

## The Crystal Structure of Germichryson

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The crystal structure of germichryson,  $C_{15}H_{15}O_4$ , has been determined by the direct method. The crystal is triclinic, space group  $P1$  with two molecules in a cell of dimensions  $a = 11.322$  (8),  $b = 7.873$  (7),  $c = 7.476$  (6) Å,  $\alpha = 110.70$  (2),  $\beta = 102.33$  (2),  $\gamma = 99.32$  (2)°,  $D_x = 1.46$  g cm<sup>-3</sup>,  $\mu$  for Cu  $K\alpha = 10.8$  cm<sup>-1</sup>. Refinement was carried out by the block-diagonal least-squares method to an  $R$  value of 0.046 for 2186 reflexions. The absolute configuration was determined from the anomalous dispersion of the O atoms for Cu  $K\alpha$  radiation. The two molecules in the asymmetric unit take different conformations at C(3) constituting conformational isomers.

### Introduction

Germichryson was extracted from *Cassia torosa* Cavanilles and the chemical structure proposed is shown in Fig. 1 apart from the configuration about the C(3) atom (Takahashi, Takido, Sankawa & Shibata, 1976). In order to establish the complete structure including the absolute configuration, the present study has been undertaken.

### Experimental

The crystals grown from ethyl acetate solutions are dark yellow, transparent plates. The cell parameters were determined by the least-squares method from the setting angles of 23 planes at  $\theta = 27$ – $44^\circ$  on a Philips PW 1100 diffractometer.

Intensities were measured by the  $\theta$ - $2\theta$  scan method with a scan speed of  $4^\circ$  min<sup>-1</sup> in  $\theta$ . The scans were repeated twice when the total counts during the first scan were less than 3000. Background was measured at each end of the scan for half the total scan time. A total of 2492 reflexions were measured within the  $\theta$  range of 3 to  $78^\circ$ , of which 138 were too weak to be observed [ $I < 2\sigma(I)$  level].

The size of the crystal used for the intensity measurements was about  $0.2 \times 0.3 \times 0.4$  mm and no absorption correction was considered to be necessary.

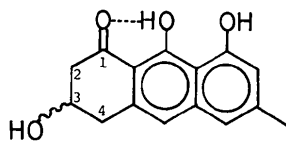


Fig. 1. Chemical structure.

The intensities were then corrected for Lorentz and polarization factors and the normalized structure factors were calculated. The  $N(z)$  test (Lipson & Woolfson, 1952) showed a hypercentric distribution of intensities. This may be explained by the fact that the symmetry of the molecule (1) is violated in part and the two molecules in a cell are arranged around the pseudo centre of symmetry.

### Determination and refinement of the structure

The crystal structure was determined by the direct method assuming the space group to be  $P\bar{1}$ . 15 atoms out of 19 comprising the whole molecule were assigned on the  $E$  map. Elucidation of the structure by the ordinary Fourier method gave 20 atoms including one extra atom and this structure could be refined to an  $R$  value of 0.11 by the block-diagonal least-squares method without any anomalous features being noticed. An extra atom, O(3) or O(3') attached to C(3) in Fig. 2, must have appeared by superposition of two molecules related by a pseudo symmetry centre, since from the chemical study it is not probable that two atoms are bonded to C(3). It is also to be noted that if one excludes one of the atoms, say an axial O(3) atom from molecule  $A$ , then we have to exclude an equatorial atom O(3') from molecule  $B$ , since the present compound was proved to be optically active.

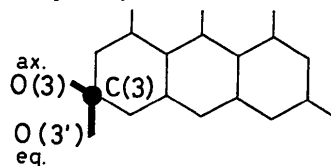


Fig. 2. Structure obtained for assumed centrosymmetric crystal. O(3) and O(3') bonded to C(3) in axial and equatorial positions are the superposition of the two atoms related by a centre of symmetry.

Table 1. *The ratios of observed and calculated Bijvoet differences, DEL, and those of Bijvoet double differences, DELA*

*DEL* and *DELA* are the quantities defined by Engel (1972).

<i>h k l</i>	$ F_o^+ $	$ F_o^- $	<i>DEL</i>	<i>DELA</i>
5-2 0	5.73	5.77	-0.43	
-5 1 1	5.11	5.15	-0.26	-0.64
-7-4 1	4.98	4.96	+0.20	-1.04
-2-5 0	4.57	4.55	+0.19	-0.46
-2-3 1	3.55	3.61	-0.54	-0.93
-7-3 5	3.48	3.38	+1.08	-2.18
2-3 3	2.97	2.98	-0.02	-1.02
-2-4 3	2.89	2.71	-1.49	-1.25
-6-4 1	2.89	2.82	-0.96	+0.11
1-2 5	2.83	2.76	+0.98	-0.09
3 3 2	2.81	2.65	-1.41	-1.25
-10 0 1	2.70	2.68	+0.27	-1.12
-6 2 5	2.58	2.55	+0.03	-0.91
6 5 0	2.54	2.38	-0.81	+0.48
2 4 4	2.44	2.46	-0.40	-0.35
1-2 3	2.41	2.28	-2.17	-0.99
2-2 5	2.37	2.44	-0.69	-1.31
-6-4 7	2.25	2.10	+2.51	-1.17
-9 0 6	2.24	2.19	+0.47	-0.49
0-9 1	2.22	2.17	+0.82	-0.86
-9 0 5	2.17	2.18	-0.08	-1.32
2 5 2	2.14	2.06	-1.44	-1.33
0 1 5	2.00	2.04	-0.57	-1.74
9-7 0	1.95	2.02	-1.71	-0.95
-3 4 3	1.92	1.94	+0.45	+1.41
-2 0 3	2.10	2.11	-0.17	
6 4 2	2.02	1.72	-3.01	

The refinement was continued by excluding O(3) from molecule *A* and O(3') from *B* and by assuming the space group to be *P1*. The *R* value was reduced to 0.083 including anisotropic temperature factors for all 38 atoms. H atoms were then located on the difference electron-density map and their positional and isotropic thermal parameters were refined along with the atomic parameters of the heavier atoms. The final *R* value was 0.046.

Finally, an attempt has been made to determine the absolute configuration by anomalous dispersion of the O atoms with Cu *K* $\alpha$  radiation. Intensities of more than 200 Friedel pairs were carefully measured of which 27 pairs have intensities strong enough to be measured above the  $3\sigma$  level and have  $|F_c(hkl)|^2/|F_c(h\bar{k}l)|^2$  values differing more than 4% from unity. The ratio of the observed and calculated Bijvoet double differences, *DELA*, defined by Engel (1972), were calculated for these 27 pairs by choosing appropriate neighbouring reflexions to correct the observed intensities for absorption. The values listed in Table 1 show that the absolute configuration must be represented by taking a coordinate system the reverse of that adopted in the intensity measurement. The final atomic coordinates listed in Table 2 are to be referred to the right-handed system to represent the absolute configuration.\*

Dispersion correction terms,  $f'$  and  $f''$ , of O and C atoms for Cu *K* $\alpha$  radiation were taken from *International Tables for X-ray Crystallography* (1974). The atomic scattering factors for these atoms were those cited in *International Tables for X-ray Crystallography* (1962) as SX-6 and SX-8 and for H atoms those given by Stewart, Davidson & Simpson (1965). The least-squares refinement was carried out using the *HBL5* program (Okaya & Ashida, 1967) with block-diagonal matrix approximations.

## Discussion

The complete structure of the molecule is now established, including the absolute configuration at C(3) which can be described as *R*. The bond lengths and bond angles of the two crystallographically independent molecules *A* and *B* are shown in Figs. 3 and 4. The standard deviations of these values are estimated as about  $\pm 0.004$  Å and  $\pm 0.3^\circ$  for C-C lengths and C-C-C angles and  $\pm 0.06$  Å and  $\pm 4^\circ$  for C-H lengths and H-C-H angles, respectively.

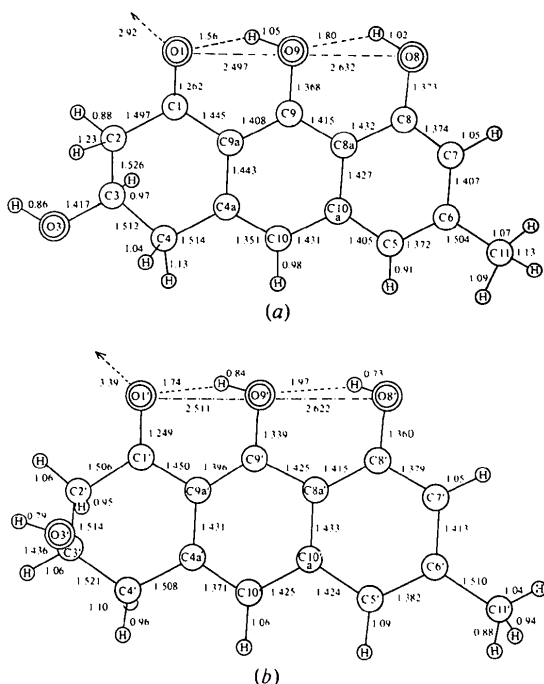


Fig. 3. Bond lengths (Å), (a) molecule *A*, (b) molecule *B*.

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33753 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Final positional parameters*For heavy atoms, parameters are multiplied by  $10^4$  and for hydrogen atoms, by  $10^3$ .

<i>A</i> (equatorial*) molecule				<i>B</i> (axial*) molecule			
	<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>
C(1)	12590 (2)	11733 (3)	2401 (4)	C(1')	6538 (3)	5116 (4)	6843 (4)
C(2)	13824 (2)	11457 (4)	2109 (4)	C(2')	5349 (3)	5485 (4)	7304 (4)
C(3)	14169 (2)	9832 (4)	2574 (4)	C(3')	4963 (3)	7020 (4)	6733 (5)
C(4)	13132 (2)	8054 (4)	1322 (4)	C(4')	6031 (3)	8804 (4)	7734 (5)
C(4a)	11884 (2)	8296 (3)	1642 (4)	C(4a')	7272 (2)	8499 (3)	7456 (4)
C(5)	8877 (2)	5464 (4)	1502 (4)	C(5')	10346 (3)	11261 (3)	7671 (4)
C(6)	7733 (2)	5626 (4)	1775 (4)	C(6')	11484 (3)	11005 (4)	7397 (4)
C(7)	7489 (2)	7409 (4)	2358 (4)	C(7')	11714 (2)	9209 (4)	6919 (4)
C(8)	8353 (2)	8964 (3)	2573 (4)	C(8')	10802 (2)	7686 (3)	6675 (4)
C(8a)	9548 (2)	8825 (3)	2273 (4)	C(8a')	9631 (2)	7899 (3)	6967 (4)
C(9)	10485 (2)	10355 (3)	2460 (3)	C(9')	8643 (2)	6398 (3)	6746 (4)
C(9a)	11648 (2)	10131 (3)	2169 (4)	C(9a')	7498 (2)	6680 (3)	7023 (4)
C(10)	10995 (2)	6836 (3)	1482 (4)	C(10')	8203 (2)	9967 (3)	7663 (4)
C(10a)	9796 (2)	7018 (3)	1728 (4)	C(10a')	9389 (2)	9714 (3)	7436 (4)
C(11)	6737 (3)	3965 (4)	1504 (5)	C(11')	12508 (3)	12651 (4)	7681 (5)
O(1)	12409 (2)	13354 (3)	2862 (3)	O(1')	6675 (2)	3486 (3)	6325 (3)
O(3)	15281 (2)	9536 (4)	2083 (4)	O(3')	4664 (2)	6468 (4)	4608 (4)
O(8)	8049 (2)	10656 (3)	3146 (3)	O(8')	11113 (2)	6017 (3)	6192 (4)
O(9)	10268 (0)	12100 (0)	2979 (0)	O(9')	8855 (2)	4691 (3)	6274 (3)
H(C2)	1352 (5)	1118 (8)	34 (8)	H(C2')	460 (4)	424 (5)	660 (6)
H'(C2)	1442 (4)	1250 (7)	251 (7)	H'(C2')	543 (4)	588 (6)	869 (6)
H(C3)	1431 (4)	1004 (6)	397 (6)	H(C3')	413 (4)	727 (6)	708 (7)
H(C4)	1306 (5)	781 (6)	-29 (7)	H(C4')	581 (4)	977 (6)	733 (6)
H'(C4)	1329 (5)	693 (7)	167 (7)	H'(C4')	604 (4)	927 (6)	931 (6)
H(C5)	898 (4)	428 (5)	122 (6)	H(C5')	999 (4)	1243 (6)	758 (6)
H(C7)	666 (4)	757 (6)	272 (6)	H(C7')	1252 (4)	901 (6)	647 (6)
H(C10)	1112 (4)	558 (6)	128 (6)	H(C10')	800 (4)	1128 (6)	787 (6)
H(C11)	610 (4)	337 (6)	0 (6)	H(C11')	1308 (4)	1244 (7)	705 (7)
H'(C11)	719 (4)	286 (7)	175 (7)	H'(C11')	1214 (4)	1347 (6)	724 (6)
H''(C11)	618 (5)	429 (7)	250 (7)	H''(C11')	1297 (5)	1349 (7)	919 (7)
H(O3)	1592 (5)	1043 (8)	234 (8)	H(O3')	398 (4)	580 (6)	410 (6)
H(O8)	869 (5)	1172 (8)	315 (7)	H(O8')	1060 (4)	535 (6)	625 (6)
H(O9)	1100 (4)	1294 (6)	277 (7)	H(O9')	824 (5)	401 (7)	637 (7)

\* Equatorial molecule means the molecule in which the O(3) atom is bonded to C(3) in the equatorial position, and similarly for the axial molecule.

Table 3. *Deviations of atoms from the least-squares planes (Å)*

Equations of the least-squares planes are referred to the orthogonal axes *X* in the *ac* plane, *Y*∥*b*\* and *Z*∥*c*; *X*, *Y* and *Z* are measured in Å. Asterisks indicate atoms not included in the least-squares calculation.

<i>A</i> (equatorial) molecule				<i>B</i> (axial) molecule			
C(1)	-0.003	C(10)	+0.028	C(1')	+0.030	C(10')	-0.010
C(4)	+0.003	C(10a)	-0.009	C(4')	-0.015	C(10a')	+0.009
C(4a)	-0.001	C(2)*	+0.024	C(4a')	-0.018	C(2')*	+0.154
C(5)	-0.013	C(3)*	+0.691	C(5')	+0.026	C(3')*	-0.538
C(6)	-0.020	O(1)*	-0.007	C(6')	+0.006	O(1')*	-0.047
C(7)	+0.021	O(3)*	+0.568	C(7')	-0.005	O(3')*	-1.956
C(8)	+0.010	O(8)*	+0.053	C(8')	-0.027	O(8')*	-0.053
C(8a)	+0.002	O(9)*	-0.006	C(8a')	+0.008	O(9')*	-0.033
C(9)	-0.014	C(11)*	-0.047	C(9')	-0.010	C(11')*	-0.049
C(9a)	-0.006			C(9a')	+0.006		

$$0.3323X + 0.1938Y + 0.9231Z = 1.332$$

$$0.3051X + 0.2144Y + 0.9279Z = 4.617$$

The mean difference in the corresponding C—C and C—O bond lengths between the two crystallographically independent molecules is  $\pm 0.016$  Å and that in the C—C—C and C—C—O angles is  $\pm 1.4^\circ$ , which lie almost within the limits of experimental error. The most significantly discordant lengths and angles are C(9)—O(9) and C(4a)—C(4)—C(3). The difference in the C(9)—O(9) bond lengths as well as those in C(1)—O(1) and C(8)—O(8) may be caused by the difference in the intermolecular hydrogen bonds linked to O(1) and O(1'). The planarity of the skeleton of the molecule is shown in Table 3. The most significantly deviated ring atoms are C(3) and C(3') and the displacement is larger for the *A* molecule which has the equatorial C—O bond.

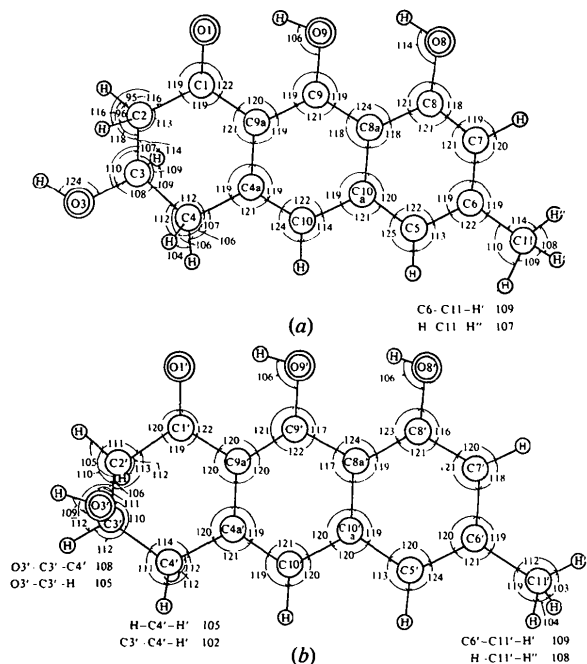


Fig. 4. Bond angles ( $^\circ$ ), (a) molecule *A*, (b) molecule *B*.

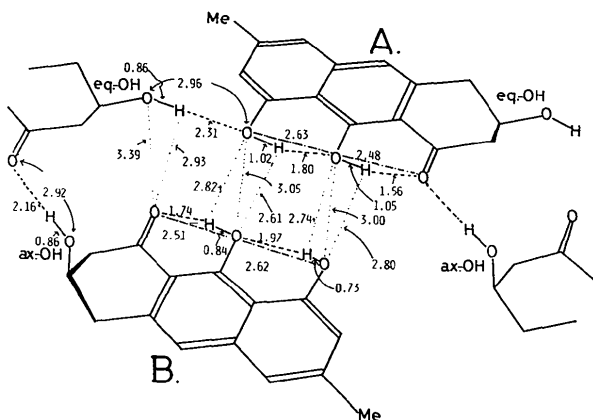


Fig. 5. Intramolecular and intermolecular hydrogen bonds. Hydrogen bonds are shown by broken lines and short intermolecular distances are shown by dotted lines.

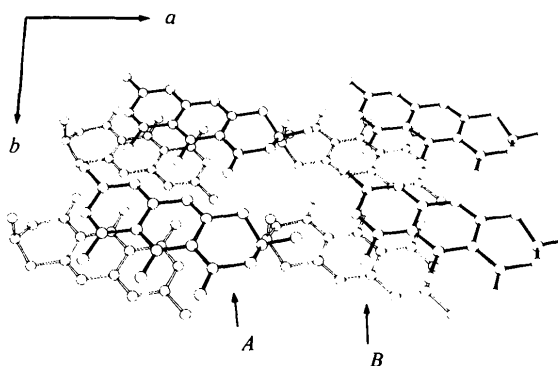


Fig. 6. Projection of the crystal structure along the *c* axis. Molecule *A* is represented by filled bonds and molecule *B* by open bonds. The figure was drawn by ORTEP (Johnson, 1965).

Interatomic distances related to the intramolecular and intermolecular hydrogen bonds are shown in Fig. 5. Fig. 6 illustrates the crystal structure projected along the *c* axis. The *A* molecules, which take the equatorial conformation at C(3)—O(3), form a chain of hydrogen bonds with the neighbouring ones along the *a* axis. The *B* molecules (axial conformation) do not form such a chain but form hydrogen bonds to the *A* molecules with their axial hydroxyl groups. It is conceivable that if the *B* molecule were the antipode of *A*, it would be related to *A* by a centre of symmetry forming the same kind of hydrogen-bond chain running antiparallel to that formed by the *A* molecule. In the present crystal, both molecules are actually related by a pseudo centre of symmetry disregarding the substituents at C(3) and this would force the C(3)—O(3) bond to take an axial conformation towards the *B* molecule. As is described above, this conformation is stabilized by the hydrogen bond between the *A* and *B* molecules. The perpendicular distances between the molecular planes given in Table 3 are 3.284 Å between *A* and *B* and 3.652 between *A* and *B* at *x*, *y*, 1 + *z*.

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