

Methyl *rac*-(1*S**,11*R**,12*S**,14*S**)-12-hydroxy-14-methyl-15-oxobicyclo-[9.3.1]pentadecane-1-carboxylate

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Key indicators

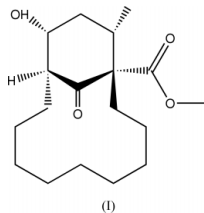
Single-crystal X-ray study
 $T = 291\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.002\text{ \AA}$
 R factor = 0.042
 wR factor = 0.131
Data-to-parameter ratio = 19.8

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

The molecule of the title compound, $\text{C}_{18}\text{H}_{30}\text{O}_4$, can be described as a *trans*-fused bicyclic system. The carbonyl group lies on the same side as the methoxycarbonyl group, while the OH group is on the opposite side. The six-membered ring has a twist formed conformation, presumably due to the presence of the methyl group next to a bulky methoxycarbonyl group. There are two local pseudo-twofold axes, one passing through two C atoms, the other through the mid-points of two C—C bonds.

Comment

The title compound, (I), was obtained in a study of the application of the domino Michael addition/Aldol condensation procedure using two different ring-sized cycloalkanones. Here, conversion of the methyl 2-oxocyclododecanoate with crotonic aldehyde under basic conditions (1,8-diazabicyclo[5.4.0]undec-7-ene) gave the bicyclic title compound, (I), as the major regio- and diastereoisomer (racemic) in 49% yield. Thus, in contrast to earlier reports (Filippini & Rodriguez (1997) of this procedure, the aldol product, starting from cyclododecanone, could be isolated, whereas the analogous product from cyclopentanone was not isolated since further conversion *via* retro-Dieckman condensation readily occurred. Stereochemical differences were assumed to be responsible for these observations, therefore the precise structure had to be determined. The title compound is formed as the *trans*-fused bicyclic compound, whereas the analogous product formed from cyclopentanone is the *cis*-fused compound. There are two local pseudo-twofold axes, one passing through the atoms C1 and C12 and the other through the mid-points of the bonds C11—C15 and C13—C14.



Experimental

To a solution of methyl-2-oxocyclododecanoate (1 equivalent) in MeOH was added DBU (1,8-diazabicyclo[5.4.0]undec-7-ene; 1 equivalent) in MeOH, and the mixture was stirred for 1 h at room temperature. Crotonaldehyde (1 equivalent) in MeOH was added slowly, and the solution was stirred for 18 h at room temperature. The solvent was then evaporated under reduced pressure, the residue dissolved in diethyl ether, acidified with HCl and the aqueous layer extracted with ether. The combined organic phases were washed with

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water and dried over magnesium sulfate. Evaporation of the solvent under reduced pressure yielded a mixture of diastereoisomers. Purification by flash chromatography, using cyclohexane–diethyl ether (2:1) as eluant, gave one diastereoisomer as crystals in 49% yield and, in addition, as an oil, a mixture of two epimers due to different orientations of the 12-hydroxy and/or the methyl group.

Crystal data

$C_{18}H_{30}O_4$	$Z = 2$
$M_r = 310.42$	$D_x = 1.171 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 8.4865 (5) \text{ \AA}$	Cell parameters from 13476 reflections
$b = 8.8025 (2) \text{ \AA}$	$\theta = 3.4\text{--}27.5^\circ$
$c = 12.2034 (2) \text{ \AA}$	$\mu = 0.08 \text{ mm}^{-1}$
$\alpha = 89.9661 (7)^\circ$	$T = 291 (1) \text{ K}$
$\beta = 87.4671 (8)^\circ$	Block, colourless
$\gamma = 75.2109 (7)^\circ$	$0.45 \times 0.40 \times 0.25 \text{ mm}$
$V = 880.51 (6) \text{ \AA}^3$	

Data collection

Nonius KappaCCD diffractometer	$R_{\text{int}} = 0.023$
ω scans at different κ angles	$\theta_{\text{max}} = 27.5^\circ$
Absorption correction: none	$h = -11 \rightarrow 11$
13476 measured reflections	$k = -10 \rightarrow 11$
4008 independent reflections	$l = -15 \rightarrow 15$
2991 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0697P)^2 + 0.0293P]$
$R[F^2 > 2\sigma(F^2)] = 0.042$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.131$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.14$	$\Delta\rho_{\text{max}} = 0.29 \text{ e \AA}^{-3}$
4008 reflections	$\Delta\rho_{\text{min}} = -0.15 \text{ e \AA}^{-3}$
202 parameters	
H-atom parameters constrained	

Table 1

Hydrogen-bonding geometry (\AA , $^\circ$).

$D\text{--}H\cdots A$	$D\text{--}H$	$H\cdots A$	$D\cdots A$	$D\text{--}H\cdots A$
$O1\text{--}H1\cdots O3^i$	0.82	2.05	2.848 (1)	164

Symmetry code: (i) $x, y - 1, z$.

H atoms were placed in calculated positions ($C\text{--}H = 0.96\text{--}0.98 \text{ \AA}$) with U_{iso} values constrained to be $1.5U_{\text{eq}}$ of the carrier atom for the methyl H atoms and $1.2U_{\text{eq}}$ for the remaining H atoms. The methyl groups were allowed to rotate but not to tip.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*; program(s) used to solve

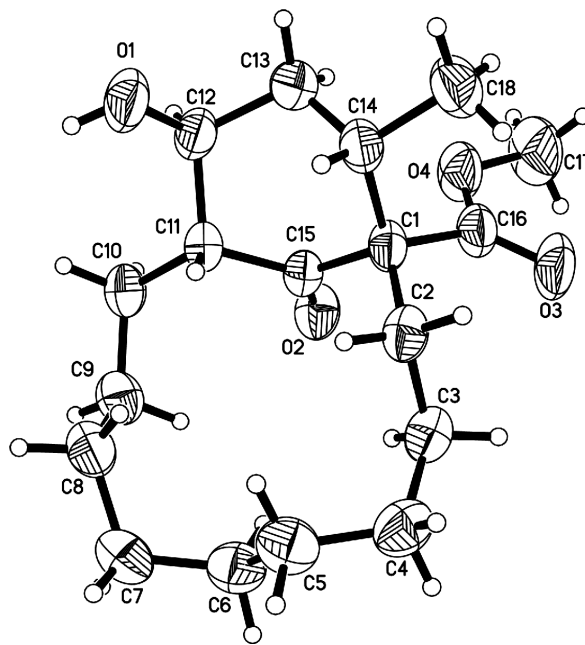


Figure 1

View of the title compound (*XP* in *SHELXTL-Plus*; Sheldrick, 1991), showing the labelling of all non-H atoms. Displacement ellipsoids are drawn at the 50% probability level.

structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELTL-Plus* (Sheldrick, 1991); software used to prepare material for publication: *SHELXL97*, *PARST95* (Nardelli, 1995) and *PLATON* (Spek, 2001).

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