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2-(2-Furylmethyl)-1-methyl-3-oxocyclohexanecarboxylic acid

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Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.002 Å
R factor = 0.039
wR factor = 0.113
Data-to-parameter ratio = 18.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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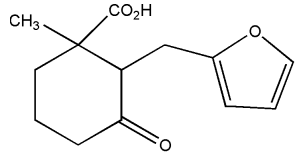
The title compound, $C_{13}H_{16}O_4$, appears as an intermediate in the synthetic pathway of furosesquiterpenes. The crystal structure is dictated by the presence of intermolecular hydrogen bonding. It is noticeable that there are rather similar C—O distances in the carboxyl group [(1.2454(14) and 1.2835 (14) Å]. In the solid state, the molecules interact in pairs, forming discrete dimers as part of a three-dimensional network.

Comment

Marine sponges and different plants are rich sources of several furosesquiterpenes (Fraga, 1988, 1990). Linearly fused furo[2,3-*b*]- and furo[3,2-*b*]decalin systems with *cis–trans* ring junctions are present in compounds such as atractylon (Honan, 1985), furodysin (Vaillancourt *et al.*, 1991), isoalantolactone (Tada *et al.*, 1993), and euryopsonal (Rivett & Wooland, 1967). As part of a program on the synthesis of furosesquiterpenes, racemic crystals of the intermediate product 2-(2-furylmethyl)-1-methyl-3-oxocyclohexanecarboxylic acid, (I), were obtained. The molecule of (I) is composed of a six- and a five-membered ring linked by the methylene group. The six-membered ring (C1–C6) (Fig. 1) adopts a chair conformation and the five-membered ring (C8–C11/O1) (Fig. 1) is planar (mean deviation = 0.0004 Å).



(I)

Geometric parameters are mostly as expected (Table 1). The angles C7—C8—C9 [134.09 (13)°] and C1—C7—C8 [114.50 (10)°] are influenced by the intramolecular environment, in particular by the intramolecular contacts C1···C8 = 2.542 (2) Å, C7···O4 = 2.779 (2) Å, and C7···O1 = 2.428 (2) Å. An important feature found in this monoclinic crystal is the existence of intermolecular hydrogen bonding. The carboxyl group serves simultaneously as a hydrogen-bond donor and acceptor. Although in compounds with a similar carboxyl-group environment to (I), single [1.320 (3) Å] C—O and double [1.217 (3) Å] C═O bonds are clearly distinguished (Shi *et al.*, 2002), it is noticeable that here both C—O bonds of the carboxyl group are rather similar [C12—O3 = 1.2835 (14) Å and C12—O2 = 1.2454 (14) Å]. Such influence of the hydrogen bonding on the C—OH and C═O distances of (I) has previously been described (Jeffrey & Saenger, 1994). The hydrogen bonding is shown in Fig. 2 and relevant

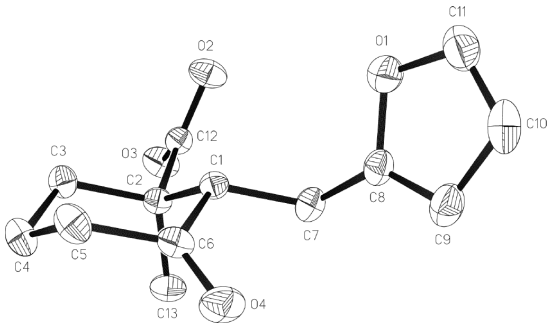


Figure 1
View of the title molecule, showing the atomic numbering and 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

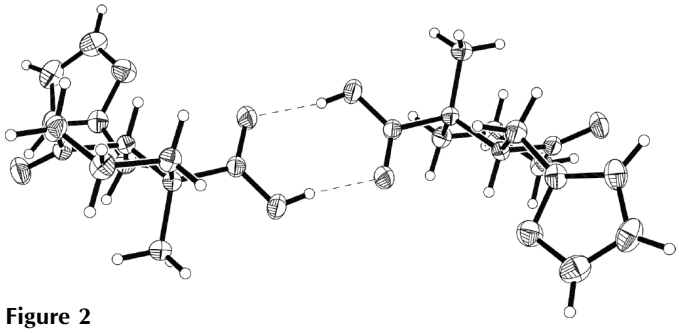


Figure 2
The intermolecular hydrogen bonding in (I). H atoms are shown as small spheres of arbitrary radii and hydrogen bonds are shown as dashed lines.

parameters are given in Table 2. As two hydrogen bonds exist between symmetry-equivalent molecules, discrete dimers are formed as part of a three-dimensional network (Fig. 3).

Experimental

The title compound, (I), was synthesized in four steps starting from Hagemann's ester. Alkylation of Hagemann's ester with 2-furylmethyl chloride in the presence of ^{t}BuOK as base afforded a C-3-alkylated product which, on alkaline hydrolytic decarboxylation, produced the furylmethylcyclohexenone derivative. This compound on treatment with KCN followed by hydrolysis, afforded the title compound, (I), as a white solid (Chakraborty *et al.*, 1997). Single crystals were grown by slow evaporation of an ethyl acetate solution of this compound.

Crystal data

$C_{13}H_{16}O_4$
M_r = 236.26
Monoclinic, $P2_1/n$
a = 6.043 (1) Å
b = 20.996 (1) Å
c = 9.372 (1) Å
β = 91.912 (1)°
V = 1188.5 (1) Å^3
Z = 4
D_x = 1.320 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4362 reflections
θ = 2.0–28.0°
μ = 0.10 mm^{-1}
T = 298 (2) K
Block, colourless
0.55 × 0.52 × 0.48 mm

Data collection

Bruker CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.948, T_{max} = 0.955
7581 measured reflections
2821 independent reflections
2338 reflections with $I > 2\sigma(I)$
R_{int} = 0.016
θ_{max} = 28.3°
$h = -6 \rightarrow 8$
$k = -27 \rightarrow 27$
$l = -11 \rightarrow 12$

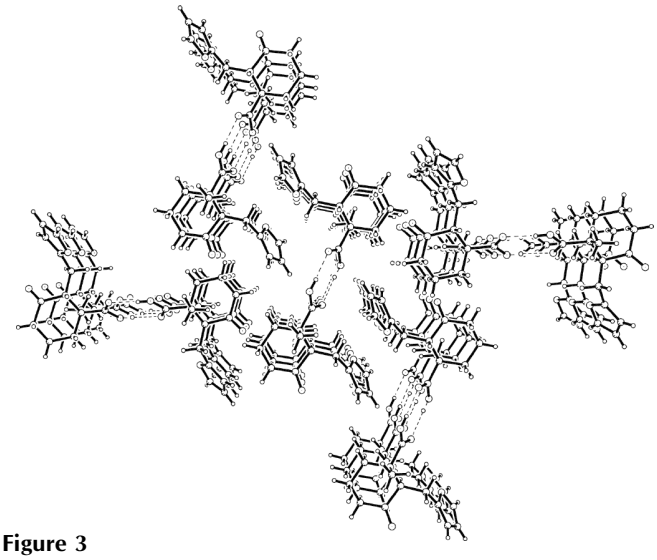


Figure 3
Packing diagram of the title compound, showing the existence of discrete dimers. Dashed lines denote the intermolecular hydrogen bonds.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.113
S = 1.04
2821 reflections
155 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0561P)^2 + 0.229P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.25 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C8	1.3657 (16)	C7—C8	1.4877 (17)
O2—C12	1.2454 (14)	C8—C9	1.3405 (18)
O3—C12	1.2835 (14)	C9—C10	1.424 (2)
O4—C6	1.2090 (15)	C10—C11	1.326 (2)
C1—C7	1.5344 (16)		
C8—O1—C11	106.63 (11)	O2—C12—O3	123.55 (10)
C5—C6—C1	115.55 (10)	O2—C12—C2	120.62 (10)
C8—C7—C1	114.50 (10)	O3—C12—C2	115.70 (10)
C9—C8—C7	134.09 (13)		
C6—C1—C2—C12	167.91 (9)	C8—C9—C10—C11	−0.04 (17)
C7—C1—C2—C12	−66.89 (12)	C9—C10—C11—O1	0.09 (18)
C6—C1—C2—C13	−69.36 (12)	C13—C2—C12—O3	34.89 (14)
C1—C7—C8—C9	116.68 (16)	C3—C2—C12—O3	−84.48 (12)
C1—C7—C8—O1	−66.77 (14)	C1—C2—C12—O3	158.34 (10)
O1—C8—C9—C10	−0.03 (16)		

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

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3A···O2^{i}	0.82	1.82	2.6327 (13)	171

Symmetry code: (i) $2-x, -y, 2-z$.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1997); software used to prepare material for publication: *SHELXTL*.

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References

Chakraborty, A., Kar, G. K. & Ray, J. K. (1997). *Tetrahedron*, **53**, 2989–2996.
Fraga, B. M. (1988). *J. Nat. Prod. Rep.* **5**, 497–521.
Fraga, B. M. (1990). *J. Nat. Prod. Rep.* **7**, 515–537.
Honan, M. (1985). *Tetrahedron Lett.* **26**, 6393–6396.
Jeffrey, G. A. & Saenger, W. (1994). *Hydrogen Bonding in Biological Structures*, p. 96. New York: Springer-Verlag.
Rivett, D. A. & Wooland, G. R. (1967). *Tetrahedron*, **23**, 2431–2436.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (1997). *SHELXS*97, *SHELXL*97 and *SHELXTL*.. University of Göttingen, Germany.
Sheldrick, G. M. (1997*b*). University of Göttingen, Germany.
Shi, H., Pan, Y. J., Wu, S. H. & Zhang, X. X. (2002). *Acta Cryst.* C**58**, o55–o56.
Siemens (1995). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Tada, M., Yamada, H., Kanamori, A. & Chiba, K. (1993). *J. Chem. Soc. Perkin Trans* 1, pp. 239–247.
Vaillancourt, V., Agharahimi, M. R., Sundaram, U. N., Richon, O., Faulkner, D. & Albizati, K. F. (1991). *J. Org. Chem.* **56**, 378–387.