Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Racemic 5-ethyl-2,6-dimethyl-4-*p*-tolyl-3-cyclohexenecarboxylic acid: an *RS* dimer

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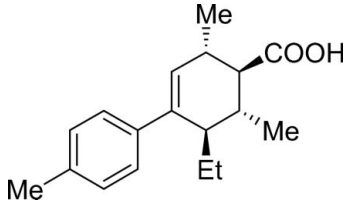
Received 16 August 2007; accepted 20 August 2007

Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.003 Å; R factor = 0.058; wR factor = 0.150; data-to-parameter ratio = 15.9.

The title compound, $C_{18}H_{24}O_2$, was synthesized to study the interaction of the two enantiomers in the solid state. The resultant racemate is made up of carboxylic acid *RS* molecules which are dimerized through their carboxyl groups by O—H···O hydrogen bonds, forming $R_2^2(8)$ rings. The dimers are interconnected *via* weak C—H···π(arene) interactions, resulting in thick two-dimensional layers.

Related literature

In the 4-*p*-methoxyphenyl analog (Xie *et al.*, 2002*a*), the racemate also consists of carboxylic acid *RS* dimers. For additional related literature, see: Bernstein *et al.* (1995); Hussain *et al.* (2006); Xie *et al.* (2002*b*, 2007).



Experimental

Crystal data

$C_{18}H_{24}O_2$
M_r = 272.37
Monoclinic, $P2_1/c$
a = 16.2786 (14) Å
b = 11.4720 (10) Å
c = 8.1035 (7) Å
β = 94.318 (5)°
V = 1509.0 (2) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.08 mm^{-1}
T = 100 (2) K
0.41 × 0.17 × 0.15 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.600, T_{max} = 0.989
19084 measured reflections
2952 independent reflections
2211 reflections with $I > 2\sigma(I)$
R_{int} = 0.054

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.058
$wR(F^2)$ = 0.150
S = 1.03
2952 reflections
186 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.55 e Å^{-3}
$\Delta\rho_{min}$ = −0.46 e Å^{-3}

Table 1
Selected torsion angles (°).

C3—C4—C12—C13	133.7 (2)	C2—C1—C6—C11	−176.17 (17)
C3—C4—C12—C17	−45.6 (3)	C7—C1—C2—C3	−170.71 (16)
C6—C1—C2—C8	−170.80 (17)	C7—C1—C6—C5	−177.26 (17)

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

*Cg*1 is the centroid of the benzene ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···O1^{i}	0.84	1.81	2.654 (2)	178
C3—H3···*Cg*1^{ii}	0.95	3.23	4.069 (2)	148

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

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT* and *SADABS* (Bruker, 2005); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *LS* in *TEXSAN* (Molecular Structure Corporation, 1997) and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PLATON*.

SX and CK are grateful to the departmental fund and Grant-in-Aid for Faculty Research from Indiana University Kokomo. We thank Professor Nigam P. Rath of the University of Missouri–St Louis for kindly collecting the low-temperature data set using a diffractometer whose purchase was made possible by funding from the National Science Foundation (CHE-0420497).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: OM2154).

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Xie, S., Kenny, C. & Robinson, P. D. (2007). *Acta Cryst.* E**63**, o1660–o1662.

 doi:10.1107/S1600536807041098

supplementary materials

Acta Cryst. (2007). E**63**, o3897 [**doi:10.1107/S1600536807041098**]

Racemic 5-ethyl-2,6-dimethyl-4-*p*-tolyl-3-cyclohexenecarboxylic acid: an *RS* dimer

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Comment

The title carboxylic acid, (I), was prepared to study the interaction of the two enantiomers in the solid state. The resultant racemate is made up of carboxylic acid *RS* dimers, a phenomenon similar to an analog compound we reported previously (Xie *et al.*, 2002*a*). The structure and atom numbering of (I) are shown in Fig. 1, which illustrates the twisted chair conformation of the cyclohexene ring. The torsion angles involving atoms C8, C2, C1, C6, and C11 are all near 180°. The C3═C4 double bond is not fully conjugated with the benzene ring due to the steric hindrance of the C5-ethyl group, a condition which causes the benzene ring plane to rotate by 44.8 (2)° with respect to the C3—C4—C5 plane. Geometric parameters of interest are given in Table 1.

Fig. 2 shows the hydrogen-bonding scheme, molecular packing and C—H···π(arene) interactions. Atom O2 acts as a donor in an intermolecular hydrogen bond to atom O1. Inversion of this interaction across (1/2, 1/2, 1) produces an $R_2^2(8)$ ring (Bernstein *et al.*, 1995), thus creating a hydrogen-bonded dimer. The dimers are interconnected *via* weak C—H···π(arene) interactions in both the b and c directions, forming thick two-dimensional layers parallel to (100). Geometry of these two interactions is given in Table 2.

Experimental

The carboxylic acid (I) was synthesized following the same method reported by Xie *et al.* (2002*a*). Purified (I) was recrystallized from hexane-ethyl acetate as colorless crystals (m.p. 490.5–492.0 K).

Refinement

The rotational orientations of the methyl H atoms were refined by the circular Fourier method available in *SHELXL97* (Sheldrick, 1997); the hydroxyl H atom position was determined in a similar manner. All H atoms were treated as riding with C—H distances ranging from 0.84 to 1.0 Å and U_{iso}(H) values equal to 1.5 (hydroxyl and methyl H atoms) or 1.2 times (all other H atoms) U_{eq} of the parent atom.

Figures

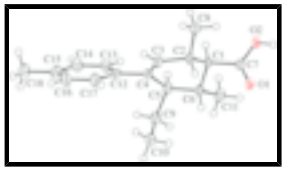

Fig. 1. The molecular structure and atom numbering scheme for (I), with displacement ellipsoids drawn at the 50% probablilty level.

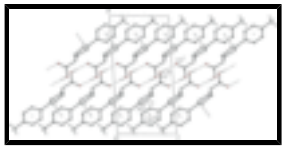

Fig. 2. Molecular packing, hydrogen bonding and C—H···π(arene) interactions in (I) as viewed down [010]. Dashed lines between red oxygen atoms represent hydrogen bonds; other dashed lines represent C—H···π(arene) interactions. [Symmetry codes: (i) $1-x$, $1-y$, $2-z$; (ii) x, $3/2-y$, $1/2+z$.]

(*RS*)-5-ethyl-2,6-dimethyl-4-*p*-tolyl-3-cyclohexenecarboxylic acid

Crystal data

$C_{18}H_{24}O_2$	F_{000} = 592
M_r = 272.37	D_x = 1.199 Mg m^{-3}
Monoclinic, $P2_1/c$	Melting point: 490.5-492 K
Hall symbol: -P 2ybc	Mo $K\alpha$ radiation λ = 0.71073 Å
a = 16.2786 (14) Å	Cell parameters from 2703 reflections
b = 11.4720 (10) Å	θ = 2.5–28.2º
c = 8.1035 (7) Å	μ = 0.08 mm^{-1}
β = 94.318 (5)º	T = 100 (2) K
V = 1509.0 (2) Å^3	Irregular fragment, colorless
Z = 4	0.41 × 0.17 × 0.15 mm

Data collection

Bruker Kappa APEX II CCD diffractometer	2952 independent reflections
Radiation source: X-ray tube	2211 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.054
T = 100(2) K	θ_{max} = 26.0º
φ and ω scans	θ_{min} = 2.2º
Absorption correction: multi-scan (SADABS; Bruker, 2005)	h = −20→20
T_{min} = 0.600, T_{max} = 0.989	k = −14→13
19084 measured reflections	l = −9→6

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.058	H-atom parameters constrained
$wR(F^2)$ = 0.150	$w = 1/[\sigma^2(F_o^2) + (0.0587P)^2 + 1.3904P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.03	$(\Delta/\sigma)_{max} < 0.001$
2952 reflections	$\Delta\rho_{max}$ = 0.55 e Å^{-3}
186 parameters	$\Delta\rho_{min}$ = −0.46 e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.40575 (9)	0.49053 (13)	0.91934 (17)	0.0244 (4)
O2	0.51667 (8)	0.52472 (14)	0.78147 (17)	0.0260 (4)
H2	0.5406	0.5183	0.8765	0.039*
C1	0.38654 (12)	0.52324 (17)	0.6275 (2)	0.0194 (4)
H1	0.4249	0.5350	0.5382	0.023*
C2	0.33118 (12)	0.63081 (17)	0.6339 (2)	0.0199 (4)
H2A	0.2996	0.6253	0.7347	0.024*
C3	0.27101 (13)	0.63237 (18)	0.4839 (3)	0.0242 (5)
H3	0.2436	0.7038	0.4571	0.029*
C4	0.25300 (12)	0.54117 (18)	0.3853 (2)	0.0218 (5)
C5	0.28849 (14)	0.42135 (19)	0.4199 (3)	0.0296 (5)
H5	0.3288	0.4069	0.3350	0.035*
C6	0.33676 (13)	0.41179 (17)	0.5894 (3)	0.0233 (5)
H6	0.2964	0.4024	0.6757	0.028*
C7	0.43691 (12)	0.51111 (16)	0.7900 (2)	0.0188 (4)
C8	0.38172 (13)	0.74326 (18)	0.6440 (3)	0.0265 (5)
H8A	0.4134	0.7496	0.5462	0.040*
H8B	0.4195	0.7420	0.7440	0.040*
H8C	0.3446	0.8103	0.6481	0.040*
C9	0.22227 (16)	0.3268 (2)	0.3955 (3)	0.0395 (6)
H9A	0.2021	0.3252	0.2771	0.047*
H9B	0.2480	0.2503	0.4225	0.047*
C10	0.14949 (17)	0.3420 (3)	0.4977 (4)	0.0529 (8)
H10A	0.1685	0.3434	0.6153	0.079*
H10B	0.1111	0.2769	0.4764	0.079*
H10C	0.1215	0.4155	0.4677	0.079*
C11	0.39292 (15)	0.30511 (19)	0.5954 (3)	0.0309 (5)
H11A	0.3599	0.2350	0.5705	0.046*
H11B	0.4211	0.2981	0.7061	0.046*
H11C	0.4338	0.3137	0.5134	0.046*
C12	0.19862 (13)	0.55613 (18)	0.2308 (3)	0.0264 (5)
C13	0.22078 (15)	0.5074 (2)	0.0822 (3)	0.0363 (6)
H13	0.2707	0.4646	0.0815	0.044*
C14	0.17192 (17)	0.5200 (3)	−0.0628 (3)	0.0451 (7)
H14	0.1888	0.4860	−0.1616	0.054*
C15	0.09955 (19)	0.5806 (3)	−0.0673 (3)	0.0482 (8)
C16	0.07687 (17)	0.6306 (3)	0.0789 (4)	0.0531 (8)
H16	0.0271	0.6739	0.0781	0.064*
C17	0.12617 (15)	0.6183 (2)	0.2270 (3)	0.0375 (6)
H17	0.1095	0.6531	0.3255	0.045*
C18	0.0446 (2)	0.5926 (3)	−0.2266 (4)	0.0746 (12)
H18A	0.0757	0.6293	−0.3116	0.112*
H18B	−0.0032	0.6409	−0.2064	0.112*
H18C	0.0259	0.5152	−0.2646	0.112*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0239 (8)	0.0327 (8)	0.0157 (7)	−0.0019 (6)	−0.0042 (6)	0.0032 (6)
O2	0.0230 (8)	0.0367 (9)	0.0174 (7)	−0.0017 (6)	−0.0054 (6)	0.0045 (7)
C1	0.0233 (10)	0.0190 (10)	0.0151 (10)	−0.0021 (8)	−0.0044 (8)	0.0008 (8)
C2	0.0244 (10)	0.0193 (10)	0.0154 (10)	0.0017 (8)	−0.0038 (8)	−0.0007 (8)
C3	0.0256 (11)	0.0241 (11)	0.0221 (11)	0.0034 (9)	−0.0042 (9)	0.0029 (9)
C4	0.0216 (10)	0.0230 (10)	0.0199 (10)	−0.0038 (8)	−0.0044 (8)	0.0042 (8)
C5	0.0380 (13)	0.0240 (11)	0.0245 (12)	−0.0038 (10)	−0.0119 (10)	0.0007 (9)
C6	0.0280 (11)	0.0192 (10)	0.0214 (11)	−0.0022 (8)	−0.0077 (8)	0.0014 (8)
C7	0.0230 (10)	0.0143 (9)	0.0183 (10)	−0.0002 (8)	−0.0038 (8)	−0.0007 (8)
C8	0.0319 (12)	0.0206 (11)	0.0263 (12)	−0.0001 (9)	−0.0033 (9)	−0.0013 (9)
C9	0.0514 (15)	0.0252 (12)	0.0379 (14)	−0.0123 (11)	−0.0234 (12)	0.0060 (10)
C10	0.0462 (16)	0.0547 (17)	0.0531 (18)	−0.0244 (14)	−0.0270 (14)	0.0263 (14)
C11	0.0401 (13)	0.0215 (11)	0.0294 (12)	0.0016 (10)	−0.0077 (10)	−0.0003 (9)
C12	0.0293 (12)	0.0235 (11)	0.0246 (11)	−0.0097 (9)	−0.0094 (9)	0.0076 (9)
C13	0.0360 (13)	0.0472 (15)	0.0244 (12)	−0.0151 (11)	−0.0060 (10)	0.0032 (11)
C14	0.0464 (16)	0.0629 (18)	0.0241 (13)	−0.0255 (14)	−0.0100 (11)	0.0075 (12)
C15	0.0627 (19)	0.0496 (16)	0.0288 (14)	−0.0275 (14)	−0.0196 (13)	0.0142 (12)
C16	0.0407 (15)	0.0444 (16)	0.069 (2)	−0.0003 (12)	−0.0292 (14)	0.0159 (15)
C17	0.0370 (13)	0.0334 (13)	0.0392 (14)	−0.0016 (10)	−0.0168 (11)	0.0046 (11)
C18	0.084 (2)	0.081 (2)	0.0512 (19)	−0.037 (2)	−0.0441 (18)	0.0289 (18)

Geometric parameters (Å, °)

O1—C7	1.221 (2)	C9—H9A	0.9900
O2—C7	1.315 (2)	C9—H9B	0.9900
O2—H2	0.8400	C10—H10A	0.9800
C1—C7	1.504 (3)	C10—H10B	0.9800
C1—C2	1.531 (3)	C10—H10C	0.9800
C1—C6	1.533 (3)	C11—H11A	0.9800
C1—H1	1.0000	C11—H11B	0.9800
C2—C3	1.503 (3)	C11—H11C	0.9800
C2—C8	1.529 (3)	C12—C17	1.377 (3)
C2—H2A	1.0000	C12—C13	1.399 (3)
C3—C4	1.336 (3)	C13—C14	1.376 (3)
C3—H3	0.9500	C13—H13	0.9500
C4—C12	1.488 (3)	C14—C15	1.366 (4)
C4—C5	1.509 (3)	C14—H14	0.9500
C5—C9	1.531 (3)	C15—C16	1.391 (4)
C5—C6	1.534 (3)	C15—C18	1.520 (3)
C5—H5	1.0000	C16—C17	1.400 (3)
C6—C11	1.526 (3)	C16—H16	0.9500
C6—H6	1.0000	C17—H17	0.9500
C8—H8A	0.9800	C18—H18A	0.9800
C8—H8B	0.9800	C18—H18B	0.9800
C8—H8C	0.9800	C18—H18C	0.9800

C9—C10	1.506 (4)		
C7—O2—H2	109.5	C10—C9—H9A	108.5
C7—C1—C2	109.17 (16)	C5—C9—H9A	108.5
C7—C1—C6	110.13 (16)	C10—C9—H9B	108.5
C2—C1—C6	112.06 (16)	C5—C9—H9B	108.5
C7—C1—H1	108.5	H9A—C9—H9B	107.5
C2—C1—H1	108.5	C9—C10—H10A	109.5
C6—C1—H1	108.5	C9—C10—H10B	109.5
C3—C2—C8	110.39 (17)	H10A—C10—H10B	109.5
C3—C2—C1	109.38 (16)	C9—C10—H10C	109.5
C8—C2—C1	111.48 (16)	H10A—C10—H10C	109.5
C3—C2—H2A	108.5	H10B—C10—H10C	109.5
C8—C2—H2A	108.5	C6—C11—H11A	109.5
C1—C2—H2A	108.5	C6—C11—H11B	109.5
C4—C3—C2	125.09 (19)	H11A—C11—H11B	109.5
C4—C3—H3	117.5	C6—C11—H11C	109.5
C2—C3—H3	117.5	H11A—C11—H11C	109.5
C3—C4—C12	120.19 (19)	H11B—C11—H11C	109.5
C3—C4—C5	122.59 (18)	C17—C12—C13	117.6 (2)
C12—C4—C5	117.18 (18)	C17—C12—C4	122.2 (2)
C4—C5—C9	111.40 (19)	C13—C12—C4	120.2 (2)
C4—C5—C6	113.25 (17)	C14—C13—C12	121.5 (3)
C9—C5—C6	111.93 (18)	C14—C13—H13	119.2
C4—C5—H5	106.6	C12—C13—H13	119.2
C9—C5—H5	106.6	C15—C14—C13	121.2 (3)
C6—C5—H5	106.6	C15—C14—H14	119.4
C11—C6—C1	110.87 (17)	C13—C14—H14	119.4
C11—C6—C5	110.55 (18)	C14—C15—C16	118.1 (2)
C1—C6—C5	110.37 (16)	C14—C15—C18	121.3 (3)
C11—C6—H6	108.3	C16—C15—C18	120.6 (3)
C1—C6—H6	108.3	C15—C16—C17	121.1 (3)
C5—C6—H6	108.3	C15—C16—H16	119.5
O1—C7—O2	122.94 (18)	C17—C16—H16	119.5
O1—C7—C1	122.33 (18)	C12—C17—C16	120.4 (3)
O2—C7—C1	114.73 (17)	C12—C17—H17	119.8
C2—C8—H8A	109.5	C16—C17—H17	119.8
C2—C8—H8B	109.5	C15—C18—H18A	109.5
H8A—C8—H8B	109.5	C15—C18—H18B	109.5
C2—C8—H8C	109.5	H18A—C18—H18B	109.5
H8A—C8—H8C	109.5	C15—C18—H18C	109.5
H8B—C8—H8C	109.5	H18A—C18—H18C	109.5
C10—C9—C5	115.0 (2)	H18B—C18—H18C	109.5
C3—C4—C12—C13	133.7 (2)	C4—C5—C6—C1	−38.9 (3)
C3—C4—C12—C17	−45.6 (3)	C9—C5—C6—C1	−165.82 (19)
C6—C1—C2—C8	−170.80 (17)	C2—C1—C7—O1	65.4 (2)
C2—C1—C6—C11	−176.17 (17)	C6—C1—C7—O1	−58.0 (2)
C7—C1—C2—C3	−170.71 (16)	C2—C1—C7—O2	−114.42 (19)
C7—C1—C6—C5	−177.26 (17)	C6—C1—C7—O2	122.14 (19)

C6—C1—C2—C3	−48.4 (2)	C4—C5—C9—C10	−56.7 (3)
C7—C1—C2—C8	66.9 (2)	C6—C5—C9—C10	71.2 (3)
C8—C2—C3—C4	139.8 (2)	C5—C4—C12—C17	136.7 (2)
C1—C2—C3—C4	16.8 (3)	C5—C4—C12—C13	−44.0 (3)
C2—C3—C4—C12	−173.91 (19)	C17—C12—C13—C14	−0.5 (3)
C2—C3—C4—C5	3.6 (3)	C4—C12—C13—C14	−179.8 (2)
C3—C4—C5—C9	135.2 (2)	C12—C13—C14—C15	−0.2 (4)
C12—C4—C5—C9	−47.2 (3)	C13—C14—C15—C16	0.8 (4)
C3—C4—C5—C6	7.9 (3)	C13—C14—C15—C18	−178.7 (2)
C12—C4—C5—C6	−174.46 (18)	C14—C15—C16—C17	−0.8 (4)
C7—C1—C6—C11	−54.4 (2)	C18—C15—C16—C17	178.8 (3)
C2—C1—C6—C5	61.0 (2)	C13—C12—C17—C16	0.5 (3)
C4—C5—C6—C11	−161.90 (19)	C4—C12—C17—C16	179.8 (2)
C9—C5—C6—C11	71.2 (3)	C15—C16—C17—C12	0.1 (4)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···O1^{i}	0.84	1.81	2.654 (2)	178
C3—H3···Cg1^{ii}	0.95	3.23	4.069 (2)	148

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

Fig. 1

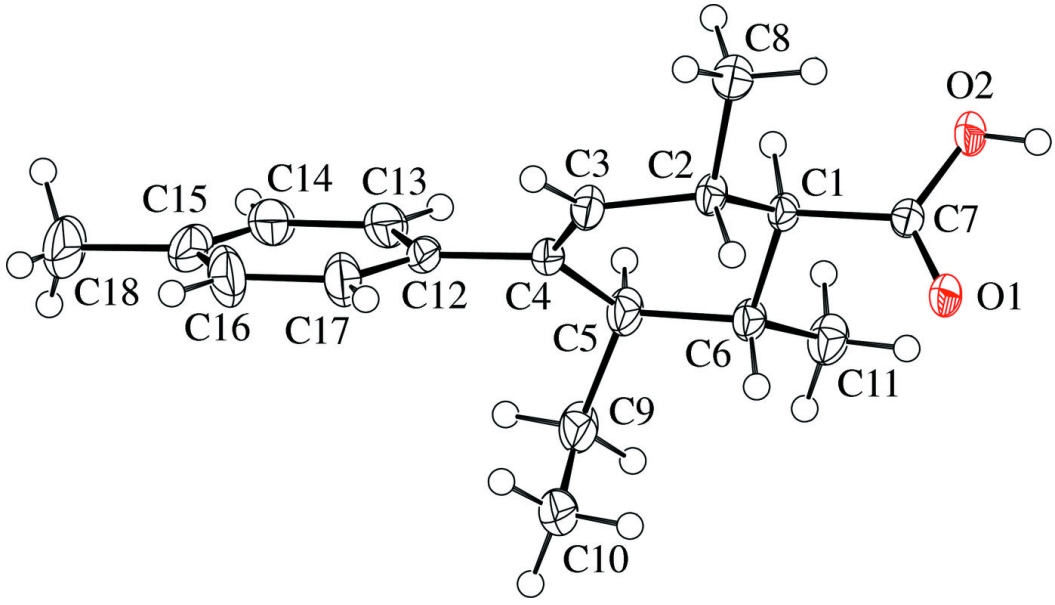

Fig. 2