Preparation of 2,3-Epoxyaldonolactones and their Conversion into 2-Fluoro-2-deoxy-aldonolactones and -sugars

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Treatment of the 2-bromo-2-deoxylactones **1**, **2** and **8** with potassium fluoride in acetonitrile or acetone gives the corresponding 2,3-epoxylactones **4**, **5** and **10**, respectively. The γ-lactones **5** and **10** were in equilibrium with the corresponding δ-lactones **7** and **12**. The 2,5-dibromo-2,5-dideoxypentonolactones **3** and **9** gave the 2,3-epoxylactones **6** and **11**, respectively, when treated with potassium carbonate in acetone. By treatment of the 2,3-epoxylactones with $Et_3N{\cdot}3HF$ at 70 °C for 3–13 days the 2-fluoro-2-deoxylactones **13**, **15** and **18** were obtained in 57–69 % yield; **15** and **18** were converted into 2-fluoro-2-deoxy-D-xylose (**17**) and -D-arabinose (**19**), respectively. Hydrolysis of **13** gave crystalline 2-fluoro-2-deoxy-L-threonic acid.

As a part of an investigation on the uses of bromodeoxyaldonolactones as substrates for the introduction of other functional groups, for example, the amino group[1,2] into aldonolactones and, subsequently, sugars, we became interested in using these lactones as substrates for the introduction of fluorine. Fluorinated carbohydrates have gained much importance for the probing of biochemical mechanisms, and consequently, the synthesis of such compounds is of importance.[3–5] One of the most common methods used is the nucleophilic displacement of reactive leaving groups, but because of the low nucleophilicity and high basicity of the fluoride ion[3,6] side reactions may occur. We have thus found that 2-bromo-2-deoxylactones could not be converted into the corresponding 2-fluoro derivatives in this way. The unprotected lactones, e.g. **2**, gave, when treated with silver or potassium fluoride in acetonitrile, the 2,3 epoxide (e.g. **5**), while the 3,5-isopropylidene derivative of **2** did not react under similar conditions. Epoxides may, however, be opened to fluorohydrins[3,4,7] and we describe in the present paper a convenient synthesis of epoxyaldonolactones and their conversion into fluorodeoxylactones.

Results and discussion

When 2-bromo-2-deoxy-L-threonolactone (**1**) was treated with potassium fluoride in acetonitrile or acetone, the 2,3-epoxylactone **4** was formed (Scheme 1). This reaction was complete within 1 h, but when the mixture was kept for 3 days, the small amount of elimination products, formed initially, disappeared, and the crude epoxylactone (55–60 %) thus obtained could be used directly for further synthesis. Similarly, the two 2-bromo-2-deoxypentonolactones **2**[8] and **8**[8] were converted into epoxylactones in high yield (85–90 %), when treated with potassium fluoride in acetonitrile for 30–60 min. In both cases the ^{13}C NMR spectra showed the presence of the γ-lactones **5** and **10** together with the δ-lactones **7** and **12**. In the case of the epoxylactones of *lyxo*-configuration the γ-lactone (**5**) and δ-lactone (**7**) could be separated by flash chromatography. However, the mixture could also be used directly in the reactions described below. By treatment of the 2,5-dibromo-2,5-dideoxy-D-xylono- (**3**)[8] or -D-arabinonolactone (**9**)[8] with potassium fluoride only slow conversion into the epoxides took place, whereas treatment with potassium carbonate in acetone[9] for 1 h gave high yields of the epoxides **6** and **11**, respectively.

Opening of epoxides with fluoride ion would be expected to require severe conditions since nucleophilic displacements with tetrabutylammonium fluoride[10] or triethylamine–hydrogen fluoride complex[11] have been performed on leaving groups adjacent to the epoxy group without interference of the latter. However, in pyranose or furanose derivatives[12,13] 2,3-epoxides have been opened with potassium hydrogen fluoride at high temperatures. The epoxylactone **4**, when treated with this reagent at different temperatures, was either unchanged or destroyed. Treatment with hydrogen fluoride at temperatures from −40 to 0 °C, or with hydrogen fluoride–boron trifluoride[14] also proved unsuccessful. We have now found that when the epoxylactone **4** was treated with the hydrogen fluoride–triethylamine complex at 70 °C for 3 days the 2-fluoro-2-deoxy-L-threonolactone (**13**) was formed as the sole product. Hydrolysis gave the crystalline 2-fluoro-2-deoxy-L-threonic acid (**14**). Treatment of the mixture of γ- and δ-2,3-epoxy-D-lyxonolactone (**5** and **7**) with $Et_3N{\cdot}3HF$ at

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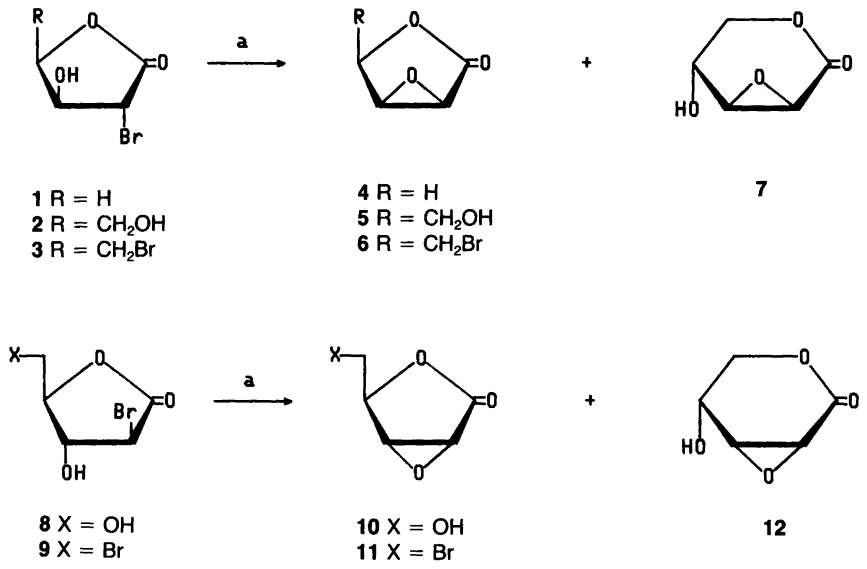
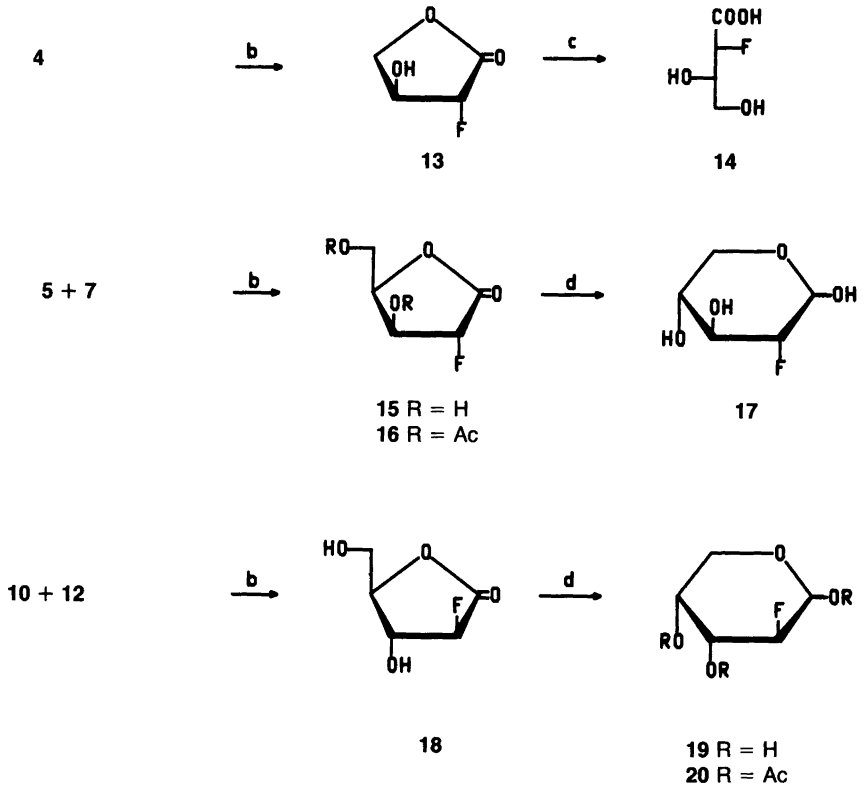


Scheme 1. a, KF/acetone or acetonitrile.

70 °C for 13 days gave the crystalline 2-fluoro-2-deoxy-D-xylonolactone (**15**) as the only detectable product in 60–65 % yield. Alternative work-up gave the syrupy diacetate **16**. Similarly, the mixture of 2,3-epoxy-γ- and -δ-D-ribonolactone (**10** and **12**) gave by a similar treatment the 2-fluoro-2-deoxy-D-arabinonolactone (**18**). The long reaction time of the epoxypentonolactones, compared with the threonolactone, is apparently due to the greater stability of the δ-lactones present. Thus, when the reaction of the mixture of **5** and **7** with $Et_3N{\cdot}3HF$ was interrupted after 3 days the reaction product consisted of a mixture of the 2-fluorolactone **15** and the unchanged δ-lactone **7**.



Scheme 2. b, $Et_3N{\cdot}3HF$; c, H_2O–HCl; d, diisoamylborane.

The structures of the fluorolactones were determined by NMR spectroscopy. The ^{13}C NMR spectrum of **16** showed a doublet at 86.7 ppm ($^1J_{CF}$=196 Hz) assigned to C-2 as the fluorine-bearing carbon. Resonances at 167.0 ($^2J_{CF}$=22 Hz) and 72.8 ppm ($^2J_{CF}$=23 Hz) were assigned to C-1 and C-3, respectively. The $^3J_{CF}$ value of C-4 (74.6 ppm) was 8.0 Hz whereas no $^4J_{CF}$ was observed for C-5 (60.0 ppm). The assignment of the signals corresponding to C-3 and C-4, respectively, was based on the C–F coupling constants, which decrease with increased distance from carbon to the fluorine.[15] The ^1H NMR spectrum of (**16**) was also in accordance with the structure proposed. Similarly, the fluorolactones **13** and **18** were shown to carry the fluorine at C-2. The lactones **15** and **18** were converted into 2-fluoro-2-deoxy-D-xylose (**17**)[13] and -D-arabinose (**19**)[16,17] respectively, confirming the structures discussed.

The regioselectivity in opening 2,3-epoxyfuranoses or pyranoses to fluorodeoxy sugars strongly depends upon the orientation of the substituents in the rest of the molecule. Thus in other cases, both 2- and/or 3-fluoro derivatives have been obtained.[7] Acyclic α,β-epoxy carboxylic esters have been opened with the hydrogen fluoride–pyridine complex to give 3-fluoro-2-hydroxy esters.[18] The epoxylactones discussed in the present work were shown to open selectively at C-2 when treated with a similar reagent. The difference between these results is not clearly understood.

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 (67.4 ppm) was used as an internal reference for ^{13}C NMR spectra and acetone (δ 2.22) for ^1H NMR spectra in D_2O. $SiMe_4$ was used as the reference for spectra in $CDCl_3$. Column chromatography was performed on silica gel 60 (40–60 μm, Merck 9385) using the flash technique. Spots were visualized on TLC either by charring with H_2SO_4 or by the NH_2OH/Fe^{3+}-reagent.[19] Potassium fluoride was dried at 150 °C *in vacuo* and kept over P_2O_5.

2,3-Anhydro-L-erythrono-1,4-lactone (**4**). 2-Bromo-2-deoxy-L-threono-1,4-lactone (**1**) (12.1 g) was dissolved in acetonitrile (80 ml), and potassium fluoride (20.4 g) was added. The mixture was stirred at room temperature for 3 days, filtered, and the filtrate was evaporated. The dark residue was dissolved in chloroform (150 ml), which was washed with water (20 ml), dried ($MgSO_4$) and evaporated, to leave syrupy **4** (3.8 g, 57 %) which was homogeneous as seen from a ^{13}C NMR spectrum ($CDCl_3$): 171.5 ppm (s, C-1), 68.7 (t, *J* 154 Hz, C-4), 55.3 (d, *J* 198 Hz), 49.6 (d, *J* 202 Hz, C-2 and C-3). The product was purified by distillation; b.p. 79 °C/1 mmHg. At low temperature the compound crystallized and was recrystallized from $CHCl_3$; m.p. 21–24 °C; $[\alpha]_D^{20}$ −25° (*c*. 2.9, $CHCl_3$). Anal. $C_4H_4O_3$: C, H.

2,3-Anhydro-D-lyxono-1,4- and -1,5-lactones (**5**) and (**7**). 2-Bromo-2-deoxy-D-xylono-1,4-lactone (**2**) (7.0 g) was refluxed for 30 min in acetonitrile (70 ml) with potassium fluoride (10.1 g). The mixture was filtered and the filtrate was concentrated and redissolved in acetone. Filtration through silica and evaporation gave a syrupy residue containing two compounds according to TLC. These were identified by ^{13}C NMR spectroscopy as 2,3-anhydro-D-lyxono-1,4-lactone (**5**) and 2,3-anhydro-D-lyxono-1,5-lactone (**7**) (3.93 g, 91 %) in the ratio 2:1. By column chromatography in ether only the fastest moving compound **7** was obtained in a pure state. ^{13}C NMR ($CDCl_3$): δ 167.2 (C-1), 69.5 (C-5), 62.9 (C-4), 53.8 and 48.8 (C-2 and C-3). ^1H NMR ($CDCl_3$, 500 MHz): δ 4.58 (dd, 1 H, H-5, $J_{4,5}$, 2.0 Hz, $J_{5,5'}$ 12.0 Hz), 4.52 (m, H-4), 4.27 (dt, H-5', $J_{4,5'}$ 1.5 Hz, $J_{3,5'}$ 1.5 Hz), 4.14 (m, OH), 3.76 (ddd, H-3, $J_{2,3}$ 4.0 Hz, $J_{3,4}$ 3.0 Hz) and 3.64 (d, H-2). IR: 1730 cm^{-1}. The 1,4-lactone (**5**) was characterized by the ^{13}C NMR spectrum ($CDCl_3$): 170.6 (C-1), 79.2 (C-4), 60.1 (C-5), 55.6 and 50.4 (C-2 and C-3).

In another experiment **2** (4.0 g) was treated in dry acetone with potassium fluoride (3.7 g) for 24 h at room temperature and worked up as described above to give 2.3 g (89 %) of a mixture of **5** and **7** (2:3). Chromatography of this in Et_2O again gave **7** (1.02 g, 41 %) which crystallized. Recrystallization from MeOH–Et_2O–hexane gave the pure compound (820 mg, 33 %); m.p. 69–71 °C; $[\alpha]_D^{20}$ −76.2° (*c* 1.2, EtOAc). Anal $C_5H_6O_4$: C, H. ^{13}C and ^1H NMR spectra were identical with those given above.

2,3-Anhydro-D-ribono-1,4- and -1,5-lactones (**10**) *and* (**12**). 2-Bromo-2-deoxy-D-arabino-1,4-lactone (**9**) (1.99 g) was treated in acetonitrile (20 ml) with potassium fluoride (2.9 g) for 1 h as described above. Work-up gave a syrup (1.05 g, 86 %) consisting of 2,3-anhydro-D-ribono-1,4-lactone (**10**) and 2,3-anhydro-D-ribono-1,5-lactone (**12**) in the proportion 2:1. The two isomers could not be separated. ^{13}C NMR [$(CD_3)_2CO$]: **10**: δ 171.2 (s, C-1), 80.1 (d, *J* 145 Hz, C-4), 60.8 (t, *J* 144 Hz, C-5), 56.6 (d, *J* 203 Hz) and 49.7 (d, *J* 204 Hz, C-2 and C-3). **12**: δ 166.7 (C-1), 65.3 (C-5), 63.5 (C-4), 55.7 and 50.0 (C-2 and C-3).

2,3-Anhydro-5-bromo-5-deoxy-D-lyxono-1,4-lactone (**6**). 2,5-Dibromo-2,5-dideoxy-D-xylono-1,4-lactone (**3**) (5 g) and potassium carbonate (20 g) was stirred in acetone (50 ml) for 1 h. The mixture was filtered and evaporated to leave a crystalline residue of **6** (3.30 g, 93 %). Recrystallization of this from EtOAc–pentane furnished a product (3.0, 84 %) with m.p. 77–78 °C $[\alpha]_D^{20}$ −116.5° (*c* 1.8 $CHCl_3$). Anal. $C_5H_5BrO_3$: C, H, Br. ^{13}C NMR ($CDCl_3$): δ 169.1 (C-1), 77.0 (C-4), 55.5 (C-2), 51.0 (C-3) and 26.0 (C-5).

2,3-Anhydro-5-bromo-5-deoxy-D-ribono-1,4-lactone (**11**). Crude syrupy 2,5-dibromo-2,5-dideoxy-D-arabino-1,4-lactone (**9**) (710 mg), containing small amounts of 2,5-dibromo-2,5-dideoxy-L-lyxono-1,4-lactone,[8] was dissolved in acetone (7 ml) containing potassium carbonate (3.0 g), and

the mixture was stirred for 1 h. Filtration and evaporation gave a colourless syrup which contained **11** as seen from the ^{13}C NMR spectrum, together with 2,3-anhydro-5-bromo-5-deoxy-L-lyxono-1,4-lactone and 2-bromo-4-hydroxypentane-2,4-dieno-1,4-lactone in the ratio 4:1:1, in ca. 70% yield. ^{13}C NMR ($CDCl_3$): **11**: δ 169.6 (C-1), 76.4 (C-4), 57.6 (C-2), 49.6 (C-3) and 30.6 (C-5).

2-Deoxy-2-fluoro-L-threono-1,4-lactone (**13**). Pure syrupy 2,3-anhydro-L-erythrono-1,4-lactone (**4**) (2.30 g) was dissolved in $Et_3N{\cdot}3HF$ (50 ml) in a polyethylene flask, connected to the atmosphere by a long polyethylene tube. The solution was kept at 70 °C for 3 days, after which time concentrated sodium carbonate solution was added (ca. 250 ml) until pH 5. The resulting solution was filtered and extracted with EtOAc (5 × 100 ml). The combined extracts were dried, filtered through silica, and concentrated to give syrupy **13** (1.56 g, 57 %). ^{13}C NMR data ($CDCl_3$): δ 170.6 (d, C-1, J_{C_1F} 22 Hz), 90.9 (d, C-2, J_{C_2F} 194 Hz), 70.7 (d, C-3, J_{C_3F} 21 Hz) and 69.1 (d, C-4, J_{C_4F} 11 Hz). ^1H NMR (500 MHz, $CDCl_3$): δ 5.12 (dd, H-2, $J_{2,3}$ 7.0 Hz, J_{2F} 51.0 Hz), 4.78 (dq, H-3, $J_{3,4} = J_{3,4'}$ 7.0 Hz, $J_{3,F}$ 17.0 Hz), 4.54 (ddd, H-4, $J_{4,4'}$ 9.5 Hz, $J_{4,F}$ 1.0 Hz) and 4.09 (dd, H-4', $J_{4',F}$ 0.0 Hz). Distillation furnished a product of b.p. 125 °C/1.5 mmHg; $[\alpha]_D^{20}$+4° (*c* 0.8, $CHCl_3$).

Crude **13** was boiled in water for 2 h, acidified with hydrochloric acid, concentrated then coevaporated with toluene to give a white crystalline solid of 2-deoxy-2-fluoro-L-threonic acid (**14**) m.p. 175–183 °C. Recrystallization in water furnished a product of m.p. 177–182 °C; $[\alpha]_D^{20}$+48° (*c* 0.04, 1 M NaOH). ^{13}C NMR (D_2O): δ 173.0 (d, C-1, J_{CF} 25 Hz), 89.7 (d, C-2, J_{CF} 185 Hz), 72.2 (d, C-3, J_{CF} 19 Hz) and 62.2 (d, C-4, J_{CF} 5 Hz). ^1H NMR (500 MHz, D_2O): δ 5.22 (dd, H-2, $J_{2,3}$ 2.0 Hz, $J_{2,F}$ 48.0 Hz), 4.19 (ddt, H-3, $J_{3,4} = J_{3,4'}$ 7.0 Hz, $J_{3,F}$ 29.0 Hz), 3.77 (ddd, H-4, $J_{4,4'}$ 12.0 Hz, $J_{4,F}$ 1.0 Hz) and 3.73 ppm (ddd, H-4', $J_{4',F}$ 1.5 Hz).

2-Deoxy-2-fluoro-D-xylono-1,4-lactone (**15**). The syrupy mixture of 2,3-anhydro-D-lyxono-1,4- and -1,5-lactones (**5** and **7**) (0.45 g) was treated with $Et_3N{\cdot}3HF$ (5 ml) in a polyethylene flask as described above for 13 days at 70 °C. Acetone (30 ml) was then added together with silica gel and the mixture was stirred for 30 min. Filtration through silica gel and concentration gave crystalline **15** (0.33 g, 64 %). Recrystallization from EtOH gave a product of m.p. 159–162 °C. $[\alpha]_D^{20}$+59° (*c* 0.2, H_2O). Anal. $C_5H_7FO_4$: C, H. ^{13}C NMR [$(CD_3)_2SO$]: δ 90.9 (d, C-2, J_{C_2F} 189 Hz), 79.6 (d, C-4, J_{C_4F} 10 Hz), 71.8 (d, C-3, J_{C_3F} 20 Hz) and 57.9 (s, C-5).

3,5-Di-O-acetyl-2-deoxy-2-fluoro-D-xylono-1,4-lactone (**16**). The mixture of **5** and **7** (0.37 g) was treated with $Et_3N{\cdot}3HF$ (3 ml) as described above. After 13 days, 4 ml of Ac_2O were added, and the mixture was stirred at room temperature for 4 h. Water was then slowly added to hydrolyse the excess of reagent and the solution was extracted with CH_2Cl_2 (3 × 25 ml). The combined extracts were dried ($MgSO_4$), concentrated and filtered through silica with $CHCl_3$ as the eluent. Evaporation of the solvent gave syrupy **16** (0.37 g, 56 %) containing some minor, unidentified impurities. Purification by flash chromatography using ether as the eluent gave a homogeneous product (0.29 g, 44 %). ^{13}C NMR ($CDCl_3$): δ 167.0 (d, C-1, J_{C_1F} 22 Hz), 86.7 (d, C-2, J_{C_2F} 196 Hz), 74.6 (d, C-4, J_{C_4F} 8 Hz), 72.8 (d, C-3, J_{C_3F} 23 Hz), 60.2 (s, C-5), 169.7, 169.3, 20.5 and 20.0 (OAc). ^1H NMR ($CDCl_3$): δ 5.64 (dt, H-3, $J_{3,F}$ 21.0 Hz, $J_{2,3} = J_{3,4}$ 7.5 Hz), 5.41 (dd, H-2, $J_{2,F}$ 52.0 Hz), 5.04 (dt, H-4, $J_{4,5} = J_{4,5'}$ 3.0 Hz), 4.30 (dd, H-5, $J_{5,5'}$ 13.0 Hz), 4.26 (ddd, $J_{5',F}$ 1.5 Hz), 2.17 and 2.12 (OAc).

2-Deoxy-2-fluoro-D-xylopyranose (**17**). A solution of diisoamylborane[20] was prepared by adding 2-methyl-2-butene (3 ml) to borane–dimethyl sulfide (10 M, 1.4 ml) in THF (10 ml) under an N_2 atmosphere, keeping the mixture at room temperature for 5 h. To this solution was added 2-deoxy-2-fluoro-D-xylono-1,4-lactone (**15**) (0.23 g) in THF (5 ml) at 0 °C, and the mixture was allowed to come to room temperature overnight. Water (10 ml) was then added and the mixture was refluxed for 1 h, concentrated to half its volume and extracted with CH_2Cl_2 (3 × 20 ml). The aqueous phase was concentrated to leave syrupy **17** (0.13 g, 56 %). ^1H NMR (500 MHz, D_2O): α-anomer: δ 5.40 (d, H-1, $J_{1,2}$ 3.5 Hz), 4.41 (ddd, H-2, $J_{2,3}$ 9.0 Hz, $J_{2,F}$ 49.0 Hz), 3.85–4.0 and 3.6–3.75 (m, H-3, H-4, H-5 and H-5'). β-Anomer: δ 4.84 (dd, H-1, $J_{1,2}$ 8.0 Hz, $J_{1,F}$ 2.5 Hz), 4.10 (dt, H-2, $J_{2,3}$ 8.0 Hz, $J_{2,F}$ 51.0 Hz) and 3.36 (t, H-5_{ax}, $J_{5,5'}$ 10.5 Hz). **17** is reported crystalline.[13]

2-Deoxy-2-fluoro-D-arabinono-1,4-lactone (**18**). The syrupy mixture of 2,3-anhydro-D-ribonolactones **10** and **12** (0.70 g) was dissolved in $Et_3N{\cdot}3HF$ (7 ml) in a polyethylene flask as described for **13** and kept at 70 °C for 12 days. Work-up as described above gave syrupy **18** (0.56 g, 69 %). Purification by flash chromatography using ether as the eluent gave a homogeneous product. $[\alpha]_D^{20}$+66° (*c* 1.6, EtOAc). Anal. $C_5H_7FO_4$: C, H. ^{13}C NMR (D_2O): δ 172.6 (d, C-1, J_{C_1F} 22 Hz), 92.8 (d, C-2, J_{C_2F} 196 Hz), 81.8 (d, C-4, J_{C_4F} 10 Hz), 71.7 (d, C-3, J_{C_3F} 21 Hz) and 60.1 (s, C-5).

2-Deoxy-2-fluoro-D-arabinopyranose (**19**). 2-Deoxy-2-fluoro-D-arabinono-1,4-lactone (**18**) (0.29 g) in THF (10 ml) was treated as above with a solution of diisoamylborane. Work-up gave colourless syrupy **19** as a mixture of anomers (0.26 g, 88 %). ^{13}C NMR (D_2O): α-anomer: δ 95.1 (d, C-1, J_{C_1F} 23 Hz), 93.2 (d, C-2, J_{C_2F} 179 Hz), 71.7 (d, C-3, J_{C_3F} 17 Hz), 69.8 (s, C-4), 67.2 (s, C-5). β-anomer: δ 91.0 (d, C-1, J_{C_1F} 21 Hz), 89.7 (d, C-2, J_{C_2F} 183 Hz), 70.0 (s, C-4), 67.8 (d, C-3, J_{C_3F} 19 Hz) and 63.1 (s, C-5). ^1H NMR (D_2O): α-anomer: δ 4.77 (dd, H-1, $J_{1,2}$ 8 Hz, $J_{1,F}$ 3 Hz), 4.34 (ddd, H-2, $J_{2,3}$ 9 Hz, $J_{2,F}$ 52 Hz) and 3.62–4.22 (m, H-3, H-4, H-5 and H-5'). β-Anomer: δ 5.44 (dd, H-1, $J_{1,2}$ 4 Hz, $J_{1,F}$ 1 Hz), 4.67 (dd, H-2, $J_{2,3}$ 10 Hz, $J_{2,F}$ 50 Hz) and 3.62–4.22 (m, H-3, H-4, H-5, H-5').

1,3,4-Tri-O-acetyl-2-deoxy-2-fluoro-α,β-D-arabinopyranose (**20**). 2-Deoxy-2-fluoro-D-arabinose (**19**) (0.20 g) was acetylated in pyridine (10 ml) with Ac_2O (4 ml) for 16 h. Work-up gave a syrupy residue, shown by ^{13}C NMR spectroscopy to be mainly **20** (0.35 g). Purification by column and preparative TLC (EtOAc–hexane 1:3) gave pure **20** as a mixture of anomers (0.12 g, 28 % based on the fluorolactone **18**). ^{13}C NMR ($CDCl_3$): α-anomer: δ 91.7 (d, C-1, J_{C_1F} 25 Hz), 86.5 (d, C-2, J_{C_2F} 186 Hz), 70.1 (d, C-3, J_{C_3F} 20 Hz), 68.0 (s, C-4) and 64.2 (s, C-5). β-Anomer: δ 89.2 (d, C-1, J_{C_1F} 22 Hz), 84.1 (d, C-2, J_{C_2F} 190 Hz), 68.7 (d, C-4, J_{C_4F} 8 Hz), 67.4 (d, C-3, J_{C_3F} 12 Hz), 62.3 (s, C-5) and 20.5 (OAc), ^1H NMR ($CDCl_3$): α-anomer: δ 5.74 (dd, H-1, $J_{1,2}$ 7.5 Hz, $J_{1,F}$ 4.8 Hz), 5.34 (m, H-4), 5.20 (ddd, H-3, $J_{2,3}$ 9.2 Hz, $J_{3,4}$ 3.5 Hz, $J_{3,F}$ 12.4 Hz), 4.67 (ddd, H-2, $J_{2,F}$ 50.9 Hz), 4.1 and 3.8 (d, H-5 and H-5′, $J_{5,5'}$ 13 Hz) and 2.1–2.2 (OAc). β-Anomer: δ 6.44 (d, H-1, $J_{1,2}$ 3.8 Hz), 5.40–5.44 (m, H-3, H-4), 4.92 (ddd, H-2, $J_{2,3}$ 9.5 Hz, $J_{2,F}$ 50.0 Hz), 4.0 and 3.8 (d, H-5, H-5′, $J_{5,5'}$ 13 Hz) and 2.0–2.1 (OAc). The ^1H NMR data for the β-anomer are in accordance with published values.[21]

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