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A dihydro- β -agarofuran sesquiterpene from *Maytenus boaria*

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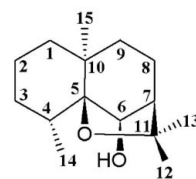
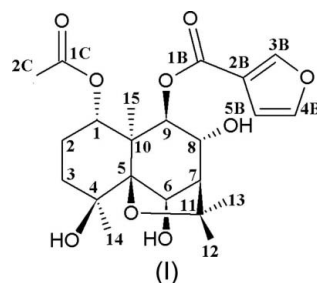
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The natural compound (1*S*,4*S*,5*S*,6*R*,7*R*,8*R*,9*R*,10*S*)-6-acetoxy-4,9,10-trihydroxy-2,2,5a,9-tetramethyloctahydro-2*H*-3,9a-methanobenzo[*b*]oxepin-5-yl furan-3-carboxylate, C₂₂H₃₀O₉, (**I**), is a β -agarofuran sesquiterpene isolated from the seeds of *Maytenus boaria* as part of a study of the secondary metabolites from Chilean flora. The compound presents a central structure formed by a decalin system esterified with acetate at site 1 and furan-3-carboxylate at site 9. The chirality of the skeleton can be described as 1*S*,4*S*,5*S*,6*R*,7*R*,8*R*,9*R*,10*S*, which is consistent with that suggested by NMR studies. Unlike previously reported structures of sesquiterpenes containing a pure dihydro- β -agarofuran skeleton, (**I**) exhibits a three-dimensional hydrogen-bonded network.

1. Introduction

Sesquiterpenes with a dihydro- β -agarofuran skeleton are perhaps the most characteristic and widespread group of secondary metabolites present in the Celastraceae family.



They have attracted the interest of extractive and synthetic organic chemists for years due to their ample range of biological properties (see, for example, Mbaning *et al.*, 2013; Céspedes *et al.*, 2001; Calderón *et al.*, 2001).

The attention ascribed to these sesquiterpenes has resulted in an extremely vast survey of reports on this family of molecules. A search in the Cambridge Structural Database (CSD; Version 5.38 and updates; Groom *et al.*, 2016) for structures having the backbone shown in Scheme 1 (but allowing for

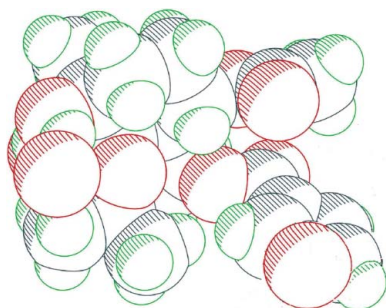


Table 1

The 15 reported structures obtained from the Cambridge Structural Database (CSD; Groom *et al.*, 2016) with the same dihydro- β -agarofuran skeleton as in (I).

Number	CSD refcode	Reference	Chemical name
1	ALEWOF	Mbaning <i>et al.</i> (2016)	5-Acetoxy-2-hydroxy-2,6,10,10-tetramethyl-4-oxo-11-oxatricyclo[7.2.1.0 ^{1,6}]dodecane-7,12-diyl dibenzoate
2	ALEXOG	Mbaning <i>et al.</i> (2016)	4,5,8-Triacetoxy-2-hydroxy-2,6,10,10-tetramethyl-11-oxatricyclo[7.2.1.0 ^{1,6}]dodecane-7,12-diyl dibenzoate hexane solvate
3	ALEYOH	Mbaning <i>et al.</i> (2016)	4-Acetoxy-5,12-bis(benzoyloxy)-2-hydroxy-2,6,10,10-tetramethyl-11-oxatricyclo[7.2.1.0 ^{1,6}]dodec-7-yl nicotinate
4	CELBRR	Smith <i>et al.</i> (1976)	Celorbicol mono- <i>p</i> -bromobenzoate
5	EJACOI	Yeboah <i>et al.</i> (2010)	2,6,10,10-Tetramethyl-4-oxo-11-oxatricyclo[7.2.1.0 ^{1,6}]dodecane-5,7-diyl bis(furan-3-carboxylate)
6	EJACOI01	Yeboah <i>et al.</i> (2010)	2,6,10,10-Tetramethyl-4-oxo-11-oxatricyclo[7.2.1.0 ^{1,6}]dodecane-5,7-diyl bis(furan-3-carboxylate)
7	ISOCEL	Smith <i>et al.</i> (1976)	Isocelorbicol
8	JAGREO	Hori <i>et al.</i> (1987)	Regelidine
9	KUXGEP	Tu <i>et al.</i> (1990)	1b,2b-Diacetoxy-9a-(3-phenyl-2-oxiranylethoxy)- β -dihydroagarofuran
10	KUXGEP10	Wang & Tu (1995)	1b,2b-Diacetoxy-9a-(3-phenyl-2-oxiranylethoxy)- β -dihydroagarofuran
11	OSOVUO	Torres-Romero <i>et al.</i> (2011)	2,6,10,10-Tetramethyl-11-oxatricyclo[7.2.1.0 ^{1,6}]dodecane-2,5,7,8,12-pentol hemihydrate
12	SIFNEA	Begley <i>et al.</i> (1990)	6- <i>O</i> -Acetyl-9- <i>O</i> -[(<i>E</i>)-cinnamoyl]-1- <i>O</i> -glycoloyl-1,4,6,9-tetrahydroxydihydroagarofuran
13	UKUBIL	Mehta & Kumaran (2003)	7-Benzoyloxy-2,6,10,10-tetramethyl-11-oxatricyclo[7.2.1.0 ^{1,6}]dodecane-3,4,12-triol
14	UKUBIL01	Kumaran & Mehta (2015)	7-Benzoyloxy-2,6,10,10-tetramethyl-11-oxatricyclo[7.2.1.0 ^{1,6}]dodecane-3,4,12-triol
15	YABZAC	Gonzalez <i>et al.</i> (1992)	(3 <i>S</i> ,4 <i>R</i> ,5 <i>R</i> ,7 <i>R</i> ,10 <i>R</i>)-3,4-Dihydroxydihydro- β -agarofuran

substitutions in the remaining sites non-explicitly marked in the Scheme) provided 15 entries (Table 1 and Fig. 1). Most of these are natural products from all over the world.

In particular, the Celastraceae family is present in Chile in the endemic genus *Maytenus*, occurring in four species, *i.e.* *M. disticha*, *M. boaria*, *M. magellanica* and *M. chubutensis*. The chemical components of *Maytenus* are dihydro- β -agarofuran sesquiterpenes which have been shown to display activity in the inhibition of acetylcholinesterase (Alarcón *et al.*, 2008) and also in reversing the drug resistance of the human leukemia CEM/VCR R cell line (Wibowo *et al.*, 2016). *Maytenus boaria* Mol. [*Celastraceae*], also called ‘maitén’, is an evergreen tree that can reach up to 25 m in height, with a gray bark trunk which can reach a diameter of 1 m at its base. It has leaves of a lanceolate form of about 3 to 9 cm in length and between 1 and 3 cm in width. Previous reports of natural compounds from the seeds of *Maytenus boaria* showed highly oxygenated sesquiterpenes with a dihydro- β -agarofuran skeleton, as determined by 1D (one-dimensional) and 2D (two-dimensional) NMR (Alarcón *et al.*, 1995). As part of our search for new compounds from Chilean flora, we report herein a new related compound with a hydroxy group at position C-4, *viz.* (1*S*,4*S*,5*S*,6*R*,7*R*,8*R*,9*R*,10*S*)-6-acetoxy-4,9,10-trihydroxy-2,2,5a,9-tetramethyloctahydro-2*H*-3,9a-methanobenzo[*b*]oxepin-5-yl furan-3-carboxylate, (I).

2. Experimental

2.1. Extraction, purification and crystallization

Dihydro- β -agarofuran sesquiterpenoid (I) (see Scheme 1) was isolated from the ethyl acetate extract of the crushed seeds of the tree *Maytenus boaria*. The seeds were collected in Temuco, IX Region of Chile, in September, 2016. The seeds (1.3 kg) were initially crushed and extracted by maceration with ethyl acetate for 3 d. The organic solvent was evaporated *in vacuo*, giving a crude extract (600 g, orange oil) which was

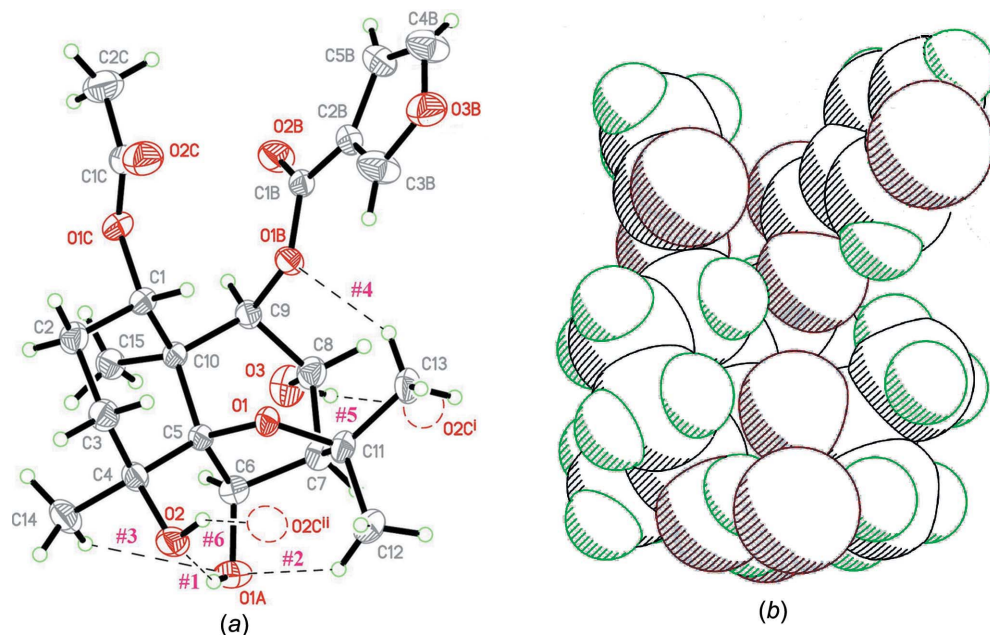
further fractionated by column chromatography, giving a primary fractioning of nine fractions (F1–F9) by using increasing eluent polarity from hexane to ethyl acetate.

Table 2

Experimental details.

Crystal data	
Chemical formula	C ₂₂ H ₃₀ O ₉
<i>M_r</i>	438.46
Crystal system, space group	Orthorhombic, <i>P</i> ₂ 12 ₁
Temperature (K)	295
<i>a</i> , <i>b</i> , <i>c</i> (Å)	9.1605 (3), 13.8069 (5), 16.8625 (7)
<i>V</i> (Å ³)	2132.74 (14)
<i>Z</i>	4
Radiation type	Cu <i>K</i> α
μ (mm ⁻¹)	0.89
Crystal size (mm)	0.40 × 0.20 × 0.20
Data collection	
Diffraction	Oxford Diffraction Gemini CCD S Ultra
Absorption correction	Multi-scan (<i>CrysAlis PRO</i> ; Oxford Diffraction, 2009)
<i>T_{min}</i> , <i>T_{max}</i>	0.78, 0.83
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	17785, 4153, 3781
<i>R_{int}</i>	0.087
(sin θ/λ) _{max} (Å ⁻¹)	0.616
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.061, 0.165, 1.03
No. of reflections	4153
No. of parameters	295
No. of restraints	3
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.28, -0.30
Absolute structure	Flack <i>x</i> determined using 1547 quotients [(<i>I</i> ⁺) - (<i>I</i> ⁻)] / [(<i>I</i> ⁺) + (<i>I</i> ⁻)] (Parsons <i>et al.</i> , 2013)
Absolute structure parameter	0.18 (15)

Computer programs: *CrysAlis PRO* (Oxford Diffraction, 2009), *SHELXS97* (Sheldrick, 2008), *XP* in *SHELXTL* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015) and *PLATON* (Spek, 2009).


Figure 3

Two molecular representations of (I), viz. (a) a displacement ellipsoid plot, drawn at the 40% probability level, and (b) a space-filling view. Only the major part of the disordered furan-3-carboxylate group is shown. Symmetry codes are defined in Table 4.

observed, followed by several overlapped intense endothermic peaks from 593 to 773 K.

2.3. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All H atoms were identified in an intermediate difference map and were treated differently in the refinement. H atoms on C atoms were idealized and their coordinates and displacement factors allowed to ride, the latter taken as $U_{\text{iso}}(\text{H}) = xU_{\text{eq}}(\text{C})$, with $\text{C}-\text{H} = 0.93 \text{ \AA}$ and $x = 1.2$ for aromatic, $\text{C}-\text{H} = 0.97 \text{ \AA}$ and $x = 1.2$ for methylene, and $\text{C}-\text{H} = 0.96 \text{ \AA}$ and $x = 1.5$ for methyl groups. H atoms attached to O atoms were refined with $\text{O}-\text{H}$ distances restrained to $0.85(1) \text{ \AA}$ and with $x = 1.2$.

The furan-2-carboxylate group presents a 180° rotational disorder around the $\text{C1B}-\text{C2B}$ bond, with an occupancy ratio of $0.83(2):0.17(2)$.

The reported absolute structure was initially assigned by matching it to the (common) configuration of the analogues in Table 1 and Fig. 1 (except for CSD refcode YABZAC; Gonzalez *et al.*, 1992). In order to confirm this assignment by an independent attempt, and taking advantage of the fact that the data set had been gathered with Cu $K\alpha$ radiation, we made refinements of the reported and inverted structures, which showed an unambiguous trend towards the former [$0.18(15):0.82(15)$, calculated *via* Parsons' method (Parsons *et al.*, 2013), using 1547 selected quotients]. When trying to investigate the possible presence of inversion twinning through a TWIN/BASF refinement (SHELXL2014; Sheldrick, 2015), the refinement converged to $0.11(29)$. Although parameters with such relatively large standard deviations could appear unreliable in conventional cases of laboratory synthesis, they could be reputed as significant when referring

Table 3

^1H (600 MHz) and ^{13}C (150 MHz) NMR data of (I) in $\text{DMSO}-d_6$.

Chemical shifts (δ) are in ppm and coupling constants (J) are in Hz. COSY is correlation spectroscopy and HMBC is heteronuclear multiple-bond correlation spectroscopy.

Position	^1H	^{13}C	COSY	HMBC
1	5.07 (<i>dd</i> , $J = 8.2, 5.2$)	72.5	2 a,b	9, 10, 15, 1C
2	1.68 (<i>m</i>) 1.45 (overlap)	22.9	3 a,b	
3	1.37 (<i>m</i>) 1.80 (<i>td</i> , $J = 16.2, 4.5$)	35.4	2 a,b	4, 7
4		82.1		
5		91.4		
6	4.78 (<i>s</i>)	73.7	7	4, 8
7	2.10 (<i>d</i> , $J = 3.8$)	57.4	6, 8	4, 5, 8, 9, 13
8	3.98 (<i>t</i> , $J = 4.3$)	72.9	7	7, 9, 10
9	4.77 (<i>d</i> , $J = 7.6$)	79.1		5, 7, 8, 15, 1B
10		49.5		
11		71.8		
12	1.46 (overlap)	26.1		
13	1.46 (overlap)	30.2		
14	1.38 (<i>s</i>)	25.7		
15	1.32 (<i>s</i>)	19.8		1, 5, 9, 10
1B		161.1		
2B		118.5		
3B	8.16 (<i>dd</i> , $J = 1.8, 0.9$)	148.4	4B	
4B	7.78 (<i>t</i> , $J = 2.2$)	144.8	3B, 5B	
5B	6.66 (<i>dd</i> , $J = 2.2, 0.9$)	109.4	4B	
1C		169.4		2C
2C	1.63 (<i>s</i>)	20.7		1C

to natural products generated by enzymatic processes (known to lead to unique enantiomeric forms), mainly when the 'handedness' assigned concurs with that suggested by NMR data, and with the configuration of a vast series of similar natural products.

2.4. NMR analysis

The molecular structure of (I) was initially determined by 1D and 2D NMR experiments. The ^1H (600 MHz in $\text{DMSO}-$

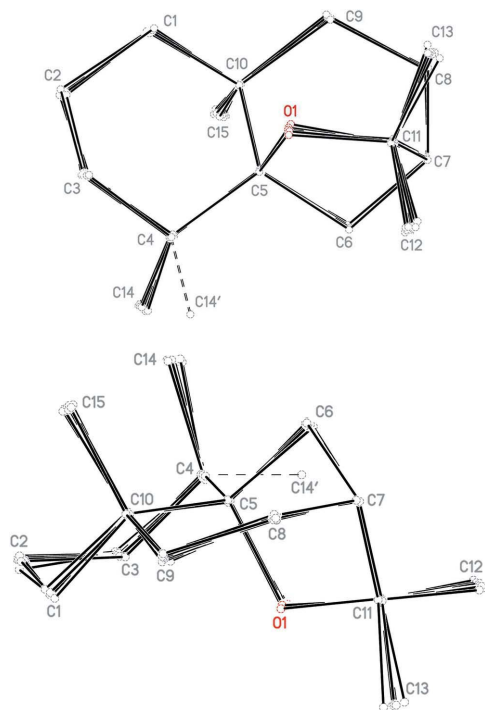


Figure 4
Two complementary views of a least-squares superposition of (I) and the molecules in the 15 reported structures with the same skeleton (Fig. 1). Note the deviation of atom C14 in YABZAC (Gonzalez *et al.*, 1992).

Table 4
Hydrogen-bond geometry (Å, °) for (I).

Code	$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
#1	O1A—H1A \cdots O2	0.851 (14)	2.02 (3)	2.769 (4)	146 (5)
#2	C12—H12C \cdots O1A	0.96	2.29	3.020 (6)	133
#3	C14—H14A \cdots O1A	0.96	2.52	3.147 (6)	123
#4	C13—H13A \cdots O1B	0.96	2.21	3.047 (4)	146
#5	O3—H3 \cdots O2C ⁱ	0.848 (14)	1.992 (18)	2.826 (4)	168 (5)
#6	O2—H2 \cdots O2C ⁱⁱ	0.854 (14)	2.39 (3)	3.120 (4)	144 (4)

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

d_6) and ^{13}C (150 MHz in $\text{DMSO}-d_6$) NMR spectra are presented in the *Supporting information* (Fig. S1). Table 3 presents relevant data from the ^1H NMR spectrum, which shows five methyl singlets and the three aromatic furanyl protons. Four protons geminal to oxygen corresponding to H1, H6, H8 and H9 are observed in the range 4–5 ppm. In addition, the spectrum displays three protons of hydroxy groups according to the heteronuclear single quantum correlation (HSQC) spectrum. The ^{13}C NMR and HSQC spectra show 22 carbon resonances as seven quaternary C atoms, including two carbonyls at 169.4 and 161.1 ppm, eight methine, two methylene and five methyl groups.

The positions of the substituents were determined from a heteronuclear multiple-bond correlation (HMBC) experiment. The correlation of methyl proton H2C at 1.63 ppm with carbonyl atom C1C at 169.4 ppm confirmed the presence of the acetyl group. Also correlations of H1 (5.07 ppm) with carbonyl atom C1C, Me15, C10 and C9 showed clearly that the acetoxy group is located at C1. Homonuclear correlation

spectroscopy ($^1\text{H}-^1\text{H}$ COSY) experiments show correlations of H1 with H2ab and from these to H3ab. Similarly, the correlation of carbonyl atom C1B at 161.1 ppm with H9 at 4.77 ppm confirmed the presence of the acetyl group at C9 on the decalin skeleton. The relative stereochemistry has been established from a study of the coupling constants in the ^1H NMR spectrum. Mbaning *et al.* (2016) reported a J value of 7.3 Hz for the axial H9; in our case, H9 has a J value of 7.6 Hz, confirming the stereochemistry of C9 as *R*. This was later confirmed by the X-ray structure determination.

3. Results and discussion

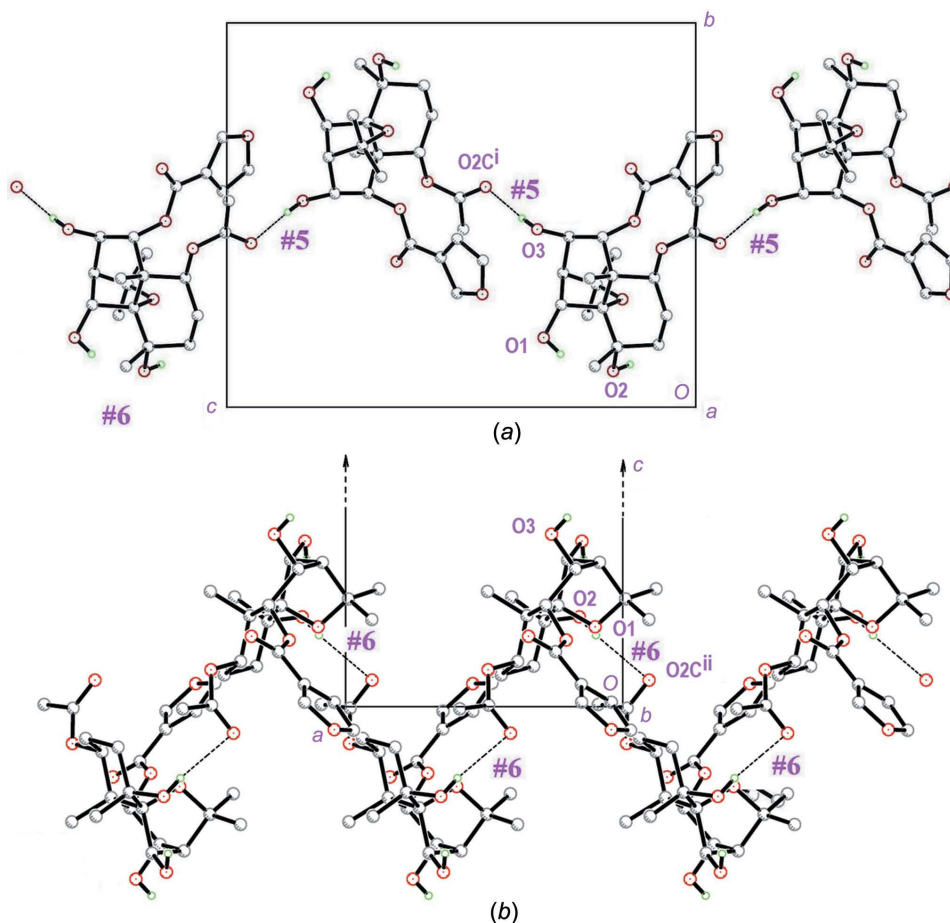
Fig. 3 shows two molecular diagrams for (I), *viz.* Fig. 3(a) an ellipsoid plot and Fig. 3(b) a space-filling view. The molecule is built up around a typical dihydro- β -agarofuran skeleton, esterified with acetate at site 1 and with furan-3-carboxylate at site 9, while sites 4, 6 and 8 are substituted with OH groups. These substituents are unexceptional, not departing from expected geometries. This particular conformation, as well as the substitution scheme in the molecule, leads to a 1*S*,4*S*,5*S*,6*R*,7*R*,8*R*,9*R*,10*S* chirality descriptor.

The central decalin system (atoms C1–C10) is in a *trans* form (H5 at C5 and H10 at C10 being antiparallel to each other), with both cyclohexane rings in chair conformations. The mean planes through the equatorial sites in each ring [that through atoms C5/C10/C2/C3, with a mean deviation of 0.025 (3) Å, and that through atoms C5/C10/C7/C8, with a mean deviation of 0.019 (4) Å] form a dihedral angle of 162.6 (3)°, confirming the nearly planar disposition. For future comparison with related compounds, we note here that methyl atoms C14 and C15 lie on the same side of the equatorial plane.

In order to investigate the geometry of the inner skeleton, we compared that in (I) with the examples in Table 1 and Fig. 1. Since four of these 15 structures contain two independent moieties ($Z' = 2$), this provided a total of 19 molecular skeletons for comparison. Striking evidence for the robustness of the group, irrespective of the substituents present, is shown in Fig. 4, where a least-squares fit of the skeletons is presented in two complementary views. The extremely low geometrical dispersion is apparent. The sole exception corresponds to CSD refcode YABZAC (Gonzalez *et al.*, 1992), where methyl atom C14 at C4 occupies a Cp3 position opposite to the remainder, thus lying opposite to atom C15 with respect to the equatorial plane.

Regarding noncovalent interactions (Table 4), the molecule possesses three potential donor sites, *i.e.* the hydroxy groups at C4, C6 and C8, and four further O atoms which could possibly act as hydrogen-bond acceptors.

The 'globular' appearance of the molecule (see Fig. 3b for a space-filling view), however, inhibits many of these potential acceptors from entering into close contacts with available donors in neighbouring molecules. This facilitates the formation of intramolecular hydrogen bonds (labelled #1 to #4 in Table 4 and represented as dotted lines in Fig. 3). Atom O1A is involved in the first three hydrogen bonds, *viz.* in #1 as the


Figure 5

A view of the perpendicular hydrogen-bonding chains in (I). (a) The [001] chain, resulting from #5 hydrogen bonds (Table 4), and (b) the [100] chain, resulting from #6 hydrogen bonds. In both cases, hydrogen bonds are drawn as broken lines. [Symmetry codes: (i) $-x + \frac{1}{2}, -y + 1, z + \frac{1}{2}$; (ii) $x - \frac{1}{2}, -y + \frac{1}{2}, -z$.]

donor of a strong $\text{O}-\text{H}\cdots\text{O}$ hydrogen bond and in #2 and #3 as an acceptor of medium-strength $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds. The remaining hydrogen bond, *i.e.* #4, has coordinated furan-3-carboxylate atom O1B as the acceptor.

Thus, the supramolecular structure in (I) is the result of only two significant intermolecular interactions, both having acetate atom O2C as the acceptor and involving the OH groups at C8 (#5 in Table 4) and C4 (#6 in Table 4) as the donors.

The role fulfilled by each one of these interactions is to generate two families of nearly perpendicular $C(9)$ chains (Bernstein *et al.*, 1995) along the 2_1 axis parallel to [001] in the case of #5 (Fig. 5a) and along the 2_1 axis parallel to [100] in the case of #6 (Fig. 5b). The combined criss-cross effect of these interactions is the linkage of both families of one-dimensional substructures into a tightly bound three-dimensional hydrogen-bonded array. Due to unavoidable overlapping, a detailed view of this linkage drawn with the full molecules is not possible, so we have resorted to a ‘topological’ view of (I), taking into account only the three interaction centres joined to the central node, as shown in the inset in Fig. 6. In this way, a clear view of the connectivity can be assessed through projections along the three crystallographic axes (Fig. 6). The role of each interaction in the three-dimensional structure can be clearly visualized.

This three-dimensional character is a rather unique property of (I), as compared with the related structures in Table 1, which generate mostly one-dimensional chains, with the sole exception of EJACOI (Yeboah *et al.*, 2010), which, due to the lack of adequate OH donors, is composed of isolated zero-dimensional units. The reason for this unique behaviour of (I) can be understood by inspection of Fig. 1. Within the large variety of substituents in the 15 compounds, compound (I) is the only one to present good hydrogen-bonding donors (OH groups) in positions 4 and 8, and a good acceptor in position 1. The result is that each molecule is attached to four different neighbours, leading to the compact network shown in Fig. 6. Thus, compound (I) appears to be rather unique in the sense that it is the only structure in the group to give rise to a well-connected three-dimensional hydrogen-bonded network.

The resulting compactness of the structure can be assessed quantitatively by the Kitaigorodsky packing index (PI) (Kitaigorodsky, 1973) of 68.9%, as calculated by *PLATON* (Spek, 2009), a value above average for pure nonpolymeric organic structures (typically in the range 65–67%). Even if the hydrogen-bonding scheme discussed above must be important for this ‘tight’ aggregation and can in principle explain the relatively high melting point of (I), there are further components not taken into account in the present analysis (such as

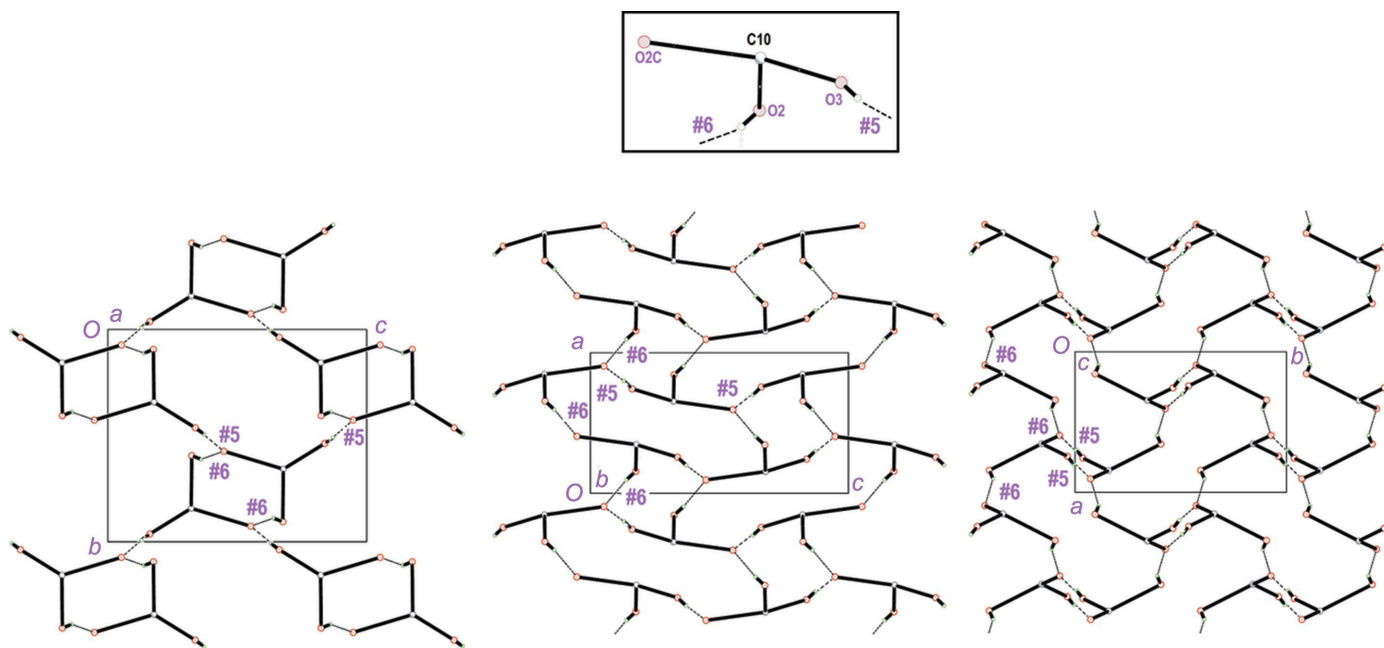


Figure 6

The connectivity of the three-dimensional hydrogen-bonded structure of (I), viewed along the three different unit-cell axes. Inset: the schematic representation used for molecule (I).

molecular polarizability, van der Waals interactions, *etc.*) leading to weak (but important) cohesive forces. Clear examples of this can be found in some related structures in Table 1, *viz.* JAGREO (Hori *et al.*, 1987), with only one OH group in its structure, but a very high melting point and a comparable PI (566 K, 68.5%), or OSOVUO (Torres-Romero *et al.*, 2011), which in spite of presenting four OH groups, generates just a one-dimensional hydrogen-bonded structure, with a rather low melting point but a large PI (454 K, 69.6%). Clarification of the individual responsibilities for these behaviours would require detailed calculations of electron-density interactions, which lie beyond the scope of this article.

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A dihydro- β -agarofuran sesquiterpene from *Maytenus boaria*

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Computing details

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2009); cell refinement: *CrysAlis PRO* (Oxford Diffraction, 2009); data reduction: *CrysAlis PRO* (Oxford Diffraction, 2009); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015) and *PLATON* (Spek, 2009).

(1S,4S,5S,6R,7R,8R,9R,10S)-6-Acetoxy-4,9,10-trihydroxy-2,2,5a,9-tetramethyloctahydro-2H-3,9a-methanobenzo[*b*]oxepin-5-yl furan-3-carboxylate

Crystal data

$C_{22}H_{30}O_9$	$D_x = 1.366 \text{ Mg m}^{-3}$
$M_r = 438.46$	Cu <i>K</i> α radiation, $\lambda = 1.54178 \text{ \AA}$
Orthorhombic, $P2_12_12_1$	Cell parameters from 5831 reflections
$a = 9.1605 (3) \text{ \AA}$	$\theta = 4.1\text{--}71.9^\circ$
$b = 13.8069 (5) \text{ \AA}$	$\mu = 0.89 \text{ mm}^{-1}$
$c = 16.8625 (7) \text{ \AA}$	$T = 295 \text{ K}$
$V = 2132.74 (14) \text{ \AA}^3$	Prisms, colourless
$Z = 4$	$0.40 \times 0.20 \times 0.20 \text{ mm}$
$F(000) = 936$	

Data collection

Oxford Diffraction Gemini CCD S Ultra diffractometer	4153 independent reflections
ω scans, thick slices	3781 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (CrysAlis PRO; Oxford Diffraction, 2009)	$R_{\text{int}} = 0.087$
$T_{\text{min}} = 0.78$, $T_{\text{max}} = 0.83$	$\theta_{\text{max}} = 71.9^\circ$, $\theta_{\text{min}} = 4.1^\circ$
17785 measured reflections	$h = -9 \rightarrow 11$
	$k = -16 \rightarrow 17$
	$l = -20 \rightarrow 20$

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.1311P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.061$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.165$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.03$	$\Delta\rho_{\text{max}} = 0.28 \text{ e \AA}^{-3}$
4153 reflections	$\Delta\rho_{\text{min}} = -0.30 \text{ e \AA}^{-3}$
295 parameters	
3 restraints	
Hydrogen site location: mixed	

Absolute structure: Flack x determined using
 1547 quotients $[(I+)-(I-)]/[(I+)+(I-)]$ (Parsons *et al.*, 2013)
 Absolute structure parameter: 0.18 (15)

Special details

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

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
O1	0.0991 (2)	0.28072 (15)	0.15650 (13)	0.0392 (5)	
O2	0.1561 (3)	0.09415 (17)	0.17624 (18)	0.0538 (6)	
H2	0.090 (4)	0.117 (3)	0.146 (2)	0.065*	
O3	0.2575 (4)	0.4631 (2)	0.33803 (15)	0.0640 (7)	
H3	0.210 (5)	0.489 (4)	0.376 (2)	0.077*	
O1A	0.1462 (4)	0.1811 (2)	0.32412 (18)	0.0645 (7)	
H1A	0.139 (7)	0.135 (3)	0.291 (3)	0.077*	
O1B	0.2037 (2)	0.48421 (15)	0.13053 (13)	0.0408 (5)	
O2B	0.3398 (3)	0.62082 (17)	0.13775 (17)	0.0560 (6)	
O3B	-0.0276 (4)	0.6172 (3)	-0.0462 (2)	0.0771 (12)	0.83 (2)
C4B'	-0.0276 (4)	0.6172 (3)	-0.0462 (2)	0.0771 (12)	0.17 (2)
H4B'	-0.1063	0.5997	-0.0781	0.093*	0.17 (2)
O1C	0.4858 (3)	0.41320 (16)	0.07259 (15)	0.0484 (6)	
O2C	0.4060 (4)	0.4272 (3)	-0.05184 (18)	0.0739 (9)	
C1	0.3791 (3)	0.3366 (2)	0.08843 (18)	0.0389 (6)	
H1	0.2895	0.3505	0.0588	0.047*	
C2	0.4377 (4)	0.2392 (2)	0.0626 (2)	0.0491 (7)	
H2A	0.5263	0.2241	0.0915	0.059*	
H2B	0.4604	0.2404	0.0064	0.059*	
C3	0.3216 (4)	0.1626 (2)	0.0793 (2)	0.0497 (8)	
H3C	0.3574	0.0999	0.0622	0.060*	
H3D	0.2347	0.1774	0.0487	0.060*	
C4	0.2810 (3)	0.1571 (2)	0.1676 (2)	0.0426 (7)	
C5	0.2342 (3)	0.2595 (2)	0.19809 (17)	0.0355 (6)	
C6	0.1984 (4)	0.2669 (2)	0.2867 (2)	0.0458 (7)	
H6	0.2846	0.2904	0.3153	0.055*	
C7	0.0840 (4)	0.3485 (3)	0.2825 (2)	0.0488 (7)	
H7	0.0258	0.3514	0.3312	0.059*	
C8	0.1700 (4)	0.4435 (3)	0.2697 (2)	0.0478 (7)	
H8	0.1005	0.4967	0.2624	0.057*	
C9	0.2780 (3)	0.4425 (2)	0.19852 (18)	0.0385 (6)	
H9	0.3587	0.4860	0.2121	0.046*	
C10	0.3460 (3)	0.34241 (19)	0.17802 (17)	0.0346 (6)	
C11	-0.0103 (3)	0.3193 (2)	0.2112 (2)	0.0472 (7)	
C12	-0.1211 (4)	0.2400 (3)	0.2310 (3)	0.0670 (11)	

H12A	-0.1601	0.2136	0.1828	0.100*	
H12B	-0.1990	0.2671	0.2621	0.100*	
H12C	-0.0739	0.1896	0.2607	0.100*	
C13	-0.0947 (4)	0.4001 (3)	0.1708 (3)	0.0580 (9)	
H13A	-0.0277	0.4482	0.1517	0.087*	
H13B	-0.1607	0.4291	0.2081	0.087*	
H13C	-0.1490	0.3740	0.1271	0.087*	
C14	0.4011 (4)	0.1066 (3)	0.2149 (3)	0.0602 (10)	
H14A	0.3830	0.1148	0.2706	0.090*	
H14B	0.4939	0.1345	0.2016	0.090*	
H14C	0.4017	0.0389	0.2022	0.090*	
C15	0.4883 (3)	0.3359 (2)	0.2259 (2)	0.0453 (7)	
H15A	0.5218	0.2700	0.2267	0.068*	
H15B	0.4709	0.3573	0.2793	0.068*	
H15C	0.5612	0.3762	0.2018	0.068*	
C1B	0.2426 (3)	0.5752 (2)	0.10788 (18)	0.0388 (6)	
C2B	0.1491 (4)	0.6089 (2)	0.04364 (19)	0.0419 (6)	
C3B	0.0408 (5)	0.5613 (3)	0.0076 (3)	0.0688 (11)	
H3B	0.0158	0.4974	0.0183	0.083*	
C4B	0.0417 (5)	0.7046 (3)	-0.0446 (2)	0.0652 (12)	0.83 (2)
H4B	0.0173	0.7576	-0.0759	0.078*	0.83 (2)
O3B'	0.0417 (5)	0.7046 (3)	-0.0446 (2)	0.0652 (12)	0.17 (2)
C5B	0.1493 (5)	0.7029 (3)	0.0085 (3)	0.0591 (9)	
H5B	0.2127	0.7535	0.0204	0.071*	
C1C	0.4837 (4)	0.4543 (3)	0.0021 (2)	0.0533 (8)	
C2C	0.5879 (6)	0.5372 (3)	-0.0036 (3)	0.0787 (14)	
H2CA	0.6419	0.5326	-0.0523	0.118*	
H2CB	0.6542	0.5353	0.0404	0.118*	
H2CC	0.5346	0.5971	-0.0027	0.118*	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0248 (9)	0.0422 (10)	0.0505 (11)	0.0010 (8)	-0.0022 (8)	0.0009 (8)
O2	0.0454 (13)	0.0396 (11)	0.0762 (16)	-0.0092 (10)	-0.0052 (12)	0.0096 (11)
O3	0.0690 (17)	0.0729 (16)	0.0502 (14)	0.0021 (14)	0.0003 (13)	-0.0198 (12)
O1A	0.0740 (18)	0.0571 (15)	0.0625 (15)	-0.0053 (13)	0.0129 (15)	0.0209 (12)
O1B	0.0363 (10)	0.0333 (9)	0.0529 (11)	-0.0017 (7)	-0.0077 (9)	0.0044 (8)
O2B	0.0496 (13)	0.0430 (12)	0.0754 (16)	-0.0118 (10)	-0.0124 (12)	0.0046 (11)
O3B	0.072 (2)	0.086 (2)	0.073 (2)	-0.0075 (18)	-0.0261 (17)	0.0179 (17)
C4B'	0.072 (2)	0.086 (2)	0.073 (2)	-0.0075 (18)	-0.0261 (17)	0.0179 (17)
O1C	0.0415 (12)	0.0480 (12)	0.0558 (13)	-0.0083 (10)	0.0079 (10)	0.0055 (10)
O2C	0.077 (2)	0.085 (2)	0.0600 (16)	0.0002 (17)	0.0053 (15)	0.0227 (15)
C1	0.0336 (14)	0.0389 (14)	0.0443 (15)	-0.0018 (11)	0.0041 (11)	0.0026 (11)
C2	0.0445 (16)	0.0458 (16)	0.0571 (18)	0.0020 (13)	0.0101 (14)	-0.0044 (14)
C3	0.0483 (18)	0.0406 (15)	0.0602 (19)	0.0021 (13)	0.0023 (15)	-0.0086 (14)
C4	0.0353 (14)	0.0322 (12)	0.0602 (18)	0.0005 (11)	-0.0034 (13)	0.0033 (12)
C5	0.0290 (12)	0.0330 (13)	0.0447 (14)	0.0009 (10)	-0.0023 (10)	0.0036 (10)

C6	0.0454 (16)	0.0452 (16)	0.0466 (16)	0.0004 (13)	0.0033 (13)	0.0079 (12)
C7	0.0429 (16)	0.0543 (17)	0.0494 (16)	0.0030 (15)	0.0112 (13)	-0.0008 (14)
C8	0.0462 (16)	0.0480 (16)	0.0490 (16)	0.0029 (14)	0.0075 (13)	-0.0085 (13)
C9	0.0353 (14)	0.0362 (13)	0.0440 (15)	0.0011 (11)	-0.0028 (11)	-0.0007 (11)
C10	0.0274 (12)	0.0340 (12)	0.0426 (13)	-0.0018 (10)	-0.0017 (11)	0.0020 (10)
C11	0.0277 (13)	0.0498 (17)	0.064 (2)	0.0011 (12)	0.0080 (13)	0.0021 (14)
C12	0.0377 (17)	0.066 (2)	0.097 (3)	-0.0071 (16)	0.0127 (19)	0.012 (2)
C13	0.0305 (15)	0.0557 (18)	0.088 (3)	0.0086 (13)	0.0011 (16)	0.0020 (18)
C14	0.052 (2)	0.0444 (17)	0.085 (3)	0.0089 (16)	-0.0139 (19)	0.0130 (17)
C15	0.0337 (14)	0.0467 (16)	0.0556 (17)	-0.0020 (12)	-0.0092 (13)	0.0030 (13)
C1B	0.0340 (14)	0.0345 (13)	0.0479 (15)	0.0018 (11)	0.0040 (12)	-0.0011 (10)
C2B	0.0393 (15)	0.0390 (14)	0.0475 (15)	0.0069 (12)	-0.0007 (12)	0.0025 (11)
C3B	0.073 (3)	0.061 (2)	0.073 (3)	-0.017 (2)	-0.024 (2)	0.0168 (19)
C4B	0.071 (2)	0.061 (2)	0.064 (2)	0.0169 (18)	-0.0047 (18)	0.0123 (16)
O3B'	0.071 (2)	0.061 (2)	0.064 (2)	0.0169 (18)	-0.0047 (18)	0.0123 (16)
C5B	0.060 (2)	0.0451 (18)	0.072 (2)	0.0044 (16)	-0.0056 (19)	0.0109 (16)
C1C	0.056 (2)	0.0459 (17)	0.058 (2)	0.0070 (15)	0.0199 (17)	0.0048 (15)
C2C	0.096 (4)	0.051 (2)	0.089 (3)	-0.011 (2)	0.037 (3)	0.008 (2)

Geometric parameters (Å, °)

O1—C5	1.453 (3)	C7—C11	1.534 (5)
O1—C11	1.463 (4)	C7—C8	1.544 (5)
O2—C4	1.445 (4)	C7—H7	0.9800
O2—H2	0.854 (14)	C8—C9	1.555 (4)
O3—C8	1.430 (4)	C8—H8	0.9800
O3—H3	0.848 (14)	C9—C10	1.555 (4)
O1A—C6	1.424 (4)	C9—H9	0.9800
O1A—H1A	0.851 (14)	C10—C15	1.536 (4)
O1B—C1B	1.360 (4)	C11—C13	1.518 (5)
O1B—C9	1.452 (4)	C11—C12	1.530 (5)
O2B—C1B	1.201 (4)	C12—H12A	0.9600
O3B—C3B	1.346 (5)	C12—H12B	0.9600
O3B—C4B	1.364 (6)	C12—H12C	0.9600
C4B'—C3B	1.346 (5)	C13—H13A	0.9600
C4B'—O3B'	1.364 (6)	C13—H13B	0.9600
C4B'—H4B'	0.9300	C13—H13C	0.9600
O1C—C1C	1.318 (5)	C14—H14A	0.9600
O1C—C1	1.465 (3)	C14—H14B	0.9600
O2C—C1C	1.214 (6)	C14—H14C	0.9600
C1—C2	1.512 (4)	C15—H15A	0.9600
C1—C10	1.543 (4)	C15—H15B	0.9600
C1—H1	0.9800	C15—H15C	0.9600
C2—C3	1.526 (5)	C1B—C2B	1.458 (4)
C2—H2A	0.9700	C2B—C3B	1.336 (5)
C2—H2B	0.9700	C2B—C5B	1.427 (5)
C3—C4	1.535 (5)	C3B—H3B	0.9300
C3—H3C	0.9700	C4B—C5B	1.331 (6)

C3—H3D	0.9700	C4B—H4B	0.9300
C4—C14	1.527 (5)	O3B'—C5B	1.331 (6)
C4—C5	1.564 (4)	C5B—H5B	0.9300
C5—C6	1.534 (4)	C1C—C2C	1.493 (6)
C5—C10	1.573 (4)	C2C—H2CA	0.9600
C6—C7	1.541 (5)	C2C—H2CB	0.9600
C6—H6	0.9800	C2C—H2CC	0.9600
C5—O1—C11	110.7 (2)	C15—C10—C1	110.2 (2)
C4—O2—H2	107 (3)	C15—C10—C9	106.0 (2)
C8—O3—H3	113 (4)	C1—C10—C9	110.0 (2)
C6—O1A—H1A	111 (4)	C15—C10—C5	113.4 (2)
C1B—O1B—C9	117.7 (2)	C1—C10—C5	107.5 (2)
C3B—O3B—C4B	106.0 (3)	C9—C10—C5	109.8 (2)
C3B—C4B'—O3B'	106.0 (3)	O1—C11—C13	109.5 (3)
C3B—C4B'—H4B'	127.0	O1—C11—C12	109.4 (3)
O3B'—C4B'—H4B'	127.0	C13—C11—C12	106.6 (3)
C1C—O1C—C1	117.8 (3)	O1—C11—C7	101.8 (2)
O1C—C1—C2	110.7 (2)	C13—C11—C7	116.4 (3)
O1C—C1—C10	105.8 (2)	C12—C11—C7	113.0 (3)
C2—C1—C10	113.5 (2)	C11—C12—H12A	109.5
O1C—C1—H1	108.9	C11—C12—H12B	109.5
C2—C1—H1	108.9	H12A—C12—H12B	109.5
C10—C1—H1	108.9	C11—C12—H12C	109.5
C1—C2—C3	108.4 (3)	H12A—C12—H12C	109.5
C1—C2—H2A	110.0	H12B—C12—H12C	109.5
C3—C2—H2A	110.0	C11—C13—H13A	109.5
C1—C2—H2B	110.0	C11—C13—H13B	109.5
C3—C2—H2B	110.0	H13A—C13—H13B	109.5
H2A—C2—H2B	108.4	C11—C13—H13C	109.5
C2—C3—C4	112.4 (3)	H13A—C13—H13C	109.5
C2—C3—H3C	109.1	H13B—C13—H13C	109.5
C4—C3—H3C	109.1	C4—C14—H14A	109.5
C2—C3—H3D	109.1	C4—C14—H14B	109.5
C4—C3—H3D	109.1	H14A—C14—H14B	109.5
H3C—C3—H3D	107.8	C4—C14—H14C	109.5
O2—C4—C14	104.0 (3)	H14A—C14—H14C	109.5
O2—C4—C3	108.6 (3)	H14B—C14—H14C	109.5
C14—C4—C3	110.8 (3)	C10—C15—H15A	109.5
O2—C4—C5	107.1 (2)	C10—C15—H15B	109.5
C14—C4—C5	116.0 (3)	H15A—C15—H15B	109.5
C3—C4—C5	109.9 (2)	C10—C15—H15C	109.5
O1—C5—C6	105.9 (2)	H15A—C15—H15C	109.5
O1—C5—C4	104.9 (2)	H15B—C15—H15C	109.5
C6—C5—C4	116.1 (2)	O2B—C1B—O1B	124.1 (3)
O1—C5—C10	107.7 (2)	O2B—C1B—C2B	125.4 (3)
C6—C5—C10	107.5 (2)	O1B—C1B—C2B	110.5 (3)
C4—C5—C10	114.1 (2)	C3B—C2B—C5B	105.0 (3)

O1A—C6—C5	116.6 (3)	C3B—C2B—C1B	128.2 (3)
O1A—C6—C7	113.6 (3)	C5B—C2B—C1B	126.8 (3)
C5—C6—C7	98.6 (2)	C2B—C3B—O3B	111.8 (4)
O1A—C6—H6	109.2	C2B—C3B—C4B'	111.8 (4)
C5—C6—H6	109.2	C2B—C3B—H3B	124.1
C7—C6—H6	109.2	O3B—C3B—H3B	124.1
C11—C7—C6	103.1 (3)	C5B—C4B—O3B	110.1 (3)
C11—C7—C8	113.6 (3)	C5B—C4B—H4B	125.0
C6—C7—C8	106.3 (3)	O3B—C4B—H4B	125.0
C11—C7—H7	111.1	C5B—O3B'—C4B'	110.1 (3)
C6—C7—H7	111.1	O3B'—C5B—C2B	107.1 (4)
C8—C7—H7	111.1	C4B—C5B—C2B	107.1 (4)
O3—C8—C7	109.5 (3)	C4B—C5B—H5B	126.4
O3—C8—C9	105.5 (3)	C2B—C5B—H5B	126.4
C7—C8—C9	115.1 (3)	O2C—C1C—O1C	123.5 (4)
O3—C8—H8	108.8	O2C—C1C—C2C	124.3 (4)
C7—C8—H8	108.8	O1C—C1C—C2C	112.3 (4)
C9—C8—H8	108.8	C1C—C2C—H2CA	109.5
O1B—C9—C10	111.4 (2)	C1C—C2C—H2CB	109.5
O1B—C9—C8	107.9 (2)	H2CA—C2C—H2CB	109.5
C10—C9—C8	115.7 (3)	C1C—C2C—H2CC	109.5
O1B—C9—H9	107.1	H2CA—C2C—H2CC	109.5
C10—C9—H9	107.1	H2CB—C2C—H2CC	109.5
C8—C9—H9	107.1		

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O2—H2 \cdots O2C ⁱ	0.85 (1)	2.39 (3)	3.120 (4)	144 (4)
O3—H3 \cdots O2C ⁱⁱ	0.85 (1)	1.99 (2)	2.826 (4)	168 (5)
O1A—H1A \cdots O2	0.85 (1)	2.02 (3)	2.769 (4)	146 (5)
C12—H12C \cdots O1A	0.96	2.29	3.020 (6)	133
C13—H13A \cdots O1B	0.96	2.21	3.047 (4)	146
C14—H14A \cdots O1A	0.96	2.52	3.147 (6)	123
C4B—H4B \cdots O2B ⁱⁱⁱ	0.93	2.56	3.421 (4)	154

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