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Structure of Dimethyl (±)-1,2,3,4,4aα,4b,9,10-Octahydro-6,7-bis(trimethylsilyl)-2β,10aβ-ethanophenanthrene-12,12-dicarboxylate

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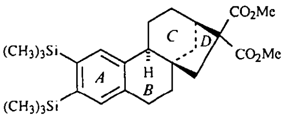
Abstract. $C_{26}H_{40}O_4Si_2$, $M_r = 472{\cdot}8$, monoclinic, $P2_1/c$, $a = 16{\cdot}432\,(2)$, $b = 9{\cdot}597\,(3)$, $c = 17{\cdot}029\,(2)$ Å, $\beta = 93{\cdot}73\,(1)°$, $V = 2680\,(1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}17$ g cm^{-3}, $\lambda(\text{Cu } K\bar{\alpha}) = 1{\cdot}5424$ Å, $\mu = 13{\cdot}9$ cm^{-1}, $F(000) = 1024$, $T = 295$ K, $R = 0{\cdot}042$ for 4337 unique observed reflections. The title compound has a phyllocladane-type framework. One of the two Si atoms is out of the mean-square plane of the phenyl ring [$d_{\text{Si}} = 0{\cdot}234\,(1)$ Å]. This feature can explain the different reactivity of the two trimethylsilyl groups.

Introduction. Kaurane and phyllocladane are two families of naturally occurring tetracyclic diterpenes exhibiting very important biological activities (Hanson, 1988). They have very close structural features with a bicyclo[3.2.1]octane arrangement of *CD* rings and a spiro *BD* ring junction in common; the only difference in structure arises from the stereochemistry of the *BC* ring junction: *cis* for the kaurane, *trans* for the phyllocladane. Two of us have recently disclosed (Gotteland & Malacria, 1989) a strategy based upon a sequence of three consecutive cycloaddition reactions, allowing a straightforward access, in high yields, to the basic skeleton of these related families of natural products (see scheme).



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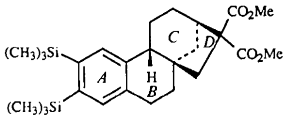

(2)

In our model study this synthetic approach gave rise to a major (90%) phyllocladane stereoisomer (1) and a minor (10%) kaurane stereoisomer (2) whose structural determination turned out to be quite difficult by NMR. We report in this paper the molecular structure of the title compound (1) having a phyllocladane-type framework. To the best of our knowledge, no structural investigations have been carried out for such a compound.

Experimental. The synthesis of the compound has been previously reported (Gotteland & Malacria, 1989). Transparent crystal from benzene/methanol (50/50), 0·25 × 0·40 × 0·40 mm. Enraf–Nonius CAD-4 diffractometer, graphite monochromator,

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Table 1. *Atomic coordinates and equivalent isotropic thermal parameters*

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

	x	*y*	*z*	B_{eq}(Å^2)
Si1	0·07858 (4)	0·08404 (8)	0·65755 (4)	3·48 (1)
Si2	0·11755 (4)	0·06995 (8)	0·87849 (4)	3·41 (1)
O1	0·4794 (1)	−0·1177 (2)	0·6189 (1)	4·83 (4)
O2	0·5515 (1)	−0·2678 (2)	0·5513 (1)	4·89 (4)
O3	0·5685 (1)	−0·5581 (2)	0·6597 (1)	4·94 (5)
O4	0·5918 (1)	−0·3599 (2)	0·7271 (1)	4·14 (4)
C1	0·1387 (1)	−0·0497 (3)	0·7183 (1)	2·82 (4)
C2	0·1497 (1)	−0·0577 (3)	0·8017 (1)	2·79 (4)
C3	0·1976 (1)	−0·1661 (3)	0·8334 (1)	3·01 (5)
C4	0·2367 (1)	−0·2647 (3)	0·7890 (1)	2·90 (5)
C5	0·2881 (2)	−0·3757 (3)	0·8311 (2)	3·77 (5)
C6	0·3104 (2)	−0·4933 (3)	0·7760 (2)	3·84 (6)
C7	0·3412 (2)	−0·4346 (3)	0·6999 (1)	3·12 (5)
C8	0·2706 (2)	−0·3567 (3)	0·6542 (1)	3·17 (5)
C9	0·2278 (1)	−0·2554 (3)	0·7073 (1)	2·77 (4)
C10	0·1781 (1)	−0·1501 (3)	0·6747 (1)	2·95 (5)
C11	0·4168 (1)	−0·3405 (3)	0·7152 (1)	3·02 (5)
C12	0·4719 (2)	−0·3666 (3)	0·6452 (1)	3·09 (5)
C13	0·4193 (2)	−0·4610 (3)	0·5879 (2)	3·74 (5)
C14	0·3577 (2)	−0·3786 (3)	0·5349 (2)	4·23 (6)
C15	0·3015 (2)	−0·2850 (3)	0·5809 (2)	3·63 (5)
C16	0·3727 (2)	−0·5477 (3)	0·6456 (2)	3·93 (6)
C17	0·4995 (2)	−0·2343 (3)	0·6057 (2)	3·58 (5)
C18	0·5821 (2)	−0·1551 (4)	0·5050 (2)	6·78 (8)
C19	0·5489 (2)	−0·4422 (3)	0·6761 (2)	3·53 (5)
C20	0·6620 (2)	−0·4210 (4)	0·7684 (2)	4·82 (7)
C21	0·1012 (2)	0·0606 (4)	0·5518 (2)	5·76 (8)
C22	0·1109 (2)	0·2664 (4)	0·6825 (2)	5·68 (8)
C23	−0·0335 (2)	0·0625 (4)	0·6626 (2)	4·87 (7)
C24	0·0157 (2)	0·1531 (3)	0·8596 (2)	4·41 (6)
C25	0·1110 (2)	−0·0252 (4)	0·9738 (2)	5·67 (8)
C26	0·1995 (2)	0·2033 (4)	0·8938 (2)	6·19 (8)

Cu *Kα* radiation, $\omega\text{–}\frac{4}{3}\theta$ scan, $2 < 2\theta < 146°$. Unit-cell parameters refined from setting angles of 25 selected reflections ($27·2 < 2\theta < 74·6°$). 5353 independent reflections, only 4337 observed [$I > 3\sigma(I)$]. $0 < h < 20$, $0 < k < 11$, $-21 < l < 21$. Standard reflection 324 showed 2% intensity variation. Lp corrections, no absorption correction. Structure solved using *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), refined by full-matrix least squares based on *F*. Non-H atoms anisotropic, H atoms located from *F* syntheses, with isotropic *B* equal to the B_{eq} of bearing C atoms. Final refinement involving the *x*, *y*, *z*, β_{ij} parameters for the non-H atoms and *x*, *y*, *z* for the H atoms. $R = 0·042$, $wR = 0·047$, $w = 1/\sigma^2$, $(\Delta/\sigma)_{max} = 0·14$, $|\Delta\rho| < 0·22$ e Å^{-3}. Computing by means of Enraf–Nonius *SDP* system (B. A. Frenz & Associates Inc., 1982), DEC Micro-VAX II computer, Centre de diffractométrie automatique de l'Université Lyon I. Scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. Atomic coordinates and equivalent isotropic thermal parameters are given in Table 1.* Main bond lengths and angles are in Table 2.

Table 2. *Main bond lengths* (Å) *and angles* (°)

Si1	C1	1·886 (2)	O1	C17	1·193 (3)	C2	C3	1·393 (3)
Si1	C21	1·876 (3)	O2	C17	1·340 (3)	C3	C4	1·394 (3)
Si1	C22	1·870 (3)	O2	C18	1·447 (4)	C4	C5	1·513 (4)
Si1	C23	1·861 (3)	O3	C19	1·196 (3)	C4	C9	1·392 (3)
Si2	C2	1·891 (2)	O4	C19	1·340 (3)	C5	C6	1·528 (4)
Si2	C24	1·862 (3)	O4	C20	1·437 (3)	C6	C7	1·529 (4)
Si2	C25	1·871 (3)	C1	C2	1·424 (3)	C7	C8	1·546 (3)
Si2	C26	1·863 (4)	C1	C10	1·401 (3)	C7	C11	1·544 (3)
C7	C16	1·538 (4)	C11	C12	1·563 (4)	C13	C14	1·531 (4)
C8	C9	1·530 (4)	C12	C13	1·552 (4)	C13	C16	1·530 (4)
C8	C15	1·540 (4)	C12	C17	1·520 (4)	C14	C15	1·539 (4)
C9	C10	1·392 (3)	C12	C19	1·522 (3)			

C1	Si1	C21	108·4 (1)	C7	C8	C15	110·4 (2)
C1	Si1	C22	112·4 (1)	C9	C8	C15	112·5 (2)
C1	Si1	C23	112·5 (1)	C4	C9	C8	121·8 (2)
C21	Si1	C22	105·0 (2)	C4	C9	C10	117·8 (2)
C21	Si1	C23	106·9 (2)	C8	C9	C10	120·4 (2)
C22	Si1	C23	111·1 (2)	C1	C10	C9	124·5 (2)
C2	Si2	C24	116·5 (1)	C7	C11	C12	106·1 (2)
C2	Si2	C25	108·5 (1)	O1	C17	O2	123·6 (3)
C4	C5	C6	112·2 (2)	O1	C17	C12	127·3 (2)
C5	C6	C7	110·7 (2)	O2	C17	C12	109·1 (2)
C6	C7	C8	109·0 (2)	O3	C19	O4	124·1 (2)
C6	C7	C11	112·4 (2)	C2	C1	C10	117·3 (2)
C6	C7	C16	113·1 (2)	Si2	C2	C1	129·2 (2)
C8	C7	C11	111·8 (2)	Si2	C2	C3	113·1 (2)
C8	C7	C16	108·0 (2)	C1	C2	C3	117·3 (2)
C11	C7	C16	102·4 (2)	C2	C3	C4	124·4 (2)
C14	C13	C16	108·6 (2)	C3	C4	C5	118·9 (2)
C13	C14	C15	113·4 (2)	C3	C4	C9	118·5 (2)
C8	C15	C14	113·1 (2)	C5	C4	C9	122·6 (2)
C7	C16	C13	101·8 (2)	C11	C12	C13	104·3 (2)
C2	Si2	C26	108·0 (1)	C11	C12	C17	114·1 (2)
C24	Si2	C25	104·9 (1)	C11	C12	C19	108·8 (2)
C24	Si2	C26	111·3 (2)	C13	C12	C17	112·3 (2)
C25	Si2	C26	107·2 (2)	C13	C12	C19	110·8 (2)
C17	O2	C18	117·2 (2)	C17	C12	C19	106·6 (2)
C19	O4	C20	116·7 (2)	C12	C13	C14	112·9 (2)
Si1	C1	C2	127·7 (2)	C12	C13	C16	101·3 (2)
Si1	C1	C10	114·9 (2)	O3	C19	C12	126·4 (2)
C7	C8	C9	111·6 (2)	O4	C19	C12	109·5 (2)

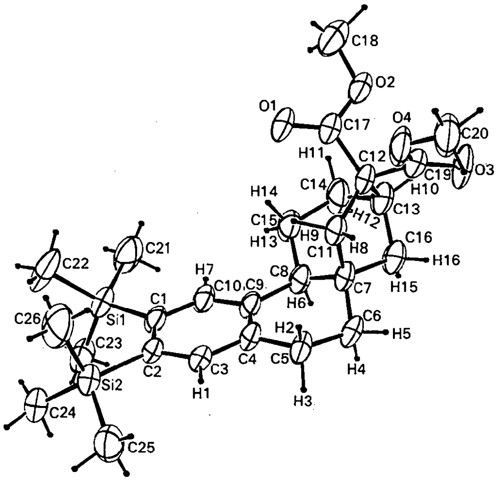

Fig. 1. *ORTEP* view of the molecule with 4% probability thermal ellipsoids. The H atoms are arbitrarily scaled.

The *ORTEP* drawing (Fig. 1) (Johnson, 1965) shows that the molecule has a phyllocladane-type framework. The different conformations of the four rings can be discussed by means of the torsion angles and the least-squares planes.

Only one of the two Si atoms lies nearly in the mean-square plane of the phenyl ring [$d_{Si1} =$

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, torsion angles and mean planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52677 (49 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0·028 (1) Å]. The other is clearly out of this plane [d_{Si2} = 0·234 (1) Å]. It has been noted (Colvin, 1981) for bis(trimethylsilyl)arylsilanes that, owing to steric acceleration, the first displacement of a silyl group (Si1) occurs 40–400 times more rapidly than does the second (Si2). An explanation of this highly regioselective desilylation could be found in the fact that the Si2 trimethylsilyl group is out of the plane defined by the phenyl ring, so determining the rate of the C—Si bond cleavage.

The *B* ring is in a half-chair conformation in which C4, C5, C8 and C9 are coplanar while C7 and C6 are symmetrically positioned. The *C* ring has a near regular chair conformation.

The *D* ring is in an envelope conformation with C16 at the flap. This conformation leads to some particularities in the ^{1}H NMR spectra. Despite its limitations (Karplus, 1963), the Karplus equation, which relates $^3J_{H-H}$ coupling constants and dihedral angles, is a very valuable model for probing molecular geometries (Colucci, Jungk & Gandour, 1985). The structure assignment of (1), made at the same time by two-dimensional NMR techniques, has revealed some surprising vicinal coupling constants especially between H16 and H10 (J_{calc} = 3·8, J_{obs} = 4·7 Hz), H12 and H10 (J_{calc} = 2·3, J_{obs} = 3 Hz) and H15 and H10 (J_{calc} = 1·2, J_{obs} = 0 Hz), which could be explained by the corresponding dihedral angles [H16—C16—C13/H10—C13—C16 = 50 (2); H12—C14—C13/H10—C13—C14 = 61 (2); H15—C16—C13/H10—C13—C16 = 108 (2)°].

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Structure of 5-Hydroxy-2,2-dimethyl-5-phenyl-2,5-dihydrofuran-3-carbonitrile

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Abstract. $C_{13}H_{13}NO_2$, M_r = 215·3, monoclinic, $P2_1/n$, a = 15·299 (4), b = 10·661 (4), c = 14·887 (3) Å, β = 90·29 (2)°, V = 2428 (2) Å^3, Z = 8, D_x = 1·18 g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, μ = 0·7 cm^{-1}, F(000) = 912, T = 294 K, R = 0·044 for 1418 observed reflections. The analysis establishes the structure of this reaction product. The two independent molecules in the asymmetric unit differ only in the orientation of the phenyl ring with respect to the furan ring. Molecular dimensions are normal; the molecules are linked by O—H···O hydrogen bonds [O···O 2·767 (5) and 2·957 (5) Å].

Introduction. The 3(2*H*)-furanone nucleus (I) occurs in a number of natural products, some of which have antitumour properties. Bullatenone (II) (Brandt & Taylor, 1954; Parker, Raphael & Wilkinson, 1958) is the simplest of these naturally occurring furanones. In an attempt to develop a short synthesis of bullatenone and its derivatives, we examined the

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