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2-Deoxy-12-oxolemnacarnol; A Case of Twinning

BY D. LOSMAN*

Collectif de Bio-Ecologie, Université Libre de Bruxelles, 50 av. F. Roosevelt, 1050 Bruxelles, Belgium

R. KARLSSON

Arrhenius Laboratory, University of Stockholm, Fack S-10405, Sweden

AND G. M. SHELDRICK

University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England

Abstract. $C_{15}H_{22}O_3$, triclinic, $P1$, $a = 13.70$ (2), $b = 7.29$ (1), $c = 7.53$ (1) Å, $\alpha = 89.6$ (1), $\beta = 109.8$ (1), $\gamma = 95.2$ (1)°, $Z = 2$, $D_m = 1.184$, $D_x = 1.180$ g cm^{-3}. The crystals are twins, with the ($1\bar{6}0$) net as twin net and a rotation angle of 180°. The twinning is explained in terms of an approximate non-crystallographic twofold screw axis. The compound was isolated from soft corals of the genera *Lemnalia* and *Paralemnalia*.

Introduction. We describe here the X-ray diffraction analysis of the title compound, which was undertaken in order to add an independent proof to the chemical analysis (Daloze, Braekman, Georget & Tursch, 1977), and to establish the configuration at C(7).

Fig. 1 shows the molecule with the absolute configuration obtained by chemical correlation with lemnacarnol (Tursch, Colin, Daloze, Losman & Karlsson, 1975).

* Present address: Laboratoire de Géochimie, Université Libre de Bruxelles, 50 av. F. Roosevelt, 1050 Bruxelles, Belgium.

A Philips PW 1100 diffractometer with graphite-monochromatized Cu $K\alpha$ radiation was used to determine lattice constants and to collect data. Two crystals were used, one for data up to 40° in θ, and another for data between 40 and 60° in θ, their volumes being respectively 3×10^{-3} and 50×10^{-3} mm^3.
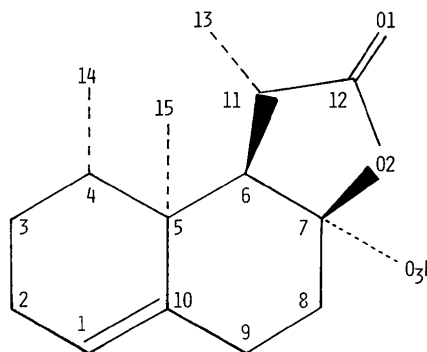

Fig. 1. The absolute configuration of 2-deoxy-12-oxolemnacarnol.

An initial unit cell was determined, identical with the correct one but with a three times longer, and used as such for data collection. We explain below how this 'data-collection unit cell' came to be interpreted as the complex unit cell of a twinned crystal and how each member of the twin was singled out.

On close examination of the data, we noticed that all very strong reflexions had as h index multiples of 3 only, and that all other non-zero intensities had their two first Miller indices, say H and K, such that $H = -(h + k)$, when $K = k$, with $h = 3n$ ($n = 0, 1, 2, \ldots n$).

We furthermore discovered the occurrence of a constant ratio between the two groups of reflexions: $I(-h - k, k, -l)/I(h,k,l) = 0.15$ for both crystals. Fig. 2 represents schematically the zero-layer of our 'data-collection lattice'. One can readily see that a lattice of this nature can be obtained by the superposition, on the black-dotted lattice, of a less intense version of itself rotated 180° around its [$\bar{1}$60] lattice row. We are thus presented here with a case of twinning; the twin plane is the ($\bar{1}$60) net, the twin index is 3. The twin operation makes reflexions $h,3k,l$ and $-h - k, 3k, -l$ overlap. The data corresponding to the larger member of the twin were kept as single-crystal data, after correcting the intensities of the double reflexions according to the algorithm:

$$(1 - Q^2)I_o(h,3k,l) = I(h,3k,l) - QI(-h - k, 3k, -l),$$

where I_o refers to single-crystal intensities, I to the measured intensities, and Q is the intensity ratio between the two members of the twin ($Q = 0.15$). It was observed that the twin obliquity is not zero by examination of the profiles of the double reflexions. The twin obliquity is 0.4°.
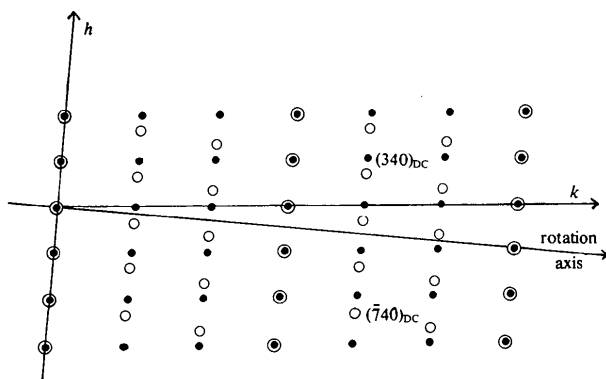

Fig. 2. Zero layer of the data-collection (DC) reciprocal lattice, where $a^*_{DC} = a^*/3$. The black dots represent the strong reflexions, the open circles the other non-zero intensities. The black-dotted lattice belongs to the larger member of the twin, the open-circled lattice to the other. A 180° rotation about [$\bar{3}$60]$^*_{DC}$ brings the open-circled lattice on to the black-dotted lattice. For instance, the point (340)$_{DC}$ corresponds to the point ($\bar{7}$40)$_{DC}$; both represent reflexion 140 of the single-crystal lattice, and the intensities are in the ratio $I(\bar{7}40)_{DC}/I(340)_{DC} = 0.15$.

Subsequent data reduction yielded 2089 unique reflexions, corrected for the Lp factor. Structure solution was first attempted with *MULTAN* (Main, Woolfson, Lessinger, Germain & Declercq, 1974), but without success. The structure was solved by application of a 'negative-quartet' figure of merit to weighted multisolution tangent refinement.

A 'pseudotangent refinement' (Roberts, Pettersen, Sheldrick, Isaacs & Kennard, 1973) was employed to select the starting set. The NQEST test (De Titta, Edmonds, Langs & Hauptman, 1975) was applied after weighted tangent refinement of 247 reflexions, and the solutions with the most negative figures of merit expanded to 461 phases before computing E maps. The two solutions with lowest NQEST gave recognizable structures: 27 atoms in chemically reasonable positions were used to calculate a difference synthesis which revealed the remaining non-hydrogen atoms.

Table 1. *Atomic coordinates* $(\times 10^3)$ *and isotropic temperature factors* $(\times 10^3)$ *for the non-hydrogen atoms of the two independent molecules*

Standard deviations are about 2 for x and about 3 for y and z.

	x	y	z	U (Å²)
C(1A)	390	125	604	81
C(2A)	406	14	776	90
C(3A)	384	−187	740	90
C(4A)	278	−232	583	64
C(5A)	279	−138	396	53
C(6A)	164	−137	253	51
C(7A)	155	−2	93	57
C(8A)	211	184	137	64
C(9A)	326	168	259	71
C(10A)	333	54	427	63
C(11A)	80	−73	334	49
C(12A)	2	−5	156	62
C(13A)	23	−223	416	59
C(14A)	246	−436	568	90
C(15A)	339	−256	299	67
O(1A)	−87	21	134	73
O(2A)	40	20	18	62
O(3A)	177	−85	−58	63
C(1B)	−394	−525	−609	71
C(2B)	−408	−640	−784	75
C(3B)	−383	−839	−739	72
C(4B)	−276	−831	−581	58
C(5B)	−279	−745	−390	52
C(6B)	−163	−697	−259	46
C(7B)	−156	−562	−90	62
C(8B)	−219	−396	−148	67
C(9B)	−331	−458	−263	70
C(10B)	−339	−574	−435	62
C(11B)	−82	−597	−331	49
C(12B)	−5	503	−158	56
C(13B)	−21	−727	−418	61
C(14B)	−240	−1027	−555	68
C(15B)	−333	−885	−292	58
O(1B)	84	−439	−136	73
O(2B)	−45	492	−20	62
O(3B)	−177	−652	57	64

Subsequent analysis showed that the second E map, ranked according to $R(\alpha)$ (Roberts et al., 1973), also yielded a sufficiently correct fragment, but the $R(\alpha)$ test was less discriminating than NQEST: the remaining six solutions of low $R(\alpha)$ were very inferior.

The structure was refined by full-matrix least squares with complex neutral-atom scattering factors. The H positions, for H attached to C, were calculated geometrically with staggered methyl groups and all C—H distances 1·08 Å. A riding model was employed during the first stages of refinement, so that the C—H vectors remained constant in magnitude and direction but not in position. All non-hydrogen atoms were refined isotropically, the H atoms being given fixed isotropic temperature factors ($U = 0·05$ Å^2). The refinement converged to an R of 12·5%.* The introduction of anisotropic C and O atoms did not improve the refinement significantly. The final atomic parameters are given in Table 1.

Table 2. Bond distances (Å), angles (°) and torsion angles (°) for the two independent molecules

Standard deviations are about 0·03 Å for the distances and 2° for the angles. An asterisk indicates significant differences between the molecules.

	Molecule A	Molecule B		Molecule A	Molecule B
C(1)—C(2)	1·49	1·51	C(5)—C(10)—C(9)	118	114
C(1)—C(10)	1·37	1·33	C(6)—C(11)—C(12)	100	104
C(2)—C(3)	1·48	1·53	C(6)—C(11)—C(13)	117	115
C(3)—C(4)	1·53	1·54	C(12)—C(11)—C(13)	108	108
C(4)—C(5)	1·57	1·58	C(11)—C(12)—O(1)	126	128
C(4)—C(14)	1·50	1·54	C(11)—C(12)—O(2)	113	111
C(5)—C(6)	1·59	1·57	O(1)—C(12)—O(2)	121	121
C(5)—C(10)	1·50	1·53	C(7)—O(2)—C(12)	109	110
C(5)—C(15)	1·58	1·54			
C(6)—C(7)	1·53	1·58			
C(6)—C(11)	1·57	1·52	C(10)—C(1)—C(2)—C(3)	18	18
C(7)—C(8)	1·48	1·53	C(2)—C(1)—C(10)—C(5)	1	3
C(7)—O(2)	1·50	1·47	C(2)—C(1)—C(10)—C(9)	−176	−177
C(7)—O(3)	1·42	1·38	C(1)—C(2)—C(3)—C(4)	−49	−50
C(8)—C(9)	1·55	1·51	C(2)—C(3)—C(4)—C(5)	60	65*
C(9)—C(10)	1·49	1·52	C(3)—C(4)—C(5)—C(6)	−165	−166
C(11)—C(12)	1·52	1·49	C(3)—C(4)—C(5)—C(10)	−41	−44
C(11)—C(13)	1·54	1·59	C(4)—C(5)—C(6)—C(7)	164	164
C(12)—O(1)	1·21	1·22	C(4)—C(5)—C(6)—C(11)	47	46
C(12)—O(2)	1·31	1·34	C(10)—C(5)—C(6)—C(7)	38	45*
			C(10)—C(5)—C(6)—C(11)	−78	−73*
C(2)—C(1)—C(10)	122	123	C(4)—C(5)—C(10)—C(1)	11	10
C(1)—C(2)—C(3)	114	112	C(4)—C(5)—C(10)—C(9)	−172	−169
C(2)—C(3)—C(4)	110	107	C(6)—C(5)—C(10)—C(1)	134	128*
C(3)—C(4)—C(5)	110	112	C(6)—C(5)—C(10)—C(9)	−48	−51
C(3)—C(4)—C(14)	111	108	C(5)—C(6)—C(7)—C(8)	−43	−47
C(5)—C(4)—C(14)	116	112	C(5)—C(6)—C(7)—O(2)	−162	−164
C(4)—C(5)—C(6)	110	107	C(5)—C(6)—C(7)—O(3)	85	80*
C(4)—C(5)—C(10)	113	109	C(11)—C(6)—C(7)—C(8)	82	83
C(4)—C(5)—C(15)	109	111	C(11)—C(6)—C(7)—O(2)	−36	−33
C(6)—C(5)—C(10)	110	112	C(11)—C(6)—C(7)—O(3)	−149	−149
C(6)—C(5)—C(15)	107	109	C(5)—C(6)—C(11)—C(12)	154	154
C(10)—C(5)—C(15)	108	109	C(7)—C(6)—C(11)—C(12)	31	30
C(5)—C(6)—C(7)	113	111	C(6)—C(7)—C(8)—C(9)	50	53
C(5)—C(6)—C(11)	117	122*	O(2)—C(7)—C(8)—C(9)	166	166
C(7)—C(6)—C(11)	101	100	O(3)—C(7)—C(8)—C(9)	−79	−76
C(6)—C(7)—C(8)	119	115	C(6)—C(7)—O(2)—C(12)	28	25
C(6)—C(7)—O(2)	103	103	C(8)—C(7)—O(2)—C(12)	−98	−97
C(6)—C(7)—O(3)	111	113	O(3)—C(7)—O(2)—C(12)	145	144
C(8)—C(7)—O(2)	107	107	C(7)—C(8)—C(9)—C(10)	−53	−56
C(8)—C(7)—O(3)	110	111	C(8)—C(9)—C(10)—C(1)	−126	−122
O(2)—C(7)—O(3)	105	107	C(8)—C(9)—C(10)—C(5)	56	57
C(7)—C(8)—C(9)	109	110	C(6)—C(11)—C(12)—O(1)	163	163
C(8)—C(9)—C(10)	110	112	C(6)—C(11)—C(12)—O(2)	−16	−18
C(1)—C(10)—C(5)	122	124	C(11)—C(12)—O(2)—C(7)	−7	−5
C(1)—C(10)—C(9)	119	121	O(1)—C(12)—O(2)—C(7)	174	174

Discussion. The structure solution confirmed the chemical analysis. The title compound is similar to lemnacarnol (Karlsson & Losman, 1976), but the exchange of the C(12) methylene group for a carbonyl group gives the molecules different conformations.

In lemnacarnol, the cyclohexane ring has the boat–twisted-boat conformation, and the five-membered ring has the envelope conformation with the smallest twist about C(6)—C(7); in 2-deoxy-12-oxolemnacarnol, the lactone ring has the smallest twist about C(12)—O(2), giving a planar ester group and making the less energetic chair conformation possible for the cyclohexane ring. Table 2 shows the torsion angles of the three rings for the two independent molecules.

The two independent molecules are related by a non-crystallographic 2_1 axis inclined approximately $1°$ to y (Fig. 3). The twinning can now be explained struc-
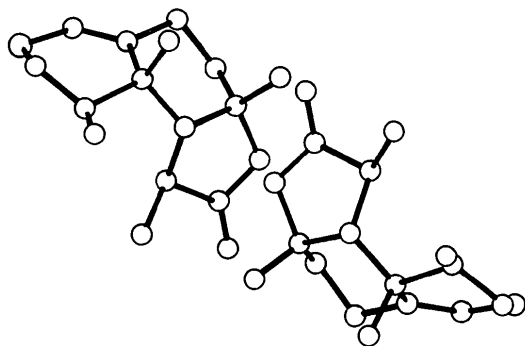

Fig. 3. The two independent molecules of 2-deoxy-12-oxo-lemnacarnol. A view down y.

turally as the sharing by the two members of the twin of the (160) crystal face to which y is nearly perpendicular. In the crystal face, the molecules have positions such that they can belong simultaneously to both twin members. The molecules are catenated by the hydrogen bonds O(3)A—O(1)B and O(3)B—O(1)A, both with an O—O distance of 2·75 Å.

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Calculations were performed with programs written by GMS.

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2-Nitro-3,5,5-trimethylcyclopentanone*†

By FADIA E. ELFEHAIL AND WALTER W. ZAJAC

Department of Chemistry, Villanova University, Villanova, PA 19085, USA

AND JOHN P. HAZEL AND GEORGE T. DE TITTA

Molecular Biophysics Department, Medical Foundation of Buffalo, 73 High Street, Buffalo, New York 14203, USA

Abstract. $C_8H_{13}O_3N$, orthorhombic, $P2_12_12_1$, $a = 8\cdot164$ (1), $b = 17\cdot119$ (3), $c = 6\cdot825$ (1) Å, $V = 953\cdot9$ Å^3; $D_m = 1\cdot19$, $D_c = 1\cdot19$ g cm^{-3} ($Z = 4$); 1021 data (769 observed); Mo $K\alpha$ ($\lambda = 0\cdot7107$ Å) on a κ-geometry diffractometer. Structure determination employed MULTAN/NQEST, and final residuals are: $R_{obs} = 0\cdot049$, $R_w = 0\cdot078$. The ring is a highly twisted C_1 half-chair; the nitro group is approximately perpen-