Acta Crystallographica Section E
**Structure Reports Online**
ISSN 1600-5368

# 2,5-Di-*O*-acetyl-3-*C*-methyl-D-lyxono-1,4-lactone

**Richard Bream,[a] David Watkin,[a] Raquel Soengas,[b] Vanessa Eastwick-Field[c] and George W. J. Fleet[b]***

[a]Chemical Crystallography, Central Chemistry Laboratory, University of Oxford, Oxford OX1 3TA, England, [b]Department of Organic Chemistry, Chemical Research Laboratory, Oxford University, Mansfield Road, Oxford OX1 3TA, England, and [c]CMS Chemicals, 9 Milton Park, Abingdon, Oxfordshire OX14 4RR, England

Correspondence e-mail: richard.bream@pmb.ox.ac.uk

**Key indicators**

Single-crystal X-ray study
*T* = 150 K
Mean σ(C–C) = 0.002 Å
*R* factor = 0.034
*wR* factor = 0.073
Data-to-parameter ratio = 10.0

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

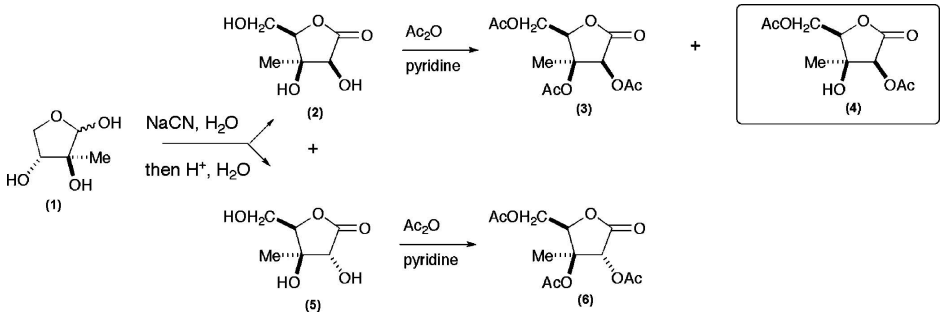


Received 25 January 2006
Accepted 3 February 2006

The structures of both lactones derived from the Kiliani ascension of 2-*C*-methyl-D-threose were defined by the crystal structure of the title compound, $C_{10}H_{14}O_7$. The structure consists of hydrogen-bonded ribbons of molecules.

## Comment

The Kiliani reaction of ketoses with cyanide, followed by acetonation, has provided a simple and environmentally friendly procedure for the generation of a set of carbohydrate scaffolds with a branched hydroxymethyl group at C-2 (Hotchkiss *et al.*, 2004; Soengas *et al.*, 2005). Branched sugar lactones bearing a C-2 methyl group may be accessed either by a Kiliani reaction on 1-deoxyketoses or by treatment of an Amadori ketose with aqueous calcium hydroxide (Hotchkiss *et al.*, 2006). X-ray crystallographic analysis has been crucial in establishing the structures of the products in these reactions (Punzo *et al.*, 2006; Watkin *et al.*, 2005; Harding *et al.*, 2005). Although these syntheses provide convenient access to C-2 carbon-branched carbohydrates, there are very few reports of sugars with a carbon branch at C-3; a 3-*C*-methyl-pentonolactone of unknown stereochemistry has been isolated from cigarette smoke (Schumacher *et al.*, 1977) and 3-*C*-methyl-D-mannose is one of the components of the tris-accharide repeating unit of the polysaccharide from *Helicobacter Pylori* (Kwon *et al.*, 2004).




3-*C*-Methyl aldonolactones should be accessible through a Kiliani reaction on a branched 2-*C*-methyl aldose. Reaction of 2-*C*-methyl-D-threose (1) with aqueous sodium cyanide afforded an inseparable mixture of the *C*-3-methyl branched lactones (2) and (5); the mixture was treated with an excess of acetic anhydride in pyridine to give a separable mixture of two triacetates (3) and (6) together with a crystalline diacetate (4) (Soengas & Fleet, 2006). Determination of the relative stereochemistry of the diacetate (4) as a lyxono-1,4-lactone by X-ray crystallographic analysis (Fig. 1) allowed unambiguous structural assigments of both the triacetates (3) and (6), and

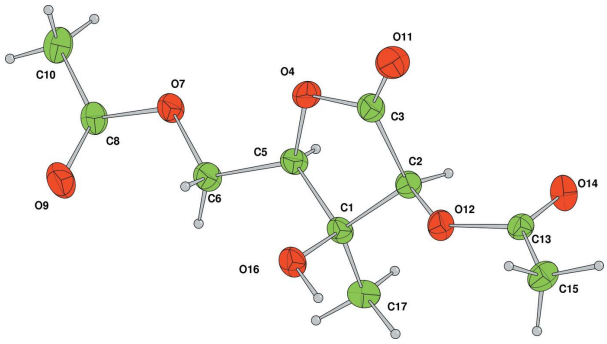



**Figure 1**
The title compound, with displacement ellipsoids drawn at the 50% probability level. The H atoms are shown as spheres of arbitary radius.

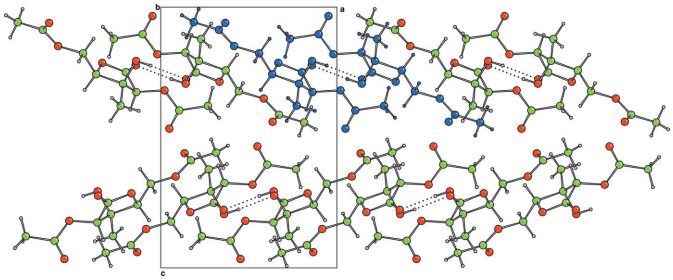


**Figure 2**
A *b*-axis projection showing layers of molecules. Dashed lines indicate hydrogen bonds.

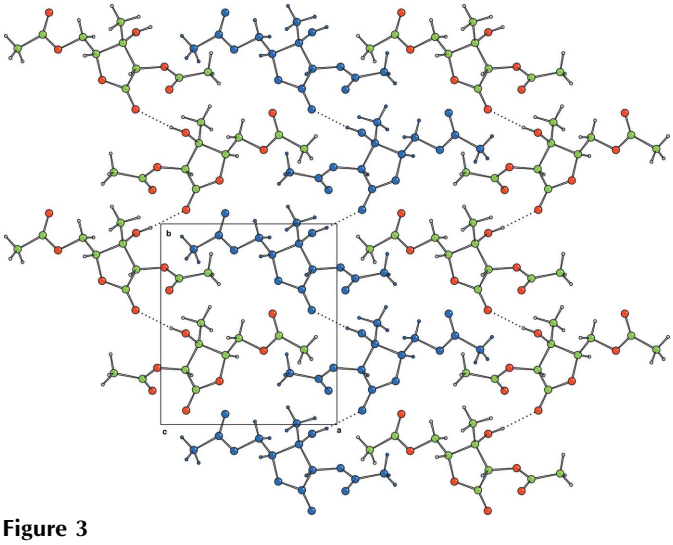


**Figure 3**
A *c*-axis projection of one layer of molecules, showing the hydrogen-bonded (dashed lines) ribbons lying parallel to *b*.

thus of the C-3 branched lyxono- (2) and xylono- (5) lactones. The use of 2-*C*-methyl-D-threose (1) as the starting material in the synthesis defines the absolute configuration of (4). Both C-2 and C-3 branched sugars are likely to increase significantly the range of carbohydrate chirons (Lichtenthaler & Peters, 2004) available for the efficient synthesis of complex homochiral targets (Simone *et al.*, 2005) and also to provide material for the first time for the study of interactions of such unnatural monosaccharides with biological receptors.

The crystal structure consists of layers of molecules lying perpendicular to the *c* axis (Fig. 2). Within each layer are interlocking zigzag ribbons of hydrogen-bonded molecules (Fig. 3).

## Experimental

The material was prepared (Soengas & Fleet, 2006) using a Kiliani reaction. The diacetate (4) was crystallized from chloroform; m.p. 521–523 K, $[\alpha]_D^{23}$ +60.0 (*c*, 1.7 in acetone).

### *Crystal data*

$C_{10}H_{14}O_7$
$M_r$ = 246.22
Orthorhombic, $P2_12_12_1$
$a$ = 8.8524 (1) Å
$b$ = 10.0821 (2) Å
$c$ = 13.1198 (2) Å
$V$ = 1170.95 (3) Å$^3$
$Z$ = 4
$D_x$ = 1.397 Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 1560 reflections
$\theta$ = 5–27°
$\mu$ = 0.12 mm$^{-1}$
$T$ = 150 K
Plate, colourless
0.20 × 0.20 × 0.08 mm

### *Data collection*

Nonius KappaCCD diffractometer
$\omega$ scans
Absorption correction: multi-scan (*DENZO/SCALEPACK*; Otwinowski & Minor, 1997)
$T_{min}$ = 0.869, $T_{max}$ = 0.990
2688 measured reflections
1545 independent reflections
1545 reflections with $I > -3.0\sigma(I)$
$R_{int}$ = 0.009
$\theta_{max}$ = 27.5°
$h = -11 \rightarrow 11$
$k = -13 \rightarrow 13$
$l = -16 \rightarrow 16$

### *Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.073
$S$ = 0.91
1545 reflections
154 parameters
H-atom parameters constrained
Modified Chebychev polynomial (Watkin, 1994; *P*rince, 1982) *w*ith the coefficients 11.3, 16.9, 8.59, 2.51
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.27 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.24 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O16—H8···O11$^{i}$ | 0.83 | 2.11 | 2.926 (2) | 167 |

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

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 = 0.93–0.98 and O—H = 0.82 Å) and displacement parameters [$U_{iso}$(H) = 1.2–1.5$U_{eq}$ of the parent atom], after which they were refined with riding constraints. In the absence of significant anomalous dispersion effects, Friedel pairs were averaged.

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*.

## References

Altomare, A., Cascarano, G., Giacovazzo, G., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.

Betteridge, P. W., Carruthers, J. R., Cooper, R. I., Prout, K. & Watkin, D. J. (2003). *J. Appl. Cryst.* **36**, 1487.
Harding, C. C., Watkin, D. J., Sawyer, N. K., Jenkinson, S. F. & Fleet, G. W. J. (2005). *Acta Cryst.* E**61**, o1472–o1474.
Hotchkiss, D. J., Jenkinson, S. F., Storer, R., Heinz, T. & Fleet, G. W. J. (2006). *Tetrahedron Lett.* **47**, 315–318.
Hotchkiss, D., Soengas, R., Simone, M. I., van Ameijde, J., Hunter, S., Cowley, A. R. & Fleet, G. W. J. (2004). *Tetrahedron Lett.* **45**, 9461–9464.
Kwon, Y. T., Lee, Y. J., Lee, K. & Kim, K. S. (2004). *Org. Lett.* **6**, 3901–3904.
Lichtenthaler, F. W. & Peters, S. (2004). *C. R. Chim.* **7**, 65–90.
Nonius (2001). *COLLECT*. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Prince, E. (1982). *Mathematical Techniques in Crystallography and Materials Science*. New York: Springer-Verlag.
Punzo, F., Watkin, D. J., Hotchkiss, D. & Fleet, G. W. J. (2006). *Acta Cryst.* E**62**, o98–o100.
Schumacher, J. N., Green, C. R., Best, F. W. & Newell, M. P. (1977). *J. Agric. Food. Chem.* **25**, 310–320.
Simone, M. I., Soengas, R., Newton, C. R., Watkin, D. J. & Fleet, G. W. J. (2005). *Tetrahedron Lett.* **46**, 5761–5765.
Soengas, R. & Fleet, G. W. J. (2006). *Tetrahedron Lett.* In preparation.
Soengas, R., Izumori, K., Simone, M. I., Watkin, D. J., Skytte, U. P., Soetaert, W. & Fleet, G. W. J. (2005). *Tetrahedron Lett.* **46**, 5755–5759.
Watkin, D. J. (1994). *Acta Cryst.* A**50**, 411–437.
Watkin, D. J., Parry, L. L., Hotchkiss, D. J., Eastwick-Field, V. & Fleet, G. W. J. (2005). *Acta Cryst.* E**61**, o3302–o3303.
Watkin, D. J., Prout, C. K. & Pearce, L. J. (1996). *CAMERON*. Chemical Crystallography Laboratory, Oxford, England.

# supporting information

*Acta Cryst.* (2006). E**62**, o977–o979 [https://doi.org/10.1107/S1600536806004211]

## 2,5-Di-*O*-acetyl-3-*C*-methyl-D-lyxono-1,4-lactone

**Richard Bream, David Watkin, Raquel Soengas, Vanessa Eastwick-Field and George W. J. Fleet**

### 2,5-Di-*O*-acetyl-3-*C*-methyl-D-lyxono-1,4-lactone

*Crystal data*

$C_{10}H_{14}O_7$
$M_r = 246.22$
Orthorhombic, $P2_12_12_1$
$a = 8.8524$ (1) Å
$b = 10.0821$ (2) Å
$c = 13.1198$ (2) Å
$V = 1170.95$ (3) Å$^3$
$Z = 4$
$F(000) = 520$
$D_x = 1.397$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 1560 reflections
$\theta = 5$–27°
$\mu = 0.12$ mm$^{-1}$
$T = 150$ K
Plate, colourless
0.20 × 0.20 × 0.08 mm

*Data collection*

Nonius KappaCCD diffractometer
Graphite monochromator
$\omega$ scans
Absorption correction: multi-scan (DENZO/SCALEPACK; Otwinowski & Minor, 1997)
$T_{min} = 0.869$, $T_{max} = 0.990$
2688 measured reflections
1545 independent reflections
1545 reflections with $I > -3.0\sigma(I)$
$R_{int} = 0.009$
$\theta_{max} = 27.5°$, $\theta_{min} = 5.1°$
$h = -11\rightarrow11$
$k = -13\rightarrow13$
$l = -16\rightarrow16$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.073$
$S = 0.91$
1545 reflections
154 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
Modified Chebychev polynomial (Watkin, 1994; *P*rince, 1982) *w*ith the coefficients 11.3, 16.9, 8.59, 2.51
$(\Delta/\sigma)_{max} = 0.000247$
$\Delta\rho_{max} = 0.27$ e Å$^{-3}$
$\Delta\rho_{min} = -0.24$ e Å$^{-3}$

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| C2 | 0.86077 (18) | 0.77278 (17) | 0.32579 (13) | 0.0218 |
| C3 | 0.8007 (2) | 0.67351 (18) | 0.24961 (15) | 0.0246 |
| O4 | 0.66668 (14) | 0.71630 (12) | 0.21387 (10) | 0.0259 |
| C5 | 0.63200 (19) | 0.84694 (16) | 0.25745 (13) | 0.0220 |
| C6 | 0.5579 (2) | 0.93071 (18) | 0.17730 (14) | 0.0265 |

| | | | | |
|---|---|---|---|---|
| O7 | 0.41613 (14) | 0.86863 (13) | 0.14924 (10) | 0.0273 |
| C18 | 0.3294 (2) | 0.94326 (18) | 0.08704 (14) | 0.0268 |
| O9 | 0.36545 (17) | 1.05300 (14) | 0.06062 (12) | 0.0388 |
| C10 | 0.1867 (2) | 0.8737 (2) | 0.05766 (17) | 0.0364 |
| O11 | 0.85646 (17) | 0.57035 (13) | 0.22296 (12) | 0.0339 |
| O12 | 1.02057 (13) | 0.78292 (13) | 0.31932 (9) | 0.0252 |
| C13 | 1.10358 (19) | 0.72849 (17) | 0.39600 (12) | 0.0213 |
| O14 | 1.04802 (15) | 0.66905 (14) | 0.46585 (9) | 0.0287 |
| C15 | 1.26726 (19) | 0.75652 (18) | 0.37875 (14) | 0.0268 |
| O16 | 0.85902 (15) | 0.95473 (13) | 0.20639 (10) | 0.0256 |
| C17 | 0.7718 (2) | 1.00576 (19) | 0.37796 (15) | 0.0293 |
| C8 | 0.78459 (19) | 0.90227 (16) | 0.29387 (14) | 0.0213 |
| H21 | 0.8338 | 0.7455 | 0.3966 | 0.0271* |
| H51 | 0.5629 | 0.8339 | 0.3181 | 0.0261* |
| H61 | 0.5387 | 1.0204 | 0.2023 | 0.0320* |
| H62 | 0.6196 | 0.9360 | 0.1157 | 0.0329* |
| H101 | 0.1203 | 0.9367 | 0.0301 | 0.0559* |
| H102 | 0.1382 | 0.8303 | 0.1174 | 0.0566* |
| H103 | 0.2129 | 0.8082 | 0.0082 | 0.0564* |
| H151 | 1.3294 | 0.6941 | 0.4221 | 0.0381* |
| H152 | 1.2888 | 0.8458 | 0.4011 | 0.0385* |
| H153 | 1.2896 | 0.7507 | 0.3076 | 0.0376* |
| H171 | 0.7183 | 1.0820 | 0.3511 | 0.0404* |
| H172 | 0.8737 | 1.0354 | 0.3990 | 0.0404* |
| H173 | 0.7197 | 0.9751 | 0.4386 | 0.0401* |
| H8 | 0.9435 | 0.9747 | 0.2287 | 0.0400* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| C2 | 0.0173 (7) | 0.0227 (7) | 0.0255 (7) | −0.0016 (7) | −0.0011 (7) | 0.0038 (7) |
| C3 | 0.0205 (8) | 0.0245 (8) | 0.0289 (8) | 0.0001 (7) | −0.0023 (7) | 0.0031 (7) |
| O4 | 0.0213 (6) | 0.0218 (5) | 0.0345 (6) | 0.0015 (5) | −0.0067 (5) | −0.0018 (5) |
| C5 | 0.0184 (7) | 0.0193 (7) | 0.0285 (8) | −0.0002 (6) | −0.0008 (7) | 0.0016 (6) |
| C6 | 0.0195 (8) | 0.0249 (8) | 0.0351 (9) | 0.0000 (7) | −0.0038 (7) | 0.0059 (8) |
| O7 | 0.0211 (6) | 0.0252 (6) | 0.0356 (7) | 0.0003 (5) | −0.0058 (5) | 0.0068 (6) |
| C18 | 0.0248 (8) | 0.0275 (8) | 0.0282 (8) | 0.0058 (7) | −0.0021 (7) | 0.0025 (7) |
| O9 | 0.0360 (8) | 0.0329 (7) | 0.0476 (8) | 0.0021 (6) | −0.0096 (7) | 0.0145 (7) |
| C10 | 0.0300 (9) | 0.0390 (10) | 0.0401 (11) | 0.0025 (9) | −0.0114 (9) | 0.0041 (9) |
| O11 | 0.0305 (7) | 0.0262 (6) | 0.0450 (8) | 0.0085 (6) | −0.0066 (7) | −0.0058 (6) |
| O12 | 0.0160 (5) | 0.0312 (6) | 0.0284 (6) | −0.0025 (5) | −0.0012 (5) | 0.0072 (6) |
| C13 | 0.0205 (7) | 0.0205 (7) | 0.0230 (7) | 0.0018 (7) | −0.0017 (6) | −0.0030 (7) |
| O14 | 0.0258 (6) | 0.0351 (7) | 0.0254 (6) | 0.0045 (6) | 0.0011 (5) | 0.0060 (6) |
| C15 | 0.0192 (8) | 0.0318 (9) | 0.0292 (8) | 0.0006 (7) | −0.0018 (7) | −0.0040 (8) |
| O16 | 0.0216 (6) | 0.0282 (6) | 0.0270 (6) | −0.0028 (5) | 0.0012 (5) | 0.0085 (5) |
| C17 | 0.0312 (10) | 0.0249 (8) | 0.0318 (9) | −0.0032 (8) | 0.0005 (8) | −0.0023 (8) |
| C8 | 0.0195 (7) | 0.0208 (7) | 0.0236 (8) | −0.0022 (6) | 0.0012 (7) | 0.0044 (7) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| C2—C3 | 1.511 (2) | C10—H101 | 0.937 |
| C2—O12 | 1.4208 (19) | C10—H102 | 0.995 |
| C2—C8 | 1.528 (2) | C10—H103 | 0.955 |
| C2—H21 | 0.997 | O12—C13 | 1.361 (2) |
| C3—O4 | 1.347 (2) | C13—O14 | 1.200 (2) |
| C3—O11 | 1.203 (2) | C13—C15 | 1.493 (2) |
| O4—C5 | 1.468 (2) | C15—H151 | 1.012 |
| C5—C6 | 1.500 (2) | C15—H152 | 0.966 |
| C5—C8 | 1.538 (2) | C15—H153 | 0.956 |
| C5—H51 | 1.012 | O16—C8 | 1.425 (2) |
| C6—O7 | 1.450 (2) | O16—H8 | 0.828 |
| C6—H61 | 0.977 | C17—C8 | 1.523 (3) |
| C6—H62 | 0.977 | C17—H171 | 0.969 |
| O7—C18 | 1.349 (2) | C17—H172 | 0.990 |
| C18—O9 | 1.203 (2) | C17—H173 | 0.970 |
| C18—C10 | 1.496 (3) | | |
| | | | |
| C3—C2—O12 | 111.00 (14) | H101—C10—H102 | 109.3 |
| C3—C2—C8 | 103.26 (14) | C18—C10—H103 | 107.1 |
| O12—C2—C8 | 111.20 (14) | H101—C10—H103 | 111.1 |
| C3—C2—H21 | 110.4 | H102—C10—H103 | 109.6 |
| O12—C2—H21 | 108.3 | C2—O12—C13 | 117.67 (13) |
| C8—C2—H21 | 112.7 | O12—C13—O14 | 122.97 (15) |
| C2—C3—O4 | 109.15 (15) | O12—C13—C15 | 109.61 (14) |
| C2—C3—O11 | 128.36 (17) | O14—C13—C15 | 127.42 (16) |
| O4—C3—O11 | 122.47 (17) | C13—C15—H151 | 108.9 |
| C3—O4—C5 | 109.63 (13) | C13—C15—H152 | 108.8 |
| O4—C5—C6 | 108.88 (14) | H151—C15—H152 | 107.6 |
| O4—C5—C8 | 105.23 (13) | C13—C15—H153 | 109.7 |
| C6—C5—C8 | 113.44 (14) | H151—C15—H153 | 113.5 |
| O4—C5—H51 | 108.4 | H152—C15—H153 | 108.2 |
| C6—C5—H51 | 111.1 | C8—O16—H8 | 102.9 |
| C8—C5—H51 | 109.5 | C8—C17—H171 | 108.5 |
| C5—C6—O7 | 108.27 (14) | C8—C17—H172 | 109.9 |
| C5—C6—H61 | 111.2 | H171—C17—H172 | 107.9 |
| O7—C6—H61 | 109.5 | C8—C17—H173 | 114.3 |
| C5—C6—H62 | 111.5 | H171—C17—H173 | 108.6 |
| O7—C6—H62 | 107.3 | H172—C17—H173 | 107.5 |
| H61—C6—H62 | 108.9 | C5—C8—C2 | 99.38 (12) |
| C6—O7—C18 | 113.90 (14) | C5—C8—C17 | 114.10 (14) |
| O7—C18—O9 | 122.45 (18) | C2—C8—C17 | 114.82 (15) |
| O7—C18—C10 | 112.03 (16) | C5—C8—O16 | 106.89 (14) |
| O9—C18—C10 | 125.51 (18) | C2—C8—O16 | 109.50 (14) |
| C18—C10—H101 | 108.2 | C17—C8—O16 | 111.32 (14) |
| C18—C10—H102 | 111.6 | | |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O16—H8···O11$^{i}$ | 0.83 | 2.11 | 2.926 (2) | 167 |

Symmetry code: (i) −*x*+2, *y*+1/2, −*z*+1/2.