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(4*S*,5*S*,6*R*,*E*)-3,5-Dimethyl-6-vinylhept-2-ene-1,4,7-triol

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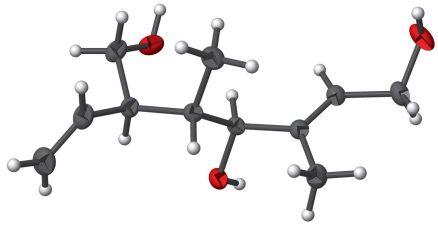
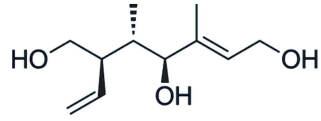
Structural data: full structural data are available from iucrdata.iucr.org

The title compound, $C_{11}H_{20}O_3$, was obtained in the course of the total syntheses of curvicollides A–C and features the same relative configuration for the central lactone moiety as that reported for the latter compounds. In the crystal, molecules are linked *via* O—H···O hydrogen bonds: all of the OH groups act as donors as well as acceptors for these bonds, hence each molecule is bound to six surrounding molecules and a three-dimensional network is formed. The absolute structure was confirmed by refinement of the Flack parameter.

3D view



Chemical scheme



Structure description

As a key precursor in the total synthesis of curvicollides A–C we obtained the title compound (I) (Fig. 1) through reductive cleavage of the benzyl ethers in (4*S*,5*S*,6*R*,*E*)-1-(benzyloxy)-6-[(benzyloxy)methyl]-3,5-dimethylocta-2,7-dien-4-ol, (II). Background to curvicollides is given by Che *et al.*, (2004) and synthetic studies of curvicollides are described by Körner & Hiersemann (2007). The stereotriade in the title compound was generated from an enantioselective transformation employing the catalytic asymmetric Gosteli–Claisen rearrangement followed by a diastereoselective reduction. The absolute configuration was determined based on the previously described stereochemical course of the catalytic asymmetric Gosteli–Claisen rearrangement using a modified Evans–Cu{(*S*,*S*)-*tert*-butyl-box}–Lewis acid catalyst. For the synthesis of the Evans–Cu{(*S*,*S*)-*tert*-butyl-box} catalyst, see: Evans *et al.* (1999) and Jaschinski & Hiersemann (2012).

In the crystal, molecules are linked *via* O—H···O hydrogen bonds (Table 1): all of the OH groups act as donors as well as acceptors for these bonds, hence each molecule is bound to six surrounding molecules and a three-dimensional network is formed Fig. 2).

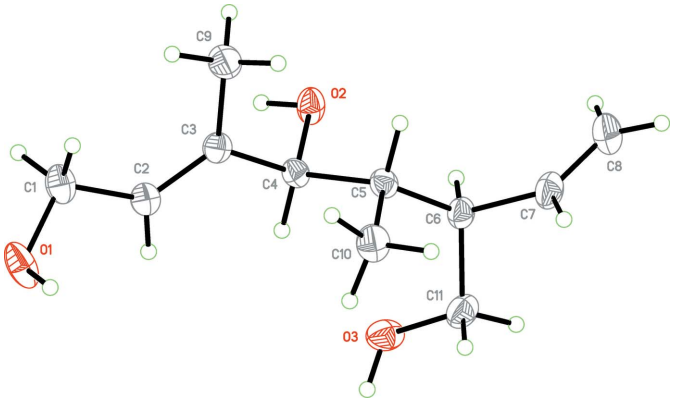


Figure 1
The molecular structure of the title compound, showing displacement ellipsoids at the 50% probability level.

Synthesis and crystallization

The synthesis of the title compound was carried out under the conditions for reductive cleavage of benzyl ethers (Liu *et al.*, 1997). To a solution of naphthalene ($C_{10}H_8$, M = 128.17 g mol^{-1}, 69.5 g, 542.35 mmol, 1.499 equiv.) in THF (300 ml), small pieces of freshly cut lithium metal (Li, M = 6.94 g mol^{-1}, 2.51 g, 361.67 mmol, 1 equiv.) were added at room temperature. Within 30 minutes, the colour of the reaction mixture turned to dark green. The reaction mixture was stirred for a further 3 h in order to completely dissolve the metal. The mixture was then transferred within 45 minutes *via* a canula to a solution of the benzylether (II) ($C_{25}H_{32}O_3$, M = 380.52 g mol^{-1}, 5.51 g, 14.48 mmol, 1 equiv) in THF (65 ml) at 195 K. After stirring for 2 h, saturated aqueous ammonium chloride solution (100 ml) was added and the mixture was allowed to reach room temperature. The phases were separated and the aqueous layer was extracted with ethyl acetate (3 × 100 ml). The combined organic phases were dried

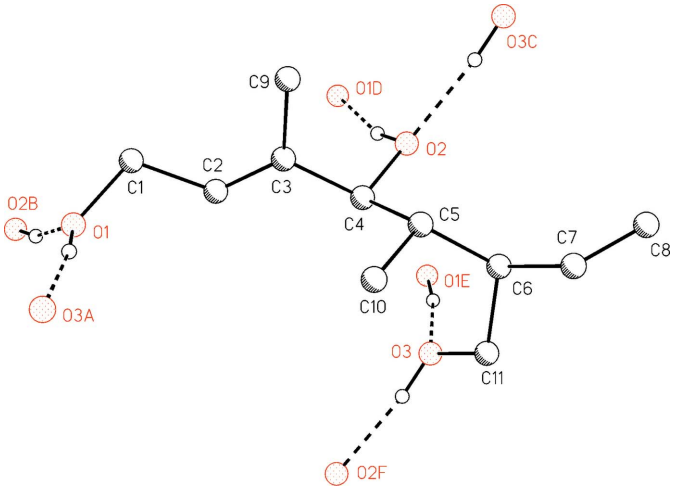


Figure 2
The molecular structure of the title compound showing the six hydrogen bonds around the molecule. H atoms on C atoms have been omitted for clarity. [Symmetry codes: (A) $x, y-1, z$; (B) $\frac{1}{2}+x, y-\frac{1}{2}, 1-z$; (C) $x-1, y, z$; (D) $x-\frac{1}{2}, \frac{1}{2}-y, 1-z$; (E) $x, 1+y, z$; (F) $1+x, y, z$.]

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

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2···O1^{i}	0.91 (2)	1.77 (2)	2.6681 (16)	166 (3)
O3—H3···O2^{ii}	0.89 (2)	1.83 (2)	2.6983 (16)	166 (2)
O1—H1···O3^{iii}	0.92 (2)	1.83 (2)	2.7458 (17)	172 (2)

Symmetry codes: (i) $x-\frac{1}{2}, -y+\frac{1}{2}, -z+1$; (ii) $x+1, y, z$; (iii) $x, y-1, z$.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{11}H_{20}O_3$
M_r	200.27
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	100
a, b, c (Å)	5.8932 (9), 7.1714 (9), 27.347 (4)
V (Å^3)	1155.7 (3)
Z	4
Radiation type	Cu $K\alpha$
μ (mm^{-1})	0.66
Crystal size (mm)	0.22 × 0.10 × 0.05
Data collection	
Diffractometer	Bruker D8 VENTURE CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2012)
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	7921, 2189, 2154
R_{int}	0.025
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.610
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.031, 0.080, 1.10
No. of reflections	2189
No. of parameters	141
No. of restraints	3
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.19, −0.17
Absolute structure	Flack x determined using 862 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons & Flack, 2004)
Absolute structure parameter	0.06 (4)

Computer programs: *SMART* and *SAINT* (Bruker, 2012), *SHELXD*, *SHELXTL-Plus* and *SHELXL97* (Sheldrick, 2008), *SHELXL2013* (Sheldrick, 2015) and *PLATON* (Spek, 2009).

($MgSO_4$), filtered and concentrated under reduced pressure. Purification of the residue by flash chromatography (cyclohexane/ethyl acetate 10/1 to 2/1 to ethyl acetate) delivered the title compound (I) ($C_{11}H_{20}O_3$, M = 200.27 g mol^{-1}, 2.58 g, 12.88 mmol, 88%) as a pale yellow solid. Single crystals of (I) were obtained by adding n-pentane (6 ml) to a solution of (I) in diethyl ether (0.4 ml). Crystallization was completed by slow evaporation of the solvent over three days and yielded (I) as colourless needles. R_f 0.28 (ethyl acetate); m.p. 335.5–337.5 K; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.85 (*d*, J = 7.3 Hz, 3 H, 5-CH_3) 1.59 (*s*, 3 H, 3-CH_3) 1.96 (*quind*, J = 7.0, 1.8 Hz, 1 H, 5-H) 2.36–2.48 (*m*, 1 H, 6-H) 3.43–3.69 (*m*, 2 H, 7-H_2) 3.84 (*d*, J = 6.6 Hz, 1 H, 4-H) 3.95 (*br s*, 1 H, OH) 4.11 (*dd*, J = 12.8, 5.9 Hz, 1 H, 1-H_a) 4.22 (*dd*, J = 12.8, 7.3 Hz, 1 H, 1-H_b) 4.94–5.15 (*m*, 3 H, CH=CH_2, OH) 5.18 (*br s*, 1 H, OH) 5.58 (*t*, J = 6.4 Hz, 1H,

2-H) 5.77 (*ddd*, *J* = 17.2, 10.4, 8.2 Hz, 1H, CH═CH_2); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 12.38 (3-CH_3) 13.91 (5-CH_3) 38.65 (CH-5) 46.54 (CH-6) 58.86 (CH_2-1) 62.73 (CH_2-7) 78.59 (CH-4) 116.48 (CH═CH_2) 125.75 (CH-2) 137.99 (CH═CH_2) 139.12 (C-3); IR (cm^{-1}): 3334 (*br s*), 2967 (*s*), 2880 (*s*), 1667 (*w*), 1634 (*w*), 1455 (*m*), 1383 (*m*) 1003 (*s*) 918 (*w*), 756 (*s*), 666 (*w*); HRMS (ESI) calculated for $C_{11}H_{20}O_3Na$ ([*M* + Na]$^+$): 223.13047, found 223.12963. Analysis calculated for $C_{11}H_{20}O_3$: C, 65.97; H, 10.07; found: C, 65.7; H, 9.9; $[\alpha]_D^{20}$ = +46 (*c* 1, $CHCl_3$).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

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full crystallographic data

IUCrData (2016). **1**, x160697 [doi:10.1107/S2414314616006970]

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Crystal data

$C_{11}H_{20}O_3$
M_r = 200.27
Orthorhombic, $P2_12_12_1$
a = 5.8932 (9) Å
b = 7.1714 (9) Å
c = 27.347 (4) Å
V = 1155.7 (3) Å^3
Z = 4
$F(000)$ = 440
D_x = 1.151 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54178 Å
Cell parameters from 7854 reflections
θ = 3.2–70.2°
μ = 0.66 mm^{-1}
T = 100 K
Plate, colourless-yellow
0.22 × 0.10 × 0.05 mm

Data collection

Bruker D8 VENTURE CCD diffractometer
Radiation source: microfocus sealed X-ray tube
Detector resolution: 7.9 pixels mm^{-1}
ω and φ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2012)
7921 measured reflections
2189 independent reflections
2154 reflections with $I > 2\sigma(I)$
R_{int} = 0.025
θ_{max} = 70.2°, θ_{min} = 3.2°
h = −7→7
k = −8→8
l = −27→33

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.080
S = 1.10
2189 reflections
141 parameters
3 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0446P)^2 + 0.1631P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.19 e Å^{-3}
$\Delta\rho_{min}$ = −0.17 e Å^{-3}
Absolute structure: Flack x determined using 862 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons & Flack, 2004)
Absolute structure parameter: 0.06 (4)

Special details

Experimental. A total of 1956 frames were collected. The total exposure time was 43.62 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data yielded a total of 7921 reflections to maximum angle of 70.22° (0.82 Å resolution), of which 2189 were independent (completeness 99.5%).

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.4533 (2)	−0.10535 (18)	0.51945 (4)	0.0343 (3)
H1	0.510 (4)	−0.150 (3)	0.5486 (7)	0.046 (6)*
O2	0.0463 (2)	0.60420 (16)	0.57604 (4)	0.0248 (3)
H2	0.038 (5)	0.598 (4)	0.5427 (7)	0.060 (8)*
O3	0.63256 (19)	0.73206 (19)	0.60174 (4)	0.0297 (3)
H3	0.771 (4)	0.686 (4)	0.5986 (9)	0.053 (7)*
C1	0.2461 (3)	−0.0061 (2)	0.52644 (6)	0.0286 (4)
H1A	0.1479	−0.0769	0.5492	0.034*
H1B	0.1656	0.0039	0.4948	0.034*
C2	0.2851 (3)	0.1850 (2)	0.54652 (5)	0.0221 (3)
H2A	0.4186	0.2471	0.5359	0.026*
C3	0.1529 (2)	0.2779 (2)	0.57773 (5)	0.0207 (3)
C4	0.2178 (2)	0.4751 (2)	0.59199 (5)	0.0195 (3)
H4	0.3642	0.5077	0.5756	0.023*
C5	0.2444 (3)	0.5057 (2)	0.64742 (5)	0.0201 (3)
H5	0.0904	0.4887	0.6621	0.024*
C6	0.3197 (3)	0.7081 (2)	0.65976 (5)	0.0216 (3)
H6	0.2309	0.7949	0.6385	0.026*
C7	0.2623 (3)	0.7525 (2)	0.71240 (5)	0.0275 (4)
H7	0.3363	0.6821	0.7371	0.033*
C8	0.1175 (3)	0.8815 (3)	0.72652 (6)	0.0362 (4)
H8A	0.0401	0.9548	0.7029	0.043*
H8B	0.0903	0.9013	0.7604	0.043*
C9	−0.0663 (3)	0.2043 (3)	0.59807 (6)	0.0302 (4)
H9A	−0.0627	0.2113	0.6339	0.045*
H9B	−0.0863	0.0743	0.5879	0.045*
H9C	−0.1928	0.2794	0.5857	0.045*
C10	0.3971 (3)	0.3580 (2)	0.67028 (6)	0.0291 (4)
H10A	0.3264	0.2350	0.6667	0.044*
H10B	0.4183	0.3856	0.7051	0.044*
H10C	0.5447	0.3583	0.6538	0.044*
C11	0.5714 (3)	0.7499 (3)	0.65208 (5)	0.0275 (3)
H11A	0.6048	0.8782	0.6633	0.033*
H11B	0.6634	0.6626	0.6719	0.033*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0504 (7)	0.0307 (6)	0.0219 (5)	0.0196 (6)	0.0061 (5)	0.0026 (5)
O2	0.0329 (6)	0.0235 (6)	0.0181 (5)	0.0067 (5)	−0.0054 (4)	−0.0018 (4)
O3	0.0228 (5)	0.0433 (7)	0.0229 (5)	−0.0026 (5)	0.0006 (4)	0.0048 (5)
C1	0.0370 (9)	0.0214 (7)	0.0274 (8)	0.0039 (7)	0.0020 (7)	−0.0028 (6)
C2	0.0257 (7)	0.0207 (7)	0.0198 (6)	0.0006 (6)	0.0006 (6)	0.0013 (6)
C3	0.0227 (7)	0.0212 (7)	0.0183 (6)	0.0001 (6)	−0.0008 (5)	0.0011 (6)
C4	0.0208 (7)	0.0205 (7)	0.0173 (6)	0.0018 (6)	0.0013 (5)	−0.0002 (5)
C5	0.0207 (7)	0.0232 (7)	0.0164 (7)	0.0014 (6)	0.0012 (5)	0.0002 (5)
C6	0.0244 (7)	0.0238 (8)	0.0165 (6)	0.0001 (6)	−0.0016 (5)	−0.0018 (6)
C7	0.0331 (8)	0.0311 (8)	0.0182 (7)	−0.0041 (8)	−0.0017 (6)	−0.0040 (6)
C8	0.0409 (9)	0.0404 (10)	0.0272 (8)	0.0006 (9)	0.0044 (7)	−0.0115 (7)
C9	0.0279 (8)	0.0274 (8)	0.0352 (8)	−0.0061 (7)	0.0073 (7)	−0.0055 (7)
C10	0.0343 (9)	0.0284 (8)	0.0245 (7)	0.0073 (8)	−0.0053 (7)	0.0009 (6)
C11	0.0274 (7)	0.0343 (9)	0.0207 (7)	−0.0060 (7)	−0.0032 (6)	−0.0008 (6)

Geometric parameters (Å, º)

O1—C1	1.426 (2)	C5—H5	1.0000
O1—H1	0.922 (19)	C6—C7	1.5125 (19)
O2—C4	1.4380 (18)	C6—C11	1.528 (2)
O2—H2	0.914 (19)	C6—H6	1.0000
O3—C11	1.4288 (18)	C7—C8	1.317 (3)
O3—H3	0.89 (2)	C7—H7	0.9500
C1—C2	1.494 (2)	C8—H8A	0.9500
C1—H1A	0.9900	C8—H8B	0.9500
C1—H1B	0.9900	C9—H9A	0.9800
C2—C3	1.334 (2)	C9—H9B	0.9800
C2—H2A	0.9500	C9—H9C	0.9800
C3—C9	1.502 (2)	C10—H10A	0.9800
C3—C4	1.516 (2)	C10—H10B	0.9800
C4—C5	1.5398 (19)	C10—H10C	0.9800
C4—H4	1.0000	C11—H11A	0.9900
C5—C10	1.524 (2)	C11—H11B	0.9900
C5—C6	1.555 (2)		
C1—O1—H1	111.6 (16)	C11—C6—C5	115.48 (13)
C4—O2—H2	107.9 (17)	C7—C6—H6	107.8
C11—O3—H3	111.0 (16)	C11—C6—H6	107.8
O1—C1—C2	112.06 (14)	C5—C6—H6	107.8
O1—C1—H1A	109.2	C8—C7—C6	124.90 (16)
C2—C1—H1A	109.2	C8—C7—H7	117.6
O1—C1—H1B	109.2	C6—C7—H7	117.6
C2—C1—H1B	109.2	C7—C8—H8A	120.0
H1A—C1—H1B	107.9	C7—C8—H8B	120.0
C3—C2—C1	127.14 (15)	H8A—C8—H8B	120.0

C3—C2—H2A	116.4	C3—C9—H9A	109.5
C1—C2—H2A	116.4	C3—C9—H9B	109.5
C2—C3—C9	124.29 (15)	H9A—C9—H9B	109.5
C2—C3—C4	118.91 (14)	C3—C9—H9C	109.5
C9—C3—C4	116.71 (13)	H9A—C9—H9C	109.5
O2—C4—C3	110.20 (11)	H9B—C9—H9C	109.5
O2—C4—C5	106.17 (11)	C5—C10—H10A	109.5
C3—C4—C5	114.31 (12)	C5—C10—H10B	109.5
O2—C4—H4	108.7	H10A—C10—H10B	109.5
C3—C4—H4	108.7	C5—C10—H10C	109.5
C5—C4—H4	108.7	H10A—C10—H10C	109.5
C10—C5—C4	111.40 (12)	H10B—C10—H10C	109.5
C10—C5—C6	113.05 (12)	O3—C11—C6	111.09 (12)
C4—C5—C6	112.07 (11)	O3—C11—H11A	109.4
C10—C5—H5	106.6	C6—C11—H11A	109.4
C4—C5—H5	106.6	O3—C11—H11B	109.4
C6—C5—H5	106.6	C6—C11—H11B	109.4
C7—C6—C11	107.85 (12)	H11A—C11—H11B	108.0
C7—C6—C5	109.84 (13)		

O1—C1—C2—C3	−145.42 (16)	C3—C4—C5—C6	177.87 (12)
C1—C2—C3—C9	−0.9 (2)	C10—C5—C6—C7	−73.56 (16)
C1—C2—C3—C4	−177.31 (14)	C4—C5—C6—C7	159.53 (12)
C2—C3—C4—O2	116.83 (15)	C10—C5—C6—C11	48.64 (17)
C9—C3—C4—O2	−59.86 (16)	C4—C5—C6—C11	−78.26 (15)
C2—C3—C4—C5	−123.71 (15)	C11—C6—C7—C8	117.18 (19)
C9—C3—C4—C5	59.60 (17)	C5—C6—C7—C8	−116.18 (19)
O2—C4—C5—C10	171.78 (13)	C7—C6—C11—O3	−173.22 (14)
C3—C4—C5—C10	50.08 (17)	C5—C6—C11—O3	63.52 (17)
O2—C4—C5—C6	−60.43 (15)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···O1^{i}	0.91 (2)	1.77 (2)	2.6681 (16)	166 (3)
O3—H3···O2^{ii}	0.89 (2)	1.83 (2)	2.6983 (16)	166 (2)
O1—H1···O3^{iii}	0.92 (2)	1.83 (2)	2.7458 (17)	172 (2)

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