C(25)	0.7202 (3)	0.3752 (1)	0.4327 (5)	0.065 (1)
C(26)	0.6164 (4)	0.3587 (1)	0.3629 (6)	0.091 (2)
C(27)	0.7772 (4)	0.4109 (1)	0.3530 (7)	0.081 (2)
C(28)	0.7314 (4)	0.3321 (1)	0.8404 (6)	0.087 (2)
C(29)	0.6898 (5)	0.2943 (2)	0.9352 (6)	0.132 (2)
C(30)	0.6637 (5)	0.3716 (2)	0.8754 (6)	0.125 (2)
C(31)	0.7805 (5)	0.4570 (2)	0.1330 (8)	0.154 (3)

† Partial occupancy (see below).

Table 2. *Geometry of hydrogen bonds and C—H···O interactions (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C(6)—H(4)···O(3*$^{\text{i}}$)	0.98	2.46	3.25 (3)	138
C(11)—H(11)···O(1)	0.98	2.51	3.122 (5)	120
N(3)—H(20)···N(2)	0.76 (4)	2.28 (4)	2.644 (5)	110 (4)
C(16)—H(21)···O(1)	0.98	2.48	2.805 (5)	99
C(20)—H(26)···O(2)	0.98	2.42	3.025 (5)	120
C(23)—H(34)···O(2)	0.98	2.22	2.706 (4)	109
C(24)—H(35)···O(3)	0.98	2.45	2.82 (1)	102
C(24)—H(35)···O(3*)	0.98	2.45	2.77 (3)	98
C(26)—H(37)···O(4)	0.98	2.22	2.713 (5)	109
C(30)—H(43)···O(4$^{\text{ii}}$)	0.98	2.52	3.427 (6)	154

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

Table 3. *Summary of bond lengths (Å)*

Bond type	Range	Mean
$C—C_{\text{aromatic}}$	1.364 (6)–1.405 (5)	1.383 (7)
$C=C$	1.318 (5)–1.355 (5)	1.337 (7)
$C—C_{\text{aliphatic}}$	1.516(7)–1.568 (5)	1.534 (6)
$C_{sp^2}—C_{sp^2}$	1.450 (6)–1.481 (6)	1.466 (8)
$C_{sp^3}—C_{sp^2}$	1.489 (5)–1.532 (5)	1.513 (6)
$N—C_{sp^2}$	1.367 (5)–1.369 (5)	1.368 (7)
$N—C_{sp^3}$	1.449 (5)–1.474 (4)	1.461 (5)
$O=C$	1.22 (1)–1.232 (5)	1.23 (1)
$O—C_{\text{carboxylate}}$	1.307 (5)	
$O—C_{\text{ester}}$	1.452 (6)	

The structure was solved by direct methods using *SIR*92 (Altomare *et al.*, 1994) and expanded using Fourier techniques (Beurskens *et al.*, 1994). All calculations were performed using *TEXSAN* (Molecular Structure Corporation, 1992) and *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988) was used for data collection and cell refinement. The amine H atoms were refined with isotropic displacement parameters. The remaining H atoms were fixed in calculated positions (methyl groups staggered, with C—H 0.98 Å and displacement parameters 20% larger than those of the parent atoms). The partial disorder of the crystal structure involves the carbonyl O(3) atom of the ester fragment. The occupancies of the two positions were adjusted as the refinement progressed to yield approximately equal displacement parameters, the final values being 0.71 and 0.29 for O(3) and O(3*), respectively. The absolute configuration was based on the known chiralities of two centers. A parallel refinement of the opposite enantiomer gave slightly higher residuals (R = 0.0392 and wR = 0.0376).

Financial support was provided by a grant to RJA from the National Cancer Institute of Canada.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, including torsion angles and contact distances, have been deposited with the IUCr (Reference: FG1120). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Humilinolide D

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Abstract

The title molecule, methyl α,10-bis(acetoxy)-4-(3-furanyl)-1,4,4a,5,6,6a,7,8,9,10,11,12b-dodecahydro-11-hydroxy-4a,7,9,9-tetramethyl-2,13-dioxo-7,11-methano-2*H*-cycloocta[*f*][2]benzopyran-8-acetate, $C_{31}H_{38}O_{11}$, consists of four six-membered rings (*A*, *B*, *C* and *D*) and a five-membered furan ring (*E*). The *A* ring is fused at C(2)—C(1)—C(10) to the *B* ring. The *B*/*C* and *C*/*D* rings are *trans-* and *cis-*fused, respectively. Rings *A*, *B*, *C* and *D* adopt conformations intermediate between twist $^2T_4$ and boat $B_{4,1}$, intermediate between half-chair $^1H_6$ and envelope ^1E, distorted chair $^1C_4$ and half-chair

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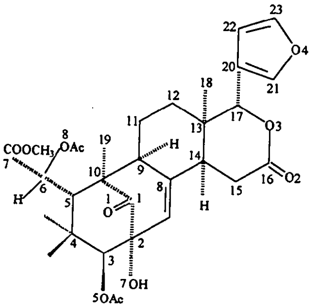
$^6H_1$, respectively. The crystal structure is stabilized by an intermolecular O—H···O hydrogen bond, three C—H···O intermolecular hydrogen bonds and van der Waals interactions.

Comment

Humilinolide D, (I), is a tetranotriterpenoid which was isolated from the seeds of *Swietenia humilis* (*Meliaceae*). Details of the source and chemical background of humilinolide D are given by Segura-Correa, Mata, Anaya, Hernández-Bautista, Villena, Soriano-García, Bye & Linares (1993).



(I)

The absolute configuration of the title compound is inferred from the known stereochemistry of humilinolide A (Segura-Correa *et al.*, 1993) deduced from chemical and X-ray studies. The Cremer & Pople (1975) ring-puckering parameters for the *A*, *B*, *C* and *D* rings are, respectively, q_2 = 0.792 (7), q_3 = 0.015 (6), Q = 0.792 (7) Å, θ = 88.9 (5), φ = −162.0 (5)°; q_2 = 0.474 (7), q_3 = 0.343 (7), Q = 0.585 (7) Å, θ = 54.1 (7), φ = −23.3 (9)°; q_2 = 0.030 (7), q_3 = 0.518 (7), Q = 0.518 (7) Å, θ = 3.3 (8), φ = −154.5 (12)°; q_2 = 0.283 (7), q_3 = −0.427 (6), Q = 0.512 (7) Å, θ = 146.4 (8), φ = 155.3 (1)°. The crystal structure is stabilized by an intermolecular hydrogen bond between the O(7)—H hydroxy group and the O(9) carbonyl group [H(7*A*)···O(9^{i}) 2.2 (7), O(7)···O(9^{i}) 2.815 (7) Å and O(7)—H···O(9^{i}) 146 (7)°; symmetry code: (i) $x-\frac{1}{2}$, $\frac{1}{2}-y$, $-z$]. There are three C—H···O interactions shorter than 3.5 Å: C(23)···O(2^{ii}) 3.292 (11), C(25)···O(7^{iii}) 3.367 (11) and C(31)···O(6^{iii}) 3.310 (12) Å [symmetry codes: (ii) $\frac{1}{2}+x$, $\frac{3}{2}-y$, $-z$; (iii) $-\frac{1}{2}-x$, $1-y$, $-\frac{1}{2}+z$].

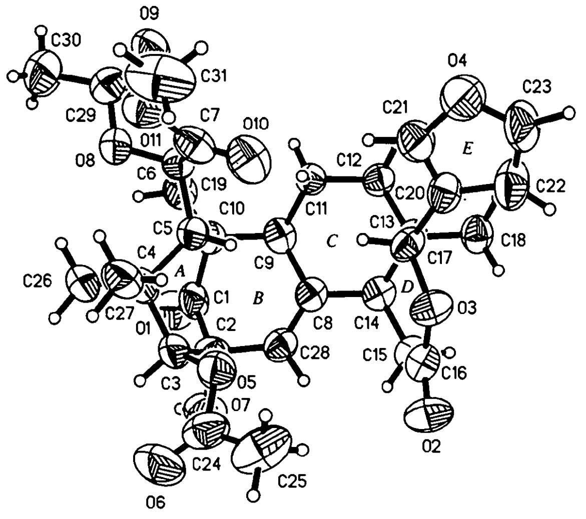


Fig. 1. The molecular structure of the title compound showing the atom labelling. Ellipsoids are plotted at the 50% probability level.

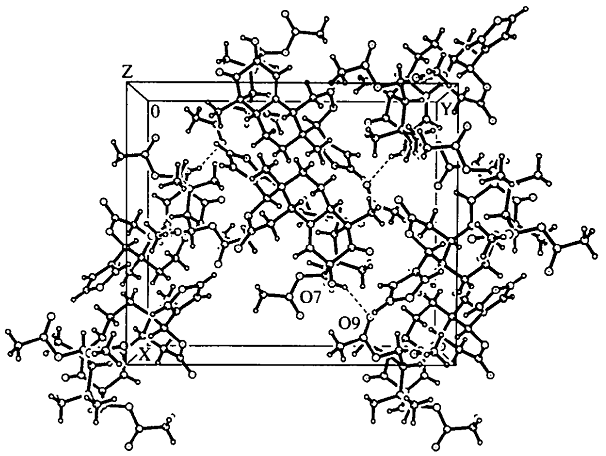


Fig. 2. A perspective drawing of the packing arrangement of the title compound. The dashed lines indicate the intermolecular hydrogen bonding.

Experimental

Crystal data

$C_{31}H_{38}O_{11}$
M_r = 586.63
Orthorhombic
$P2_12_12_1$
a = 14.510 (1) Å
b = 17.248 (1) Å
c = 11.908 (2) Å
V = 2980 (1) Å^3
Z = 4
D_x = 1.307 Mg m^{-3}

Cu $K\alpha$ radiation
λ = 1.54184 Å
Cell parameters from 25 reflections
θ = 32.7–40.0°
μ = 0.83 mm^{-1}
T = 296 K
Prism
0.40 × 0.33 × 0.22 mm
Colourless

Data collection

Rigaku AFC-5*R* diffractometer
ω scans
Absorption correction: ψ scan (North, Phillips & Mathews, 1968)
T_{min} = 0.94, T_{max} = 1.00
2551 measured reflections
2526 independent reflections

1854 observed reflections [$F > 4\sigma(F)$]
θ_{max} = 60.25°
$h = 0 \rightarrow 16$
$k = 0 \rightarrow 19$
$l = 0 \rightarrow 13$
3 standard reflections monitored every 150 reflections
intensity decay: 5%

Refinement

Refinement on F
$R = 0.0562$
$wR = 0.0651$
$S = 1.32$
1854 reflections
382 parameters
H atoms refined isotropically

$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\max} = 0.032$
$\Delta\rho_{\max} = 0.15$ e Å^{-3}
$\Delta\rho_{\min} = -0.21$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *SHELXTL-Plus* (Sheldrick, 1991)

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	$U_{\rm eq}$
O(1)	−0.1010 (4)	0.2521 (3)	0.1708 (5)	0.080 (2)
O(2)	−0.0912 (4)	0.6691 (3)	0.1978 (5)	0.081 (2)
O(3)	0.0317 (3)	0.6407 (3)	0.0996 (4)	0.061 (2)
O(4)	0.2552 (4)	0.6514 (3)	−0.1569 (5)	0.091 (2)
O(5)	−0.1966 (3)	0.4745 (3)	−0.0180 (5)	0.066 (2)
O(6)	−0.3502 (4)	0.4727 (4)	−0.0142 (8)	0.127 (4)
O(7)	−0.2200 (4)	0.3722 (3)	0.1980 (6)	0.084 (2)
O(8)	0.0067 (3)	0.2691 (3)	−0.2224 (4)	0.067 (2)
O(9)	0.1575 (3)	0.2486 (3)	−0.2525 (5)	0.081 (2)
O(10)	0.0473 (4)	0.4730 (3)	−0.2342 (5)	0.080 (2)
O(11)	0.0301 (4)	0.3792 (3)	−0.3649 (5)	0.079 (2)
C(1)	−0.0871 (5)	0.3082 (4)	0.1128 (7)	0.059 (3)
C(2)	−0.1488 (5)	0.3781 (4)	0.1158 (7)	0.061 (3)
C(3)	−0.1925 (5)	0.3919 (4)	−0.0003 (7)	0.062 (3)
C(4)	−0.1425 (5)	0.3509 (4)	−0.0981 (7)	0.058 (3)
C(5)	−0.0359 (5)	0.3605 (4)	−0.0735 (6)	0.051 (2)
C(6)	0.0285 (5)	0.3419 (4)	−0.1733 (5)	0.051 (2)
C(7)	0.0345 (5)	0.4064 (5)	−0.2618 (8)	0.063 (3)
C(8)	0.0021 (5)	0.4425 (3)	0.1603 (6)	0.047 (2)
C(9)	0.0578 (5)	0.3770 (4)	0.1086 (6)	0.052 (2)
C(10)	−0.0034 (5)	0.3201 (3)	0.0378 (6)	0.050 (2)
C(11)	0.1404 (4)	0.4083 (3)	0.0432 (6)	0.051 (2)
C(12)	0.1960 (4)	0.4667 (3)	0.1108 (6)	0.053 (2)
C(13)	0.1403 (5)	0.5340 (4)	0.1578 (6)	0.051 (2)
C(14)	0.0587 (5)	0.5020 (4)	0.2247 (6)	0.051 (2)
C(15)	0.0028 (5)	0.5682 (4)	0.2738 (6)	0.056 (2)
C(16)	−0.0252 (6)	0.6285 (4)	0.1894 (6)	0.059 (3)
C(17)	0.0980 (5)	0.5818 (4)	0.0617 (6)	0.052 (2)
C(18)	0.2025 (5)	0.5832 (4)	0.2328 (6)	0.061 (3)
C(19)	0.0459 (5)	0.2422 (4)	0.0221 (6)	0.062 (3)
C(20)	0.1660 (5)	0.6248 (4)	−0.0100 (6)	0.057 (3)
C(21)	0.1909 (6)	0.6032 (4)	−0.1138 (7)	0.070 (3)
C(22)	0.2166 (6)	0.6918 (4)	0.0127 (8)	0.084 (4)
C(23)	0.2699 (7)	0.7047 (5)	−0.0779 (8)	0.091 (4)
C(24)	−0.2803 (6)	0.5083 (5)	−0.0190 (8)	0.078 (4)
C(25)	−0.2720 (7)	0.5938 (5)	−0.0237 (7)	0.102 (4)
C(26)	−0.1747 (5)	0.2670 (4)	−0.1020 (8)	0.079 (3)
C(27)	−0.1692 (5)	0.3891 (5)	−0.2091 (7)	0.079 (3)
C(28)	−0.0892 (5)	0.4437 (4)	0.1578 (6)	0.056 (3)
C(29)	0.0808 (6)	0.2265 (5)	−0.2589 (7)	0.070 (3)
C(30)	0.0515 (7)	0.1520 (5)	−0.3074 (9)	0.127 (5)
C(31)	0.0441 (7)	0.4354 (6)	−0.4531 (7)	0.116 (5)

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

O(1)—C(1)	1.207 (9)	O(2)—C(16)	1.191 (10)
O(3)—C(16)	1.367 (9)	O(3)—C(17)	1.470 (8)
O(4)—C(21)	1.351 (10)	O(4)—C(23)	1.333 (11)
O(5)—C(3)	1.442 (8)	O(5)—C(24)	1.347 (10)
O(6)—C(24)	1.187 (11)	O(7)—C(2)	1.427 (10)
O(8)—C(6)	1.420 (8)	O(8)—C(29)	1.372 (10)
O(9)—C(29)	1.178 (10)	O(10)—C(7)	1.210 (10)
O(11)—C(7)	1.316 (11)	O(11)—C(31)	1.443 (11)
C(1)—C(2)	1.502 (10)	C(1)—C(10)	1.521 (10)
C(2)—C(3)	1.540 (12)	C(2)—C(28)	1.509 (10)
C(3)—C(4)	1.543 (11)	C(4)—C(5)	1.583 (9)
C(4)—C(26)	1.522 (10)	C(4)—C(27)	1.527 (11)
C(5)—C(6)	1.545 (9)	C(5)—C(10)	1.571 (9)
C(6)—C(7)	1.536 (11)	C(8)—C(9)	1.519 (9)
C(8)—C(14)	1.521 (9)	C(8)—C(28)	1.326 (10)
C(9)—C(10)	1.569 (9)	C(9)—C(11)	1.528 (9)
C(10)—C(19)	1.533 (9)	C(11)—C(12)	1.523 (9)
C(12)—C(13)	1.520 (9)	C(13)—C(14)	1.532 (9)
C(13)—C(17)	1.538 (9)	C(13)—C(18)	1.527 (10)
C(14)—C(15)	1.517 (9)	C(15)—C(16)	1.503 (10)
C(17)—C(20)	1.502 (10)	C(20)—C(21)	1.341 (11)
C(20)—C(22)	1.396 (11)	C(22)—C(23)	1.346 (13)
C(24)—C(25)	1.481 (12)	C(29)—C(30)	1.472 (12)
C(16)—O(3)—C(17)	122.0 (5)	C(14)—C(13)—C(17)	105.7 (5)
C(3)—O(5)—C(24)	117.7 (6)	C(14)—C(13)—C(18)	110.7 (6)
C(7)—O(11)—C(31)	115.6 (7)	C(8)—C(14)—C(13)	113.5 (5)
O(1)—C(1)—C(10)	125.2 (6)	C(13)—C(14)—C(15)	110.0 (5)
O(7)—C(2)—C(1)	113.0 (6)	O(2)—C(16)—O(3)	117.4 (7)
C(1)—C(2)—C(3)	110.3 (6)	O(3)—C(16)—C(15)	117.8 (6)
C(1)—C(2)—C(28)	105.5 (6)	O(3)—C(17)—C(20)	105.2 (5)
O(5)—C(3)—C(2)	107.5 (6)	C(17)—C(20)—C(21)	124.3 (6)
C(2)—C(3)—C(4)	114.4 (6)	C(21)—C(20)—C(22)	105.5 (7)
C(3)—C(4)—C(26)	108.3 (6)	C(20)—C(22)—C(23)	106.5 (8)
C(3)—C(4)—C(27)	109.6 (6)	O(5)—C(24)—O(6)	123.1 (8)
C(26)—C(4)—C(27)	107.8 (6)	O(6)—C(24)—C(25)	125.9 (9)
C(4)—C(5)—C(10)	113.8 (5)	O(8)—C(29)—O(9)	123.1 (7)
O(8)—C(6)—C(5)	111.5 (5)	O(9)—C(29)—C(30)	125.5 (8)
C(21)—O(4)—C(23)	105.5 (7)	O(10)—C(7)—O(11)	126.9 (8)
C(6)—O(8)—C(29)	115.5 (6)	O(11)—C(7)—C(6)	112.3 (7)
O(1)—C(1)—C(2)	122.1 (7)	C(9)—C(8)—C(28)	122.3 (6)
C(2)—C(1)—C(10)	112.5 (6)	C(8)—C(9)—C(10)	112.5 (5)
O(7)—C(2)—C(3)	109.2 (6)	C(10)—C(9)—C(11)	113.0 (6)
O(7)—C(2)—C(28)	104.0 (6)	C(1)—C(10)—C(9)	102.8 (5)
C(3)—C(2)—C(28)	114.7 (6)	C(1)—C(10)—C(19)	109.1 (5)
O(5)—C(3)—C(4)	111.2 (6)	C(9)—C(10)—C(19)	110.5 (5)
C(3)—C(4)—C(5)	105.8 (6)	C(11)—C(12)—C(13)	114.7 (5)
C(5)—C(4)—C(26)	113.9 (6)	C(12)—C(13)—C(17)	110.4 (5)
C(5)—C(4)—C(27)	111.3 (6)	C(12)—C(13)—C(18)	109.0 (5)
C(4)—C(5)—C(6)	115.3 (6)	C(17)—C(13)—C(18)	111.9 (5)
C(6)—C(5)—C(10)	112.0 (5)	C(8)—C(14)—C(15)	114.5 (6)
O(8)—C(6)—C(7)	111.8 (6)	C(14)—C(15)—C(16)	114.1 (6)
C(5)—C(6)—C(7)	114.3 (6)	O(2)—C(16)—C(15)	124.7 (7)
O(10)—C(7)—C(6)	120.7 (8)	O(3)—C(17)—C(13)	113.8 (5)
C(9)—C(8)—C(14)	114.8 (6)	C(13)—C(17)—C(20)	115.2 (6)
C(14)—C(8)—C(28)	122.7 (6)	C(17)—C(20)—C(22)	130.2 (7)
C(8)—C(9)—C(11)	111.2 (5)	O(4)—C(21)—C(20)	111.4 (7)
C(1)—C(10)—C(5)	108.3 (5)	O(4)—C(23)—C(22)	111.1 (8)
C(5)—C(10)—C(9)	110.2 (5)	O(5)—C(24)—C(25)	110.9 (7)
C(5)—C(10)—C(19)	115.2 (6)	C(2)—C(28)—C(8)	124.7 (6)
C(9)—C(11)—C(12)	112.3 (6)	O(8)—C(29)—C(30)	111.4 (7)
C(12)—C(13)—C(14)	109.1 (5)		

The H atoms of the CH and CH_2 groups were allowed to ride on their bonded C atoms and refined. The H atom bonded to atom O(7) was located on a difference Fourier map at an advanced stage of anisotropic refinement and its coordinates refined. The structure solution and refinement were carried out using *SHELXTL-Plus* (Sheldrick, 1991). *PARST* (Nardelli, 1983) was used for geometrical calculations.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SZ1030). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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