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Crystal structure of 7,7-dimethyl-6-methylidenetricyclo[6.2.1.0^{1,5}]undecane-2-carboxylic acid

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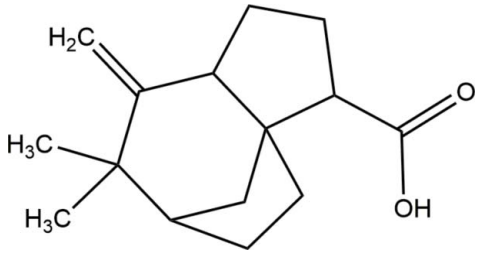
In the title compound, $C_{15}H_{22}O_2$, both five-membered rings display an envelope conformation whereas the six-membered ring displays a chair conformation. In the crystal, pairs of O—H···O hydrogen bonds between carboxylic groups link molecules, related by a twofold rotation axis, into supramolecular dimers.

Keywords: crystal structure; *inula graveolens*; hydrogen bonding.

CCDC reference: 1041493

1. Related literature

For background to the title compound, which was extracted from the air-dried aerial parts of *inula graveolens* see: Chiappini & Fardella (1980); Rustaiyan *et al.* (1987). For related structures, see: Turner *et al.* (1980); Harlow & Simonsen (1977); Dastlik *et al.* (1992).



2. Experimental

2.1. Crystal data

$C_{15}H_{22}O_2$ M_r = 234.33
Orthorhombic, $C222_1$
a = 7.6400 (3) Å
b = 16.1700 (5) Å
c = 21.3406 (9) Å
V = 2636.39 (17) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.08 mm^{-1}
T = 150 K
0.30 × 0.18 × 0.04 mm

2.2. Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*DENZO*/*SCALEPACK*; Otwinowski & Minor, 1997)
T_{min} = 0.978, T_{max} = 0.997
8814 measured reflections
2978 independent reflections
2327 reflections with $I > 2\sigma(I)$
R_{int} = 0.052

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.103
S = 1.07
2978 reflections
157 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.15 e Å^{-3}
$\Delta\rho_{min}$ = −0.15 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O2^{i}	0.84	1.81	2.646 (3)	174

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

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor 1997); data reduction: *HKL DENZO* (Otwinowski & Minor 1997) and *SCALEPACK*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1992); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP99* for Windows (Farrugia, 2012); software used to prepare material for publication: *WinGX* publication routines (Farrugia, 2012) and *CHEMDRAW Ultra* (Cambridge Soft, 2001).

Acknowledgements

The authors extend their appreciation to Constantine 1 University and Cardiff University for supporting this research.

Supporting information for this paper is available from the IUCr electronic archives (Reference: XU5833).

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supporting information

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Crystal structure of 7,7-dimethyl-6-methylidenetricyclo[6.2.1.$0^{1,5}$]undecane-2-carboxylic acid

Noureddine Beghidja, Samir Benayache, Fadila Benayache, David W. Knight and Benson M. Kariuki

S1. Comment

Inula graveolens have consistently been the subject of research interest (Chiappini & Fardella, 1980; Rustaiyan *et al.*, 1987). Our interest is the extracts from aerial parts of Algerian species such as stems, flowers and leaves. The asymmetric unit of the crystal structure consists of a single molecule (Fig. 1). Both five-membered rings display an envelope conformation (with C4 and C8 as the flap atoms) whereas the six-membered ring displays a chair conformation.

The structure consists of pairs of molecules linked by the classic dimeric carbocylic acid hydrogen bonding interaction (Fig 2). Structures of some related compounds have been reported (Turner *et al.*, 1980; Harlow & Simonsen, 1977; Dastlik *et al.*, 1992).

S2. Experimental

The air-dried aerial parts of *inula graveolens* (500 g) were extracted with acetone/Et_2O (1:1) at room temperature. The solution was filtered off and concentrated under reduced pressure to give a pale yellow gum (9 g). The gum was subjected to successive column chromatography (silica gel) and TLC (silica gel, PF254). Eleven fractions were obtained. Fraction 9 gave a material which crystallized as colourless crystals with a melting point of 450 K.

S3. Refinement

H atoms were positioned geometrically and refined using a riding model with U_{iso}(H) constrained to be 1.2 times U_{eq} for the atom it is bonded to (except for methyl groups where it was 1.5 times with free rotation about the C—C bond).

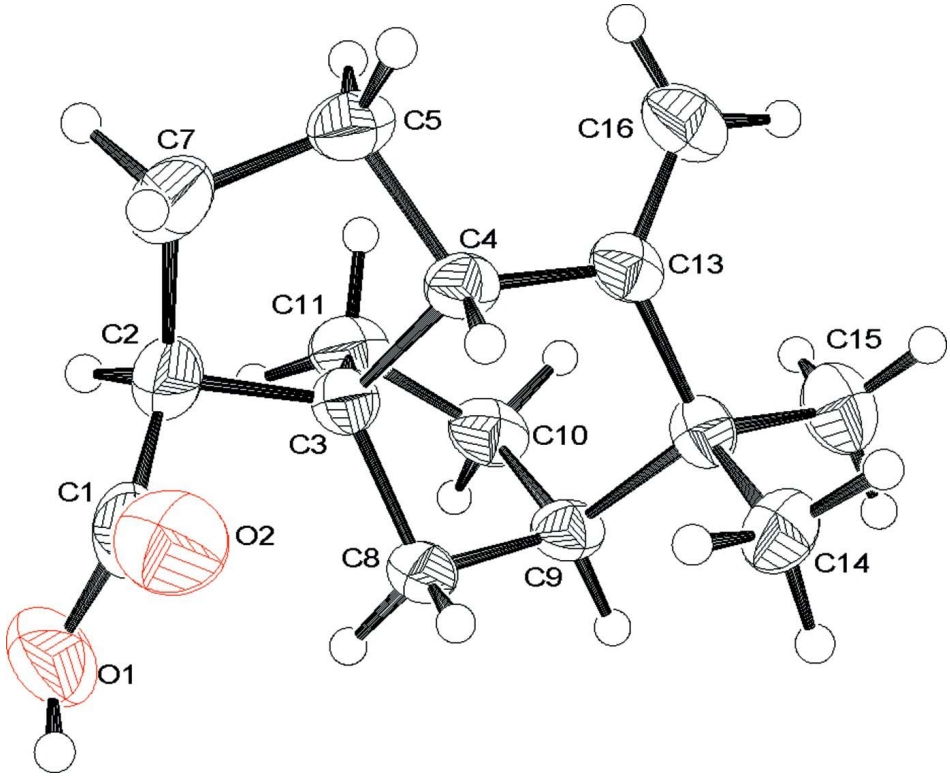

Figure 1

A molecule showing atom labels and 50% probability displacement ellipsoids for non-H atoms.

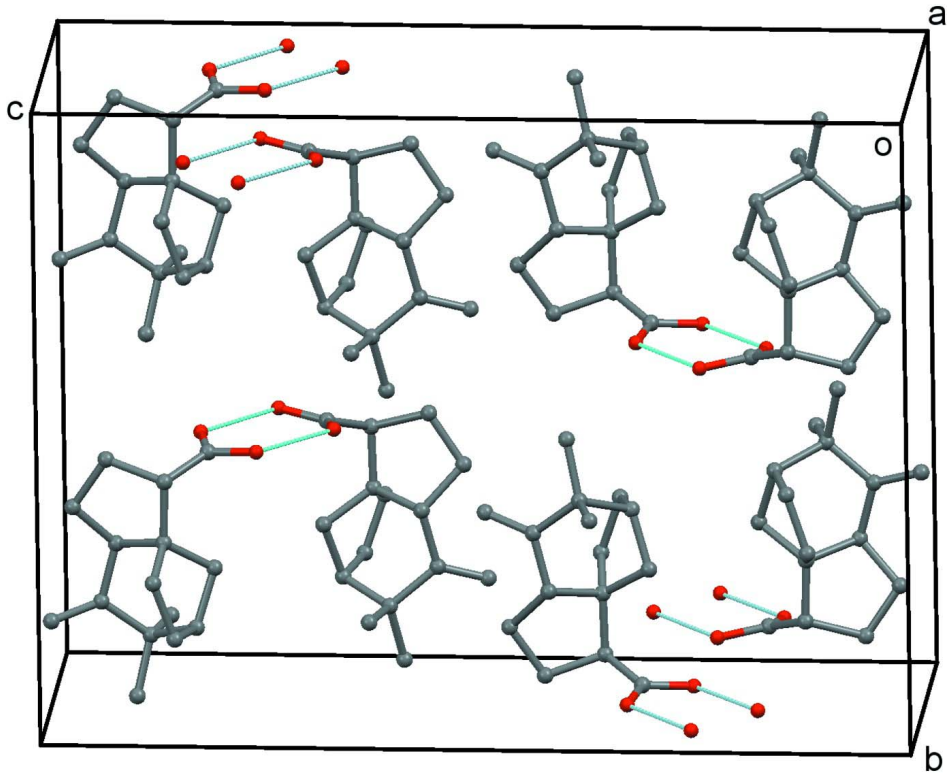

Figure 2

Crystal packing in the structure with H atoms omitted and hydrogen bonds shown as dotted lines.

7,7-Dimethyl-6-methylidenetricyclo[6.2.1.0^{1,5}]undecane-2-carboxylic acid

Crystal data

$C_{15}H_{22}O_2$
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Orthorhombic, $C222_1$
a = 7.6400 (3) Å
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c = 21.3406 (9) Å
V = 2636.39 (17) Å^3
Z = 8
F(000) = 1024
D_x = 1.181 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2327 reflections
θ = 2.7–27.4°
μ = 0.08 mm^{-1}
T = 150 K
Plate, colourless
0.30 × 0.18 × 0.04 mm

Data collection

Nonius KappaCCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
CCD slices, ω and phi scans
Absorption correction: multi-scan (*DENZO*/*SCALEPACK*; Otwinowski & Minor, 1997)
T_{min} = 0.978, T_{max} = 0.997
8814 measured reflections
2978 independent reflections
2327 reflections with $I > 2\sigma(I)$
R_{int} = 0.052
θ_{max} = 27.4°, θ_{min} = 2.7°
h = −9→8
k = −20→20
l = −27→27

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.103$
$S = 1.07$
2978 reflections
157 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0392P)^2 + 0.6557P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.15$ e Å^{-3}
$\Delta\rho_{min} = -0.15$ e Å^{-3}

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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 $F^2 > 2\sigma(F^2)$ 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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.3233 (3)	0.41972 (11)	0.18712 (10)	0.0496 (5)
C2	0.1890 (3)	0.39139 (12)	0.14061 (9)	0.0469 (5)
H2	0.0705	0.4118	0.1532	0.056*
C3	0.1900 (2)	0.29473 (10)	0.13886 (8)	0.0351 (4)
C4	0.3048 (2)	0.27610 (11)	0.08041 (7)	0.0331 (4)
H4	0.4293	0.2879	0.0918	0.040*
C5	0.2468 (3)	0.34157 (11)	0.03307 (8)	0.0419 (4)
H5A	0.3350	0.3485	−0.0005	0.050*
H5B	0.1330	0.3268	0.0139	0.050*
C7	0.2312 (3)	0.41978 (13)	0.07268 (9)	0.0586 (6)
H7A	0.1365	0.4556	0.0564	0.070*
H7B	0.3423	0.4513	0.0718	0.070*
C8	0.2606 (3)	0.24567 (10)	0.19461 (7)	0.0355 (4)
H8A	0.2004	0.2609	0.2340	0.043*
H8B	0.3884	0.2534	0.1997	0.043*
C9	0.2161 (2)	0.15726 (11)	0.17434 (7)	0.0348 (4)
H9	0.2277	0.1182	0.2104	0.042*
C10	0.0230 (2)	0.16680 (12)	0.15525 (8)	0.0415 (4)
H10A	−0.0550	0.1569	0.1915	0.050*
H10B	−0.0075	0.1273	0.1215	0.050*
C11	0.0058 (3)	0.25713 (12)	0.13183 (9)	0.0422 (5)
H11A	−0.0323	0.2584	0.0875	0.051*
H11B	−0.0801	0.2880	0.1575	0.051*
C12	0.3311 (2)	0.12798 (11)	0.11790 (8)	0.0345 (4)
C13	0.2924 (2)	0.18576 (11)	0.06300 (7)	0.0330 (4)

C14	0.5274 (2)	0.13066 (12)	0.13538 (9)	0.0428 (4)
H14A	0.5965	0.1063	0.1014	0.064*
H14B	0.5465	0.0992	0.1740	0.064*
H14C	0.5634	0.1882	0.1418	0.064*
C15	0.2877 (3)	0.03737 (11)	0.10297 (9)	0.0504 (5)
H15A	0.1635	0.0326	0.0922	0.076*
H15B	0.3129	0.0030	0.1397	0.076*
H15C	0.3591	0.0187	0.0675	0.076*
C16	0.2421 (2)	0.16103 (13)	0.00671 (8)	0.0462 (5)
H16A	0.2123	0.2007	−0.0244	0.055*
H16B	0.2358	0.1037	−0.0026	0.055*
O1	0.2608 (2)	0.42962 (10)	0.24438 (7)	0.0639 (4)
H1	0.3442	0.4330	0.2699	0.096*
O2	0.4779 (2)	0.42873 (9)	0.17426 (7)	0.0606 (4)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0665 (16)	0.0313 (9)	0.0511 (12)	0.0092 (10)	0.0070 (11)	−0.0002 (9)
C2	0.0534 (13)	0.0419 (10)	0.0455 (11)	0.0164 (9)	0.0036 (10)	0.0009 (9)
C3	0.0345 (10)	0.0406 (10)	0.0302 (8)	0.0087 (8)	0.0013 (8)	−0.0016 (7)
C4	0.0282 (9)	0.0425 (9)	0.0286 (8)	0.0027 (8)	0.0001 (7)	0.0016 (7)
C5	0.0381 (11)	0.0547 (11)	0.0329 (8)	0.0078 (9)	0.0026 (8)	0.0100 (8)
C7	0.0752 (17)	0.0499 (12)	0.0507 (11)	0.0192 (11)	0.0035 (11)	0.0137 (9)
C8	0.0405 (10)	0.0413 (10)	0.0248 (8)	0.0060 (8)	0.0006 (7)	−0.0018 (7)
C9	0.0345 (10)	0.0433 (10)	0.0265 (8)	0.0004 (8)	0.0025 (7)	0.0029 (7)
C10	0.0338 (10)	0.0583 (12)	0.0326 (9)	−0.0032 (9)	0.0092 (8)	0.0004 (8)
C11	0.0310 (10)	0.0622 (12)	0.0335 (9)	0.0088 (9)	0.0067 (8)	0.0038 (8)
C12	0.0348 (10)	0.0347 (9)	0.0341 (9)	0.0009 (8)	0.0049 (8)	−0.0032 (7)
C13	0.0237 (9)	0.0458 (10)	0.0296 (8)	−0.0001 (7)	0.0063 (7)	−0.0030 (7)
C14	0.0360 (11)	0.0432 (10)	0.0492 (11)	0.0064 (8)	−0.0006 (8)	0.0046 (9)
C15	0.0534 (14)	0.0422 (11)	0.0558 (12)	−0.0047 (9)	0.0107 (11)	−0.0075 (9)
C16	0.0405 (12)	0.0621 (12)	0.0361 (9)	−0.0022 (10)	0.0062 (9)	−0.0090 (9)
O1	0.0667 (11)	0.0715 (9)	0.0536 (8)	0.0157 (8)	0.0057 (8)	−0.0223 (8)
O2	0.0667 (11)	0.0592 (9)	0.0560 (9)	−0.0160 (8)	0.0063 (8)	0.0078 (7)

Geometric parameters (Å, º)

C1—O2	1.221 (3)	C9—C12	1.564 (2)
C1—O1	1.322 (2)	C9—H9	1.0000
C1—C2	1.499 (3)	C10—C11	1.549 (3)
C2—C7	1.555 (3)	C10—H10A	0.9900
C2—C3	1.564 (2)	C10—H10B	0.9900
C2—H2	1.0000	C11—H11A	0.9900
C3—C8	1.529 (2)	C11—H11B	0.9900
C3—C11	1.540 (3)	C12—C13	1.527 (2)
C3—C4	1.554 (2)	C12—C15	1.536 (2)
C4—C13	1.510 (2)	C12—C14	1.546 (3)

C4—C5	1.529 (2)	C13—C16	1.323 (2)
C4—H4	1.0000	C14—H14A	0.9800
C5—C7	1.526 (3)	C14—H14B	0.9800
C5—H5A	0.9900	C14—H14C	0.9800
C5—H5B	0.9900	C15—H15A	0.9800
C7—H7A	0.9900	C15—H15B	0.9800
C7—H7B	0.9900	C15—H15C	0.9800
C8—C9	1.532 (2)	C16—H16A	0.9500
C8—H8A	0.9900	C16—H16B	0.9500
C8—H8B	0.9900	O1—H1	0.8400
C9—C10	1.538 (3)		

O2—C1—O1	122.9 (2)	C10—C9—C12	111.40 (14)
O2—C1—C2	123.34 (19)	C8—C9—H9	110.6
O1—C1—C2	113.7 (2)	C10—C9—H9	110.6
C1—C2—C7	112.66 (19)	C12—C9—H9	110.6
C1—C2—C3	108.54 (15)	C9—C10—C11	105.13 (15)
C7—C2—C3	105.77 (15)	C9—C10—H10A	110.7
C1—C2—H2	109.9	C11—C10—H10A	110.7
C7—C2—H2	109.9	C9—C10—H10B	110.7
C3—C2—H2	109.9	C11—C10—H10B	110.7
C8—C3—C11	101.16 (14)	H10A—C10—H10B	108.8
C8—C3—C4	108.95 (13)	C3—C11—C10	105.28 (14)
C11—C3—C4	111.16 (14)	C3—C11—H11A	110.7
C8—C3—C2	120.12 (14)	C10—C11—H11A	110.7
C11—C3—C2	113.12 (15)	C3—C11—H11B	110.7
C4—C3—C2	102.45 (14)	C10—C11—H11B	110.7
C13—C4—C5	119.27 (15)	H11A—C11—H11B	108.8
C13—C4—C3	110.45 (14)	C13—C12—C15	112.50 (15)
C5—C4—C3	103.45 (13)	C13—C12—C14	110.84 (14)
C13—C4—H4	107.7	C15—C12—C14	106.63 (15)
C5—C4—H4	107.7	C13—C12—C9	107.26 (13)
C3—C4—H4	107.7	C15—C12—C9	109.12 (15)
C7—C5—C4	103.33 (14)	C14—C12—C9	110.51 (14)
C7—C5—H5A	111.1	C16—C13—C4	122.27 (17)
C4—C5—H5A	111.1	C16—C13—C12	124.60 (17)
C7—C5—H5B	111.1	C4—C13—C12	113.00 (14)
C4—C5—H5B	111.1	C12—C14—H14A	109.5
H5A—C5—H5B	109.1	C12—C14—H14B	109.5
C5—C7—C2	106.75 (16)	H14A—C14—H14B	109.5
C5—C7—H7A	110.4	C12—C14—H14C	109.5
C2—C7—H7A	110.4	H14A—C14—H14C	109.5
C5—C7—H7B	110.4	H14B—C14—H14C	109.5
C2—C7—H7B	110.4	C12—C15—H15A	109.5
H7A—C7—H7B	108.6	C12—C15—H15B	109.5
C3—C8—C9	100.72 (13)	H15A—C15—H15B	109.5
C3—C8—H8A	111.6	C12—C15—H15C	109.5
C9—C8—H8A	111.6	H15A—C15—H15C	109.5

C3—C8—H8B	111.6	H15B—C15—H15C	109.5
C9—C8—H8B	111.6	C13—C16—H16A	120.0
H8A—C8—H8B	109.4	C13—C16—H16B	120.0
C8—C9—C10	101.20 (14)	H16A—C16—H16B	120.0
C8—C9—C12	112.04 (14)	C1—O1—H1	109.5

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O2^{i}	0.84	1.81	2.646 (3)	174

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