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2,3,4aβ,8aβ-Tetramethyl-4a,5,8,8a-tetrahydro-1-naphthoquin-4α-yl Benzoate,* $C_{21}H_{24}O_3$

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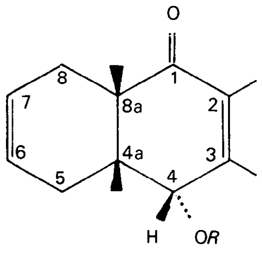
Abstract. $M_r = 324{\cdot}4$, triclinic, $P\bar{1}$, $a = 9{\cdot}6506\,(7)$, $b = 11{\cdot}0330\,(8)$, $c = 8{\cdot}5530\,(7)$ Å, $\alpha = 93{\cdot}078\,(7)$, $\beta = 91{\cdot}122\,(6)$, $\gamma = 94{\cdot}345\,(6)°$, $V = 906{\cdot}5\,(1)$ Å^3, $Z = 2$, $D_x = 1{\cdot}189$ g cm^{-3}, $F(000) = 348$, $T = 294$ K, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71073$ Å, $\mu = 0{\cdot}73$ cm^{-1}, $R = 0{\cdot}048$ for 2961 reflexions. The tetrahydronaphthoquinol ring system has a conformation typical for derivatives with a 4α substituent.

Introduction. The crystal structure of the benzoate has been determined in the course of a study of the solid-state photochemistry of substituted tetrahydronaphthoquinols (Secco & Trotter, 1982).



$R = C_6H_5CO$–

Experimental. CAD-4 diffractometer, crystal faces {100}, {001}, {101}, {010}, dimensions 0·4 × 0·6 × 0·7 mm, D_m not measured, monochromatized Mo $K\alpha$ radiation, cell parameters from $\sin^2\theta$ values for 21 reflections ($\theta = 5 - 19°$), intensity data for $0 < \theta \leq 27{\cdot}5°$, ω–$(4/3)\theta$ scans, ω scan angle $(0{\cdot}85 + 0{\cdot}35\tan\theta)°$, extended by 25% in each direction for background, scan speeds 1 to 10° min^{-1}, horizontal aperture $(2{\cdot}00 + \tan\theta)$ mm, vertical aperture 4 mm, three standard reflexions, Lp but no absorption corrections; 4130 reflections, 2961 (72%) with $I \geq 3\sigma(I)$, $\sigma^2(I) = S + 2B + [0{\cdot}04(S-B)]^2$, S = scan count, B = time-corrected background. Direct methods, full-matrix least squares on F, H atoms from a difference map refined isotropically,† $w = (0{\cdot}0329 + 0{\cdot}02117|F_o| - 0{\cdot}00227|F_o|^2 + 0{\cdot}0002221|F|^3)^{-1}$, final $R = 0{\cdot}048$, $R_w = 0{\cdot}069$ for 2961 reflexions with $I \geq 3\sigma(I)$, $R = 0{\cdot}066$ for all 4130 reflexions, $S = 0{\cdot}98$, mean and maximum shifts on final cycle 0·04 and 0·60σ, final difference synthesis ±0·25 e Å^{-3}. Scattering factors from Cromer & Mann (1968) and Stewart, Davidson & Simpson (1965). No correction for secondary extinction.

Discussion. Final atomic parameters in Table 1.‡

The conformation of the tetrahydronaphthoquinol ring system (Fig. 1) is typical of that of other molecules in the series which have 4α substituents, *i.e.* *anti* or *trans* to the bridgehead 4β-methyl groups (Greenhough & Trotter, 1981; Secco & Trotter, 1982). The ring system is twisted, with a C(4a1)—C(4a)—C(8a)—C(8a1) torsion angle of 61·7 (2)°, the corresponding value in the parent hydroxy compound being 63·0 (2)° (Greenhough & Trotter, 1980). The 4α-C_6H_5COO— substituent occupies a pseudo-equatorial position on the half-chair cyclohexenone ring. The parameters relevant to photochemical reactivity are: H1(5)···C(3) = 2·79 (2) Å, $\tau_C = 53°$, $\Delta_C = 79{\cdot}2\,(4)°$, C(2)···C(5) = 3·335 (2) Å [corresponding values in the parent tetramethyl-hydroxy compound are 2·78 (2) Å, 52°,

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* IUPAC name: 2,3,4aβ,8aβ-tetramethyl-1(4*H*)-oxo-4a,5,8,8a-tetrahydro-4α-naphthyl benzoate.

† Computer programs include locally written programs for data processing and locally modified versions of *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), *ORFLS* (Busing, Martin & Levy, 1962) and *ORFFE* (Busing, Martin & Levy, 1964), *FORDAP* (A. Zalkin), and *ORTEP*II (Johnson, 1976).

‡ Lists of structure factors, thermal parameters, bond distances and angles involving H atoms, and a packing diagram have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38729 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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77·5 (5)°, 3·30 Å (Greenhough & Trotter, 1980)]. The parent compound is photochemically reactive in the solid state, but the major photoproduct is the (2+2) cycloaddition solution product, suggesting local melting of the crystal during irradiation (Appel, Jiang, Scheffer & Walsh, 1983). The photochemistry of the benzoate has not been studied.

Bond distances and angles (Table 2) are very similar to those in the parent compound (Greenhough & Trotter, 1980), the only significant differences being associated with the replacement of the 4-OH by the benzoyloxy group. C(4)—O(2), 1·458 (2) Å in the benzoate, is increased in length by 0·026 Å (7σ) relative to the parent compound, 1·432 (3) Å, with accompanying small reductions (4σ and 2σ) in C(4)—C(3) and C(4)—C(4a). The C(3)—C(4)—C(4a) angle increases [from 114·2 (2) to 116·0 (1)°] with an accompanying decrease in C(3)—C(4)—O(2) [109·9 (2) to 107·1 (1)°].

Table 1. *Final positional (fractional* $\times 10^5$, *for* H $\times 10^3$) *and isotropic thermal parameters* ($Å^2 \times 10^3$) *with e.s.d.'s in parentheses*

$$U_{\rm eq} = \tfrac{1}{3}\sum_i\sum_j U_{ij}a^*_i a^*_j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}/U_{\rm iso}$
C(1)	25512 (17)	32039 (15)	14889 (18)	49
C(2)	39973 (17)	30238 (15)	19942 (18)	49
C(21)	44023 (32)	35223 (31)	36293 (26)	81
C(3)	48443 (16)	24439 (14)	10389 (19)	48
C(31)	62788 (22)	21470 (25)	15284 (33)	72
C(4)	43705 (15)	19718 (14)	−5824 (18)	43
C(4a)	30731 (16)	24979 (14)	−12384 (18)	45
C(4a1)	25778 (26)	17504 (22)	−27410 (27)	67
C(5)	34181 (20)	38341 (16)	−16484 (22)	56
C(6)	21515 (27)	45115 (20)	−18821 (26)	73
C(7)	9104 (27)	41402 (22)	−13973 (29)	79
C(8)	6309 (20)	30061 (22)	−5607 (31)	72
C(8a)	19525 (16)	24643 (15)	401 (20)	50
C(8a1)	15626 (23)	11784 (20)	5807 (33)	70
C(9)	60895 (17)	13697 (14)	−24243 (20)	51
C(10)	71968 (16)	18525 (15)	−34592 (18)	48
C(11)	75341 (18)	30890 (17)	−35420 (21)	54
C(12)	85671 (20)	34989 (21)	−45293 (23)	64
C(13)	92613 (20)	26737 (23)	−54296 (24)	70
C(14)	89279 (22)	14433 (24)	−53397 (25)	73
C(15)	79079 (20)	10261 (19)	−43671 (24)	63
O(1)	18479 (15)	38662 (14)	22714 (17)	74
O(2)	55046 (11)	22731 (9)	−16300 (14)	51
O(3)	57558 (17)	3051 (12)	−23095 (20)	81
H1(21)	464 (4)	293 (4)	426 (5)	151 (15)
H2(21)	527 (5)	391 (4)	388 (5)	162 (15)
H3(21)	365 (4)	394 (3)	424 (5)	152 (13)
H1(31)	653 (4)	140 (4)	108 (5)	166 (15)
H2(31)	691 (3)	269 (3)	100 (3)	97 (8)
H3(31)	646 (3)	233 (3)	268 (4)	119 (10)
H(4)	424 (2)	107 (2)	−57 (2)	53 (5)
H1(4a1)	227 (3)	101 (2)	−247 (3)	89 (8)
H2(4a1)	183 (3)	209 (2)	−325 (3)	98 (8)
H3(4a1)	329 (2)	170 (2)	−358 (3)	76 (6)
H1(5)	393 (2)	383 (2)	−262 (3)	70 (6)
H2(5)	405 (2)	427 (2)	−85 (2)	58 (5)
H(6)	225 (2)	530 (2)	−241 (3)	77 (6)
H(7)	16 (3)	460 (2)	−159 (3)	84 (7)
H1(8)	14 (2)	239 (2)	−119 (3)	81 (7)
H2(8)	6 (3)	316 (2)	40 (3)	92 (7)
H1(8a1)	116 (3)	60 (2)	−37 (3)	101 (8)
H2(8a1)	229 (3)	79 (2)	111 (3)	84 (7)
H3(8a1)	93 (4)	118 (3)	138 (4)	126 (11)
H(11)	707 (2)	366 (2)	−293 (3)	75 (6)
H(12)	871 (3)	434 (2)	−456 (3)	82 (7)
H(13)	992 (3)	297 (2)	−615 (3)	86 (7)
H(14)	944 (3)	83 (2)	−594 (3)	87 (7)
H(15)	772 (2)	19 (2)	−426 (3)	79 (7)

The dimensions of the benzoyloxy group are normal: C=O = 1·204 (2), C—O = 1·342 (2), C(carboxyl)—C(phenyl) = 1·487 (2), C—C(phenyl) = 1·370–1·395 (3) Å, C(4)—O(2)—C(9) = 119·1 (1)°. Intermolecular distances correspond to normal van der Waals interactions; the shortest contacts are C···O = 3·291 (2), C···C = 3·480 (3) Å.

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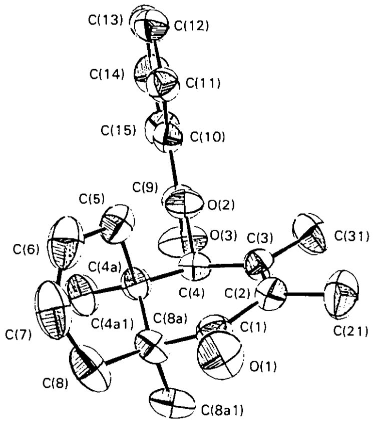

Fig. 1. Diagram of the tetramethyltetrahydronaphthoquinyl benzoate (50% thermal ellipsoids, H atoms omitted).

Table 2. *Bond lengths* (Å) *and angles* (°) *with estimated standard deviations in parentheses*

C(1)—C(2)	1·484 (2)	C(6)—C(7)	1·318 (4)
C(1)—C(8a)	1·526 (2)	C(7)—C(8)	1·484 (4)
C(1)—O(1)	1·218 (2)	C(8)—C(8a)	1·540 (3)
C(2)—C(21)	1·508 (3)	C(8a)—C(8a1)	1·538 (3)
C(2)—C(3)	1·339 (2)	C(9)—C(10)	1·487 (2)
C(3)—C(31)	1·503 (2)	C(9)—O(3)	1·204 (2)
C(3)—C(4)	1·505 (2)	C(9)—O(2)	1·342 (2)
C(4)—C(4a)	1·529 (2)	C(10)—C(11)	1·384 (2)
C(4)—O(2)	1·458 (2)	C(10)—C(15)	1·395 (2)
C(4a)—C(4a1)	1·537 (2)	C(11)—C(12)	1·385 (2)
C(4a)—C(5)	1·547 (2)	C(12)—C(13)	1·381 (3)
C(4a)—C(8a)	1·553 (2)	C(13)—C(14)	1·378 (3)
C(5)—C(6)	1·496 (3)	C(14)—C(15)	1·370 (3)

C(2)—C(1)—C(8a)	117·86 (14)	C(6)—C(7)—C(8)	123·3 (2)
C(2)—C(1)—O(1)	120·36 (15)	C(7)—C(8)—C(8a)	113·8 (2)
C(8a)—C(1)—O(1)	121·63 (15)	C(1)—C(8a)—C(4a)	108·12 (12)
C(1)—C(2)—C(21)	115·1 (2)	C(1)—C(8a)—C(8)	110·27 (14)
C(1)—C(2)—C(3)	120·75 (14)	C(1)—C(8a)—C(8a1)	105·8 (2)
C(21)—C(2)—C(3)	124·2 (2)	C(4a)—C(8a)—C(8)	110·1 (2)
C(2)—C(3)—C(31)	123·2 (2)	C(4a)—C(8a)—C(8a1)	113·44 (15)
C(2)—C(3)—C(4)	121·29 (14)	C(8)—C(8a)—C(8a1)	109·0 (2)
C(31)—C(3)—C(4)	115·4 (2)	C(10)—C(9)—O(3)	124·55 (15)
C(3)—C(4)—C(4a)	115·97 (13)	C(10)—C(9)—O(2)	111·38 (13)
C(3)—C(4)—O(2)	107·09 (12)	O(3)—C(9)—O(2)	124·07 (15)
C(4a)—C(4)—O(2)	107·31 (12)	C(9)—C(10)—C(11)	121·90 (14)
C(4)—C(4a)—C(4a1)	108·92 (14)	C(9)—C(10)—C(15)	118·5 (2)
C(4)—C(4a)—C(5)	110·07 (13)	C(11)—C(10)—C(15)	119·6 (2)
C(4)—C(4a)—C(8a)	108·23 (12)	C(10)—C(11)—C(12)	120·0 (2)
C(4a1)—C(4a)—C(5)	108·6 (2)	C(11)—C(12)—C(13)	120·0 (2)
C(4a1)—C(4a)—C(8a)	112·10 (15)	C(12)—C(13)—C(14)	119·9 (2)
C(5)—C(4a)—C(8a)	108·90 (13)	C(13)—C(14)—C(15)	120·7 (2)
C(4a)—C(5)—C(6)	113·0 (2)	C(10)—C(15)—C(14)	119·8 (2)
C(5)—C(6)—C(7)	123·5 (2)	C(4)—O(2)—C(9)	119·11 (12)

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Vaginatin, $C_{20}H_{30}O_4$

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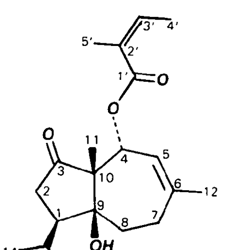
Abstract. $M_r = 334{\cdot}5$, orthorhombic, $P2_12_12_1$, $a = 12{\cdot}993\,(7)$, $b = 7{\cdot}979\,(3)$, $c = 18{\cdot}64\,(1)$ Å, $U = 1932\,(1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}15$ Mg m^{-3}, $\lambda(\text{Mo }K\alpha) = 0{\cdot}71073$ Å, $\mu = 0{\cdot}084$ mm^{-1}, $F(000) = 728$, $T = 293$ K. Final $R = 0{\cdot}055$ for 1446 observed reflections. The proposed constitution of this sesquiterpenoid from *Selinum vaginatum* was confirmed, and the relative configurations of the four chiral centers were established. It appears to be a biological oxidation product of carotol.



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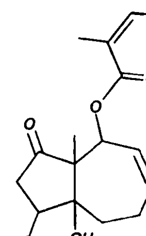

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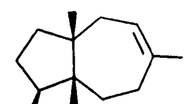

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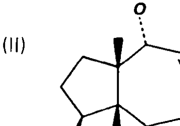

(IV)

Introduction. Vaginatin was isolated from *Selinum vaginatum* (Mesta, Paknikar & Bhattacharyya, 1968) and the partial structure (II) was assigned (Rajendran, Paknikar, Trivedi & Bhattacharyya, 1978). A crystal-structure analysis was performed to check the constitution and to establish the stereochemistry.

Experimental. Crystal dimensions 0·3 × 0·3 × 0·3 mm. Syntex $P2_1$ four-circle diffractometer. Cell constants from 15 reflections with $5 \leq 2\theta \leq 25°$. No absorption correction. $2\theta_{\max} = 50°$. Range of *hkl*: 0–15, 0–9, 0–22. Three check reflections collected after every 100 data points showed no appreciable crystal decay. 1446 of 2014 reflections with $I > 3\sigma(I)$ used in F^2 refinement $R_{\text{int}} = 0{\cdot}055$. Structure solved by *MULTAN*80 (Main *et al.*, 1980) using 150 highest *E* values; all 24 non-H atoms found in first *E* map. Refinement of non-H atoms with isotropic temperature factors gave $R = 0{\cdot}125$, refinement with anisotropic temperature factors led to $R = 0{\cdot}091$, final refinement (217 parameters) was of non-H atoms after adding H atoms in calculated positions with isotropic temperature factors; $wR = 0{\cdot}067$, $S = 2{\cdot}6$, weighting scheme of Corfield, Doedens & Ibers (1967), with $p = 0{\cdot}04$. $(\Delta/\sigma)_{\max} = 0{\cdot}11$. $\Delta\rho = -0{\cdot}3$–$0{\cdot}3$ e Å^{-3}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1962). Least-squares refinement program *NUCLS* (Doedens & Ibers, 1967), plotter program *ORTEP* (Johnson, 1965).

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