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rac-(1*R*,11*R*,14*S*,18*R*)-Methyl 18-hydroxy-19-oxotricyclo[9.7.1.0^{1,14}]nonadecane-11-carboxylate

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Key indicators

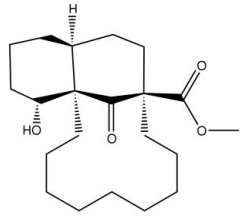
Single-crystal X-ray study
T = 291 K
Mean σ(C–C) = 0.004 Å
Disorder in main residue
R factor = 0.043
wR factor = 0.071
Data-to-parameter ratio = 15.0

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

The investigated crystal of the title compound, $C_{21}H_{34}O_4$, contains two molecules in the asymmetric unit. One molecule shows disorder for two atoms in the 12-membered ring. The two independent molecules show only slight conformational differences. Four molecules are linked *via* two O—H···O hydrogen bonds [O···O = 2.816 (2) Å and O—H···O = 163°; O···O = 2.764 (2) Å and O—H···O = 163°] and a centrosymmetric 16-membered heterocycle containing four hydrogen bonds is formed.

Comment

The title compound, (I), was obtained in a study of the application of the one-pot tandem hydroformylation/aldol condensation of ethyl 12-allyl-15-oxobicyclo[9.3.1]pentadecane-1-carboxylate, which was obtained by 1,4-conjugate addition of allytrimethylsilane in the presence of titanium tetrachloride (Rahm & Pereyre, 1977). Owing to the complex tricyclic structure of the title compound, (I), bearing four stereogenic centres, an X-ray analysis had to be performed. The tricyclic structure is determined to be a *cis*-fused decalin system attached to the cyclododecanone in the positions α,α' to its carbonyl group. Thus, both the Michael addition and the subsequent hydroformylation/aldol condensation occur from the side of the carbonyl group of the bicyclic starting compound, whereas the OH group is on the opposite side. Both six-membered rings have a chair conformation.



(I)

The two crystallographically independent molecules show only slight conformational differences as is indicated by the torsion angles. Four molecules are linked *via* two O—H···O hydrogen bonds [O···O = 2.816 (2) Å and O—H···O = 163°; O···O = 2.764 (2) Å and O—H···O = 163°] and a centrosymmetric 16-membered heterocycle (H1′—O1′—C18′—C1′—C19′—O2′···H1—O1···H1$'^{i}$—O1$'^{i}$—C18$'^{i}$—C1$'^{i}$—C19$'^{i}$—O2$'^{i}$···H1^{i}—O1^{i}···) is formed [symmetry code: (i) $2-x, 2-y, -z$].

Experimental

A solution of methyl 12-allyl-15-oxobicyclo[9.3.1]pentadecane-1-carboxylate (1 equivalent), BIPHEPHOS (2,2′-bis{[(2,2′-bisphenoxy)phosphino]oxy}-3,3′,5,5′-tetra-*tert*-butyl-1,1′-biphenyl; 4 mol%), *p*-toluenesulfonic acid (5 mol%) and [Rh(acac)(CO)$_2$] (1 mol%) in

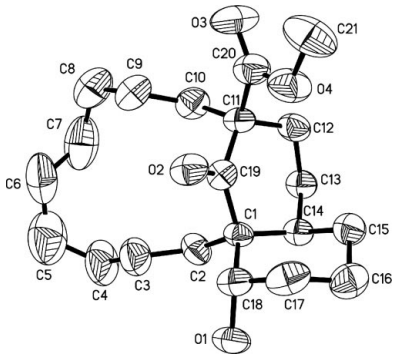


Figure 1
View of one of the independent molecules of the title compound (*XP* in *SHELXTL*; Sheldrick, 1991), showing the labelling of all non-H atoms. Displacement ellipsoids are shown at the 30% probability level. H atoms have been omitted for clarity.

anhydrous dichloromethane (20 ml) was placed in an autoclave. After flushing with argon, the reactor was pressurized with 10 bar carbon monoxide and 10 bar hydrogen, magnetically stirred and heated to 333 K for 3 d. The autoclave was then allowed to cool to room temperature. After expanding the *syn* gas, the remaining solution was filtered through alumina using MTBE (methyl *tert*-butyl ether) as eluant. The solvent was removed by rotary evaporation and the residue was analysed by gas chromatography. The residue was subjected to silica-gel column chromatography using a solution of cyclohexane/diethyl ether (10:1) as eluant. Recrystallization from diethyl ether gave the title compound in 43% yield. Spectroscopic data, ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.01 (*bs*, 1H, OH), 3.67 (*s*, 3H, CH_3), 2.38 (*m*, 2H, CH_{2ring}), 2.07 (*m*, 2H, CH_{2ring}), 1.81 (*m*, 4H, CH_{2ring}), 1.75 (*m*, 2H, CH_{2ring}), 1.54 (*m*, 7H, CH_{2ring}), 1.34 (*m*, 13H, CH_{2ring}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.83 (CO), 174.11 (CO), 68.64 (CH—OH), 62.16 (C_q), 58.86 (C_q), 53.90 (CH_3), 37.77 (CH_{2ring}), 32.51 (CH_{2ring}), 31.10 (CH_{2ring}), 29.50 (CH_{2ring}), 28.58 (CH_{2ring}), 27.86 (CH_{2ring}), 24.83 (CH_{2ring}), 24.42 (CH_{2ring}), 24.22 (CH_{2ring}), 24.03 (CH_{2ring}), 23.87 (CH_{2ring}), 23.55 (CH_{2ring}), 22.56 (CH_{2ring}), 21.75 (CH_{2ring}), 20.83 (CH_{2ring}); MS–LR (EI, 70 eV): *m*/*z* (%) = 350 (M^+, 5.65), 338 (6.17), 306 (16.15), 294 (6.27), 282 (5.99), 246, (8.84), 210 (6.92), 184 (39.45), 105 (100), 93 (13.36), 81 (36.17), 69 (29.34), 55 (53.59), 41 (68.86), 29 (52.27), 18 (9.43); High Resolution MS (EI, 70 eV): calculated: 350.2457, found 350.2484; IR (Pressling, KBr), ν (cm^{-1}): 3506 (*s*), 2936 (*s*), 2865 (*s*), 2850 (*s*), 1737 (*s*), 1680 (*s*), 1467 (*m*), 1446 (*s*), 1277 (*m*), 1245 (*m*), 1186 (*m*), 1102 (*m*), 815 (*m*); elemental analysis calculated: C 71.96, H 9.78%; found: C 71.8, H 10.0%.

Crystal data

$C_{21}H_{34}O_4$
M_r = 350.48
Monoclinic, $P2_1/n$
a = 10.5029 (9) Å
b = 11.0460 (2) Å
c = 34.5904 (9) Å
β = 97.0550 (10)°
V = 3982.6 (4) Å^3
Z = 8
D_x = 1.169 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 31011 reflections
θ = 3.0–25.3°
μ = 0.08 mm^{-1}
T = 291 (1) K
Block, colourless
0.20 × 0.15 × 0.15 mm

Data collection

Nonius KappaCCD diffractometer
ω scans
Absorption correction: none
31011 measured reflections
7110 independent reflections
2449 reflections with $I > 2\sigma(I)$
R_{int} = 0.044
θ_{max} = 25.3°
$h = -12 \rightarrow 12$
$k = -13 \rightarrow 13$
$l = -41 \rightarrow 41$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.071
S = 0.91
7110 reflections
474 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0101P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.14 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.00321 (18)

Table 1
Selected torsion angles (°).

C19—C1—C2—C3	−62.8 (3)	C19′—C1′—C2′—C3′	−66.3 (3)
C1—C2—C3—C4	172.9 (2)	C1′—C2′—C3′—C4′	172.5 (2)
C2—C3—C4—C5	−143.3 (3)	C2′—C3′—C4′—C5′*A*	−142.4 (7)
C3—C4—C5—C6	47.7 (5)	C3′—C4′—C5′*A*—C6′	47.1 (11)
C4—C5—C6—C7	55.7 (4)	C4′—C5′*A*—C6′—C7′*A*	62.2 (9)
C5—C6—C7—C8	−158.7 (3)	C5′*A*—C6′—C7′*A*—C8′	−154.4 (5)
C6—C7—C8—C9	75.5 (3)	C6′—C7′*A*—C8′—C9′	68.9 (5)
C7—C8—C9—C10	74.5 (3)	C7′*A*—C8′—C9′—C10′	81.1 (4)
C8—C9—C10—C11	−168.8 (2)	C8′—C9′—C10′—C11′	−172.7 (2)
C9—C10—C11—C19	55.1 (3)	C9′—C10′—C11′—C19′	53.4 (3)
C19—C11—C12—C13	35.2 (3)	C19′—C11′—C12′—C13′	38.4 (3)
C11—C12—C13—C14	−52.6 (3)	C11′—C12′—C13′—C14′	−54.4 (3)
C12—C13—C14—C1	62.1 (3)	C12′—C13′—C14′—C1′	62.0 (3)
C19—C1—C14—C13	−52.9 (2)	C18′—C1′—C14′—C15′	−48.7 (3)
C18—C1—C14—C15	−47.8 (3)	C19′—C1′—C14′—C13′	−52.3 (3)
C1—C14—C15—C16	54.2 (3)	C1′—C14′—C15′—C16′	54.7 (3)
C14—C15—C16—C17	−58.7 (3)	C14′—C15′—C16′—C17′	−58.3 (3)
C15—C16—C17—C18	60.0 (3)	C15′—C16′—C17′—C18′	58.3 (3)
C16—C17—C18—C1	−55.7 (3)	C16′—C17′—C18′—C1′	−55.6 (3)
C14—C1—C18—C17	48.3 (3)	C14′—C1′—C18′—C17′	49.5 (3)
C14—C1—C19—C11	38.4 (3)	C14′—C1′—C19′—C11′	39.2 (3)
C2—C1—C19—C11	−81.7 (3)	C2′—C1′—C19′—C11′	−80.3 (3)
C10—C11—C19—C1	93.4 (2)	C12′—C11′—C19′—C1′	−32.5 (3)
C12—C11—C19—C1	−29.5 (3)	C10′—C11′—C19′—C1′	90.6 (2)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O2′	0.82	2.02	2.816 (2)	163
O1′—H1′···O1^{i}	0.82	1.97	2.764 (2)	163

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

H atoms were placed in calculated positions, with U_{iso} values constrained to be 1.5 times U_{eq} of the carrier atom for the methyl–H and the hydroxyl–H and 1.2 times U_{eq} for the remaining H atoms. The methyl and the hydroxyl groups were allowed to rotate but not to tip. For the disordered positions of atoms C5′ and C7′, two split positions (C5′/C5′*A* and C7′/C7′*A*) were refined anisotropically, each with an occupancy factor 0.5.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus* (Sheldrick, 1991); software used to prepare material for publication: *SHELXL*97, *PARST*95 (Nardelli, 1995) and *PLATON* (Spek, 2001).

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