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(2*R*,3*R*,4*R*)-Methyl 2-bromo-3,4-dihydroxy-3,4-*O*-isopropylidenetetrahydrofuran-2-carboxylate

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Key indicators

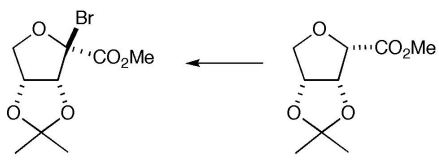
Single-crystal X-ray study
T = 190 K
Mean σ(C–C) = 0.006 Å
R factor = 0.050
wR factor = 0.097
Data-to-parameter ratio = 18.2

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

The relative configuration of the quaternary C atom in the title bromide, $C_9H_{13}BrO_5$, prepared by bromination of the parent ester, has been determined by X-ray crystallographic analysis; the absolute configuration is known from the synthesis.

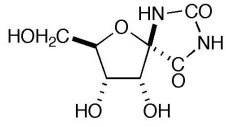
Comment

The bromination of tetrahydrofuran (THF) carboxylic acid esters to give α-bromoesters (Smith *et al.*, 1999) is a key step in the synthesis of anomeric α-sugar amino acids (Estevez, Estevez *et al.*, 1994; Estevez, Ardron *et al.*, 1994). Such intermediates have also been used in the synthesis of biologically active spirohydantoins, such as the herbicide hydantocidin (3) (Fairbanks & Fleet, 1995; Fairbanks *et al.* 1993) and a powerful glycogen phosphorylase inhibitor (4) (Bichard *et al.*, 1995; Krulle *et al.*, 1997).

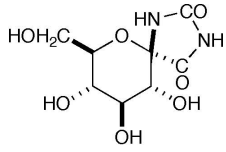


(1)

(2)



(3)



(4)

In a programme directed towards the synthesis of novel nucleosides of erythrose bearing a carbon substituent at the anomeric position, the protected THF ester (2) (Sanjayan *et al.*, 2003) was treated with *N*-bromosuccinimide in trichloroethane in the presence of benzoyl peroxide; a single crystalline bromide was formed in 72% isolated yield. There is no reliable spectroscopic technique available in this case to allow the assignment of configuration of the quaternary C atom; X-ray crystallography firmly established the structure of the bromide as the β-anomer (1). The absolute configuration of (1) is determined by the use of D-ribose as the starting material for the synthesis.

The slightly large displacement parameters for atoms Br1, O3, O7, O9, C14 and C15 could be explained in terms of flexing of the two five-membered rings. Concerted rocking of the whole molecule is unlikely (R_{TLS} = 0.334). The crystal packing is unexceptional, apart from a short Br1···H152^{i} contact of 2.92 Å [symmetry code: (i) $-x+1, y+\frac{1}{2}, -z+\frac{1}{2}$].

Experimental

The title compound was crystallized from ethyl acetate/hexane. Full details of the synthesis will be published separately (Stewart *et al.*, 2005).

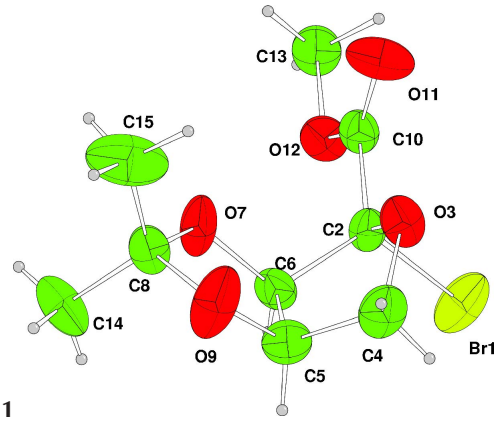


Figure 1
The molecular structure of the title compound, with displacement ellipsoids drawn at the 50% probability level and H atoms with arbitrary radii.

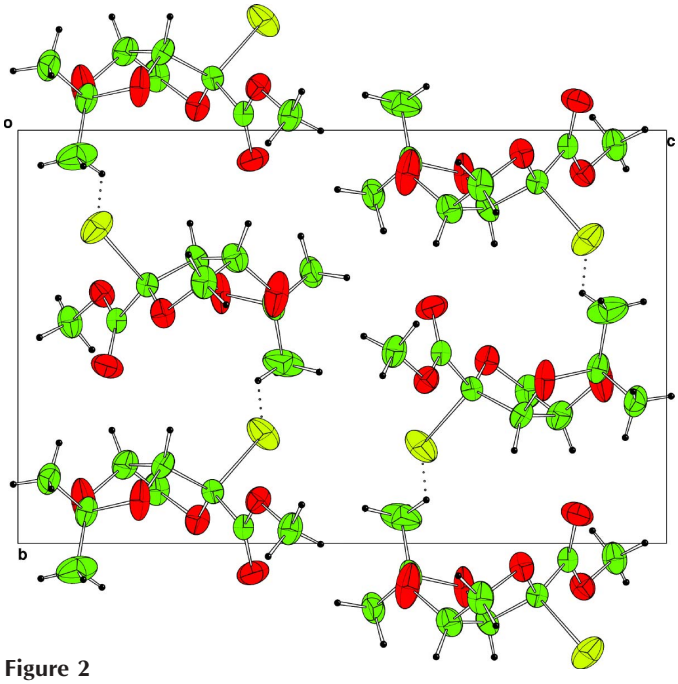


Figure 2
Packing diagram of the title structure, viewed parallel to the *a* axis. The short Br1···H152^{i} contact [symmetry code: (i) $-x+1, y+\frac{1}{2}, -z+\frac{1}{2}$] is shown as a dotted line.

Crystal data

$C_9H_{13}BrO_5$
M_r = 281.10
Orthorhombic, $P2_12_12_1$
a = 6.6195 (2) Å
b = 10.4127 (3) Å
c = 16.3294 (7) Å
V = 1125.53 (7) Å^3
Z = 4
D_x = 1.659 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1434 reflections
θ = 5–27°
μ = 3.65 mm^{-1}
T = 190 K
Plate, colourless
0.40 × 0.30 × 0.10 mm

Data collection

Nonius KappaCCD diffractometer
ω scans
Absorption correction: multi-scan (*DENZO*/*SCALEPACK*; Otwinowski & Minor, 1997)
T_{min} = 0.30, T_{max} = 0.69
8664 measured reflections
2490 independent reflections
2490 reflections with $I > -3\sigma(I)$
R_{int} = 0.051
θ_{max} = 27.5°
$h = -8 \rightarrow 8$
$k = -13 \rightarrow 13$
$l = -20 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.097
S = 0.97
2490 reflections
137 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F^2) + 0.02 + 2.65P]$ where $P = [\max(F_o^2,0) + 2F_c^2]/3$
$(\Delta/\sigma)_{max}$ = 0.005
$\Delta\rho_{max}$ = 0.63 e Å^{-3}
$\Delta\rho_{min}$ = −0.62 e Å^{-3}
Absolute structure: Flack (1983), 902 Friedel pairs
Flack parameter: 0.049 (17)

Table 1
Selected geometric parameters (Å, °).

Br1—C2	2.007 (4)	C6—O7	1.409 (5)
C2—O3	1.368 (4)	O7—C8	1.430 (5)
C2—C6	1.530 (5)	C8—O9	1.417 (5)
C2—C10	1.517 (5)	C8—C14	1.483 (6)
O3—C4	1.451 (5)	C8—C15	1.491 (7)
C4—C5	1.503 (6)	C10—O11	1.189 (5)
C5—C6	1.530 (6)	C10—O12	1.330 (5)
C5—O9	1.433 (5)	O12—C13	1.444 (5)
Br1—C2—O3	109.4 (2)	C2—C6—O7	108.3 (3)
Br1—C2—C6	107.9 (3)	C6—O7—C8	109.8 (3)
O3—C2—C6	107.3 (3)	O7—C8—O9	106.1 (3)
Br1—C2—C10	106.1 (2)	O7—C8—C14	109.7 (4)
O3—C2—C10	109.6 (3)	O9—C8—C14	112.2 (4)
C6—C2—C10	116.3 (3)	O7—C8—C15	109.0 (4)
C2—O3—C4	106.5 (3)	O9—C8—C15	107.1 (4)
O3—C4—C5	104.7 (3)	C14—C8—C15	112.5 (5)
C4—C5—C6	105.0 (3)	C5—O9—C8	108.7 (3)
C4—C5—O9	107.6 (4)	C2—C10—O11	124.6 (4)
C6—C5—O9	105.3 (3)	C2—C10—O12	110.3 (3)
C5—C6—C2	102.8 (3)	O11—C10—O12	125.0 (4)
C5—C6—O7	105.1 (3)	C10—O12—C13	116.4 (3)

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 0.93–98 Å), with U_{iso}(H) in the range 1.2–1.5 times U_{eq}(C), after which they 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. (2005). E**61**, o1718–o1720 [https://doi.org/10.1107/S1600536805014467]

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$c = 16.3294$ (7) Å
$V = 1125.53$ (7) Å^3
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$F(000) = 568$
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Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 1434 reflections
$\theta = 5$–27°
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$\theta_{max} = 27.5°$, $\theta_{min} = 5.2°$
$h = -8 \rightarrow 8$
$k = -13 \rightarrow 13$
$l = -20 \rightarrow 21$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.097$
$S = 0.97$
2490 reflections
137 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F^2) + 0.02 + 2.65P]$ where $P = (\max(F_o^2,0) + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.005$
$\Delta\rho_{max} = 0.63$ e Å^{-3}
$\Delta\rho_{min} = -0.62$ e Å^{-3}
Absolute structure: Flack (1983), 902 Friedel pairs
Absolute structure parameter: 0.049 (17)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.40041 (8)	0.26467 (5)	0.87830 (3)	0.0666
C2	0.3161 (6)	0.1256 (4)	0.8004 (2)	0.0334

O3	0.4825 (4)	0.0570 (3)	0.77676 (17)	0.0449
C4	0.5809 (7)	0.1316 (5)	0.7132 (3)	0.0516
C5	0.4105 (7)	0.1904 (4)	0.6652 (3)	0.0484
C6	0.2299 (6)	0.1897 (4)	0.7237 (2)	0.0397
O7	0.0891 (5)	0.1051 (4)	0.68791 (16)	0.0564
C8	0.1484 (6)	0.0765 (4)	0.6057 (2)	0.0414
O9	0.3581 (5)	0.1025 (5)	0.6012 (2)	0.0746
C10	0.1732 (6)	0.0392 (4)	0.8477 (2)	0.0358
O11	0.2036 (6)	−0.0710 (3)	0.8622 (2)	0.0615
O12	0.0096 (4)	0.1043 (3)	0.87037 (19)	0.0429
C13	−0.1357 (7)	0.0355 (5)	0.9197 (3)	0.0509
C14	0.0299 (9)	0.1562 (5)	0.5478 (3)	0.0605
C15	0.1220 (12)	−0.0637 (5)	0.5908 (4)	0.0836
H41	0.6604	0.1987	0.7370	0.0711*
H42	0.6639	0.0779	0.6791	0.0705*
H51	0.4451	0.2740	0.6450	0.0670*
H61	0.1786	0.2747	0.7346	0.0558*
H131	−0.2400	0.0937	0.9376	0.0930*
H132	−0.0653	−0.0017	0.9667	0.0928*
H133	−0.1956	−0.0312	0.8859	0.0925*
H141	0.0810	0.1434	0.4929	0.1087*
H142	0.0452	0.2435	0.5636	0.1090*
H143	−0.1104	0.1323	0.5512	0.1090*
H151	0.1609	−0.0850	0.5356	0.1530*
H152	0.2099	−0.1056	0.6296	0.1529*
H153	−0.0182	−0.0870	0.6009	0.1525*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0606 (3)	0.0705 (3)	0.0688 (3)	−0.0177 (3)	−0.0020 (3)	−0.0282 (3)
C2	0.0279 (17)	0.039 (2)	0.0328 (18)	0.0008 (15)	−0.0013 (15)	−0.0015 (16)
O3	0.0349 (14)	0.0595 (18)	0.0404 (15)	0.0086 (13)	0.0038 (12)	0.0044 (14)
C4	0.035 (2)	0.074 (3)	0.047 (2)	−0.009 (2)	0.009 (2)	0.000 (2)
C5	0.042 (2)	0.057 (2)	0.046 (2)	−0.009 (2)	0.008 (2)	0.0081 (19)
C6	0.035 (2)	0.048 (2)	0.036 (2)	−0.0019 (17)	0.0014 (16)	0.0114 (17)
O7	0.0287 (14)	0.112 (3)	0.0281 (13)	−0.0181 (18)	−0.0001 (12)	0.0057 (15)
C8	0.0295 (19)	0.061 (2)	0.033 (2)	0.0020 (17)	0.0039 (15)	0.0075 (17)
O9	0.0402 (18)	0.142 (4)	0.0415 (18)	−0.029 (2)	0.0120 (14)	−0.018 (2)
C10	0.0373 (19)	0.042 (2)	0.0276 (18)	−0.0001 (17)	0.0006 (15)	0.0000 (15)
O11	0.077 (2)	0.0389 (17)	0.068 (2)	0.0101 (15)	0.025 (2)	0.0120 (16)
O12	0.0361 (14)	0.0498 (15)	0.0427 (15)	0.0026 (12)	0.0082 (13)	0.0060 (14)
C13	0.043 (3)	0.069 (3)	0.040 (2)	−0.007 (2)	0.008 (2)	0.007 (2)
C14	0.081 (4)	0.065 (3)	0.035 (2)	0.027 (3)	−0.002 (2)	0.007 (2)
C15	0.086 (4)	0.051 (3)	0.115 (5)	0.020 (3)	0.040 (4)	0.016 (3)

Geometric parameters (Å, º)

Br1—C2	2.007 (4)	C8—C14	1.483 (6)
C2—O3	1.368 (4)	C8—C15	1.491 (7)
C2—C6	1.530 (5)	C10—O11	1.189 (5)
C2—C10	1.517 (5)	C10—O12	1.330 (5)
O3—C4	1.451 (5)	O12—C13	1.444 (5)
C4—C5	1.503 (6)	C13—H131	0.964
C4—H41	0.957	C13—H132	0.977
C4—H42	0.962	C13—H133	0.972
C5—C6	1.530 (6)	C14—H141	0.967
C5—O9	1.433 (5)	C14—H142	0.951
C5—H51	0.959	C14—H143	0.963
C6—O7	1.409 (5)	C15—H151	0.964
C6—H61	0.964	C15—H152	0.964
O7—C8	1.430 (5)	C15—H153	0.973
C8—O9	1.417 (5)		
Br1—C2—O3	109.4 (2)	O9—C8—C14	112.2 (4)
Br1—C2—C6	107.9 (3)	O7—C8—C15	109.0 (4)
O3—C2—C6	107.3 (3)	O9—C8—C15	107.1 (4)
Br1—C2—C10	106.1 (2)	C14—C8—C15	112.5 (5)
O3—C2—C10	109.6 (3)	C5—O9—C8	108.7 (3)
C6—C2—C10	116.3 (3)	C2—C10—O11	124.6 (4)
C2—O3—C4	106.5 (3)	C2—C10—O12	110.3 (3)
O3—C4—C5	104.7 (3)	O11—C10—O12	125.0 (4)
O3—C4—H41	110.3	C10—O12—C13	116.4 (3)
C5—C4—H41	109.1	O12—C13—H131	109.6
O3—C4—H42	111.0	O12—C13—H132	108.4
C5—C4—H42	111.3	H131—C13—H132	110.7
H41—C4—H42	110.2	O12—C13—H133	108.0
C4—C5—C6	105.0 (3)	H131—C13—H133	109.2
C4—C5—O9	107.6 (4)	H132—C13—H133	110.9
C6—C5—O9	105.3 (3)	C8—C14—H141	109.2
C4—C5—H51	111.7	C8—C14—H142	107.8
C6—C5—H51	113.9	H141—C14—H142	110.3
O9—C5—H51	112.8	C8—C14—H143	109.1
C5—C6—C2	102.8 (3)	H141—C14—H143	110.9
C5—C6—O7	105.1 (3)	H142—C14—H143	109.5
C2—C6—O7	108.3 (3)	C8—C15—H151	110.3
C5—C6—H61	112.7	C8—C15—H152	105.4
C2—C6—H61	112.4	H151—C15—H152	110.5
O7—C6—H61	114.7	C8—C15—H153	109.1
C6—O7—C8	109.8 (3)	H151—C15—H153	110.9
O7—C8—O9	106.1 (3)	H152—C15—H153	110.6
O7—C8—C14	109.7 (4)		