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REACTION OF ACETYL HYPOFLUORITE WITH PYRANOID AND FURANOID GLYCALS[1]

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ABSTRACT

The regiospecific *syn*-addition of acetyl hypofluorite to glycals derived from pentopyranoses led to mixtures of stereoisomers. Stereospecific reactions occurred with furanoid glycals, the direction of addition being governed by the nature of the substituent at C-3. Whereas a benzyloxy group caused attack from the opposite, less-hindered face of the double bond, a hydroxyl group induced addition from the same side. From these reactions, 2-deoxy-2-fluoro derivatives of β-D-arabino-, α-D-ribo-, β-D-lyxo-, and α-D-xylo-pyranose as well as β-D-manno-, α-D-gluco-, α-D-ribo-, and β-D-arabino-furanose were obtained; their ^{1}H-, ^{13}C-, and ^{19}F-n.m.r. data are given.

INTRODUCTION

The stereoselective synthesis of sugars fluorinated at C-2 still constitutes a challenging problem[2,3]. Epoxide cleavage by fluoride yields mixtures of isomers. Substitution of a sulfonyloxy group as well as direct displacement of HO-2 often fail because of elimination and neighboring-group or solvent participation, respectively. The smooth introduction of fluorine has been accomplished when trifluoromethanesulfonate (triflate)[3] or imidazolsulfonate (imidazylate)[4] were the leaving groups.

The strict regiospecificity and high stereoselectivity reported for the electrophilic *syn*-addition of acetyl hypofluorite[5] across the double bond of some pyranoid glycals (1,5-anhydro-2-deoxy-hex-1-enitols and -pent-1-enitols)[6], giving 2-deoxy-2-fluoropyranoses, prompted a study of this reaction with glycals derived from pentopyranoses, and hexo- and pentofuranoses.

RESULTS AND DISCUSSION

Reactions with pyranoid glycals. — 3,4-Di-*O*-acetyl-D-arabinal[7] (**1**), when treated with gaseous acetyl hypofluorite[8] in acetic acid at room temperature, gave

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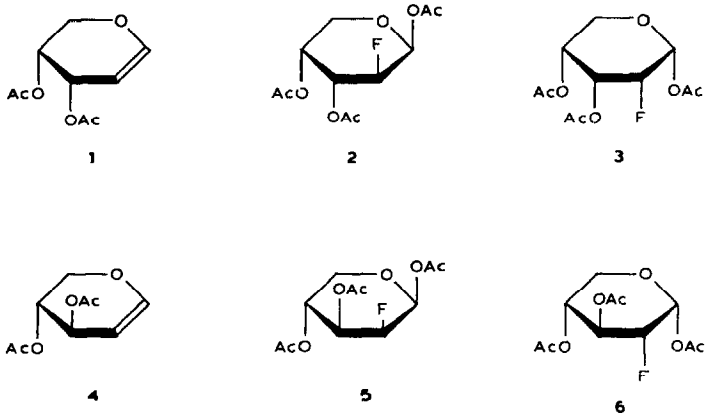


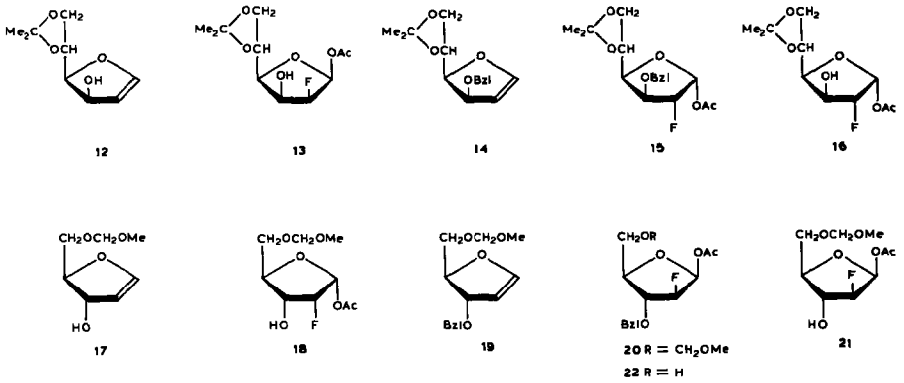
a 6:1 mixture of 1,3,4-tri-*O*-acetyl-2-deoxy-2-fluoro-β-D-arabinopyranose[6] (**2**) and 1,3,4-tri-*O*-acetyl-2-deoxy-2-fluoro-α-D-ribopyranose (**3**). A similar reaction of 3,4-di-*O*-acetyl-D-xylal[7] (**4**) gave a 7:4 mixture of 1,3,4-tri-*O*-acetyl-2-deoxy-2-fluoro-β-D-lyxopyranose (**5**) and 1,3,4-tri-*O*-acetyl-2-deoxy-2-fluoro-α-D-xylopyranose (**6**).

The addition of trifluoromethyl hypofluorite, in trichlorofluoromethane at −78°, to **1** gave a 40:1 mixture of β-D-*arabino* and α-D-*ribo* products[9]; under similar conditions, **4** gave a 7:1 mixture of β-D-*lyxo* and α-D-*xylo* products[10]. The poorer stereoselectivity observed in our experiments prompted a re-investigation of the reactions of 3,4,6-tri-*O*-acetyl-D-glucal (**7**) and 3,4,6-tri-*O*-acetyl-D-galactal (**10**), which have been repeatedly described[6,8,11]. We obtained similar results [**7** gave a 5:2 mixture of the tetra-acetates of 2-deoxy-2-fluoro-α-D-gluco- (**8**) and -β-D-manno-pyranose (**9**), whereas **10** gave only the α-D-*galacto* isomer (**11**)]. Thus, the findings with **1** and **4** must reflect the higher susceptibility of pentopyranoses and their derivatives[12,13], especially in their transition state, to such solvent-dependent polar interactions as the anomeric, the gauche, and the Δ^2-effects[14].

Reactions with furanoid glycals. — Treatment of 1,4-anhydro-2-deoxy-5,6-*O*-isopropylidene-D-*arabino*-hex-1-enitol[15] (**12**) or 1,4-anhydro-2-deoxy-5-*O*-methoxymethyl-D-*erythro*-pent-1-enitol[15] (**17**) with gaseous acetyl hypofluorite[8] in dichloromethane–hexane at room temperature gave a complex mixture with one product strongly preponderating. ^{19}F-N.m.r. spectroscopy of the components, isolated by chromatography, revealed that fluorine was present only in each main product and suggested that the other products were formed as a result of rearrangements[15].

The structures of the fluorinated compounds were established, from the spectroscopic data, as 1-*O*-acetyl-2-deoxy-2-fluoro-5,6-*O*-isopropylidene-β-D-mannofuranose (**13**, obtained from **12** in 47% yield) and 1-*O*-acetyl-2-deoxy-2-fluoro-5-*O*-methoxymethyl-α-D-ribofuranose (**18**, isolated from the reaction of **17** in 30% yield).

Addition of acetyl hypofluorite across double bonds generally occurs from the less-hindered face[6], the stereoselectivity depending on effects of polarity (in



substrate and solvent) and on the relative stabilities of ionic intermediates[11]. In each of our reactions, exclusive attack from the sterically more-hindered side was revealed by the configuration of the sole addition product.

In seeking the cause of this phenomenon, the 3-*O*-benzyl derivatives **14** (of **12**) and **19** (of **17**) were treated with acetyl hypofluorite. Only the main product from **14** contained fluorine, and the n.m.r. data indicated it to be 1-*O*-acetyl-3-*O*-benzyl-2-deoxy-2-fluoro-5,6-*O*-isopropylidene-α-D-glucofuranose (**15**). Two fluorinated products were isolated after the reaction of **19**, and the n.m.r. data indicated them to have identical configurations and to be 1-*O*-acetyl-3-*O*-benzyl-2-deoxy-2-fluoro-5-*O*-methoxymethyl-β-D-arabinofuranose (**20**) and its *O*-de(methoxymethylated) analogue **22**.

In order to compare these products with those obtained from the reaction of glycals having HO-3 unprotected, the benzyl groups in **15** and **20** were hydrogenolysed to yield 1-*O*-acetyl-2-deoxy-2-fluoro-5,6-*O*-isopropylidene-α-D-glucofuranose (**16**) and 1-*O*-acetyl-2-deoxy-2-fluoro-5-*O*-methoxymethyl-β-D-arabinofuranose (**21**), respectively. The clear-cut spectral differences within the pairs of stereoisomers (**13/16** and **18/21**) confirmed the occurrence of two different steric courses of the addition reaction. Thus, with the 3-*O*-protected compounds **14** and **19**, attack occurred solely from the less-hindered face, but reaction with acetyl hypofluorite occurred on the same side as the hydroxyl group when HO-3 was unsubstituted (**12** and **17**), presumably because the resulting transition state was stabilised. This dualism parallels that observed in the reaction of protected and unprotected glycals with peroxy acids[16].

N.m.r. spectroscopy. — The configurations of all of the fluorinated products were assigned on the basis of the n.m.r. data, especially those referring to positions 1–3 (see Tables I–V).

For pyranoid derivatives, some differences in conformation could also be deduced. The hexopyranose derivatives **8, 9,** and **11**[6] and the α-D-xylopyranose derivative **6** adopt the $^4C_1$ conformation (indicated by the $^3J_{H,H}$ values); the equatorial positions of F-2 and H-1 in **6, 8,** and **11** and their antiperiplanar relationship in **9** were reflected by the $^3J_{H,F}$ values (0 and 19 Hz). The $^1C_4$ conformation

TABLE I

^{1}H-N.M.R. DATA FOR THE PYRANOID DERIVATIVES[a]

Atom	**2**[b]	**3**	**5**	**6**	**8**[b]	**9**	**11**[b]
H-1	6.44 *4.0(2)*	6.06 *8.4(F)* *2.7(2)*	5.90 *12.0(F)* *2.0(2)*	6.30 *4.0(2)*	6.46 *4.0(2)*	5.81 *19.0(F)*	6.48 *4.0(2)*
H-2	4.94 *48.0(F)* *4.0(1)* *10.0(3)*	4.72 *46.9(F)* *2.7(1)* *3.2(3)*	4.83 *48.0(F)* *2.0(1)* *3.0(3)*	4.58 *48.0(F)* *4.0(1)* *10.0(3)*	4.64 *52.0(F)* *4.0(1)* *9.6(3)*	4.87 *51.2(F)* *2.4(3)*	4.90 *49.0(F)* *4.0(1)* *10.0(3)*
H-3		5.48 *17.7(F)* *3.2(2)* *3.5(4)*	5.18 *17.6(F)* *3.0(2)* *7.5(4)*	5.49 *12.0(F)* *10.0(2)* *10.0(4)*	5.56 *12.0(F)* *9.6(2)* *9.6(4)*	5.07 *27.0(F)* *2.4(2)* *10.0(4)*	5.40 *11.0(F)* *10.0(2)* *3.0(4)*
H-4	5.3–5.5 (m)	5.10 *3.5(3)* *3.5(5')* *6.9(5)*	5.03 *7.5(3)* *4.0(5)* *6.0(5')*	4.94 *10.0(3)* *6.0(5)* *10.5(5')*	5.08 *9.6(3)* *9.6(5)*	5.37 *10.0(3)* *10.0(5)*	5.51 *3.5(F)* *3.0(3)* *1.2(5)*
H-5	4.05 *13.5(5')* *2.5(4)*	4.06 *6.9(4)* *12.1(5')*	4.10 *4.0(4)* *12.8(5')*	4.01 *6.0(4)* *11.1(5')*		3.81 *10.0(4)* *4.8(6)* *2.3(6')*	4.32 *1.2(4)* *6.5(6)* *6.5(6')*
H-5'/6	3.82 *13.5(5)* *5.0(4)*	3.73 *3.5(4)* *12.1(5)*	3.49 *6.0(4)* *12.8(5)*	3.80 *10.5(4)* *11.1(5)*	3.9–4.1 (m)	4.30 *4.8(5)* *12.5(6')*	
H-6'					4.22 *12.5(6)* *4.0(5)*	4.16 *2.3(5)* *12.5(6)*	4.10 *6.5(5)*

[a]Chemical shifts on the δ scale, J in Hz. Signals of AcO protons are omitted. The J values are given in italics with the coupled nucleus in brackets.

strongly preponderates for the β-D-arabinopyranose derivative[6] **2** (indicated by the $^3J_{H,H}$ values, no $J_{F,H-1}$, and the $J_{F,C-4}$ value of 7 Hz, which is consistent with a dihedral angle of ~180°). For the pentopyranose derivatives **3** and **5**, a ~1:1 equilibrium of the two chair forms was determined[13] from the value of $J_{H-4,H-5}$ and from the magnitudes of $J_{F,H-1}$ and $J_{F,H-3}$, which were close to the mean of the theoretical values for a diequatorial or diaxial relationship (0 or 19 Hz for $J_{F,H-1}$; 11 or 27 Hz for $J_{F,H-3}$).

In the ^{13}C-n.m.r. spectra of the furanoid glycals, the resonances for C-3 and C-4 were discriminated on the basis of the "alkylation shift" (+6 p.p.m.), which contrasts with assignments made recently[17] for **17** and related structures.

TABLE II

^{13}C-N.M.R. DATA FOR THE PYRANOID DERIVATIVES[a]

Atom	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**
C-1	147.8	89.5 *22*	88.9 *20*	148.2	89.6 *19*	88.8 *21*	145.8	88.8 *22*	90.4 *15*	145.5	89.0 *22*
C-2	97.5	84.3 *191*	84.0 *198*	97.6	84.7 *193*	86.6 *194*	99.2	86.6 *194*	86.5 *191*	99.0	84.1 *191*
C-3	62.8+[b]	67.8 *19*	67.2 *17*	63.8+	68.6 *18*	70.2 *19*	67.6+	71.0 *19*	71.3 *17*	63.9+	68.2 *19*
C-4	65.9+	69.0 *7*	65.3	67.3+	67.7 *3*	68.3 *8*	67.4+	67.9 *8*	65.0	63.8+	67.8 *7*
C-5	62.8+	62.5	61.0	63.6+	61.8	60.6	74.1+	70.0	73.1	72.8+	68.6
C-6							61.5	61.8	61.7	62.0	61.0

[a]Chemical shifts on the δ scale, J in Hz. The $J_{C,F}$ values are given in italics. The data for acetyl carbons are omitted. [b]Assignments marked + are tentative.

TABLE III

^{1}H-N.M.R. DATA FOR THE FURANOID DERIVATIVES[a]

Atom	**12**[15]	**13**	**14**	**15**	**16**	**17**[15,17]	**18**	**19**	**20**	**21**
H-1	6.59 *2.8(2)* *0.8(3)*	6.22 *4.8(2)*	6.62 *2.5(2)*	6.34 *4.0(2)* *6.9(F)*	6.34 *4.0(2)* *6.4(F)*	6.58 *2.6(2)* *1.2(3)*	6.39 *4.4(2)* *2.4(F)*	6.59 *2.5(2)* *1.0(3)*	6.32 *4.0(2)*	6.30 *4.5(2)*
H-2	5.25 *2.8(1)* *2.8(3)* *0.5(4)*	5.12 *49.0(F)* *4.8(1)* *4.8(3)*	5.28 *2.5(1)* *2.5(3)*	5.06 *50.8(F)* *4.0(1)* *2.6(3)*	5.01 *50.8(F)* *4.0(1)* *3.0(3)*	5.19 *2.6(1)* *2.6(3)*	5.08 *51.3(F)* *4.4(1)* *5.5(3)*	5.18 *2.5(1)* *2.5(3)*	5.16 *51.3(F)* *4.0(1)* *5.2(3)*	5.02 *52.6(F)* *4.5(1)* *6.9(3)*
H-3	4.93 *2.8(2)* *6.5(4)* *0.8(1)*	4.44 *4.8(2)* *4.2(4)*	4.66 *2.5(2)* *7.0(4)*	4.32 *13.0(F)* *2.6(2)* *4.4(4)*	4.60 *15.0(F)* *3.0(2)* *4.7(4)*	4.78 *2.6(2)* *3.0(4)* *7.5(OH)* *1.2(1)*	4.30 *6.4(F)* *6.4(4)* *5.5(2)* *6.5(OH)*		4.26 *17.0(F)* *5.2(2)* *5.2(4)*	4.56 *17.2(F)* *6.9(2)* *6.8(4)*
H-4	4.18 *6.5(3)* *7.5(5)* *0.5(2)*	4.09 *1.8(F)* *4.2(3)* *6.3(5)*	4.43 *7.0(3)* *5.0(5)*		4.21 *4.7(3)* *8.2(5)*	4.48 *3.0(3)* *5.7(5')* *6.2(5)*	4.38 *6.4(3)* *3.2(5)* *3.2(5')*	4.6–4.7 (m)	4.18 *5.2(3)* *5.0(5)* *5.0(5')*	4.06 *6.8(3)* *5.5(5)* *5.5(5')*
H-5	4.52 *7.5(4)* *6.3(6)* *5.2(6')*	4.38 *6.3(4)* *6.3(6)* *5.8(6')*	4.60 *5.0(4)* *6.4(6)* *6.4(6')*	4.3–4.5 (m)	4.30 *8.2(4)* *6.0(6)* *4.7(6')*	3.62 *6.2(4)* *10.5(5')*		3.58 *6.5(4)* *10.5(5')*		3.74 *5.5(4)* *10.0(5')*
H-5'/6	4.17 *6.3(5)* *8.5(6')*	4.00 *6.3(5)* *8.4(6')*	4.12 *6.4(5)* *8.6(6')*	4.12 *5.7(5)* *8.7(6')*	4.14 *6.0(5)* *8.7(6')*	3.58 *5.7(4)* *10.5(5)*	3.71 *3.2(4)*	3.53 *5.0(4)* *10.5(5)*	3.65 *5.0(4)*	3.70 *5.5(4)* *10.0(5)*
H-6'	4.03 *5.2(5)* *8.5(6)*	3.96 *5.8(5)* *8.4(6)*	4.00 *6.4(5)* *8.6(6)*	4.00 *5.3(5)* *8.7(6)*	3.99 *4.7(5)* *8.7(6)*					

[a]Chemical shifts on the δ scale, J in Hz. The J values are given in italics with the coupled nucleus in brackets. Data for the protecting groups are omitted.

TABLE IV

^{13}C-N.M.R. DATA FOR THE FURANOID DERIVATIVES[a]

Atom	**12**	**13**[b]	**14**	**15**[b]	**16**	**17**[17]	**18**	**19**	**20**	**21**
C-1	150.4	92.8 *25*	150.8	94.8 *22*	95.0 *17*	150.2	94.2 *16*	153.1	93.7 *18*	93.3 *18*
C-2	104.2	89.0 *200*	102.2	93.6 *195*	95.3 *196*	103.5	88.0 *200*	100.8	94.0 *200*	94.6 *200*
C-3	73.1[+c]	68.2 *20*	79.5	80.4 *25*	74.5 *26*	76.0	69.9 *17*	82.8	80.5 *21*	74.6 *22*
C-4	84.9	81.6 *10*	84.4	80.4 *10*	81.0 *4*	87.9	84.7 *3*	85.1	81.1 *9*	81.2 *10*
C-5	72.9[+]	74.2	73.4[+]	73.6[+]	73.8	67.8	66.7	67.8[+]	68.4[+]	68.7
C-6	67.0	66.0	66.2	66.2	67.6					
CMe_2	109.4 27.0 25.4	108.4 26.2 24.6	108.6 26.8 25.5	108.8 26.2 25.0	110.2 27.1 25.4					
CH_2OMe						96.9 55.5	96.6 55.4	96.9 55.6	96.8 55.6	97.1 55.7
$CH_2(Ph)$			71.3[+]	72.8[+]				69.8[+]	72.6[+]	
COMe		169.2		169.2						
		20.0		20.0	21.1		21.2		21.3	21.3

[a]Chemical shifts on the δ scale, J in Hz. The J values are given in italics. [b]Obtained from solutions in acetone-d_6 (δ 29.83). [c]Assignments marked + may be interchangeable.

TABLE V

^{19}F-N.M.R. DATA[a]

Pyranoid derivatives						
2[6]	**3**	**5**	**6**	**8**[6]	**9**	**11**[6]
−207.7	−202.9	−201.0	−195.9	−202.9	−220.2	−209.7
Furanoid derivatives						
13	**15**	**16**	**18**	**20**	**21**	**22**
−215.7	−202.5	−205.2	−216.8	−203.4	−208.0	−203.4

[a]Chemical shifts in p.p.m. from the ^{19}F signal for $CFCl_3$.

EXPERIMENTAL

General. — T.l.c. was performed on silica gel (Merck, 5554) and column chromatography on silica gel 60 (230–400 mesh, Merck, 9385)[18]. Melting points, determined with a Tottoli apparatus, are uncorrected. Optical rotations were measured with a Perkin–Elmer 141 polarimeter. N.m.r. spectra were recorded with a Bruker WM 400, WM 300, WM 250, WH 90, or Varian 200 instrument, usually for solutions in $CDCl_3$ (internal Me_4Si for ^{1}H; $CDCl_3$ for ^{13}C, 77.27 p.p.m.).

Glycals **1** and **4**[7], **7**[19], **10**[20], and **12** and **17**[15] were prepared according to literature methods.

*1,4-Anhydro-3-*O*-benzyl-2-deoxy-5,6-*O*-isopropylidene-*D*-*arabino*-hex-1-enitol* (**14**). — To a solution of **12** (1.2 g, 6.5 mmol) in tetrahydrofuran was added sodium hydride (0.15 g, 6.6 mmol) at 0° with stirring. After 30 min, a catalytic amount of tetrabutylammonium iodide and benzyl bromide[21] (1.1 g, 6.5 mmol) were added. The mixture was stored for 18 h at 35° and then concentrated. Column chromatography (toluene–ethyl acetate, 3:1) of the residue gave **14** (1.2 g, 67%), isolated as a syrup, $[\alpha]_D^{20}$ −28° (*c* 2.4, chloroform), R_F 0.86.

Anal. Calc. for $C_{16}H_{20}O_4$: C, 69.54; H, 7.30. Found: C, 69.30; H, 7.09.

*1,4-Anhydro-3-*O*-benzyl-2-deoxy-5-*O*-methoxymethyl-*D*-erythro-pent-1-enitol* (**19**). — Reaction of **17** (1.0 g, 6.2 mmol) as described above for **14**, but for 3 h at 35°, gave **19** (1.34 g, 85%), isolated as a syrup, $[\alpha]_D^{20}$ +116° (*c* 1.7, chloroform), R_F (toluene–ethyl acetate, 3:1) 0.82.

Anal. Calc. for $C_{14}H_{18}O_4$: C, 67.18; H, 7.24. Found: C, 66.92; H, 7.05.

Reactions with acetyl hypofluorite. — Generation of, and transformations with, (gaseous) acetyl hypofluorite were carried out at room temperature in the apparatus recently described[22]. After quantitative reaction of the substrate (as determined by t.l.c.), the solvent was evaporated and the products were isolated by column chromatography. The results are collected in Table VI.

TABLE VI

REACTIONS WITH ACETYL HYPOFLUORITE

Substrate	*Solvent*[a]	*Reaction time (h)*	*Chromatography eluant*[b]	*Product(s)*	*M.p.*	$[\alpha]_D^{20}$ [c]	R_F[d]
1 (0.50 g, 2.50 mmol)	A (30 mL)	2.0	C	**2**[6] (0.38 g, 55%)	122–124°	−189 (0.4)	0.32 (G)
				3 (0.06 g, 9%)	syrup		0.23 (G)
4 (0.47 g, 2.35 mmol)	A (30 mL)	2.5	C	**5**[e] (0.30 g, 54%)	syrup	−60 (1.1)	0.38 (H)
				6[f] (0.20 g, 31%)	87–90°	+106.5 (0.5)	0.48 (H)
7 (0.40 g, 1.47 mmol)	A (30 mL)	1.5	D	**8**[6] (0.25 g, 49%)	syrup	+147 (1.0)	0.21 (G)
				9 (0.10 g, 20%)	syrup	−10 (0.3)	0.13 (G)
10 (0.50 g, 1.83 mmol)	A (40 mL)	1.0	D	**11**[6] (0.49 g, 74%)	syrup	+146 (0.8)	0.24 (G)
12 (0.30 g, 1.61 mmol)	B (60 mL)	2.5	E	**13**[g] (0.20 g, 47%)	syrup	−43 (0.7)	0.35 (I)
14 (0.30 g, 1.08 mmol)	B (40 mL)	2.0	F	**15**[h] (0.23 g, 61%)	syrup	+26 (2.8)	0.81 (I)
17 (0.30 g, 2.08 mmol)	B (40 mL)	2.0	E	**18**[i] (0.15 g, 30%)	syrup	+17 (1.0)	0.51 (K)
19 (0.40 g, 1.60 mmol)	B (40 mL)	2.0	F	**20**[j] (0.26 g, 51%)	syrup	−10 (1.0)	0.44 (L)
				22[k] (0.05 g, 12%)	syrup	+14 (0.9)	0.23 (L)

[a] A, Acetic acid; B, dichloromethane–hexane (1:3). [b] C, Ethyl acetate–toluene (1:10); D, ethyl acetate–toluene (1:4); E, ethyl acetate–cyclohexane (1:2); F, ethyl acetate–cyclohexane (1:3). [c] In chloroform (*c* in brackets). [d] G, Ethyl acetate–toluene (1:4); H, ethyl acetate–toluene (1:3); I, ethyl acetate–cyclohexane (1:1); K, ethyl acetate–cyclohexane (2:1); L, ethyl acetate–cyclohexane (1:3). [e] *Anal.* Calc. for $C_{11}H_{15}FO_7$: C, 47.48; H, 5.43. Found: C, 47.35; H, 5.44. [f] *Anal.* Calc. for $C_{11}H_{15}FO_7$: C, 47.48; H, 5.43. Found: C, 47.46; H, 5.30. [g] *Anal.* Calc. for $C_{11}H_{17}FO_6$: C, 50.00; H, 6.48. Found: C, 49.84; H, 6.33. [h] *Anal.* Calc. for $C_{18}H_{23}FO_6$: C, 61.00; H, 6.54. Found: C, 60.83; H, 6.31. [i] *Anal.* Calc. for $C_9H_{15}FO_6$: C, 45.38; H, 6.35. Found: C, 45.42; H, 6.30. [j] *Anal.* Calc. for $C_{16}H_{21}FO_6$: C, 58.53; H, 6.45. Found: C, 58.12; H, 6.20. [k] N.m.r. data ($CDCl_3$): ^1H, δ 6.35 (d, 1 H, $J_{1,2}$ 4 Hz, H-1), 5.16 (ddd, 1 H, $J_{F,2}$ 51, $J_{2,3}$ 5 Hz, H-2), benzyl ether (4.6 and 7.4), acetyl (2.1); ^{19}F, δ −203.4 (*J* 53 and 16 Hz).

Hydrogenolysis of benzyl ethers. — A 3% solution in ethyl acetate of the benzyl ether (**15** or **20**) was hydrogenolysed in the presence of an equivalent amount of 10% Pd–C at 1 atm. and room temperature. After quantitative reaction (t.l.c.), the mixture was filtered and the solvent was evaporated. The following compounds were prepared in this way.

1-*O*-Acetyl-2-deoxy-2-fluoro-5,6-*O*-isopropylidene-α-D-glucofuranose (**16**), isolated as a syrup, $[\alpha]_D^{20}$ +36° (*c* 1.8, chloroform), R_F (ethyl acetate–cyclohexane, 1:1) 0.48.

Anal. Calc. for $C_{11}H_{17}FO_6$: C, 50.00; H, 6.48. Found: C, 49.74; H, 6.39.

1-*O*-Acetyl-2-deoxy-2-fluoro-5-*O*-methoxymethyl-β-D-arabinofuranose (**21**), isolated as a syrup, $[\alpha]_D^{20}$ −43.5° (*c* 0.8, chloroform), R_F (ethyl acetate–cyclohexane, 1:2) 0.49.

Anal. Calc. for $C_9H_{15}FO_6$: C, 45.38; H, 6.35. Found: C, 45.30; H, 6.28.

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