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## The Crystal Structure and Absolute Configuration of Lactucin

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The crystal structure and absolute configuration of lactucin,  $C_{15}H_{16}O_5$ , have been determined by single-crystal X-ray crystallographic techniques. Crystals of the sesquiterpenoid lactone isolated from *Lactuca virosa* are monoclinic, space group  $P2_1$ , with  $a = 7.097$  (3),  $b = 11.091$  (5),  $c = 8.713$  (4) Å,  $\beta = 110.40$  (3)° and  $Z = 2$ . The structure was solved by direct methods and refined to  $R = 3.2\%$ . Estimated standard deviations of the bond lengths not involving hydrogen are 0.002–0.004 Å. Anomalous scattering from oxygen was used to determine the absolute configuration.

### Introduction

Lactucin is one of the bitter principles of *Lactuca virosa*. It was the first compound of a group of sesquiterpenoid lactones to be isolated having a carbonyl group at the C(2) position of the guaiane skeleton and a cross-conjugated system of double bonds. Until recently (Barton & Narayanan, 1958) it seemed as if lactucin was the only sesquiterpenoid lactone of this type possessing a  $5\beta$  hydrogen atom. A new interpretation of ORD data, however (Bachelor & Ito, 1973), revised this to the  $5\alpha$  configuration, which we now confirm (Fig. 1).

### Experimental

Whitish crystals obtained from an acetone solution were examined by standard X-ray crystallographic film techniques. They were found to be monoclinic. The optical activity together with the space-group ex-

tinctions ( $0k0$  absent for  $k = 2n + 1$ ) led to the space group  $P2_1$ . A summary of the most important crystallographic data is given in Table 1.

Intensity data were collected on an 'off-line' four-circle Siemens single-crystal diffractometer with a

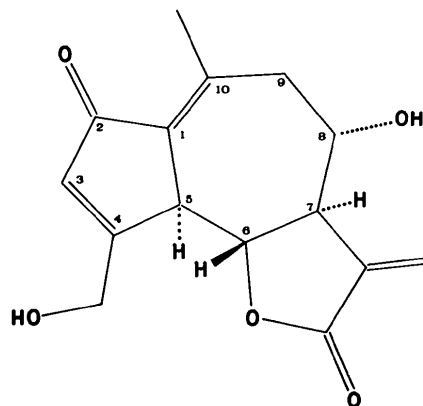


Fig. 1. Lactucin configuration.

Table 1. *Crystallographic data*

Lactucin, C <sub>15</sub> H <sub>16</sub> O <sub>5</sub>	$D_{\text{exp}} = 1.42 \text{ g cm}^{-3}$
$M_r = 276.1$	$D_x = 1.426$
$a = 7.097 (3) \text{ \AA}$	$\mu(\text{Cu } K\alpha) = 9.1 \text{ cm}^{-1}$
$b = 11.091 (5)$	Space group: $P2_1$
$c = 8.713 (4)$	$Z = 2$
$\beta = 110.40 (3)^\circ$	Number of reflexions
$V = 642.4 \text{ \AA}^3$	$[I > 2\sigma(I)]: 1277$
	$R = 3.2\%$

crystal of dimensions  $0.25 \times 0.4 \times 0.3 \text{ mm}$  mounted along **c**. The  $\omega/2\theta$  scan technique using the five-value method (Allen, Rogers & Troughton, 1971) at a speed of  $1^\circ \text{ min}^{-1}$  in  $\theta$  was used throughout. In the range  $3.5^\circ \leq \theta \leq 70^\circ$  1287 reflexions were recorded using Ni-filtered Cu  $K\alpha$  radiation, of which only 10 were considered unobserved ( $I < 2\sigma$ ).

### Structure determination and refinement

The structure was solved by direct methods with the aid of the XRAY 72 series of programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). After routine data reduction the intensities were put on an absolute scale and normalized structure factors,  $E$ , were calculated. An inspection of the  $|E|$  values and their occurrence in the  $\Sigma_2$  triplets led to the starting set which was used for expansion with the tangent formula. After the origin was defined and the enantiomorph fixed, the phases of 227 reflexions ( $|E| \geq 1.4$ ) were determined by the tangent formula and these yielded the solution. After

Table 2. *Final positional parameters ( $\times 10^4$ ) for the non-hydrogen atoms with standard deviations in parentheses*

	<i>x</i>	<i>y</i>	<i>z</i>
O(1)	5853 (2)	3340 (2)	8453 (1)
O(2)	-159 (3)	3436 (2)	-572 (2)
O(3)	1983 (3)	-28 (1)	4946 (2)
O(4)	2046 (2)	1887 (1)	4158 (1)
O(5)	671 (2)	7000 (-)	3227 (1)
C(1)	2688 (2)	5267 (2)	4585 (2)
C(2)	1214 (2)	5948 (2)	3222 (2)
C(3)	565 (3)	5146 (2)	1799 (2)
C(4)	1501 (2)	4080 (2)	2163 (2)
C(5)	2943 (2)	4028 (2)	3929 (2)
C(6)	2479 (2)	3057 (2)	4986 (2)
C(7)	4228 (2)	2783 (2)	6589 (2)
C(8)	4435 (3)	3723 (2)	7927 (2)
C(9)	5115 (2)	4941 (2)	7451 (2)
C(10)	3557 (2)	5668 (2)	6140 (2)
C(11)	3809 (3)	1495 (2)	6901 (2)
C(12)	2529 (3)	992 (2)	5295 (3)
C(13)	4447 (4)	816 (2)	8236 (3)
C(14)	1294 (3)	3092 (2)	943 (2)
C(15)	3053 (3)	6855 (2)	6721 (2)

Table 3. *Final positional ( $\times 10^3$ ) and thermal ( $\text{\AA}^2 \times 10^2$ ) parameters for the hydrogen atoms with standard deviations in parentheses*

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
H(1)	694 (6)	333 (5)	927 (5)	7.9 (11)
H(2)	-15 (4)	289 (4)	-137 (4)	5.3 (8)
H(3)	-42 (5)	537 (4)	75 (4)	6.4 (9)
H(5)	434 (3)	390 (2)	397 (2)	2.5 (5)
H(6)	134 (3)	327 (2)	515 (2)	2.2 (4)
H(7)	542 (3)	271 (2)	631 (2)	2.9 (5)
H(8)	321 (3)	375 (2)	804 (2)	1.8 (4)
H(91)	627 (3)	478 (2)	717 (3)	2.7 (5)
H(92)	580 (5)	541 (4)	851 (4)	6.4 (8)
H(131)	527 (4)	112 (3)	932 (4)	5.3 (7)
H(132)	403 (5)	0 (4)	819 (4)	5.2 (8)
H(141)	266 (4)	298 (3)	82 (3)	4.4 (6)
H(142)	96 (4)	229 (3)	137 (4)	4.6 (6)
H(151)	215 (8)	640 (7)	739 (6)	10.1 (14)
H(152)	441 (6)	728 (4)	749 (5)	6.5 (9)
H(153)	238 (4)	734 (3)	610 (4)	4.7 (7)

Thermal parameters have the form  $T_{(\text{iso})} = \exp(-8\pi^2 U \sin^2\theta/\lambda^2)$ .

Table 4. *Calculated and observed Bijvoet differences*

<i>h k l</i>	$D_{\text{calc}}$	$D_{\text{obs}} = F_o(hkl) - F_o(h\bar{k}l)$
6 5 0	-	-----
-6 5 0	-	---
1 11 0	+	++++
-1 11 0	+	++++
-5 5 2	-	-----
-2 6 4	-	-----
-4 5 5	-	+
2 10 5	-	++
2 6 6	+	++++
-1 1 7	+	-
0 5 7	+	++++
0 8 7	+	++++
1 2 8	+	++++

The number of signs indicates the level of the difference:  $+ D < \sigma$ ;  $++ 2\sigma > D > \sigma$ ;  $+++ 3\sigma > D > 2\sigma$ ;  $++++ D > 3\sigma$ .

computation of an  $E_{\text{map}}$  ( $R_{\text{Karle}} = 0.24$ ) all non-hydrogen atoms were located among the 25 highest peaks.

The five O and the fifteen C atoms were refined with the *CRLSQ* link of the XRAY 72 system. The scattering factor for H was taken from Stewart, Davidson & Simpson (1965) and those for the remaining atoms were from Cromer & Mann (1968). The real and imaginary parts of the anomalous scattering correction terms for O and C (Cromer & Liberman, 1970) were used from the beginning in the refinement process. As the origin is not fixed by symmetry in the polar space group  $P2_1$ , the *y* coordinate of O(5) was held constant at 0.7000. The refinement proceeded smoothly and converged at  $R = 10.7\%$  with isotropic thermal parameters. After introduction of anisotropic vibrational terms  $R$  fell to 7.5%.



was used to select reflexions with the highest probability of observable Bijvoet differences  $D$  [ $= |F_c(hkl)| - |F_c(\bar{h}\bar{k}\bar{l})|$ ] (Hope & De la Camp, 1969).

Eleven reflexion pairs were accordingly selected. As it is very inconvenient with a quarter  $\chi$ -circle geometry to measure the reflexions  $hkl$  and  $\bar{h}\bar{k}\bar{l}$ , the symmetry-related pairs  $hkl$  and  $\bar{h}\bar{k}\bar{l}$  were measured. The scanning time was increased to  $0.1^\circ \text{ min}^{-1}$ . The data for these reflexions were subjected to all the usual corrections, including absorption. The calculated and observed Bijvoet differences are shown in Table 4.

The remeasurement of the Bijvoet pairs confirms essentially the absolute configuration obtained by the Hamilton method. All tables and figures correspond to this correct absolute configuration.

### Description of the structure

The relatively flat molecules are stacked parallel to the (201) planes in the crystal. There are two types of hydrogen bonds connecting the atom O(2) with O'(1) and O'(5), respectively, where O'(1) belongs to the translational neighbour at  $x-1, y, z-1$ , and O'(5) is at  $\bar{x}, \frac{1}{2}+y, \bar{z}$ . The separations are  $\text{O}(2)\cdots\text{O}'(1) = 2.840 \text{ \AA}$  and  $\text{O}(2)\cdots\text{O}'(5) = 2.727 \text{ \AA}$ ; the corresponding O—H $\cdots$ O contacts are 2.03 and 1.82  $\text{\AA}$ . The multiple sequence of hydrogen bonds is shown by a schematic (010) projection (Fig. 6).

The bond lengths, the bond angles and the torsion angles are shown in Figs. 3–5 while Fig. 2 shows a plot of the molecule with the thermal parameters. Table 5 lists the bond lengths involving the H atoms.

The cyclopentenone ring is forced into an almost planar form by the keto group at C(2) and by the  $sp^2$ -hybridized carbon atom C(1). The bond length

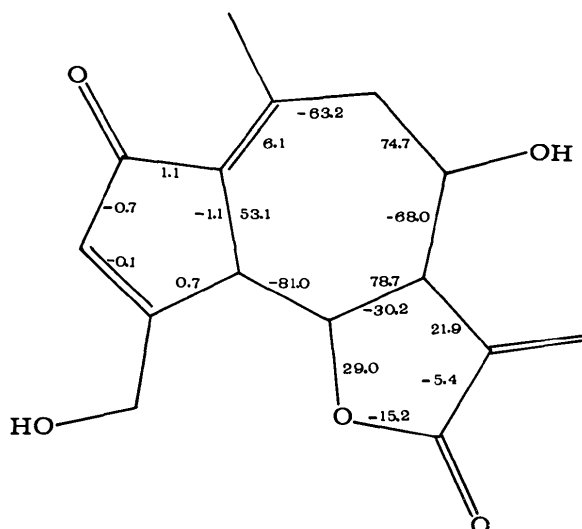


Fig. 5. Torsion angles ( $^\circ$ ).

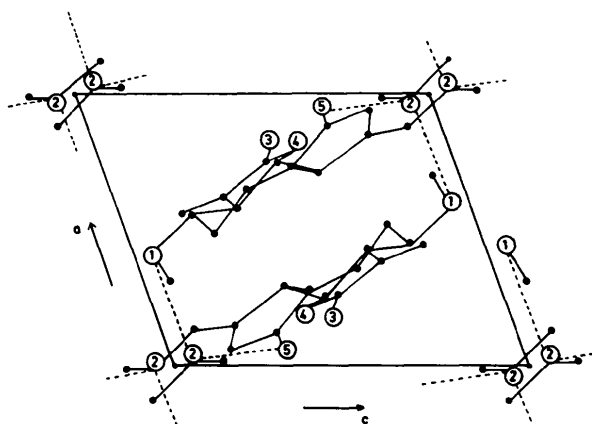


Fig. 6. (010) projection showing the hydrogen bonds.

Table 5. Bond lengths ( $\text{\AA}$ ) involving the hydrogen atoms with standard deviations in parentheses

O(1)—H(1)	0.84 (5)	C(9)—H(92)	1.03 (3)
O(2)—H(2)	0.93 (4)	C(13)—H(131)	0.98 (3)
C(3)—H(3)	0.97 (3)	C(13)—H(132)	0.94 (4)
C(5)—H(5)	0.99 (2)	C(14)—H(141)	1.02 (3)
C(6)—H(6)	0.90 (2)	C(14)—H(142)	1.02 (4)
C(7)—H(7)	0.96 (2)	C(15)—H(151)	1.12 (7)
C(8)—H(8)	0.91 (2)	C(15)—H(152)	1.07 (4)
C(9)—H(91)	0.95 (3)	C(15)—H(153)	0.79 (3)

C(2)—C(3) [1.463 (3)  $\text{\AA}$ ] shows the influence of conjugation between the keto group and the double bond C(3)—C(4). The fusion to the cycloheptene ring is quasi-*trans* with torsion angles in the five- and seven-membered ring of  $-1.1^\circ$  and  $53.1^\circ$  respectively. The cycloheptene moiety has a slightly distorted chair conformation.

The lactone ring is not planar but approximates to an envelope conformation with C(6) as the flap being 0.47  $\text{\AA}$  out of the plane formed by a least-squares fit to the other four ring atoms. The fusion to the seven-membered ring is *trans* with torsion angles of  $78.7^\circ$  and  $-30.2^\circ$ . The pseudorotational angle (Altona, Geise & Romers, 1968) is  $\Delta = 20.6^\circ$  while  $\phi_0 = -30.2^\circ$  for the five-membered lactone ring. This is another sesquiterpenoid lactone with the H atom at C(7) in an  $\alpha$  configuration.

The C(1)—C(10) double bond [1.353 (2)  $\text{\AA}$ ] seems to be relatively long. This may be attributed to tension at the  $sp^2$ -hybridized bridge atom C(1), belonging to a nearly coplanar sequence of atoms O(5), C(2), C(1), C(10), C(15) with significant non-bonded repulsions between O(5) and C(15), which are only 2.926  $\text{\AA}$  from each other. Similar conditions are met in the lactone ring; the separation O(1) $\cdots$ C(13) is 3.036  $\text{\AA}$ . The splaying of the angles involved is obvious.

The rest of the bond lengths and angles lie in the expected ranges.

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## Structure Cristalline et Moléculaire de la Méthoxycarbonyl-5 Phényl-4 (Phényl-4 $\Delta$ 1-pyrazolinyl-3)-4 $\Delta$ 2-Pyrazolinecarbonitrile-5

PAR YVON DÉLUGEARD, LOÏC TOUPET ET JEAN-CLAUDE MESSAGER

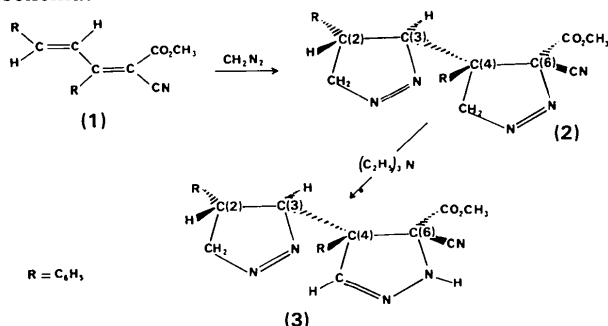
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The crystal and molecular structure of  $C_{21}H_{19}N_5O_2$  has been determined by a single-crystal three-dimensional X-ray analysis. The crystals are monoclinic, space group  $P2_1/c$  with  $a = 8.895$  (8),  $b = 17.788$  (14),  $c = 12.126$  (10) Å,  $\beta = 99.43$  (20)° and  $Z = 4$ . The structure, solved by direct methods, has been refined by full-matrix least-squares analysis to a final conventional  $R$  index of 0.077 for 2818 reflexions. The present work has been carried out to determine unambiguously the relative configuration of the C(3) and C(4) carbon atoms which link the two pyrazoline rings. The geometry and the conformation of the molecule are discussed. Some comments about the use of the *MULTAN* system are also made.

### Introduction

Le dérivé diénique (1) conduit, par réaction avec un excès de diazométhane,  $CH_2N_2$ , à la formation de la bipyrazoline de formule (2). L'un des cycles  $\Delta$ 1-pyrazoline de (2) s'isomérisé en milieu basique donnant le dérivé  $\Delta$ 1-pyrazolinyl  $\Delta$ 2-pyrazoline (3) selon le schéma:



L'addition de la première molécule de  $CH_2N_2$  constitue l'étape cinétique de la réaction, aucun monoadduit n'ayant été mis en évidence (Martelli & Carrié, 1977). De plus, un seul dérivé étant obtenu lors de l'addition de la deuxième molécule de  $CH_2N_2$ , l'induction asymétrique est totale, la réaction est une *cis* addition stéréospécifique de sorte que les configurations relatives de C(2) et C(3) d'une part et de C(4) et C(6) d'autre part sont connues.

Cependant, la configuration relative de C(3) et C(4) déterminante pour la discussion de l'induction asymétrique observée, n'a pu être précisée. Cette induction asymétrique est un aspect important de la réaction de cycloaddition et aucune étude systématique n'a été réalisée jusqu'ici. L'analyse cristallographique s'est alors avérée nécessaire. Les cristaux du dérivé (2) étant impropres à l'examen, nous avons entrepris l'étude structurale du dérivé (3), ce qui nous a permis en outre de préciser les caractéristiques géométriques d'une