Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SZ1046). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C**52**, 107–110

14-Membered Macrocycles: Methyl *trans*-(10*E*)-5-Methyl-8-methylene-11,15-dioxobicyclo[12.3.0]heptadec-4-ene-14-carboxylate, (I), and Methyl *trans*-(2*E*,10*E*)-10-Methyl-7-methylene-4,17-dioxobicyclo[12.3.0]-heptadeca-2,10-diene-1-carboxylate, (II)

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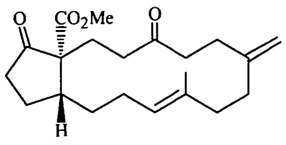
Abstract

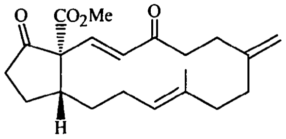
A new series of functionalized 14-membered ring compounds were synthesized by an intramolecular Michael reaction. The structures of the title compounds (I) and (II) ($C_{21}H_{30}O_4$ and $C_{21}H_{28}O_4$, respectively) were determined by single-crystal X-ray diffraction in order to confirm their relative stereochemistries.

Comment

The intramolecular Michael reaction has been used successfully for the synthesis of medium sized (nine- and ten-membered) rings (Deslongchamps & Roy, 1986). Recently, the formation of 14-membered rings was reported using pseudo-high-dilution techniques (Girard & Deslongchamps, 1992). In order to verify the relative ease of macrocyclization of five-membered β-ketoesters with enones and ynones, a series of new 14-membered ring compounds were synthesized from precursors differing in the nature of their Michael acceptors and in the hybridization state of one C atom (Berthiaume & Deslongchamps, 1995). X-ray diffraction analysis of the products was undertaken in order to confirm the structure and relative stereochemistry, not possible by conventional spectroscopic analysis. We report here the crystal structures of the two title 14-membered ring macrocycles, (I) and (II).



(I)



(II)

The results show the ring junction to be *trans* in both molecules and the olefin geometries to be *trans* in (I) and *trans,trans* in (II). The global conformations of the molecules are very similar. In both compounds, the methylene moiety is facing the five-membered ring. The methyl carboxylate group is equatorial to the plane defined by the atoms forming the 14-membered ring, whereas the five-membered ring is axial to this plane. In (I), C20 and C21 are facing down on the same side of the macrocycle as the five-membered ring, whereas the C4═O3 carbonyl group is facing up. In (II), C20 and C21 are also facing down, whereas the C4═O3 carbonyl group is in the plane of the 14-membered ring. Puckering analysis on the five-membered ring shows an envelope conformation in (I) and (II). C15 is 0.508 (2) Å from the plane defined by C1, C14, C16 and C17 in (I). C14 is 0.524 (10) Å from the plane defined by C1, C15, C16 and C17 in (II). In compound (I), there is no transannular close contact. In (II), the O3 ketone group and C2═C3 *trans* double bond are conjugated, as shown by the C3—C4 bond distance [1.462 (7) Å] and the O3—C4—C3—C2 torsion angle [2.6 (4)°]. This particular rigid geometry is such that H3 (attached to C3) interacts strongly with H14 (attached to C14) [2.08 (7) Å]. No abnormally short contacts were observed.

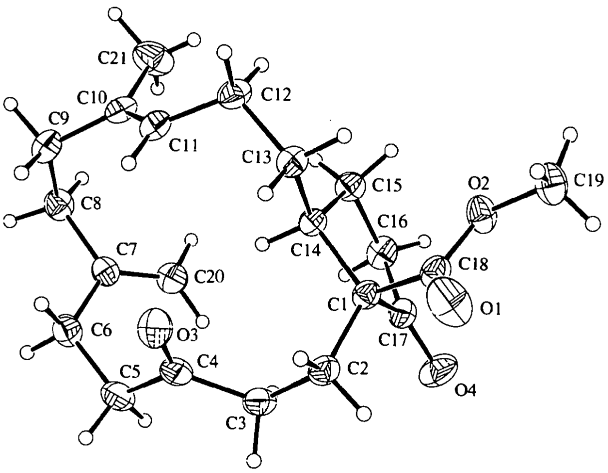


Fig. 1. *ORTEP*II (Johnson, 1976) perspective view of (I) showing the labeling of the non-H atoms. Displacement ellipsoids are shown at the 30% probability level and H atoms are drawn as small circles of arbitrary radii.

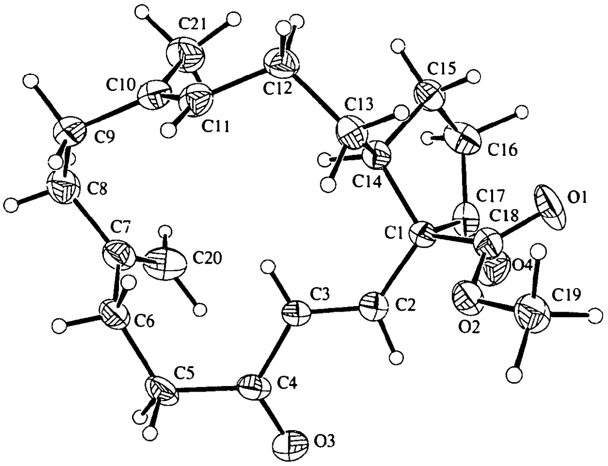


Fig. 2. *ORTEP*II (Johnson, 1976) perspective view of (II) showing the labeling of the non-H atoms. Displacement ellipsoids are shown at the 30% probability level and H atoms are drawn as small circles of arbitrary radii.

Experimental

Compounds (I) and (II) were prepared according to Berthiaume & Deslongchamps (1995).

Compound (I)

Crystal data

$C_{21}H_{30}O_4$
$M_r = 346.46$
Triclinic
$P\bar{1}$
$a = 7.3972\ (3)$ Å
$b = 9.7969\ (6)$ Å
$c = 13.3883\ (8)$ Å
$\alpha = 95.405\ (5)°$
$\beta = 96.186\ (4)°$
$\gamma = 91.666\ (4)°$
$V = 959.55\ (9)$ Å^3
$Z = 2$
$D_x = 1.199$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 24 reflections
$\theta = 15.0$–$20.0°$
$\mu = 0.08$ mm^{-1}
$T = 293$ K
Irregular
0.50 × 0.50 × 0.50 mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
4818 measured reflections
3366 independent reflections
2690 observed reflections [$I_{\rm net} > 2.5\sigma(I_{\rm net})$]

$R_{\rm int} = 0.009$
$\theta_{\rm max} = 24.91°$
$h = -8 \rightarrow 8$
$k = 0 \rightarrow 11$
$l = -15 \rightarrow 15$
2 standard reflections frequency: 60 min intensity decay: 2%

Refinement

Refinement on F
$R = 0.037$
$wR = 0.060$
$S = 1.68$
2690 reflections
227 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F) + 0.0009F^2]$
$(\Delta/\sigma)_{\rm max} = 0.019$

$\Delta\rho_{\rm max} = 0.32$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.20$ e Å^{-3}
Extinction correction: Larson (1970)
Extinction coefficient: $4.5\ (2) \times 10^4$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (I)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
C1	0.36405 (17)	0.03491 (14)	0.20893 (10)	0.0382 (7)
C2	0.4905 (2)	−0.05969 (15)	0.15247 (11)	0.0473 (8)
C3	0.3961 (2)	−0.18210 (16)	0.08706 (11)	0.0501 (8)
C4	0.37940 (19)	−0.31289 (16)	0.13672 (11)	0.0453 (7)
C5	0.2726 (2)	−0.43274 (17)	0.07582 (12)	0.0560 (9)
C6	0.1481 (2)	−0.50809 (15)	0.13709 (12)	0.0513 (9)
C7	−0.01598 (19)	−0.43398 (14)	0.16758 (10)	0.0429 (7)
C8	−0.1175 (2)	−0.49971 (16)	0.24325 (12)	0.0515 (8)
C9	−0.0169 (2)	−0.48327 (17)	0.35091 (12)	0.0524 (8)
C10	0.0061 (2)	−0.33666 (16)	0.39605 (10)	0.0458 (8)
C11	0.1683 (2)	−0.27148 (16)	0.40859 (11)	0.0450 (8)
C12	0.2145 (2)	−0.12616 (16)	0.44984 (11)	0.0492 (8)
C13	0.33504 (19)	−0.04951 (15)	0.38573 (10)	0.0429 (7)
C14	0.24332 (17)	−0.03470 (13)	0.27963 (10)	0.0359 (6)
C15	0.06602 (19)	0.04312 (15)	0.27589 (11)	0.0447 (8)
C16	0.0352 (2)	0.08167 (17)	0.16842 (12)	0.0518 (8)
C17	0.2204 (2)	0.09536 (15)	0.13374 (11)	0.0451 (7)
C18	0.48163 (19)	0.15423 (15)	0.26501 (11)	0.0443 (8)
C19	0.4857 (2)	0.36633 (17)	0.36510 (14)	0.0589 (9)
C20	−0.0716 (2)	−0.31972 (17)	0.13158 (12)	0.0525 (8)
C21	−0.1654 (3)	−0.2721 (2)	0.42272 (16)	0.0742 (11)
O1	0.64383 (15)	0.16100 (14)	0.27381 (12)	0.0850 (9)
O2	0.38393 (13)	0.25175 (10)	0.30689 (9)	0.0518 (6)
O3	0.45325 (15)	−0.32487 (11)	0.22076 (9)	0.0577 (6)
O4	0.25594 (17)	0.14199 (14)	0.05802 (9)	0.0700 (8)

Table 2. *Selected geometric parameters (Å, °) for* (I)

C1—C2	1.542 (2)	C9—C10	1.502 (2)
C1—C14	1.558 (2)	C10—C11	1.329 (2)
C1—C17	1.553 (2)	C10—C21	1.497 (2)
C1—C18	1.524 (2)	C11—C12	1.494 (2)
C2—C3	1.521 (2)	C12—C13	1.531 (2)
C3—C4	1.506 (2)	C13—C14	1.528 (2)
C4—C5	1.515 (2)	C14—C15	1.535 (2)
C4—O3	1.214 (2)	C15—C16	1.517 (2)
C5—C6	1.518 (2)	C16—C17	1.500 (2)
C6—C7	1.506 (2)	C17—O4	1.201 (2)
C7—C8	1.504 (2)	C18—O1	1.192 (2)
C7—C20	1.319 (2)	C18—O2	1.333 (2)
C8—C9	1.541 (2)	C19—O2	1.447 (2)
C2—C1—C14	116.1 (1)	C9—C10—C21	115.0 (1)
C2—C1—C17	111.0 (1)	C11—C10—C21	123.9 (1)
C2—C1—C18	107.4 (1)	C10—C11—C12	128.0 (1)
C14—C1—C17	102.4 (1)	C11—C12—C13	113.5 (1)
C14—C1—C18	112.0 (1)	C12—C13—C14	113.2 (1)
C17—C1—C18	107.6 (1)	C1—C14—C13	115.3 (1)
C1—C2—C3	115.3 (1)	C1—C14—C15	105.9 (1)
C2—C3—C4	116.4 (1)	C1—C14—H14	106.8 (7)
C3—C4—C5	117.3 (1)	C13—C14—C15	115.0 (1)
C3—C4—O3	122.2 (1)	C14—C15—C16	104.4 (1)
C5—C4—O3	120.6 (1)	C15—C16—C17	106.01 (12)
C4—C5—C6	113.0 (1)	C1—C17—C16	109.9 (1)
C5—C6—C7	116.8 (1)	C1—C17—O4	123.7 (1)
C6—C7—C8	115.4 (1)	C16—C17—O4	126.4 (1)
C6—C7—C20	123.9 (1)	C1—C18—O1	125.0 (1)
C8—C7—C20	120.7 (1)	C1—C18—O2	112.8 (1)
C7—C8—C9	113.5 (1)	O1—C18—O2	122.2 (1)
C8—C9—C10	113.4 (1)	C18—O2—C19	116.3 (1)
C9—C10—C11	121.0 (1)		

Compound (II)

Crystal data

$C_{21}H_{28}O_4$
$M_r = 344.45$
Triclinic
$P\bar{1}$
$a = 9.5791\ (13)$ Å
$b = 9.883\ (3)$ Å
$c = 12.2588\ (12)$ Å
$\alpha = 73.344\ (17)°$
$\beta = 68.083\ (17)°$
$\gamma = 64.290\ (18)°$
$V = 959.2\ (4)$ Å^3
$Z = 2$
$D_x = 1.193$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 24 reflections
$\theta = 20.0–25.0°$
$\mu = 0.08$ mm^{-1}
$T = 293$ K
Prism
0.25 × 0.25 × 0.25 mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2466 measured reflections
2466 independent reflections
1898 observed reflections [$I_{net} > 2.5\sigma(I_{net})$]

$\theta_{max} = 22.43°$
$h = -8 \rightarrow 9$
$k = 0 \rightarrow 10$
$l = -12 \rightarrow 13$
2 standard reflections
frequency: 60 min
intensity decay: 2%

Refinement

Refinement on F
$R = 0.073$
$wR = 0.083$
$S = 4.83$
1898 reflections
227 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F) + 0.00005F^2]$
$(\Delta/\sigma)_{max} = 0.011$

$\Delta\rho_{max} = 0.29$ e Å^{-3}
$\Delta\rho_{min} = -0.24$ e Å^{-3}
Extinction correction: Larson (1970)
Extinction coefficient: 0.8 (1) × 10^4
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for* (II)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
O1	0.1515 (5)	0.6736 (5)	0.3455 (4)	0.076 (4)
O2	0.3470 (4)	0.5258 (4)	0.4299 (3)	0.049 (3)
O3	0.8783 (5)	0.2742 (5)	0.2115 (4)	0.076 (4)
O4	0.4141 (5)	0.6519 (5)	0.0745 (4)	0.070 (4)
C1	0.3685 (6)	0.4663 (6)	0.2482 (5)	0.041 (4)
C2	0.5448 (6)	0.3925 (6)	0.2396 (4)	0.039 (4)
C3	0.6326 (6)	0.2465 (6)	0.2543 (5)	0.040 (4)
C4	0.8070 (6)	0.1879 (7)	0.2369 (5)	0.046 (5)
C5	0.9011 (7)	0.0175 (7)	0.2518 (5)	0.053 (5)
C6	0.8167 (6)	−0.0893 (6)	0.2729 (5)	0.048 (4)
C7	0.7714 (7)	−0.0978 (7)	0.1727 (6)	0.051 (5)
C8	0.7087 (7)	−0.2203 (7)	0.1907 (6)	0.061 (5)
C9	0.5608 (7)	−0.2152 (6)	0.2946 (6)	0.056 (5)
C10	0.4137 (7)	−0.0706 (6)	0.2946 (5)	0.047 (5)
C11	0.3403 (7)	0.0036 (6)	0.3876 (5)	0.048 (5)
C12	0.1899 (7)	0.1441 (6)	0.4053 (5)	0.049 (4)
C13	0.2255 (6)	0.2851 (6)	0.3963 (5)	0.046 (4)
C14	0.2824 (6)	0.3549 (6)	0.2675 (5)	0.044 (4)
C15	0.1447 (7)	0.4505 (6)	0.2097 (5)	0.054 (5)
C16	0.2132 (7)	0.5484 (7)	0.1024 (6)	0.065 (5)
C17	0.3397 (7)	0.5705 (6)	0.1325 (5)	0.051 (5)
C18	0.2751 (7)	0.5689 (6)	0.3447 (5)	0.046 (5)
C19	0.2649 (7)	0.6154 (7)	0.5277 (5)	0.059 (5)
C20	0.7897 (8)	−0.0074 (8)	0.0701 (6)	0.070 (6)
C21	0.3604 (7)	−0.0238 (7)	0.1850 (6)	0.068 (6)

Table 4. *Selected geometric parameters (Å, °) for* (II)

C1—C2	1.496 (7)	C9—C10	1.510 (8)
C1—C14	1.562 (7)	C10—C11	1.329 (8)
C1—C17	1.536 (8)	C10—C21	1.493 (8)
C1—C18	1.530 (7)	C11—C12	1.502 (8)
C2—C3	1.317 (8)	C12—C13	1.538 (7)
C3—C4	1.462 (7)	C13—C14	1.525 (8)
C4—C5	1.520 (8)	C14—C15	1.538 (7)
C4—O3	1.218 (7)	C15—C16	1.507 (9)
C5—C6	1.505 (8)	C16—C17	1.504 (8)
C6—C7	1.479 (8)	C17—O4	1.205 (8)
C7—C8	1.502 (8)	C18—O1	1.186 (7)
C7—C20	1.319 (10)	C18—O2	1.332 (7)
C8—C9	1.504 (9)	C19—O2	1.463 (6)
C2—C1—C14	115.2 (4)	C9—C10—C11	120.5 (5)
C2—C1—C17	111.5 (4)	C9—C10—C21	114.6 (5)
C2—C1—C18	111.7 (4)	C11—C10—C21	124.9 (5)
C14—C1—C17	103.2 (4)	C10—C11—C12	127.9 (5)
C14—C1—C18	109.1 (4)	C11—C12—C13	112.5 (4)
C17—C1—C18	105.3 (4)	C12—C13—C14	112.0 (4)
C1—C2—C3	128.1 (5)	C1—C14—C13	115.0 (4)
C2—C3—C4	123.0 (5)	C1—C14—C15	103.5 (4)
C3—C4—C5	120.0 (5)	C13—C14—C15	113.8 (4)
C3—C4—O3	120.7 (5)	C14—C15—C16	105.5 (4)
C5—C4—O3	119.3 (5)	C15—C16—C17	105.5 (5)
C4—C5—C6	119.5 (4)	C1—C17—C16	109.6 (5)
C5—C6—C7	118.0 (5)	C1—C17—O4	123.5 (5)
C6—C7—C8	116.8 (5)	C16—C17—O4	126.8 (5)
C6—C7—C20	122.9 (5)	C1—C18—O1	124.4 (5)
C8—C7—C20	120.3 (5)	C1—C18—O2	112.2 (5)
C7—C8—C9	115.2 (5)	O1—C18—O2	123.4 (5)
C8—C9—C10	116.4 (5)	C18—O2—C19	116.3 (4)

For both compounds, data collection: *NRCCAD DATCOL*; cell refinement: *NRCCAD TRUANG*; data reduction: *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989) *DATRD2*;

program(s) used to solve structures: *NRCVAX SOLVER*; program(s) used to refine structures: *NRCVAX LSTSQ*; molecular graphics: *NRCVAX ORTEP*; software used to prepare material for publication: *NRCVAX TABLES*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: SZ1039). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tricoccin S_{43}

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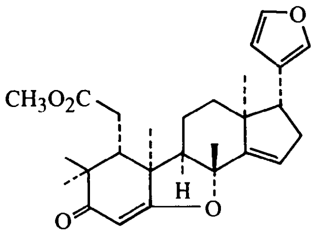
(Received 27 September 1994; accepted 1 February 1995)

Abstract

In methyl (1*S*,2*S*,8*S*,9*S*,10*S*,13*S*,17*S*)-17-(3-furyl)-2,2,8-trimethyl-3-oxo-6-oxa-7-norandrosta-4,14-dien-1-yl-methylcarboxylate, $C_{27}H_{34}O_5$, several C—C bonds and C—C—C angles deviate significantly from their expected values. The two six-membered rings, *A* and *C*, have slightly distorted sofa and boat conformations. Two of the five-membered rings, *B* and *D*, have half-chair and envelope conformations, and the terminal five-membered ring is nearly planar. The structure is stabilized by van der Waals interactions.

Comment

The title compound, (I), was isolated by Epe & Mondon (Herz, Grisebach & Kirby, 1983) from *Cneorum tricoccin L.*, a shrub with hairless leaves, yellow blossoms and red fruits, native to coastal areas of the western Mediterranean. Crystals were grown from ethanol–acetone solution at room temperature.



(I)

Several C—C bonds and C—C—C angles involved in the fused-ring systems deviate by more than 3σ from their expected values, presumably as a result of the strain introduced by axial substitutions with bulky groups (Hall & Maslen, 1965; Gzella, Zaprutko, Wrezciono & Jaskolski, 1987; Sekar, Parthasarathy, Kundu & Barik, 1992, 1993). Ring *A* has a slightly distorted sofa conformation with a mean torsion angle of 23.5 (7)°. The ring puckering is pronounced near atom C5 and less so near C2. Ring *B* has a half-chair conformation and ring *C* has a slightly distorted boat conformation with a mean torsion angle of 37.2 (6)°. The puckering is high at atom C11 and low at C14. Ring *D* has an envelope conformation. Ring *E* is planar within the 4σ level. The structure is stabilized by van der Waals forces.

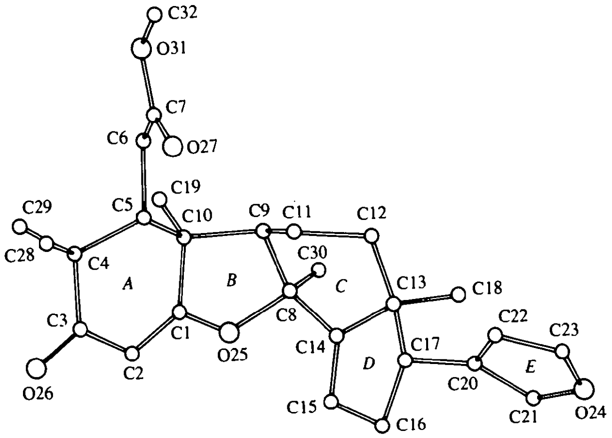


Fig. 1. A perspective view of the title molecule with the atom numbering and ring labels indicated.

Experimental

Crystal data

$C_{27}H_{34}O_5$ | Cu *K*α radiation
M_r = 438.56 | λ = 1.5418 Å

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‡ Contribution No. 850.

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