Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NS1006). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(14α,22*E*)-14-Hydroxyergosta-4,7,22-triene-3,6-dione, $C_{28}H_{40}O_3$

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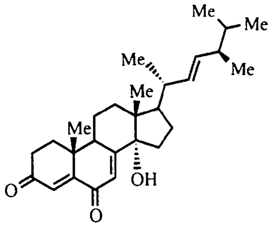
Abstract

The rings *A*, *B*, *C* and *D* in the title compound adopt twist, sofa, chair and twist conformations, respectively. The C17 side chain has an extended conformation. There is an intermolecular hydrogen bond between the O3 carbonyl and the O14 hydroxy groups.

Comment

The title compound, (I), is a natural product which has been isolated from *Phellinus igniarius*. To determine the structure unequivocally, an X-ray analysis has been undertaken.



(I)

An *ORTEP*II (Johnson, 1976) drawing of the title compound, together with the atomic numbering and ring-labelling scheme, is shown in Fig. 1. Ring *A* adopts a twist conformation with atoms C1 and C2 deviating 0.384 (2) and −0.265 (2) Å, respectively, from the least-squares planes defined by C3, C4, C5 and C10. Ring *B* adopts a sofa conformation with the C10 atom deviating 0.610 (2) Å from the least-squares plane defined by the other five atoms in the ring. The *C* ring has a chair conformation and ring *D* adopts a twist conformation with the C13 and C14 atoms deviating −0.509 (2) and 0.227 (2) Å, respectively, from the plane defined by the other three atoms in the ring. The alkyl chain attached to atom C17 has an extended conformation.

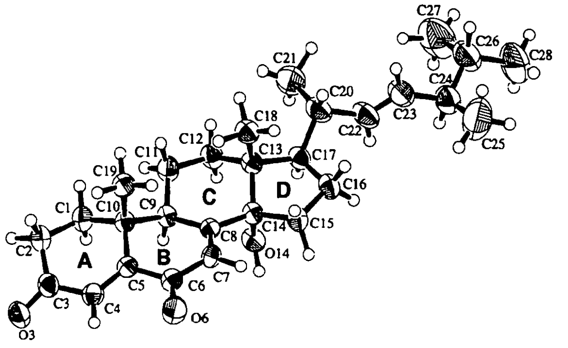


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the title compound showing the atomic numbering and ring-labelling schemes. Displacement ellipsoids are shown at the 50% probability level for non-H atoms and H atoms are shown as small spheres of arbitrary radii.

The C22═C23 bond is relatively short for a C═C double bond. The C6—C7 bond is significantly shorter than the C5—C6 bond. The exocyclic bond angles around atom C17 are highly asymmetric. Other bond lengths and angles are within normal ranges.

There is an intermolecular hydrogen bond between the O14 hydroxy group and the O3$(1 - x, -\frac{1}{2} + y, -z)$ carbonyl group [O14···O3 = 2.928 (2) Å, O14—H···O3 = 156.9 (7)°]. There is also a short contact of 3.092 (2) Å between the C4 atom and the O3 atom at $(1 - x, -\frac{1}{2} + y, -1 - z)$, but judging from the C4—H···O3 angle of 77.5 (9)°, it cannot be classed as a hydrogen bond.

Experimental

The crystals were grown from an ethanol solution.

Crystal data

$C_{28}H_{40}O_3$
$M_r = 424.62$
Monoclinic
$P2_1$
$a = 21.900\,(7)$ Å
$b = 6.368\,(2)$ Å
$c = 8.939\,(2)$ Å
$\beta = 93.51\,(2)°$
$V = 1244.3\,(6)$ Å^3
$Z = 2$
$D_x = 1.13$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 30$–$35°$
$\mu = 0.556$ mm^{-1}
$T = 293\,(2)$ K
Plate
0.5 × 0.3 × 0.02 mm
Colourless

Data collection

Enraf–Nonius CAD-4 Turbo diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2875 measured reflections
2832 independent reflections
2581 observed reflections [$F > 3\sigma(F)$]

$R_{\rm int} = 0.054$
$\theta_{\rm max} = 74.9°$
$h = 0 \rightarrow 27$
$k = -7 \rightarrow 0$
$l = -11 \rightarrow 11$
3 standard reflections
frequency: 60 min
intensity decay: 2.5%

Refinement

Refinement on F
$R = 0.039$
$wR = 0.047$
$S = 2.30$
2581 reflections
436 parameters
H atoms: see below
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\rm max} = 0.11$

$\Delta\rho_{\rm max} = 0.23$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.15$ e Å^{-3}
Extinction correction: $|F_{\rm calc}|/(1 + gI_{\rm calc})$
Extinction coefficient: $g = 1.155 \times 10^{-5}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$$B_{\rm eq} = (4/3)\textstyle\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
O3	0.52949 (7)	0.614	−0.4137 (2)	5.04 (4)
O6	0.49875 (7)	−0.0515 (4)	−0.1319 (2)	4.96 (4)
O14	0.35584 (6)	0.2720 (3)	0.2705 (1)	3.69 (3)
C1	0.3802 (1)	0.5734 (4)	−0.2741 (2)	3.78 (4)
C2	0.4206 (1)	0.6030 (4)	−0.4068 (2)	3.99 (4)
C3	0.48420 (9)	0.5260 (4)	−0.3698 (2)	3.81 (4)
C4	0.48956 (9)	0.3347 (4)	−0.2787 (2)	3.55 (4)
C5	0.44327 (8)	0.2556 (4)	−0.2060 (2)	3.04 (3)
C6	0.45418 (8)	0.0583 (4)	−0.1172 (2)	3.38 (4)
C7	0.40956 (9)	0.0083 (4)	−0.0074 (2)	3.24 (3)
C8	0.36576 (7)	0.1436 (3)	0.0273 (2)	2.83 (3)
C9	0.35542 (8)	0.3504 (4)	−0.0536 (2)	2.99 (3)
C10	0.37955 (8)	0.3479 (4)	−0.2143 (2)	2.98 (3)
C11	0.2890 (1)	0.4287 (4)	−0.0548 (2)	3.99 (4)
C12	0.2565 (1)	0.3948 (4)	0.0902 (2)	3.85 (4)
C13	0.26175 (8)	0.1667 (4)	0.1415 (2)	3.23 (3)
C14	0.33057 (8)	0.1156 (4)	0.1673 (2)	3.05 (3)
C15	0.33190 (9)	−0.0963 (4)	0.2457 (2)	3.72 (4)
C16	0.27590 (9)	−0.0868 (4)	0.3439 (2)	3.88 (4)
C17	0.23956 (9)	0.1131 (4)	0.2987 (2)	3.60 (4)
C18	0.2321 (1)	0.0174 (5)	0.0229 (2)	4.05 (4)
C19	0.3406 (1)	0.2050 (4)	−0.3225 (2)	3.74 (4)
C20	0.1706 (1)	0.0862 (5)	0.3179 (3)	4.91 (5)
C21	0.1331 (1)	0.2816 (9)	0.2758 (5)	8.0 (1)
C22	0.1616 (1)	0.0284 (5)	0.4789 (3)	5.08 (5)
C23	0.1277 (1)	−0.1214 (6)	0.5256 (3)	5.66 (6)
C24	0.1209 (1)	−0.1810 (7)	0.6874 (3)	6.14 (7)
C25	0.1466 (3)	−0.402 (1)	0.7122 (6)	11.5 (2)
C26	0.0550 (1)	−0.1589 (7)	0.7332 (3)	6.85 (8)
C27	0.0312 (3)	0.058 (1)	0.7076 (7)	10.8 (2)
C28	0.0486 (2)	−0.223 (1)	0.8946 (5)	10.8 (1)

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

O3—C3	1.224 (2)	O6—C6	1.214 (2)
O14—C14	1.446 (2)	C1—C2	1.534 (3)
C1—C10	1.532 (3)	C2—C3	1.495 (3)
C3—C4	1.464 (3)	C4—C5	1.336 (3)
C5—C6	1.497 (3)	C5—C10	1.511 (3)
C6—C7	1.462 (2)	C7—C8	1.340 (3)
C8—C9	1.512 (3)	C8—C14	1.519 (2)
C9—C10	1.561 (2)	C9—C11	1.538 (3)
C10—C19	1.547 (3)	C11—C12	1.530 (3)
C12—C13	1.525 (3)	C13—C14	1.545 (3)
C13—C17	1.552 (2)	C13—C18	1.539 (3)
C14—C15	1.519 (3)	C15—C16	1.553 (3)
C16—C17	1.541 (3)	C17—C20	1.540 (3)
C20—C21	1.525 (5)	C20—C22	1.509 (3)
C22—C23	1.293 (4)	C23—C24	1.511 (4)
C2—C1—C10	113.7 (2)	C11—C12—C13	111.0 (2)
C1—C2—C3	111.3 (2)	C12—C13—C14	107.4 (2)
O3—C3—C2	122.8 (2)	C12—C13—C17	117.3 (2)
O3—C3—C4	121.2 (2)	C12—C13—C18	111.2 (2)
C2—C3—C4	115.9 (2)	C14—C13—C17	100.1 (1)
C3—C4—C5	123.1 (2)	C14—C13—C18	109.9 (2)
C4—C5—C6	118.2 (2)	C17—C13—C18	110.2 (2)
C4—C5—C10	123.8 (2)	O14—C14—C8	104.6 (1)
C6—C5—C10	117.9 (1)	O14—C14—C13	106.4 (1)
O6—C6—C5	121.9 (2)	O14—C14—C15	108.8 (1)
O6—C6—C7	121.5 (2)	C8—C14—C13	113.1 (1)
C5—C6—C7	116.5 (2)	C8—C14—C15	119.1 (2)
C6—C7—C8	122.2 (2)	C13—C14—C15	104.2 (1)
C7—C8—C9	122.5 (2)	C14—C15—C16	103.4 (2)
C7—C8—C14	121.5 (2)	C15—C16—C17	107.3 (2)
C9—C8—C14	115.2 (1)	C13—C17—C16	103.4 (2)
C8—C9—C10	112.4 (1)	C13—C17—C20	119.3 (2)
C8—C9—C11	113.5 (2)	C16—C17—C20	111.9 (2)
C10—C9—C11	111.8 (1)	C17—C20—C21	113.5 (2)
C1—C10—C5	110.7 (2)	C17—C20—C22	108.6 (2)
C1—C10—C9	108.7 (1)	C21—C20—C22	109.5 (2)
C1—C10—C19	110.5 (2)	C20—C22—C23	126.7 (2)
C5—C10—C9	108.9 (1)	C22—C23—C24	125.9 (3)
C5—C10—C19	105.9 (2)	C9—C11—C12	115.9 (2)
C9—C10—C19	112.2 (1)		
C1—C2—C3—C4	38.2 (3)	C9—C8—C14—C13	49.8 (2)
C2—C1—C10—C5	42.6 (2)	C11—C9—C8—C14	−37.9 (2)
C3—C2—C1—C10	−54.0 (3)	C13—C14—C15—C16	−34.3 (2)
C5—C6—C7—C8	−8.6 (3)	C14—C13—C17—C16	−39.7 (2)
C6—C5—C10—C9	46.3 (2)	C15—C14—C13—C17	46.5 (2)
C7—C6—C5—C10	−19.5 (2)	C17—C20—C22—C23	−132.5 (3)
C8—C9—C11—C12	39.3 (3)	C22—C23—C24—C26	119.0 (4)
C1—C10—C5—C4	−17.4 (2)	C9—C11—C12—C13	−51.7 (3)
C2—C3—C4—C5	−13.6 (3)	C11—C12—C13—C14	59.6 (2)
C3—C4—C5—C10	2.7 (3)	C13—C17—C16—C15	19.7 (2)
C5—C10—C9—C8	−47.1 (2)	C14—C15—C16—C17	8.8 (2)

C6—C7—C8—C9	5.5 (3)	C16—C17—C20—C22	57.4 (3)
C7—C8—C9—C10	23.9 (2)	C20—C22—C23—C24	178.0 (3)
C8—C14—C13—C12	−59.7 (2)		

All non-H atoms were located by direct methods. All H atoms were found from difference Fourier maps. All non-H atoms were refined anisotropically and H atoms isotropically.

Data collection: *CAD*-4 *Software* (Enraf-Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *CAD*-4 *Software*. Program(s) used to solve structure: *MITHRIL* (Gilmore, 1984). Program(s) used to refine structure: *TEXSAN* (Molecular Structure Corporation, 1992). Molecular graphics: *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KH1087). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(2′*S*,3′*S*,4′*R*)-5′-*O*-Benzoyl-3′-deoxy-3′β-diethylphosphono-2′-*O*-*tert*-butyldimethylsilyluridine

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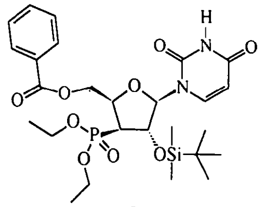
Abstract

3′-Hydroxy-3′-diethylphosphononucleosides readily undergo radical deoxygenation under modified Barton conditions to give two diastereomers of the parent diethyl phosphonate. However, the stereochemistry of the diastereomers is difficult to establish by spectral means. When the major product of one such reaction was obtained in crystalline form, a single crystal diffraction analysis was conducted on that diastereomer, the title compound, $C_{26}H_{39}N_2O_9PSi$.

Comment

A modified Barton deoxygenation protocol suitable for deoxygenation of tertiary alcohols was reported by Dolan & MacMillan in 1985, but there have been few applications of this methodology in carbohydrate or nucleoside systems (Matsusda, Takenuki, Sasaki & Ueda, 1991; Kakefuda, Yoshimura, Sasaki & Matsuda, 1993; Serra, Dewynter, Montero & Imbach, 1994). In all previous cases, the stereochemistry of the products was assigned by analysis of the NMR spectra. After deoxygenation of 5′-*O*-benzoyl-3′α-diethylphosphono-3′β-hydroxy-2′-*O*-*tert*-butyldimethylsilyluridine *via* this procedure (McEldoon & Wiemer, 1995), the 3′-stereochemistry of the title product, (I), was established by a single-crystal diffraction analysis.



(I)

The diffraction analysis revealed an intermolecular hydrogen bond between the H atom of N3 and the phosphoryl O atom [N3···O5^i 2.924 (7), H3···O5^i 2.17 (5) Å, N3—H3···O5^i 176 (5)°; symmetry code: (i) $x - 1/2, -y + 1/2, -z + 1$]. It also established that the ribose ring adopts an O4′,C4′ half-chair conformation. The conformation about the glycosidic bond is *anti* [O4′—C1—N1—C2 = 242.7 (5)°].

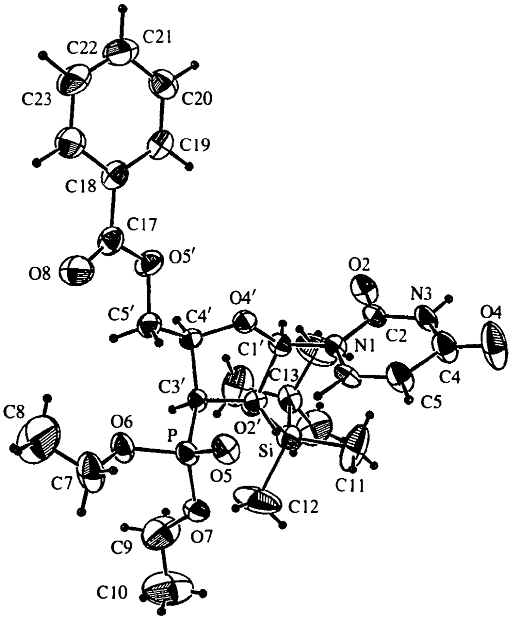


Fig. 1. An *ORTEP*II (Johnson, 1976) drawing of the title compound with the atomic numbering scheme. Displacement ellipsoids are plotted at the 35% probability level.

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