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1β-(4-Methoxybenzyl)-8α-vinyl-7-oxabicyclo[4.3.0]nonan-6β-ol

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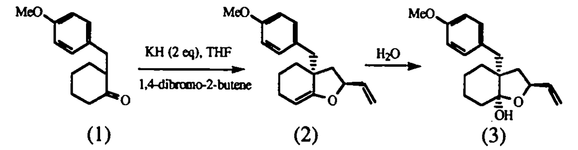
Abstract

The crystal structure analysis of 1β-(4-methoxybenzyl)-8α-vinyl-7-oxabicyclo[4.3.0]nonan-6β-ol, $C_{18}H_{24}O_3$, reveals that the unit cell consists of two dimers, each formed by the linkage of double head-to-head hydrogen bonds between hemiacetal groups.

Comment

In our search for novel methods of stereoselective formation of remote stereocenters, we developed a route for the synthesis of 4-hydroxyketone derivatives *via* temporarily formed bicyclic systems such as (2). Compound (2) was prepared from potassium hydride treatment of the 2-substituted cycloketone (1) and 1,4-dibromo-2-butene in tetrahydrofuran (Wang, Chen & Zhao, 1994), but the determination of the relative stereochemistry of (2) by ^1H and ^{13}C NMR spectra was difficult. Recrystallization of the corresponding hydrate product, (3), from a mixture of cyclohexane and ethyl acetate gave colorless needles. A single-crystal X-ray analysis indicates that the vinyl group is located on the concave face of structure (3).



(1) (2) (3)

Structural features of the bicyclic rings are shown in Fig. 1. The cyclopentane and cyclohexane rings are *cis* fused. The dihedral angle between the cyclopentane ring and atoms C12, C13, C15 and C16 of the cyclohexane ring is 96.4°. The cyclohexane ring is in a distorted chair conformation with atoms C2 and O3 at equatorial positions, and atoms C17 and O1 at axial positions. The torsion angle C12—C13—C14—C15 on one side of the distorted ring is −59.9°, which exceeds the mean value of 52.9° by 7.0°. There is a compensation of 8.3° on the other side (C12—C11—C16—C15) from a flattening effect. The cyclopentane ring adopts a half-chair conformation [torsion angles ω_1 (C11—O1—C1—C2), ω_2 (O1—C1—C2—C16), ω_3 (C1—C2—C16—C11), ω_4 (C2—C16—C11—O1) and ω_5 (C16—C11—O1—C1) of 16.5, 10.3, −30.4, 40.8 and −36.6°, respectively], which is also distorted from the ideal half-chair conformation of cyclopentane [torsion angles ω_1 = 14.4, ω_2 = 14.4, ω_3 = −37.8, ω_4 = 46.7 and ω_5 = −37.8°] (Geise, Altona & Romers, 1967; Altona, Geise & Romers, 1968). The C3=C4 double bond is approximately parallel to the O1—C1 bond, with a torsion angle O1—C1—C3=C4 of 3.2°.

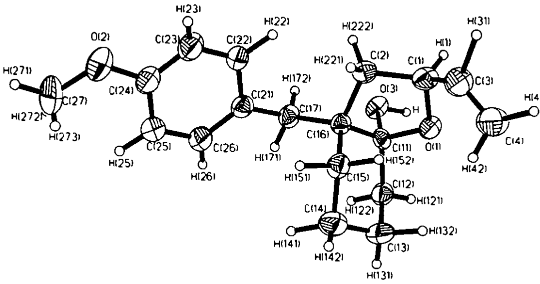


Fig. 1. The molecular structure and atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

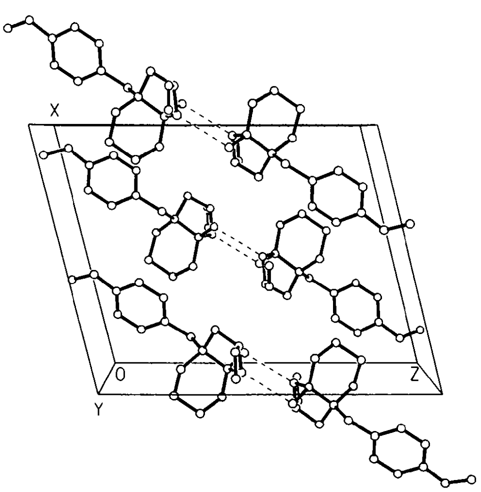


Fig. 2. The packing arrangement as viewed along **b**. Hydrogen bonds are shown by dashed lines.

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As shown in Fig. 2, which is viewed down the *b* axis, the intermolecular packing is dictated by two hydrogen bonds, O3—H···O1′ and O3′—H···O1, resulting in dimers related by an inversion center [symmetry code: (′) $1-x, -y, 1-z$; H···O1′ and H′···O1 2.02 Å, O3—H···O1′ and O3—H′···O1 164°].

Experimental

Crystal data

$C_{18}H_{24}O_3$
$M_r = 288.39$
Monoclinic
$P2_1/a$
$a = 12.525$ (3) Å
$b = 8.490$ (2) Å
$c = 15.697$ (6) Å
$\beta = 104.19$ (3)°
$V = 1618$ Å^3
$Z = 4$
$D_x = 1.184$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 8.1$–14.2°
$\mu = 0.0738$ mm^{-1}
$T = 299$ K
Needle
0.4 × 0.4 × 0.3 mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3166 measured reflections
2936 independent reflections
1546 observed reflections $[I > 3\sigma(I)]$

$R_{\rm int} = 0.027$
$\theta_{\rm max} = 25°$
$h = -14 \rightarrow 14$
$k = 0 \rightarrow 10$
$l = 0 \rightarrow 18$
3 standard reflections monitored every 200 reflections intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.057$
$wR(F^2) = 0.061$
$S = 5.7$
1546 reflections
286 parameters
H atoms refined isotropically
Unit weights for all observed reflections

$(\Delta/\sigma)_{\rm max} = 0.64$
$\Delta\rho_{\rm max} = 0.24$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.22$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$B_{\rm eq} = (4/3)\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	$B_{\rm eq}$
O1	0.4614 (2)	0.1336 (2)	0.5758 (1)	3.39 (3)
O2	0.0942 (3)	−0.1058 (7)	0.9653 (2)	7.45 (9)
O3	0.4151 (2)	−0.1294 (3)	0.5573 (1)	3.68 (3)
C1	0.3522 (2)	0.1985 (4)	0.5625 (2)	3.58 (5)
C2	0.2965 (2)	0.1067 (4)	0.6243 (2)	3.69 (5)
C3	0.3556 (3)	0.3733 (4)	0.5740 (2)	4.59 (6)
C4	0.4461 (4)	0.4581 (5)	0.5899 (4)	5.85 (9)
C11	0.4644 (2)	−0.0146 (3)	0.6194 (2)	3.24 (4)
C12	0.5838 (2)	−0.0547 (4)	0.6601 (2)	3.99 (5)
C13	0.6349 (3)	0.0511 (5)	0.7381 (3)	5.63 (8)
C14	0.5647 (3)	0.0527 (5)	0.8047 (3)	5.46 (8)
C15	0.4510 (2)	0.1135 (5)	0.7597 (2)	4.20 (5)
C16	0.3901 (2)	0.0110 (3)	0.6834 (2)	3.16 (4)
C17	0.3517 (2)	−0.1476 (3)	0.7141 (2)	3.97 (5)
C21	0.2870 (2)	−0.1356 (4)	0.7840 (2)	3.82 (5)
C22	0.1850 (2)	−0.0626 (5)	0.7658 (2)	4.29 (5)
C23	0.1226 (3)	−0.0545 (6)	0.8278 (3)	5.25 (7)
C24	0.1629 (3)	−0.1202 (6)	0.9098 (2)	5.31 (7)
C25	0.2637 (3)	−0.1939 (5)	0.9294 (3)	5.80 (8)
C26	0.3260 (3)	−0.1981 (5)	0.8669 (3)	5.13 (7)
C27	0.1220 (5)	−0.181 (1)	1.0447 (3)	9.6 (2)

Table 2. *Selected geometric parameters (Å, °)*

O1—C1	1.442 (2)	C13—C14	1.521 (3)
O1—C11	1.429 (2)	C14—C15	1.516 (3)
O2—C24	1.371 (2)	C15—C16	1.525 (2)
O2—C27	1.367 (4)	C16—C17	1.547 (2)
O3—C11	1.410 (3)	C17—C21	1.519 (2)
C1—C2	1.538 (3)	C21—C22	1.386 (2)
C1—C3	1.494 (2)	C21—C26	1.379 (3)
C2—C16	1.536 (3)	C22—C23	1.391 (3)
C3—C4	1.314 (3)	C23—C24	1.380 (3)
C11—C12	1.514 (3)	C24—C25	1.375 (4)
C11—C16	1.542 (1)	C25—C26	1.395 (3)
C12—C13	1.527 (3)		
C1—O1—C11	108.6 (2)	C11—C12—C13	112.5 (2)
C24—O2—C27	118.7 (3)	C12—C13—C14	111.0 (2)
O1—C1—C2	106.1 (1)	C13—C14—C15	108.5 (2)
O1—C1—C3	111.3 (1)	O3—C11—C12	110.9 (1)
C2—C1—C3	115.5 (1)	C2—C16—C11	100.1 (1)
C1—C2—C16	104.6 (2)	C2—C16—C15	109.5 (1)
C1—C3—C4	124.4 (1)	C2—C16—C17	113.6 (1)
O1—C11—O3	108.7 (1)	C11—C16—C15	109.0 (1)
O1—C11—C12	107.9 (1)	C11—C16—C17	111.3 (2)
O1—C11—C16	103.8 (2)	C15—C16—C17	112.7 (1)
C16—C17—C21	115.4 (1)	C14—C15—C16	113.8 (2)
C17—C21—C22	120.6 (1)	C22—C23—C24	119.6 (2)
C17—C21—C26	121.9 (1)	O2—C24—C23	114.4 (2)
C22—C21—C26	117.6 (1)	O2—C24—C25	125.8 (2)
C21—C22—C23	121.8 (2)	C23—C24—C25	119.9 (2)
O3—C11—C16	108.4 (1)	C24—C25—C26	119.7 (3)
C12—C11—C16	116.7 (1)	C21—C26—C25	121.5 (2)

The non-H atoms were refined anisotropically and all H atoms were located in difference maps and refined isotropically. Backgrounds were obtained from the analysis of scan profile (Blessing, Coppens & Becker, 1974) and data were collected using *CAD*-4 *Software* (Enraf–Nonius, 1989). The structure was solved by direct methods and refined using the *SDP-Plus* (Frenz, 1985) program package on a PDP 11/44 computer.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CR1175). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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