

925 reflections, $S = 2.41$ (refined enantiomorph, $wR = 0.057$, rejected at 99.5% significance level), 117 parameters [0.037, 0.041, 1.61 for 691 reflections (enantiomorph, $wR = 0.043$, rejected at 99.5% level), 119 parameters, including extinction correction, $g = 6.3(5) \times 10^4$], $R = 0.099$ for all 1336 reflections [0.087 for all 1207 reflections], $\Delta/\sigma = 0.09$ (mean), 0.36 (maximum) [0.03, 0.32], maximum final difference density -1.2 to $+1.8$ [-0.7 to $+0.4$] $e \text{ \AA}^{-3}$. Thermal parameters interpretable in terms of rigid-body motion for the fenchone derivative, bond lengths corrected for libration.

Discussion. Final positional parameters are in Table 1, and other data have been deposited.* The molecular structures (Fig. 1) are similar to those of other camphor derivatives (e.g. Rettig & Trotter, 1986). The analyses have established the absolute configurations (Fig. 1) for the (–)-enantiomorphs obtained from (+)-3-endo-9-

* Lists of anisotropic thermal parameters, H-atom positions, torsion angles and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43529 (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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Structure and Absolute Configuration of (1*R*,2*R*,4*R*)-2-[2-(4-Bromobenzoyloxy)ethyl]-1-methylbicyclo[2.1.1]hexan-5-one*

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Abstract. $C_{16}H_{17}BrO_3$, $M_r = 337.22$, orthorhombic, $P2_12_12_1$, $a = 7.253(1)$, $b = 7.949(2)$, $c = 26.520(2)$ \AA , $V = 1529.0(4)$ \AA^3 , $Z = 4$, $D_x = 1.464(1)$ g cm^{-3} , $Mo K\alpha$, $\lambda_{\alpha_1} = 0.70930$ \AA , $\mu = 27$ cm^{-1} , $F(000) = 688$, $T = 295$ K, $R = 0.047$ for 647 reflections. The bicyclohexane ring system contains a folded four-membered ring and two five-membered rings with envelope conformations. The bond distances in the ring system are slightly elongated, but otherwise molecular dimensions are close to expected values.

Introduction. The crystal structure analysis was undertaken to determine the structure and absolute configuration of an unusual rearrangement by-product

* IUPAC name: (1'*R*,2'*R*,4'*R*)-2-(1'-methyl-5'-oxo-2'-bicyclo[2.1.1]hexyl)ethyl 4-bromobenzoate.

dibromocamphor (Money, 1985; Antoniadis *et al.*, 1987). Bond distances and angles (Table 2) are close to normal values, with mean dimensions (identical in the two molecules): C–Br 1.97(1), C=O 1.21(1), C(sp^3)–C(sp^2) 1.52(1), C(sp^3)–C(sp^3) 1.54(1) \AA ; the C(1)–C(7)–C(4) bridgehead angles are 95.3(8) and 95.7(8)°. Intermolecular distances correspond to van der Waals interactions; shortest distances of each type in the two structures are: Br...Br 3.950(2), 3.719(2); Br...O 3.42(1), >4.5; Br...C 3.84(1), 3.81(1); C...C 3.81(2), 3.58(2); O...C 3.48(1), 3.28(1) \AA .

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formed in an enantiospecific synthesis from camphor of California red scale pheromone (Hutchinson & Money, 1986).

Experimental. Colourless needles along **b**, dimensions 0.14 × 0.75 × 0.18 mm, faces {010}, {001}, {101}, Enraf–Nonius CAD-4F diffractometer, lattice parameters from 25 reflections with $\theta = 10$ –18°. Intensities for $\theta \leq 22^\circ$ (rapid fall off in intensity with angle, as a result of poor crystal quality; efforts to obtain better crystals were unsuccessful), hkl : 0 to 7, 0 to 8, 0 to 28, ω – θ scan, ω scan width (0.70 + 0.35tan θ)° at 0.75–6.7° min^{–1}, extended 25% on each side for background measurement, three standard reflections (no decay), Lp and absorption corrections, transmission factors 0.62–0.78, 1200 unique reflections measured, 647 with $I \geq \sigma(I)$, where $\sigma^2(I) =$

$S + 4(B_1 + B_2) + (0.04I)^2$, $S = \text{scan}$, B_1 and $B_2 =$ background counts. Structure by Patterson and Fourier methods, refined by full-matrix least squares on F , H atoms in calculated positions, $w = 1/\sigma^2(F)$, scattering factors from *International Tables for X-ray Crystallography* (1974), locally written, or locally modified versions of standard computer programs, final $R = 0.047$, $wR = 0.041$ for 647 reflexions (refined enantiomorph gave significantly poorer agreement, $wR = 0.044$), $S = 1.62$, 181 parameters, $R = 0.122$ for all

Table 1. Final positional (fractional $\times 10^4$, Br $\times 10^5$) and isotropic thermal parameters ($\times 10^3 \text{ \AA}^2$) with estimated standard deviations in parentheses

	x	y	z	U_{eq}
Br	17088 (24)	16231 (26)	22107 (4)	134
O(1)	7021 (12)	9506 (11)	5458 (3)	72
O(2)	6477 (8)	3394 (10)	4321 (2)	67
O(3)	8918 (12)	2754 (16)	3862 (3)	115
C(1)	6255 (13)	6781 (16)	5877 (3)	44
C(2)	7270 (16)	5263 (14)	5608 (4)	48
C(3)	9322 (14)	5843 (15)	5659 (4)	48
C(4)	9047 (15)	7530 (15)	5948 (4)	54
C(5)	7388 (15)	8282 (19)	5674 (4)	48
C(6)	7579 (15)	7008 (16)	6346 (3)	69
C(7)	4178 (14)	6779 (19)	5914 (4)	73
C(8)	6578 (15)	5028 (12)	5067 (3)	48
C(9)	7544 (13)	3661 (14)	4780 (4)	59
C(10)	7327 (19)	2926 (16)	3888 (4)	65
C(11)	5885 (18)	2681 (15)	3486 (3)	53
C(12)	4037 (17)	3080 (15)	3545 (3)	52
C(13)	2829 (14)	2810 (14)	3168 (4)	64
C(14)	3441 (19)	2085 (16)	2729 (4)	72
C(15)	5224 (25)	1685 (20)	2659 (3)	84
C(16)	6475 (17)	1963 (15)	3035 (4)	72

$U_{\text{eq}} = \frac{1}{3}$ trace of diagonalized U tensor.

Table 2. Bond lengths (\AA) and angles ($^\circ$) with estimated standard deviations in parentheses

Br—C(14)	1.899 (11)	C(3)—C(4)	1.559 (13)
O(1)—C(5)	1.160 (13)	C(4)—C(5)	1.528 (15)
O(2)—C(9)	1.459 (10)	C(4)—C(6)	1.554 (14)
O(2)—C(10)	1.355 (11)	C(8)—C(9)	1.500 (12)
O(3)—C(10)	1.164 (12)	C(10)—C(11)	1.506 (15)
C(1)—C(2)	1.584 (14)	C(11)—C(12)	1.387 (13)
C(1)—C(5)	1.55 (2)	C(11)—C(16)	1.391 (13)
C(1)—C(6)	1.581 (13)	C(12)—C(13)	1.347 (13)
C(1)—C(7)	1.510 (12)	C(13)—C(14)	1.373 (14)
C(2)—C(3)	1.563 (14)	C(14)—C(15)	1.34 (2)
C(2)—C(8)	1.531 (12)	C(15)—C(16)	1.37 (2)
C(9)—O(2)—C(10)	120.5 (9)	C(1)—C(6)—C(4)	85.0 (6)
C(2)—C(1)—C(5)	100.6 (8)	C(2)—C(8)—C(9)	114.2 (9)
C(2)—C(1)—C(6)	99.2 (8)	O(2)—C(9)—C(8)	106.3 (8)
C(2)—C(1)—C(7)	119.5 (11)	O(2)—C(10)—O(3)	122.2 (11)
C(5)—C(1)—C(6)	82.1 (8)	O(2)—C(10)—C(11)	108.6 (11)
C(5)—C(1)—C(7)	123.6 (10)	O(3)—C(10)—C(11)	129.1 (11)
C(6)—C(1)—C(7)	123.7 (8)	C(10)—C(11)—C(12)	124.1 (11)
C(1)—C(2)—C(3)	100.3 (9)	C(10)—C(11)—C(16)	116.6 (11)
C(1)—C(2)—C(8)	111.3 (8)	C(12)—C(11)—C(16)	119.3 (10)
C(3)—C(2)—C(8)	115.4 (9)	C(11)—C(12)—C(13)	120.5 (10)
C(2)—C(3)—C(4)	100.0 (8)	C(12)—C(13)—C(14)	119.1 (11)
C(3)—C(4)—C(5)	101.7 (8)	Br—C(14)—C(13)	118.8 (11)
C(3)—C(4)—C(6)	101.1 (8)	Br—C(14)—C(15)	119.3 (10)
C(5)—C(4)—C(6)	83.6 (8)	C(13)—C(14)—C(15)	121.9 (10)
O(1)—C(5)—C(1)	134.2 (11)	C(14)—C(15)—C(16)	119.8 (10)
O(1)—C(5)—C(4)	138.1 (12)	C(11)—C(16)—C(15)	119.3 (11)
C(1)—C(5)—C(4)	87.1 (9)		

1200 reflections, $\Delta/\sigma = 0.003$ (mean), 0.02 (maximum), maximum final difference density 0.35 e \AA^{-3} .

Discussion. Final positional parameters are in Table 1, and other data have been deposited.* The molecule (Fig. 1) contains a bicyclo[2.1.1]hexane ring system, which has close to C_{2v} symmetry. The crystal analysis has established that the compound formed in the enantiospecific synthesis has the (1*R*,2*R*,4*R*) configuration; the corresponding *tert*-butyldimethylsilyl derivative ($R = \text{SiMe}_2\text{Bu}^t$ in Fig. 1) has $[\alpha]_D = +54.1^\circ$ (Hutchinson & Money, 1986). Both five-membered rings have envelope conformations, with the C(1)—C(2)—C(3)—C(4) grouping nearly planar, and the C(5) and C(6) atoms significantly displaced, torsion angles about the C(1)—C(2) and C(3)—C(4) bonds being in the range $40.5\text{--}43.2$ (9°). The four-membered C(1)—C(5)—C(4)—C(6) ring is folded, with mean torsion angle about the ring bonds of 34.5 (4°). Bond lengths and angles (Table 2) are generally close to expected values. Within the ring system bond lengths are slightly elongated, the mean $C(sp^3)\text{—}C(sp^3)$ distance being 1.57 (1) and $C(sp^2)\text{—}C(sp^3)$ 1.54 (1) \AA . In the four-

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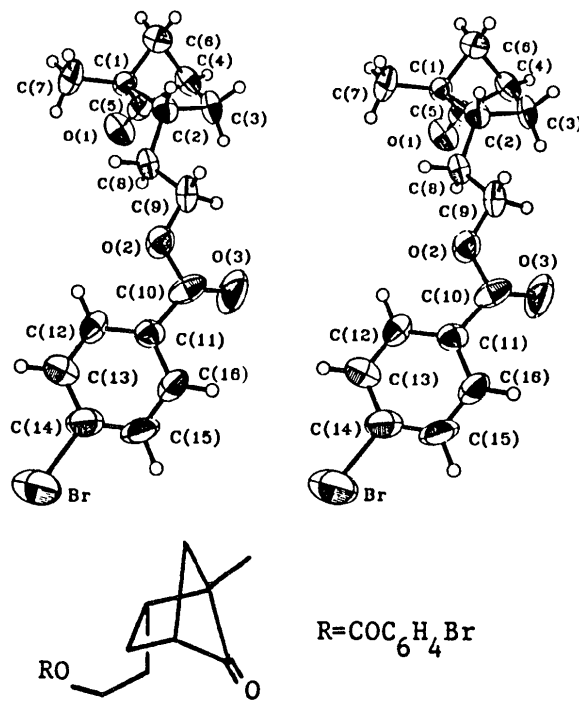


Fig. 1. Stereoview of the bicyclohexanone derivative.

membered ring the angle at the sp^2 -hybridized C(5) atom is $87.1(9)^\circ$, and at the other three atoms $82.1-85.0(8)^\circ$. Intermolecular distances correspond to van der Waals interactions; the shortest contacts are O(3) \cdots C(13) 3.38 (1), O(1) \cdots O(3) 3.61 (1), Br \cdots C(7) 3.72 (1) Å.

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Structure of 2-Methyl-4-phenyl-3-butyn-2-ol

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Abstract. $C_{11}H_{12}O$, $M_r = 160.22$, orthorhombic, $Pca2_1$, $a = 35.454(8)$, $b = 6.024(1)$, $c = 13.606(1)$ Å, $V = 2905.9(8)$ Å³, $Z = 12$, $D_x = 1.099$ g cm⁻³, $\lambda(Mo K\alpha) = 0.71073$ Å, $\mu = 0.6$ cm⁻¹, $F(000) = 1032$, room temperature, $R = 0.0486$ for 2183 unique reflections. The asymmetric unit contains three molecules which exhibit almost identical shapes and sizes. They only differ in the orientation of the phenyl ring relative to the C-O axis. A hydrogen-bonding system connects the O atoms and produces spirals parallel to the **b** direction that are held together solely by van der Waals forces. The position of the ethynyl group is in accordance with IR measurements, where an intramolecular OH $\cdots\pi$ hydrogen-bond interaction has been suggested.

Introduction. Visser & Van der Maas (1983) have studied α -ethynyl alcohols in solution by means of IR spectroscopy. From this study it follows that the hydroxyl-H atom is involved in an OH $\cdots\pi$ interaction. Lin, Okaya, Chiou & le Noble (1982) have reported a similar hydrogen bond in 2-ethynyladamantan-2-ol, which is structurally related to the title compound. The presence of an electron-withdrawing phenyl ring in 2-methyl-4-phenyl-3-butyn-2-ol influences the charge on the C atoms of the ethynyl group and weakens the OH $\cdots\pi$ interaction (Visser & Van der Maas, 1984). However, the IR measurements indicated that in solution only the OH-*gauche* conformation is present. The X-ray analysis was undertaken to compare this finding with the molecular stereochemistry in the crystalline state.

Experimental. The compound was kindly donated by Professor L. Brandsma. Data were obtained on an Enraf-Nonius CAD-4F diffractometer with Zr-filtered Mo $K\alpha$ radiation. Lattice constants from 16 reflections in the range of $22 < 2\theta < 26^\circ$; ω - 2θ mode, $\Delta\omega = (0.60 + 0.35\tan\theta)^\circ$. Reflections were measured up to $2\theta = 50^\circ$. The crystal is orthorhombic with space group $Pca2_1$, with three independent molecules in the asymmetric unit. On the exposure to X-rays the crystal (initial dimensions 1.0 × 0.5 × 0.5 mm) started to decay and disappeared gradually; however, the reflections maintained their relative intensities. Four periodically measured standard reflections (125, $\bar{1}25$, $1\bar{2}\bar{5}$, $\bar{1}\bar{2}5$) showed relative intensity variations less than 10%. Two crystals were used to collect the full data set. The first crystal disappeared completely, whereas the data collection from the second one was continued until the intensities reached about 15% of their original values. The intensities were corrected for this decrease as well as for Lorentz and polarization effects, but not for absorption. Variance $\sigma^2(I)$ calculated based on counting statistics plus a term $(PI)^2$ where $P (= 0.073)$ is the instability constant (McCandlish, Stout & Andrews, 1975). First crystal: 1690 reflections, $-42 \leq h \leq -12$; second crystal: 2992 reflections, $0 \leq h \leq 29$; both crystals: $0 \leq k \leq 16$, $0 \leq l \leq 7$. The data sets were merged using the common reference transitions and with averaging over Friedel pairs (internal consistency index 0.16, based on intensity values); 2664 independent reflections were left.

2183 reflections with $I > 1.5\sigma(I)$ were considered observed and used in the calculations. The structure was solved with *SHELXS84* (Sheldrick, 1984); the best *E* map gave all non-H atoms. To specify the origin an

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