Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

(3*S*,4*S*,5*R*)-3-Hydroxy-4-methyl-5-vinyltetrahydropyran-2-one

Marleen Körner, Markus Schürmann, Hans Preut* and M. Hiersemann

Fachbereich Chemie, Universität Dortmund, Otto-Hahn-Strasse 6, 44221 Dortmund, Germany
Correspondence e-mail: hans.preut@udo.edu

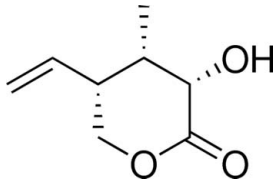
Received 19 April 2007; accepted 9 May 2007

Key indicators: single-crystal X-ray study; T = 173 K; mean σ(C–C) = 0.003 Å; R factor = 0.029; wR factor = 0.058; data-to-parameter ratio = 7.2.

The title compound, $C_8H_{12}O_3$, was synthesized to prove the relative configuration in the projected total synthesis of curvicollides A–C. In the crystal structure, molecules are linked *via* a bifurcated O—H···O hydrogen bond and a chain of molecules is formed along the *a* axis.

Related literature

For related literature, see: Abraham, Körner & Hiersemann (2004); Abraham, Körner *et al.* (2004); Evans *et al.* (1999); Körner & Hiersemann (2006, 2007); Oikawa *et al.* (1982).



Experimental

Crystal data

$C_8H_{12}O_3$
M_r = 156.18
Orthorhombic, $P2_12_12_1$
a = 5.4490 (5) Å
b = 6.4489 (5) Å
c = 22.2203 (14) Å
V = 780.82 (11) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 173 (1) K
0.45 × 0.40 × 0.40 mm

Data collection

Nonius KappaCCD area-detector diffractometer
Absorption correction: none
7057 measured reflections
1075 independent reflections
727 reflections with $I > 2\sigma(I)$
R_{int} = 0.026

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.058
S = 0.90
1075 reflections
149 parameters
All H-atom parameters refined
$\Delta\rho_{max}$ = 0.15 e Å^{-3}
$\Delta\rho_{min}$ = −0.14 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3O···O2^{i}	0.88 (2)	2.32 (2)	2.9881 (18)	133.0 (17)
O3—H3O···O3^{i}	0.88 (2)	2.06 (2)	2.8713 (8)	153.1 (19)

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

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus* (Sheldrick, 1991); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RZ2139).

References

Abraham, L., Körner, M. & Hiersemann, M. (2004). *Tetrahedron Lett.* **45**, 3647–3650.
Abraham, L., Körner, M., Schwab, P. & Hiersemann, M. (2004). *Adv. Synth. Catal.* **346**, 1281–1294.
Evans, D. A., Miller, S. J., Lectka, T. & Matt, P. V. (1999). *J. Am. Chem. Soc.* **121**, 7559–7573.
Körner, M. & Hiersemann, M. (2006). *Synlett*, pp. 121–123.
Körner, M. & Hiersemann, M. (2007). Manuscript in preparation.
Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
Oikawa, Y., Yoshioka, T. & Yonemitsu, O. (1982). *Tetrahedron Lett.* **23**, 885–888.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Sheldrick, G. M. (1991). *SHELXTL-Plus*. Release 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

  doi:10.1107/S1600536807022854

supplementary materials

Acta Cryst. (2007). E**63**, o3012 [**doi:10.1107/S1600536807022854**]

(3*S*,4S,5*R*)-3-Hydroxy-4-methyl-5-vinyltetrahydropyran-2-one

M. Körner, M. Schürmann, H. Preut and M. Hiersemann

Comment

The title compound, (I), was synthesized to proof the relative configuration in the projected total synthesis of curvicollides A—C using a catalytic asymmetric Claisen rearrangement (Abraham, Körner *et al.*, 2004; Abraham, Körner & Hiersemann, 2004) and a diastereoselective reduction with K-Selectride (Körner & Hiersemann, 2006). In order to verify the assumed relative configuration of methyl-4-(benzyloxymethyl)-2-hydroxy-3-methylhex-5-enoate (the preparation of this intermediate will be described elsewhere; Körner & Hiersemann, 2007), the δ-lactone, (I), was prepared. Fig. 1 shows that the relative configuration of C2, C3 and C4 is as expected. The configuration of the chiral C atoms in (I) (C2 S, C3 S and C4 *R*) were assigned based on the previously described stereochemical course of the catalytic asymmetric Claisen rearrangement (CAC) using the chiral Lewis acid [Cu{(*S*,*S*)-*tert*-Butyl-box}] $(H_2O)_2(SbF_6)_2$ (Evans *et al.*, 1999). In the crystal the molecules are linked *via* a bifurcated O—H ··· O hydrogen bridge (Table 1) and a chain of molecules is formed along the *a* axis.

Experimental

The synthesis of (I) was carried out under the conditions of the oxidative removal of the benzyl protecting group (Oikawa *et al.*, 1982). To a solution of (2*S*,3S,4*R*)-Methyl-4-(benzyloxymethyl)-2-hydroxy-3-methylhex-5-enoate (200 mg, 0.72 mmol, 1.0 eq) in dry dichloromethane (4 ml) and pH 7 buffer (1 ml) was added 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (0.49 g, 2.16 mmol, 3.0 eq) at 273 K. The orange mixture was stirred at room temperature for 3 days and filtered through a pad of celite and $MgSO_4$. The solvents were removed under reduced pressure. Flash chromatography (isohexane/ethyl acetate 20/1 to 10/1) afforded (I) (78 mg, 0.49 mmol, 69%) as colourless crystals. Single crystals of (I) were obtained by vapor diffusion recrystallization technique from isohexane and ethyl acetate to yield colourless cuboids: mp 357 K; R_f = 0.5 (isohexane/ethyl acetate 1/1); ^{1}H NMR (400 MHz, $CDCl_3$, δ) 0.96 (d, J = 7.0 Hz, 3H), 2.42–2.46 (m, 1H), 2.93–2.95 (m, 1H), 3.28 (br. s, 1H), 4.20–4.35 (m, 1H + 2H), 5.10–5.21 (m, 2H), 5.68 (ddd, J = 17.4, 10.5, 6.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, δ) 7.4 (CH_3), 36.0 (CH), 40.8 (CH), 69.9 (CH_2), 71.4 (CH), 118.5 (CH_2=), 133.9 (CH=), 174.2 (C=O); IR (in substance) ν 3250–3500, 2920, 1740 cm^{-1}; Anal. Calcd. for $C_8H_{12}O_3$: C, 61.5; H, 7.7. Found: C, 61.7; H, 7.7; $[\alpha]^{25}_D$ +18.1 (c 0.42, $CHCl_3$).

Refinement

H atoms were refined isotropically. In the absence of significant anomalous scattering effects, Friedel pairs were merged in the final refinement.

Figures

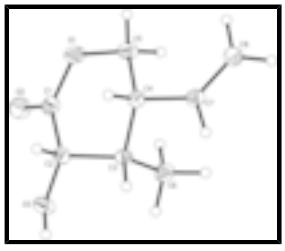


Fig. 1. The molecular structure of the title compound, showing the labelling of all non-H atoms. Displacement ellipsoids are shown at the 30% probability level.

(3*S*,4S,5*R*)-3-Hydroxy-4-methyl-5-vinyltetrahydropyran-2-one

Crystal data

$C_8H_{12}O_3$	F_{000} = 336
M_r = 156.18	D_x = 1.329 Mg m^{-3}
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: P 2ac 2ab	Cell parameters from 7057 reflections
a = 5.4490 (5) Å	θ = 3.3–27.5º
b = 6.4489 (5) Å	μ = 0.10 mm^{-1}
c = 22.2203 (14) Å	T = 173 (1) K
V = 780.82 (11) Å^3	Block, colourless
Z = 4	0.45 × 0.40 × 0.40 mm

Data collection

Nonius KappaCCD area-detector diffractometer	1075 independent reflections
Radiation source: fine-focus sealed tube	727 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.026
Detector resolution: 19 vertical, 18 horizontal pixels mm^{-1}	θ_{max} = 27.5º
T = 173(1) K	θ_{min} = 3.3º
289 frames via ω rotation (Δω = 1°) and two times 20 s per frame (three sets at different κ–angles) scans	h = −7→7
Absorption correction: none	k = −8→8
7057 measured reflections	l = −28→28

Refinement

Refinement on F^2	All H-atom parameters refined
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0305P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.029	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2)$ = 0.058	$\Delta\rho_{max}$ = 0.15 e Å^{-3}
S = 0.90	$\Delta\rho_{min}$ = −0.14 e Å^{-3}

1075 reflections

149 parameters

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

Extinction correction: SHELXL97 (Sheldrick, 1997), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.048 (5)

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.

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 ($Å^2$)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.5199 (2)	0.8726 (2)	0.82549 (5)	0.0360 (4)
O2	0.6965 (2)	0.6799 (2)	0.89410 (6)	0.0410 (4)
O3	0.3787 (2)	0.7650 (2)	0.98007 (5)	0.0361 (4)
H3O	0.249 (4)	0.769 (4)	1.0033 (10)	0.058 (7)*
C1	0.5252 (3)	0.7878 (3)	0.88106 (7)	0.0296 (5)
C2	0.3065 (3)	0.8247 (3)	0.92142 (7)	0.0272 (4)
H2	0.178 (3)	0.732 (3)	0.9067 (7)	0.028 (5)*
C3	0.2162 (3)	1.0476 (3)	0.91739 (7)	0.0256 (5)
H3	0.064 (3)	1.055 (3)	0.9395 (6)	0.021 (4)*
C4	0.1557 (3)	1.0900 (3)	0.85078 (8)	0.0262 (4)
H4	0.041 (3)	0.986 (3)	0.8395 (7)	0.024 (5)*
C5	0.3836 (3)	1.0619 (3)	0.81287 (8)	0.0330 (5)
H5A	0.338 (3)	1.055 (2)	0.7706 (8)	0.025 (4)*
H5B	0.502 (3)	1.182 (3)	0.8212 (7)	0.030 (5)*
C6	0.3998 (4)	1.1984 (4)	0.94473 (9)	0.0358 (5)
H6A	0.415 (3)	1.169 (3)	0.9876 (8)	0.033 (5)*
H6B	0.561 (4)	1.184 (3)	0.9246 (8)	0.046 (6)*
H6C	0.335 (4)	1.347 (4)	0.9409 (8)	0.050 (6)*
C7	0.0438 (3)	1.3007 (3)	0.84232 (8)	0.0297 (5)
H7	−0.073 (3)	1.337 (3)	0.8724 (7)	0.033 (5)*
C8	0.0979 (4)	1.4381 (3)	0.80057 (9)	0.0360 (5)
H8A	0.020 (3)	1.575 (3)	0.8003 (7)	0.034 (5)*
H8B	0.225 (4)	1.415 (3)	0.7692 (9)	0.050 (6)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0363 (7)	0.0428 (9)	0.0288 (7)	0.0135 (7)	0.0068 (6)	0.0009 (6)
O2	0.0334 (8)	0.0448 (9)	0.0448 (8)	0.0126 (8)	0.0043 (6)	0.0038 (7)
O3	0.0334 (7)	0.0450 (10)	0.0300 (7)	0.0077 (7)	0.0038 (6)	0.0099 (7)
C1	0.0289 (10)	0.0290 (12)	0.0308 (10)	0.0010 (10)	−0.0019 (8)	−0.0027 (9)
C2	0.0262 (9)	0.0285 (11)	0.0269 (9)	0.0007 (9)	−0.0012 (8)	0.0017 (8)
C3	0.0218 (9)	0.0284 (12)	0.0267 (9)	−0.0006 (9)	0.0045 (8)	0.0006 (8)
C4	0.0231 (9)	0.0282 (12)	0.0274 (9)	0.0000 (9)	−0.0006 (8)	−0.0011 (9)
C5	0.0315 (11)	0.0398 (14)	0.0278 (10)	0.0082 (11)	−0.0002 (9)	0.0023 (10)
C6	0.0391 (12)	0.0372 (14)	0.0311 (11)	−0.0045 (11)	−0.0003 (9)	−0.0027 (10)
C7	0.0264 (10)	0.0348 (12)	0.0278 (9)	0.0028 (9)	0.0012 (8)	−0.0002 (9)
C8	0.0400 (12)	0.0348 (14)	0.0333 (11)	0.0043 (11)	−0.0018 (10)	0.0012 (11)

Geometric parameters (Å, °)

O1—C1	1.351 (2)	C4—C5	1.512 (3)
O1—C5	1.456 (2)	C4—H4	0.952 (18)
O2—C1	1.200 (2)	C5—H5A	0.973 (17)
O3—C2	1.415 (2)	C5—H5B	1.024 (19)
O3—H3O	0.88 (2)	C6—H6A	0.974 (18)
C1—C2	1.510 (2)	C6—H6B	0.99 (2)
C2—C3	1.522 (3)	C6—H6C	1.02 (2)
C2—H2	0.977 (19)	C7—C8	1.316 (3)
C3—C6	1.522 (3)	C7—H7	0.952 (18)
C3—C4	1.541 (2)	C8—H8A	0.98 (2)
C3—H3	0.964 (17)	C8—H8B	1.00 (2)
C4—C7	1.502 (3)		
C1—O1—C5	121.78 (14)	C5—C4—H4	108.0 (10)
C2—O3—H3O	108.0 (14)	C3—C4—H4	105.5 (10)
O2—C1—O1	118.19 (16)	O1—C5—C4	114.33 (15)
O2—C1—C2	124.20 (16)	O1—C5—H5A	106.3 (10)
O1—C1—C2	117.49 (16)	C4—C5—H5A	109.5 (10)
O3—C2—C1	106.53 (14)	O1—C5—H5B	106.0 (9)
O3—C2—C3	113.67 (15)	C4—C5—H5B	109.2 (9)
C1—C2—C3	111.67 (16)	H5A—C5—H5B	111.6 (13)
O3—C2—H2	110.0 (10)	C3—C6—H6A	109.0 (11)
C1—C2—H2	105.7 (10)	C3—C6—H6B	110.2 (12)
C3—C2—H2	109.0 (10)	H6A—C6—H6B	110.3 (15)
C2—C3—C6	111.57 (15)	C3—C6—H6C	109.7 (12)
C2—C3—C4	107.06 (14)	H6A—C6—H6C	106.9 (16)
C6—C3—C4	114.26 (17)	H6B—C6—H6C	110.7 (19)
C2—C3—H3	107.0 (11)	C8—C7—C4	127.34 (18)
C6—C3—H3	109.4 (10)	C8—C7—H7	118.7 (12)
C4—C3—H3	107.2 (9)	C4—C7—H7	113.9 (12)
C7—C4—C5	111.85 (16)	C7—C8—H8A	120.9 (10)

C7—C4—C3	111.58 (15)	C7—C8—H8B	123.2 (13)
C5—C4—C3	109.76 (15)	H8A—C8—H8B	115.8 (17)
C7—C4—H4	109.9 (10)		
C5—O1—C1—O2	−155.30 (18)	C2—C3—C4—C7	175.08 (14)
C5—O1—C1—C2	28.4 (2)	C6—C3—C4—C7	−60.9 (2)
O2—C1—C2—O3	17.4 (3)	C2—C3—C4—C5	−60.4 (2)
O1—C1—C2—O3	−166.52 (16)	C6—C3—C4—C5	63.7 (2)
O2—C1—C2—C3	142.05 (19)	C1—O1—C5—C4	−31.6 (3)
O1—C1—C2—C3	−41.9 (2)	C7—C4—C5—O1	171.65 (15)
O3—C2—C3—C6	52.0 (2)	C3—C4—C5—O1	47.2 (2)
C1—C2—C3—C6	−68.52 (19)	C5—C4—C7—C8	11.9 (3)
O3—C2—C3—C4	177.73 (15)	C3—C4—C7—C8	135.3 (2)
C1—C2—C3—C4	57.18 (19)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3O···O2^{i}	0.88 (2)	2.32 (2)	2.9881 (18)	133.0 (17)
O3—H3O···O3^{i}	0.88 (2)	2.06 (2)	2.8713 (8)	153.1 (19)

Symmetry codes: (i) *x*−1/2, −*y*+3/2, −*z*+2.

Fig. 1