Data collection

Enraf-Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
5324 measured reflections
2379 independent reflections
1337 observed reflections [$I > 3.0\sigma(I)$]
$R_{\rm int}$ = 0.11
$\theta_{\rm max}$ = 22.98°
$h = 0 \rightarrow 16$
$k = -7 \rightarrow 7$
$l = -21 \rightarrow 21$
3 standard reflections
frequency: 180 min
intensity variation: 1.17%

Refinement

Refinement on F
R = 0.060
wR = 0.074
S = 1.095
1337 reflections
254 parameters
H atoms refined with U = 1.3 × U of bonded atom
$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0121F_o^4]$
$(\Delta/\sigma)_{\rm max}$ = 0.001
$\Delta\rho_{\rm max}$ = 0.3639 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.2917 e Å^{-3}
Extinction correction: isotropic (Zachariasen, 1963)
Extinction coefficient: 0.77 × 10^{-6}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Data collection: *CAD*-4 (Enraf-Nonius, 1977). Cell refinement: *SET*4 (de Boer & Duisenberg, 1984). Data reduction: *MolEN PROCESS* (Fair, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *MolEN LSFM*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *MolEN BTABLE PTABLE CIFIN*.

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

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

	x	y	z	$U_{\rm eq}$
O1	0.9411 (2)	−0.1286 (5)	0.0839 (2)	0.027 (2)
O2	1.1718 (2)	0.0764 (5)	0.1009 (2)	0.036 (2)
O3	0.9339 (2)	0.2599 (5)	0.0195 (1)	0.028 (1)
O4	0.8296 (2)	0.2229 (5)	0.1386 (2)	0.031 (1)
O5	0.7939 (2)	0.5436 (6)	0.1825 (2)	0.047 (2)
C1	0.9601 (3)	−0.0146 (8)	0.1508 (2)	0.028 (2)
C2	1.0385 (3)	−0.0767 (7)	0.1229 (2)	0.024 (2)
C3	1.0869 (3)	0.0873 (7)	0.0932 (2)	0.024 (2)
C4	1.0323 (3)	0.2861 (8)	0.0627 (2)	0.030 (2)
C5	0.9535 (3)	0.3419 (7)	0.0911 (2)	0.025 (2)
C6	0.9313 (3)	0.2167 (7)	0.1484 (2)	0.022 (2)
C7	0.9785 (3)	0.3213 (8)	0.2226 (2)	0.032 (2)
C8	0.9040 (4)	0.306 (1)	0.2591 (3)	0.048 (3)
C9	0.8118 (3)	0.3277 (9)	0.1972 (3)	0.039 (2)
O1′	0.6250 (2)	0.3333 (5)	−0.0988 (2)	0.034 (2)
O2′	0.7773 (2)	0.5187 (6)	−0.1948 (2)	0.056 (2)
O3′	0.5532 (2)	0.6886 (5)	−0.1832 (2)	0.030 (2)
O4′	0.5521 (2)	0.6973 (5)	−0.0313 (1)	0.024 (1)
O5′	0.6062 (2)	0.5664 (5)	0.0865 (2)	0.030 (2)
C1′	0.6794 (3)	0.4804 (8)	−0.0478 (2)	0.029 (2)
C2′	0.7162 (3)	0.4002 (8)	−0.1040 (3)	0.036 (2)
C3′	0.7179 (3)	0.5387 (8)	−0.1647 (2)	0.033 (2)
C4′	0.6518 (3)	0.7253 (8)	−0.1804 (2)	0.030 (2)
C5′	0.6149 (3)	0.8038 (7)	−0.1237 (2)	0.022 (2)
C6′	0.6399 (3)	0.7030 (7)	−0.0504 (2)	0.021 (2)
C7′	0.7090 (3)	0.8429 (8)	0.0086 (2)	0.030 (2)
C8′	0.6522 (3)	0.9112 (8)	0.0568 (2)	0.030 (2)
C9′	0.5729 (3)	0.7470 (7)	0.0435 (2)	0.027 (2)

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71582 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR1079]

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Dimethyl 9-[(*S*)-(−)-*N*-Acetylalanyloxy]methyl-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate

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Abstract

The molecule of $C_{26}H_{25}NO_7$ has normal dimensions, with the carboxymethyl group that is remote from the 9-substituent conjugated with the C11=C12 double bond and the adjacent carboxymethyl group out of conjugation. Molecules are linked by N—H···O hydrogen bonds.

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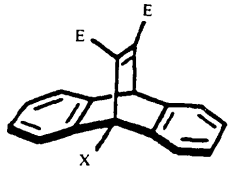
Comment

The structure of (I) was determined as part of a study of asymmetric induction in di-π-methane rearrangements.



(I)

E = CO_2Me
(−)
X = $CH_2OCOCH(Me)NHCOMe$

The molecule has normal geometry and dimensions (Pokkuluri, Scheffer & Trotter, 1993). The carboxymethyl group remote from the 9-substituent is conjugated with the C11=C12 double bond [C11—C12—C15—O4 = −13.9 (6)°, $\cos^2$(angle) = 0.94]; the group adjacent to the 9-substituent is out of conjugation [C12—C11—C13—O2 = 114.4 (4)°, $\cos^2$(angle) = 0.17]. The difference is not reflected in the C—CO_2Me bond lengths, which are essentially equal [1.488 (5) and 1.481 (5) Å]. The difference in orientation of the two ester groups is presumably a result of steric repulsion between the non-conjugated group and the adjacent bulky 9-substituent. In additon, this ester group is also involved in an intermolecular hydrogen bond, N—H···O2$(1-x, \frac{1}{2}+y, \frac{1}{2}-z)$: N···O = 3.014 (5), N—H = 0.92 (6), H···O = 2.22 (6) Å, N—H···O = 143°.

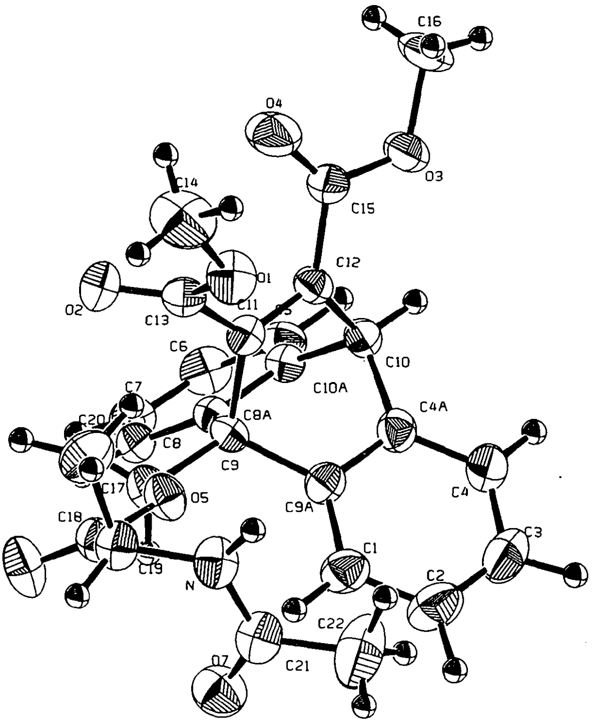


Fig. 1. View of the molecule with 50% probability ellipsoids.

Experimental

Crystal data

$C_{26}H_{25}NO_7$
$M_r = 463.49$
Orthorhombic
$P2_12_12_1$
$a = 18.914$ (4) Å
$b = 14.345$ (1) Å
$c = 8.622$ (1) Å
$V = 2339.3$ (5) Å^3
$Z = 4$
$D_x = 1.32$ Mg m^{-3}
Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å

Cell parameters from 25 reflections
$\theta = 25$–$39°$
$\mu = 0.76$ mm^{-1}
$T = 294$ K
Prism
0.30 × 0.30 × 0.20 mm
Colourless
Crystal source: Chen, Garcia-Garibay & Scheffer (1989)

Data collection

Rigaku AFC-6 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
($T_{\min} = 0.97$, $T_{\max} = 1.00$)
2818 measured reflections
2818 independent reflections
1941 observed reflections
[$I > 3\sigma(I)$]

$\theta_{\max} = 77.6°$
$h = 0 \rightarrow 23$
$k = 0 \rightarrow 18$
$l = 0 \rightarrow 10$
3 standard reflections monitored every 150 reflections
intensity variation: none

Refinement

Refinement on F
$R = 0.038$
$wR = 0.048$
$S = 1.39$
1941 reflections
308 + 100 H parameters
H-atoms refined isotropically
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\max} = 0.02$
$\Delta\rho_{\max} = 0.14$ e Å^{-3}
$\Delta\rho_{\min} = -0.18$ e Å^{-3}

Extinction correction: *TEXSAN* (Molecular Structure Corporation, 1990)
Extinction coefficient: 0.31×10^{-5}
Atomic scattering factors from *TEXSAN*
Absolute configuration: from the known configuration of (*S*)-(−)-alanine (Chen, Garcia-Garibay & Scheffer, 1989)

Data collection, cell refinement, data reduction, structure solution and refinement, and graphical representation were carried out using *TEXSAN* (Molecular Structure Corporation, 1990). The structure was determined by direct methods.

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

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

	x	y	z	U_{eq}
O1	0.4373 (1)	0.8802 (2)	0.3912 (3)	0.051
O2	0.4954 (1)	0.7561 (2)	0.2954 (4)	0.047
O3	0.2430 (1)	0.7351 (2)	0.4978 (3)	0.045
O4	0.3590 (2)	0.7364 (3)	0.5407 (3)	0.071
O5	0.4698 (1)	0.8912 (2)	0.0103 (3)	0.038
O6	0.5708 (1)	0.8678 (2)	−0.1203 (4)	0.054
O7	0.4678 (2)	1.0537 (2)	−0.2248 (4)	0.057
N	0.4971 (2)	1.0768 (2)	0.0231 (5)	0.046
C1	0.3176 (2)	0.9146 (3)	−0.1197 (5)	0.046
C2	0.2563 (3)	0.9619 (3)	−0.1560 (6)	0.061
C3	0.1928 (3)	0.9383 (3)	−0.0867 (6)	0.062
C4	0.1898 (2)	0.8668 (3)	0.0207 (5)	0.049

C4*A*	0.2512 (2)	0.8193 (2)	0.0600 (4)	0.037
C5	0.2550 (2)	0.5724 (3)	0.0490 (5)	0.040
C6	0.2893 (2)	0.5073 (3)	−0.0439 (5)	0.045
C7	0.3539 (2)	0.5283 (3)	−0.1098 (5)	0.043
C8	0.3852 (2)	0.6152 (3)	−0.0891 (4)	0.035
C8*A*	0.3511 (2)	0.6800 (2)	0.0015 (4)	0.030
C9	0.3765 (2)	0.7799 (2)	0.0388 (4)	0.030
C9*A*	0.3155 (2)	0.8430 (2)	−0.0113 (4)	0.035
C10	0.2573 (2)	0.7377 (3)	0.1693 (4)	0.034
C10*A*	0.2865 (2)	0.6582 (2)	0.0719 (4)	0.031
C11	0.3774 (2)	0.7845 (2)	0.2163 (4)	0.031
C12	0.3159 (2)	0.7603 (2)	0.2841 (4)	0.032
C13	0.4430 (2)	0.8039 (3)	0.3044 (4)	0.036
C14	0.4909 (3)	0.8921 (6)	0.5077 (7)	0.074
C15	0.3098 (2)	0.7451 (3)	0.4543 (4)	0.038
C16	0.2318 (3)	0.7165 (5)	0.6616 (5)	0.058
C17	0.4468 (2)	0.7992 (3)	−0.0386 (5)	0.037
C18	0.5339 (2)	0.9173 (3)	−0.0420 (5)	0.039
C19	0.5558 (2)	1.0122 (3)	0.0139 (5)	0.041
C20	0.5904 (3)	1.0055 (4)	0.1718 (6)	0.060
C21	0.4580 (2)	1.0946 (3)	−0.1027 (5)	0.047
C22	0.4005 (4)	1.1653 (5)	−0.084 (1)	0.082

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

C1—C2	1.379 (6)	C11—C12	1.347 (5)
C1—C9*A*	1.389 (5)	C11—C13	1.481 (5)
C2—C3	1.384 (7)	C12—C15	1.488 (5)
C3—C4	1.383 (7)	C18—C19	1.502 (5)
C4—C4*A*	1.388 (5)	C19—C20	1.514 (6)
C4*A*—C9*A*	1.404 (5)	C21—C22	1.496 (7)
C4*A*—C10	1.507 (5)	C19—N	1.448 (5)
C5—C6	1.391 (6)	C21—N	1.337 (5)
C5—C10*A*	1.382 (5)	C13—O1	1.330 (5)
C6—C7	1.381 (6)	C13—O2	1.208 (4)
C7—C8	1.392 (5)	C14—O1	1.437 (6)
C8—C8*A*	1.375 (5)	C15—O3	1.326 (4)
C8*A*—C9	1.545 (4)	C15—O4	1.199 (4)
C8*A*—C10*A*	1.400 (4)	C16—O3	1.453 (5)
C9—C9*A*	1.529 (5)	C17—O5	1.452 (4)
C9—C11	1.532 (5)	C18—O5	1.347 (4)
C9—C17	1.513 (5)	C18—O6	1.203 (5)
C10—C10*A*	1.520 (5)	C21—O7	1.219 (5)
C10—C12	1.521 (5)		
C2—C1—C9*A*	119.5 (4)	C8*A*—C10*A*—C10	112.9 (3)
C1—C2—C3	120.8 (4)	C9—C11—C12	114.4 (3)
C2—C3—C4	120.4 (4)	C9—C11—C13	122.0 (3)
C3—C4—C4*A*	119.5 (4)	C12—C11—C13	123.3 (3)
C4—C4*A*—C9*A*	119.9 (3)	C10—C12—C11	113.7 (3)
C4—C4*A*—C10	126.7 (3)	C10—C12—C15	123.6 (3)
C9A—C4*A*—C10	113.3 (3)	C11—C12—C15	122.2 (3)
C6—C5—C10*A*	118.6 (3)	C11—C13—O1	112.0 (3)
C5—C6—C7	120.2 (4)	C11—C13—O2	123.2 (3)
C6—C7—C8	121.3 (4)	O1—C13—O2	124.7 (3)
C7—C8—C8*A*	118.6 (3)	C12—C15—O3	111.6 (3)
C8—C8*A*—C9	126.8 (3)	C12—C15—O4	124.6 (4)
C8—C8*A*—C10*A*	120.3 (3)	O3—C15—O4	123.6 (3)
C9—C8*A*—C10*A*	112.9 (3)	C9—C17—O5	107.6 (3)
C8*A*—C9—C9*A*	104.8 (3)	C19—C18—O5	113.1 (3)
C8*A*—C9—C11	104.6 (3)	C19—C18—O6	123.7 (3)
C8*A*—C9—C17	110.6 (3)	O5—C18—O6	123.1 (3)
C9*A*—C9—C11	105.4 (3)	C18—C19—C20	110.5 (4)
C9*A*—C9—C17	115.5 (3)	C18—C19—N	112.7 (3)
C11—C9—C17	115.0 (3)	C20—C19—N	108.8 (4)
C1—C9*A*—C4*A*	119.9 (3)	C22—C21—N	116.4 (5)
C1—C9*A*—C9	127.3 (3)	C22—C21—O7	122.0 (5)
C4*A*—C9*A*—C9	112.7 (3)	N—C21—O7	121.6 (4)
C4*A*—C10—C10*A*	105.4 (3)	C19—N—C21	120.1 (4)
C4*A*—C10—C12	107.3 (3)	C13—O1—C14	115.7 (4)
C10*A*—C10—C12	104.8 (3)	C15—O3—C16	115.7 (3)
C5—C10*A*—C8*A*	120.9 (3)	C17—O5—C18	115.2 (3)
C5—C10*A*—C10	126.2 (3)		

We thank the Natural Sciences and Engineering Research Council of Canada for financial support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and stereo molecular and packing diagrams have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71586 (31 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: BR1047]

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Pokkuluri, P. R., Scheffer, J. R. & Trotter, J. (1993). *Acta Cryst.* **B49**, 107-116.

Acta Cryst. (1994). **C50**, 278–281

Structure of a Mixed Crystal of α- and β-Pipitzol (1:1), $C_{15}H_{20}O_3.C_{15}H_{20}O_3$

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Abstract

The structure of a mixed crystal (1:1, space group $P1$) of α- and β-pipitzol {[3*R*-(3α,3aβ,7β,8aα)]- and [3*R*-(3α,3aα,7α,8aβ)]-1,2,3,7,8,8a-hexahydro-5-hydroxy-3,6,8,8-tetramethyl-4*H*-3a,7-methanoazulene-4,9-dione} is described. The two molecules are enantiomeric at three C centres, but have the same (*R*) configuration at one C atom and are linked into α/β pairs about pseudo centres of symmetry by O—H· · ·O hydrogen bonds.

Comment

Pipitzol is isolated from the roots of *Perezia michoacana* as a mixture of the α and β diastereoisomers. The material is formed from the sesquiterpene quinone, perezone, which has a single chiral centre (Sánchez, Basurto & Joseph-Nathan, 1984). Intramolecular addition of the side-chain double bond of perezone onto the two faces of the quinone gives rise to the pipitzols, while generating three additional chiral centres. Thus α- and β-pipitzol are enantiomeric at three centres, but have the same configuration at C3. Crystal structures have been determined for several derivatives, in particular a mixed crystal (1:1) of the acetates of the α- and β-isomers (see Soriano-

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