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3,4:5,6-Di-*O*-isopropylidene-3-*C*-hydroxymethyl-D-altrono-1,3′-lactone

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Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.003 Å
R factor = 0.029
wR factor = 0.070
Data-to-parameter ratio = 8.2

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

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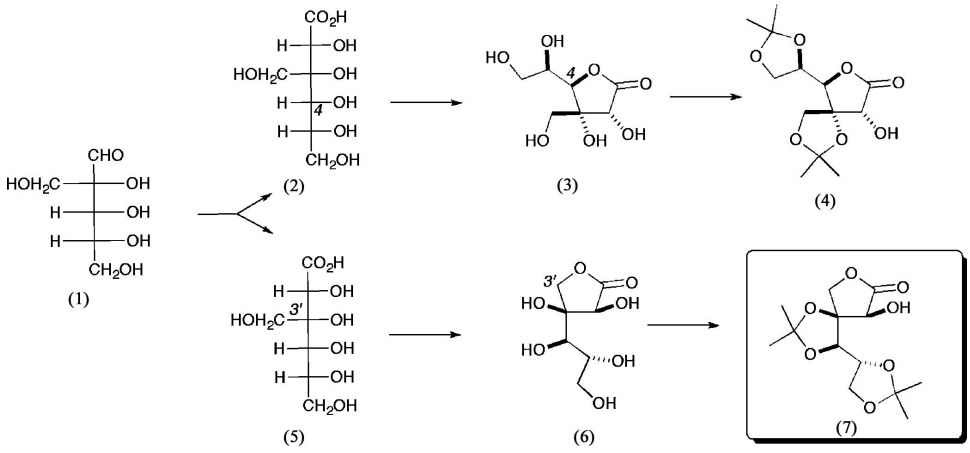
The title compound, $C_{13}H_{20}O_7$, a rare example of a sugar with a carbon branch at C-3, is one of the major products isolated from the treatment of D-hamamelose with cyanide (the Kiliani reaction), followed by protection as a diacetonide. The material crystallizes with two molecules in the asymmetric unit, related to each other by a non-crystallographic twofold axis.

Comment

The value of the Kiliani reaction of cyanide with ketoses (Hotchkiss *et al.*, 2004; Soengas *et al.*, 2005) and 1-deoxyketoses (Hotchkiss *et al.*, 2006) has been recognized for the easy synthesis of carbohydrate scaffolds with branched carbon chains at C-2 of the sugar. Such branched sugars are powerful intermediates for the synthesis of enantiomerically pure bioactive compounds (Simone *et al.*, 2005).



Examples of carbohydrates with a carbon branch at C-3 are very rare, although the synthesis of a crystalline derivative of 3-*C*-methyl-D-lyxono-1,4-lactone from the Kiliani reaction on 2-*C*-methyl-D-threose has been reported (Bream *et al.*, 2006). This paper reports a short synthesis of two carbohydrates with a branch at C-3 of a hexose from the Kiliani reaction of D-hamamelose, (1), which may be prepared in two steps from D-ribose (Ho, 1978; Hricoviniova-Bilikovaa *et al.*, 1999; Hricoviniova *et al.*, 2005). Thus, treatment of (1) with sodium cyanide in water gives a mixture of the diastereomeric 3-*C*-hydroxymethylhexonic acids, (2) and (5). Treatment of the crude reaction mixture of (2) and (5) with acid in dimethoxypropane induces cyclization to the respective lactones, (3) and (6), together with subsequent formation of the diacetonides, (4) and (7); experimental details for the procedure are given below.

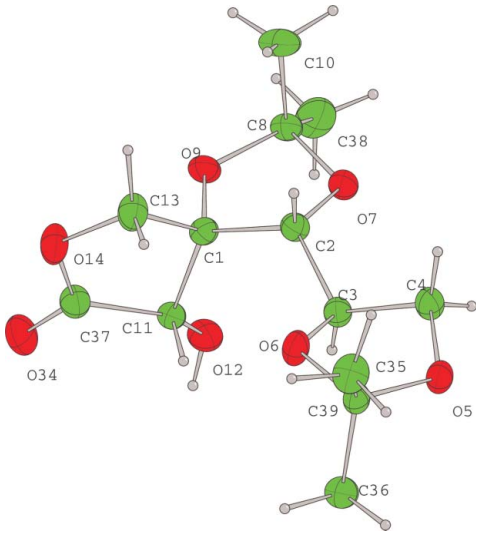


Figure 1
One of the two independent molecules of the title compound, with displacement ellipsoids drawn at the 50% probability level. H atoms are shown as spheres of arbitary radii. The second molecule has a similar geometry and is numbered by adding 100 to equivalent atoms in the first molecule.

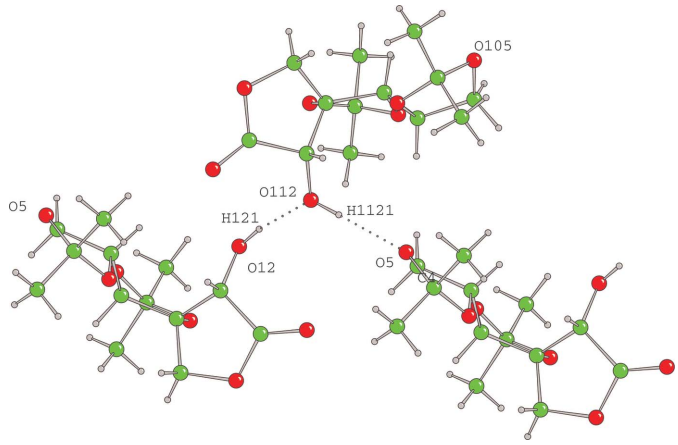


Figure 2
Part of the hydrogen-bonding network, showing the formation of columns, two molecules wide, linking the two independent molecules. Hydrogen bonds are shown as dotted lines. The columns run parallel to the *b* axis and there are no interactions between columns. Note that atom O5 is involved in the hydrogen bonding but atom O105 is not.

The possible combinations for the formation of different diacetonides from acids (2) and (5) are numerous. Thus, it is seen that 1,4-lactones can be formed from either the C-4 hydroxyl group of the sugar [to give (3)] or the C-3′ hydroxyl group [to give (6)], and from each of these products several different diacetonides may arise. Only X-ray crystallographic analysis can resolve the structural ambiguities that arise in this reaction. This paper firmly identifies the relative configuration of the four stereocentres in the altrono-diacetonide, (7). The absolute configuration of (7) is determined by the use of D-ribose as the starting material for the synthesis. The crystal structure of the allono-lactone, (4), is reported in a subsequent paper (Cowley *et al.*, 2006).

Compound (7) crystallizes with two molecules in the asymmetric unit, related by a well-defined non-crystallographic twofold axis. After mapping the molecules together by least-squares, the r.m.s. positional deviation of the non-H atoms is 0.378 Å, and the r.m.s. deviation in equivalent bond lengths is 0.009 Å. The major difference between the two molecules is at O5 and O105, where the envelope flap is on opposite sides of the plane of the rest of the ring.

The crystal structure of (7) is built up of infinite columns, two molecules wide, connected by hydrogen bonds (Table 1). Note that atom O105 is not involved in the network, and is thus free to adopt a different comformation from O5.

Experimental

The synthesis of 3,4:5,6-di-*O*-isopropylidene-3-*C*-hydroxymethyl-D-altrono-1,3′-lactone, (7), and 3,3′:5,6-di-*O*-isopropylidene-3-*C*-hydroxymethyl-D-allono-1,4-lactone, (4), was carried out as follows. Sodium cyanide (1.04 g, 21.184 mmol) was added to a solution of D-hamamelose, (1) (1.26 g, 7.007 mmol), in water (80 ml). The reaction mixture was stirred at room temperature for 24 h and then heated to reflux for a further 24 h. The solution was then passed through an ion-exchange resin [Amberlite IR-120 (H^+)]. The water was removed *in vacuo* to give a dark-yellow oily residue (1.32 g), which was then treated with dimethoxypropane (18 ml) and *para*-toluenesulfonic acid monohydrate (119 mg, catalyst). The reaction mixture was stirred at room temperature for 36 h, quenched with solid sodium bicarbonate and concentrated *in vacuo*. The residue was partitioned between dichloromethane (200 ml) and water (40 ml). The aqueous phase was washed twice with dichloromethane (2 × 160 ml). The organic layers were combined, dried (magnesium sulfate) and concentrated *in vacuo* to give a residue which was purified by flash chromatography (ethyl acetate-hexane, 1:3 to 1:2 to 1:1) to give 3,4:5,6-di-*O*-isopropylidene-3-*C*-hydroxymethyl-D-altrono-1,3′-lactone, (7) (R_f 0.56) (254 mg), and 3-*C*-hydroxymethyl-3,3′:5,6-di-*O*-isopropylidene-D-allono-1,4-lactone, (4) (R_f 0.44) (251 mg) (25% combined yield, 1.75 mmol). Data for (7): m.p. 321–323 K (dichloromethane–cyclohexane as colourless chunky crystals); *m*/*z* (MS ES$^-$): 287.2 [*M*−H]$^-$, 100%); HRMS (MS ES$^+$), found: 311.1101 [*M*+Na]$^+$; $C_{13}H_{20}NaO_7$ requires 311.1101; $[\alpha]_D^{23}$: 5.8 (*c*, 0.23 in acetone); IR (ν_{max}, thin film, cm^{-1}): 3439 (*br*, OH), 2989 (CH), 1797 (*sh*, C=O); ^{1}H NMR ($CDCl_3$, 400 MHz, δ, p.p.m.): 1.35, 1.43, 1.44, 1.50 [12H, 4*s*, 2 C(CH_3)$_2$], 2.60–2.70 (1H, *br s*, OH2), 3.87 (1H, *d*, $J_{H4,H5}$ = 9.3 Hz, H4), 4.00 (1H, *dd*, $J_{H6,H6'}$ = 9.0 Hz, $J_{H6,H5}$ = 4.4 Hz, H6), 4.21 (1H, *dd*, $J_{H6',H6}$ = 9.0 Hz, $J_{H6',H5}$ = 6.1 Hz, H6′), 4.32 (2H, 2*s*, H3′ and H3″), 4.31–4.39 (1H, *m*, H5), 4.75–4.80 (1H, *br s*, H2); ^{13}C NMR ($CDCl_3$, 100 MHz, δ, p.p.m.): 25.0, 25.4, 26.8, 26.9 [2 C(CH_3)$_2$], 67.9 (C6), 68.5 (C2), 73.1 (C5), 74.3 (C3′), 77.7 (C4), 85.8 (C3), 110.3, 111.1 [2 C(CH_3)$_2$], 174.7 (C=O).

The sample for X-ray crystallographic analysis of (7) was grown by vapour diffusion of cyclohexane into a saturated solution of the material in dichlorormethane until crystals formed. Data for the allono-lactone, (4), are given in Bream *et al.* (2006).

Crystal data

$C_{13}H_{20}O_7$
M_r = 288.30
Monoclinic, $P2_1$
a = 11.5720 (2) Å
b = 9.2793 (2) Å
c = 13.1937 (3) Å
β = 90.5971 (8)°
V = 1416.66 (5) Å^3
Z = 4
D_x = 1.352 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.11 mm^{-1}
T = 150 K
Block, colourless
0.55 × 0.50 × 0.45 mm

Data collection

Nonius KappaCCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*DENZO*/*SCALEPACK*; Otwinowski & Minor, 1997)
T_{min} = 0.73, T_{max} = 0.95
17056 measured reflections
3374 independent reflections
2956 reflections with $I > 3\sigma(I)$
R_{int} = 0.028
θ_{max} = 27.5°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.070
S = 0.97
2956 reflections
361 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F^2) + (0.03P)^2 + 0.33P]$ where $P = [\max(F_o^2,0) + 2F_c^2]/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.19 e Å^{-3}
$\Delta\rho_{min}$ = −0.16 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O12—H121···O112^{i}	0.84	1.98	2.813 (2)	170
O112—H1121···O5^{i}	0.83	1.98	2.806 (2)	169

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

In the absence of significant anomalous scattering, Friedel pairs were merged and the absolute configuration was assigned from the known configuration of the starting materials. The values of T_{min} and T_{max} were computed by the multi-scan inter-frame scaling, and take into account factors other than simple absorption (Görbitz, 1999). 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 and O—H = 0.82 Å) and U_{iso}(H) (in the range 1.2–1.5 times U_{eq} of the parent atom), after which the positions were refined with riding constraints.

Data collection: *COLLECT* (Nonius, 2001); cell refinement: *DENZO*/*SCALEPACK*; data reduction: *DENZO*/*SCALEPACK* (Otwinowski & Minor, 1997); 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

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$\beta = 90.5971$ (8)°
$V = 1416.66$ (5) Å^3
$Z = 4$
$F(000) = 616$
$D_x = 1.352$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2974 reflections
$\theta = 1$–27°
$\mu = 0.11$ mm^{-1}
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Block, colourless
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Graphite monochromator
ω scans
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$R_{int} = 0.028$
$\theta_{max} = 27.5°$, $\theta_{min} = 1.5°$
$h = -14 \rightarrow 15$
$k = -12 \rightarrow 10$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.070$
$S = 0.97$
2956 reflections
361 parameters
1 restraint
Primary atom site location: structure-invariant direct methods
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
Method = Modified Sheldrick $w = 1/[\sigma^2(F^2) + (0.03P)^2 + 0.33P]$ where $P = [\max(F_o^2,0) + 2F_c^2]/3$
$(\Delta/\sigma)_{max} = 0.000313$
$\Delta\rho_{max} = 0.19$ e Å^{-3}
$\Delta\rho_{min} = -0.16$ e Å^{-3}

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

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.44755 (15)	0.7690 (2)	0.28314 (14)	0.0217
C2	0.41152 (16)	0.9276 (2)	0.29530 (14)	0.0222
C3	0.29565 (16)	0.9692 (2)	0.24929 (14)	0.0223
C4	0.26104 (17)	1.1237 (2)	0.27130 (14)	0.0257

O5	0.19260 (11)	1.16063 (16)	0.18344 (10)	0.0267
O6	0.30920 (11)	0.97016 (17)	0.14152 (9)	0.0275
O7	0.40438 (11)	0.94553 (16)	0.40241 (10)	0.0258
C8	0.48830 (17)	0.8519 (2)	0.44709 (15)	0.0271
O9	0.49147 (11)	0.72881 (17)	0.38093 (10)	0.0275
C10	0.60708 (18)	0.9206 (3)	0.4514 (2)	0.0435
C11	0.35681 (15)	0.6579 (2)	0.25106 (14)	0.0216
O12	0.28235 (11)	0.61758 (18)	0.32832 (11)	0.0301
C13	0.53828 (18)	0.7441 (2)	0.20166 (17)	0.0305
O14	0.53436 (12)	0.58976 (17)	0.18066 (12)	0.0335
H21	0.4715	0.9900	0.2669	0.0268*
H31	0.2366	0.8990	0.2690	0.0255*
O34	0.40973 (14)	0.40971 (18)	0.20661 (13)	0.0395
C35	0.30089 (19)	1.1675 (3)	0.02637 (17)	0.0349
C36	0.12885 (17)	1.0048 (2)	0.05030 (16)	0.0315
C37	0.43223 (17)	0.5359 (3)	0.21210 (15)	0.0274
C38	0.4456 (2)	0.8060 (3)	0.54949 (17)	0.0427
C39	0.23279 (16)	1.0761 (2)	0.09879 (14)	0.0228
H41	0.3289	1.1871	0.2747	0.0305*
H42	0.2143	1.1331	0.3324	0.0311*
C101	0.08842 (15)	0.9233 (2)	0.70134 (14)	0.0231
H101	0.6603	0.8461	0.4689	0.0653*
C102	0.12099 (15)	0.7655 (2)	0.68734 (14)	0.0223
H102	0.6084	0.9962	0.5029	0.0654*
C103	0.10873 (17)	0.6687 (2)	0.77894 (15)	0.0234
H103	0.6280	0.9590	0.3853	0.0640*
C104	0.16111 (18)	0.5186 (2)	0.76614 (17)	0.0307
O105	0.27298 (12)	0.53161 (19)	0.81266 (11)	0.0344
O106	0.17451 (12)	0.73092 (17)	0.86006 (10)	0.0305
O107	0.04067 (12)	0.71858 (18)	0.61155 (10)	0.0293
C108	0.01997 (17)	0.8379 (3)	0.54473 (14)	0.0279
O109	0.04252 (12)	0.96432 (17)	0.60534 (10)	0.0287
C110	0.1011 (2)	0.8372 (4)	0.45547 (17)	0.0454
C111	0.00104 (16)	0.9631 (2)	0.78410 (15)	0.0231
H111	0.3146	0.6970	0.1919	0.0264*
O112	−0.11611 (10)	0.93697 (16)	0.76295 (10)	0.0267
C113	0.18790 (18)	1.0229 (3)	0.73016 (17)	0.0323
O114	0.13331 (13)	1.15310 (18)	0.76873 (13)	0.0376
H121	0.2271	0.5684	0.3058	0.0454*
H131	0.6159	0.7709	0.2269	0.0364*
H132	0.5162	0.7985	0.1388	0.0368*
O134	−0.04290 (15)	1.21648 (19)	0.81995 (14)	0.0461
C135	0.3715 (2)	0.7065 (4)	0.9153 (2)	0.0541
C136	0.2135 (2)	0.5534 (3)	0.98838 (17)	0.0401
C137	0.02296 (19)	1.1247 (2)	0.79402 (16)	0.0314
C138	−0.10483 (18)	0.8358 (3)	0.51261 (17)	0.0363
C139	0.25957 (17)	0.6287 (3)	0.89522 (16)	0.0291
H351	0.3384	1.1036	−0.0203	0.0526*

H352	0.3585	1.2243	0.0646	0.0505*
H353	0.2498	1.2327	−0.0106	0.0517*
H361	0.1540	0.9449	−0.0068	0.0463*
H362	0.0767	1.0795	0.0251	0.0460*
H363	0.0913	0.9441	0.1009	0.0464*
H381	0.5024	0.7404	0.5807	0.0632*
H382	0.4368	0.8905	0.5918	0.0634*
H383	0.3710	0.7558	0.5405	0.0627*
H1021	0.2003	0.7598	0.6619	0.0266*
H1031	0.0275	0.6611	0.7981	0.0274*
H1041	0.1145	0.4435	0.7999	0.0373*
H1042	0.1694	0.4940	0.6947	0.0369*
H1101	0.0824	0.9194	0.4109	0.0677*
H1102	0.1816	0.8432	0.4780	0.0660*
H1103	0.0887	0.7501	0.4153	0.0671*
H1111	0.0230	0.9192	0.8494	0.0266*
H1121	−0.1342	0.8567	0.7863	0.0411*
H1131	0.2382	0.9802	0.7852	0.0377*
H1132	0.2350	1.0455	0.6720	0.0386*
H1351	0.4291	0.6367	0.9360	0.0807*
H1352	0.3618	0.7787	0.9687	0.0806*
H1353	0.3948	0.7532	0.8537	0.0799*
H1361	0.2758	0.4927	1.0143	0.0593*
H1362	0.1923	0.6260	1.0383	0.0598*
H1363	0.1487	0.4927	0.9686	0.0595*
H1381	−0.1196	0.9170	0.4694	0.0537*
H1382	−0.1533	0.8416	0.5714	0.0535*
H1383	−0.1222	0.7490	0.4772	0.0542*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0207 (8)	0.0216 (10)	0.0228 (9)	0.0013 (8)	−0.0020 (7)	0.0005 (8)
C2	0.0217 (8)	0.0221 (10)	0.0228 (9)	−0.0010 (8)	0.0004 (7)	−0.0015 (8)
C3	0.0235 (8)	0.0211 (10)	0.0224 (9)	0.0014 (8)	0.0002 (7)	−0.0009 (8)
C4	0.0310 (9)	0.0234 (10)	0.0228 (9)	0.0054 (8)	−0.0029 (7)	−0.0008 (8)
O5	0.0289 (7)	0.0268 (8)	0.0244 (7)	0.0094 (6)	−0.0021 (5)	−0.0034 (6)
O6	0.0326 (7)	0.0288 (8)	0.0210 (7)	0.0126 (7)	−0.0012 (5)	−0.0007 (6)
O7	0.0276 (6)	0.0274 (8)	0.0223 (7)	0.0044 (6)	−0.0043 (5)	−0.0035 (6)
C8	0.0259 (9)	0.0269 (11)	0.0283 (10)	0.0015 (9)	−0.0081 (8)	−0.0032 (9)
O9	0.0296 (7)	0.0247 (7)	0.0281 (7)	0.0023 (6)	−0.0115 (6)	−0.0020 (6)
C10	0.0302 (11)	0.0437 (15)	0.0562 (15)	−0.0043 (11)	−0.0163 (10)	−0.0093 (12)
C11	0.0211 (8)	0.0208 (10)	0.0228 (9)	−0.0001 (8)	−0.0021 (7)	−0.0017 (8)
O12	0.0245 (6)	0.0319 (8)	0.0341 (8)	−0.0082 (6)	0.0054 (5)	−0.0035 (7)
C13	0.0284 (10)	0.0249 (11)	0.0385 (12)	0.0006 (9)	0.0087 (9)	−0.0020 (9)
O14	0.0326 (8)	0.0256 (8)	0.0426 (9)	0.0031 (6)	0.0119 (6)	−0.0051 (7)
O34	0.0435 (9)	0.0228 (8)	0.0524 (10)	−0.0006 (7)	0.0015 (7)	−0.0077 (8)
C35	0.0356 (11)	0.0328 (13)	0.0363 (11)	0.0001 (10)	0.0063 (9)	0.0044 (10)

C36	0.0293 (10)	0.0289 (12)	0.0361 (11)	0.0006 (9)	−0.0050 (8)	−0.0033 (9)
C37	0.0287 (10)	0.0273 (11)	0.0263 (10)	0.0027 (9)	0.0004 (8)	−0.0025 (9)
C38	0.0454 (13)	0.0539 (17)	0.0286 (11)	0.0118 (12)	−0.0041 (10)	0.0034 (11)
C39	0.0246 (9)	0.0199 (10)	0.0238 (9)	0.0042 (8)	−0.0006 (7)	0.0000 (8)
C101	0.0211 (8)	0.0244 (10)	0.0237 (9)	−0.0025 (8)	−0.0023 (7)	0.0045 (8)
C102	0.0184 (8)	0.0273 (11)	0.0211 (9)	0.0025 (8)	−0.0018 (7)	−0.0026 (8)
C103	0.0239 (8)	0.0210 (10)	0.0252 (9)	0.0018 (8)	−0.0016 (7)	−0.0031 (8)
C104	0.0340 (11)	0.0232 (11)	0.0349 (11)	0.0061 (9)	−0.0069 (9)	−0.0051 (9)
O105	0.0292 (7)	0.0346 (9)	0.0393 (8)	0.0101 (7)	−0.0037 (6)	−0.0078 (7)
O106	0.0423 (8)	0.0231 (8)	0.0259 (7)	0.0090 (7)	−0.0117 (6)	−0.0036 (6)
O107	0.0341 (7)	0.0283 (8)	0.0253 (7)	0.0022 (7)	−0.0081 (6)	−0.0027 (6)
C108	0.0290 (10)	0.0340 (12)	0.0206 (9)	0.0038 (9)	−0.0013 (7)	0.0010 (9)
O109	0.0335 (7)	0.0291 (8)	0.0235 (7)	0.0011 (7)	−0.0032 (6)	0.0062 (6)
C110	0.0404 (13)	0.0674 (19)	0.0285 (11)	0.0068 (13)	0.0051 (9)	0.0020 (13)
C111	0.0239 (9)	0.0196 (10)	0.0257 (9)	0.0002 (8)	−0.0013 (7)	0.0011 (8)
O112	0.0212 (6)	0.0223 (8)	0.0365 (8)	0.0007 (6)	0.0016 (5)	0.0058 (6)
C113	0.0281 (10)	0.0278 (12)	0.0408 (12)	−0.0041 (9)	−0.0024 (9)	0.0022 (10)
O114	0.0376 (8)	0.0239 (8)	0.0513 (10)	−0.0084 (7)	−0.0039 (7)	−0.0012 (8)
O134	0.0565 (10)	0.0236 (8)	0.0585 (11)	0.0053 (8)	0.0080 (8)	−0.0077 (8)
C135	0.0344 (12)	0.0558 (18)	0.0719 (19)	−0.0060 (13)	−0.0106 (12)	−0.0082 (16)
C136	0.0522 (13)	0.0326 (13)	0.0353 (12)	0.0049 (11)	−0.0094 (10)	0.0057 (10)
C137	0.0388 (11)	0.0216 (11)	0.0337 (11)	−0.0018 (9)	−0.0029 (9)	−0.0019 (9)
C138	0.0298 (10)	0.0479 (14)	0.0309 (11)	−0.0017 (11)	−0.0059 (9)	0.0049 (11)
C139	0.0275 (9)	0.0251 (11)	0.0345 (11)	0.0053 (9)	−0.0066 (8)	−0.0016 (9)

Geometric parameters (Å, º)

C1—C2	1.539 (3)	C101—C102	1.524 (3)
C1—O9	1.431 (2)	C101—O109	1.420 (2)
C1—C11	1.528 (3)	C101—C111	1.541 (3)
C1—C13	1.528 (3)	C101—C113	1.521 (3)
C2—C3	1.516 (2)	C102—C103	1.514 (3)
C2—O7	1.426 (2)	C102—O107	1.426 (2)
C2—H21	0.981	C102—H1021	0.982
C3—C4	1.517 (3)	C103—C104	1.529 (3)
C3—O6	1.432 (2)	C103—O106	1.429 (2)
C3—H31	0.980	C103—H1031	0.979
C4—O5	1.439 (2)	C104—O105	1.432 (2)
C4—H41	0.982	C104—H1041	0.990
C4—H42	0.979	C104—H1042	0.975
O5—C39	1.446 (2)	O105—C139	1.423 (3)
O6—C39	1.434 (2)	O106—C139	1.440 (2)
O7—C8	1.426 (2)	O107—C108	1.434 (3)
C8—O9	1.438 (3)	C108—O109	1.442 (3)
C8—C10	1.516 (3)	C108—C110	1.514 (3)
C8—C38	1.505 (3)	C108—C138	1.501 (3)
C10—H101	0.952	C110—H1101	0.986
C10—H102	0.976	C110—H1102	0.977

C10—H103	0.975	C110—H1103	0.976
C11—O12	1.393 (2)	C111—O112	1.402 (2)
C11—C37	1.522 (3)	C111—C137	1.527 (3)
C11—H111	0.986	C111—H1111	0.984
O12—H121	0.837	O112—H1121	0.834
C13—O14	1.460 (3)	C113—O114	1.458 (3)
C13—H131	0.986	C113—H1131	1.007
C13—H132	1.002	C113—H1132	0.969
O14—C37	1.353 (3)	O114—C137	1.349 (3)
O34—C37	1.201 (3)	O134—C137	1.195 (3)
C35—C39	1.506 (3)	C135—C139	1.503 (3)
C35—H351	0.961	C135—H1351	0.967
C35—H352	0.984	C135—H1352	0.979
C35—H353	0.974	C135—H1353	0.962
C36—C39	1.509 (3)	C136—C139	1.516 (3)
C36—H361	0.983	C136—H1361	0.974
C36—H362	0.974	C136—H1362	0.975
C36—H363	0.979	C136—H1363	0.972
C38—H381	0.984	C138—H1381	0.959
C38—H382	0.969	C138—H1382	0.964
C38—H383	0.987	C138—H1383	0.951

C2—C1—O9	104.43 (16)	C102—C101—O109	103.91 (16)
C2—C1—C11	119.21 (15)	C102—C101—C111	118.76 (17)
O9—C1—C11	108.09 (16)	O109—C101—C111	109.00 (15)
C2—C1—C13	114.00 (17)	C102—C101—C113	115.24 (16)
O9—C1—C13	110.78 (15)	O109—C101—C113	109.56 (16)
C11—C1—C13	100.29 (16)	C111—C101—C113	100.24 (16)
C1—C2—C3	116.18 (16)	C101—C102—C103	116.63 (16)
C1—C2—O7	103.50 (16)	C101—C102—O107	102.58 (15)
C3—C2—O7	107.88 (14)	C103—C102—O107	108.24 (16)
C1—C2—H21	109.3	C101—C102—H1021	109.1
C3—C2—H21	108.9	C103—C102—H1021	109.6
O7—C2—H21	111.0	O107—C102—H1021	110.4
C2—C3—C4	113.45 (16)	C102—C103—C104	114.32 (17)
C2—C3—O6	107.07 (14)	C102—C103—O106	107.72 (16)
C4—C3—O6	102.47 (16)	C104—C103—O106	104.02 (15)
C2—C3—H31	109.9	C102—C103—H1031	110.3
C4—C3—H31	113.0	C104—C103—H1031	110.2
O6—C3—H31	110.6	O106—C103—H1031	110.0
C3—C4—O5	102.43 (15)	C103—C104—O105	103.49 (16)
C3—C4—H41	111.2	C103—C104—H1041	111.9
O5—C4—H41	109.1	O105—C104—H1041	111.2
C3—C4—H42	113.0	C103—C104—H1042	111.3
O5—C4—H42	109.7	O105—C104—H1042	109.6
H41—C4—H42	111.0	H1041—C104—H1042	109.3
C4—O5—C39	108.32 (14)	C104—O105—C139	106.04 (14)
C3—O6—C39	108.74 (14)	C103—O106—C139	109.39 (15)

C2—O7—C8	107.00 (14)	C102—O107—C108	107.39 (16)
O7—C8—O9	104.75 (14)	O107—C108—O109	105.02 (13)
O7—C8—C10	111.89 (19)	O107—C108—C110	111.94 (19)
O9—C8—C10	109.14 (18)	O109—C108—C110	108.98 (19)
O7—C8—C38	108.36 (18)	O107—C108—C138	108.52 (18)
O9—C8—C38	109.30 (19)	O109—C108—C138	109.59 (18)
C10—C8—C38	113.05 (19)	C110—C108—C138	112.51 (17)
C8—O9—C1	109.22 (15)	C108—O109—C101	109.89 (15)
C8—C10—H101	106.7	C108—C110—H1101	109.1
C8—C10—H102	109.7	C108—C110—H1102	111.1
H101—C10—H102	110.4	H1101—C110—H1102	109.9
C8—C10—H103	110.7	C108—C110—H1103	109.7
H101—C10—H103	108.4	H1101—C110—H1103	106.6
H102—C10—H103	110.9	H1102—C110—H1103	110.3
C1—C11—O12	114.02 (16)	C101—C111—O112	117.24 (16)
C1—C11—C37	101.57 (15)	C101—C111—C137	100.75 (17)
O12—C11—C37	114.12 (17)	O112—C111—C137	110.25 (17)
C1—C11—H111	107.8	C101—C111—H1111	110.9
O12—C11—H111	111.9	O112—C111—H1111	110.1
C37—C11—H111	106.7	C137—C111—H1111	106.8
C11—O12—H121	111.3	C111—O112—H1121	109.1
C1—C13—O14	105.16 (17)	C101—C113—O114	105.14 (16)
C1—C13—H131	110.7	C101—C113—H1131	111.8
O14—C13—H131	109.8	O114—C113—H1131	108.8
C1—C13—H132	109.6	C101—C113—H1132	111.4
O14—C13—H132	109.3	O114—C113—H1132	110.2
H131—C13—H132	112.1	H1131—C113—H1132	109.3
C13—O14—C37	109.28 (16)	C113—O114—C137	109.82 (16)
C39—C35—H351	107.5	C139—C135—H1351	108.6
C39—C35—H352	109.4	C139—C135—H1352	110.5
H351—C35—H352	110.5	H1351—C135—H1352	109.8
C39—C35—H353	110.4	C139—C135—H1353	108.4
H351—C35—H353	109.8	H1351—C135—H1353	110.0
H352—C35—H353	109.2	H1352—C135—H1353	109.6
C39—C36—H361	109.4	C139—C136—H1361	106.6
C39—C36—H362	108.7	C139—C136—H1362	108.9
H361—C36—H362	109.2	H1361—C136—H1362	110.6
C39—C36—H363	108.7	C139—C136—H1363	109.0
H361—C36—H363	109.5	H1361—C136—H1363	109.0
H362—C36—H363	111.3	H1362—C136—H1363	112.6
C11—C37—O14	109.54 (18)	C111—C137—O114	109.12 (18)
C11—C37—O34	128.4 (2)	C111—C137—O134	128.2 (2)
O14—C37—O34	122.1 (2)	O114—C137—O134	122.7 (2)
C8—C38—H381	109.1	C108—C138—H1381	108.9
C8—C38—H382	109.0	C108—C138—H1382	109.8
H381—C38—H382	109.5	H1381—C138—H1382	109.4
C8—C38—H383	108.7	C108—C138—H1383	110.3
H381—C38—H383	109.8	H1381—C138—H1383	109.8

H382—C38—H383	110.8	H1382—C138—H1383	108.7
C36—C39—C35	113.44 (17)	C136—C139—C135	112.83 (19)
C36—C39—O5	107.69 (15)	C136—C139—O106	108.64 (17)
C35—C39—O5	111.06 (17)	C135—C139—O106	109.0 (2)
C36—C39—O6	110.60 (17)	C136—C139—O105	111.78 (19)
C35—C39—O6	108.11 (15)	C135—C139—O105	109.76 (19)
O5—C39—O6	105.68 (14)	O106—C139—O105	104.48 (15)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O12—H121···O112^{i}	0.84	1.98	2.813 (2)	170
O112—H1121···O5^{i}	0.83	1.98	2.806 (2)	169

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