molecular interaction; the usual 90° torsion angle could bring adjacent molecules even closer together with a reduction in stability of the crystal lattice.

The phenyl and carbonyl groups are both able to adopt the preferred bisected conformation (Jason & Ibers, 1977) with respect to the cyclopropane ring C(4)—C(5)—C(6), unlike the situation in the isomeric bis[(1-phenyl-1-cyclopropyl)carbonyl] peroxide where there are steric constraints (Bethell, Chadwick, Harding & Maling, 1982). Further, the C—C bond lengths in the three-membered ring show a combination of vicinal bond lengthening and distal bond shortening as previously noted (Allen, 1980), the effect of the carbonyl group appearing to dominate as in the isomeric peroxide. This effect is exaggerated in the bond lengths of the cyclopropane ring C(16)—C(17)—C(18) since the attached carbonyl group adopts the bisected conformation but the phenyl group is twisted from it by some 30°. It should be noted, however, that the orbital interaction implied by these effects does not appear to lead to lengthening of the C=O bond which is substantially shorter than such bonds in unconjugated acyloxy groups (Allen, 1981), in common with other diacyl peroxides. We also note that, in the present compound as in its isomer, the carbonyl group adopts the bisected conformation in which its O atom lies

vertically above the three-membered ring. Bearing in mind the parallelism of behaviour often noted between cyclopropyl and vinyl groups (e.g. Noe & Young, 1982), this preference is analogous to that for the s-cis conformation found in trans-cinnamoyl peroxide.

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Stereochemistry and Absolute Structure of (+)-8β-Acetoxy-12-(4-bromobenzoyloxy)-13,14,15,16-tetranorlabdane,* C23H35BrO4

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Abstract. $M_r = 479.5$, orthorhombic, $P2_12_12_1$, $a = 7.3547$ (6), $b = 11.0209$ (10), $c = 30.025$ (3) Å, $V = 2433.7$ (3) Å^3, $Z = 4$, $D_x = 1.308$ Mg m^{-3}, Mo $K\bar{\alpha}$, $\lambda = 0.71069$ Å, $\mu = 1.693$ mm^{-1}, $F(000) = 1008$, room temperature, $R = 4.6\%$ for 2519 observed reflections (mostly Friedel pairs), $[\alpha]_D^{20°C} +31.6°$ (1.2% in CHCl$_3$), m.p. 382–384 K. The absolute configuration for chiral centres was confirmed by least-squares refinement to a high degree of precision using a new procedure for absolute structure assessment. The six-membered rings are trans-fused and both are in the chair conformation.

Introduction. Ambergris fragrances display a strong stereochemistry–odour relationship to norlabdane derivatives, Ambrox® (1) being the most typical example (Ohloff, 1982). The two diastereoisomeric ethers (2) and (3) differ in tonality and odour strength from (1). The steric effect at receptor level is held responsible for

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* (+)-12-(4-Bromobenzoyloxy)-13,14,15,16-tetranorlabdan-8β-yl acetate.

the different sensory activity. For the verification of this hypothesis (Ohloff, 1982) we need a precise conformational analysis of the 1,4-diols (4)–(6), precursors of the tricyclic ethers (1)–(3). In this communication we describe the synthesis and the determination of the structure by X-ray diffraction analysis of the 8β-acetoxy-12-(p-bromobenzoyloxy) derivative (Fig. 1) of diol (5). These compounds are derived with retention of configuration from (+)-norambreinolide, of which the absolute configuration is known (Buchecker et al., 1973; Klyne & Buckingham, 1978).

(1) (2) (3)

(4) (5) (6)
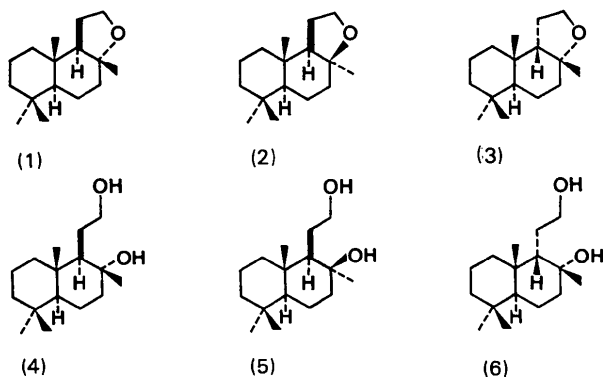
Experimental. 219 mg (1 mmol) p-brombenzoyl chloride (Fluka) were added to a stirred solution of 254 mg (1 mmol) of diol (5) (Hinder & Stoll, 1953) in 3 ml dimethylaniline under cooling (ice bath). After stirring for 10 h at room temperature the reaction mixture was diluted with ether (100 ml) and washed with cold diluted H_2SO_4 (2×), cold $NaHCO_3$ solution (1×), and brine (2×). After evaporation of the solvent the product was chromatographed on silica gel with cyclohexane/ether (9:1) as eluent to yield 410 mg of the monoester. This intermediate was dissolved in 3 ml dimethylaniline, and 102 mg (1 mmol) acetic anhydride

Fig. 1. The chemical structure of the title compound showing the numbering scheme.

and 78 mg acetyl chloride were added (stirring, ice bath). After 20 h at 313 K the reaction mixture was treated as above. The crude yield of the title compound was recrystallized from pentane to yield 320 mg pure product.

Crystal of average dimensions $0.37 \times 0.35 \times 0.19$ mm, with faces (102), (10$\bar{2}$), {012}, {001} and ($\bar{1}$00) (cleavage plane) cut from the tip of a colourless

Table 1. *Fractional coordinates and, for non-hydrogen atoms, equivalent isotropic temperature factors, U_{eq}, ($\mathring{A}^2 \times 10^2$) with e.s.d.'s in parentheses*

U_{eq} is the average of the eigenvalues of U.

	x	y	z	U_{eq}
C(1)	−0.0374 (8)	0.1068 (5)	0.13344 (24)	5.44 (21)
C(2)	−0.1054 (12)	0.0230 (7)	0.1696 (3)	7.6 (3)
C(3)	0.0506 (13)	−0.0501 (7)	0.1899 (3)	8.2 (3)
C(4)	0.2052 (11)	0.0280 (6)	0.20885 (24)	6.4 (3)
C(5)	0.2639 (9)	0.1190 (5)	0.17239 (22)	5.16 (21)
C(6)	0.4248 (10)	0.1995 (5)	0.18510 (20)	5.56 (19)
C(7)	0.5009 (9)	0.2567 (7)	0.1429 (3)	6.22 (24)
C(8)	0.3680 (7)	0.3345 (5)	0.11746 (20)	4.48 (18)
C(9)	0.1901 (9)	0.2628 (5)	0.10873 (18)	4.40 (18)
C(10)	0.1064 (9)	0.1977 (5)	0.15093 (18)	4.71 (17)
C(11)	0.3658 (13)	−0.0575 (6)	0.2182 (3)	8.6 (3)
C(12)	0.1515 (13)	0.0858 (7)	0.25252 (24)	7.5 (3)
C(13)	0.4522 (11)	0.3773 (7)	0.07371 (23)	7.0 (3)
O(14)	0.3124 (6)	0.4383 (4)	0.14437 (14)	5.40 (14)
C(15)	0.4267 (14)	0.5236 (6)	0.15709 (23)	7.0 (3)
O(16)	0.5839 (11)	0.5302 (6)	0.14748 (21)	10.1 (3)
C(17)	0.3345 (16)	0.6121 (7)	0.1873 (3)	9.4 (4)
C(18)	0.0486 (9)	0.3404 (5)	0.08334 (19)	5.45 (22)
C(19)	0.0190 (10)	0.2981 (6)	0.03620 (22)	6.42 (24)
O(20)	−0.1005 (7)	0.3808 (4)	0.01322 (13)	5.80 (14)
C(21)	−0.0286 (10)	0.4733 (8)	−0.0082 (3)	6.9 (3)
O(22)	0.1325 (9)	0.4880 (8)	−0.0113 (3)	11.8 (3)
C(23)	−0.1671 (10)	0.5571 (6)	−0.02756 (20)	5.68 (23)
C(24)	−0.1105 (13)	0.6560 (9)	−0.0532 (3)	9.5 (4)
C(25)	−0.2348 (14)	0.7319 (8)	−0.0723 (3)	9.2 (4)
C(26)	−0.4115 (13)	0.7141 (5)	−0.06487 (22)	6.21 (23)
C(27)	−0.4728 (10)	0.6199 (6)	−0.03894 (25)	6.31 (25)
C(28)	−0.3485 (9)	0.5429 (6)	−0.02060 (23)	5.52 (23)
Br(29)	−0.58695 (15)	0.81688 (7)	−0.09365 (3)	8.47 (3)
C(30)	0.0247 (8)	0.2876 (5)	0.18253 (22)	5.01 (20)
H(11)	−0.138 (9)	0.151 (5)	0.1214 (21)	
H(12)	0.034 (9)	0.056 (5)	0.1068 (20)	
H(21)	−0.171 (9)	0.058 (6)	0.1947 (22)	
H(22)	−0.192 (9)	−0.040 (6)	0.1545 (22)	
H(31)	0.002 (9)	−0.101 (5)	0.2088 (22)	
H(32)	0.101 (11)	−0.102 (5)	0.1652 (21)	
H(5)	0.302 (9)	0.067 (6)	0.1451 (21)	
H(61)	0.376 (10)	0.270 (5)	0.2080 (21)	
H(62)	0.535 (9)	0.149 (5)	0.1983 (21)	
H(71)	0.604 (10)	0.305 (6)	0.1512 (19)	
H(72)	0.565 (10)	0.198 (5)	0.1249 (19)	
H(9)	0.224 (8)	0.191 (6)	0.0914 (23)	
H(111)	0.474 (9)	−0.018 (6)	0.2335 (21)	
H(112)	0.335 (9)	−0.124 (6)	0.2352 (21)	
H(113)	0.395 (11)	−0.097 (5)	0.1871 (21)	
H(121)	0.135 (9)	0.024 (5)	0.2740 (22)	
H(122)	0.256 (9)	0.152 (5)	0.2683 (21)	
H(123)	0.027 (10)	0.132 (6)	0.2513 (23)	
H(131)	0.369 (9)	0.440 (5)	0.0580 (21)	
H(132)	0.572 (11)	0.419 (5)	0.0762 (20)	
H(133)	0.472 (9)	0.301 (6)	0.0536 (20)	
H(171)	0.218 (9)	0.641 (5)	0.1692 (22)	
H(172)	0.280 (9)	0.568 (6)	0.2144 (22)	
H(173)	0.448 (9)	0.667 (6)	0.1909 (20)	
H(181)	−0.065 (9)	0.340 (5)	0.0985 (21)	
H(182)	0.088 (11)	0.427 (5)	0.0836 (20)	
H(191)	0.132 (9)	0.294 (5)	0.0208 (20)	
H(192)	−0.040 (9)	0.213 (5)	0.0335 (20)	
H(24)	0.020 (9)	0.661 (5)	−0.0560 (21)	
H(25)	−0.179 (9)	0.792 (5)	−0.0839 (20)	
H(27)	−0.605 (11)	0.609 (5)	−0.0340 (20)	
H(28)	−0.381 (10)	0.481 (5)	0.0014 (21)	
H(301)	−0.059 (10)	0.253 (5)	0.2042 (22)	
H(302)	0.120 (10)	0.337 (5)	0.2024 (20)	
H(303)	−0.039 (9)	0.349 (5)	0.1689 (22)	
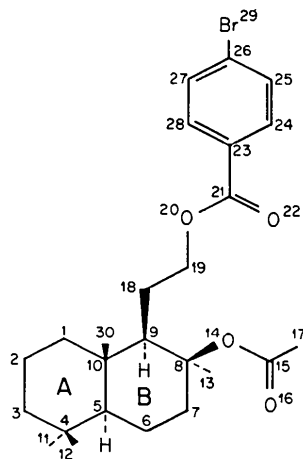
needle; Philips PW 1100 diffractometer, graphite-monochromated Mo $K\alpha$; cell dimensions from 24 reflections [$2\theta = 35$–$41°$, $\lambda(\text{Mo } K\alpha_1) = 0.70930$ Å]; data collection: $\sin\theta/\lambda < 0.53$ Å^{-1}, h 0–7, k 0–11, l 0–31 and all anti-reflections of these, $\omega/2\theta$ scans. ω-scan angle $(0.8 + 0.7 \tan\theta)°$; correction for steady decrease (2.4%) of three standard reflections ($\bar{2},0,\bar{16}$, 080, $\bar{503}$); 1787 independent Friedel pairs, 2519 reflections with $F \geq 3\sigma(F)$; Lorentz–polarization and analytical absorption corrections (min. 0.56, max. 0.74); systematic absences $h00$ $h = 2n + 1$, $0k0$ $k = 2n + 1$, $00l$ $l = 2n + 1$; distribution of data $\langle E^2-1\rangle = 0.704$ indicated non-centrosymmetric space group; structure solved by *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); blocked-matrix least squares using F values. 378 parameters refined: one scale factor, one isotropic secondary-extinction parameter, one enantiomorph-polarity parameter, atomic positional parameters for all atoms (including H atoms) and anisotropic temperature factors for all non-H atoms. Isotropic ($U = 0.07$ Å^2) H atoms initially placed at 1.09 Å from C atoms. $wR = 4.9\%$, $S = 13.2$, $w(F) = \exp[23.0(\sin\theta/\lambda)^2]/\sigma^2(F)$ (Dunitz & Seiler, 1973), max. and average ratio of |shift| to error for non-H atomic parameters, 0.09 and 0.005 respectively, for H atomic parameters 1.9 and 0.34 respectively, and |shift| to error for secondary-extinction parameter 3.7 in the final cycle, max. and min. height in the final difference electron density map of 0.34 and -0.46 e Å^{-3}. Secondary-extinction parameter, type 1, Lorentzian distribution of 0.74 (5) $\times 10^{-4}$ (Becker & Coppens, 1974a,b) and absolute structure parameter, x, (Flack, 1983) of 0.012 (21); all programs and measurement procedures were tested successfully for absolute-configuration determination by measuring intensity data for a crystal of potassium hydrogen L-(+)-tartrate; atomic scattering factors for neutral isolated atoms and f' and f'' from Cromer & Waber (1974); all calculations performed with a local version of *XRAY*76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) and *ORTEP*II (Johnson, 1976).
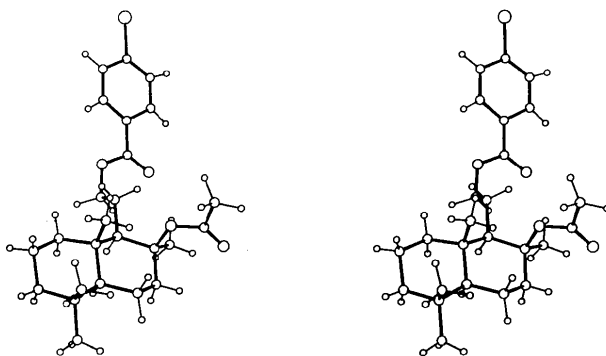
Table 2. *Bond distances and torsion angles*

(*a*) Interatomic distances (Å) with e.s.d.'s in parentheses

C(1)–C(2)	1.510 (11)	C(10)–C(30)	1.498 (8)
C(1)–C(10)	1.549 (9)	O(14)–C(15)	1.317 (9)
C(2)–C(3)	1.529 (12)	C(15)–O(16)	1.194 (13)
C(3)–C(4)	1.535 (12)	C(15)–C(17)	1.495 (12)
C(4)–C(5)	1.546 (10)	C(18)–C(19)	1.506 (9)
C(4)–C(11)	1.537 (11)	C(19)–O(20)	1.442 (9)
C(4)–C(12)	1.510 (10)	O(20)–C(21)	1.317 (9)
C(5)–C(6)	1.527 (10)	C(21)–O(22)	1.199 (10)
C(5)–C(10)	1.584 (9)	C(21)–C(23)	1.493 (11)
C(6)–C(7)	1.523 (10)	C(23)–C(24)	1.398 (12)
C(7)–C(8)	1.507 (10)	C(23)–C(28)	1.360 (10)
C(8)–C(9)	1.551 (8)	C(24)–C(25)	1.365 (14)
C(8)–C(13)	1.527 (9)	C(25)–C(26)	1.333 (14)
C(8)–O(14)	1.460 (7)	C(26)–C(27)	1.374 (10)
C(9)–C(10)	1.581 (8)	C(26)–Br(29)	1.922 (8)
C(9)–C(18)	1.548 (9)	C(27)–C(28)	1.363 (10)

(*b*) Torsion angles (°) with e.s.d.'s in parentheses around rings A and B. Angles start at the junction bond C(5)–C(10) and are given in counter-clockwise order:

Ring A: −55.0 (7); 56.4 (7); −59.1 (8); 56.5 (9); −51.5 (9); 52.5 (7)
Ring B: 58.6 (6); −62.7 (7); 59.9 (7); −52.1 (7); 49.1 (7); −52.3 (6)

Discussion. Final positional parameters and, for non-hydrogen atoms, equivalent isotropic temperature factors are given in Table 1.* Since the absolute-structure parameter x refined to 0.012 (21), the chirality of the crystal and of the coordinates is the same. They are referred to right-handed axes and the correct absolute configuration of the molecule is shown in Fig. 2. Bond distances for non-H atoms and torsion angles around the rings A and B are to be found in Table 2. Bond angles to aliphatic and aromatic C are in the range 104.8 to 116.0 (6)° and 117.8 to 122.6 (8)° respectively, and C–H bond distances are in the range 0.85 to 1.11 (6) Å. Rings A and B are in the chair conformation, and are *trans*-fused. Hence the methyl group at C(8) and side chain at C(9) are attached in an ideal equatorial position.

Fig. 2. Stereopair showing the configuration of the molecule.

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The Structure of (1*RS*,7*SR*,8a*RS*)-4,7-Dimethyl-1,2,3,5,6,7,8,8a-octahydro-1-naphthoic Acid, $C_{13}H_{20}O_2$*

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Abstract. $M_r = 208.3$, monoclinic, $P2_1/n$, $a = 9.597$ (2), $b = 9.461$ (1), $c = 13.065$ (2) Å, $\beta = 93.75$ (1)°, $V = 1183.7$ Å^3, D_m (flotation) = 1.152, $D_x = 1.169$ Mg m^{-3}, $Z = 4$, μ(Mo $K\alpha$) = 1.03 mm^{-1}, λ(Mo $K\alpha$) = 0.7107 Å, $F(000) = 456.0$, $T = 293$ K. $R = 0.043$ for 575 observed reflections. Ring *A* has the half-chair form while ring *B* has the chair form. The dihedral angle between ring planes is 46.8 (7)°. Bond lengths and angles resemble those in capsidiol.

Introduction. The title compound (I) was synthesized to correlate with a number of naturally occurring compounds having the carbon skeleton of cadalene. It was obtained by reacting a conjugated diene with ethyl acrylate followed by saponification of the Diels–Alder adduct (Shankaran & Rao, 1983).

Experimental. Crystal ~0.30 × 0.30 × 0.22 mm. Nonius CAD-4F-11 M diffractometer, graphite-monochromated Mo $K\alpha$ radiation, $\omega/2\theta$ scan mode, scan speed 1° min^{-1}, $\theta < 24°$, h 0 to 10, k 0 to 10, l −14 to 14. 1982 reflections collected, 575 judged significant ($|F_o| > 3\sigma|F_o|$), lattice parameters from 25 reflections ($15° < 2\theta < 35°$), three standard reflections ($30\bar{3}$, $\bar{1}12$ and $\bar{1}25$) every 2000 s, 4% variation in intensity. No corrections for absorption. Structure solved by direct methods using Sayre-equation program (Long, 1965). Full-matrix least-squares refinement (on *F*) of scale factors, positional and anisotropic thermal parameters (isotropic thermal parameters for H atoms, initial H positions calculated by stereochemistry) converged to $R = 0.043$ and $R_w = 0.040$, $S = 2.09$; $\sum w(|F_o| - |F_c|)^2$ minimized, $w = (3.5 + 1.0 |F_o| +$ $0.025 |F_o|^2)^{-1}$. $(\Delta/\sigma)_{max} = 0.1$. Final $\Delta\rho$ excursions $< |0.3|$ e Å^{-3}. No correction for secondary extinction. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Programs *LALS* (Gantzel, Sparks & Trueblood, 1961) for refinement, *NRC*-12 and *NRC*-22 (Ahmed, Hall, Pippy & Huber, 1973) for bond lengths, bond angles, mean planes and torsion angles.†

Discussion. The atomic parameters with their e.s.d.'s and equivalent isotropic temperature factors are given in Table 1. Bond lengths and bond angles involving the non-hydrogen atoms are given in Table 2. Fig. 1 shows the chemical formula together with the numbering of the atoms. Fig. 2 shows the packing of the molecules in the unit cell.

The purpose of this work was to determine the stereochemistry; the nomenclature of the compound being established subsequently. Ring *A* is in a half-chair conformation owing to C(4a) being sp^2-hybridized, while ring *B* is in the chair conformation (Hilderbrandt, Wieser & Montogomery, 1973). The dihedral angle between the mean planes of the two rings is 46.8 (7)°. The molecules form dimers around the centre of symmetry by hydrogen bonding through carboxylic groups, the O—H···O distance being 2.639 (6) Å [O—H = 1.08 (8), H···O = 1.57 (8) Å, ∠ O—H···O = 171 (7)°]. All other contacts are of the normal van der Waals type.

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