

The Crystal Structure and Absolute Configuration of Cedryl Chromate

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Cedryl chromate crystallizes in the space group $P2_1$, $a = 6.06 \pm 0.02$, $b = 14.68 \pm 0.02$, $c = 16.45 \pm 0.02$ Å and $\beta = 95^\circ 30' \pm 5'$, with two molecules of $(C_{15}H_{25})_2CrO_4$ per unit cell. The crystal structure was solved using the anomalous scattering of Cu $K\alpha$ radiation by the chromium atoms to determine some of the phases of visually estimated three-dimensional data. Further data collected on a linear diffractometer with Mo $K\alpha$ radiation were used for the final refinement. The R index for 1115 observed reflexions is 0.085. The two cedryl units in the asymmetric unit are essentially the same except that the different environment at each end of the molecule causes one of the five-membered rings to take up different conformations. The absolute configuration of cedryl chromate was determined by anomalous dispersion and the result agrees with earlier chemical work on (+)-cedrol.

Introduction

The molecular structure of (+)-cedrol and its absolute configuration have been deduced previously by Stork & Clarke (1961) by chemical methods. A crystallographic investigation of the structure of cedryl chromate has been carried out to confirm the structure and, as the anomalous dispersion method (with Cu $K\alpha$ radiation) has been used for phase determination, the absolute configuration of cedryl chromate has also been directly determined.

During the course of the structure determination it was found that the two cedryl groups in the molecule occurred in slightly different configurations. To confirm the reality of this difference it was necessary to carry out a redetermination of the structure using data not significantly affected by anomalous dispersion and absorption effects and obtained from Mo $K\alpha$ radiation.

Crystal data

Single crystals of cedryl chromate, $(C_{15}H_{25})_2CrO_4$, prepared by the method of Fieser & Ourisson (1953) and recrystallized from petroleum spirit, are orange coloured plates elongated parallel to the a axis with the (001) and (00 $\bar{1}$) faces prominent.

Monoclinic: $a = 6.06 \pm 0.02$, $b = 14.68 \pm 0.02$, $c = 16.45 \pm 0.02$ Å, $\beta = 95^\circ 30' \pm 5'$, $D_o = 1.20$ g.cm $^{-3}$, $D_c = 1.21$ g.cm $^{-3}$ for $Z = 2$, $\mu = 36$ cm $^{-1}$ for Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å) and $\mu = 4.5$ cm $^{-1}$ for Mo $K\alpha$ radiation ($\lambda = 0.7107$).

The space group was determined from oscillation

and Weissenberg photographs. Absent spectra were $0k0$ for k odd and since the molecule is optically active the space group is determined uniquely as $P2_1$ (C_2^1).

Intensity data

The intensities of the visual data were recorded for the layers $h = 0 \rightarrow 4$ using multiple-film equi-inclination Weissenberg photographs with Cu $K\alpha$ radiation (data set I); chromium has a large imaginary component ($\Delta f'' = 2.6$) for Cu $K\alpha$ radiation (Dauben & Templeton, 1955). The fluorescent effect was reduced by covering the gap in the layer line screens with thin nickel foil. As the crystals disintegrated under the action of the X-rays, three small crystals were required to collect all the data. The upper layer photographs were taken with the l rows central so that the intensities of the hkl and $hk\bar{l}$ reflexions could be compared for the determination of the Bijvoet differences. The choice of k and \bar{k} for the $0kl$ reflexions was carefully maintained in the upper layers to obtain a completely consistent set of data.

The number of reflexions observed, 1580, represents only 57% of the number possible within the Cu sphere, the high temperature factor accounting for most of the unobserved reflexions.

The intensities of the hkl , $h\bar{k}l$, $hk\bar{l}$, $h\bar{k}\bar{l}$ reflexions were estimated visually, and corrections for spot shape on the upper layer films were made (Scoulaudi, 1953). Lorentz and polarization factors were applied in the usual way. The crystals were very small (~ 0.1 mm dimensions) and no correction was made for absorption.

The scaling of each layer of reflexions was carried out by the method of Wilson (1942). It is important in the anomalous dispersion method that the systematic errors due to scaling, as well as the random errors

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of the estimation of the intensities should be as small as possible. It was shown (Amirthalingam & Grant, 1963) that small errors in these have no serious effect on the phases determined except when the phase is near 90° . Although the nickel foil lessens the fluorescent effect, the top films were all slightly fogged making the estimation on these films difficult and increasing the errors in the intensities.

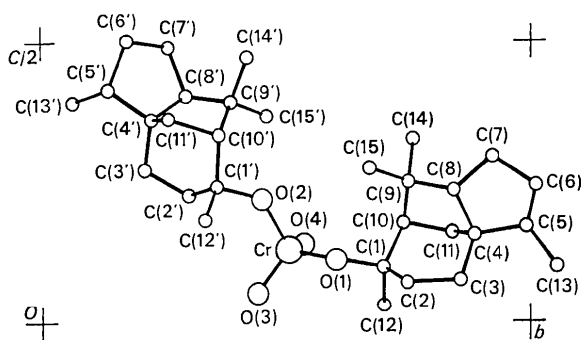


Fig. 1. Molecule of cedryl chromate viewed along the a axis.

A better set of data with no significant anomalous dispersion and absorption effects was later collected for refinement purposes. A single crystal of approximately $0.02 \times 0.05 \times 0.1$ mm dimensions was mounted along the b axis and the intensities of 1115 observed reflexions were collected for the layers $k=0 \rightarrow 14$ on a linear diffractometer with Mo $K\alpha$ radiation and a balanced filter technique (data set II). Again Lorentz and polarization corrections were made but no absorption corrections were applied. Since the oscillation angles were different for the upper layers, appropriate scale factors were applied to put the data on the same scale.

Structure determination

Using data set I, the x and z coordinates of the chromium atom was found from the (100) and (010) Patterson projections, the intensities used in the calculation being the average intensity of the Bijvoet pairs. The origin was chosen midway between the chromium atoms, making them centrosymmetrically related and using the values $x=0.110$, $y=0.250$ and $z=0.124$. The values of the contribution of the anomalous scattering

Table 1. Atomic coordinates and thermal parameters

Anisotropic temperature factors are of the form $\exp[-(h^2b_{11} + k^2b_{22} + l^2b_{33} + klb_{23} + hlb_{13} + hkb_{12})]$.

All values for the non-hydrogen atom are multiplied by 10^4 and the hydrogen atoms coordinates are multiplied by 10^3 .

	x/a	y/b	z/c	b_{11}	b_{22}	b_{33}	b_{23}	b_{13}	b_{12}
Cr	1078 (4)	2495 (2)	1224 (2)	283	53	45	7	38	3
O(1)	2716 (14)	3429 (6)	1026 (7)	203	45	63	-7	-31	8
O(2)	2304 (18)	1917 (6)	2110 (7)	422	44	56	-5	7	54
O(3)	-1284 (21)	2879 (8)	1355 (11)	375	74	145	59	3	4
O(4)	793 (23)	1840 (8)	445 (8)	671	60	59	-25	75	56
C(1)	2335 (23)	4420 (9)	883 (9)	286	50	25	7	56	98
C(2)	4522 (26)	4799 (10)	606 (9)	388	54	36	-3	154	-66
C(3)	4550 (21)	5866 (8)	651 (9)	181	34	48	5	65	13
C(4)	3745 (21)	6228 (8)	1454 (9)	222	41	30	-1	-81	38
C(5)	4071 (23)	7267 (11)	1593 (10)	232	76	47	-11	46	-65
C(6)	5993 (29)	7335 (11)	2284 (11)	497	65	56	-33	47	-14
C(7)	5646 (26)	6514 (12)	2809 (10)	385	80	33	-33	-92	-32
C(8)	4978 (25)	5750 (9)	2223 (10)	293	58	39	-13	50	17
C(9)	3556 (26)	4907 (10)	2405 (9)	375	47	45	37	87	-9
C(10)	1711 (21)	4872 (10)	1693 (10)	140	54	39	24	27	8
C(11)	1346 (22)	5893 (9)	1513 (9)	191	50	43	35	117	2
C(12)	404 (25)	4486 (10)	205 (7)	231	73	25	1	15	134
C(13)	4545 (39)	7832 (11)	891 (2)	781	69	48	-10	63	-85
C(14)	2278 (28)	5087 (14)	3218 (10)	387	128	25	-17	53	-150
C(15)	4975 (30)	4059 (11)	2607 (11)	432	74	44	-3	-51	128
C(1')	3017 (24)	1005 (10)	2318 (9)	312	62	33	-48	99	-66
C(2')	882 (27)	428 (12)	2205 (10)	323	95	29	19	63	168
C(3')	1160 (24)	-494 (12)	2675 (10)	219	92	43	3	1	-24
C(4')	2411 (28)	-361 (11)	3539 (11)	384	69	41	-31	65	-36
C(5')	2559 (28)	-1252 (12)	4083 (12)	427	80	71	125	-19	-26
C(6')	2711 (39)	-865 (16)	4971 (13)	898	94	50	44	-33	-77
C(7')	1134 (36)	13 (17)	4921 (14)	663	117	83	-27	181	-230
C(8')	1237 (25)	381 (11)	4029 (10)	249	98	38	20	76	-20
C(9')	2479 (26)	1295 (10)	3870 (10)	420	68	32	13	98	1
C(10')	4052 (23)	1041 (11)	3222 (9)	173	77	39	-34	51	-140
C(11')	4612 (26)	24 (10)	3487 (10)	300	50	36	22	-11	26
C(12')	4678 (29)	744 (13)	1692 (11)	495	99	47	18	111	147
C(13')	839 (36)	-2002 (14)	3914 (11)	650	105	33	-2	4	-40
C(14')	4082 (41)	1609 (16)	4629 (14)	724	102	69	-25	-11	-174
C(15')	820 (37)	2052 (13)	3681 (12)	785	83	39	-23	89	82

Table 1 (cont.)

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> (Å) ²
H(1)	581	453	99	4·2
H(2)	459	459	0	4·2
H(3)	614	610	60	3·0
H(4)	345	614	17	3·0
H(5)	260	751	180	4·4
H(6)	745	732	203	6·4
H(7)	578	797	258	6·4
H(8)	711	638	319	5·7
H(9)	438	666	322	5·7
H(10)	637	545	204	5·3
H(11)	37	449	191	4·0
H(12)	31	600	97	4·2
H(13)	59	623	200	4·2
H(14)	-67	392	17	5·0
H(15)	-58	506	25	5·0
H(16)	102	450	-40	5·0
H(17)	367	850	83	6·4
H(18)	617	797	88	6·4
H(19)	390	749	34	6·4
H(20)	217	575	333	5·2
H(21)	68	482	315	5·2
H(22)	318	479	374	5·2
H(23)	575	375	217	5·7
H(24)	613	422	307	5·7
H(25)	386	356	279	5·7
H(1')	-49	76	240	4·6
H(2')	50	24	157	4·5
H(3')	-38	-75	274	5·6
H(4')	211	-92	235	5·6
H(5')	400	-160	396	4·8
H(6')	221	-135	535	7·2
H(7')	437	-68	511	7·2
H(8')	-41	-19	505	6·5
H(9')	185	46	538	6·5
H(10')	-36	51	378	5·3
H(11')	539	150	325	5·4
H(12')	535	-30	300	4·5
H(13')	563	1	401	4·5
H(14')	500	0	179	5·0
H(15')	397	85	109	5·0
H(16')	613	112	180	5·0
H(17')	67	-233	450	7·6
H(18')	-67	-177	366	7·6
H(19')	142	-252	351	7·6
H(20')	317	183	517	7·9
H(21')	508	108	487	7·9
H(22')	499	218	450	7·9
H(23')	167	267	375	7·7
H(24')	7	201	312	7·7
H(25')	-28	205	414	7·7

The ambiguity in the phase angle so deduced was resolved by giving F_A the sign of F_{Cr} .

By this method the phases of 668 out of a total of 1580 reflexions were established and used to solve the structure.

The (100) electron density projection was first calculated using the anomalous dispersion determined phases for 113 out of the 199 observed $0kl$ reflexions and the heavy-atom phases for some of the remaining reflexions. The map showed no false symmetry and few spurious peaks. It was possible to assign the positions for the oxygen atoms and to fit the cedryl groups with reasonable certainty. Structure factors based on these atomic positions gave an *R* index of 0·35, which was reduced to 0·20 by difference synthesis and one cycle of least-squares refinement.

A three-dimensional electron density map was then calculated using the latest phases for the $0kl$ reflexions,

Table 2. Observed and calculated structure factors

H(1)			100 0 0	581 453 99	306	306	100 0 0
H(2)			100 0 0	459 459 0	459	459	100 0 0
H(3)			100 0 0	614 610 60	213	213	100 0 0
H(4)			100 0 0	345 614 17	210	210	100 0 0
H(5)			100 0 0	260 751 180	180	180	100 0 0
H(6)			100 0 0	745 732 203	203	203	100 0 0
H(7)			100 0 0	578 797 258	258	258	100 0 0
H(8)			100 0 0	711 638 319	319	319	100 0 0
H(9)			100 0 0	438 666 322	322	322	100 0 0
H(10)			100 0 0	637 545 204	204	204	100 0 0
H(11)			100 0 0	37 449 191	191	191	100 0 0
H(12)			100 0 0	31 600 97	97	97	100 0 0
H(13)			100 0 0	59 623 200	200	200	100 0 0
H(14)			100 0 0	-67 392 17	17	17	100 0 0
H(15)			100 0 0	-58 506 25	25	25	100 0 0
H(16)			100 0 0	102 450 -40	450	450	100 0 0
H(17)			100 0 0	367 850 83	83	83	100 0 0
H(18)			100 0 0	617 797 88	88	88	100 0 0
H(19)			100 0 0	390 749 34	34	34	100 0 0
H(20)			100 0 0	217 575 333	333	333	100 0 0
H(21)			100 0 0	68 482 315	315	315	100 0 0
H(22)			100 0 0	318 479 374	374	374	100 0 0
H(23)			100 0 0	575 375 217	217	217	100 0 0
H(24)			100 0 0	613 422 307	307	307	100 0 0
H(25)			100 0 0	386 356 279	279	279	100 0 0
H(1')			0 100 0	-49 76 240	240	240	0 100 0
H(2')			0 100 0	50 24 157	157	157	0 100 0
H(3')			0 100 0	-38 -75 274	274	274	0 100 0
H(4')			0 100 0	211 -92 235	235	235	0 100 0
H(5')			0 100 0	400 -160 396	396	396	0 100 0
H(6')			0 100 0	221 -135 535	535	535	0 100 0
H(7')			0 100 0	437 -68 511	511	511	0 100 0
H(8')			0 100 0	-41 -19 505	505	505	0 100 0
H(9')			0 100 0	185 46 538	538	538	0 100 0
H(10')			0 100 0	-36 51 378	378	378	0 100 0
H(11')			0 100 0	539 150 325	325	325	0 100 0
H(12')			0 100 0	535 -30 300	300	300	0 100 0
H(13')			0 100 0	563 1 401	401	401	0 100 0
H(14')			0 100 0	500 0 179	179	179	0 100 0
H(15')			0 100 0	397 85 109	109	109	0 100 0
H(16')			0 100 0	613 112 180	180	180	0 100 0
H(17')			0 100 0	67 -233 450	450	450	0 100 0
H(18')			0 100 0	-67 -177 366	366	366	0 100 0
H(19')			0 100 0	142 -252 351	351	351	0 100 0
H(20')			0 100 0	317 183 517	517	517	0 100 0
H(21')			0 100 0	508 108 487	487	487	0 100 0
H(22')			0 100 0	499 218 450	450	450	0 100 0
H(23')			0 100 0	167 267 375	375	375	0 100 0
H(24')			0 100 0	7 201 312	312	312	0 100 0
H(25')			0 100 0	-28 205 414	414	414	0 100 0

to the imaginary part of the structure factor $\Delta B = (F_{Cr}/f_{Cr})\Delta f''$ where ($\Delta f'' = 2\cdot6$) were calculated for all observed reflexions (the real dispersion component $\Delta f' = 0\cdot1$ was ignored). The intensity values corrected for anomalous dispersion were calculated from $I = |F|^2 = \frac{1}{2}(I_1 + I_2) - (\Delta B)^2$ where $I_1 = I(hkl)$ and $I_2 = I(\bar{h}\bar{k}\bar{l})$.

The real and imaginary parts of the structure factors were given by

$$F_A^2 = \frac{1}{2}(I_1 + I_2) - (\Delta B)^2 - \frac{(I_1 - I_2)^2}{16(\Delta B)^2},$$

and

$$F_B = \frac{(I_1 + I_2)}{4(\Delta B)} \text{ (Ramachandran \& Raman, 1956).}$$

the phases deduced by the anomalous dispersion method and 127 heavy-atom phases for those reflexions with $I_1 - I_2 \approx 0$. There were no prominent peaks due to false symmetry, confirming that the ambiguity in the phases had been sufficiently resolved by assuming the phases nearer to that of the chromium atom.

A knowledge of the y and z coordinates of the atoms enabled 25 out of the 34 atoms to be identified and their x coordinates established with certainty. Three cycles of structure factors and electron density maps were required to locate the remaining atoms and the R index at this stage was 0.23.

Refinement

Continuing to use data set I, the structure was refined by 5 cycles of block-diagonal least squares with isotropic temperature factors, the R index being 0.18 at this stage. It was evident from an electron density map that the two cedryl units in the asymmetric unit were identical except that the plane containing C(5), C(6) and C(7) takes up two positions relative to the rest of the molecule in the two units, Fig. 1. With relatively poor visual data and a non-centrosymmetric space group it was possible that the difference was not real but a result of the way in which the molecule had been built up from successive electron density maps.

The structure was partly redetermined using data set II. From the last cycle of least squares using data set I, the coordinates of the following atoms were used to phase an electron density map using data set II; Cr, O(1) to O(4), C(1) to C(4), C(8) to C(12), C(14), C(15), C(1') to C(4'), C(8') to C(12'), C(14'), C(15'). The positions of the 8 missing carbon atoms (C(5), C(6), C(7) and C(13) in each unit) were found from the electron density map. These atoms were in the positions originally found using data set I and the difference between the two units was confirmed. The refinement was continued, using data set II, by 3 cycles of least-squares before hydrogen atoms were included. From the geometry of the molecule, hydrogen atom coordinates were calculated for those atoms not attached to methyl groups. From the resulting electron density map, the best defined hydrogen atom of each methyl group was used to calculate the positions of the remaining two hydrogen atoms of each group. These positional parameters were not included in any subsequent least-squares refinement and the isotropic temperature factor for each hydrogen was assumed to be that of its attached carbon and was not refined.

Least-squares refinement was carried out (block-diagonal program for the IBM 1620 series) using absolute weights (Grant, Killean & Lawrence, 1969) and isotropic temperature factors were used for each atom. After three cycles of refinement the R index was 0.10 and $\sum \omega |\Delta F|^2 / (m-n) = 2.493$. Further refinement was carried out using anisotropic temperature factors for the chromium, oxygen and carbon atoms; the hydrogen positions and isotropic temperature factors were

not refined. Seventeen reflexions with $|\Delta F| > 3\sigma(F)$ were given zero weight. Three cycles of refinement reduced R to 0.0853 and $\sum \omega |\Delta F|^2 / (m-n) = 1.378$. The final atomic coordinates and temperature factors are shown in Table 1 and the observed and calculated structure factors in Table 2.

Molecular geometry

The bond-lengths and angles and their standard deviations are given in Tables 3 and 4. The four Cr-O bond-lengths show that the chromate group approximates to a $(\text{CrO}_4)^-$ ion. The bond-lengths Cr-O(3) (1.57 Å), Cr-O(4) (1.59 Å) are not significantly different from those found in $(\text{NH}_4)_2\text{CrO}_4$ (Gatehouse & Leverett, 1969), whereas Cr-O(1) (1.74 Å) and Cr-O(2) (1.79 Å) lie between these values and the sum of the covalent radii (1.90 Å). The chromate group is tetrahedral within the accuracy of the structure determination.

Table 3. Bond lengths with standard deviations

Cr—O(1)	1.74 (1) Å	O(2)—C(1')	1.44 (2) Å
Cr—O(2)	1.79 (1)	C(1')—C(2')	1.55 (2)
Cr—O(3)	1.57 (1)	C(2')—C(3')	1.56 (2)
Cr—O(4)	1.59 (1)	C(3')—C(4')	1.55 (2)
O(1)—C(1)	1.49 (2)	C(4')—C(5')	1.58 (2)
C(1)—C(2)	1.54 (2)	C(5')—C(6')	1.56 (3)
C(2)—C(3)	1.57 (2)	C(6')—C(7')	1.59 (3)
C(3)—C(4)	1.54 (2)	C(7')—C(8')	1.58 (3)
C(4)—C(5)	1.55 (2)	C(8')—C(9')	1.57 (2)
C(5)—C(6)	1.54 (2)	C(9')—C(10')	1.54 (2)
C(6)—C(7)	1.51 (2)	C(10')—C(11')	1.58 (2)
C(7)—C(8)	1.52 (2)	C(11')—C(10')	1.56 (2)
C(8)—C(9)	1.55 (2)	C(11')—C(12')	1.55 (2)
C(9)—C(10)	1.54 (2)	C(4')—C(8')	1.57 (2)
C(10)—C(11)	1.54 (2)	C(4')—C(11')	1.46 (2)
C(1)—C(10)	1.56 (2)	C(5')—C(13')	1.52 (3)
C(1)—C(12)	1.54 (2)	C(9')—C(14')	1.58 (3)
C(4)—C(8)	1.57 (2)	C(9')—C(15')	1.51 (3)
C(4)—C(11)	1.55 (2)		
C(5)—C(13)	1.48 (2)		
C(9)—C(14)	1.63 (2)		
C(9)—C(15)	1.53 (2)		

The structures of both cedryl groups are the same (with the exception mentioned above and discussed below) and are in complete agreement with the structure of (+)-cedrol found by chemical studies (Stork & Clarke, 1961).

The six-membered ring is chair shaped and the five-membered rings are *cis*-fused, the ring [C(4), C(8), C(9), C(10), C(11)] being in the envelope form and the ring [C(4), C(5), C(6), C(7), C(8)] in half-chair form, Fig. 1. The bond lengths and angles are as expected and are similar to those found in the cedrene skeleton in shellolic bromo-lactone (Gabe, 1962).

A survey of all the molecular contacts showed no distances shorter than the usual van der Waals distances, the shortest of these being given in Table 5.

Table 4. Bond angles with standard deviations

O(1)—Cr—O(2)	109.0 (0.5)°
O(1)—Cr—O(3)	106.7 (0.5)
O(1)—Cr—O(4)	110.2 (0.6)
O(2)—Cr—O(3)	111.8 (0.7)
O(2)—Cr—O(4)	111.9 (0.6)
O(3)—Cr—O(4)	107.2 (0.8)
Cr—O(1)—C(1)	135.7 (0.8)
O(1)—C(1)—C(2)	106.1 (1.0)
O(1)—C(1)—C(10)	109.0 (1.1)
O(1)—C(1)—C(12)	105.7 (1.1)
C(1)—C(2)—C(3)	110.8 (1.1)
C(2)—C(3)—C(4)	112.3 (1.1)
C(3)—C(4)—C(5)	114.9 (1.1)
C(3)—C(4)—C(8)	111.8 (1.0)
C(3)—C(4)—C(11)	108.6 (1.1)
C(5)—C(4)—C(8)	106.0 (1.1)
C(5)—C(4)—C(11)	114.1 (1.0)
C(8)—C(4)—C(11)	100.6 (1.1)
C(4)—C(5)—C(6)	104.6 (1.2)
C(4)—C(5)—C(13)	117.8 (1.3)
C(6)—C(5)—C(13)	110.7 (1.4)
C(5)—C(6)—C(7)	103.5 (1.3)
C(6)—C(7)—C(8)	105.6 (1.3)
C(4)—C(8)—C(7)	105.1 (1.1)
C(4)—C(8)—C(9)	106.6 (1.2)
C(7)—C(8)—C(9)	126.2 (1.3)
C(8)—C(9)—C(10)	104.8 (1.2)
C(8)—C(9)—C(14)	110.2 (1.3)
C(10)—C(9)—C(15)	119.3 (1.3)
C(14)—C(9)—C(15)	104.7 (1.3)
C(1)—C(10)—C(11)	106.9 (1.1)
C(1)—C(10)—C(9)	116.2 (1.1)
C(9)—C(10)—C(11)	101.1 (1.1)
C(4)—C(11)—C(10)	101.6 (1.0)
Cr—O(2)—C(1')	136.8 (0.9)
O(2)—C(1')—C(2')	104.8 (1.2)
O(2)—C(1')—C(10')	105.9 (1.2)
O(2)—C(1')—C(12')	105.8 (1.2)
C(1')—C(2')—C(3')	111.2 (1.3)
C(2')—C(3')—C(4')	112.0 (1.3)
C(3')—C(4')—C(5')	114.0 (1.3)
C(3')—C(4')—C(8')	110.4 (1.3)
C(3')—C(4')—C(11')	111.2 (1.3)
C(5')—C(4')—C(8')	107.0 (1.3)
C(5')—C(4')—C(11')	111.0 (1.4)
C(8')—C(4')—C(11')	102.6 (1.3)
C(4')—C(5')—C(6')	102.5 (1.5)
C(4')—C(5')—C(13')	119.8 (1.6)
C(6')—C(5')—C(13')	114.5 (1.6)
C(5')—C(6')—C(7')	105.6 (1.7)
C(6')—C(7')—C(8')	104.2 (1.6)
C(4')—C(8')—C(7')	107.0 (1.5)
C(4')—C(8')—C(9')	105.3 (1.2)
C(7')—C(8')—C(9')	121.2 (1.5)
C(8')—C(9')—C(10')	104.2 (1.2)
C(8')—C(9')—C(14')	112.7 (1.4)
C(10')—C(9')—C(15')	118.6 (1.4)
C(14')—C(9')—C(15')	107.2 (1.5)
C(1')—C(10')—C(11')	106.5 (1.2)
C(1')—C(10')—C(9')	116.9 (1.2)
C(9')—C(10')—C(11')	99.7 (1.1)
C(4')—C(11')—C(10')	102.3 (1.2)

Table 5. Short non-bonded intermolecular distances

C(13) → O(1)	(1-x, ½+y, z̄)	3.79 Å
C(13) → O(3)	(x̄, ½+y, z̄)	3.99
C(13) → O(4)	(x̄, ½+y, z̄)	3.94
C(13) → C(2)	(1-x, ½+y, z̄)	3.85
C(13') → C(6)	(1-x, ½+y, z̄)	3.94

The two cedryl groups

The difference between the two groups in the molecule of cedryl chromate found in this structure is that the plane containing the atoms C(5), C(6) and C(7) in one of the five-membered rings takes up two different positions. The atom C(6') is *cis* to the methyl C(14') in one group but the atom C(6) is *trans* to the methyl C(14) in the other. Fig. 2(a) shows the two groups superimposed taking C(4) as a common point and aligning the bond C(4)–C(3) and C(4)–C(8); Fig. 2(b) gives another view of the superposition. An examination of

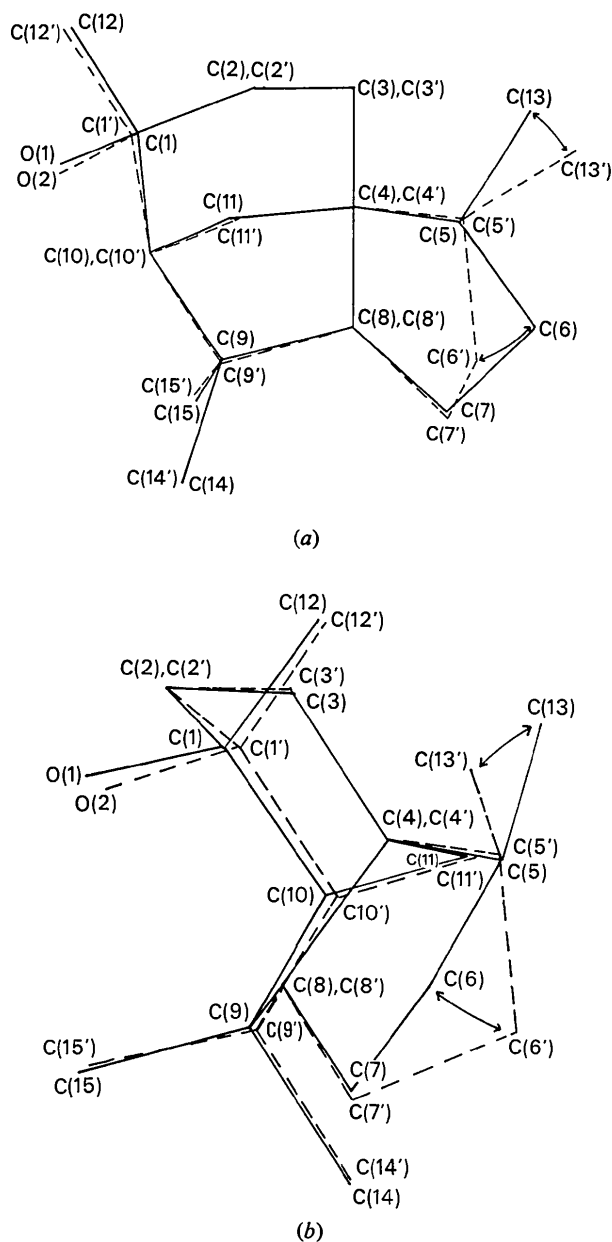


Fig. 2. Two views of the cedryl units when superimposed.

the positions of the atoms around the points $y=1, z=0$ and $y=0, z=\frac{1}{2}$ in Fig. 3 shows greater overcrowding in the former case (Table 5). The distance between the methyl at C(13) of the primary molecule (x, y, z) and O(4) of the molecule at $(\bar{x}, \frac{1}{2}+y, \bar{z})$ is 3.94 Å and the distance between the same methyl and O(1) of the molecule at $(1-x, \frac{1}{2}+y, \bar{z})$ is 3.79 Å. This methyl is held closely between these oxygen atoms. The ring atom

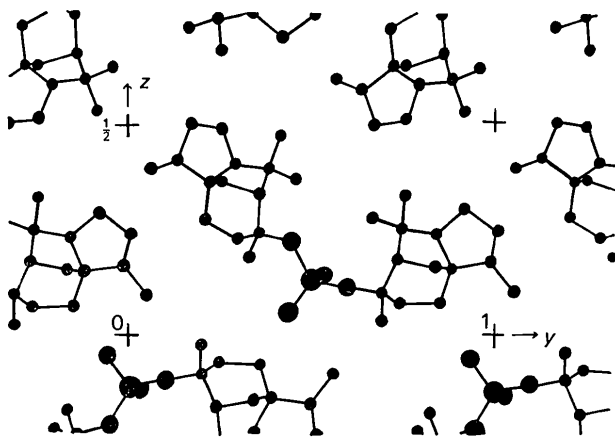


Fig. 3. Molecular packing viewed along the a axis.

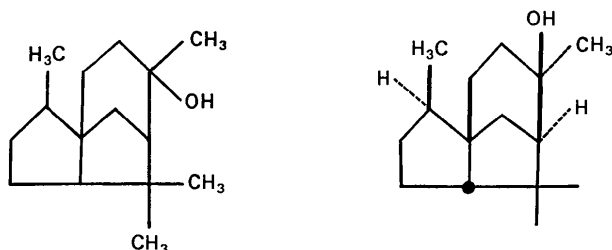


Fig. 4. (+)-cedrol.

C(6) moves into a position to preserve the tetrahedral arrangement at each carbon atom and becomes *trans* to the methyl C(14).

The absolute configuration

Provided precautions are taken in the indexing of the Weissenberg photographs (Peerdeman & Bijvoet, 1956; Raman, 1958; Ramaseshan, 1964) the structure as determined by the anomalous dispersion method will be in the absolute configuration. Fig. 1 then shows the absolute configuration of the molecule of cedryl chromate and that of (+)-cedrol, deduced from it, is shown in Fig. 4. This is the same as that deduced by Stork & Clarke (1961) from chemical studies.

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The Crystal and Molecular Structure of Difluoromalonic Acid

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Difluoromalonic acid crystallizes in the monoclinic space group $P2_1/c$ with cell dimensions $a=9.59$, $b=5.61$, $c=9.80$ Å, $\beta=115.1^\circ$ and $Z=4$. The crystal is a racemate of two conformational antipodes. The acid molecules in the infinite chains are connected by hydrogen bonds between carboxyl groups across centres of symmetry.

Introduction

In the crystal structure of α -substituted monocarboxylic acids, such as propionic acid (Strieter & Templeton, 1962), fluoroacetic acid (Kanters, 1972), glycollic

acid (Pijper, 1971) and several amino-acids (*e.g.* Kanters, Kroon, Beurskens & Vliegthart, 1966), it is found that the carboxylic acid group is nearly coplanar with the α -substituent. It appears that such a planar arrangement is favoured. These findings are in accord-