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## Structure of the 2,5-Dimethyl Ether of Avarol,\* a Sesquiterpenoid Hydroquinone from the Marine Sponge *Dysidea avara*

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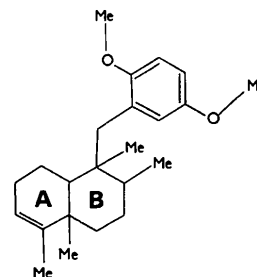
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**Abstract.**  $C_{23}H_{34}O_2$ ,  $M_r = 342.53$ , monoclinic,  $P2_1$ ,  $a = 17.200$  (9),  $b = 6.599$  (4),  $c = 19.316$  (12) Å,  $\beta = 111.67$  (4)°,  $V = 2037$  (2) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.12$  Mg m<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.5418$  Å,  $\mu(\text{Cu } K\alpha) = 0.50$  mm<sup>-1</sup>,  $F(000) = 752$ , room temperature, final  $R = 0.056$  for 2825 independent observed reflections and 451 parameters. The two independent molecules in the asymmetric unit show identical features except for the different orientation of the hydroquinone fragment with respect to the  $C_{15}$  sesquiterpene moiety, due to crystal packing requirements. Of the two *trans*-connected six-carbon-atom rings forming the sesquiterpene system the cyclohexene ring *A* has a conformation intermediate between the sofa and half-chair forms, while the cyclohexane ring *B* shows a slightly distorted chair conformation.

**Introduction.** The title compound is the 2,5-dimethyl ether of avarol, a sesquiterpenoid hydroquinone extracted from the sponge *Dysidea avara* (Minale, Riccio & Sodano, 1974). Its absolute stereochemistry has been stated by De Rosa, Minale, Riccio & Sodano (1976) by spectroscopic and chemical methods. Some doubts about the correctness of these assignments were raised by Djura, Stierle, Sullivan, Faulkner, Arnold & Clardy (1980), owing to the inconsistency of physical

data reported for a reaction product common to two different chemical pathways starting from avarol and aureol. Recently, Cariello, De Nicola Giudici & Zanetti (1980) have reported that avarol is active in inducing development aberrations in sea-urchin eggs.



**Experimental.** Needle-shaped crystal (from ethanol), elongated along **b**,  $0.5 \times 0.12 \times 0.12$  mm, Enraf-Nonius CAD-4 diffractometer, Ni-filtered  $\text{Cu } K\alpha$  radiation, cell dimensions determined by a least-squares procedure applied to the setting angles of 20 reflections in the  $\theta$  range  $10 \leq \theta \leq 13^\circ$ . 2825 unique observed reflections [ $I_o > 3\sigma(I_o)$ ] out of the total 3784 measured by the  $\omega/\theta$  scan technique with  $\theta \leq 65^\circ$ ,  $0 \leq h \leq 19$ ,  $0 \leq k \leq 7$ ,  $-21 \leq l \leq 21$ . Three monitoring reflections, intensity variation < 4%. Lp correction, absorption ignored. Structure solved by direct methods: *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Full-matrix least squares

\* Avarol = |1R(1 $\alpha$ ,2 $\beta$ ,4 $\alpha\beta$ ,8 $\alpha\beta$ )|-2-|(1,2,3,4,4a,7,8,8a-octahydro-1,2,4a,5-tetramethyl-1-naphthalenyl)methyl|-1,4-benzenediol.

minimized  $\sum w(\Delta F)^2$ ,  $w = 1/\sigma^2(F)$ . The  $y$  coordinate of C(1) was fixed to define the origin. H atoms, located in part from  $\Delta F$  synthesis and in part at their calculated stereochemical positions, were included in the structure-factor calculations with isotropic thermal factors derived from those of the carrier atoms, but not refined. 451 refined parameters included overall scale factor, positional and anisotropic thermal parameters of the non-hydrogen atoms and a correction for secondary extinction [ $g$  coefficient =  $3.47(1) \times 10^{-6}$ ]. Final  $R = 0.056$ ,  $wR = 0.074$ ,  $S = 1.90$ . Final  $\Delta/\sigma_{(\max)} = 0.04$ ; final difference electron density within  $\pm 0.20 e \text{ \AA}^{-3}$ .

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974), all calculations performed by the Enraf-Nonius (1979) system of programs (SDP) on a PDP 11/34 computer. Final atomic parameters of the non-hydrogen atoms are listed in Table 1.\*

**Discussion.** The conformations of the two independent molecules, together with the atom-labelling scheme, are shown in Fig. 1.

The present analysis confirms the correctness of the stereochemistry assigned by De Rosa *et al.* (1976), removing the doubts raised by Djura *et al.* (1980).

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43682 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The intramolecular dimensions involving the non-hydrogen atoms are given in Table 2. Excluding from the comparison the ill-defined C(15) of molecule 2, all differences in bond lengths and valency angles between the two independent molecules are less than  $4\sigma$  and are hardly significant.

Furthermore, the two molecules show a high degree of conformational correspondence (Table 2). In fact, even in view of the weakness of the intermolecular packing forces, all differences in torsion angles ( $\Delta < 4\sigma$ ) appear devoid of any real significance, except those concerning the rotations around the C(9)–C(11) and C(11)–C(16) single bonds, which are due to packing requirements. Hereinafter, only values averaged on both molecules will be mentioned.

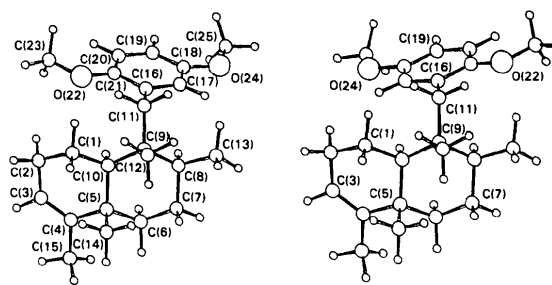


Fig. 1. Perspective view of molecule 1 on the left-hand side, and molecule 2 on the right-hand side, together with the atom-labelling scheme.

Table 1. Fractional atomic coordinates ( $\times 10^4$ ) and equivalent isotropic thermal parameters ( $\text{\AA}^2 \times 10$ ) of the non-hydrogen atoms with *e.s.d.*'s in parentheses

$$B_{eq} = \frac{1}{3} \sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$$

|       | Molecule 1 |           |          |          | Molecule 2 |            |          |          |
|-------|------------|-----------|----------|----------|------------|------------|----------|----------|
|       | $x$        | $y$       | $z$      | $B_{eq}$ | $x$        | $y$        | $z$      | $B_{eq}$ |
| C(1)  | 1940 (2)   | 5084      | 8467 (2) | 50 (1)   | 5036 (3)   | 14634 (8)  | 7484 (2) | 62 (1)   |
| C(2)  | 2357 (2)   | 7087 (9)  | 8812 (2) | 57 (1)   | 4090 (3)   | 14559 (12) | 7254 (3) | 89 (2)   |
| C(3)  | 1969 (3)   | 8018 (7)  | 9309 (2) | 52 (1)   | 3824 (3)   | 13510 (13) | 7812 (3) | 91 (2)   |
| C(4)  | 1265 (2)   | 7398 (6)  | 9361 (2) | 46 (1)   | 4315 (2)   | 12404 (9)  | 8382 (2) | 63 (1)   |
| C(5)  | 771 (2)    | 5589 (6)  | 8927 (2) | 42 (1)   | 5254 (2)   | 12248 (7)  | 8564 (2) | 49 (1)   |
| C(6)  | -172 (2)   | 5959 (8)  | 8671 (2) | 52 (1)   | 5595 (3)   | 10137 (7)  | 8856 (2) | 55 (1)   |
| C(7)  | -669 (2)   | 4251 (9)  | 8189 (2) | 61 (1)   | 6493 (3)   | 9876 (7)   | 8942 (2) | 56 (1)   |
| C(8)  | -462 (2)   | 3911 (7)  | 7493 (2) | 52 (1)   | 6648 (2)   | 10165 (6)  | 8223 (2) | 45 (1)   |
| C(9)  | 483 (2)    | 3633 (6)  | 7663 (2) | 44 (1)   | 6313 (2)   | 12237 (6)  | 7848 (2) | 42 (1)   |
| C(10) | 995 (2)    | 5259 (6)  | 8224 (2) | 40 (1)   | 5416 (2)   | 12583 (6)  | 7832 (2) | 44 (1)   |
| C(11) | 642 (2)    | 3837 (6)  | 6917 (2) | 47 (1)   | 6306 (2)   | 12194 (7)  | 7031 (2) | 49 (1)   |
| C(12) | 784 (3)    | 1452 (6)  | 7938 (3) | 62 (1)   | 6914 (3)   | 13988 (7)  | 8242 (2) | 59 (1)   |
| C(13) | -1011 (3)  | 2176 (10) | 7033 (3) | 77 (1)   | 7571 (3)   | 9771 (8)   | 8364 (3) | 64 (1)   |
| C(14) | 1011 (3)   | 3782 (7)  | 9487 (2) | 54 (1)   | 5671 (3)   | 13827 (8)  | 9196 (2) | 63 (1)   |
| C(15) | 935 (3)    | 8460 (7)  | 9899 (2) | 60 (1)   | 3952 (3)   | 11349 (14) | 8864 (4) | 106 (2)  |
| C(16) | 332 (2)    | 5695 (6)  | 6431 (2) | 43 (1)   | 5809 (2)   | 10554 (7)  | 6509 (2) | 47 (1)   |
| C(17) | -485 (2)   | 5773 (7)  | 5940 (2) | 50 (1)   | 4955 (3)   | 10612 (8)  | 6187 (2) | 55 (1)   |
| C(18) | -793 (2)   | 7393 (8)  | 5449 (2) | 54 (1)   | 4490 (2)   | 9103 (9)   | 5713 (2) | 58 (1)   |
| C(19) | -261 (3)   | 8950 (7)  | 5437 (2) | 55 (1)   | 4897 (3)   | 7488 (9)   | 5537 (2) | 63 (1)   |
| C(20) | 564 (3)    | 8868 (7)  | 5916 (2) | 52 (1)   | 5764 (3)   | 7439 (8)   | 5834 (2) | 61 (1)   |
| C(21) | 873 (2)    | 7293 (7)  | 6412 (2) | 45 (1)   | 6221 (2)   | 8919 (7)   | 6313 (2) | 51 (1)   |
| O(22) | 1687 (2)   | 7126 (5)  | 6882 (1) | 55 (1)   | 7075 (2)   | 9006 (6)   | 6600 (2) | 68 (1)   |
| C(23) | 2259 (3)   | 8668 (9)  | 6859 (3) | 69 (1)   | 7518 (3)   | 7427 (10)  | 6424 (3) | 87 (1)   |
| O(24) | -1619 (2)  | 7215 (7)  | 4995 (2) | 73 (1)   | 3635 (2)   | 9393 (8)   | 5437 (2) | 80 (1)   |
| C(25) | -1966 (4)  | 8748 (12) | 4455 (3) | 92 (2)   | 3129 (4)   | 7911 (12)  | 4952 (3) | 93 (2)   |



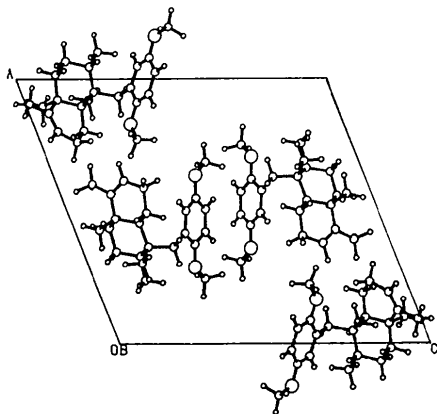


Fig. 2. Projection of the crystal structure down *b*.

C(12) and C(14). This interaction is also responsible for the flattening of ring *B* at C(9). Analogously, the widening of angle C(9)–C(8)–C(13) to 114.2 (4)° is a demand of the interaction C(12)···C(13), while the short contact (1.96 Å) between two H atoms at C(1) and C(11) causes the angle C(1)–C(10)–C(9) to widen to 114.4 (3)°.

Otherwise, the widening of the angle C(9)–C(11)–C(16) to 119.1 (4)° is probably due to requirements of the packing of the hydroquinone fragment which, in this way, becomes perpendicular to the mean plane through the sesquiterpene system

[interplanar angles: 91 (1) for molecule 1 and 86 (1)° for molecule 2].

The crystal packing, illustrated in Fig. 2, shows weak van der Waals contacts.

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## Structure of *N*-Benzoyl-5'-*O*-*tert*-butyldimethylsilyl-2'-deoxyadenosine Monohydrate

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**Abstract.** C<sub>23</sub>H<sub>31</sub>N<sub>5</sub>O<sub>4</sub>Si.H<sub>2</sub>O, *M*<sub>r</sub> = 487.6, orthorhombic, *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, *a* = 18.642 (2), *b* = 8.032 (1), *c* = 16.825 (2) Å, *V* = 2519.3 (1) Å<sup>3</sup>, *Z* = 4, *D*<sub>x</sub> = 1.286 g cm<sup>-3</sup>, λ(Cu *K*α) = 1.5418 Å, μ = 10.85 cm<sup>-1</sup>, *F*(000) = 1040, *T* = 283 K, *R* = 0.067 for 1664 unique observed reflections. The glycosidic torsion angle, χ = 161.8 (10)°, is in the *anti* conformation. The deoxyribose ring has a C3'-*exo* (C2'-*endo*) pucker and the conformation around the C5'–C4' bond is *gauche*–

*gauche*. The mean Si–C bond length is 1.861 (6) Å (three evaluations), and the Si–O5' bond length is 1.658 (6) Å. The crystal structure is stabilized by a fully satisfied hydrogen-bond network involving the water of crystallization and by stacking interactions between the phenyl ring and the base. Finally, there are weakly polar C–H···O interactions between C8 and O5' and between the δ(+) edge of the phenyl ring and the water of crystallization.