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#### Key indicators

Single-crystal X-ray study  
 T = 150 K  
 Mean  $\sigma(\text{C}-\text{C}) = 0.002 \text{ \AA}$   
 R factor = 0.030  
 wR factor = 0.098  
 Data-to-parameter ratio = 9.6

For details of how these key indicators were  
 automatically derived from the article, see  
<http://journals.iucr.org/e>.

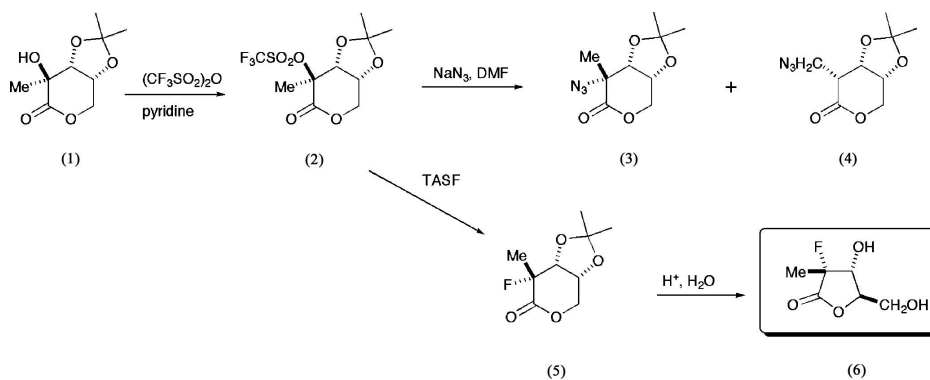
## 2-Deoxy-2-fluoro-2-C-methyl-D-ribo- 1,4-lactone (fluoromethylrib)

The relative stereochemistry of the fluoro substituent (as *ribo*) and the ring size of the lactone (as five) in the title compound,  $\text{C}_6\text{H}_9\text{FO}_4$ , have been established by X-ray crystallographic analysis.

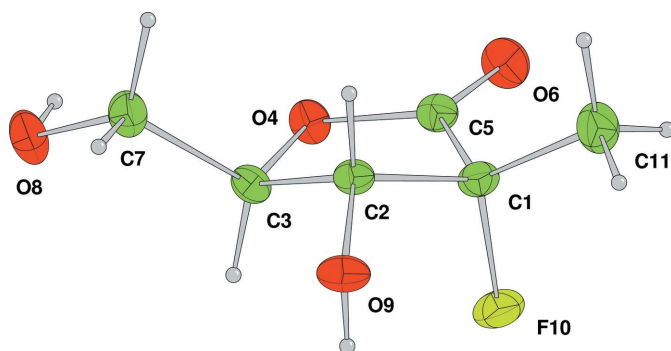
Received 7 February 2006  
 Accepted 20 February 2006

### Comment

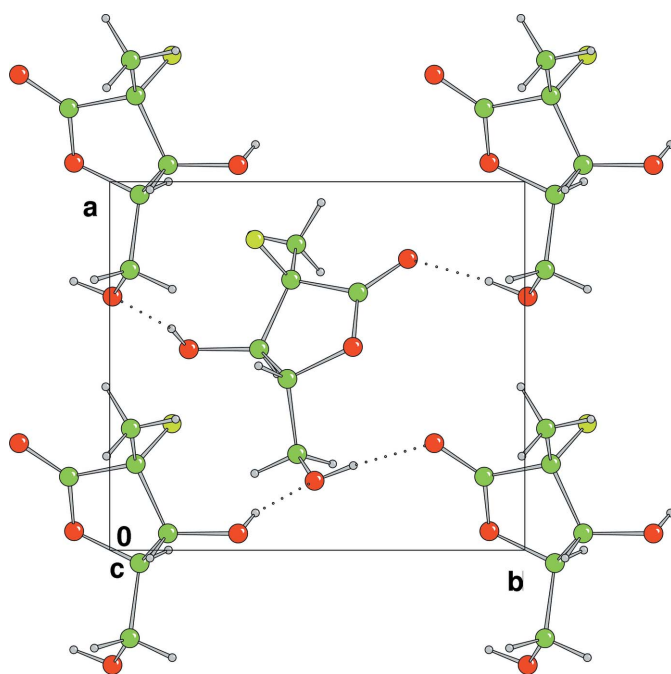
Until recently, carbohydrate building blocks with branched carbon chains have not been readily available in large quantities (Bols, 1996; Lichtenthaler & Peters, 2004). The Kiliani reaction of ketoses with cyanide, followed by acetonation (Hotchkiss *et al.*, 2004; Soengas *et al.*, 2005), provides access to a novel class of carbohydrate scaffold which contains a branched hydroxymethyl carbon chain. Branched sugars bearing a C-2 alkyl group are also available from the Kiliani reaction of cyanide with 1-deoxyketoses, themselves prepared by addition of organometallic reagents to sugar lactones. Thus, reaction of cyanide with a protected 1-deoxy-D-ribose afforded the isopropylidene derivative of arabinono-1,5-lactone (1) (Hotchkiss *et al.*, 2006), shown to crystallize in a boat conformation (Punzo, Watkin, Jenkinson & Fleet, 2005).



Protected sugar lactones such as (1) allow modification of the tertiary alcohol group to introduce other functional groups at the quaternary centre; hitherto, there have been very few strategies for the synthesis of branched carbohydrates with a non-oxygen functional group at a quaternary position. Esterification of the free hydroxyl group in (1) with triflic anhydride in pyridine afforded the trifluoromethanesulfonate (2). Reaction of (2) with sodium azide in dimethylformamide gave the *ribo*-azide (3) as the major product in good yield, even though the overall reaction is a nucleophilic displacement at a very hindered position; this reaction is very unlikely to be an  $\text{S}_{\text{N}}2$  reaction, so the stereochemistry at C-2 of the azide (3) was established by X-ray crystallographic analysis (Punzo, Watkin, Jenkinson, Cruz & Fleet, 2005), showing that the reaction



**Figure 1**  
The molecular structure of the title compound, with displacement ellipsoids drawn at the 50% probability level. H atoms are shown as spheres of arbitrary radius.



**Figure 2**  
A *c*-axis projection. The molecules are linked by hydrogen bonds (dashed lines) into pleated sheets perpendicular to *c*.

proceeded with inversion of configuration to give the ribonolactone (3) in a boat conformation with the C-2 methyl group in a hindered flagpole position. A minor product was also formed during the azide displacement reaction and was proven by X-ray analysis to have the *ribo*-configuration (4) (Punzo *et al.*, 2006). It is noteworthy that the 1,5-lactones (1), (3) and (4) all adopt a boat conformation in the solid state.

When the trifluoromethanesulfonate (2) was treated with tris(dimethylamino)sulfur trimethylsilyl difluoride – an excellent source of nucleophilic fluoride – fluorolactone (5) was isolated as the major product. Removal of the isopropylidene protecting group by treatment with aqueous acid gave the title unprotected fluorolactone, (6). The crystal structure reported in this paper (Fig. 1) establishes the relative *ribo*-stereochemistry in both (5) and (6), and also shows that deprotection of the ketal (5) is accompanied by contraction of

the six-ring lactone in (5) to give a five-ring lactone in (6). The quaternary fluoride (6) is likely to be a powerful intermediate for the synthesis of a novel class of carbohydrate in which a F atom is attached to a quaternary centre. The absolute configuration of (6) was established by the use of D-erythrulactone as the starting material for the preparation of (1).

The crystal structure consists of pleated sheets lying perpendicular to *c*, with molecules linked by hydrogen bonds (Fig. 2). There is a short contact between adjacent sheets [ $2.86 \text{ \AA}$  for  $\text{O9} \cdots \text{C5}(\frac{1}{2} + x, \frac{1}{2} - y, 1 - z)$ ].

## Experimental

The fluorolactone (6) (Mayes *et al.*, 2006) was crystallized from ethyl acetate:heptane (8:1), m.p. 415–416 K;  $[\alpha]_{20}^D +129.3^\circ$  ( $c = 0.9$  in  $\text{CH}_3\text{CN}$ ).

### Crystal data

$\text{C}_6\text{H}_9\text{FO}_4$   
 $M_r = 164.13$   
 Orthorhombic,  $P2_12_12_1$   
 $a = 7.3570$  (2)  $\text{\AA}$   
 $b = 8.2864$  (2)  $\text{\AA}$   
 $c = 11.7886$  (3)  $\text{\AA}$   
 $V = 718.67$  (3)  $\text{\AA}^3$   
 $Z = 4$   
 $D_x = 1.517 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation  
 Cell parameters from 900 reflections  
 $\theta = 1\text{--}27^\circ$   
 $\mu = 0.14 \text{ mm}^{-1}$   
 $T = 150 \text{ K}$   
 Block, colourless  
 $0.60 \times 0.40 \times 0.40 \text{ mm}$

### Data collection

Nonius KappaCCD diffractometer  
 $\omega$  scans  
 Absorption correction: multi-scan  
 (DENZO/SCALEPACK;  
 Otwinowski & Minor, 1997)  
 $T_{\min} = 0.64$ ,  $T_{\max} = 0.94$   
 1612 measured reflections

964 independent reflections  
 958 reflections with  $I > -3\sigma(I)$   
 $R_{\text{int}} = 0.008$   
 $\theta_{\max} = 27.5^\circ$   
 $h = -9 \rightarrow 9$   
 $k = -10 \rightarrow 10$   
 $l = -14 \rightarrow 14$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.030$   
 $wR(F^2) = 0.098$   
 $S = 0.91$   
 958 reflections  
 100 parameters

H-atom parameters constrained  
 $w = 1/[\sigma^2(F^2) + (0.1P)^2]$   
 where  $P = [\text{max}(F_o^2, 0) + 2F_c^2]/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.22 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.18 \text{ e \AA}^{-3}$

**Table 1**

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D\text{--}H \cdots A$	$D\text{--}H$	$H \cdots A$	$D \cdots A$	$D\text{--}H \cdots A$
$\text{O9--H6} \cdots \text{O8}^i$	0.82	1.90	2.701 (2)	165
$\text{O8--H7} \cdots \text{O6}^ii$	0.84	2.01	2.804 (2)	157

Symmetry codes: (i)  $x - \frac{1}{2}, -y - \frac{1}{2}, -z + 2$ ; (ii)  $x + \frac{1}{2}, -y + \frac{1}{2}, -z + 2$ .

The H atoms were all located in a difference map, but those attached to C atoms were repositioned geometrically. The H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C–H in the range 0.93–0.98, O–H = 0.82  $\text{\AA}$ ) and  $U_{\text{iso}}(\text{H})$  (in the range 1.2–1.5 times  $U_{\text{eq}}$  of the parent atom), after which the positions were refined with riding constraints.

Data collection: COLLECT (Nonius, 2001); cell refinement: DENZO/SCALEPACK (Otwinowski & Minor, 1997); data reduction: DENZO/SCALEPACK; program(s) used to solve structure:

SIR92 (Altomare *et al.*, 1994); program(s) used to refine structure: CRYSTALS (Betteridge *et al.*, 2003); molecular graphics: CAMERON (Watkin *et al.*, 1996); software used to prepare material for publication: CRYSTALS.

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## supporting information

*Acta Cryst.* (2006). E62, o1208–o1210 [https://doi.org/10.1107/S1600536806006337]

## 2-Deoxy-2-fluoro-2-C-methyl-D-ribo-1,4-lactone (fluoromethylrib)

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#### Crystal data

$C_6H_9FO_4$

$M_r = 164.13$

Orthorhombic,  $P2_12_12_1$

$a = 7.3570$  (2) Å

$b = 8.2864$  (2) Å

$c = 11.7886$  (3) Å

$V = 718.67$  (3) Å<sup>3</sup>

$Z = 4$

$F(000) = 344$

$D_x = 1.517$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 900 reflections

$\theta = 1\text{--}27^\circ$

$\mu = 0.14$  mm<sup>-1</sup>

$T = 150$  K

Block, colourless

$0.60 \times 0.40 \times 0.40$  mm

#### Data collection

Nonius KappaCCD  
diffractometer

Graphite monochromator

$\omega$  scans

Absorption correction: multi-scan

(DENZO/SCALEPACK; Otwinowski & Minor,  
1997)

$T_{\min} = 0.64$ ,  $T_{\max} = 0.94$

1612 measured reflections

964 independent reflections

958 reflections with  $I > -3\sigma(I)$

$R_{\text{int}} = 0.008$

$\theta_{\max} = 27.5^\circ$ ,  $\theta_{\min} = 3.0^\circ$

$h = -9 \rightarrow 9$

$k = -10 \rightarrow 10$

$l = -14 \rightarrow 14$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.030$

$wR(F^2) = 0.098$

$S = 0.91$

958 reflections

100 parameters

0 restraints

Primary atom site location: structure-invariant  
direct methods

Hydrogen site location: inferred from  
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F^2) + (0.1P)^2]$

where  $P = [\max(F_o^2, 0) + 2F_c^2]/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.22$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.18$  e Å<sup>-3</sup>

#### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å<sup>2</sup>)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.26615 (19)	-0.06271 (16)	0.80936 (11)	0.0189
C2	0.45465 (18)	-0.13941 (14)	0.81193 (11)	0.0165
C3	0.53478 (17)	-0.07250 (16)	0.92219 (11)	0.0174

O4	0.44849 (12)	0.08566 (11)	0.93581 (9)	0.0193
C5	0.30033 (19)	0.09816 (14)	0.87060 (11)	0.0184
O6	0.20970 (13)	0.21809 (11)	0.86637 (9)	0.0266
C7	0.7384 (2)	-0.04800 (18)	0.91928 (13)	0.0223
O8	0.81162 (14)	-0.00656 (11)	1.02682 (10)	0.0284
O9	0.45498 (14)	-0.30961 (9)	0.80642 (8)	0.0214
F10	0.15671 (11)	-0.15009 (10)	0.88691 (8)	0.0270
C11	0.1703 (2)	-0.05096 (18)	0.69793 (13)	0.0289
H21	0.5219	-0.0960	0.7483	0.0171*
H31	0.4997	-0.1418	0.9867	0.0184*
H71	0.7913	-0.1502	0.8971	0.0248*
H72	0.7657	0.0375	0.8615	0.0253*
H111	0.0568	0.0094	0.7100	0.0416*
H6	0.3993	-0.3510	0.8589	0.0318*
H7	0.7703	0.0866	1.0403	0.0405*
H1	0.1448	-0.1591	0.6721	0.0420*
H2	0.2452	0.0073	0.6451	0.0406*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.0190 (7)	0.0156 (5)	0.0222 (7)	-0.0029 (5)	0.0005 (5)	0.0018 (5)
C2	0.0179 (7)	0.0144 (5)	0.0172 (6)	-0.0005 (5)	0.0018 (5)	0.0002 (4)
C3	0.0202 (6)	0.0129 (5)	0.0192 (6)	0.0046 (5)	-0.0004 (5)	0.0008 (5)
O4	0.0221 (5)	0.0150 (4)	0.0209 (5)	0.0043 (4)	-0.0017 (4)	-0.0037 (4)
C5	0.0193 (6)	0.0169 (6)	0.0189 (7)	-0.0003 (5)	0.0023 (5)	0.0007 (5)
O6	0.0258 (6)	0.0207 (5)	0.0333 (7)	0.0078 (4)	0.0012 (5)	-0.0014 (4)
C7	0.0197 (6)	0.0229 (6)	0.0244 (8)	0.0022 (5)	-0.0035 (5)	-0.0001 (5)
O8	0.0311 (5)	0.0206 (4)	0.0334 (6)	0.0043 (4)	-0.0154 (5)	-0.0012 (4)
O9	0.0281 (6)	0.0128 (4)	0.0231 (5)	0.0017 (4)	0.0076 (4)	-0.0012 (4)
F10	0.0202 (4)	0.0260 (5)	0.0347 (5)	-0.0024 (4)	0.0068 (4)	0.0059 (4)
C11	0.0315 (8)	0.0240 (7)	0.0313 (9)	-0.0023 (7)	-0.0107 (7)	0.0007 (6)

*Geometric parameters (Å, °)*

C1—C2	1.5258 (19)	O4—C5	1.3378 (16)
C1—C5	1.5367 (17)	C5—O6	1.1978 (17)
C1—F10	1.4171 (15)	C7—O8	1.4195 (18)
C1—C11	1.4941 (17)	C7—H71	0.968
C2—C3	1.5311 (18)	C7—H72	1.003
C2—O9	1.4118 (13)	O8—H7	0.845
C2—H21	0.968	O9—H6	0.818
C3—O4	1.4651 (16)	C11—H111	0.984
C3—C7	1.512 (2)	C11—H1	0.964
C3—H31	0.987	C11—H2	0.961
C2—C1—C5	101.73 (10)	C3—O4—C5	111.06 (10)
C2—C1—F10	106.90 (10)	C1—C5—O4	109.64 (10)

C5—C1—F10	103.48 (10)	C1—C5—O6	127.52 (12)
C2—C1—C11	118.26 (12)	O4—C5—O6	122.80 (12)
C5—C1—C11	115.71 (11)	C3—C7—O8	112.83 (12)
F10—C1—C11	109.41 (11)	C3—C7—H71	106.7
C1—C2—C3	102.47 (10)	O8—C7—H71	107.5
C1—C2—O9	114.63 (11)	C3—C7—H72	107.9
C3—C2—O9	113.59 (11)	O8—C7—H72	111.1
C1—C2—H21	107.1	H71—C7—H72	110.8
C3—C2—H21	109.1	C7—O8—H7	104.6
O9—C2—H21	109.5	C2—O9—H6	112.5
C2—C3—O4	104.49 (10)	C1—C11—H111	107.9
C2—C3—C7	114.26 (12)	C1—C11—H1	108.0
O4—C3—C7	108.16 (11)	H111—C11—H1	110.7
C2—C3—H31	110.1	C1—C11—H2	109.4
O4—C3—H31	108.8	H111—C11—H2	108.9
C7—C3—H31	110.8	H1—C11—H2	112.0

*Hydrogen-bond geometry (Å, °)*

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
O9—H6 $\cdots$ O8 <sup>i</sup>	0.82	1.90	2.701 (2)	165
O8—H7 $\cdots$ O6 <sup>ii</sup>	0.84	2.01	2.804 (2)	157

Symmetry codes: (i)  $x-1/2, -y-1/2, -z+2$ ; (ii)  $x+1/2, -y+1/2, -z+2$ .