

C(212)	0.5901 (6)	0.1764 (5)	0.8998 (3)	0.0556
C(213)	0.4662 (7)	0.1864 (7)	0.7343 (4)	0.0501
O(214)	0.3793 (6)	0.1592 (5)	0.6697 (4)	0.0722
C(301)	0.0188 (5)	0.2197 (6)	0.5053 (3)	0.0471
C(302)	0.0822 (7)	-0.1677 (7)	0.5699 (3)	0.0490
C(303)	0.0397 (7)	-0.2026 (7)	0.6304 (4)	0.0637
C(304)	-0.0600 (7)	-0.2947 (8)	0.6294 (3)	0.0677
C(305)	-0.1258 (6)	-0.3416 (7)	0.5660 (3)	0.0614
C(306)	-0.0872 (5)	-0.3050 (6)	0.5054 (3)	0.0548
C(307)	0.0586 (5)	-0.1911 (6)	0.4395 (3)	0.0464
C(308)	0.1827 (5)	-0.2139 (6)	0.4308 (3)	0.0599
C(309)	0.2184 (6)	-0.1910 (7)	0.3673 (3)	0.0712
C(310)	0.1299 (6)	-0.1485 (8)	0.3100 (4)	0.0689
C(311)	0.0062 (6)	-0.1251 (6)	0.3173 (3)	0.0643
C(312)	-0.0308 (5)	-0.1469 (5)	0.3805 (3)	0.0518
C(313)	0.1807 (8)	-0.0631 (8)	0.5784 (5)	0.0593
O(314)	0.2884 (5)	-0.0951 (5)	0.6243 (3)	0.0648
C(401)	0.0259 (6)	0.2543 (6)	0.4955 (3)	0.0445
C(402)	0.0684 (6)	0.3153 (7)	0.5610 (3)	0.0469
C(403)	0.0122 (6)	0.2794 (7)	0.6171 (3)	0.0583
C(404)	-0.0788 (7)	0.1774 (7)	0.6127 (4)	0.0667
C(405)	-0.1172 (6)	0.1149 (7)	0.5487 (3)	0.0606
C(406)	-0.0063 (6)	0.1517 (5)	0.4920 (3)	0.0517
C(407)	0.0716 (6)	0.2922 (6)	0.4331 (3)	0.0469
C(408)	0.0527 (6)	0.4236 (6)	0.4059 (3)	0.0556
C(409)	0.0866 (6)	0.4551 (6)	0.3428 (3)	0.0658
C(410)	0.1414 (7)	0.3604 (7)	0.3048 (4)	0.0674
C(411)	0.1621 (7)	0.2310 (6)	0.3327 (3)	0.0710
C(412)	0.1262 (6)	0.1967 (6)	0.3945 (3)	0.0593
C(413)	0.1674 (7)	0.4196 (7)	0.5739 (5)	0.0549
O(414)	0.2562 (5)	0.4022 (6)	0.6335 (3)	0.0664

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989). Data reduction: *CRYSTALS* (Watkin, Carruthers & Betteridge, 1985). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *CRYSTALS*. Molecular graphics: *CAMERON* (Pearce, Watkin & Prout, 1992). Software used to prepare material for publication: *CRYSTALS*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PA1180). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Studies on Avarol Derivatives. 2',5'-Di-acetylavarol from *Dysidea Avara*

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Abstract

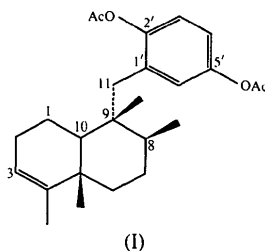
The X-ray analysis of the natural product 2',5'-diacetylavarol [De Giulio, De Rosa, Di Vincenzo & Strazzullo (1990). *Tetrahedron*, **46**, 7971–7976], 2-[(1,2,3,4,4a,7,8,8a-octahydro-1,2,4a,5-tetramethyl-1-naphthyl)methyl]-1,4-benzenediyl diacetate, C₂₅H₃₄O₄, is reported. Short intramolecular contacts between the bulky substituents of the bicyclic system cause significant distortions of the molecular geometry. The $\Delta^{3,4}$ cyclohexene ring adopts a conformation intermediate between half chair and half boat, and the cyclohexane ring is in a nearly ideal chair conformation. The hydroquinone system is almost perpendicular to the *trans*-fused sesquiterpene residue. The acetyl groups are

oriented on the opposite sides of the aromatic ring with the carbonyl O atoms *cis* relative to their respective ring C atoms. Crystal packing exhibits normal van der Waals interactions.

Comment

This study is part of a program of structural and biological investigations concerning the analysis of the structural features (Giordano & Puliti, 1987; Puliti, De Rosa & Mattia, 1994, 1995) and pharmacological properties (De Rosa, De Giulio & Strazzullo, 1991, and references therein) of the avarol–avarone pair and its derivatives.

2',5'-Diacetylavarol, (I), has been isolated recently as a minor secondary metabolite from the marine sponge *Dysidea avara* and characterized mainly by spectral data (De Giulio, De Rosa, Di Vincenzo & Strazzullo, 1990). Its biological and pharmacological properties were tested extensively and compared with those of several avarol–avarone derivatives (De Giulio, De Rosa, Strazzullo, Diliberto, Obino, Marongiu, Pani & La Colla, 1991).



A perspective view of the final X-ray model of (I) is shown in Fig. 1. The molecular geometry is in good agreement with those of closely related molecules (Giordano & Puliti, 1987; Puliti, De Rosa & Mattia, 1994, 1995). The presence of short intramolecular contacts between the bulky substituents of the bicyclic system causes significant distortions with respect to normal C_{sp^2} and C_{sp^3} geometry. In particular, the endocyclic bond distances involving the atomic sequence C5, C10, C9 and C8 reach values greater than 1.550 Å, and the C4–C5 bond, adjacent to the double bond, is lengthened to 1.533 (3) Å. Similarly, the angles C5–C10–C9 [116.8 (2)°], C10–C5–C14 [114.6 (2)°], C7–C8–C9 [114.2 (2)°] and C9–C8–C13 [113.8 (2)°] are increased. Furthermore, the large value of angle C9–C11–C1' and the long distances involving atom C11 partially relieve the steric strain between the sesquiterpene and hydroquinone residues. Similar geometrical features are present in avarol-related molecules, such as arenarol diacetate (Schmitz, Lakshmi, Powell & van der Helm, 1984).

The $\Delta^{3,4}$ cyclohexene ring adopts a conformation intermediate between a half chair and a half boat. Atoms C1 and C10 are displaced by 0.235 (3) and

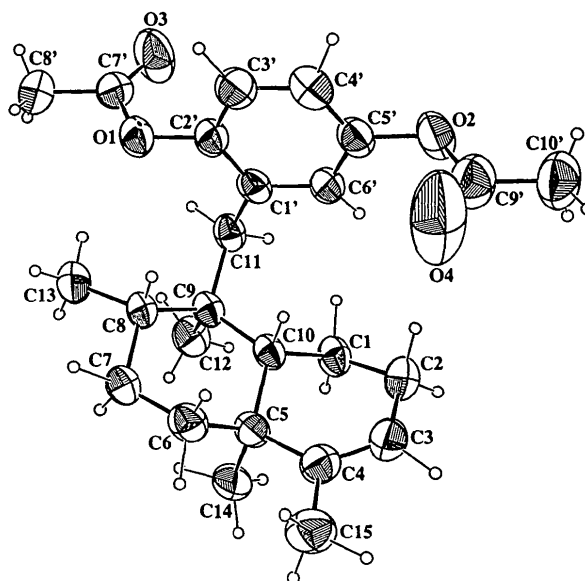


Fig. 1. A perspective view of the title molecule with the atomic numbering scheme for the non-H atoms. Displacement ellipsoids are plotted at the 30% probability level.

0.545 (2) Å, respectively, on opposite sides of the best plane through the remaining ring atoms. Deviation from ideal C_2 (HC) and C_5 (HB) symmetries can be measured by the asymmetry parameters: $\Delta C_2[C3-C4] = 11.2$ (4) and $\Delta C_5[C3] = 13.5$ (4)° (Duax, Weeks & Rohrer, 1976). The cyclohexane ring approximates an ideal chair with $Q = 0.544$ (3) Å, $\theta = 8.6$ (3) and $\varphi_2 = -23$ (2)° for the atomic sequence C6, C7–C10, C5, according to the Cremer & Pople (1975) puckering parameters. With respect to the ideal chair form, atom C9 is slightly more flattened than C6, with distances of 0.594 (2) and 0.686 (3) Å, respectively, from the best plane through atoms C5, C7, C8 and C10. In this ring, the mean intracycle torsion angle value is 52.8 (5)°.

The aromatic ring is strictly planar. Atoms O1 and O2 deviate by 0.042 (2) and 0.094 (2) Å, respectively, in opposite directions from the ring plane. The two acetyl groups protrude on opposite sides of the hydroquinone system and their carbonyl atoms O3 and O4 are *cis* to ring atoms C2' and C5', respectively. The acetyl group at O2 refines with a high displacement parameter. As shown in Fig. 1, atom O4 has a particularly large anisotropic component in the direction perpendicular to the acetyl plane, corresponding to a maximum r.m.s. displacement of 0.70 (1) Å, compared with the minimum value of 0.245 (3) Å. A restrained refinement, including two alternative acetyl groups differently tilted around C5'–O2 and O2–C9', gave a small improvement of the discrepancy index (0.042 *versus* 0.047). Atomic parameters pertinent to the restrained refinement are given in the deposited supplementary material.

The benzenediol–diacetate system is oriented in order to optimize intramolecular contacts. The *trans* con-

formation of the C11—C1' bond with respect to the C9—C12 bond is a recurring feature in avarol-type molecules. As a consequence, the hydroquinone ring is roughly perpendicular to the bicyclic system. In the present structure, the dihedral angle between the two weighted best planes is 91.30(6)°. It is worth noting that the hydroquinone ring is rotated approximately 180° around the C11—C1' bond with respect to avarol and its monoacetyl derivative structures (Puliti, De Rosa & Mattia, 1994, 1995). Both orientations were found in the two molecules which form the asymmetric unit of the dimethylavarol crystal (Giordano & Puliti, 1987). The orientation of the hydroquinone system in (I) is the same as in arenarol diacetate, which has a disubstituted hydroquinone unit linked to an enantiomeric rearranged sesquiterpene skeleton similar to avarol, but *cis* fused (Schmitz, Lakshmi, Powell & van der Helm, 1984). The superposition of 17 pairs of corresponding atoms in the two molecules is within 0.18 Å, with an r.m.s. deviation of 0.08 Å.

The crystal packing is governed by normal van der Waals interactions. The shortest intermolecular contacts are O3···C6'(1/2 + x, 1/2 - y, -z) 3.290(3) and C14···C8'(x - 1, y, z) 3.617(4) Å.

Experimental

Crystals of 2-[(1,2,3,4,4a,7,8,8a-octahydro-1,2,4a,5-tetramethyl-1-naphthyl)methyl]-1,4-benzenediyl diacetate were obtained by slow evaporation of an *n*-hexane-ethyl ether solution.

Crystal data

C₂₅H₃₄O₄
M_r = 398.55
 Orthorhombic
*P*2₁2₁2₁
a = 10.184(2) Å
b = 13.362(1) Å
c = 16.429(1) Å
V = 2235.6(8) Å³
Z = 4
D_x = 1.184 Mg m⁻³

Data collection

Enraf-Nonius CAD-4F
 diffractometer
ω-2*θ* scans
 Absorption correction:
 none
 2609 measured reflections
 2609 independent reflections
 2545 observed reflections
 [*I* ≥ 2.5σ(*I*)]

Refinement

Refinement on *F*
R = 0.047
wR = 0.055

Cu Kα radiation
 λ = 1.5418 Å
 Cell parameters from 24
 reflections
 θ = 25–29°
 μ = 0.590 mm⁻¹
T = 293 K
 Prism
 0.5 × 0.5 × 0.3 mm
 Colourless

θ_{max} = 75°
h = 0 → 12
k = 0 → 16
l = 0 → 20
 4 standard reflections
 frequency: 240 min
 intensity decay: 4%

(Δ/σ)_{max} = 0.01
 Δρ_{max} = 0.24 e Å⁻³
 Δρ_{min} = -0.24 e Å⁻³

S = 1.08
 2545 reflections
 263 parameters
 H-atom parameters not
 refined
w = 1/[σ²(*F_o*) + (0.02*F_o*)²
 + 4] (Killean &
 Lawrence, 1969)

Extinction correction:
 Stout & Jensen (1968)
 Extinction coefficient:
 3.3(1) × 10⁻⁶
 Atomic scattering factors
 from *International Tables*
 for *X-ray Crystallography*
 (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$B_{eq} = (1/3)\sum_i\sum_j B_{ij}a_i^*a_j^*a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B_{eq}</i>
O1	0.6602(2)	0.0063(1)	0.0151(1)	4.28(3)
O2	0.5093(2)	0.2967(1)	-0.2060(1)	5.14(4)
O3	0.7488(3)	0.1207(2)	0.0963(2)	7.82(6)
O4	0.4318(5)	0.1923(2)	-0.2940(2)	16.9(1)
C1	0.1275(3)	0.1327(3)	-0.0508(2)	4.06(5)
C2	0.0849(3)	0.1672(2)	-0.1351(2)	4.94(6)
C3	0.0392(3)	0.0820(2)	-0.1873(2)	4.69(6)
C4	0.0559(3)	-0.0147(2)	-0.1704(2)	4.14(5)
C5	0.1195(2)	-0.0498(2)	-0.0908(2)	3.47(4)
C6	0.2081(3)	-0.1404(2)	-0.1065(2)	4.21(5)
C7	0.2803(3)	-0.1722(2)	-0.0297(2)	4.78(6)
C8	0.3650(3)	-0.0893(2)	0.0067(2)	3.76(5)
C9	0.2913(2)	0.0115(2)	0.0199(1)	3.35(4)
C10	0.2083(2)	0.0360(2)	-0.0567(1)	3.20(4)
C11	0.3966(3)	0.0954(2)	0.0338(1)	3.59(4)
C12	0.2090(3)	0.0097(2)	0.0990(2)	4.55(5)
C13	0.4307(3)	-0.1304(2)	0.0843(2)	5.44(6)
C14	0.0051(3)	-0.0803(2)	-0.0346(2)	4.33(5)
C15	0.0069(4)	-0.0938(3)	-0.2278(2)	6.04(7)
C1'	0.4923(2)	0.1204(2)	-0.0341(1)	3.43(4)
C2'	0.6178(3)	0.0815(2)	-0.0400(2)	3.77(5)
C3'	0.7062(3)	0.1085(2)	-0.0994(2)	4.67(6)
C4'	0.6697(3)	0.1797(2)	-0.1573(2)	4.78(6)
C5'	0.5460(3)	0.2197(2)	-0.1523(2)	4.04(5)
C6'	0.4585(3)	0.1921(2)	-0.0925(2)	3.71(5)
C7'	0.7297(3)	0.0353(2)	0.0807(2)	4.20(5)
C8'	0.7742(3)	-0.0507(2)	0.1309(2)	5.04(6)
C9'	0.4459(4)	0.2742(3)	-0.2736(2)	6.49(8)
C10'	0.3988(4)	0.3641(3)	-0.3174(2)	7.40(9)

Table 2. Selected geometric parameters (Å, °)

O1—C2'	1.420(3)	C7—C8	1.527(3)
O1—C7'	1.347(3)	C8—C9	1.557(3)
O2—C5'	1.406(3)	C8—C13	1.540(4)
O2—C9'	1.319(4)	C9—C10	1.552(3)
O3—C7'	1.185(3)	C9—C11	1.568(3)
O4—C9'	1.154(4)	C9—C12	1.547(3)
C1—C2	1.523(4)	C11—C1'	1.517(3)
C1—C10	1.536(3)	C1'—C2'	1.383(4)
C2—C3	1.499(4)	C1'—C6'	1.400(3)
C3—C4	1.333(4)	C2'—C3'	1.376(4)
C4—C5	1.533(3)	C3'—C4'	1.397(4)
C4—C15	1.502(4)	C4'—C5'	1.371(4)
C5—C6	1.533(3)	C5'—C6'	1.376(4)
C5—C10	1.563(3)	C7'—C8'	1.486(4)
C5—C14	1.541(3)	C9'—C10'	1.481(5)
C6—C7	1.521(4)		
C2'—O1—C7'	117.8(2)	C11—C9—C12	105.1(2)
C5'—O2—C9'	119.5(2)	C1—C10—C5	109.2(2)
C2—C1—C10	110.5(2)	C1—C10—C9	114.7(2)
C1—C2—C3	112.2(2)	C5—C10—C9	116.8(2)
C2—C3—C4	125.3(3)	C9—C11—C1'	119.3(2)
C3—C4—C5	121.8(2)	C11—C1'—C2'	124.2(2)
C3—C4—C15	120.6(3)	C11—C1'—C6'	119.8(2)
C5—C4—C15	117.5(2)	C2'—C1'—C6'	115.9(2)
C4—C5—C6	110.2(2)	O1—C2'—C1'	120.2(2)
C4—C5—C10	109.0(2)	O1—C2'—C3'	116.0(2)
C4—C5—C14	105.8(2)	C1'—C2'—C3'	123.8(2)
C6—C5—C10	107.4(2)	C2'—C3'—C4'	119.2(3)

C6—C5—C14	109.7 (2)	C3'—C4'—C5'	117.9 (3)
C10—C5—C14	114.6 (2)	O2—C5'—C4'	119.4 (3)
C5—C6—C7	111.4 (2)	O2—C5'—C6'	118.1 (2)
C6—C7—C8	113.3 (2)	C4'—C5'—C6'	122.3 (2)
C7—C8—C9	114.2 (2)	C1'—C6'—C5'	120.9 (2)
C7—C8—C13	108.1 (2)	O1—C7'—O3	122.5 (3)
C9—C8—C13	113.8 (2)	O1—C7'—C8'	112.4 (2)
C8—C9—C10	109.4 (2)	O3—C7'—C8'	125.1 (3)
C8—C9—C11	108.0 (2)	O2—C9'—O4	121.4 (4)
C8—C9—C12	111.4 (2)	O2—C9'—C10'	112.5 (3)
C10—C9—C11	109.8 (2)	O4—C9'—C10'	126.0 (4)
C10—C9—C12	112.9 (2)		
C7'—O1—C2'—C1'	-96.6 (3)	C13—C8—C9—C12	-44.1 (3)
C2'—O1—C7'—O3	4.9 (4)	C2—C3—C4—C5	3.4 (4)
C9'—O2—C5'—C4'	95.1 (3)	C8—C9—C11—C1'	63.3 (3)
C5'—O2—C9'—O4	-8.1 (6)	C9—C11—C1'—C2'	-96.2 (3)
C4—C5—C10—C9	-174.7 (2)	C6'—C1'—C2'—O1	-178.3 (2)
C14—C5—C10—C9	66.9 (3)	C3'—C4'—C5'—O2	175.5 (2)

The equipment of the CIMCF of the University 'Federico II' of Naples was used for collection of the crystallographic data. H atoms were placed on the basis of geometrical considerations and ΔF map suggestions in the case of the hydroxy and methyl groups. All H atoms were included with B_{iso} values fixed at the values of B_{eq} of their respective parent atoms. The structure was solved using *MULTAN11/82* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982). All calculations were performed using Enraf-Nonius *SDP* software (B. A. Frenz & Associates Inc., 1985) on a MicroVAX 3100 computer.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and the atomic parameters of the restrained refinement have been deposited with the IUCr (Reference: NA1165). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Configuration and Conformation of (3*S*,3*aR*,4*R*,7*S*,7*aS*)-4-Methyl-7-(2-propyl)-2-oxo-2,3,3*a*,4,5,6,7,7*a*-octahydro-3-benzofurancarboxylic Acid

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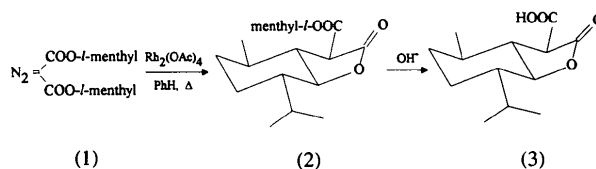
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Abstract

The crystal structure determination of the title compound, C₁₃H₂₀O₄, together with the knowledge of the configuration of the starting menthyl reagent, define both its absolute configuration and that of the menthyl ester from which it is obtained by hydrolysis. The structure of the title compound in the crystal is compared with that obtained for the isolated molecule by molecular-mechanics energy minimization. The largest discrepancies are observed for the carboxyl group which, in the crystal, is involved in hydrogen bonding with the same group of an adjacent molecule packed about a twofold axis of the $P2_12_12$ space group. The conformation of the molecule is discussed.

Comment

The catalytic decomposition of di(1*R*,3*S*,4*S*)-(–)-menthlyldiazomalonate, (1), in the presence of rhodium-(II) acetate dimer gave exclusive formation of the bicyclic γ -lactone (2) by intramolecular carbenic attack on a methylenic C—H bond of the menthyl ring, according to the scheme below.



The crystal structure analysis of the acid (3), obtained by hydrolysis of the ester (2), was carried out to establish the configurations at the chiral centres of these