

(–)-5-endo,6-exo-Dihydroxycamphene

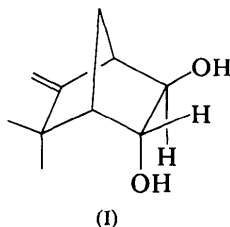
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Abstract. C₁₀H₁₆O₂, $M_r = 168.24$, tetragonal, $I4_1$, $a = 16.385$ (2), $c = 14.879$ (2) Å, $V = 3994.5$ Å³, $Z = 16$ (two molecules per asymmetric unit), $D_x = 1.12$ Mg m⁻³. Cu radiation, $R = 0.047$ for 772 reflexions (diffractometer data). The norbornane skeleton is slightly distorted as a result of intramolecular steric repulsion. Molecules are linked in the crystal by a double helical system of hydrogen bonds.

Introduction. A simple synthetic route from camphor to 5,6-dihydroxycamphenes has been developed with a view to assessing the potential phytohormone activity of these compounds (Allen, Lamb, Money & Salisbury, 1979). The present study of the 5-endo,6-exo isomer (I) was undertaken to provide structural data to assist in the interpretation of the biological function of these molecules.



A colourless needle crystal was used ($0.2 \times 0.2 \times 0.4$ mm), and unit-cell data were obtained by a least-squares fit of 25 $\sin \theta$ values measured on a GE XRD-6 diffractometer with Cu $K\alpha$ radiation. Intensity data were measured on an Enraf–Nonius CAD-4F diffractometer, with Cu $K\alpha$ (Ni filter), $\theta \leq 60^\circ$, $\omega/2\theta$ scan of $(0.80 + 0.15 \tan \theta)^\circ$ in ω extended 25% on either side for background measurement, variable scan speed, and check reflexion measurement every hour. Of 1557 reflexions with $\theta \leq 60^\circ$, 772 had intensities greater than $3\sigma[\sigma^2(I) = S + B + (0.04S)^2]$, where $S =$ scan, $B =$ time-corrected background count] (most of the weaker reflexions were at high angle). No absorption corrections were applied.

The structure was determined by direct methods, 226 reflexions with $|E| \geq 1.35$ being used; 11,10,1 was used to fix the origin, and eight pairs of sets of phases were developed by assigning two values to each of 220, 8,7,11, 0,9,11, and 022 to initiate tangent refinement. The E map from the best solution gave positions for about two thirds of the atoms in the two independent

molecules, and the remainder were located on a subsequent F_o map. A subsequent difference map gave positions for only about one half of the H atoms; from these, positions could be calculated for all the H atoms, including those involved in hydrogen bonding, with the assumption of ideal geometry. Refinement was completed by full-matrix least-squares methods, with minimization of $\sum w(|F_o| - |F_c|)^2$, with $w = 1/\sigma^2(F)$; anisotropic thermal parameters were used for C and O atoms, H atoms were included but not refined, and an extinction parameter was refined. Final R was 0.047 for 772 reflexions (217 parameters). The final positional parameters are in Table 1.* The absolute configuration is established from the chemical preparation.

* Lists of thermal parameters, calculated hydrogen parameters, molecular dimensions, and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34743 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final positional parameters (fractional, $\times 10^4$) with estimated standard deviations in parentheses

Unprimed atoms are in molecule 1, primed atoms in molecule 2.

	x	y	z
O(5)	1490 (5)	1809 (6)	2136 (8)
O(6)	1317 (6)	2544 (6)	0
C(1)	-64 (8)	2227 (11)	567 (12)
C(2)	-475 (8)	1562 (11)	1058 (11)
C(3)	-400 (8)	1784 (9)	2048 (11)
C(4)	163 (8)	2547 (8)	2002 (10)
C(5)	1026 (8)	2367 (7)	1624 (10)
C(6)	858 (7)	2066 (7)	640 (9)
C(7)	-186 (10)	2986 (11)	1165 (13)
C(8)	-782 (13)	886 (16)	708 (15)
C(9)	-69 (9)	1084 (8)	2641 (12)
C(10)	-1243 (9)	2040 (12)	2455 (14)
O(5')	3665 (6)	2683 (5)	3231 (7)
O(6')	3138 (5)	1578 (5)	1510 (8)
C(1')	4594 (7)	1938 (8)	1234 (10)
C(2')	5105 (7)	2693 (9)	1304 (11)
C(3')	5380 (8)	2758 (8)	2275 (10)
C(4')	4951 (7)	1988 (7)	2690 (10)
C(5')	4016 (8)	2045 (8)	2698 (10)
C(6')	3788 (7)	2148 (7)	1708 (10)
C(7')	5031 (8)	1369 (8)	1917 (10)
C(8')	5274 (10)	3195 (11)	631 (13)
C(9')	5132 (11)	3607 (9)	2684 (13)
C(10')	6325 (9)	2669 (11)	2361 (14)

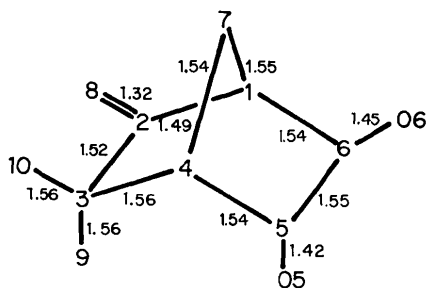


Fig. 1. Mean molecular dimensions (Å and deg) ($\sigma = 0.01\text{--}0.02$ Å and $0.6\text{--}1.1^\circ$); $C(2)\text{--}C(3)\text{--}C(9) = 112^\circ$, $C(4)\text{--}C(3)\text{--}C(10) = 109^\circ$.

Discussion. The geometry and dimensions* of the norbornane skeleton (Fig. 1) are generally normal; the one significant distortion (observed in both molecules) is an increase in the exocyclic angles at C(3), C(4), and C(5), to $114\text{--}116^\circ$, presumably as a result of steric repulsion between O(5) and C(9) (distance 2.94 Å).

Molecules are linked in the crystal by a double helical system of hydrogen bonds (Fig. 2).

We thank Dr T. Money for crystals, the Natural Sciences and Engineering Council Canada for financial support, and the University of British Columbia Computing Centre for assistance.

* See previous footnote.

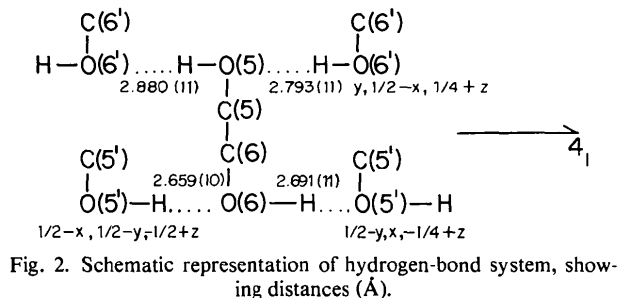
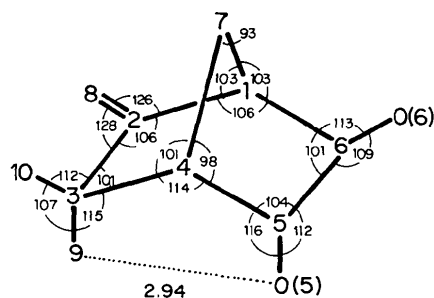


Fig. 2. Schematic representation of hydrogen-bond system, showing distances (Å).

Reference

- ALLEN, M. S., LAMB, N., MONEY, T. & SALISBURY, P. (1979). *J. Chem. Soc. Chem. Commun.* p. 112.

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Decahydro-5-methylene-2-oxo-6 β -trimethylsiloxy-[3 α ,6 α ,8 $\alpha\beta$]-3 α ,6-methano-3 α -azulenecarboxylic Acid Methyl Ester

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Abstract. $C_{17}H_{26}O_4Si$, monoclinic, $C2/c$, $a = 35.663$ (13), $b = 6.608$ (4), $c = 15.165$ (5) Å, $\beta = 94.44$ (3) $^\circ$, $M_r = 322.48$, $U = 3563.1$ Å 3 , $Z = 8$, $D_m = 1.205$ (floatation, aqueous KI), $D_c = 1.202$ Mg m $^{-3}$, $F(000) = 1392$; Mo $K\alpha$ radiation ($\lambda_{m1} = 0.70926$ Å, $\mu = 0.108$ mm $^{-1}$). The structure was solved by direct methods and refined by full-matrix least squares to $R = 0.063$ using 1614 diffractometer reflexions. The position of the methoxycarbonyl group on the azulene precursor has been established as 3 α .

Introduction. The title compound (Fig. 1) was prepared as an intermediate during studies toward the synthesis

of gibberellic acid (Stork, Still & Singh, 1979). The structure determination was undertaken to establish the position of the methoxycarbonyl group on the azulene precursor. The four possibilities were 1 α , 1 β , 3 α , or 3 β .

The quality of the crystal used for data collection (approximate dimensions $0.2 \times 0.6 \times 0.3$ mm) was examined on the diffractometer, by taking ω scans of several strong low-angle reflexions, and judged to be acceptable. The average width of the peaks at half height was 0.23° . Intensity data, in the range $3 \leq 2\theta \leq 55^\circ$, were collected at 301 K employing the $\omega\text{--}2\theta$ scan technique on an Enraf–Nonius CAD-4F κ -geometry