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rac-2,7-Bis(2-hydroxy-2-propyl)-*trans*-oxepane

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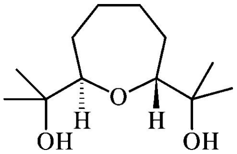
Key indicators: single-crystal X-ray study; T = 173 K; mean σ(C–C) = 0.002 Å; R factor = 0.044; wR factor = 0.102; data-to-parameter ratio = 14.1.

The title compound, $C_{12}H_{24}O_3$, was prepared by the RuO_4-catalyzed oxidative cyclization of 2,9-dimethyldeca-2,8-diene. The crystal structure determination has shown unambigously that ring closure produced the *trans* stereoisomer. Intramolecular O—H⋯O hydrogen bonding generates an $S(8)$ ring motif. Intermolecular O—H⋯O hydrogen bonding leads to the formation of infinite $C_2^2(4)$ chains running along the a axis.

Related literature

For related literature, see: Albarella *et al.* (2001); Brown & Keily (2001); de Champdoré *et al.* (1998); Charlsen *et al.* (1981); Donohoe & Butterworth (2003); Hoberg (1998); Luger *et al.* (1991); Matsumura *et al.* (2000); Piccialli (2000); Piccialli & Caserta (2004); Piccialli & Cavallo (2001); Roth & Stark (2006); Roth *et al.* (2005).



Experimental

Crystal data

$C_{12}H_{24}O_3$
M_r = 216.31
Orthorhombic, $Pbca$
a = 8.4400 (16) Å
b = 16.473 (3) Å
c = 18.470 (5) Å
V = 2567.9 (10) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.08 mm^{-1}
T = 173 (2) K
0.25 × 0.20 × 0.10 mm

Data collection

Bruker-Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker–Nonius, 2002)
T_{min} = 0.978, T_{max} = 0.988
20554 measured reflections
2926 independent reflections
1811 reflections with $I > 2\sigma(I)$
R_{int} = 0.082

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.102
S = 1.02
2926 reflections
208 parameters
Only H-atom coordinates refined
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.17 e Å^{-3}

Table 1
Selected bond angles (°).

O1—C7—C6	108.51 (12)

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O2—H2O⋯O3^i	0.819 (18)	1.859 (18)	2.6705 (16)	170.7 (17)
O3—H3O⋯O2	0.824 (18)	1.873 (18)	2.6921 (17)	172.4 (17)

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

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DIRAX/LSQ* (Duisenberg *et al.*, 2000); data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB2377).

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supplementary materials

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rac-2,7-Bis(2-hydroxy-2-propyl)-*trans*-oxepane

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Comment

Ruthenium tetroxide is able to catalyze the stereoselective synthesis of 2,5-bishydroxyalkyl-substituted THF and/or THP rings from 1,5- and 1,6-dienes, respectively, *via* oxygen transfer to the diene system, in the presence of sodium periodate as reoxidant (Charlsen *et al.*, 1981; Piccialli, 2000; Piccialli & Cavallo, 2001; Albarella *et al.*, 2001; Roth *et al.*, 2005; Roth & Stark, 2006). Related oxidative cyclization processes, mediated by other transition metal-oxo species such as OsO_4, MnO_4^-, RuO_4^-, are also known (Brown & Keily, 2001; de Champdoré *et al.*, 1998; Piccialli & Caserta, 2004; Donohoe & Butterworth, 2003). We decided to investigate the same oxidative transformation on 1,7-dienes envisaging that the process could lead to the formation of oxepane rings as well.

Seven-membered oxacycles are present in many biologically active natural products such as Laurencia acetogenin metabolites and ether marine toxin. In these compounds the oxepane ring is very often 2,7 dialkylsubstituted. While some efficient methods toward the stereoselective synthesis of 2,7-*cis*-oxepanes have been developed, few methods have been so far devised to generate the 2,7-*trans*-oxepane system (Hoberg, 1998; Matsumura *et al.*, 2000). Thus, taking into account the electrophilic character of RuO_4, and precedents from the oxidation of 1,5- and 1,6-dienes, 2,9-dimethyldeca-2,8-diene was initially selected as a good substrate to test this possibility.

In this paper we report that the ruthenium-catalyzed oxidative cyclization of 2,9-dimethyldeca-2,8-diene gives the *trans*-oxepane diol product, (I). The X-ray analysis showed that the (*R*,*R*), (S,*S*) racemic mixture is formed, with the molecule in *trans*-configuration (Fig. 1 and Table 1). The oxepane ring adopts a twisted-chair conformation (Table 1) as usually found in oxepane derivatives (Luger *et al.*, 1991). This conformation appears also to be the one adopted by mono-*p*-bromobenzoate derivative of (I) in solution as indicated by NOE data and J values.

This is the first report dealing with the synthesis of an oxepane product through oxidative cyclization of an 1,7-diene.

Crystal packing with indication of H bonds is shown in Fig. 2. Hydrogen bonds are summarized in Table 2. There is an intramolecular hydrogen bond, whose graph set descriptor is S(8), from O3 donor to O2 acceptor, leading to the formation of an eight-membered ring.

Molecules in the crystals are linked through intermolecular O—H···O bonds forming chains running along a, whose graph set descriptor is $C^2_2(4)$. The rows are generated by the glide planes normal to *c* axis.

Experimental

The oxidative cyclization was accomplished as shown in Scheme 1. Ru-catalyzed oxidative cyclizations of dienes are generally conducted in solvent mixtures containing water (e.g $EtOAc/CH_3CN/H_2O$, 3:3:1) to dissolve $NaIO_4$ that acts as the final oxidant. However, exclusion of water from the reaction mixture has recently been demonstrated to increase the yields of the THF diols obtained from the oxidation of 1,5-dienes. (Roth *et al.*, 2005). Therefore, after some experimentation, the process was run in EtOAc/CH_3CN (1:1) with $NaIO_4$ (7 equiv.) supported on wet silica. These conditions proved very effective giving *trans*-oxepane (I) in an isolated 63% yield (HPLC, hexane/EtOAc, 7:3, Rt= 34 min) with >95% stereoselectivity level.

In particular, to a suspension of $NaIO_4$ supported on wet silica (7 eqiv, 1.90 g) in EtOAc/CH_3CN (1:1, 5.8 ml) was added 2,9-dimethyldeca-2,8-diene in EtOAc/CH_3CN (1:1, 0.5 ml). Then, $RuCl_3$ (160 µ*L* of a 0.1 *M* stock solution in EtOAc, 5 mol %) was added *via* syringe, at 273 K under stirring. After 15 min reaction, TLC analysis (I_2) showed complete consumption of the diene and formation of a product at R_f 0.6 (EtOAc/hexane, 7:3). The process was quenched by addition of a few drops of isopropylalcohol. The mixture was filtered and the solid washed with EtOAc and MeOH and the crude mixture chromatographed over a Si-gel column (25 × 0.5 cm). Elution with EtOAc-petroleum ether (1:1, 50 ml) gave 20 mg (63%) of the pure oxepane diol (I).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 3.63 (1*H*, dd, J=10.6, 2.2, H-3/H-8), 1.94, 1.87 (2H each, H_2-4/H_2-7), 1.52, 1.37 (2H each, H_2-5/H_2-6), 1.22, 1.16 (6H each, 4 *x* Me). ^{13}C NMR (75 MHz, $CDCl_3$) δ 82.6, 73.9, 29.6, 27.8, 27.7, 24.2.

Single crystals of (I) suitable for structure determination were obtained from a chloroform solution by slow evaporation at room temperature.

Refinement

The H atoms were located in difference maps and their coordinates were refined with U_{iso}(H) = U_{eq}(carrier).

Figures

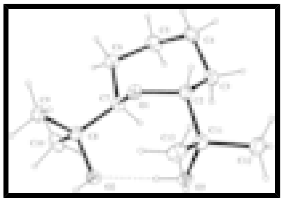


Fig. 1. View of the (*R*,*R*) enantiomer of (I). Displacement ellipsoids are drawn at 30% probability level (arbitrary spheres for the H atoms).

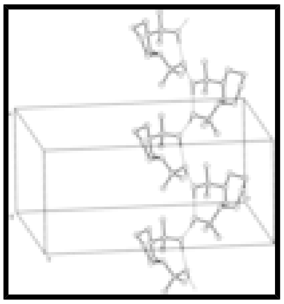


Fig. 2. Partial crystal packing of (I) showing H bonding patterns as dashed lines.

Fig. 3. The reaction scheme for the formation of (I).

rac-2,7-bis(2-hydroxy-2-propyl)-*trans*-oxepane

Crystal data

$C_{12}H_{24}O_3$

$M_r = 216.31$

Orthorhombic, *Pbca*

Hall symbol: -P 2ac 2ab

$a = 8.4400\ (16)$ Å

$b = 16.473\ (3)$ Å

$c = 18.470\ (5)$ Å

$V = 2567.9\ (10)$ Å^3

$Z = 8$

$F_{000} = 960$

$D_x = 1.119$ Mg m^{-3}

Mo *K*α radiation
λ = 0.71073 Å

Cell parameters from 86 reflections

θ = 3.4–19.5°

μ = 0.08 mm^{-1}

$T = 173\ (2)$ K

Prism, colourless

0.25 × 0.20 × 0.10 mm

Data collection

Bruker-Nonius KappaCCD diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

Detector resolution: 9 pixels mm^{-1}

$T = 173(2)$ K

CCD rotation images, thick slices scans

Absorption correction: multi-scan (SADABS; Bruker–Nonius, 2002)

$T_{min} = 0.978$, $T_{max} = 0.988$

20554 measured reflections

2926 independent reflections

1811 reflections with $I > 2\sigma(I)$

$R_{int} = 0.082$

$\theta_{max} = 27.5°$

$\theta_{min} = 3.3°$

$h = -10 \rightarrow 10$

$k = -17 \rightarrow 21$

$l = -23 \rightarrow 21$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.044$

$wR(F^2) = 0.102$

$S = 1.02$

2926 reflections

208 parameters

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: difference Fourier map

Only H-atom coordinates refined

$w = 1/[\sigma^2(F_o^2) + (0.038P)^2 + 0.5591P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.24$ e Å^{-3}

$\Delta\rho_{min} = -0.17$ e Å^{-3}

Extinction correction: none

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	0.00809 (12)	0.04118 (6)	0.90900 (5)	0.0255 (3)
O2	−0.10634 (13)	0.07424 (7)	0.77014 (6)	0.0345 (3)
H2O	−0.185 (2)	0.0479 (11)	0.7584 (9)	0.035*
O3	0.15740 (14)	−0.01681 (7)	0.78139 (5)	0.0312 (3)
H3O	0.072 (2)	0.0072 (11)	0.7781 (8)	0.031*
C2	0.15237 (18)	−0.00501 (9)	0.91339 (8)	0.0270 (4)
H2	0.1361 (17)	−0.0388 (10)	0.9560 (8)	0.027*
C3	0.2978 (2)	0.04707 (11)	0.92827 (9)	0.0323 (4)
H3A	0.3339 (18)	0.0754 (10)	0.8836 (9)	0.032*
H3B	0.382 (2)	0.0112 (10)	0.9424 (9)	0.032*
C4	0.2726 (2)	0.10787 (11)	0.98981 (9)	0.0379 (4)
H4A	0.207 (2)	0.0818 (10)	1.0290 (8)	0.038*
H4B	0.377 (2)	0.1205 (10)	1.0105 (9)	0.038*
C5	0.1973 (2)	0.18820 (11)	0.96685 (10)	0.0385 (4)
H5A	0.265 (2)	0.2133 (10)	0.9287 (9)	0.039*
H5B	0.199 (2)	0.2266 (10)	1.0091 (9)	0.039*
C6	0.0286 (2)	0.18288 (10)	0.93785 (9)	0.0320 (4)
H6A	−0.0038 (19)	0.2358 (10)	0.9216 (8)	0.032*
H6B	−0.044 (2)	0.1686 (9)	0.9770 (8)	0.032*
C7	0.01118 (18)	0.12087 (9)	0.87740 (8)	0.0253 (3)
H7	0.1026 (19)	0.1262 (9)	0.8431 (8)	0.025*
C8	−0.13765 (18)	0.12793 (10)	0.82998 (8)	0.0291 (4)
C9	−0.2878 (2)	0.10296 (12)	0.86928 (10)	0.0355 (4)
H9A	−0.283 (2)	0.0472 (11)	0.8852 (9)	0.035*
H9B	−0.307 (2)	0.1363 (10)	0.9119 (9)	0.035*
H9C	−0.378 (2)	0.1079 (10)	0.8360 (9)	0.035*
C10	−0.1541 (3)	0.21341 (12)	0.79847 (12)	0.0451 (5)
H10A	−0.186 (2)	0.2511 (12)	0.8354 (10)	0.045*
H10B	−0.237 (2)	0.2126 (11)	0.7604 (9)	0.045*
H10C	−0.052 (2)	0.2298 (11)	0.7752 (9)	0.045*
C11	0.16319 (19)	−0.06260 (9)	0.84775 (8)	0.0295 (4)
C12	0.3197 (2)	−0.10858 (12)	0.84672 (11)	0.0413 (4)
H12A	0.409 (2)	−0.0726 (11)	0.8373 (9)	0.041*
H12B	0.333 (2)	−0.1365 (11)	0.8936 (10)	0.041*
H12C	0.312 (2)	−0.1483 (11)	0.8092 (9)	0.041*
C13	0.0240 (2)	−0.12139 (11)	0.84791 (10)	0.0368 (4)
H13A	0.027 (2)	−0.1555 (10)	0.8037 (9)	0.037*
H13B	0.029 (2)	−0.1577 (10)	0.8913 (9)	0.037*

H13C	−0.073 (2)	−0.0938 (11)	0.8474 (8)	0.037*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0243 (6)	0.0224 (5)	0.0297 (5)	−0.0022 (4)	0.0025 (4)	0.0020 (4)
O2	0.0261 (6)	0.0472 (7)	0.0303 (6)	−0.0026 (5)	−0.0022 (5)	−0.0071 (5)
O3	0.0292 (6)	0.0370 (6)	0.0273 (5)	0.0035 (5)	0.0049 (5)	0.0028 (5)
C2	0.0270 (9)	0.0261 (8)	0.0277 (8)	0.0022 (6)	0.0017 (6)	0.0056 (7)
C3	0.0276 (9)	0.0351 (9)	0.0343 (9)	0.0010 (7)	−0.0036 (7)	0.0039 (7)
C4	0.0336 (10)	0.0432 (10)	0.0370 (9)	−0.0037 (8)	−0.0111 (8)	−0.0037 (8)
C5	0.0402 (11)	0.0325 (9)	0.0429 (10)	−0.0081 (8)	−0.0085 (8)	−0.0067 (8)
C6	0.0356 (10)	0.0237 (9)	0.0365 (9)	−0.0020 (7)	−0.0015 (7)	−0.0013 (7)
C7	0.0262 (8)	0.0214 (8)	0.0284 (8)	−0.0036 (6)	0.0007 (7)	0.0025 (6)
C8	0.0261 (9)	0.0314 (8)	0.0298 (8)	−0.0001 (7)	0.0000 (6)	−0.0021 (7)
C9	0.0255 (9)	0.0433 (11)	0.0376 (10)	−0.0003 (8)	0.0025 (7)	−0.0068 (8)
C10	0.0416 (12)	0.0424 (11)	0.0515 (11)	0.0029 (9)	−0.0118 (9)	0.0111 (9)
C11	0.0328 (9)	0.0273 (8)	0.0284 (8)	0.0019 (7)	0.0047 (7)	0.0038 (6)
C12	0.0433 (11)	0.0372 (10)	0.0434 (10)	0.0118 (9)	0.0052 (9)	0.0008 (9)
C13	0.0450 (11)	0.0290 (9)	0.0365 (10)	−0.0052 (8)	0.0051 (8)	−0.0043 (8)

Geometric parameters (Å, °)

C7—O1	1.4368 (17)	C6—H6B	0.978 (17)
C2—O1	1.4382 (18)	C7—C8	1.536 (2)
O2—C8	1.4399 (18)	C7—H7	1.002 (16)
O2—H2O	0.819 (18)	C8—C9	1.518 (2)
O3—C11	1.4400 (18)	C8—C10	1.530 (2)
O3—H3O	0.824 (18)	C9—H9A	0.965 (18)
C2—C3	1.523 (2)	C9—H9B	0.973 (17)
C2—C11	1.542 (2)	C9—H9C	0.982 (17)
C2—H2	0.974 (16)	C10—H10A	0.963 (19)
C3—C4	1.530 (2)	C10—H10B	0.990 (19)
C3—H3A	0.995 (16)	C10—H10C	1.000 (19)
C3—H3B	0.958 (17)	C11—C12	1.522 (2)
C4—C5	1.528 (3)	C11—C13	1.523 (2)
C4—H4A	1.006 (17)	C12—H12A	0.972 (19)
C4—H4B	0.982 (18)	C12—H12B	0.986 (18)
C5—C6	1.523 (2)	C12—H12C	0.956 (18)
C5—H5A	0.997 (18)	C13—H13A	0.992 (17)
C5—H5B	1.004 (18)	C13—H13B	1.001 (17)
C6—C7	1.520 (2)	C13—H13C	0.938 (18)
C6—H6A	0.961 (17)		
C7—O1—C2	119.40 (11)	C8—C7—H7	105.2 (8)
C8—O2—H2O	112.4 (12)	O2—C8—C9	110.73 (13)
C11—O3—H3O	110.0 (11)	O2—C8—C10	106.86 (14)
O1—C2—C3	113.24 (12)	C9—C8—C10	110.82 (15)
O1—C2—C11	109.35 (12)	O2—C8—C7	103.95 (12)

C3—C2—C11	116.16 (13)	C9—C8—C7	112.94 (13)
O1—C2—H2	103.2 (9)	C10—C8—C7	111.16 (14)
C3—C2—H2	106.9 (9)	C8—C9—H9A	111.7 (10)
C11—C2—H2	107.0 (9)	C8—C9—H9B	111.7 (10)
C2—C3—C4	113.03 (14)	H9A—C9—H9B	107.3 (13)
C2—C3—H3A	111.2 (9)	C8—C9—H9C	108.9 (10)
C4—C3—H3A	110.5 (9)	H9A—C9—H9C	107.6 (14)
C2—C3—H3B	107.3 (10)	H9B—C9—H9C	109.5 (14)
C4—C3—H3B	107.7 (10)	C8—C10—H10A	110.5 (11)
H3A—C3—H3B	106.7 (13)	C8—C10—H10B	108.7 (10)
C5—C4—C3	114.74 (14)	H10A—C10—H10B	108.3 (15)
C5—C4—H4A	109.9 (10)	C8—C10—H10C	109.5 (11)
C3—C4—H4A	109.3 (10)	H10A—C10—H10C	112.0 (15)
C5—C4—H4B	107.3 (10)	H10B—C10—H10C	107.7 (14)
C3—C4—H4B	107.7 (10)	O3—C11—C12	106.22 (13)
H4A—C4—H4B	107.6 (13)	O3—C11—C13	107.98 (13)
C6—C5—C4	115.89 (15)	C12—C11—C13	110.66 (15)
C6—C5—H5A	108.1 (10)	O3—C11—C2	110.18 (12)
C4—C5—H5A	108.4 (10)	C12—C11—C2	111.54 (14)
C6—C5—H5B	108.8 (10)	C13—C11—C2	110.12 (13)
C4—C5—H5B	108.9 (9)	C11—C12—H12A	111.6 (11)
H5A—C5—H5B	106.2 (13)	C11—C12—H12B	108.6 (10)
C7—C6—C5	112.79 (14)	H12A—C12—H12B	110.7 (14)
C7—C6—H6A	110.7 (9)	C11—C12—H12C	106.9 (11)
C5—C6—H6A	108.9 (10)	H12A—C12—H12C	109.8 (14)
C7—C6—H6B	108.7 (9)	H12B—C12—H12C	109.0 (14)
C5—C6—H6B	110.0 (10)	C11—C13—H13A	109.8 (10)
H6A—C6—H6B	105.6 (13)	C11—C13—H13B	110.6 (10)
O1—C7—C6	108.51 (12)	H13A—C13—H13B	108.7 (13)
O1—C7—C8	106.62 (12)	C11—C13—H13C	111.5 (11)
C6—C7—C8	116.56 (13)	H13A—C13—H13C	106.8 (14)
O1—C7—H7	110.6 (9)	H13B—C13—H13C	109.4 (14)
C6—C7—H7	109.3 (9)		

C7—O1—C2—C3	35.73 (17)	C6—C7—C8—O2	168.50 (13)
C7—O1—C2—C11	−95.51 (14)	O1—C7—C8—C9	49.88 (17)
O1—C2—C3—C4	47.03 (18)	C6—C7—C8—C9	−71.42 (18)
C11—C2—C3—C4	174.81 (13)	O1—C7—C8—C10	175.18 (13)
C2—C3—C4—C5	−85.78 (19)	C6—C7—C8—C10	53.88 (19)
C3—C4—C5—C6	64.5 (2)	O1—C2—C11—O3	58.09 (16)
C4—C5—C6—C7	−52.3 (2)	C3—C2—C11—O3	−71.58 (17)
C2—O1—C7—C6	−95.30 (14)	O1—C2—C11—C12	175.81 (13)
C2—O1—C7—C8	138.41 (12)	C3—C2—C11—C12	46.14 (19)
C5—C6—C7—O1	77.03 (17)	O1—C2—C11—C13	−60.91 (16)
C5—C6—C7—C8	−162.67 (14)	C3—C2—C11—C13	169.41 (14)
O1—C7—C8—O2	−70.20 (14)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*

O2—H2O···O3^{i}	0.819 (18)	1.859 (18)	2.6705 (16)	170.7 (17)
O3—H3O···O2	0.824 (18)	1.873 (18)	2.6921 (17)	172.4 (17)

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

Fig. 1

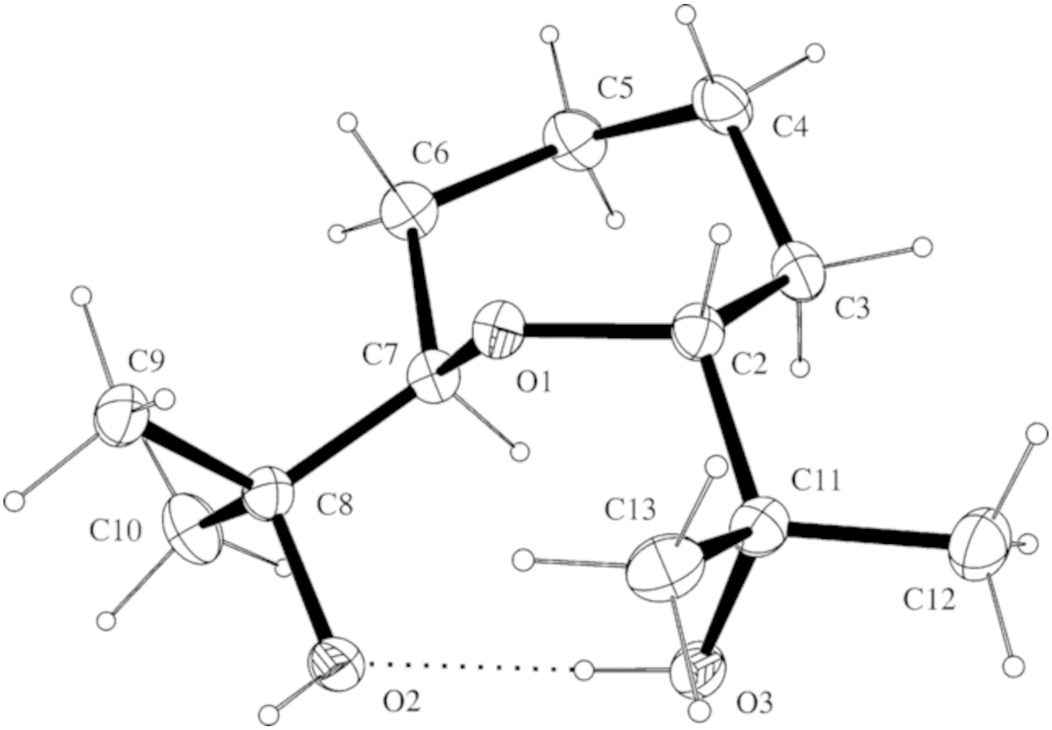


Fig. 2

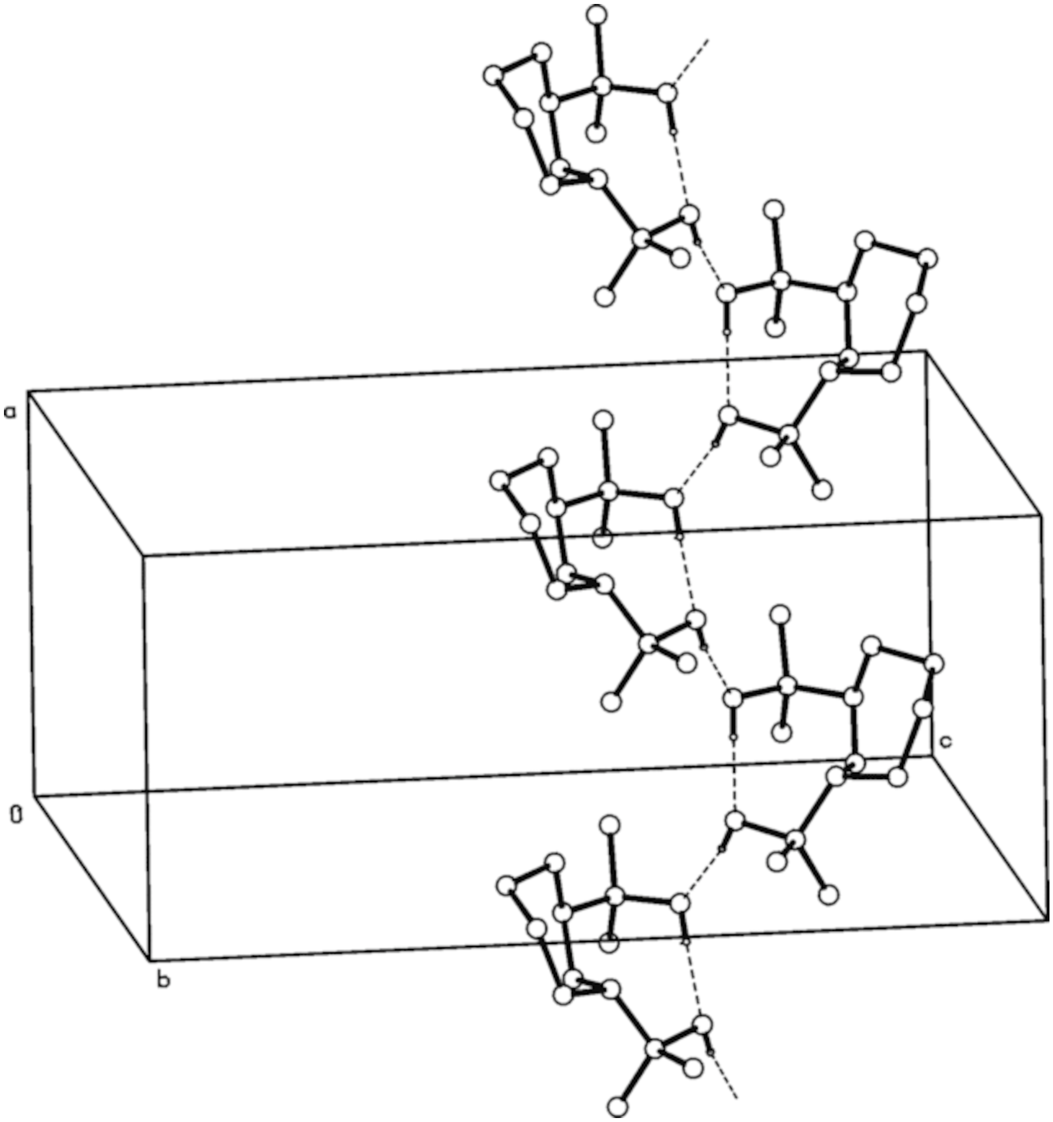
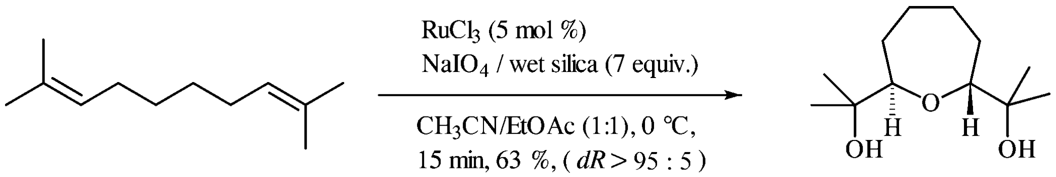


Fig. 3


$RuCl_3$ (5 mol %)
$NaIO_4$ / wet silica (7 equiv.)
CH_3CN/EtOAc (1:1), 0 °C,
15 min, 63 %, (*dR* > 95 : 5)
O
H
H
OH
OH

(I)