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**Crystal Structure
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2-[3-Furyl(hydroxy)methyl]-2,3-dimethylcyclohexanone[1]

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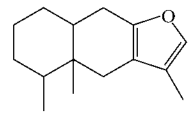
In the molecule of the title compound, $C_{13}H_{18}O_3$, there is a *syn* relationship between the two vicinal methyl groups. The six-membered ring adopts a chair conformation, with one equatorial and two axial groups, and the furyl group is almost parallel to the ketone group. Intermolecular hydrogen bonds [O—H···O═C 2.814 (3) Å] form chains along [100].

Comment

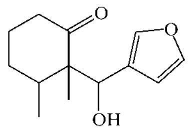
Many sesquiterpenes possessing a furan ring have been isolated from plant species and among them, the furanoeremophilanes, (I), are the most abundant (Hikino & Konno, 1976; Kuroyanagi *et al.*, 1985; Torres *et al.*, 1999). The interesting linearly fused furo[2,3-*b*]decalin framework, containing *syn*-vicinal dimethyl groups at atoms C-4a and C-5, of these compounds, together with the biological activities shown by some of them, have attracted the attention of many synthetic chemists (Irie *et al.*, 1982; Jacobi *et al.*, 1984; Koike *et al.*, 1999; Miyashita *et al.*, 1980; Tada *et al.*, 1980; Yamakawa *et al.*, 1983). We have designed a strategy for the synthesis of the basic skeleton (I), in which the key step is the preparation of compounds such as the ketol (II). Since NMR analyses of (II*a*) and (II*b*) did not allow conclusive assignment of the relative stereochemistry of the methyl groups, we carried out the X-ray analysis of (II*a*), which unequivocally established this relationship as *syn*.

The molecular structure of (II*a*) is shown in Fig. 1, and selected bond distances, angles and torsion angles are listed in Table 1. The cyclohexanone ring adopts a chair conformation, with the C3-methyl and C2-hydroxymethyl groups in *anti*-diaxial orientations. This is an unexpected and unusual result since, in principle, the *anti*-diequatorial conformer, (II*a*′) (obtained by flipping the cyclohexanone ring), should be more stable.

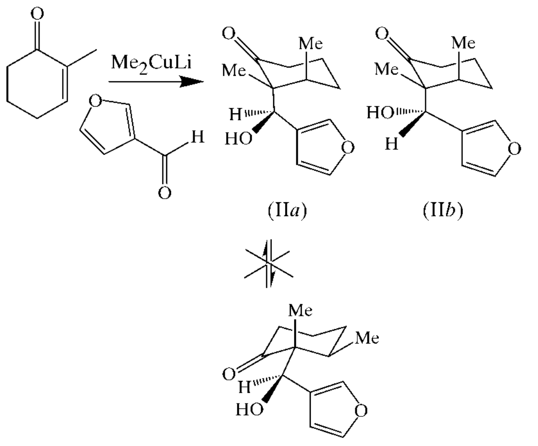
The carbonyl and methyl (C8) groups on C2 are almost coplanar, with an O1—C1—C2—C8 torsion angle of −1.8 (4)° and a mean deviation from the plane of the four atoms of 0.007 Å; the C2—C7—O2 hydroxy moiety is almost perpendicular [86.84 (14)°] to this four-atom plane. This geometry does not allow intramolecular hydrogen bonding between the hydroxy and ketone groups. The C1(═O1)—C2—C6 fragment of the cyclohexanone ring is practically planar, within experimental error [the maximum deviation from the plane is −0.020 (3) Å for atom C1], and the C1═O1 bond distance [1.227 (3) Å] is within the normal range. Similar results were found in previously reported cyclohexanones (Barluenga *et al.*, 1993; Brunner & Maas, 1995; Hernández-Ortega *et al.*, 2001; Rowland *et al.*, 1998).



(I)



(II)



(II*a*′)

The furyl group is essentially planar, within experimental error (the mean deviation from the plane is 0.0018 Å). This

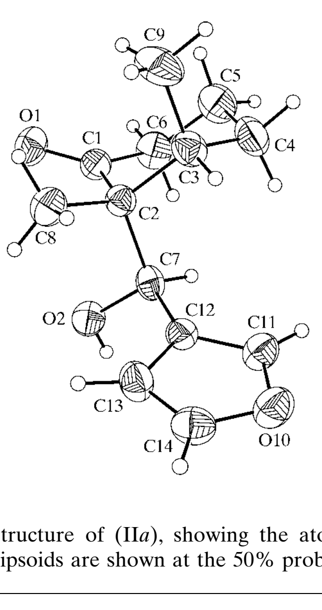


Figure 1
The molecular structure of (II*a*), showing the atom-labelling scheme. Displacement ellipsoids are shown at the 50% probability level.

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group is almost parallel to the ketone group [12.82 (9)°] and is inclined at an angle of 47.23 (17)° to the best plane described by atoms C2, C3, C5 and C6 of the cyclohexanone ring (the mean deviation from this plane is 0.0051 Å).

The molecules are stacked in the crystal along the *a* axis, with the cyclohexanone and furyl groups almost perpendicular to the *ac* plane (Fig. 2). The molecules are linked by intermolecular hydrogen bonds between the hydroxy and ring carbonyl groups (Table 2). The preference for intermolecular as opposed to intramolecular hydrogen bonding is due to the orientation of the 3-furyl(hydroxy)methyl group on the cyclohexanone ring.

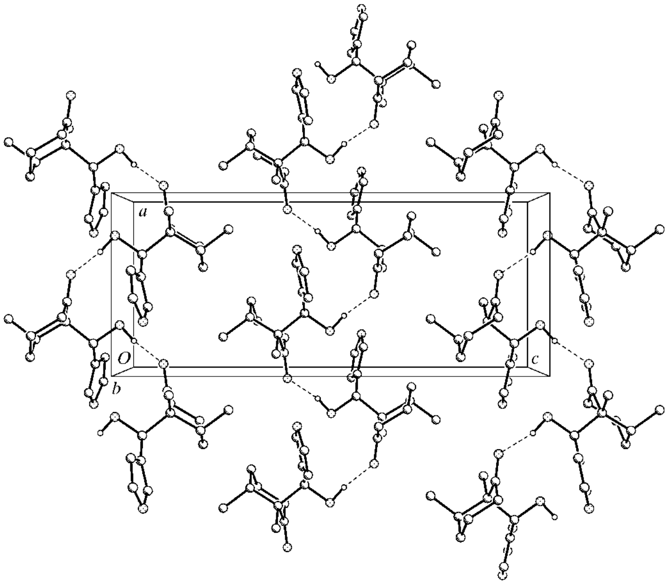

Figure 2
The crystal packing of (II*a*) projected on to the *ab* plane. The intermolecular hydrogen bonds are along the *a* axis.

Experimental

A solution of 2-methyl-2-cyclohexenone (15 mmol) in anhydrous ether (15 ml) was added dropwise to a stirred solution of lithium dimethylcuprate (30 mmol) in anhydrous ether (200 ml) at 268 K under a nitrogen atmosphere. A yellow precipitate was obtained, and after stirring for 30 min, a 1 *M* ethereal solution of zinc chloride (30 ml) was added, followed by a solution of furan-3-carbaldehyde (18.75 mmol) in anhydrous ether (15 ml). Stirring was continued for 15 min at 268 K, and the reaction mixture was then poured into 20% aqueous ammonium chloride (350 ml). After separation, the aqueous phase was extracted with ether (2 × 30 ml). The combined ethereal phases were washed with 10% aqueous ammonium chloride (2 × 30 ml) and brine (2 × 30 ml), and were then dried and concentrated. The crude product was separated by column chromatography, yielding two compounds. The most polar product [(II*a*) in 28% yield] was obtained as colorless prisms (m.p. 360–361 K) after purification and recrystallization from ether–hexane. The epimeric stereochemical relationship between (II*a*) and (II*b*) was established by oxidation (Jones) of each diastereoisomer to the same *β*-diketone.

Crystal data

$C_{13}H_{18}O_3$
$M_r = 222.27$
Orthorhombic, $P2_12_12_1$
$a = 7.962$ (3) Å
$b = 8.249$ (4) Å
$c = 18.931$ (9) Å
$V = 1243.3$ (10) Å^3
$Z = 4$
$D_x = 1.187$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 512 reflections
$\theta = 2.7$–29.1°
$\mu = 0.08$ mm^{-1}
$T = 293$ (2) K
Prism, colorless
0.24 × 0.20 × 0.14 mm

Data collection

Bruker CCD area-detector diffractometer
φ and ω scans
11 179 measured reflections
1667 independent reflections
1045 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.149$
$\theta_{\rm max} = 27.5°$
$h = -10 \rightarrow 10$
$k = -10 \rightarrow 10$
$l = -24 \rightarrow 24$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.098$
$S = 0.99$
1667 reflections
149 parameters

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0271P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.021$
$\Delta\rho_{\rm max} = 0.15$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.12$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.227 (3)	O10—C14	1.356 (3)
O2—C7	1.436 (3)	O10—C11	1.364 (3)
C1—C2	1.529 (4)	C11—C12	1.347 (3)
C2—C8	1.532 (3)	C12—C13	1.430 (4)
C2—C7	1.554 (4)	C13—C14	1.335 (4)
C2—C3	1.558 (4)		
O1—C1—C6	121.4 (3)	C14—O10—C11	105.4 (2)
O1—C1—C2	121.6 (3)	C12—C11—O10	111.8 (3)
C6—C1—C2	116.9 (2)	C11—C12—C13	104.7 (3)
C1—C2—C8	110.2 (2)	C14—C13—C12	107.1 (3)
C1—C2—C7	107.1 (2)	C13—C14—O10	111.1 (3)
O2—C7—C2	106.5 (2)		
O1—C1—C2—C8	−1.8 (4)	C1—C2—C7—O2	−56.5 (3)
O1—C1—C2—C7	117.3 (3)	C8—C2—C7—O2	63.0 (3)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···O1$^{\rm i}$	0.80 (3)	2.02 (3)	2.814 (3)	172 (3)

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

The positional parameters of the hydroxy H atom were refined, while those of the other H atoms were calculated geometrically (C—H = 0.93–0.98 Å). All H atoms were fixed with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}$ of the attached non-H atom. The absolute configuration could not be determined.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT-Plus* (Bruker, 1999); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1367). Services for accessing these data are described at the back of the journal.

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