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Key indicators

Single-crystal X-ray study
 $T = 190$ K
Mean $\sigma(C-C) = 0.006$ 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>.

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

The relative configuration of the quaternary C atom in the title bromide, C₉H₁₃BrO₅, prepared by bromination of the parent ester, has been determined by X-ray crystallographic analysis; the absolute configuration is known from the synthesis.

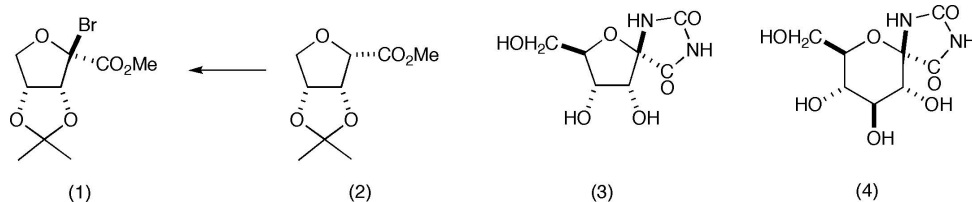
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Comment

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 spirohydantoin, 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).



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...H15ⁱ 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).

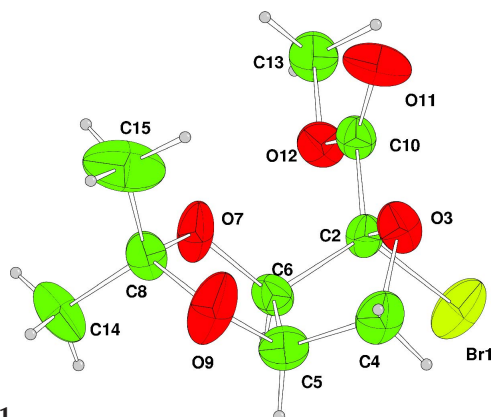


Figure 1
The molecular structure of the title compound, with displacement ellipsoids drawn at the 50% probability level and H atoms with arbitrary radii.

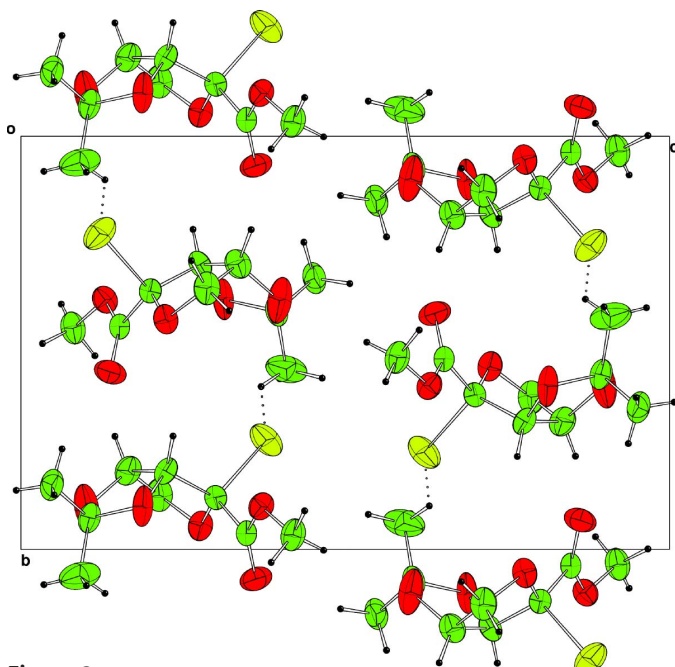


Figure 2
Packing diagram of the title structure, viewed parallel to the *a* axis. The short Br1...H152ⁱ contact [symmetry code: (i) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$] is shown as a dotted line.

Crystal data

$C_9H_{13}BrO_5$
 $M_r = 281.10$
Orthorhombic, $P2_12_1$
 $a = 6.6195$ (2) Å
 $b = 10.4127$ (3) Å
 $c = 16.3294$ (7) Å
 $V = 1125.53$ (7) Å³
 $Z = 4$
 $D_x = 1.659$ Mg m⁻³

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

Mo $K\alpha$ radiation
Cell parameters from 1434 reflections
 $\theta = 5-27^\circ$
 $\mu = 3.65$ mm⁻¹
 $T = 190$ K
Plate, colourless
 $0.40 \times 0.30 \times 0.10$ mm

2490 independent reflections
2490 reflections with $I > -3\sigma(I)$
 $R_{\text{int}} = 0.051$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = -8 \rightarrow 8$
 $k = -13 \rightarrow 13$
 $l = -20 \rightarrow 21$

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 $P = [\max(F_o^2, 0) + 2F_c^2]/3$
 $(\Delta/\sigma)_{\text{max}} = 0.005$
 $\Delta\rho_{\text{max}} = 0.63$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.62$ 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 0.93–0.98 Å), with $U_{\text{iso}}(\text{H})$ in the range 1.2–1.5 times $U_{\text{eq}}(\text{C})$, 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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