Acta Crystallographica Section E
**Structure Reports Online**
ISSN 1600-5368

# The product of a regiospecific and stereoselective ene-reaction of a polycyclic terpenoid system

**Antonio Abad,[a] Consuelo Agulló,[a] Ana C. Cuñat,[a] Ismael Navarro[a] and Carmen Ramírez de Arellano[b]***

[a]Departamento de Química Orgánica, Facultad de Química, Universidad de Valencia, 46100-Burjassot, Valencia, Spain, and [b]Departamento de Química Orgánica, Facultad de Farmacia, Universidad de Valencia, 46100-Burjassot, Valencia, Spain

Correspondence e-mail: mcra@uv.es

**Key indicators**

Single-crystal X-ray study
$T$ = 293 K
Mean $\sigma$(C–C) = 0.004 Å
$R$ factor = 0.049
$wR$ factor = 0.123
Data-to-parameter ratio = 14.4

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

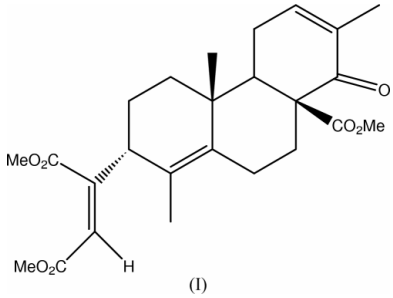
© 2001 International Union of Crystallography
Printed in Great Britain – all rights reserved

The X-ray structure of dimethyl ($Z$)-[(8a$S$,2$R$,4a$R$,4b$R$)-8a-methoxycarbonyl-1,4a,7-trimethyl-8-oxo-2,3,4,4a,4b,5,8,8a,9,-10-decahydrophenanthren-2-yl]-2-butenedioate, $C_{25}H_{32}O_7$, confirmed its relative configuration. The structure shows the bend in the molecular skeleton as found for similar compounds. Weak intermolecular C—H···O interactions have been found in the crystal.

Received 4 May 2001
Accepted 21 May 2001
Online 31 May 2001

## Comment

Compound (I) is obtained by a regiospecific and stereoselective ene-reaction of the A-ring methylcyclohexene moiety of a polycyclic terpenoid system with dimethylacetylenedicarboxylate (DMAD). The synthesis of the compound has been already reported (Abad *et al.*, 2001). After the ene reaction the configuration for C8, C9 and C10 was known to be $S$, $R$ and $R$, respectively (see Fig. 1). An $R$ configuration for the newly generated stereo centre C3 was postulated after NOESY experiments. The X-ray structure analysis confirms the relative $R$ configuration of C3 as well as other structural facts.




(I)

The structure shows the bend in the molecular skeleton as found for similar compounds (Cambie *et al.*, 1999), with a dihedral angle of 44.7 (2)° between the mean planes of the $A$ and $C$ rings. Ring $B$ is in the expected chair conformation. Rings $A$ and $C$ are in a half-chair conformation with atoms C2 and C9 out of the mean plane, respectively. The acetate group at C8 has the C22—O6 bond oriented towards the centre of the $C$ ring. The dimethyl butenedioate moiety at C3 is in an axial position with the double bond C15═C16 towards the molecular skeleton. Two intermolecular C$sp^3$—H···O═C close contacts have been found (C18—H18$B$···O7$^{i}$ and C20—H20$B$···O7$^{ii}$, Table 1), that form infinite zigzag chains parallel to the $b$ and $a$ axes, respectively. These two zigzag chains form a molecular layer perpendicular to the $c$ axis. Other much weaker C$sp^3$—H···O═C interactions connect the molecular layers described above (C24—H24$A$···O3$^{iii}$ and C25—H25$C$···O3$^{ii}$).

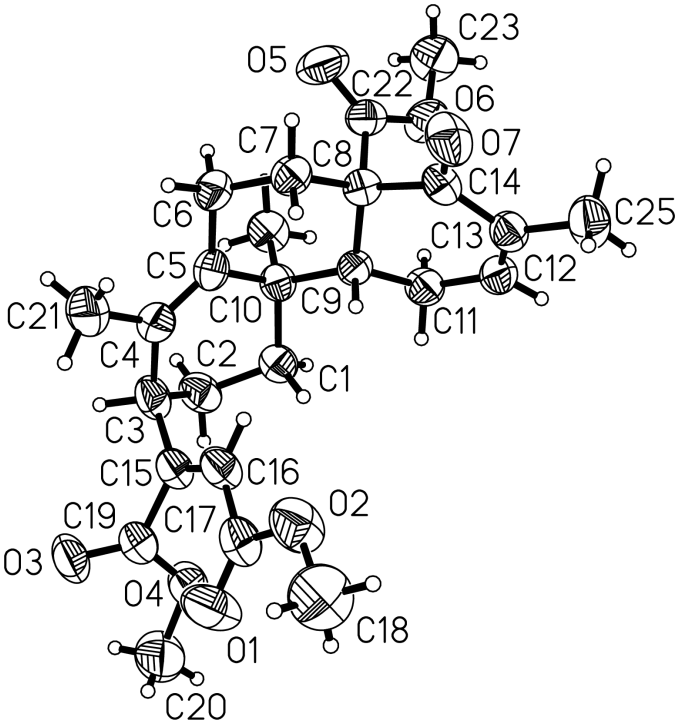



**Figure 1**
Displacement ellipsoid plot (50% probability level) with the usual diterpene labelling scheme.

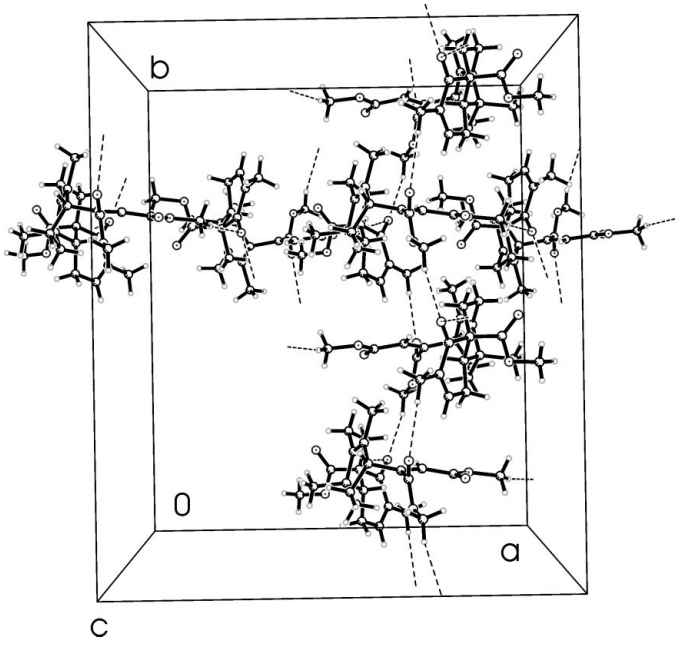



**Figure 2**
Crystal packing. Broken lines indicate the C—H···O close contacts.

## Experimental

Single crystals of (I) were grown by slow evaporation of a methanol solution.

*Crystal data*

$C_{25}H_{32}O_7$
$M_r$ = 444.51
Orthorhombic, $P2_12_12_1$
$a$ = 11.810 (2) Å
$b$ = 13.985 (3) Å
$c$ = 14.434 (3) Å
$V$ = 2384.0 (8) Å$^3$
$Z$ = 4
$D_x$ = 1.238 Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta$ = 10–12°
$\mu$ = 0.09 mm$^{-1}$
$T$ = 293 (2) K
Block, colourless
0.64 × 0.62 × 0.44 mm

*Data collection*

Nonius CAD-4 diffractometer
$\omega$- scans
Absorption correction: none
6144 measured reflections
4163 independent reflections
3049 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.030
$\theta_{max}$ = 25.0°
$h = -14 \rightarrow 4$
$k = -16 \rightarrow 16$
$l = 0 \rightarrow 17$
3 standard reflections every 250 reflections intensity decay: 1.8%

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.123
$S$ = 1.09
4163 reflections
290 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0417P)^2 + 0.6085P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.15 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.14 e Å$^{-3}$
Extinction correction: *SHELXL*
Extinction coefficient: 0.0069 (9)
Absolute structure: (Flack, 1983)
Flack parameter = 0.5 (16)

**Table 1**
Close contacts (Å, °).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| C18—H18$B$···O7$^{i}$ | 0.96 | 2.47 | 3.424 (5) | 170 |
| C20—H20$B$···O7$^{ii}$ | 0.96 | 2.42 | 3.344 (5) | 161 |
| C25—H25$C$···O3$^{ii}$ | 0.96 | 2.70 | 3.607 (5) | 158 |
| C24—H24$A$···O3$^{iii}$ | 0.96 | 2.84 | 3.755 (4) | 160 |

Symmetry codes: (i) $-x, \frac{1}{2}+y, \frac{3}{2}-z$; (ii) $\frac{1}{2}+x, \frac{1}{2}-y, 2-z$; (iii) $-x, y-\frac{1}{2}, \frac{5}{2}-z$.

The absolute structure could not be determined with a Flack parameter of 0.5 (16), and was assumed based on the synthesis of the title compound (Abad *et al.*, 2001).

Data collection: *CAD*-4/*PC* (Enraf–Nonius, 1996); cell refinement: *CAD*-4/*PC*; data reduction: *MolEN* (Fair, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97; molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXL*97.

We are grateful to the Ministerio de Educación y Cultura of Spain for financial support (Project No PB98–1421–C02–01).

## References

Abad, A., Agulló, C., Cuñat,A. C., Navarro, I. & Ramírez de Arellano, M. C. (2001). *J. Chem.* Research. In the press.
Bruker (1997) *SHELXTL*. Version 5.1. Bruker AXS, Madison, Wisconsin 53719 USA.
Cambie, R. C., Rickard, C. E. F., Rutledge, P. S. & Yang, X. S. (1999). *Acta Cryst.* C**55**, 112–114.
Enraf–Nonius (1996). *CAD*-4/*PC* Software. Version 2.0. Enraf–Nonius, Delft, The Netherlands.
Fair, C. K. (1997). *MolEN*. Version 2.2. Enraf–Nonius, Delft, The Netherlands.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.