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16β-(Acetyloxy)-3β-[(2,6-dideoxy-3-*O*-methyl-L-*arabino*-hexopyranosyl)oxy]-14-hydroxycard-20(22)-enolide Dihydrate

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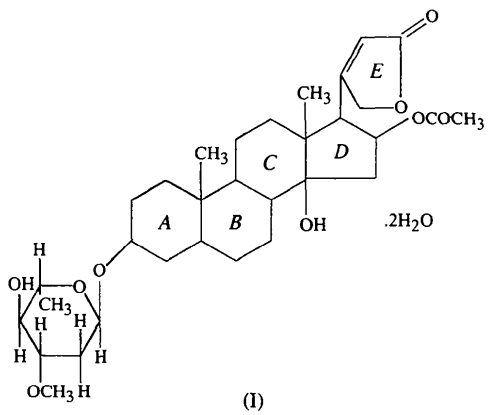
Abstract

In the title compound, $C_{32}H_{48}O_9.2H_2O$, all three six-membered rings of the cardenolide skeleton have chair conformations. The five-membered ring, the γ-lactone ring and the sugar ring adopt envelope, half-chair and envelope conformations, respectively. The crystal structure is stabilized by short C—H···O and O—H···O intramolecular hydrogen bonds. Several intermolecular interactions of the C—H···O type are also present.

Comment

The crystal and molecular structure of the title compound, (I), was investigated in order to determine the conformation and crystal packing, and also to confirm the stereochemistry of the molecule.



(I)

Bond distances and angles are quite similar to those of related compounds. The C(1)—C(2) and C(1)—C(6) bond distances are significantly shorter than the normal value of 1.533 Å for a C—C bond length in *n*-hydrocarbons (Bartell, 1959), but are in agreement with those of a previously reported structure (Soriano-García *et al.*, 1987). The molecules consist of three six-membered rings (*A*, *B* and *C*), one five-membered ring (*D*), a γ-lactone ring (*E*) and a sugar ring (*F*). The *A*/*B* and *C*/*D* ring junctions are *trans*. According to the torsion angle (Table 2) and puckering parameter values (φ_2, θ_2 and Q), the six-membered rings, *A*, *B* and *C*, occur in chair ($^1C_4$), chair ($^1C_4$), chair ($^4C_1$) conformations, respectively, while the *D*, *E* and *F* rings adopt envelope, half-chair and envelope (E_5) conformations, respectively (Boeyens, 1978).

The O—H···O hydrogen-bonding scheme is given in Table 3. The hydroxy groups interact with the water molecules, with O···O distances of 2.821 (5) and 2.741 (5) Å, respectively. One of the water molecules (*OW*1) participates in O—H···O hydrogen bonds with the hydroxy O1 and carbonyl O3 atoms, with O···O distances of 2.825 (5) and 2.847 (5) Å, respectively. The other water molecule (*OW*2) interacts with the O9 and O5 atoms, with O···O distances of 2.793 (5) and 2.837 (5) Å, respectively (Allen, Kennard & Taylor, 1983).

There is a short intramolecular C—H···O hydrogen bond (H17···O5 2.317, C17···O5 2.637 Å, C17—H17···O5 100.6°) which stabilizes the molecule internally. In addition, there are several C—H···O intermolecular interactions with C···O distances in the range 3.323–3.883 Å and C—H···O angles in the range

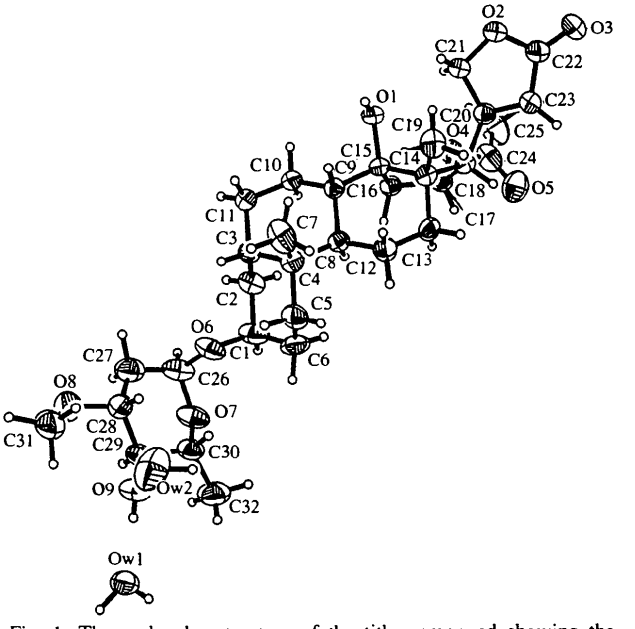


Fig. 1. The molecular structure of the title compound showing the atom-labelling scheme and 50% probability displacement ellipsoids.

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125.3–176.4°. These ranges are conventionally employed to characterize C—H···O hydrogen-bond interactions (Desiraju, 1991), some of which involve bifurcated-donor and/or bifurcated-acceptor atoms (Jeffrey & Saenger, 1991). The molecules in the crystal are stabilized through intermolecular hydrogen bonds forming a zigzag arrangement (Fig. 2).

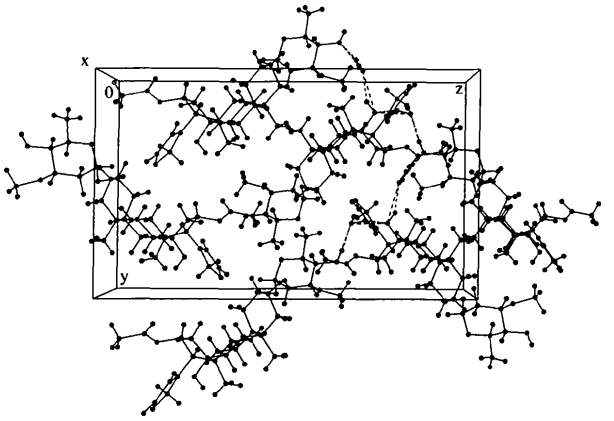

Fig. 2. A perspective drawing of the crystal packing showing the zigzag arrangement of molecules.

Experimental

Crystals of the title compound were obtained from a chloroform solution of commercially available material by slow evaporation of the solvent at room temperature.

Crystal data

$C_{32}H_{48}O_9.2H_2O$
M_r = 612.74
Orthorhombic
$P2_12_12_1$
a = 9.534 (4) Å
b = 14.283 (4) Å
c = 24.020 (5) Å
V = 3270.9 (18) Å^3
Z = 4
D_x = 1.244 Mg m^{-3}
Cu $K\alpha$ radiation
λ = 1.54178 Å
Cell parameters from 24 reflections
θ = 10–30°
μ = 0.765 mm^{-1}
T = 293 (2) K
Rectangular
0.25 × 0.22 × 0.18 mm
Colourless

Data collection

$P4$ diffractometer
$\theta/2\theta$ scans
Absorption correction: none
3221 measured reflections
3031 independent reflections
2942 observed reflections [$I > 2\sigma(I)$]
R_{int} = 0.0207
θ_{max} = 56.74°
$h = -1 \rightarrow 10$
$k = -1 \rightarrow 15$
$l = -1 \rightarrow 26$
3 standard reflections monitored every 200 reflections
intensity decay: 2.5%

Refinement

Refinement on F^2
$R(F)$ = 0.0383
$wR(F^2)$ = 0.1044
S = 1.109
3031 reflections
587 parameters
All H atoms refined isotropically
$w = 1/[\sigma^2(F_o^2) + (0.0602P)^2 + 0.9230P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.039
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: taken from the sugar substituent

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

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

	x	y	z	U_{eq}
C1	0.6945 (5)	1.0205 (2)	0.9269 (2)	0.0577 (10)
C2	0.7075 (5)	0.9425 (3)	0.88465 (15)	0.0490 (8)
C3	0.6755 (3)	0.8464 (2)	0.90966 (13)	0.0399 (7)
C4	0.5298 (4)	0.8407 (2)	0.93757 (12)	0.0406 (7)
C5	0.5179 (5)	0.9245 (3)	0.97887 (14)	0.0557 (9)
C6	0.5519 (5)	1.0190 (3)	0.9534 (2)	0.0627 (11)
C7	0.5201 (5)	0.7510 (3)	0.9725 (2)	0.0641 (11)
C8	0.4129 (3)	0.8427 (2)	0.89253 (11)	0.0348 (7)
C9	0.4326 (3)	0.7636 (2)	0.84925 (12)	0.0332 (6)
C10	0.5773 (3)	0.7685 (2)	0.82258 (14)	0.0398 (7)
C11	0.6937 (4)	0.7684 (3)	0.8664 (2)	0.0489 (9)
C12	0.2648 (4)	0.8391 (3)	0.91652 (13)	0.0469 (8)
C13	0.1526 (4)	0.8416 (3)	0.87126 (13)	0.0423 (7)
C14	0.1646 (3)	0.7592 (2)	0.82979 (12)	0.0357 (7)
C15	0.3153 (3)	0.7592 (2)	0.80554 (11)	0.0317 (6)
C16	0.3139 (3)	0.8404 (2)	0.76382 (12)	0.0367 (7)
C17	0.1622 (3)	0.8528 (2)	0.74509 (12)	0.0354 (7)
C18	0.0702 (3)	0.7837 (2)	0.77847 (12)	0.0361 (7)
C19	0.1203 (4)	0.6674 (3)	0.8587 (2)	0.0489 (8)
C20	0.0112 (3)	0.7048 (2)	0.74396 (12)	0.0388 (7)
C21	0.0883 (4)	0.6266 (3)	0.7151 (2)	0.0471 (8)
C22	−0.1445 (4)	0.6140 (2)	0.69534 (15)	0.0499 (8)
C23	−0.1239 (4)	0.6955 (2)	0.73134 (14)	0.0460 (8)
C24	0.0452 (5)	0.8772 (3)	0.6591 (2)	0.0613 (10)
C25	0.0482 (7)	0.8570 (5)	0.5982 (2)	0.096 (2)
C26	0.9189 (5)	1.0643 (3)	0.9645 (2)	0.0605 (11)
C27	1.0370 (5)	1.0244 (3)	0.9983 (2)	0.0648 (11)
C28	1.0235 (4)	1.0376 (3)	1.0598 (2)	0.0542 (9)
C29	0.9832 (4)	1.1389 (2)	1.07300 (15)	0.0513 (9)
C30	0.8562 (4)	1.1663 (2)	1.03938 (14)	0.0507 (9)
C31	1.1538 (6)	0.9830 (3)	1.1403 (2)	0.0815 (14)
C32	0.8039 (7)	1.2650 (3)	1.0485 (2)	0.0791 (14)
O1	0.3358 (2)	0.67634 (14)	0.77133 (8)	0.0370 (5)
O2	−0.0195 (3)	0.5748 (2)	0.68516 (10)	0.0524 (6)
O3	−0.2511 (3)	0.5805 (2)	0.67625 (13)	0.0695 (8)
O4	0.1526 (2)	0.8365 (2)	0.68553 (8)	0.0455 (5)
O5	−0.0389 (4)	0.9254 (2)	0.6832 (2)	0.0885 (10)
O6	0.7995 (3)	1.0072 (2)	0.97005 (10)	0.0575 (7)
O7	0.8869 (3)	1.1585 (2)	0.98078 (9)	0.0623 (7)
O8	1.1560 (3)	1.0090 (2)	1.0837 (2)	0.0811 (9)
O9	0.9554 (3)	1.1472 (2)	1.13076 (10)	0.0608 (7)
OW1	1.0121 (4)	1.3232 (2)	1.17041 (11)	0.0624 (7)
OW2	0.8200 (4)	1.0131 (2)	1.1962 (2)	0.0989 (13)

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

C1—O6	1.454 (5)	C17—O4	1.452 (4)
C1—C6	1.501 (6)	C17—C18	1.544 (4)
C1—C2	1.511 (5)	C18—C20	1.508 (4)
C2—C3	1.530 (5)	C20—C23	1.330 (5)
C3—C11	1.533 (4)	C20—C21	1.505 (5)
C3—C4	1.545 (5)	C21—O2	1.457 (4)
C4—C7	1.535 (5)	C22—O3	1.213 (5)
C4—C8	1.553 (4)	C22—O2	1.339 (4)
C4—C5	1.559 (5)	C22—C23	1.463 (5)
C5—C6	1.517 (6)	C24—O5	1.206 (5)
C8—C12	1.526 (4)	C24—O4	1.337 (5)
C8—C9	1.546 (4)	C24—C25	1.491 (6)
C9—C10	1.523 (4)	C26—O6	1.406 (5)

C9—C15	1.535 (4)	C26—O7	1.435 (5)
C10—C11	1.529 (5)	C26—C27	1.500 (6)
C12—C13	1.525 (5)	C27—C28	1.497 (6)
C13—C14	1.546 (4)	C28—O8	1.446 (5)
C14—C19	1.543 (4)	C28—C29	1.530 (5)
C14—C15	1.551 (4)	C29—O9	1.418 (4)
C14—C18	1.566 (4)	C29—C30	1.507 (5)
C15—O1	1.454 (3)	C30—O7	1.442 (4)
C15—C16	1.532 (4)	C30—C32	1.511 (6)
C16—C17	1.526 (4)	C31—O8	1.409 (6)
O6—C1—C6	108.6 (3)	C17—C16—C15	106.8 (2)
O6—C1—C2	109.0 (3)	O4—C17—C16	109.4 (2)
C6—C1—C2	110.3 (3)	O4—C17—C18	111.9 (2)
C1—C2—C3	112.5 (3)	C16—C17—C18	108.1 (2)
C2—C3—C11	111.3 (3)	C20—C18—C17	113.8 (2)
C2—C3—C4	113.3 (3)	C20—C18—C14	118.7 (2)
C11—C3—C4	111.0 (3)	C17—C18—C14	103.0 (2)
C7—C4—C3	109.6 (3)	C23—C20—C21	107.1 (3)
C7—C4—C8	110.6 (3)	C23—C20—C18	124.1 (3)
C3—C4—C8	110.0 (2)	C21—C20—C18	128.7 (3)
C7—C4—C5	106.8 (3)	O2—C21—C20	105.1 (3)
C3—C4—C5	107.6 (3)	O3—C22—O2	120.8 (3)
C8—C4—C5	112.2 (3)	O3—C22—C23	130.4 (3)
C6—C5—C4	114.2 (3)	O2—C22—C23	108.8 (3)
C1—C6—C5	112.2 (3)	C20—C23—C22	110.1 (3)
C12—C8—C9	110.0 (3)	O5—C24—O4	121.9 (4)
C12—C8—C4	113.6 (2)	O5—C24—C25	126.5 (4)
C9—C8—C4	111.6 (2)	O4—C24—C25	111.5 (5)
C10—C9—C15	112.0 (2)	O6—C26—O7	110.2 (3)
C10—C9—C8	111.0 (2)	O6—C26—C27	109.6 (3)
C15—C9—C8	113.7 (2)	O7—C26—C27	111.6 (3)
C9—C10—C11	111.6 (3)	C28—C27—C26	115.0 (4)
C10—C11—C3	112.6 (3)	O8—C28—C27	106.3 (3)
C8—C12—C13	112.3 (2)	O8—C28—C29	113.9 (3)
C12—C13—C14	112.9 (3)	C27—C28—C29	110.2 (3)
C19—C14—C13	109.7 (3)	O9—C29—C30	110.7 (3)
C19—C14—C15	115.0 (3)	O9—C29—C28	109.2 (3)
C13—C14—C15	108.1 (2)	C30—C29—C28	109.7 (3)
C19—C14—C18	112.8 (3)	O7—C30—C29	109.9 (3)
C13—C14—C18	107.2 (2)	O7—C30—C32	106.2 (3)
C15—C14—C18	103.7 (2)	C29—C30—C32	115.5 (3)
O1—C15—C16	104.3 (2)	C22—O2—C21	109.0 (2)
O1—C15—C9	108.8 (2)	C24—O4—C17	116.5 (3)
C16—C15—C9	115.0 (2)	C26—O6—C1	114.4 (3)
O1—C15—C14	109.7 (2)	C26—O7—C30	112.4 (3)
C16—C15—C14	103.7 (2)	C31—O8—C28	116.3 (4)
C9—C15—C14	114.7 (2)		

C6—C1—C2—C3	−55.3 (4)	C18—C14—C15—C16	37.9 (3)
C1—C2—C3—C4	55.8 (4)	C13—C14—C15—C9	50.6 (3)
C11—C3—C4—C8	−55.2 (4)	C14—C15—C16—C17	−25.9 (3)
C2—C3—C4—C5	−51.5 (3)	C15—C16—C17—C18	3.8 (3)
C3—C4—C5—C6	51.8 (4)	C16—C17—C18—C14	19.4 (3)
C2—C1—C6—C5	54.9 (4)	C15—C14—C18—C17	−35.1 (3)
C4—C5—C6—C1	−55.4 (5)	C23—C20—C21—O2	0.6 (4)
C3—C4—C8—C9	56.0 (3)	C21—C20—C23—C22	0.4 (4)
C4—C8—C9—C10	−55.7 (3)	O2—C22—C23—C20	−1.3 (4)
C12—C8—C9—C15	49.9 (3)	O6—C26—C27—C28	−74.3 (4)
C8—C9—C10—C11	54.3 (3)	C26—C27—C28—C29	−46.8 (5)
C9—C10—C11—C3	−54.8 (4)	C27—C28—C29—C30	52.0 (4)
C4—C3—C11—C10	55.2 (4)	C28—C29—C30—O7	−60.2 (4)
C9—C8—C12—C13	−54.4 (4)	C23—C22—O2—C21	1.7 (4)
C8—C12—C13—C14	59.4 (4)	C20—C21—O2—C22	−1.4 (4)
C12—C13—C14—C15	−54.9 (3)	C27—C26—O7—C30	−55.5 (4)
C8—C9—C15—C14	−50.2 (3)	C29—C30—O7—C26	62.7 (4)

Table 3. *Hydrogen-bonding geometry* (Å, °)

D—H···*A*	H···*A*	*D*···*A*	*D*—H···*A*
O1—HO1···*OW2*^{i}	2.05 (3)	2.821 (5)	149 (3)
O9—HO9···*OW1*	1.95 (3)	2.741 (5)	174 (3)
OW1—H1*W1*···O3^{ii}	2.06 (3)	2.847 (5)	166 (3)
OW1—H2*W1*···O1^{iii}	1.80 (3)	2.825 (5)	162 (3)
OW2—H1*W2*···O9	1.83 (3)	2.793 (5)	168 (3)
OW2—H2*W2*···O5^{ii}	1.82 (3)	2.837 (5)	163 (3)

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

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Data collection: *P*4 diffractometer software. Cell refinement: *XSCANS* (Siemens, 1991). Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1990). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HR1054). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis(phenylsulfonyl)methane, $(PhSO_2)_2CH_2$, and Dibromobis(phenylsulfonyl)methane, $(PhSO_2)_2CBr_2$

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Abstract

In bis(phenylsulfonyl)methane, $C_{13}H_{12}O_4S_2$, the central C—S bond lengths are 1.786 (2) and 1.786 (3) Å, while