Crystal Structure of 1-Hydroxymethyl-4-methyl-7-oxabicyclo[4,3,0]non-4-en-8-one

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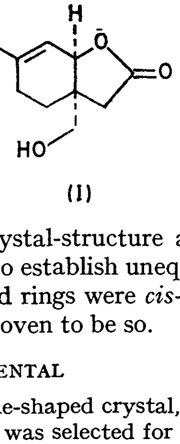
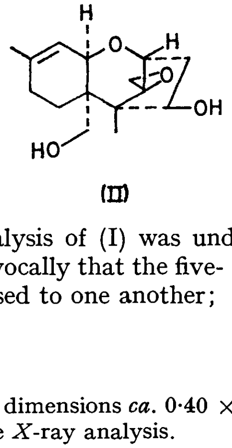
Crystals of the title compound are monoclinic, $a = 7{\cdot}973$, $b = 6{\cdot}249$, $c = 9{\cdot}444$ Å, $\beta = 95{\cdot}8°$, $Z = 2$, with space group $P2_1$. The structure was determined from diffractometer data by direct methods, and refined by full-matrix least-squares to R 0·068 for 681 data. The two rings are *cis*-fused and the molecules are hydrogen-bonded in chains parallel to the *a* axis. Bond lengths and angles are generally normal.

THE title compound (I) is a key intermediate in a projected synthesis of the sesquiterpenoid verrucarol (II),[1] a close relation of the recently synthesised trichodermin.[2]



(I)



(II)

The crystal-structure analysis of (I) was undertaken in order to establish unequivocally that the five- and six-membered rings were *cis*-fused to one another; this has in fact proven to be so.

EXPERIMENTAL

A needle-shaped crystal, of dimensions *ca.* 0·40 × 0·25 × 0·05 mm, was selected for the *X*-ray analysis.

Cell dimensions were established by means of a least-squares refinement of the positions of a number of reflexions as determined on a Hilger and Watts Y 290 computer-controlled, four-circle diffractometer using a Zr-filter to give Mo-K_α radiation ($\lambda = 0{\cdot}71069$ Å; 1 Å = 100 pm).

Crystal Data.—$C_{10}H_{14}O_3$, $M = 182{\cdot}2$, Monoclinic, $a = 7{\cdot}973(4)$, $b = 6{\cdot}249(5)$, $c = 9{\cdot}444(4)$ Å, $\beta = 95{\cdot}8°(0{\cdot}1°)$, $U = 468{\cdot}1$ Å^3, $Z = 2$, $D_c = 1{\cdot}292$. μ(Mo-K_α) = 1·02 cm^{-1}. Space group $P2_1$ (C_2^2); no molecular symmetry required.

The intensities of 1106 independent reflexions (0—*h*, 0—*k*, *l*—*l*) out to θ 27° weremeasured on the diffractometer with Mo-K_α radiation. An ω—2θ scan was carried out (80 steps of 0·01°, 1 s^{-1}) and 20 s were spent on each of two stationary background counts.

Corrections for the Lorentz and polarization factors were applied to the intensities, but none was made for absorption, which was assumed to be negligible.

Structure Solution and Refinement.—$|E|$ values, with linear isotropic and anisotropic corrections, were calculated from a Wilson plot for the 979 reflexions with $|F_o| \neq 0$ and scaled to $\langle|E|^2\rangle = 1$. The $|E|$ statistics are given in Table 1.

TABLE 1

$|E|$ statistics

Quantity	Obs.	Theoretical Centro-symmetric	Non-centro-symmetric
$\langle\|E\|\rangle$	0·901	0·798	0·886
$\langle\|E\|^2\rangle$	1·000	1·000	1·000
$\langle\|E^2 - 1\|\rangle$	0·680	0·968	0·736
% >3·0	0·00	0·27	0·01
>2·0	1·12	4·55	1·83
>1·0	37·07	31·73	36·79

Overall isotropic temperature factor B 2·967 Å^2.

The structure was solved by an application of tangent-formula refinement[3] to the 149 reflexions with $|E_o| > 1{\cdot}35$.

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[1] S. Malchenko, Ph.D. Thesis, University of Glasgow, 1972.

[2] E. W. Colvin, R. A. Raphael, and (in part) J. S. Roberts, *Chem. Comm.*, 1971, 858.

[3] J. Karle and H. Hauptman, *Acta Cryst.*, 1956, **9**, 635.

The phases of four reflexions were fixed, three to define the origin, the fourth to define the enantiomorph. Initially the phase of one other reflexion was also defined arbitarily, and allowed to refine, but no satisfactory results were obtained until two such ' starting phases ' were included in the calculation; this led to a total of 48 possible combinations of values (Table 2).

TABLE 2

Starting reflexions for the tangent formula

h	k	l	$\lvert E\rvert$	Phases (°)	Description
4	1	9	2·39	0	Origin
6	0	−7	2·26	180	
3	1	0	2·17	0	
5	1	7	2·52	a	Enantiomorph
3	4	6	2·12	b	' Starting phases '
0	1	1	1·83	c	

Possible values (°) for a: 45, 90, 135; b: ±45, ±135; c: ±45, ±135.

The correct solution was found from the set of values with $a = 90°$, $b = 225°$ and $c = 90°$, which yielded R_K [$= \Sigma||E_o| - |E_c||/\Sigma|E_o|$] of 0·16, *cf.* from 0·21 to 0·29 for some other sets of values. An E map was calculated, and revealed the positions of all the non-hydrogen atoms.

Full-matrix least-squares refinement was carried out; initially all 979 data with $|F_o| \neq 0$ were included, but latterly only the 681 with $I > 2\sigma(I)$. Two cycles of refinement with isotropic vibrational parameters (R 0·164 for 979 data) were followed by six cycles with anisotropic vibrational parameters (R 0·106 for 681 data). All the hydrogen atoms were located in a difference-Fourier map and their positions (only) were allowed to refine subsequently. A weighting scheme was also introduced, such that $\sqrt{w} = 1$ for $|F_o| \leqslant p$, and $\sqrt{w} = p/|F_o|$ for $|F_o| > p$; the ultimate value of p was 13. Refinement converged after a further five cycles with R 0·068 and R' 0·089 ($R' = [\Sigma w\Delta^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$) for 681 data. Atom scattering factors for oxygen, carbon, and hydrogen were taken from ref. 4. Observed and calculated structure amplitudes with phases are listed in Supplementary Publication No. SUP 20581 (3 pp., 1 microfiche).*

Atomic co-ordinates are listed in Table 3, and vibrational parameters in Table 4, with estimated standard deviations derived from the inverse of the least-squares matrix.

TABLE 3

(*a*) Fractional co-ordinates (×10⁵) with standard deviations in parentheses

	x	y	z
C(1)	17650(107)	−2958(187)	22789(88)
C(2)	16421(104)	−4197(198)	6939(93)
C(3)	23230(103)	9800(215)	−1044(92)
C(4)	32037(135)	29539(223)	5115(109)
C(5)	28238(113)	34094(179)	20292(98)
C(6)	29776(88)	14145(171)	29529(78)
C(7)	22015(96)	17845(202)	43552(88)
C(8	3344(93)	13297(188)	39812(93)
O(9)	1207(61)	2270(0)	27604(58)
C(10)	23017(144)	6643(284)	−17021(103)
C(11)	47643(102)	6029(195)	32074(90)
O(12)	57372(77)	21528(176)	39812(79)
O(13)	−8293(62)	18529(164)	46200(59)

(*b*) Fractional co-ordinates (×10³) for the hydrogen atoms, which are numbered according to the atoms to which they are attached. Standard deviations are: mean σ (X) = 0·10, mean σ (Y) = 0·13, mean σ (Z) = 0·10 Å

	x	y	z
H(1)	198	−145	243
H(2)	114	−159	38
H(4a)	426	260	28
H(4b)	307	418	3
H(5a)	349	463	233
H(5b)	168	395	209
H(7a)	279	42	503
H(7b)	240	315	463
H(10a)	166	−45	−214
H(10b)	151	179	−230
H(10c)	339	98	−198
H(11a)	523	−13	248
H(11b)	496	−68	379
H(12)	671	171	401

TABLE 4

Anisotropic vibrational parameters (Å² × 10³) * with standard deviations in parentheses

	U_{11}	U_{22}	U_{33}	U_{23}	U_{31}	U_{12}
C(1)	39(4)	29(5)	44(5)	−4(4)	5(3)	2(4)
C(2)	37(4)	50(6)	50(5)	−10(5)	0(3)	−1(4)
C(3)	37(4)	78(8)	37(4)	4(5)	7(4)	18(5)
C(4)	50(5)	57(7)	59(7)	1(6)	17(5)	−4(5)
C(5)	34(4)	38(6)	55(5)	−8(5)	5(4)	−11(4)
C(6)	25(3)	37(5)	34(4)	−11(4)	−1(3)	1(4)
C(7)	31(4)	44(6)	44(5)	−2(5)	7(3)	−3(4)
C(8)	28(4)	53(6)	58(5)	−1(5)	6(4)	−1(4)
O(9)	30(3)	46(4)	47(3)	−6(3)	0(2)	−11(3)
C(10)	54(6)	89(10)	52(6)	−11(6)	−1(5)	20(7)
C(11)	37(4)	47(6)	35(4)	2(5)	−6(3)	6(4)
O(12)	30(3)	82(6)	91(5)	−24(5)	2(3)	1(4)
O(13)	28(3)	71(5)	52(3)	−6(4)	−12(2)	−3(3)

* In the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* \cos\alpha^* + 2U_{31}lhc^*a^* \cos\beta^* + 2U_{12}hka^*b^* \cos\gamma^*)]$

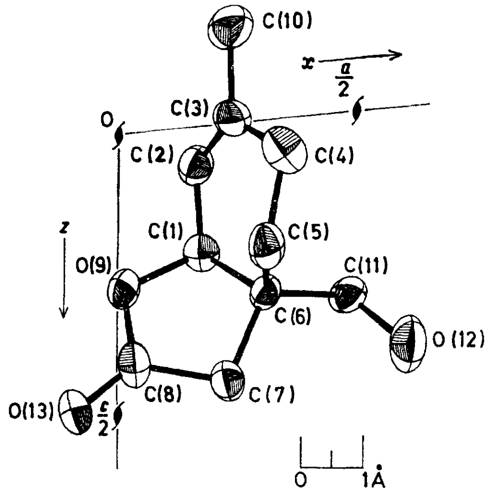

FIGURE 1 The crystal-chemical unit (CCU) as seen in its b-axial projection, showing arbitrary crystallographic numbering system

DISCUSSION

Figure 1 shows the structure in its b-axial projection, together with the crystallographic numbering system used, and Figure 2 the arrangement of the molecules in the crystal. Symmetry-related units are designated as

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* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are sent as full size copies).

[4] ' International Tables for X-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

follows: I $1 + x, y, z$, and II $-x, -\frac{1}{2} + y, 1 - z$. Interatomic distances and bond angles are given in Table 5, the displacements of some of the atoms from two planes in Table 6, and torsion angles in Table 7.

The conformation of the six-membered ring is a flattened version of the half-chair form for cyclohexene,[5] this flattening resulting from the *cis*-fusion of the five- and six-membered rings. Atoms C(1), C(2), C(3), C(4), and C(10) are closely coplanar (Table 6), as would be expected with a double bond between C(2) and C(3), and atoms C(5) and C(6) are displaced from the plane by 0·37 and −0·36 Å respectively, *cf.* the values of ±0·43 Å suggested for an ideal cyclohexene[6] (and those of 0·22 and −0·47 Å found in verrucarin-A *p*-iodobenzenesulphonate[7]). The flattening of the ring is also apparent in the reduction of the torsion angle C(5)–C(6)–C(1)–C(2) from the 56° appropriate for cyclohexene to 39°, which is similar to the 33° of the corresponding O(9)–C(1)–C(6)–C(7) torsion angle in the five-membered ring. Similarly the torsion angle C(3)–C(4)–C(5)–C(6) is, at 47°, less than the predicted value of 56°; the effect in this case is less, however, as this angle is further away from the junction of the rings.

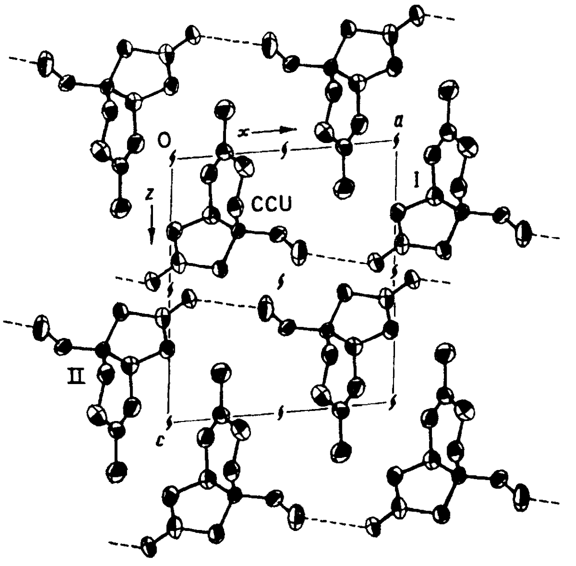

FIGURE 2 The arrangement of the molecules in the crystal

TABLE 5

Interatomic distances (Å) and bond angles (deg.), with standard deviations in parentheses

C(1)–C(2)	1·492(12)	C(5)–C(6)	1·519(14)
C(1)–C(6)	1·536(14)	C(6)–C(7)	1·534(11)
C(1)–O(9)	1·467(11)	C(6)–C(11)	1·509(12)
C(2)–C(3)	1·308(15)	C(7)–C(8)	1·522(12)
C(3)–C(4)	1·507(18)	C(8)–O(9)	1·339(11)
C(3)–C(10)	1·520(13)	C(8)–O(13)	1·202(11)
C(4)–C(5)	1·521(14)	C(11)–O(12)	1·400(14)

C(6)–C(1)–C(2)	115·3(7)	C(5)–C(6)–C(1)	108·8(6)
O(9)–C(1)–C(2)	110·6(6)	C(5)–C(6)–C(11)	112·8(6)
C(6)–C(1)–O(9)	105·2(5)	C(1)–C(6)–C(7)	99·8(5)
C(1)–C(2)–C(3)	123·7(7)	C(1)–C(6)–C(11)	112·2(6)
C(2)–C(3)–C(4)	122·0(8)	C(7)–C(6)–C(11)	111·7(6)
C(2)–C(3)–C(10)	121·4(8)	C(6)–C(7)–C(8)	104·0(6)
C(4)–C(3)–C(10)	116·6(7)	C(7)–C(8)–O(9)	109·4(5)
C(3)–C(4)–C(5)	112·8(7)	C(7)–C(8)–O(13)	128·3(5)
C(4)–C(5)–C(6)	112·0(9)	O(13)–C(8)–O(9)	122·3(5)
C(5)–C(6)–C(7)	110·8(6)	C(8)–O(9)–C(1)	109·9(5)
		C(6)–C(11)–O(12)	108·4(7)

O(12)–H(12)	0·82(12)
H(12) · · · $O(13^{I})$	1·99(11)
O(12) · · · $O(13^{I})$	2·750(8)

TABLE 6

Displacements (Å) of atoms from planes

Plane (1): C(1)—(4), C(10)

C(1) −0·036, C(2) 0·043, C(3) 0·019, C(4) 0·004, C(10) −0·030, C(5) 0·375, C(6) −0·362

Plane (2): C(7), C(8), O(9), O(13)

C(7) 0·001, C(8) −0·005, O(9) 0·001, O(13) 0·002, C(1) −0·095, C(6) 0·457

TABLE 7

(*a*) Torsion angles (deg.). The angle *A–B–C–D* is defined as positive if when viewed along the *B–C* bond atom *A* has to be rotated clockwise to eclipse atom *D*

C(6)–C(1)–C(2)–C(3)	−9	C(3)–C(4)–C(5)–C(6)	47
O(9)–C(1)–C(2)–C(3)	110	C(4)–C(5)–C(6)–C(1)	−58
C(2)–C(1)–C(6)–C(5)	39	C(4)–C(5)–C(6)–C(7)	−167
C(2)–C(1)–C(6)–C(7)	155	C(4)–C(5)–C(6)–C(11)	67
C(2)–C(1)–C(6)–C(11)	−86	C(1)–C(6)–C(7)–C(8)	−30
O(9)–C(1)–C(6)–C(5)	−83	C(5)–C(6)–C(7)–C(8)	85
O(9)–C(1)–C(6)–C(7)	33	C(11)–C(6)–C(7)–C(8)	−149
O(9)–C(1)–C(6)–C(11)	152	C(1)–C(6)–C(11)–O(12)	−173
C(2)–C(1)–O(9)–C(8)	−150	C(5)–C(6)–C(11)–O(12)	64
C(6)–C(1)–O(9)–C(8)	−25	C(7)–C(6)–C(11)–O(12)	−61
C(1)–C(2)–C(3)–C(4)	−4	C(6)–C(7)–C(8)–O(9)	17
C(1)–C(2)–C(3)–C(10)	174	C(6)–C(7)–C(8)–O(13)	−162
C(2)–C(3)–C(4)–C(5)	−15	C(7)–C(8)–O(9)–C(1)	4
C(10)–C(3)–C(4)–C(5)	167	O(13)–C(8)–O(9)–C(1)	−176

(*b*) Comparison of the torsion angles (deg.) in the six-membered ring with values appropriate to cyclohexane and cyclohexene

	Present work	Cyclohexene [a]	Cyclohexane [b]
C(1)–C(2)–C(3)–C(4)	−4	0	56
C(2)–C(3)–C(4)–C(5)	−15	−19	−56
C(3)–C(4)–C(5)–C(6)	47	56	56
C(4)–C(5)–C(6)–C(1)	−58	−76	−56
C(5)–C(6)–C(1)–C(2)	39	56	56
C(6)–C(1)–C(2)–C(3)	−9	−19	−56

[a] Ref. 5. [b] H. R. Buys and H. J. Geise, *Tetrahedron Letters*, 1970, 2991.

The conformation of the five-membered lactone ring is almost an envelope; atom C(1) is close to the plane through C(7), C(8), O(9), and O(13), whilst atom C(6) is displaced by 0·46 Å from this plane (Table 6).

Bond lengths are as expected: the $C(sp^3)$–$C(sp^3)$ bond distances are 1·509—1·536, mean 1·524 Å, whilst the $C(sp^3)$–$C(sp^2)$ bond distances range from 1·492 to 1·522, mean 1·510 Å. In the γ-lactone the $C(sp^2)$–O bond [C(8)–O(9) 1·339(11) Å] is significantly shorter than the $C(sp^3)$–O bond [C(1)–O(9) 1·467(11) Å]; this distinction is customary in lactones and esters.[8]

In the crystal structure the molecules are linked into

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[5] J. B. Hendrikson, *J. Amer. Chem. Soc.*, 1961, **83**, 4537.

[6] E. J. Corey and R. A. Sneen, *J. Amer. Chem. Soc.*, 1955, **77**, 2505.

[7] A. T. McPhail and G. A. Sim, *J. Chem. Soc.* (*C*), 1966, 1394.

[8] *Chem. Soc. Special Publ.* No. 11, 1958.

chains along the *a* direction by hydrogen bonds, O(12) $\cdots$ O(13$^{\text{I}}$) 2·750(8) Å. There are no unusual intermolecular contents; those <3·5 Å are C(8) $\cdots$ O(13$^{\text{II}}$) 3·102, O(9) $\cdots$ O(13$^{\text{II}}$) 3·257, O(13) $\cdots$ O(13$^{\text{II}}$) 3·440, and C(7) $\cdots$ O(13$^{\text{II}}$) 3·441 Å.

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[2/1930 *Received, 14th August, 1972*]

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[9] '*X*-Ray' System of Crystallographic Programs, J. M. Stewart, *et al.*, Computer Science Center, University of Maryland, 1970.