

(3*R*,4*aS*,5*R*)-3-Hydroxy-5-isopropenyl-3,8-dimethyl-4,4*a*,5,6-tetrahydro-2(3*H*)-naphthalenone

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Received 16 January 2001

Accepted 30 January 2001

In the crystal structure of $C_{15}H_{20}O_2$, molecules are associated by intermolecular hydrogen bonds between the hydroxy function and a keto group [$O \cdots O$ 2.770 (2) Å], forming chains along the [100] direction in the crystal. Both six-membered rings in the decalin unit adopt envelope conformations; one section of the molecule, encompassing the extended conjugation of a $C=C$ double bond with an enone functionality [$C=C-C=O = 175.6$ (2)° and $C=C-C=C = 176.6$ (2)°], is flat, whilst the rest of the molecule is folded relative to the constrained part. The stereochemistry was determined from the *R*-(-)-carvone starting material.

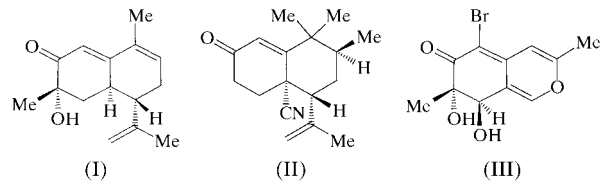
Comment

Several terpenoid-based substances found in natural products have been derived from marine and plant life using commercial or synthetic sources. Of these, sesquiterpene representatives are often valuable intermediates in the synthesis of a wide variety of complex natural products (Davidson *et al.*, 1990). Some show antibacterial activity whilst others have potential use in medical applications, for example *Artemisia annua* is used in antimalarial medicines (Ngo & Brown, 1999).

Although there are limited approaches to forming fused-ring structures, the conversion of enantiomeric forms of carvone to cadinane-based sesquiterpenes using the Mukaiyama–Michael reaction with other cyclization steps provides one route to the parent skeleton. The synthesis and analytical properties of the title compound, (I), have been reported by Baranovsky *et al.* (1998), which was identified as the most stable diastereoisomer for the proceeding construction of related sesquiterpene analogues. The *R* configuration at C5 [from the *R*-(-)-carvone starting material] is retained, thus the configuration at the other chiral atoms, C3 and C4*a*, is *R* and *S*, respectively.

Compound (I) is similar to the unsaturated cyano species (4*aR*,5*S*,7*R*)-4*a*-cyano-5-isopropenyl-7,8,8-trimethyl-4,4*a*,5,6,7,8-hexahydronaphthalen-(2*H*)-one, (II) (Jansen *et al.*, 2000;

Ellis & Spek, 2000). A ring-puckering analysis (Evans & Boeyens, 1989; Spek, 2000) of the two six-membered rings in (I) revealed the following parameters: $Q = 0.480$ (2) Å, $\theta = 126.1$ (2)° and $\varphi = 6.0$ (3)° (for C1–C8*a*), and $Q = 0.451$ (2) Å, $\theta = 124.7$ (3)° and $\varphi = 235.7$ (3)° (for C5–C4*a*). The puckering parameters within the non-carvone ring of (I) are essentially



the same as its counterpart in (II), with both adopting envelope conformations. Since the carvone ring in (I) is additionally constrained at C7/C8, the 'upper' part is flattened [$C7=C8-C8a=C1 = 176.6$ (2)° and $C8a=C1-C2=O2 = 175.6$ (2)°] changing the ring conformation from a half-chair in (II) to an envelope form in (I).

The most significant geometric differences in the decalin units of (I) and (II) are a result of the extended conjugation and the presence of different functional groups. Thus, C1–C2 in (I) is shorter than the corresponding bond in (II) [1.447 (3) *versus* 1.471 (5) Å] and likewise for C7–C8 [1.339 (3) *versus* 1.549 (5) Å], although the latter is related to the change in hybridization at C8. The bond parameters within the isopropenyl group of (I) are consistent with a more localized system compared with those in (II), which tend towards positional disorder.

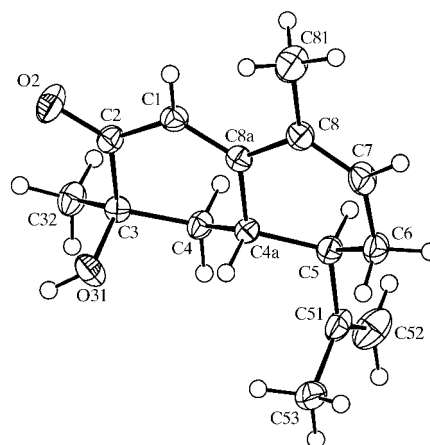


Figure 1
Displacement ellipsoid plot of (I) (PLATON; Spek, 2000) drawn at the 50% probability level.

The configuration of the keto and hydroxy functionalities are similar to those in 5-bromo-8-hydroxy-7,8-dihydro-3,7-dimethyl-2-benzopyran-6-one, (III) (Engel & Kruger, 1976). In (I), the molecules are stabilized by strong intermolecular hydroxy–keto hydrogen bonding (Table 2), forming a zigzag pattern along the [100] direction in the crystal. In (III), the hydrogen-bonding system is more complex, due to the four independent molecules in the asymmetric unit, although pairs of molecules form similar hydroxy–keto motifs along the [110] direction.

Experimental

The synthesis of (I) has been described previously (Baranovsky *et al.*, 1998). The compound was recrystallized from a diethyl ether/hexane mixture.

Crystal data

$C_{15}H_{20}O_2$	Mo $K\alpha$ radiation
$M_r = 232.31$	Cell parameters from 25 reflections
Orthorhombic, $P2_12_12_1$	$\theta = 9\text{--}15^\circ$
$a = 8.6663$ (9) Å	$\mu = 0.077$ mm $^{-1}$
$b = 9.671$ (3) Å	$T = 150$ (2) K
$c = 15.470$ (4) Å	Plate, colourless
$V = 1296.6$ (5) Å 3	$0.50 \times 0.37 \times 0.20$ mm
$Z = 4$	
$D_x = 1.190$ Mg m $^{-3}$	

Data collection

Enraf–Nonius CAD-4T diffractometer	$\theta_{\max} = 27.47^\circ$
ω scans	$h = -11 \rightarrow 0$
3441 measured reflections	$k = -12 \rightarrow 0$
1720 independent reflections	$l = -20 \rightarrow 20$
1457 reflections with $I > 2\sigma(I)$	3 standard reflections
$R_{\text{int}} = 0.035$	frequency: 60 min
	intensity decay: 2.2%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0572P)^2 + 0.1030P]$
$R[F^2 > 2\sigma(F^2)] = 0.040$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.100$	$(\Delta/\sigma)_{\max} < 0.002$
$S = 1.019$	$\Delta\rho_{\max} = 0.21$ e Å $^{-3}$
1720 reflections	$\Delta\rho_{\min} = -0.21$ e Å $^{-3}$
161 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 1

Selected geometric parameters (Å, °).

C1—C2	1.447 (3)	C7—C8	1.339 (3)
C1—C8a	1.352 (3)	C8—C8a	1.463 (3)
C2—O2	1.231 (2)	C51—C52	1.323 (3)
C3—O31	1.429 (2)	C51—C53	1.503 (3)
C6—C7	1.486 (3)		
C8a—C1—C2—O2	175.6 (2)	C7—C8—C8a—C1	176.6 (2)

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O31—H31 \cdots O2 ⁱ	0.86 (3)	1.91 (3)	2.770 (2)	171 (3)

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

Due to the absence of anomalous scatterers, the absolute configuration could not be established reliably. The *SHELXL97* (Sheldrick, 1997) value for the Flack x parameter (Flack, 1983) was 0.10 (17). The absolute configuration was therefore chosen with respect to *R*-(−)-carvone, the starting material in the synthesis. In the final refinement cycles, the Friedel-related reflections were merged. All H atoms, except those on methyl and hydroxy groups, were placed in idealized positions and were constrained to ride on their C atoms, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. Methyl H atoms were constrained to ideal geometries, with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$, and allowed to rotate freely about their C—C bonds. The hydroxy H atom (H31) was located in the Fourier map and its coordinates and displacement parameter were allowed to refine freely.

Data collection: locally modified *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *SET4* (de Boer & Duisenberg, 1984); data reduction: *HELENA* (Spek, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2000); software used to prepare material for publication: *PLATON*.

Crystals of (I) were kindly provided by Dr T. M. Meulemans and Professor Dr A. de Groot, Wageningen University, The Netherlands. The investigations were supported by the Netherlands Foundation for Chemical Research (SON), with financial aid from the Netherlands Organization of Scientific Research (NWO).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1617). Services for accessing these data are described at the back of the journal.

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