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The Crystal Structure of 2-*cis*-4-Hydroxyretinoic Acid γ -Lactone*

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2-*cis*-4-Hydroxyretinoic acid γ -lactone, C₂₀H₂₆O₂, is triclinic (*P* $\bar{1}$) with $a = 18.67$ (2), $b = 7.51$ (1), $c = 6.87$ (1) Å, $\alpha = 111.04$ (12), $\beta = 83.77$ (12), $\gamma = 98.96$ (12)°, $D_c = 1.12$ g cm⁻³ for $Z = 2$. The structure was solved by Patterson and Fourier methods and refined to an R of 0.072. The double-bond system in the molecule is in the all-*trans* configuration except where the chain is attached to the cyclohexene ring. Here the double bonds are in a near *s-cis* configuration, with a dihedral angle of 45.2° between the planes of the chain and the ring. The five-membered butenolide ring is planar, and is almost coplanar with the chain.

Introduction

During studies of the reaction of *trans*- β -ionylideneacetaldehyde with 3-methylbut-2-enolide by Dr B.V. Burger and Mr F.E. Greeff of the Department of Chemistry, University of Stellenbosch, two products were formed which could not be identified by n.m.r. or other methods at their disposal. They were thought to be the isomers depicted in Fig. 1(a) and (b), but no certainty could be reached on this point. Crystals of these two compounds were therefore submitted to the authors for structure analysis. Here we report the structure of one product which was found to be 2-*cis*-4-hydroxyretinoic acid γ -lactone [Fig. 1(c)]. The structure of the other isomer has also been determined and is illustrated in Fig. 1(d). It differs in the *cis*-linkage at C(10) and will be reported fully later.

Experimental

Yellow crystals of 2-*cis*-4-hydroxyretinoic acid were provided by Burger & Greeff. Weissenberg photographs indicated that the crystals were triclinic (*P* $\bar{1}$)

with $a = 18.67$ (2), $b = 7.51$ (1), $c = 6.87$ (1) Å, $\alpha = 111.04$ (12), $\beta = 83.77$ (12), $\gamma = 98.96$ (12)° and $D_c = 1.12$ g cm⁻³ for $Z = 2$. The density was measured as 1.12 g cm⁻³ by flotation in potassium iodide solution.

A crystal with dimensions 0.9 × 1.0 × 1.1 mm was used to collect intensities on a Philips PW 1100 diffractometer at 20°C with graphite-monochromated Mo $K\alpha$ radiation. 2174 reflexions were measured by the ω scan technique between 3 and 22° θ . A scan speed of 0.04° s⁻¹ and a scan width of 1.2° were employed. The background was counted for half the scanning time on both sides of each reflexion. 218 were rejected as unobserved by the criterion $I < 1.65\sigma(I)$, where $\sigma(I) = [(0.02N_o)^2 + N_o + K^2N_b]^{1/2}$, N_o is the gross count, N_b the background count and K the ratio of scan to background time.

During data collection repetition of three standard reflexions every hour showed that the crystal was stable as the maximum intensity variation was 0.6% from its mean value.

Lorentz and polarization factors were applied to give relative structure factors. No absorption corrections were made as μR was only 0.04. The scattering factors for C and O were those of Cromer & Mann (1968), and for H those of Stewart, Davidson & Simpson (1965).

* C.S.I.R. – R. Fis. 689.

Table 1. *Positional and thermal parameters*

Positional parameters are given as fractional coordinates ($\times 10^4$) and thermal parameters ($\times 10^4$) are given according to the expression $T = \exp[-2\pi^2(a^{*2}h^2U_{11} + b^{*2}k^2U_{22} + c^{*2}l^2U_{33} + 2a^*b^*hkU_{12} + 2a^*c^*hlU_{13} + 2b^*c^*klU_{23})]$. Standard deviations are given in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃	Isotropic <i>B</i> (Å ²)
C(1)	8494 (2)	9282 (5)	3981 (6)	338 (18)	673 (23)	533 (22)	170 (16)	139 (15)	299 (19)	6.44
C(2)	9005 (2)	9579 (7)	2225 (7)	526 (24)	915 (33)	572 (26)	315 (24)	300 (20)	317 (24)	5.34
C(3)	9491 (3)	1462 (8)	2820 (9)	574 (27)	1137 (41)	811 (32)	179 (27)	387 (25)	557 (31)	3.99
C(4)	9067 (2)	3054 (7)	4109 (7)	511 (24)	803 (31)	732 (28)	-57 (22)	211 (22)	373 (25)	3.37
C(5)	1257 (2)	7199 (6)	3835 (6)	302 (17)	736 (25)	516 (21)	-53 (16)	81 (15)	236 (18)	3.69
C(6)	1626 (2)	9269 (5)	4247 (5)	208 (15)	681 (23)	432 (20)	58 (15)	73 (13)	266 (18)	3.24
C(7)	2118 (2)	9506 (5)	2501 (5)	318 (19)	673 (23)	384 (19)	31 (16)	73 (14)	216 (17)	3.34
C(8)	2788 (2)	423 (5)	2581 (5)	335 (19)	579 (21)	342 (18)	41 (15)	87 (14)	176 (16)	3.40
C(9)	3277 (2)	509 (5)	808 (5)	313 (18)	572 (20)	369 (18)	39 (15)	116 (14)	173 (15)	3.42
C(10)	3943 (2)	1487 (5)	1172 (5)	364 (19)	553 (21)	332 (17)	20 (16)	115 (15)	146 (16)	3.02
C(11)	4507 (2)	1689 (5)	9650 (5)	385 (20)	556 (22)	340 (17)	69 (17)	130 (16)	124 (16)	3.32
C(12)	5146 (2)	2759 (5)	55 (5)	313 (18)	510 (19)	355 (17)	79 (15)	151 (13)	151 (15)	4.11
C(13)	5747 (2)	3133 (5)	8674 (5)	334 (17)	534 (20)	432 (19)	107 (14)	197 (14)	183 (16)	5.29
C(14)	6238 (2)	4351 (6)	9854 (6)	300 (20)	646 (26)	565 (24)	-29 (18)	233 (18)	212 (20)	5.18
C(15)	5998 (2)	4857 (7)	2026 (6)	426 (23)	872 (31)	469 (25)	-131 (22)	111 (19)	125 (23)	3.95
C(16)	5751 (2)	2253 (9)	6375 (7)	523 (29)	962 (39)	435 (25)	-18 (26)	258 (20)	235 (25)	5.41
C(17)	3017 (2)	9498 (9)	8661 (7)	393 (24)	1073 (39)	430 (24)	-69 (26)	121 (18)	265 (27)	5.16
C(18)	1814 (2)	5794 (7)	2990 (9)	673 (31)	620 (30)	678 (32)	26 (24)	158 (25)	208 (26)	5.67
C(19)	688 (2)	6653 (11)	2234 (10)	543 (30)	1019 (46)	849 (38)	-175 (28)	-123 (26)	351 (35)	5.63
C(20)	8153 (3)	7268 (8)	3541 (9)	846 (39)	700 (34)	631 (34)	278 (28)	328 (26)	191 (28)	6.59
O(1)	5324 (1)	3807 (3)	2089 (3)	343 (13)	797 (18)	315 (13)	-73 (12)	128 (10)	133 (12)	4.11
O(2)	6255 (2)	5924 (7)	3595 (5)	712 (22)	1746 (41)	518 (20)	-530 (25)	62 (17)	-48 (23)	8.63
H(21)	8730 (19)	9508 (49)	1138 (59)							3.38

Solution of the structure

The orientation of the conjugated planar chains was deduced from a sharpened Patterson map. In general intramolecular vectors defining the direction and orientation of a chain will yield a row of peaks passing through the origin while the vectors between two centrosymmetrically related chains will yield a row of peaks parallel to the row through the origin. The separation of these rows indicates the distance between the chains.

Such an arrangement was evident, and it was possible to locate the $2x, 2y, 2z$ vector peak which defined the interaction between the central atoms C(9), C(9') of the two chains. The position of C(9) was then calculated from the coordinates of the vector peak. The positions of the remaining chain atoms were calculated from a knowledge of the orientation and length of the intramolecular vectors.

A Fourier synthesis was phased on these atomic positions and the remaining non-hydrogen atoms were located. Full-matrix least-squares refinement was carried out with the program *CRYLSQ* of the X-RAY 72 system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). After several cycles of isotropic and anisotropic refinement with unit weighting, *R* was 0.108, where $R = \sum w(|F_o| - |F_c|) / \sum |F_o|$. The function minimized was $\sum w(|F_o| - |F_c|)^2$.

A difference map was computed in which all the hydrogen atoms were located. Each hydrogen atom was given an isotropic temperature factor equal to the overall *B* value determined from a Wilson plot

Table 1 (cont.)

	<i>x</i>	<i>y</i>	<i>z</i>	Isotropic <i>B</i> (Å ²)
H(22)	9227 (20)	8549 (54)	1734 (57)	3.38
H(31)	9693 (19)	1754 (48)	1659 (59)	3.38
H(32)	-133 (20)	1391 (49)	3744 (56)	3.38
H(41)	9344 (20)	4285 (55)	4497 (54)	3.38
H(42)	8654 (20)	2899 (48)	3095 (55)	3.38
H(7)	1936 (19)	8857 (50)	1200 (61)	3.38
H(8)	2978 (19)	1012 (51)	3811 (61)	3.38
H(10)	4050 (19)	2064 (51)	2405 (62)	3.38
H(11)	5565 (20)	8912 (54)	1559 (62)	3.38
H(14)	3433 (21)	5183 (53)	468 (59)	3.38
H(161)	3993 (22)	7150 (55)	3985 (62)	3.38
H(162)	4294 (19)	9109 (58)	4027 (55)	3.38
H(163)	4606 (21)	7545 (51)	4256 (57)	3.38
H(171)	6740 (21)	192 (51)	2255 (62)	3.38
H(172)	7121 (21)	1691 (56)	1584 (58)	3.38
H(173)	7336 (21)	-91 (51)	1509 (54)	3.38
H(181)	1618 (19)	4592 (59)	2739 (54)	3.38
H(182)	1959 (20)	5799 (51)	1795 (63)	3.38
H(183)	2169 (20)	6166 (51)	4021 (59)	3.38
H(191)	385 (21)	7558 (54)	2773 (57)	3.38
H(192)	535 (20)	5348 (58)	1819 (54)	3.38
H(193)	870 (19)	6919 (50)	1042 (61)	3.38
H(201)	7917 (22)	6954 (59)	2586 (65)	3.38
H(202)	7991 (19)	7061 (49)	4708 (62)	3.38
H(203)	8377 (21)	6512 (56)	2883 (62)	3.38

(3.38 \AA^2). A weighting factor of $(\sin \theta / 0.35) \times (10.0 / F_o)$ was applied to all reflexions with $\sin \theta < 0.35$ and $F > 10.0$. Unit weights were applied to the remaining reflexions. At the end of the refinement $R = 0.072$ and $R_w = 0.083$.

Final values of the atomic positional and thermal parameters are given in Table 1. Figs. 2 and 3 show bond lengths and angles with the e.s.d.'s of the least

significant figures in parentheses. Bond lengths involving H atoms are given in Table 2.*

The labelling scheme for the atoms is given in Fig. 1(e).

Discussion

The crystal structure is closely related to the structures of vitamin A, carotene and canthaxanthin. In all these compounds the chain has an all-*trans* con-

* The table of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30393 (12 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

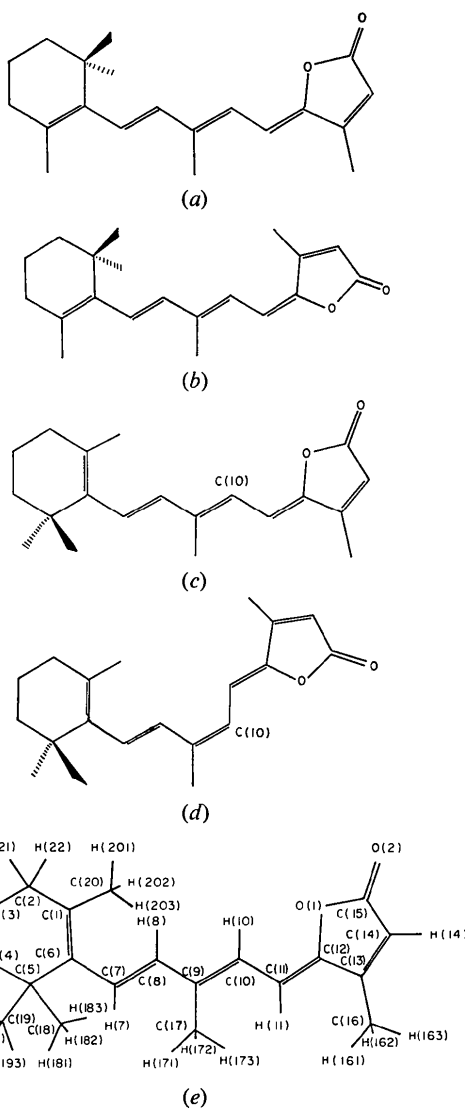


Fig. 1. (a), (b) Proposed conformations of the two isomers before structure elucidation. (c) Conformation of the *trans*-isomer. (d) Conformation of the *cis*-isomer. (e) Labelling scheme for the atoms.

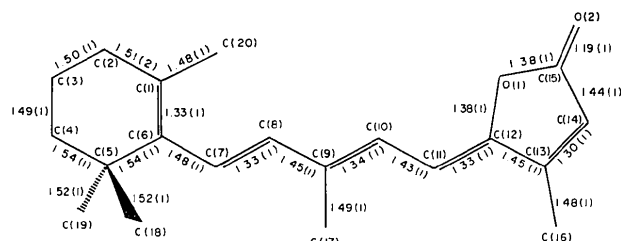


Fig. 2. Bond lengths.

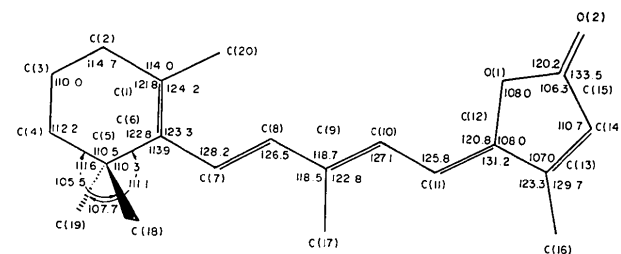


Fig. 3. Bond angles.

Table 2. Bond lengths involving hydrogen atoms, with *e.s.d.*'s in parentheses

C(2)—H(21)	0.93 (4) Å	C(16)—H(163)	0.89 (5) Å
C(2)—H(22)	0.88 (4)	C(17)—H(171)	0.82 (4)
C(3)—H(31)	0.93 (4)	C(17)—H(172)	0.85 (4)
C(3)—H(32)	1.01 (4)	C(17)—H(173)	0.89 (5)
C(4)—H(41)	0.95 (4)	C(18)—H(181)	0.88 (4)
C(4)—H(42)	1.06 (4)	C(18)—H(182)	0.84 (4)
C(7)—H(7)	0.92 (4)	C(18)—H(183)	0.96 (4)
C(8)—H(8)	0.88 (4)	C(19)—H(191)	0.90 (4)
C(10)—H(10)	0.83 (4)	C(19)—H(192)	0.92 (4)
C(11)—H(11)	0.81 (4)	C(19)—H(193)	0.93 (4)
C(14)—H(14)	0.71 (4)	C(20)—H(201)	0.77 (4)
C(16)—H(161)	0.69 (4)	C(20)—H(202)	0.88 (4)
C(16)—H(162)	0.95 (4)	C(20)—H(203)	0.74 (4)

figuration except for the almost *s-cis* configuration about the single bond from the chain to the six-membered ring.

Planarity of the molecule

The planarities of three sections of the molecule were considered: (a) C(1), C(2), C(5), C(6) and C(20) of the cyclohexene ring, (b) the chain between C(6) and C(12) [including C(17)], and (c) the atoms of the butenolide ring: C(12), C(13), C(14), C(15), C(16), O(1) and O(2). The least-squares planes are given in Table 3. All three portions were found to be planar, the maximum deviations of atoms being 0.005, 0.055 and 0.022 Å, respectively.

In the cyclohexene ring only C(1), C(2), C(5), C(6) and C(20) were used in the calculation of the least-squares plane. C(3) and C(4) were found to lie on different sides, being almost equidistant from it (−0.33 and 0.39 Å) thereby giving the ring a puckered character. The puckering of the ring leaves the hydrogen atoms H(31) and H(32) in a staggered conformation with respect to H(41) and H(42).

Table 3. Deviations (\AA) of atoms from least-squares planes

(a) Deviations of the atoms from the best plane through C(1), C(2), C(5), C(6) and C(20)			
C(1)	0.002	C(20)	-0.003
C(2)	0.001	C(3)	-0.333
C(5)	-0.004	C(4)	0.394
C(6)	0.005		
(b) Deviations of the atoms from the best plane through C(6), C(7), C(8), C(9), C(10), C(11), C(12) and C(17)			
C(6)	0.048	C(10)	-0.006
C(7)	-0.030	C(11)	0.055
C(8)	-0.035	C(12)	-0.018
C(9)	-0.015	C(17)	0.001
(c) Deviations of the atoms from the best plane through C(12), C(13), C(14), C(15), C(16), O(1) and O(2)			
C(12)	-0.011	C(16)	-0.013
C(13)	0.005	O(1)	0.015
C(14)	0.020	O(2)	-0.022
C(15)	0.005		

The dihedral angle between the plane of the cyclohexene ring and the plane of the chain was 45.2° . This agrees with values found in related structures. The reason for this twisting has been attributed largely to steric effects.

In contrast, the 5-membered butenolide ring was found to be almost coplanar with the chain, the dihedral angle being only 7.49° .

Bond lengths and angles

The bond lengths and angles reported here agree with those found in related structures reported by Sly (1964), Bart & MacGillavry (1968) and Hamanaka, Mitsui, Ashida & Kakudo (1972).

The double and single bonds in the chain have mean values of 1.333 and 1.453 \AA , respectively, as expected for conjugated systems. The three C-CH₃ bond distances are shorter than expected, and average 1.483 \AA .

The C-O and C=O bond distances of 1.38 and 1.19 \AA are normal.

The C(2)-C(3) and C(3)-C(4) bond distances of the cyclohexene ring are contracted. In most other related compounds substantial disorder in C(4), C(18) and C(19) was observed. A difference synthesis computed after the final refinement showed no appreciable dis-

order in the positions of these atoms. This was confirmed by the fact that C(3) and C(4) were found to be equidistant from but on opposite sides of the least-squares plane defined by C(1), C(2), C(5), C(6) and C(20). However, a small degree of disorder cannot be entirely discounted, and could well be used to explain the slight shortening of these bonds.

Thermal parameters of the atoms at both ends of the molecule, in particular O(2), were noticeably larger than the thermal parameters of the atoms forming the conjugated chain. Isotropic temperature factors of all the atoms are given in Table 1.

Although all the hydrogen atoms were clearly identified in the final stages of refinement, and no free rotation of any of the methyl groups was evident, some of the C-H bond distances were found to be abnormally short.

The C-C-C bond angles in the chain, except for C(8)-C(9)-C(10), have a mean value of 126.9° , whereas C(8)-C(9)-C(10) has the much reduced value of 118.7° . This in-plane bending can be attributed to steric hindrance between the methyl group C(17) and neighbouring hydrogen atoms and results in a slight curving of the chain.

The angles in the planar butenolide ring are all close to the theoretical value of 108° . The tetrahedral angles around C(5) show no gross deviation from their expected values. The values of the bond angles in the cyclohexene ring are typical of those found in this class of compound.

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