Refinement

Refinement on F^2
$R(F) = 0.0496$
$wR(F^2) = 0.1423$
$S = 1.033$
2870 reflections
189 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0449P)^2 + 2.508P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.018$
$\Delta\rho_{\max} = 0.285$ e Å^{-3}
$\Delta\rho_{\min} = -0.229$ e Å^{-3}
Extinction correction: *SHELXTL*
Extinction coefficient: 0.0043 (10)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

B—O1	1.461 (3)	O1—C1	1.410 (3)
B—O2	1.471 (3)	O2—C2	1.403 (3)
B—O3	1.473 (3)	O3—C3	1.394 (3)
B—O4	1.464 (3)	O4—C4	1.417 (3)
O1—B—O2	112.4 (2)	O3—B—O4	113.6 (2)
O1—B—O3	113.9 (2)	C1—O1—B	115.40 (18)
O1—B—O4	102.95 (18)	C2—O2—B	115.73 (19)
O2—B—O3	101.24 (19)	C3—O3—B	119.9 (2)
O2—B—O4	113.2 (2)	C4—O4—B	114.41 (18)
O4—B—O1—C1	−172.7 (2)	O2—B—O3—C3	−161.0 (2)
O3—B—O2—C2	179.3 (2)	O1—B—O4—C4	−179.6 (2)

H atoms were placed geometrically and refined with a riding model (including free rotation about *X*—Me bonds) and with $U_{\rm iso}$ constrained to be 1.2 (1.5 for methyl groups) times $U_{\rm eq}$ of the carrier atom.

Data collection: *DIF4* (Stoe & Cie, 1988). Cell refinement: *DIF4*. Data reduction: local programs. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1994). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL* and local programs.

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: AB1461). 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. (1997). C**53**, 753–755

(2*R*,3*R*,4*S*)-3-(*tert*-Butyldiphenylsiloxy)-4-hydroxy-3-methylhex-5-ene-1,2-diyl Diacetate

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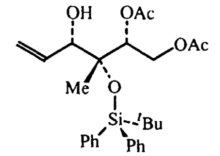
Abstract

The crystal structure and absolute configuration of the title compound, $C_{27}H_{36}O_6Si$, have been determined. The molecules are linked through hydrogen bonds between the hydroxy and acetoxy groups. The dihedral angle between the planes of the phenyl rings is 55.4 (1)°.

Comment

The diphenyl-*tert*-butylsilyl substituent was found to be an effective steric directing group for the substrate-controlled diastereoselective synthesis of allenylcarbinols from chiral allenals (Marshall & Tang, 1993). This methodology was applied to synthesize the title compound, (I), as part of a study on enantioselective synthesis of carbohydrate precursors (Marshall & Tang, 1994). The crystal structure was determined in order to establish the stereochemistry of the reaction product.



(I)

The least-squares planes of the phenyl rings are inclined by 13.3 (1) and 47.6 (1)° with respect to the Si, C21, C31 plane. Bond lengths and angles within both rings show distortion patterns from perfect hexagons, similar to the distortion already reported in other Si compounds (Karle, Karle & Nielsen, 1986; Tomlins, Lydon, Akrigg & Sheldrick, 1985). Both Si—C bond lengths are longer than 1.87 (2) Å, the average value observed in 51 other *tert*-butyldiphenylsilyloxy groups found in the April 1996 edition of the Cambridge Structural Database (Allen & Kennard, 1993). Also, the Si—C bond to the *tert*-butyl group of 1.900 (2) Å is longer than average. The torsion angle C4—O2—Si—C41 of 156.2 (2)° differs from an ideal *trans* conformation to a greater extent than observed in the majority of structures containing the *tert*-butyldiphenylsilyloxy group.

In the acetoxy groups, the bond distances do not differ significantly from those reported previously (Lewinski, Marshall & Beaudoin, 1994). Both groups are in their usual conformation with the C—H bond *cis* to the carbonyl group.

The crystal packing is stabilized by one hydrogen bond between the hydroxyl and acetoxy group of the molecule at $(1-x, y-\frac{1}{2}, 1-z)$, with O1···O6 2.871 (3), H1···O6 2.11 (3) Å and O1—H1···O6 158 (3)°. All other contacts are of the van der Waals type.

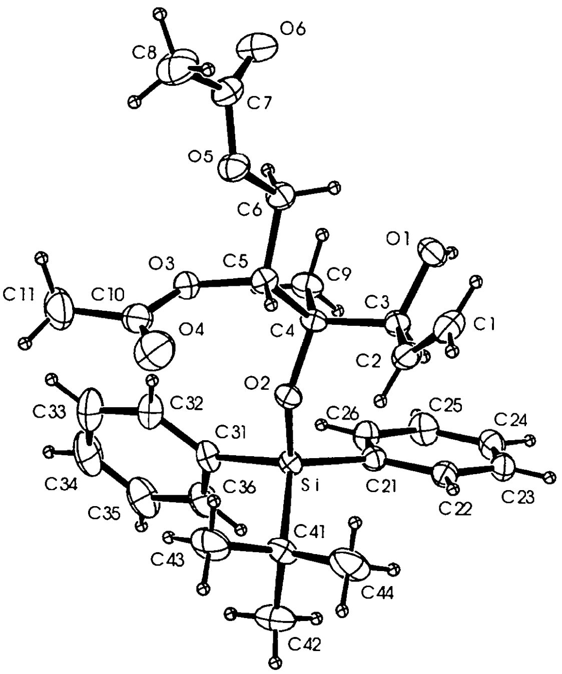


Fig. 1. The molecular structure of the title compound. Displacement ellipsoids are shown at the 25% probability level and H atoms are drawn with arbitrary radii.

Experimental

The title compound was obtained as described elsewhere (Marshall & Tang, 1994). Crystals were grown by slow evaporation from diethyl ether.

Crystal data

$C_{27}H_{36}O_6Si$
$M_r = 484.65$
Monoclinic
$P2_1$
$a = 10.838\ (1)$ Å
$b = 9.347\ (1)$ Å
$c = 13.456\ (1)$ Å
$\beta = 92.30\ (1)°$
$V = 1362.0\ (2)$ Å^3
$Z = 2$
$D_x = 1.182$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 14.0$–$17.5°$
$\mu = 0.123$ mm^{-1}
$T = 293\ (2)$ K
Prismatic
0.6 × 0.5 × 0.4 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
4964 measured reflections
4755 independent reflections
4485 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.0235$
$\theta_{\rm max} = 24.97°$
$h = -12 \rightarrow 12$
$k = -11 \rightarrow 11$
$l = 0 \rightarrow 15$
3 standard reflections
frequency: 120 min
intensity decay: 0.5%

Refinement

Refinement on F^2
$R(F) = 0.0317$
$wR(F^2) = 0.0869$
$S = 1.021$
4755 reflections
352 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0596P)^2 + 0.1165P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.002$
$\Delta\rho_{\rm max} = 0.135$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.150$ e Å^{-3}

Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.016 (2)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: Flack (1983)
Flack parameter = −0.05 (10)

Table 1. *Selected geometric parameters (Å, °)*

Si—O2	1.6441 (12)	O5—C6	1.444 (2)
Si—C31	1.885 (2)	O6—C7	1.187 (3)
Si—C21	1.887 (2)	C1—C2	1.304 (3)
Si—C41	1.900 (2)	C2—C3	1.495 (3)
O1—C3	1.419 (2)	C3—C4	1.557 (2)
O2—C4	1.433 (2)	C4—C9	1.520 (2)
O3—C10	1.343 (3)	C4—C5	1.541 (2)
O3—C5	1.445 (2)	C5—C6	1.506 (3)
O4—C10	1.188 (4)	C7—C8	1.502 (3)
O5—C7	1.330 (3)	C10—C11	1.507 (4)
O2—Si—C31	110.08 (8)	C9—C4—C5	111.9 (2)
O2—Si—C21	112.73 (7)	O2—C4—C3	106.22 (13)
C31—Si—C21	107.73 (8)	C9—C4—C3	111.39 (15)
O2—Si—C41	103.60 (8)	C5—C4—C3	110.18 (13)
C31—Si—C41	107.92 (9)	O3—C5—C6	105.90 (15)
C21—Si—C41	114.64 (9)	O3—C5—C4	109.15 (13)
C4—O2—Si	135.43 (10)	C6—C5—C4	114.18 (15)
C10—O3—C5	117.8 (2)	O5—C6—C5	106.4 (2)
C7—O5—C6	116.6 (2)	O6—C7—O5	124.2 (2)
C1—C2—C3	125.7 (2)	O6—C7—C8	124.6 (2)
O1—C3—C2	110.1 (2)	O5—C7—C8	111.2 (2)
O1—C3—C4	112.0 (2)	O4—C10—O3	124.0 (3)
C2—C3—C4	112.44 (15)	O4—C10—C11	126.3 (3)
O2—C4—C9	111.19 (14)	O3—C10—C11	109.7 (3)
O2—C4—C5	105.62 (13)		

Positions of H atoms were calculated and included as riding atoms in the structure-factor calculations, except for H1, which was found on a difference Fourier map and refined. The absolute configuration was assigned according to the Flack parameter (Flack, 1983) and was in agreement with the configuration assigned previously from ^{1}H NMR spectra (Marshall & Tang, 1994). To validate this assignment, both enantiomorphs were refined. The value of the Flack parameter for the inverted structure [$x = 1.05\ (10)$] confidently confirms the correctness of the assigned absolute configuration.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure:

*SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *PARST* (Nardelli, 1983).

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: NA1274). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Two Dolabrane-type Diterpenoids

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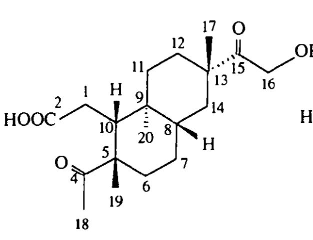
Abstract

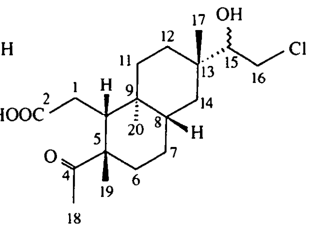
The crystal structures of two dolabrane diterpenes, *ent*-2-seco-3-nor-5α,4,15-dioxo-16-hydroxydolabran-2-oic acid, $C_{19}H_{30}O_5$, (I), and *ent*-2-seco-3-nor-5α,16-chloro-15-hydroxydolabran-2-oic acid, $C_{19}H_{31}ClO_4$, (II), have been determined at room temperature. They revealed the presence of two *trans*-fused rings having a chair conformation and they confirmed previous NMR studies showing that the C9 substituent is *trans* with respect to those at C8 and C10. Furthermore, we observed that the longer C_{sp^3}—C_{sp^3} distances occur for C9—C10 and C5—C10, which is in agreement with the values found in other diterpenes. These are the first reported crystal structures of dolabrane molecules.

Comment

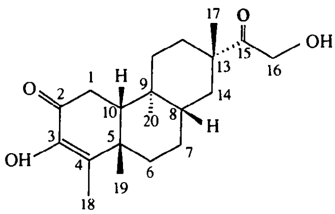
The present work is part of a study concerning the structure and pharmacological activity of diterpene derivatives (Kijjoa *et al.*, 1994; Kijjoa, Pinto, Anantachoke, Gedris & Herz, 1995; Paya *et al.*, 1997). Compounds (I) and (II) belong to a series of dolabrane-type diterpenoids, isolated from *Endospermum diadenum* Airy Shaw (Euphorbiaceae), the only representative of this genus found in Thailand (Kijjoa *et al.*, 1994). They are natural products with potential pharmacological interest since the plant from which they were isolated is used in folk medicine for the relief of fever and skin infections.



(I)



(II)



(III)

Compounds (I) and (II) are similar to the tricyclic diterpene (III), in which C3 is substituted for O3, opening the ring structure. X-ray diffraction studies were performed in order to confirm the NMR studies and to obtain more detailed information about the three-dimensional structure of the molecules.

The compounds both present a bicyclic system with a chair conformation, as shown by the torsion angles around each of the rings. In both compounds, the C20 atom is in a *trans* position relative to the H8 and H10 atoms. The longest C_{sp^3}—C_{sp^3} distances occur in both compounds at bonds C5—C10 and C10—C9, which have respective values of 1.559 (2) and 1.564 (2) Å for compound (I), and 1.563 (2) and 1.563 (2) Å for compound (II). These elongated bonds have been