IUCrData

ISSN 2414-3146

Limonin isolated from the seeds of *Citrus limetta* (Indian sweet lemon)

A. K. Bauri,[a] Sabine Foro[b] and Quynh Nguyen Do Nhu[c]*

[a]Bioorganic Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India, [b]FB Material-und Geowissenschaften, Technische Universität Darmstadt, Alarich-Weiss-Strasse 2, 64287 Darmstadt, Germany, and [c]Accident and Emergency Department, Franco Vietnamese Hospital, 7 Nguyen Luong Bang Street, Ho Chi Minh City, Vietnam. *Correspondence e-mail: nguyendonhuquynh@yahoo.com

Received 18 January 2016
Accepted 27 January 2016

Edited by H. Stoeckli-Evans, University of Neuchâtel, Switzerland

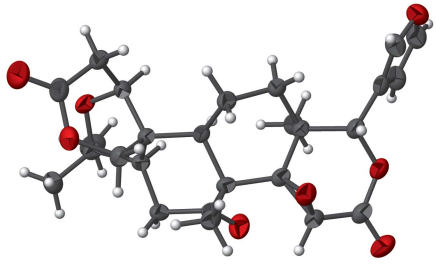
Keywords: crystal structure; limonin; tetracyclic terpenoid; polyoxgenated; antiproliferative; C—H···O hydrogen bonding.

CCDC reference: 1450293

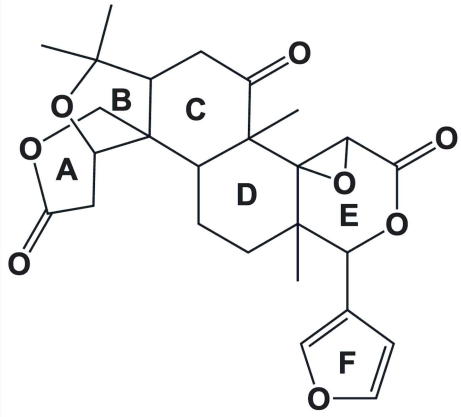
Structural data: full structural data are available from iucrdata.iucr.org

The title molecule, $C_{26}H_{30}O_8$ [systematic name: (4a*S*,14b*R*)-12-(furan-3-yl)-6,6,8a,12a-tetramethyldecahydro-1*H*,3*H*-oxireno[2,3-*d*]pyrano[4′,3′:3,3a]isobenzofuro[5,4-*f*]isochromene-3,8,10(6*H*,9a*H*)-trione], commonly known as limonin, is an antiproliferative polyoxgenated bioactive molecule. It comprises a fused cyclic system containing a cyclohexane (*D*), a cyclohexanone (*C*), a furan (*B*), an epoxide and two lactone rings (*A* and *E*). In addition to these rings, a second furan ring (*F*) is present as a substituent. Only the cyclohexane (*D*) ring has a chair conformation; the other six-membered rings (*A*, *C* and *E*) have twist-boat conformations due to steric hinderance or bonding strain. In the crystal, molecules are linked by C—H···O hydrogen bonds, forming a three-dimensional structure.

3D view



Chemical scheme



Structure description

The fruit of *Citrus limetta* or Indian sweet lemon, is popularly known as *Mousombi* in Mumbai, India. It was procured from local markets for chemical profiling of the seeds in our search for antiproliferative compounds. The roles of citrous limonoids as functional chemicals in agricultural foods have been reviewed (Berhow *et al.*, 2000). The juices of *Citrus limetta* possess a pleasant aroma and have been used as a natural antioxidant and preservative in various food industries, whereas its seeds are quiet bitter in taste. The seeds have been segregated in two parts such as pericarp (outer coat/peel of the seeds) and seed kernel (inner part of the seeds). The inner part of the seeds is quiet soft and comparatively heavier than the pericarp which was extracted with methanol. The chemical analysis of this extract revealed that the major constituent is a pale-yellow oil, a glycerol ester of different long-chain fatty acid mixtures. Besides this oil, this extract is a

OPEN ACCESS

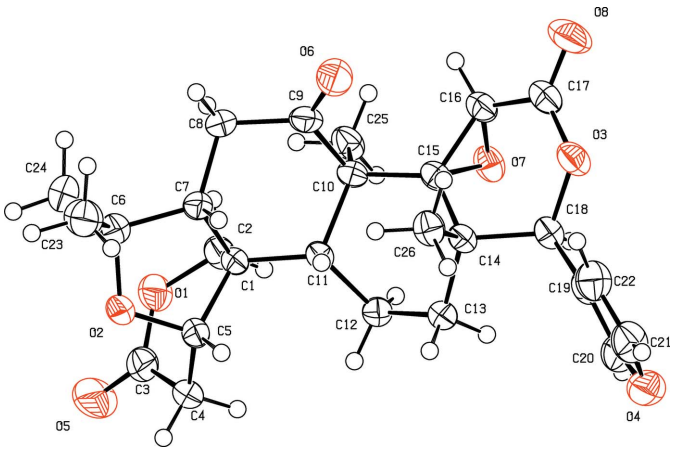


Figure 1
The molecular structure of the title compound, showing the atom labelling and displacement ellipsoids drawn at the 50% probability level

rich source of some limonoids and their glycosides. Limonoids are highly oxygenated tetracyclic terpenoids. Herein we report on the extraction and crystal structure of the major constituent, the title compound limonin.

A view of the molecular structure of the title compound is shown in Fig. 1. The molecule is composed of a series of fused rings. It contains a cyclohexane ring (*D*) with a chair conformation, a cyclohexanone and two lactone rings (*D*, *A* and *E*) with twist-boat conformations, a furan (*B*) and an epoxide ring. In addition to these rings, a second furan ring (*F*) with a flat conformation is present as a substituent. In the crystal, a three-dimensional structure is formed by molecules being linked by C—H···O hydrogen bonds (Table 1 and Fig. 2).

Synthesis and crystallization

The source of the title compound is a citrus fruit known as *sweet lemon*. The crude product has been separated by column chromatography over silica gel by gradient solvent elution. In order to purify the target molecule, it was subjected to preparative thin layer chromtography followed by crystallization. Crystals suitable for X-ray diffraction were obtained by recrystallization of the title compound from hexane–ethylacetate (4:1) at room temperature by slow evaporation.

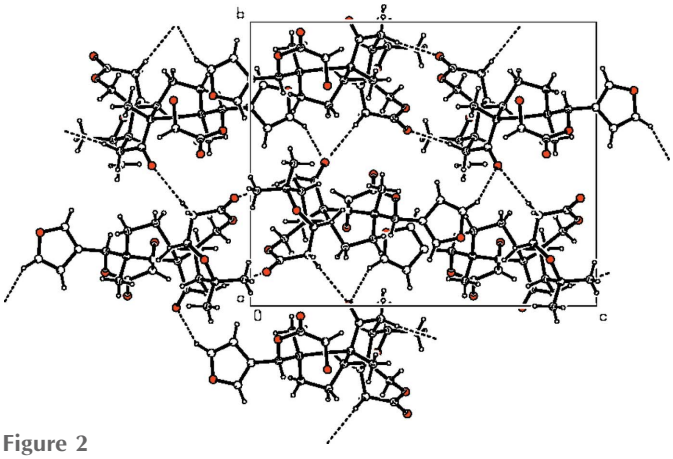


Figure 2
The crystal packing of the title compound, viewed along the *a* axis. The C—H···O hydrogen bonds are shown as dashed lines (see Table 1).

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C8—H8*A*···O5^{i}	0.97	2.35	3.313 (3)	171
C4—H4*A*···O6^{ii}	0.97	2.54	3.442 (3)	156
C21—H21···O6^{iii}	0.93	2.52	3.135 (3)	124

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{26}H_{30}O_8$
M_r	470.50
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	299
a, *b*, *c* (Å)	8.877 (1), 14.533 (2), 17.748 (2)
V (Å^3)	2289.7 (5)
Z	4
Radiation type	Cu *Kα*
μ (mm^{-1})	0.84
Crystal size (mm)	0.28 × 0.22 × 0.15
Data collection	
Diffractometer	Enraf–Nonius CAD-4
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	5062, 4081, 3659
R_{int}	0.018
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.597
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.036, 0.110, 1.10
No. of reflections	4081
No. of parameters	308
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.20, −0.14
Absolute structure	Flack (1983); 1742 Friedel pairs
Absolute structure parameter	−0.2 (2)

Computer programs: *CAD-4-PC Software* (Enraf–Nonius, 1996), *REDU4* (Stoe & Cie, 1987), *SHELXS97* (Sheldrick, 2008), *SHELXL97* (Sheldrick, 2008), *PLATON* (Spek, 2009).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The final refined Flack *x* parameter is −0.2 (2), and the Hooft *y* parameter is −0.02 (10), which despite using Cu *Kα* radiation does not justify the determination of the absolute structure.

Acknowledgements

The authors thank Professor Dr Hartmut Fuess, FG Strukturforschung, FB Material-und Geowissenschaften, Technische Universität Darmstadt, Alarich-Weiss-Strasse 2, 64287 Darmstadt, for diffractometer time.

References

Berhow, M. A., Hasegawa, S. & Manners, G. D. (2000). Editors. *Citrous limonoids: Functional Chemicals in Agriculture Food*. ACS Symposium Series, Vol. 758, Washington, DC: Oxford Press.

Enraf–Nonius (1996). *CAD-4-PC Software*. Enraf–Nonius, Delft, The Netherlands.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

Stoe & Cie (1987). *REDU4*. Stoe & Cie GmbH, Darmstadt, Germany.

full crystallographic data

IUCrData (2016). **1**, x160172 [https://doi.org/10.1107/S2414314616001723]

Limonin isolated from the seeds of *Citrus limetta* (Indian sweet lemon)

A. K. Bauri, Sabine Foro and Quynh Nguyen Do Nhu

(4a*S*,14b*R*)-12-(Furan-3-yl)-6,6,8a,12a-tetramethyldecahydro-1*H*,3*H*-oxireno[2,3-*d*]pyrano[4′,3′:3,3a]isobenzofuro[5,4-*f*]isochromene-3,8,10(6*H*,9a*H*)-trione

Crystal data

$C_{26}H_{30}O_8$
M_r = 470.50
Orthorhombic, $P2_12_12_1$
Hall symbol: P 2ac 2ab
a = 8.877 (1) Å
b = 14.533 (2) Å
c = 17.748 (2) Å
V = 2289.7 (5) Å^3
Z = 4
$F(000)$ = 1000
D_x = 1.365 Mg m^{-3}
Melting point: 320 K
Cu $K\alpha$ radiation, λ = 1.54180 Å
Cell parameters from 25 reflections
θ = 5.6–20.1°
μ = 0.84 mm^{-1}
T = 299 K
Prism, colourless
0.28 × 0.22 × 0.15 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\omega/2\theta$ scans
5062 measured reflections
4081 independent reflections
3659 reflections with $I > 2\sigma(I)$
R_{int} = 0.018
θ_{max} = 67.0°, θ_{min} = 3.9°
h = −10→10
k = −17→1
l = −21→1
3 standard reflections every 120 min
intensity decay: 1.0%

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.110
S = 1.10
4081 reflections
308 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0611P)^2 + 0.4711P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.14 e Å^{-3}
Extinction correction: SHELXL97 (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0025 (3)
Absolute structure: Flack (1983); 1742 Friedel pairs
Absolute structure parameter: −0.2 (2)

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.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.6003 (2)	0.80012 (14)	0.33749 (12)	0.0269 (4)
C2	0.5523 (3)	0.73683 (17)	0.40261 (13)	0.0351 (5)
H2A	0.4863	0.7715	0.4357	0.042*
H2B	0.4935	0.6867	0.3817	0.042*
C3	0.7945 (3)	0.66158 (18)	0.41522 (15)	0.0435 (6)
C4	0.8133 (3)	0.68083 (16)	0.33300 (13)	0.0381 (6)
H4A	0.7519	0.6387	0.3038	0.046*
H4B	0.9177	0.6722	0.3185	0.046*
C5	0.7656 (2)	0.77923 (16)	0.31750 (13)	0.0308 (5)
H5	0.7855	0.7952	0.2648	0.037*
C6	0.7664 (3)	0.91464 (17)	0.39612 (14)	0.0380 (6)
C7	0.6193 (2)	0.90414 (15)	0.35240 (13)	0.0301 (5)
H7	0.6422	0.9299	0.3027	0.036*
C8	0.4757 (3)	0.95437 (16)	0.37654 (14)	0.0339 (5)
H8A	0.4382	0.9291	0.4235	0.041*
H8B	0.4961	1.0193	0.3838	0.041*
C9	0.3599 (3)	0.94112 (16)	0.31414 (13)	0.0333 (5)
C10	0.3312 (2)	0.84126 (15)	0.28916 (12)	0.0291 (5)
C11	0.4883 (2)	0.79615 (14)	0.27056 (12)	0.0260 (4)
H11	0.5325	0.8381	0.2334	0.031*
C12	0.4600 (3)	0.70816 (15)	0.22574 (12)	0.0313 (5)
H12A	0.3807	0.6723	0.2493	0.038*
H12B	0.5507	0.6710	0.2241	0.038*
C13	0.4129 (3)	0.73613 (16)	0.14529 (13)	0.0324 (5)
H13A	0.3583	0.6854	0.1226	0.039*
H13B	0.5030	0.7464	0.1156	0.039*
C14	0.3128 (2)	0.82416 (14)	0.14136 (12)	0.0277 (4)
C15	0.2343 (2)	0.83565 (15)	0.21743 (13)	0.0289 (5)
C16	0.0807 (3)	0.87401 (17)	0.21645 (14)	0.0356 (5)
H16	0.0484	0.9054	0.2626	0.043*
C17	0.0162 (3)	0.90980 (17)	0.14487 (15)	0.0392 (5)
C18	0.1886 (2)	0.80715 (16)	0.08166 (13)	0.0317 (5)
H18	0.1360	0.7500	0.0945	0.038*
C19	0.2444 (2)	0.79965 (17)	0.00200 (13)	0.0334 (5)
C20	0.2693 (3)	0.7219 (2)	−0.03703 (14)	0.0429 (6)

H20	0.2550	0.6629	−0.0181	0.051*
C21	0.3232 (3)	0.8340 (2)	−0.11317 (15)	0.0474 (6)
H21	0.3533	0.8663	−0.1558	0.057*
C22	0.2793 (3)	0.87306 (19)	−0.04913 (14)	0.0449 (6)
H22	0.2725	0.9358	−0.0394	0.054*
C23	0.8507 (3)	1.0017 (2)	0.37485 (19)	0.0556 (8)
H23A	0.7888	1.0543	0.3855	0.067*
H23B	0.8744	1.0003	0.3221	0.067*
H23C	0.9421	1.0055	0.4035	0.067*
C24	0.7532 (3)	0.9063 (2)	0.48154 (15)	0.0520 (7)
H24A	0.7134	0.8469	0.4943	0.062*
H24B	0.6871	0.9534	0.5002	0.062*
H24C	0.8510	0.9135	0.5039	0.062*
C25	0.2427 (3)	0.79570 (18)	0.35395 (13)	0.0373 (5)
H25A	0.1498	0.8282	0.3617	0.045*
H25B	0.3017	0.7977	0.3992	0.045*
H25C	0.2214	0.7328	0.3412	0.045*
C26	0.4005 (3)	0.91202 (16)	0.12044 (13)	0.0352 (5)
H26A	0.4466	0.9042	0.0719	0.042*
H26B	0.4771	0.9232	0.1575	0.042*
H26C	0.3325	0.9634	0.1188	0.042*
O1	0.6722 (2)	0.69751 (13)	0.44804 (9)	0.0437 (4)
O2	0.85351 (17)	0.83682 (12)	0.36687 (10)	0.0387 (4)
O3	0.07834 (18)	0.88186 (12)	0.07995 (10)	0.0396 (4)
O4	0.3184 (2)	0.74096 (14)	−0.10816 (10)	0.0492 (5)
O5	0.8815 (3)	0.62005 (18)	0.45340 (13)	0.0760 (8)
O6	0.2971 (2)	1.00559 (12)	0.28523 (11)	0.0510 (5)
O7	0.10294 (17)	0.77602 (11)	0.22248 (9)	0.0362 (4)
O8	−0.0850 (2)	0.96443 (15)	0.14442 (12)	0.0605 (6)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0224 (10)	0.0306 (11)	0.0277 (10)	0.0021 (9)	−0.0003 (8)	−0.0015 (9)
C2	0.0297 (11)	0.0435 (13)	0.0322 (12)	0.0020 (10)	−0.0006 (9)	0.0040 (10)
C3	0.0466 (14)	0.0428 (13)	0.0411 (14)	0.0106 (12)	−0.0133 (12)	−0.0042 (11)
C4	0.0320 (12)	0.0407 (13)	0.0415 (13)	0.0111 (10)	−0.0066 (10)	−0.0083 (11)
C5	0.0252 (10)	0.0383 (12)	0.0290 (11)	0.0011 (9)	−0.0015 (9)	−0.0037 (10)
C6	0.0277 (11)	0.0408 (13)	0.0456 (14)	0.0019 (10)	−0.0039 (10)	−0.0119 (11)
C7	0.0264 (10)	0.0334 (11)	0.0304 (11)	0.0005 (9)	0.0017 (9)	−0.0050 (9)
C8	0.0324 (11)	0.0347 (12)	0.0346 (12)	0.0045 (9)	0.0007 (10)	−0.0097 (9)
C9	0.0286 (11)	0.0347 (12)	0.0367 (12)	0.0059 (9)	0.0052 (10)	−0.0042 (10)
C10	0.0229 (10)	0.0333 (11)	0.0311 (11)	0.0024 (9)	0.0044 (9)	−0.0016 (9)
C11	0.0231 (9)	0.0294 (10)	0.0256 (10)	0.0016 (9)	−0.0002 (8)	0.0033 (9)
C12	0.0307 (11)	0.0291 (11)	0.0340 (11)	0.0024 (9)	−0.0024 (9)	−0.0026 (10)
C13	0.0290 (11)	0.0362 (11)	0.0319 (11)	0.0055 (9)	−0.0026 (9)	−0.0036 (9)
C14	0.0224 (10)	0.0317 (11)	0.0291 (11)	0.0018 (9)	0.0000 (9)	0.0022 (9)
C15	0.0225 (10)	0.0299 (11)	0.0342 (12)	−0.0001 (9)	0.0016 (9)	0.0031 (9)

C16	0.0244 (11)	0.0456 (13)	0.0367 (12)	0.0051 (10)	0.0002 (10)	−0.0022 (11)
C17	0.0260 (11)	0.0446 (13)	0.0470 (14)	0.0032 (10)	−0.0019 (10)	0.0012 (12)
C18	0.0257 (10)	0.0361 (11)	0.0333 (11)	0.0001 (9)	−0.0016 (9)	0.0040 (9)
C19	0.0268 (10)	0.0425 (12)	0.0308 (11)	0.0030 (10)	−0.0062 (9)	0.0044 (10)
C20	0.0473 (14)	0.0503 (15)	0.0311 (12)	0.0024 (12)	−0.0012 (11)	0.0058 (11)
C21	0.0476 (14)	0.0596 (16)	0.0349 (13)	0.0010 (13)	−0.0020 (12)	0.0113 (12)
C22	0.0501 (15)	0.0464 (14)	0.0380 (14)	0.0011 (12)	−0.0050 (12)	0.0090 (12)
C23	0.0387 (14)	0.0449 (15)	0.083 (2)	−0.0059 (12)	−0.0018 (15)	−0.0158 (15)
C24	0.0479 (15)	0.0638 (18)	0.0444 (15)	0.0069 (14)	−0.0124 (12)	−0.0194 (13)
C25	0.0262 (10)	0.0519 (14)	0.0339 (11)	0.0020 (11)	0.0029 (10)	0.0050 (11)
C26	0.0316 (11)	0.0386 (13)	0.0353 (12)	−0.0048 (10)	0.0001 (10)	0.0045 (10)
O1	0.0458 (9)	0.0531 (10)	0.0321 (8)	0.0094 (9)	−0.0067 (8)	0.0054 (8)
O2	0.0231 (7)	0.0424 (9)	0.0505 (10)	0.0022 (7)	−0.0053 (7)	−0.0140 (8)
O3	0.0308 (8)	0.0491 (10)	0.0391 (9)	0.0090 (8)	−0.0037 (7)	0.0060 (8)
O4	0.0526 (11)	0.0624 (12)	0.0326 (9)	0.0133 (10)	0.0019 (8)	−0.0004 (8)
O5	0.0822 (16)	0.0946 (17)	0.0512 (12)	0.0491 (15)	−0.0201 (12)	0.0015 (12)
O6	0.0601 (12)	0.0371 (9)	0.0557 (11)	0.0131 (9)	−0.0180 (10)	−0.0032 (9)
O7	0.0242 (7)	0.0445 (9)	0.0398 (9)	−0.0063 (7)	0.0002 (7)	0.0057 (8)
O8	0.0461 (11)	0.0700 (14)	0.0656 (13)	0.0286 (11)	−0.0029 (10)	0.0012 (11)

Geometric parameters (Å, º)

C1—C2	1.537 (3)	C13—H13A	0.9700
C1—C5	1.540 (3)	C13—H13B	0.9700
C1—C7	1.544 (3)	C14—C15	1.529 (3)
C1—C11	1.550 (3)	C14—C26	1.541 (3)
C2—O1	1.453 (3)	C14—C18	1.549 (3)
C2—H2A	0.9700	C15—O7	1.455 (3)
C2—H2B	0.9700	C15—C16	1.473 (3)
C3—O5	1.192 (3)	C16—O7	1.442 (3)
C3—O1	1.338 (3)	C16—C17	1.488 (3)
C3—C4	1.495 (4)	C16—H16	0.9800
C4—C5	1.517 (3)	C17—O8	1.199 (3)
C4—H4A	0.9700	C17—O3	1.341 (3)
C4—H4B	0.9700	C18—O3	1.462 (3)
C5—O2	1.441 (3)	C18—C19	1.502 (3)
C5—H5	0.9800	C18—H18	0.9800
C6—O2	1.465 (3)	C19—C20	1.344 (4)
C6—C23	1.517 (4)	C19—C22	1.434 (3)
C6—C24	1.525 (4)	C20—O4	1.364 (3)
C6—C7	1.526 (3)	C20—H20	0.9300
C7—C8	1.531 (3)	C21—C22	1.329 (4)
C7—H7	0.9800	C21—O4	1.356 (3)
C8—C9	1.523 (3)	C21—H21	0.9300
C8—H8A	0.9700	C22—H22	0.9300
C8—H8B	0.9700	C23—H23A	0.9600
C9—O6	1.205 (3)	C23—H23B	0.9600
C9—C10	1.539 (3)	C23—H23C	0.9600

C10—C15	1.539 (3)	C24—H24A	0.9600
C10—C25	1.542 (3)	C24—H24B	0.9600
C10—C11	1.576 (3)	C24—H24C	0.9600
C11—C12	1.527 (3)	C25—H25A	0.9600
C11—H11	0.9800	C25—H25B	0.9600
C12—C13	1.542 (3)	C25—H25C	0.9600
C12—H12A	0.9700	C26—H26A	0.9600
C12—H12B	0.9700	C26—H26B	0.9600
C13—C14	1.559 (3)	C26—H26C	0.9600

C2—C1—C5	108.63 (18)	C14—C13—H13B	108.7
C2—C1—C7	119.16 (18)	H13A—C13—H13B	107.6
C5—C1—C7	97.37 (17)	C15—C14—C26	110.65 (18)
C2—C1—C11	112.09 (17)	C15—C14—C18	107.29 (17)
C5—C1—C11	115.28 (17)	C26—C14—C18	109.09 (17)
C7—C1—C11	103.77 (16)	C15—C14—C13	108.06 (18)
O1—C2—C1	116.69 (18)	C26—C14—C13	113.74 (18)
O1—C2—H2A	108.1	C18—C14—C13	107.77 (17)
C1—C2—H2A	108.1	O7—C15—C16	58.99 (14)
O1—C2—H2B	108.1	O7—C15—C14	110.77 (18)
C1—C2—H2B	108.1	C16—C15—C14	116.94 (19)
H2A—C2—H2B	107.3	O7—C15—C10	115.37 (18)
O5—C3—O1	118.4 (3)	C16—C15—C10	120.47 (19)
O5—C3—C4	125.3 (3)	C14—C15—C10	118.79 (17)
O1—C3—C4	116.3 (2)	O7—C16—C15	59.90 (14)
C3—C4—C5	108.80 (19)	O7—C16—C17	117.5 (2)
C3—C4—H4A	109.9	C15—C16—C17	119.9 (2)
C5—C4—H4A	109.9	O7—C16—H16	116.0
C3—C4—H4B	109.9	C15—C16—H16	116.0
C5—C4—H4B	109.9	C17—C16—H16	116.0
H4A—C4—H4B	108.3	O8—C17—O3	120.2 (2)
O2—C5—C4	106.62 (18)	O8—C17—C16	121.7 (2)
O2—C5—C1	105.16 (17)	O3—C17—C16	118.0 (2)
C4—C5—C1	114.23 (19)	O3—C18—C19	104.78 (17)
O2—C5—H5	110.2	O3—C18—C14	111.85 (18)
C4—C5—H5	110.2	C19—C18—C14	114.90 (18)
C1—C5—H5	110.2	O3—C18—H18	108.4
O2—C6—C23	107.2 (2)	C19—C18—H18	108.4
O2—C6—C24	109.4 (2)	C14—C18—H18	108.4
C23—C6—C24	110.5 (2)	C20—C19—C22	105.3 (2)
O2—C6—C7	101.20 (17)	C20—C19—C18	126.9 (2)
C23—C6—C7	112.2 (2)	C22—C19—C18	127.8 (2)
C24—C6—C7	115.6 (2)	C19—C20—O4	111.0 (2)
C6—C7—C8	121.51 (18)	C19—C20—H20	124.5
C6—C7—C1	106.18 (18)	O4—C20—H20	124.5
C8—C7—C1	115.07 (18)	C22—C21—O4	111.2 (2)
C6—C7—H7	104.0	C22—C21—H21	124.4
C8—C7—H7	104.0	O4—C21—H21	124.4

C1—C7—H7	104.0	C21—C22—C19	106.7 (3)
C9—C8—C7	107.36 (18)	C21—C22—H22	126.7
C9—C8—H8A	110.2	C19—C22—H22	126.7
C7—C8—H8A	110.2	C6—C23—H23A	109.5
C9—C8—H8B	110.2	C6—C23—H23B	109.5
C7—C8—H8B	110.2	H23A—C23—H23B	109.5
H8A—C8—H8B	108.5	C6—C23—H23C	109.5
O6—C9—C8	121.6 (2)	H23A—C23—H23C	109.5
O6—C9—C10	122.3 (2)	H23B—C23—H23C	109.5
C8—C9—C10	116.13 (19)	C6—C24—H24A	109.5
C9—C10—C15	112.40 (18)	C6—C24—H24B	109.5
C9—C10—C25	105.94 (18)	H24A—C24—H24B	109.5
C15—C10—C25	108.01 (18)	C6—C24—H24C	109.5
C9—C10—C11	107.82 (17)	H24A—C24—H24C	109.5
C15—C10—C11	107.42 (17)	H24B—C24—H24C	109.5
C25—C10—C11	115.37 (18)	C10—C25—H25A	109.5
C12—C11—C1	122.43 (17)	C10—C25—H25B	109.5
C12—C11—C10	108.15 (17)	H25A—C25—H25B	109.5
C1—C11—C10	113.04 (16)	C10—C25—H25C	109.5
C12—C11—H11	103.7	H25A—C25—H25C	109.5
C1—C11—H11	103.7	H25B—C25—H25C	109.5
C10—C11—H11	103.7	C14—C26—H26A	109.5
C11—C12—C13	107.83 (17)	C14—C26—H26B	109.5
C11—C12—H12A	110.1	H26A—C26—H26B	109.5
C13—C12—H12A	110.1	C14—C26—H26C	109.5
C11—C12—H12B	110.1	H26A—C26—H26C	109.5
C13—C12—H12B	110.1	H26B—C26—H26C	109.5
H12A—C12—H12B	108.5	C3—O1—C2	120.44 (19)
C12—C13—C14	114.34 (18)	C5—O2—C6	112.20 (16)
C12—C13—H13A	108.7	C17—O3—C18	118.86 (18)
C14—C13—H13A	108.7	C21—O4—C20	105.9 (2)
C12—C13—H13B	108.7	C16—O7—C15	61.11 (14)

C5—C1—C2—O1	20.7 (3)	C26—C14—C15—C16	89.4 (2)
C7—C1—C2—O1	−89.3 (3)	C18—C14—C15—C16	−29.5 (3)
C11—C1—C2—O1	149.30 (19)	C13—C14—C15—C16	−145.5 (2)
O5—C3—C4—C5	−138.2 (3)	C26—C14—C15—C10	−68.8 (2)
O1—C3—C4—C5	39.2 (3)	C18—C14—C15—C10	172.33 (18)
C3—C4—C5—O2	55.3 (2)	C13—C14—C15—C10	56.4 (2)
C3—C4—C5—C1	−60.4 (3)	C9—C10—C15—O7	−127.9 (2)
C2—C1—C5—O2	−87.3 (2)	C25—C10—C15—O7	−11.4 (3)
C7—C1—C5—O2	36.9 (2)	C11—C10—C15—O7	113.65 (19)
C11—C1—C5—O2	145.95 (18)	C9—C10—C15—C16	−60.4 (3)
C2—C1—C5—C4	29.2 (2)	C25—C10—C15—C16	56.1 (3)
C7—C1—C5—C4	153.43 (18)	C11—C10—C15—C16	−178.84 (19)
C11—C1—C5—C4	−97.5 (2)	C9—C10—C15—C14	97.0 (2)
O2—C6—C7—C8	164.4 (2)	C25—C10—C15—C14	−146.51 (19)
C23—C6—C7—C8	−81.6 (3)	C11—C10—C15—C14	−21.5 (3)

C24—C6—C7—C8	46.4 (3)	C14—C15—C16—O7	99.1 (2)
O2—C6—C7—C1	30.4 (2)	C10—C15—C16—O7	−103.1 (2)
C23—C6—C7—C1	144.3 (2)	O7—C15—C16—C17	−106.4 (2)
C24—C6—C7—C1	−87.6 (2)	C14—C15—C16—C17	−7.2 (3)
C2—C1—C7—C6	74.7 (2)	C10—C15—C16—C17	150.5 (2)
C5—C1—C7—C6	−41.4 (2)	O7—C16—C17—O8	133.0 (3)
C11—C1—C7—C6	−159.81 (17)	C15—C16—C17—O8	−157.7 (2)
C2—C1—C7—C8	−62.7 (3)	O7—C16—C17—O3	−49.5 (3)
C5—C1—C7—C8	−178.88 (19)	C15—C16—C17—O3	19.8 (3)
C11—C1—C7—C8	62.8 (2)	C15—C14—C18—O3	57.3 (2)
C6—C7—C8—C9	170.9 (2)	C26—C14—C18—O3	−62.6 (2)
C1—C7—C8—C9	−58.7 (3)	C13—C14—C18—O3	173.45 (17)
C7—C8—C9—O6	−126.2 (2)	C15—C14—C18—C19	176.59 (18)
C7—C8—C9—C10	52.3 (3)	C26—C14—C18—C19	56.7 (2)
O6—C9—C10—C15	8.4 (3)	C13—C14—C18—C19	−67.3 (2)
C8—C9—C10—C15	−170.14 (18)	O3—C18—C19—C20	−137.6 (2)
O6—C9—C10—C25	−109.3 (3)	C14—C18—C19—C20	99.3 (3)
C8—C9—C10—C25	72.1 (2)	O3—C18—C19—C22	41.0 (3)
O6—C9—C10—C11	126.6 (2)	C14—C18—C19—C22	−82.2 (3)
C8—C9—C10—C11	−51.9 (2)	C22—C19—C20—O4	0.6 (3)
C2—C1—C11—C12	−62.9 (2)	C18—C19—C20—O4	179.4 (2)
C5—C1—C11—C12	62.1 (3)	O4—C21—C22—C19	0.6 (3)
C7—C1—C11—C12	167.29 (19)	C20—C19—C22—C21	−0.7 (3)
C2—C1—C11—C10	69.3 (2)	C18—C19—C22—C21	−179.5 (2)
C5—C1—C11—C10	−165.73 (18)	O5—C3—O1—C2	−170.9 (3)
C7—C1—C11—C10	−60.5 (2)	C4—C3—O1—C2	11.6 (3)
C9—C10—C11—C12	−164.55 (17)	C1—C2—O1—C3	−44.8 (3)
C15—C10—C11—C12	−43.2 (2)	C4—C5—O2—C6	−142.4 (2)
C25—C10—C11—C12	77.3 (2)	C1—C5—O2—C6	−20.8 (2)
C9—C10—C11—C1	56.6 (2)	C23—C6—O2—C5	−123.5 (2)
C15—C10—C11—C1	177.98 (17)	C24—C6—O2—C5	116.6 (2)
C25—C10—C11—C1	−61.5 (2)	C7—C6—O2—C5	−5.8 (2)
C1—C11—C12—C13	−151.99 (19)	O8—C17—O3—C18	−172.6 (2)
C10—C11—C12—C13	73.9 (2)	C16—C17—O3—C18	9.8 (3)
C11—C12—C13—C14	−36.6 (2)	C19—C18—O3—C17	−175.0 (2)
C12—C13—C14—C15	−23.7 (2)	C14—C18—O3—C17	−49.9 (3)
C12—C13—C14—C26	99.6 (2)	C22—C21—O4—C20	−0.2 (3)
C12—C13—C14—C18	−139.37 (19)	C19—C20—O4—C21	−0.3 (3)
C26—C14—C15—O7	154.24 (17)	C17—C16—O7—C15	110.4 (2)
C18—C14—C15—O7	35.3 (2)	C14—C15—O7—C16	−109.7 (2)
C13—C14—C15—O7	−80.6 (2)	C10—C15—O7—C16	111.7 (2)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C8—H8*A*···O5^{i}	0.97	2.35	3.313 (3)	171

C4—H4*A*···O6^{ii}	0.97	2.54	3.442 (3)	156
C21—H21···O6^{iii}	0.93	2.52	3.135 (3)	124

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