

Received 11 November 2020

Accepted 22 December 2020

Edited by A. S. Batsanov, University of Durham,
England**Keywords:** crystal structure; natural product;
lawinal; flavanone.**CCDC reference:** 2051848**Supporting information:** this article has
supporting information at journals.iucr.org/e

Isolation and crystal structure of lawinal

Virayu Suthiphasilp,^a Pornphimol Meesakul,^a Christopher Richardson,^b Stephen G. Pyne^b and Surat Laphookhieo^{a*}^aCenter of Chemical Innovation for Sustainability (CIS) and School of Science, Mae Fah Luang University, Chiang Rai 57100, Thailand, and ^bSchool of Chemistry and Molecular Bioscience, University of Wollongong, Wollongong, New South Wales 2522, Australia. *Correspondence e-mail: surat.lap@mfu.ac.th

The structure of the natural product lawinal [systematic name: (–)-(2*S*)-5,7-dihydroxy-6-methyl-4-oxo-2-phenylchromane-8-carbaldehyde, C₁₇H₁₄O₅] at 150 K is reported. The compound crystallizes with monoclinic (*I*2) symmetry and with *Z*' = 2. The absolute configuration could not be determined reliably from X-ray analysis only. However, our analysis returns the *S*-configuration at the C-2 position, consistent with previous stereochemical assignment from specific rotation. The independent molecules form into alternating hydrogen-bonded chains with C–H...O=CH intermolecular linkages that run parallel to the crystallographic *a* axis and are extended into the *ac* plane by π – π interactions between their phenyl substituents.

1. Chemical context

The small flowering plants of the *Desmos* genus belong to the Annonaceae family, which comprises about 33 species and is distributed widely throughout Southern Asia and northern Australia (Brophy *et al.*, 2002; Clement *et al.*, 2017). Several species of this genus have been used as Chinese folk medicines (Wu *et al.*, 2003). The aerial part of *D. chinensis* has been used as an analgesic agent, and to treat vertigo, and parturition (Kummee & Intaraksa, 2008; Rahman *et al.*, 2003). In Thailand it is widely used traditionally to treat fever and dysentery (Bunyapraphatsara *et al.*, 2000). The petroleum ether extracts of *D. cochinchinensis* roots have mainly been explored for their antimalarial activity (Liao *et al.*, 1989). The *Desmos* genus is well known as an abundant source of flavonoids (Meesakul *et al.*, 2019; Bajgai *et al.*, 2011; Kuo *et al.*, 2015), and their 2*S* absolute configuration has been commonly found (Meesakul *et al.*, 2019; Kuo *et al.*, 2015). Flavonoids exhibit interesting biological activities, including inhibition of HIV-1 replication in H9 lymphocytic cells (Wu *et al.*, 2003), antibacterial properties (Liao *et al.*, 1989) and show activities as α -glucosidase inhibitors (Meesakul *et al.*, 2019), antioxidants (Miller, 1996), aromatase and lipoxygenase inhibitors (Bajgai *et al.*, 2011).

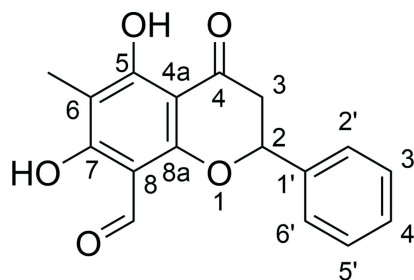
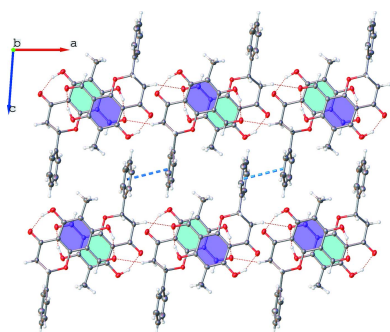


Table 1
 Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$C3-H3B\cdots O9A^i$	0.99	2.32	3.252 (3)	158
$C3A-H3AB\cdots O9^{ii}$	0.99	2.31	3.248 (3)	157
$O7A-H7A\cdots O9A$	0.94 (3)	1.67 (3)	2.572 (2)	159 (4)
$O5-H5\cdots O4$	0.94 (3)	1.70 (3)	2.579 (2)	154 (3)
$O7-H7\cdots O9$	0.95 (3)	1.67 (3)	2.585 (2)	162 (3)
$O5A-H5A\cdots O4A$	0.94 (3)	1.70 (3)	2.574 (2)	153 (3)

Symmetry codes: (i) $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$.

Herein, we report the isolation and crystal structure of the flavonoid, $(-)(2S)$ -5,7-dihydroxy-6-methyl-4-oxo-2-phenylchromane-8-carbaldehyde, commonly known as lawinal, isolated from the twig extract of *D. dumosus*.

2. Structural commentary

Lawinal crystallizes in the space group $I2$ with $Z' = 2$. Because of the large standard deviation of the Flack parameter [$-0.1(5)$], the absolute configuration cannot be assigned from the X-ray data (Parsons *et al.*, 2013). We explored applying the Bayesian statistical approach promoted by Hooft *et al.* (2008). Given that the compound comes from a natural product source and thus should be enantiopure, the analysis, as implemented in *PLATON* (Spek, 2020), returned a $P2(\text{true})$ value of 0.992 for the *S*-configuration at C2 in each molecule (Fig. 1). This is consistent with the stereochemical assignment by the method of specific rotation (Prawat *et al.*, 2012; Wu *et al.*, 2005).

The unique molecules adopt extremely similar conformations and an overlay of the molecular structures is shown in Fig. 2. The hydroxyl groups attached to C5 and C7 on each unique molecule act as hydrogen-bond donors to the ketone and aldehyde functionalities, respectively. The positions of the hydroxyl hydrogen atoms were refined, the relatively long $D-H$ distances (Table 1) indicating strong intramolecular stabilization. The hydrogen bond $O7-H7\cdots O9$ is responsible for

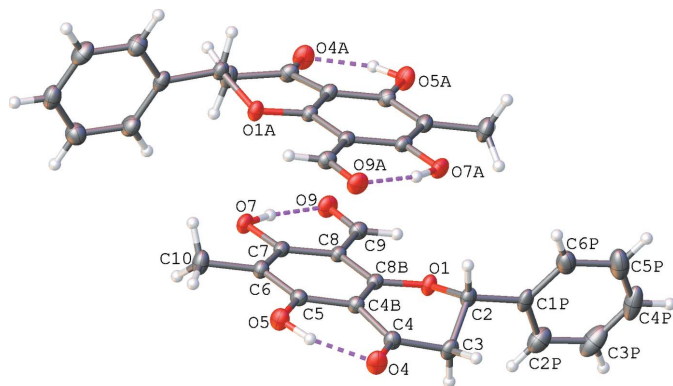


Figure 1
 The contents of the asymmetric unit with complete atom labelling of one molecule and selected heteroatom labelling of the second molecule, for clarity. Intramolecular hydrogen bonds are shown as dashed magenta lines. Displacement ellipsoids are plotted at the 50% probability level.

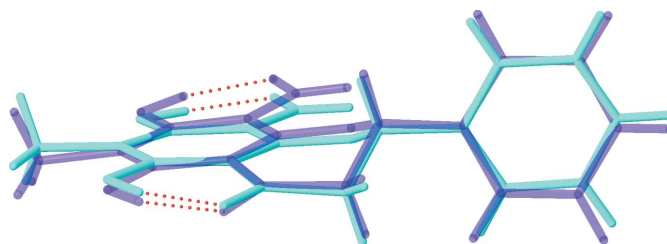


Figure 2
 An overlay of the independent molecules in the asymmetric unit. The dotted lines represent the intramolecular hydrogen bonds.

bringing the aldehyde group into approximate coplanarity with the chromanone ring system. In contrast, the phenyl substituents attached to C2 in each molecule are approximately orthogonal to the chromanone ring systems [plane-to-plane angles of $99.4(1)$ and $97.5(1)^\circ$ to the phenyl rings of the chromanones].

3. Supramolecular features

The shortest intermolecular contacts to hydrogen-bond acceptors of the unique molecules come from the pseudo-equatorial $C-H$ bonds in the CH_2 moieties of the chromanone rings to the aldehyde oxygen atoms, O9 and O9A (Table 1). These $C-H\cdots O=CH$ connections assemble the unique molecules into alternating chains that propagate parallel to the crystallographic a -axis, as shown in Fig. 3. The supramolecular alignment of these hydrogen bonded chains are controlled by $\pi-\pi$ interactions of phenyl rings from

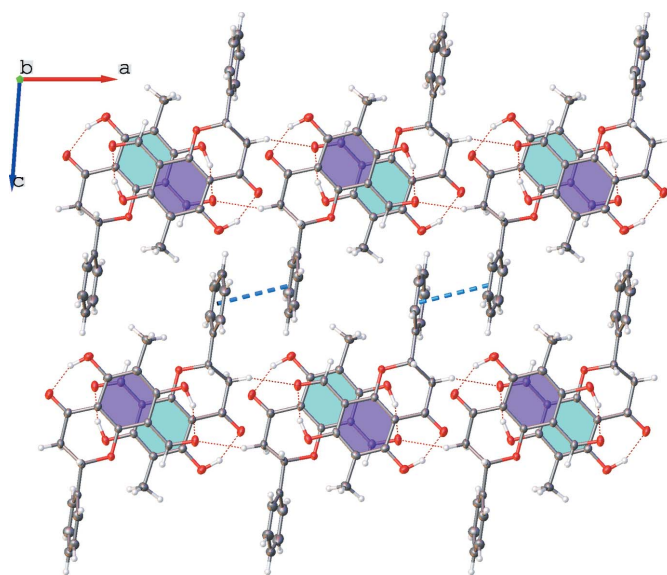


Figure 3
 A view parallel to the crystallographic b -axis, with intramolecular and intermolecular hydrogen bonds shown as dotted red lines and the $\pi-\pi$ interactions as dashed blue lines. The intermolecular hydrogen bonds link molecules into chains propagating along the crystallographic a -axis direction and the $\pi-\pi$ interactions link the hydrogen-bonded chains into two-dimensional sheets in the crystallographic ac plane. Displacement ellipsoids are plotted at the 50% probability level.

adjacent chains. This links the chains into two-dimensional sheets in the *ac* plane. The plane-to-plane angle between phenyl rings is $4.7 (1)^\circ$ and the distance from plane centroid to plane centroid, as indicated by the blue dashed line in Fig. 3, is $3.821 (2) \text{ \AA}$.

4. Synthesis and crystallization

Plant Material

Desmos dumosus twigs were collected from Doi Tung, Chiang Rai Province, Thailand, in February 2016. The plant was identified by Mr Matin Van de Bult (Doi Tung Development Project, Chiang Rai, Thailand). The specimen (MFU-NPR0110) was deposited at Mae Fah Luang University's Natural Products Research Laboratory.

Extraction and Isolation

Air-dried twigs of *D. dumosus* (7.00 kg) were extracted for three days at room temperature with EtOAc (20 L). Removal of the solvent under reduced pressure provided the crude extract (92.7 g), which was subjected to column chromatography over silica gel using a gradient of hexanes and EtOAc (100% hexanes to 100% EtOAc) to afford 12 fractions (D1-D12). Fraction D5 (7.70 g) was further fractionated by column chromatography over Sephadex-LH 20 resin eluting with 100% MeOH to provide nine subfractions (D5A-D5I). Subfraction D5E (1.45 g) was further separated by column chromatography over silica gel (1:4, *v/v* EtOAc/hexanes) to give lawinal (35.5 mg) as a faint yellow-coloured solid.

Crystallization and characterization data

Crystals grew from slow evaporation of a 1:4 dichloromethane:methanol solution. M.p. 488–489 K [Lit. (Prawat *et al.*, 2012) 487 K]; $[\alpha]_{\text{D}}^{25} -52.4$ (*c* 0.2, CH_2Cl_2); ECD (3.4×10^{-4}) λ_{max} ($\Delta\epsilon$) 298 (+4.66), 276 (−4.88), and 228 (+3.82); ^1H NMR (CDCl_3 , 500 MHz) δ_{H} 12.85 (1H, *s*, OH-5), 13.00 (1H, *s*, OH-7), 10.11 (1H, *s*, CHO), 7.45 (5H, *m*, H-2'–H-6'), 5.57 (1H, *dd*, *J* = 13.0, 3.2 Hz, H-2), 3.16 (1H, *dd*, *J* = 17.3, 13.0 Hz, H α -3), 2.93 (1H, *dd*, *J* = 17.3, 3.2 Hz, H β -3), 2.02 (3H, *s*, CH_3); ^{13}C NMR (CDCl_3 , 125 MHz) δ_{C} 6.0 (CH_3), 42.8 (C-3), 80.3 (C2), 101.3 (C4a), 104.1 (C8), 105.7 (C6), 126.1 (C2', C6'), 129.1 (C3', C4', C5'), 137.6 (C1'), 164.7 (C8a), 166.6 (C5), 168.8 (C7), 191.3 (CHO), 195.3 (C4).

5. Refinement

The data were collected using Mo $K\alpha$ radiation, therefore anomalous dispersion effects are small. The crystal structure itself is pseudo-centrosymmetric. Indeed, a structural solution can be successfully obtained in a centrosymmetric space group, although this results in an unsatisfactory refinement, with apparent disorder about the stereogenic center, as expected. The actual inversion symmetry is, of course, incompatible with the natural origin and optical activity of the compound. Crystal data, data collection and structure refinement details are summarized in Table 2. Tertiary C(H), secondary C(H,H), primary C(H,H,H) and aromatic H atoms were placed in geometrically idealized positions (C–H = 1.00, 0.99, 0.98, and 0.95 Å, respectively) and refined in riding

Table 2

Experimental details.

Crystal data	
Chemical formula	$\text{C}_{17}\text{H}_{14}\text{O}_5$
M_r	298.28
Crystal system, space group	Monoclinic, <i>I</i> 2
Temperature (K)	150
<i>a</i> , <i>b</i> , <i>c</i> (Å)	18.9581 (14), 6.6461 (4), 22.4043 (16)
β ($^\circ$)	94.163 (7)
<i>V</i> (Å ³)	2815.4 (3)
<i>Z</i>	8
Radiation type	Mo $K\alpha$
μ (mm ^{−1})	0.10
Crystal size (mm)	0.42 × 0.19 × 0.16
Data collection	
Diffractometer	Rigaku XtaLAB Mini II
Absorption correction	Multi-scan (<i>CrysAlis PRO</i> ; Rigaku OD, 2018)
T_{min} , T_{max}	0.728, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	33601, 7914, 6451
R_{int}	0.072
$(\sin \theta/\lambda)_{\text{max}}$ (Å ^{−1})	0.718
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, <i>S</i>	0.053, 0.144, 1.02
No. of reflections	7914
No. of parameters	415
No. of restraints	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ^{−3})	0.39, −0.32
Absolute structure	Flack <i>x</i> determined using 2350 quotients $[(I^+) - (I^-)] / [(I^+) + (I^-)]$ (Parsons <i>et al.</i> , 2013)
Absolute structure parameter	−0.1 (5)

Computer programs: *CrysAlis PRO* (Rigaku OD, 2018), *SHELXS* (Sheldrick, 2008), *SHELXL* (Sheldrick, 2015) and *OLEX2* (Dolomanov *et al.*, 2009).

models with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{C})$. The methyl group attached to C-6 was refined as a rotating body. The hydroxylic H atoms were refined unconstrained in isotropic approximation.

Acknowledgements

The University of Wollongong is acknowledged for providing laboratory facilities.

Funding information

Funding for this research was provided by: Thailand Science Research and Innovation (grant No. DBG6280007; student-ship No. PHD/0133/2559 to V. Suthiphasilp); Mae Fah Luang University.

References

- Bajgai, S. P., Prachyawarakorn, V., Mahidol, C., Ruchirawat, S. & Kittakoop, P. (2011). *Phytochemistry*, **72**, 2062–2067.
 Brophy, J. J., Goldsack, R. J. & Forster, P. I. (2002). *J. Essent. Oil Res.* **14**, 298–301.
 Bunyapraphatsara, N., Dechsree, S., Yoosook, C., Herunsalee, A. & Panpisutchai, Y. (2000). *Phytomedicine*, **6**, 421–424.

- Clement, J. A., Ondeyka, J. G. & Goetz, M. A. (2017). *Phytochemistry Lett.* **22**, 117–121.
- Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
- Hooft, R. W. W., Straver, L. H. & Spek, A. L. (2008). *J. Appl. Cryst.* **41**, 96–103.
- Kummee, S. & Intaraksa, N. (2008). *Songklanakarin J. Sci. Technol.* **30**, 635–639.
- Kuo, P. C., Thang, T. D., Huang, G. J., Huang, B. S., Hoa, L. T. M., Yang, M. & Wu, T. (2015). *Chem. Nat. Compd.* **51**, 152–155.
- Liao, S. X., Han, G. Y., Zhang, Y. R., Zheng, Q. T. & He, C. H. (1989). *Yao xue xue bao.* **24**, 110–113.
- Meesakul, P., Richardson, C., Pyne, S. G. & Laphookhieo, S. (2019). *J. Nat. Prod.* **82**, 741–747.
- Miller, A. L. (1996). *Alt. Med. Rev.* **1**, 103–111.
- Parsons, S., Flack, H. D. & Wagner, T. (2013). *Acta Cryst.* **B69**, 249–259.
- Prawat, U., Phupornprasert, D., Butsuri, A., Salae, A.-W., Boonsri, S. & Tuntiwachwuttikul, P. (2012). *Phytochemistry Lett.* **5**, 809–813.
- Rahman, M. M., Qais, N. & Rashid, M. A. (2003). *Fitoterapia*, **74**, 511–514.
- Rigaku OD (2018). *CrysAlis PRO*. Rigaku Oxford Diffraction, Yarnton, England.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Sheldrick, G. M. (2015). *Acta Cryst.* **C71**, 3–8.
- Spek, A. L. (2020). *Acta Cryst.* **E76**, 1–11.
- Wu, J. H., Shi, N., Pan, M. X., Wang, X. H. & Yi, Y. H. (2005). *Chin. Pharm. J.* **40**, 495–497.
- Wu, J. H., Wang, X. H., Yi, Y. H. & Lee, K. H. (2003). *Bioorg. Med. Chem. Lett.* **13**, 1813–1815.

supporting information

Acta Cryst. (2021). E77, 75-78 [https://doi.org/10.1107/S2056989020016540]

Isolation and crystal structure of lawinal

Virayu Suthiphasilp, Pornphimol Meesakul, Christopher Richardson, Stephen G. Pyne and Surat Laphookhieo

Computing details

Data collection: *CrysAlis PRO* (Rigaku OD, 2018); cell refinement: *CrysAlis PRO* (Rigaku OD, 2018); data reduction: *CrysAlis PRO* (Rigaku OD, 2018); program(s) used to solve structure: *SHELXS* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

(2S)-5,7-Dihydroxy-6-methyl-4-oxo-2-phenylchromane-8-carbaldehyde

Crystal data

$C_{17}H_{14}O_5$	$F(000) = 1248$
$M_r = 298.28$	$D_x = 1.407 \text{ Mg m}^{-3}$
Monoclinic, <i>I</i> 2	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$a = 18.9581 (14) \text{ \AA}$	Cell parameters from 12756 reflections
$b = 6.6461 (4) \text{ \AA}$	$\theta = 2.1\text{--}30.6^\circ$
$c = 22.4043 (16) \text{ \AA}$	$\mu = 0.10 \text{ mm}^{-1}$
$\beta = 94.163 (7)^\circ$	$T = 150 \text{ K}$
$V = 2815.4 (3) \text{ \AA}^3$	Block, clear colourless
$Z = 8$	$0.42 \times 0.19 \times 0.16 \text{ mm}$

Data collection

Rigaku XtaLAB Mini II diffractometer	33601 measured reflections
Radiation source: fine-focus sealed X-ray tube, Rigaku (Mo) X-ray Source	7914 independent reflections
Graphite monochromator	6451 reflections with $I > 2\sigma(I)$
ω scans	$R_{\text{int}} = 0.072$
Absorption correction: multi-scan (<i>CrysAlisPro</i> ; Rigaku OD, 2018)	$\theta_{\text{max}} = 30.7^\circ$, $\theta_{\text{min}} = 2.2^\circ$
$T_{\text{min}} = 0.728$, $T_{\text{max}} = 1.000$	$h = -26 \rightarrow 26$
	$k = -9 \rightarrow 9$
	$l = -32 \rightarrow 32$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Hydrogen site location: mixed
$R[F^2 > 2\sigma(F^2)] = 0.053$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.144$	$w = 1/[\sigma^2(F_o^2) + (0.0925P)^2]$
$S = 1.02$	where $P = (F_o^2 + 2F_c^2)/3$
7914 reflections	$(\Delta/\sigma)_{\text{max}} < 0.001$
415 parameters	$\Delta\rho_{\text{max}} = 0.39 \text{ e \AA}^{-3}$
1 restraint	

$$\Delta\rho_{\min} = -0.32 \text{ e } \text{\AA}^{-3}$$

Absolute structure: Flack x determined using
2350 quotients $[(F^+)-(F^-)]/[(F^+)+(F^-)]$ (Parsons *et al.*, 2013)

Absolute structure parameter: -0.1 (5)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.57571 (8)	0.2436 (3)	0.16037 (6)	0.0205 (4)
O4	0.73983 (8)	0.1600 (3)	0.28806 (7)	0.0284 (4)
O5	0.64990 (9)	0.1903 (3)	0.36865 (6)	0.0248 (4)
O7	0.40722 (8)	0.2205 (3)	0.30729 (7)	0.0220 (4)
O9	0.37112 (8)	0.2498 (3)	0.19412 (7)	0.0262 (4)
C2	0.64822 (11)	0.3054 (4)	0.14926 (8)	0.0204 (4)
H2	0.655815	0.445414	0.164727	0.024*
C3	0.70093 (11)	0.1669 (4)	0.18367 (9)	0.0225 (5)
H3A	0.693728	0.026481	0.169839	0.027*
H3B	0.749831	0.207369	0.176389	0.027*
C4	0.69015 (11)	0.1811 (4)	0.24939 (9)	0.0205 (4)
C5	0.59854 (11)	0.2066 (3)	0.32465 (9)	0.0184 (4)
C6	0.52807 (11)	0.2131 (4)	0.34014 (9)	0.0193 (5)
C7	0.47547 (11)	0.2219 (3)	0.29309 (9)	0.0173 (4)
C8	0.49093 (11)	0.2327 (3)	0.23198 (9)	0.0163 (4)
C9	0.43514 (11)	0.2491 (4)	0.18501 (9)	0.0203 (5)
H9	0.447893	0.259941	0.144908	0.024*
C10	0.50961 (12)	0.2053 (5)	0.40436 (9)	0.0280 (6)
H10A	0.488694	0.333896	0.415220	0.042*
H10B	0.552530	0.180389	0.430374	0.042*
H10C	0.475581	0.096640	0.409285	0.042*
C4B	0.61711 (12)	0.2130 (4)	0.26415 (9)	0.0177 (4)
C8B	0.56271 (11)	0.2306 (3)	0.21864 (9)	0.0165 (4)
C1P	0.65328 (11)	0.3085 (4)	0.08262 (9)	0.0243 (5)
C2P	0.64364 (13)	0.1363 (5)	0.04797 (11)	0.0366 (6)
H2P	0.633195	0.011407	0.065971	0.044*
C3P	0.64952 (15)	0.1489 (6)	-0.01417 (12)	0.0462 (8)
H3P	0.642758	0.032115	-0.038366	0.055*
C4P	0.66512 (13)	0.3311 (7)	-0.04014 (10)	0.0448 (8)
H4P	0.669125	0.338660	-0.082103	0.054*
C5P	0.67485 (13)	0.5008 (6)	-0.00559 (10)	0.0430 (7)
H5P	0.685672	0.625104	-0.023760	0.052*
C6P	0.66898 (12)	0.4918 (5)	0.05540 (10)	0.0324 (6)
H6P	0.675579	0.609940	0.079017	0.039*
O1A	0.42391 (8)	0.7039 (3)	0.34098 (6)	0.0201 (3)

O4A	0.26002 (9)	0.6903 (3)	0.21057 (7)	0.0290 (4)
O5A	0.35043 (9)	0.7514 (3)	0.13220 (7)	0.0280 (4)
O7A	0.59290 (8)	0.7443 (3)	0.19545 (7)	0.0233 (4)
O9A	0.62819 (8)	0.7220 (3)	0.30829 (7)	0.0267 (4)
C2A	0.35218 (11)	0.7575 (4)	0.35631 (9)	0.0206 (5)
H2A	0.345949	0.906404	0.352371	0.025*
C3A	0.29726 (11)	0.6534 (4)	0.31422 (9)	0.0243 (5)
H3AA	0.299403	0.506440	0.321265	0.029*
H3AB	0.249480	0.700565	0.322737	0.029*
C4A	0.30940 (12)	0.6959 (4)	0.25019 (9)	0.0211 (4)
C5A	0.40185 (12)	0.7439 (3)	0.17646 (9)	0.0202 (5)
C6A	0.47233 (12)	0.7487 (4)	0.16168 (9)	0.0212 (5)
C7A	0.52461 (11)	0.7395 (3)	0.20899 (9)	0.0188 (4)
C8A	0.50869 (11)	0.7268 (3)	0.26992 (9)	0.0173 (4)
C9A	0.56451 (11)	0.7198 (4)	0.31718 (9)	0.0204 (5)
H9A	0.551698	0.713108	0.357350	0.024*
C10A	0.49126 (13)	0.7599 (5)	0.09739 (9)	0.0307 (6)
H10D	0.451210	0.712862	0.070936	0.046*
H10E	0.532553	0.674776	0.092114	0.046*
H10F	0.502307	0.899468	0.087429	0.046*
C4AA	0.38250 (12)	0.7287 (4)	0.23673 (9)	0.0187 (4)
C8AA	0.43682 (11)	0.7208 (3)	0.28291 (9)	0.0167 (4)
C1PA	0.34755 (12)	0.6990 (4)	0.42113 (9)	0.0223 (5)
C2PA	0.33826 (12)	0.5001 (4)	0.43833 (9)	0.0278 (5)
H2PA	0.335466	0.396820	0.408958	0.033*
C3PA	0.33302 (13)	0.4515 (4)	0.49835 (10)	0.0316 (6)
H3PA	0.326462	0.315656	0.509901	0.038*
C4PA	0.33746 (12)	0.6031 (5)	0.54122 (10)	0.0302 (6)
H4PA	0.333388	0.570378	0.582103	0.036*
C5PA	0.34774 (13)	0.8014 (5)	0.52490 (10)	0.0317 (6)
H5PA	0.351439	0.904073	0.554461	0.038*
C6PA	0.35263 (12)	0.8490 (4)	0.46478 (9)	0.0281 (5)
H6PA	0.359485	0.984872	0.453403	0.034*
H7A	0.616 (2)	0.742 (6)	0.2338 (15)	0.060 (11)*
H5	0.6917 (17)	0.176 (6)	0.3492 (13)	0.049 (9)*
H7	0.3847 (18)	0.226 (6)	0.2681 (13)	0.042 (9)*
H5A	0.3078 (17)	0.733 (5)	0.1507 (13)	0.041 (9)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0133 (7)	0.0324 (10)	0.0158 (6)	-0.0003 (6)	0.0016 (5)	-0.0005 (6)
O4	0.0144 (7)	0.0437 (11)	0.0265 (8)	0.0028 (7)	-0.0028 (6)	0.0037 (7)
O5	0.0194 (8)	0.0352 (10)	0.0193 (7)	0.0010 (7)	-0.0026 (6)	0.0004 (7)
O7	0.0152 (8)	0.0282 (10)	0.0233 (7)	-0.0001 (6)	0.0062 (6)	0.0003 (6)
O9	0.0131 (8)	0.0363 (11)	0.0295 (8)	0.0006 (7)	0.0032 (6)	0.0018 (7)
C2	0.0136 (9)	0.0281 (12)	0.0198 (9)	0.0000 (8)	0.0031 (7)	0.0003 (8)
C3	0.0126 (9)	0.0326 (13)	0.0225 (9)	0.0021 (9)	0.0028 (7)	-0.0008 (9)

C4	0.0167 (10)	0.0247 (11)	0.0200 (9)	0.0009 (8)	0.0011 (7)	0.0024 (8)
C5	0.0182 (11)	0.0191 (11)	0.0178 (9)	0.0010 (8)	-0.0002 (8)	0.0002 (8)
C6	0.0183 (11)	0.0224 (12)	0.0176 (9)	0.0003 (8)	0.0030 (8)	0.0001 (8)
C7	0.0158 (11)	0.0167 (11)	0.0199 (9)	0.0000 (8)	0.0041 (8)	-0.0001 (8)
C8	0.0139 (10)	0.0177 (11)	0.0172 (8)	0.0003 (8)	0.0017 (7)	-0.0006 (7)
C9	0.0165 (11)	0.0222 (11)	0.0221 (10)	0.0001 (8)	0.0013 (8)	-0.0009 (8)
C10	0.0227 (12)	0.0425 (16)	0.0194 (10)	-0.0009 (10)	0.0045 (9)	0.0010 (10)
C4B	0.0157 (10)	0.0203 (11)	0.0168 (9)	0.0003 (8)	-0.0005 (7)	-0.0004 (8)
C8B	0.0142 (10)	0.0170 (11)	0.0184 (9)	-0.0003 (8)	0.0014 (8)	-0.0008 (8)
C1P	0.0128 (10)	0.0411 (15)	0.0195 (9)	0.0030 (9)	0.0044 (7)	0.0003 (9)
C2P	0.0278 (13)	0.0468 (17)	0.0355 (12)	-0.0015 (12)	0.0054 (10)	-0.0102 (12)
C3P	0.0294 (14)	0.075 (2)	0.0339 (13)	0.0016 (15)	-0.0012 (10)	-0.0245 (15)
C4P	0.0223 (13)	0.090 (3)	0.0218 (10)	0.0010 (15)	0.0026 (9)	0.0013 (15)
C5P	0.0309 (14)	0.069 (2)	0.0297 (12)	0.0013 (14)	0.0033 (10)	0.0158 (14)
C6P	0.0259 (13)	0.0431 (16)	0.0286 (11)	0.0053 (11)	0.0042 (9)	0.0083 (11)
O1A	0.0137 (7)	0.0304 (9)	0.0165 (6)	0.0004 (6)	0.0017 (5)	0.0003 (6)
O4A	0.0154 (8)	0.0450 (12)	0.0261 (8)	0.0013 (7)	-0.0028 (6)	0.0000 (8)
O5A	0.0226 (9)	0.0426 (11)	0.0183 (7)	0.0018 (8)	-0.0019 (6)	-0.0020 (7)
O7A	0.0159 (8)	0.0285 (10)	0.0264 (8)	-0.0009 (6)	0.0071 (6)	-0.0023 (7)
O9A	0.0136 (8)	0.0353 (11)	0.0310 (8)	0.0012 (7)	0.0015 (6)	-0.0002 (7)
C2A	0.0155 (10)	0.0272 (12)	0.0195 (9)	0.0034 (8)	0.0035 (8)	0.0009 (8)
C3A	0.0136 (9)	0.0376 (14)	0.0218 (9)	-0.0006 (9)	0.0022 (7)	0.0000 (9)
C4A	0.0156 (10)	0.0258 (12)	0.0215 (9)	0.0022 (9)	-0.0014 (7)	-0.0023 (8)
C5A	0.0208 (11)	0.0220 (12)	0.0174 (9)	0.0010 (8)	-0.0008 (8)	-0.0022 (8)
C6A	0.0231 (12)	0.0217 (12)	0.0192 (9)	0.0004 (9)	0.0045 (8)	-0.0015 (8)
C7A	0.0150 (11)	0.0179 (11)	0.0240 (10)	-0.0005 (8)	0.0050 (8)	-0.0022 (9)
C8A	0.0153 (11)	0.0174 (11)	0.0193 (9)	0.0002 (8)	0.0015 (8)	-0.0009 (7)
C9A	0.0141 (10)	0.0230 (12)	0.0238 (10)	-0.0005 (8)	0.0003 (8)	-0.0011 (8)
C10A	0.0266 (13)	0.0455 (16)	0.0207 (10)	0.0016 (11)	0.0069 (9)	-0.0020 (10)
C4AA	0.0154 (10)	0.0230 (11)	0.0177 (9)	0.0015 (8)	-0.0001 (8)	-0.0026 (8)
C8AA	0.0151 (10)	0.0183 (11)	0.0168 (9)	0.0001 (8)	0.0015 (7)	-0.0018 (8)
C1PA	0.0156 (10)	0.0330 (13)	0.0185 (9)	0.0028 (9)	0.0030 (8)	-0.0028 (9)
C2PA	0.0306 (13)	0.0321 (13)	0.0210 (10)	0.0037 (10)	0.0030 (9)	-0.0037 (9)
C3PA	0.0332 (14)	0.0327 (14)	0.0290 (11)	0.0004 (11)	0.0030 (10)	0.0029 (10)
C4PA	0.0230 (12)	0.0446 (16)	0.0233 (10)	0.0030 (11)	0.0045 (9)	0.0020 (10)
C5PA	0.0284 (13)	0.0407 (16)	0.0259 (11)	0.0015 (11)	0.0018 (9)	-0.0113 (11)
C6PA	0.0262 (12)	0.0306 (13)	0.0278 (10)	-0.0031 (10)	0.0044 (9)	-0.0041 (10)

Geometric parameters (Å, °)

O1—C2	1.473 (2)	O1A—C2A	1.470 (2)
O1—C8B	1.349 (2)	O1A—C8AA	1.346 (2)
O4—C4	1.241 (3)	O4A—C4A	1.243 (3)
O5—C5	1.339 (3)	O5A—C5A	1.340 (3)
O5—H5	0.94 (3)	O5A—H5A	0.94 (3)
O7—C7	1.355 (2)	O7A—C7A	1.351 (2)
O7—H7	0.95 (3)	O7A—H7A	0.94 (3)
O9—C9	1.245 (3)	O9A—C9A	1.238 (2)

C2—H2	1.0000	C2A—H2A	1.0000
C2—C3	1.526 (3)	C2A—C3A	1.520 (3)
C2—C1P	1.503 (3)	C2A—C1PA	1.512 (3)
C3—H3A	0.9900	C3A—H3AA	0.9900
C3—H3B	0.9900	C3A—H3AB	0.9900
C3—C4	1.504 (3)	C3A—C4A	1.496 (3)
C4—C4B	1.462 (3)	C4A—C4AA	1.456 (3)
C5—C6	1.405 (3)	C5A—C6A	1.400 (3)
C5—C4B	1.426 (3)	C5A—C4AA	1.428 (3)
C6—C7	1.399 (3)	C6A—C7A	1.399 (3)
C6—C10	1.506 (2)	C6A—C10A	1.511 (2)
C7—C8	1.423 (2)	C7A—C8A	1.422 (3)
C8—C9	1.441 (3)	C8A—C9A	1.442 (3)
C8—C8B	1.414 (3)	C8A—C8AA	1.414 (3)
C9—H9	0.9500	C9A—H9A	0.9500
C10—H10A	0.9800	C10A—H10D	0.9800
C10—H10B	0.9800	C10A—H10E	0.9800
C10—H10C	0.9800	C10A—H10F	0.9800
C4B—C8B	1.401 (3)	C4AA—C8AA	1.407 (3)
C1P—C2P	1.387 (4)	C1PA—C2PA	1.392 (4)
C1P—C6P	1.404 (4)	C1PA—C6PA	1.394 (3)
C2P—H2P	0.9500	C2PA—H2PA	0.9500
C2P—C3P	1.407 (3)	C2PA—C3PA	1.393 (3)
C3P—H3P	0.9500	C3PA—H3PA	0.9500
C3P—C4P	1.384 (5)	C3PA—C4PA	1.390 (4)
C4P—H4P	0.9500	C4PA—H4PA	0.9500
C4P—C5P	1.373 (5)	C4PA—C5PA	1.385 (4)
C5P—H5P	0.9500	C5PA—H5PA	0.9500
C5P—C6P	1.380 (3)	C5PA—C6PA	1.393 (3)
C6P—H6P	0.9500	C6PA—H6PA	0.9500
C8B—O1—C2	114.82 (16)	C8AA—O1A—C2A	116.23 (16)
C5—O5—H5	105.1 (18)	C5A—O5A—H5A	105.8 (18)
C7—O7—H7	99 (2)	C7A—O7A—H7A	101 (2)
O1—C2—H2	108.3	O1A—C2A—H2A	108.9
O1—C2—C3	109.37 (18)	O1A—C2A—C3A	110.40 (17)
O1—C2—C1P	107.42 (17)	O1A—C2A—C1PA	106.34 (17)
C3—C2—H2	108.3	C3A—C2A—H2A	108.9
C1P—C2—H2	108.3	C1PA—C2A—H2A	108.9
C1P—C2—C3	115.06 (18)	C1PA—C2A—C3A	113.22 (18)
C2—C3—H3A	109.9	C2A—C3A—H3AA	109.4
C2—C3—H3B	109.9	C2A—C3A—H3AB	109.4
H3A—C3—H3B	108.3	H3AA—C3A—H3AB	108.0
C4—C3—C2	109.05 (17)	C4A—C3A—C2A	111.28 (19)
C4—C3—H3A	109.9	C4A—C3A—H3AA	109.4
C4—C3—H3B	109.9	C4A—C3A—H3AB	109.4
O4—C4—C3	121.76 (19)	O4A—C4A—C3A	121.2 (2)
O4—C4—C4B	122.81 (18)	O4A—C4A—C4AA	122.38 (19)

C4B—C4—C3	115.38 (19)	C4AA—C4A—C3A	116.23 (19)
O5—C5—C6	118.33 (17)	O5A—C5A—C6A	118.67 (18)
O5—C5—C4B	119.06 (18)	O5A—C5A—C4AA	118.64 (19)
C6—C5—C4B	122.6 (2)	C6A—C5A—C4AA	122.7 (2)
C5—C6—C10	121.7 (2)	C5A—C6A—C10A	121.5 (2)
C7—C6—C5	116.99 (17)	C7A—C6A—C5A	117.11 (18)
C7—C6—C10	121.26 (19)	C7A—C6A—C10A	121.33 (19)
O7—C7—C6	117.62 (17)	O7A—C7A—C6A	117.80 (18)
O7—C7—C8	119.6 (2)	O7A—C7A—C8A	119.4 (2)
C6—C7—C8	122.82 (18)	C6A—C7A—C8A	122.82 (18)
C7—C8—C9	121.00 (18)	C7A—C8A—C9A	120.75 (18)
C8B—C8—C7	118.1 (2)	C8AA—C8A—C7A	118.3 (2)
C8B—C8—C9	120.86 (17)	C8AA—C8A—C9A	120.95 (18)
O9—C9—C8	123.58 (18)	O9A—C9A—C8A	123.61 (19)
O9—C9—H9	118.2	O9A—C9A—H9A	118.2
C8—C9—H9	118.2	C8A—C9A—H9A	118.2
C6—C10—H10A	109.5	C6A—C10A—H10D	109.5
C6—C10—H10B	109.5	C6A—C10A—H10E	109.5
C6—C10—H10C	109.5	C6A—C10A—H10F	109.5
H10A—C10—H10B	109.5	H10D—C10A—H10E	109.5
H10A—C10—H10C	109.5	H10D—C10A—H10F	109.5
H10B—C10—H10C	109.5	H10E—C10A—H10F	109.5
C5—C4B—C4	120.9 (2)	C5A—C4AA—C4A	121.3 (2)
C8B—C4B—C4	120.43 (17)	C8AA—C4AA—C4A	119.93 (18)
C8B—C4B—C5	118.34 (19)	C8AA—C4AA—C5A	118.26 (19)
O1—C8B—C8	116.75 (19)	O1A—C8AA—C8A	116.55 (19)
O1—C8B—C4B	122.21 (18)	O1A—C8AA—C4AA	122.63 (18)
C4B—C8B—C8	121.03 (18)	C4AA—C8AA—C8A	120.81 (18)
C2P—C1P—C2	122.0 (2)	C2PA—C1PA—C2A	121.8 (2)
C2P—C1P—C6P	119.7 (2)	C2PA—C1PA—C6PA	119.2 (2)
C6P—C1P—C2	118.3 (2)	C6PA—C1PA—C2A	119.0 (2)
C1P—C2P—H2P	120.4	C1PA—C2PA—H2PA	119.8
C1P—C2P—C3P	119.2 (3)	C1PA—C2PA—C3PA	120.5 (2)
C3P—C2P—H2P	120.4	C3PA—C2PA—H2PA	119.8
C2P—C3P—H3P	119.9	C2PA—C3PA—H3PA	120.2
C4P—C3P—C2P	120.2 (3)	C4PA—C3PA—C2PA	119.6 (3)
C4P—C3P—H3P	119.9	C4PA—C3PA—H3PA	120.2
C3P—C4P—H4P	119.8	C3PA—C4PA—H4PA	119.7
C5P—C4P—C3P	120.4 (2)	C5PA—C4PA—C3PA	120.6 (2)
C5P—C4P—H4P	119.8	C5PA—C4PA—H4PA	119.7
C4P—C5P—H5P	119.8	C4PA—C5PA—H5PA	120.3
C4P—C5P—C6P	120.4 (3)	C4PA—C5PA—C6PA	119.4 (2)
C6P—C5P—H5P	119.8	C6PA—C5PA—H5PA	120.3
C1P—C6P—H6P	119.9	C1PA—C6PA—H6PA	119.7
C5P—C6P—C1P	120.2 (3)	C5PA—C6PA—C1PA	120.6 (2)
C5P—C6P—H6P	119.9	C5PA—C6PA—H6PA	119.7
O1—C2—C3—C4	-59.6 (2)	O1A—C2A—C3A—C4A	-53.9 (3)

O1—C2—C1P—C2P	-62.0 (3)	O1A—C2A—C1PA—C2PA	-77.6 (3)
O1—C2—C1P—C6P	118.7 (2)	O1A—C2A—C1PA—C6PA	102.6 (2)
O4—C4—C4B—C5	-4.7 (4)	O4A—C4A—C4AA—C5A	-3.9 (4)
O4—C4—C4B—C8B	-178.3 (2)	O4A—C4A—C4AA—C8AA	-175.9 (2)
O5—C5—C6—C7	-177.4 (2)	O5A—C5A—C6A—C7A	-179.7 (2)
O5—C5—C6—C10	0.9 (4)	O5A—C5A—C6A—C10A	-0.6 (4)
O5—C5—C4B—C4	6.4 (3)	O5A—C5A—C4AA—C4A	7.9 (3)
O5—C5—C4B—C8B	-179.9 (2)	O5A—C5A—C4AA—C8AA	180.0 (2)
O7—C7—C8—C9	2.1 (3)	O7A—C7A—C8A—C9A	0.2 (3)
O7—C7—C8—C8B	-179.0 (2)	O7A—C7A—C8A—C8AA	-179.6 (2)
C2—O1—C8B—C8	161.36 (19)	C2A—O1A—C8AA—C8A	162.39 (19)
C2—O1—C8B—C4B	-19.5 (3)	C2A—O1A—C8AA—C4AA	-18.7 (3)
C2—C3—C4—O4	-148.6 (2)	C2A—C3A—C4A—O4A	-153.9 (2)
C2—C3—C4—C4B	33.8 (3)	C2A—C3A—C4A—C4AA	30.6 (3)
C2—C1P—C2P—C3P	-179.6 (2)	C2A—C1PA—C2PA—C3PA	-178.9 (2)
C2—C1P—C6P—C5P	179.3 (2)	C2A—C1PA—C6PA—C5PA	179.2 (2)
C3—C2—C1P—C2P	60.1 (3)	C3A—C2A—C1PA—C2PA	43.9 (3)
C3—C2—C1P—C6P	-119.3 (2)	C3A—C2A—C1PA—C6PA	-136.0 (2)
C3—C4—C4B—C5	172.9 (2)	C3A—C4A—C4AA—C5A	171.6 (2)
C3—C4—C4B—C8B	-0.7 (3)	C3A—C4A—C4AA—C8AA	-0.4 (3)
C4—C4B—C8B—O1	-8.2 (3)	C4A—C4AA—C8AA—O1A	-6.9 (3)
C4—C4B—C8B—C8	170.9 (2)	C4A—C4AA—C8AA—C8A	172.0 (2)
C5—C6—C7—O7	177.5 (2)	C5A—C6A—C7A—O7A	-179.9 (2)
C5—C6—C7—C8	-2.6 (3)	C5A—C6A—C7A—C8A	-0.3 (3)
C5—C4B—C8B—O1	178.0 (2)	C5A—C4AA—C8AA—O1A	-179.1 (2)
C5—C4B—C8B—C8	-2.9 (3)	C5A—C4AA—C8AA—C8A	-0.3 (3)
C6—C5—C4B—C4	-172.4 (2)	C6A—C5A—C4AA—C4A	-171.3 (2)
C6—C5—C4B—C8B	1.3 (4)	C6A—C5A—C4AA—C8AA	0.8 (4)
C6—C7—C8—C9	-177.7 (2)	C6A—C7A—C8A—C9A	-179.3 (2)
C6—C7—C8—C8B	1.2 (3)	C6A—C7A—C8A—C8AA	0.8 (3)
C7—C8—C9—O9	-1.9 (4)	C7A—C8A—C9A—O9A	-0.8 (4)
C7—C8—C8B—O1	-179.16 (19)	C7A—C8A—C8AA—O1A	178.5 (2)
C7—C8—C8B—C4B	1.7 (3)	C7A—C8A—C8AA—C4AA	-0.5 (3)
C9—C8—C8B—O1	-0.3 (3)	C9A—C8A—C8AA—O1A	-1.4 (3)
C9—C8—C8B—C4B	-179.5 (2)	C9A—C8A—C8AA—C4AA	179.7 (2)
C10—C6—C7—O7	-0.8 (3)	C10A—C6A—C7A—O7A	1.1 (3)
C10—C6—C7—C8	179.0 (2)	C10A—C6A—C7A—C8A	-179.4 (2)
C4B—C5—C6—C7	1.3 (3)	C4AA—C5A—C6A—C7A	-0.5 (4)
C4B—C5—C6—C10	179.7 (2)	C4AA—C5A—C6A—C10A	178.6 (2)
C8B—O1—C2—C3	53.6 (2)	C8AA—O1A—C2A—C3A	49.0 (3)
C8B—O1—C2—C1P	179.10 (19)	C8AA—O1A—C2A—C1PA	172.20 (19)
C8B—C8—C9—O9	179.3 (2)	C8AA—C8A—C9A—O9A	179.0 (2)
C1P—C2—C3—C4	179.4 (2)	C1PA—C2A—C3A—C4A	-173.03 (19)
C1P—C2P—C3P—C4P	0.3 (4)	C1PA—C2PA—C3PA—C4PA	-0.3 (4)
C2P—C1P—C6P—C5P	0.0 (4)	C2PA—C1PA—C6PA—C5PA	-0.7 (4)
C2P—C3P—C4P—C5P	-0.1 (4)	C2PA—C3PA—C4PA—C5PA	-0.7 (4)
C3P—C4P—C5P—C6P	-0.2 (4)	C3PA—C4PA—C5PA—C6PA	0.9 (4)
C4P—C5P—C6P—C1P	0.3 (4)	C4PA—C5PA—C6PA—C1PA	-0.3 (4)

C6P—C1P—C2P—C3P -0.3 (4) C6PA—C1PA—C2PA—C3PA 0.9 (4)

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>
C3—H3B \cdots O9A ⁱ	0.99	2.32	3.252 (3)	158
C3A—H3AB \cdots O9 ⁱⁱ	0.99	2.31	3.248 (3)	157
O7A—H7A \cdots O9A	0.94 (3)	1.67 (3)	2.572 (2)	159 (4)
O5—H5 \cdots O4	0.94 (3)	1.70 (3)	2.579 (2)	154 (3)
O7—H7 \cdots O9	0.95 (3)	1.67 (3)	2.585 (2)	162 (3)
O5A—H5A \cdots O4A	0.94 (3)	1.70 (3)	2.574 (2)	153 (3)

Symmetry codes: (i) $-x+3/2, y-1/2, -z+1/2$; (ii) $-x+1/2, y+1/2, -z+1/2$.