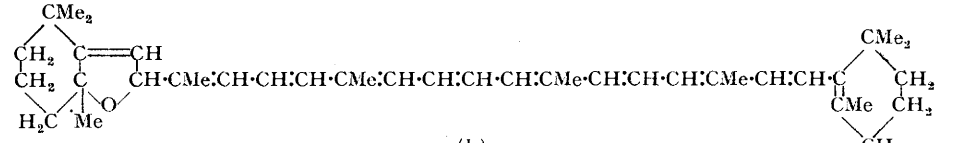
NOTE.

X-Ray Investigation of Some Oxidation Products of β-Carotene. By R. F. HUNTER, T. R. LOMER, V. VAND, and N. E. WILLIAMS

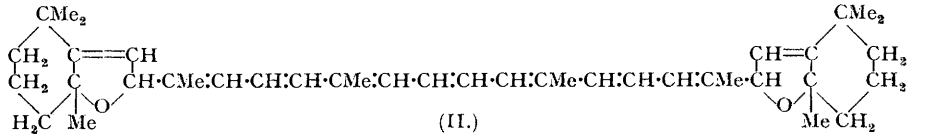
IT appeared desirable to supplement the chemical and spectroscopic evidence of structure of the crystalline products formed in the study of oxidation of β-carotene by oxygen (Hunter and Krakenberger, *J.*, 1947, 1) by *X*-ray measurements on carefully purified specimens of the carotenoids prepared by methods given in the literature. It also appeared probable that such data would enable us to obtain some information with regard to oxidation in the crystalline state.

The unit cell for β-carotene was determined by Taylor (*Z. Krist.*, 1937, **96**, 150) from single crystal measurements, who showed that it has a monoclinic cell of $a = 7{\cdot}75$, $b = 9{\cdot}5$, and $c = 25{\cdot}0$ A., $\beta = 105°$, containing two molecules per unit cell at co-ordinates 0,0,0, and $0,\frac{1}{2},\frac{1}{2}$, the space group being $C_{2h}^5 - P2_1/c$.

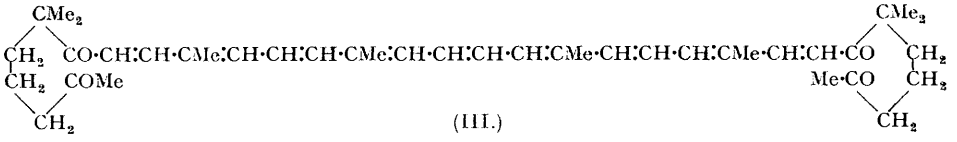
X-Ray diffraction data are now reported for all-*trans*-β-carotene, mutatochrome (I) (formerly regarded as " β-carotene oxide ", Karrer and Jucker, *Helv. Chim. Acta*, 1945, **28**, 427), aurochrome to which Karrer and Jucker have assigned the formula (II), and β-carotenone (III).



(I.)



(II.)



(III.)

No crystals large enough for a complete *X*-ray analysis by a single crystal method could be obtained. However, as the unit cell of β-carotene was already known, and as the powder patterns of its oxidation products are closely related, it was possible to index the diffraction lines on their powder photographs and so deduce the probable unit cells of the compounds studied, under the assumption that their unit cells do not differ greatly from that of β-carotene. A graphical method of indexing the powder photo-

graphs, which will be described elsewhere, has been used. As the resolving power of our powder camera is relatively high, it has been possible to determine the unit cell of β-carotene from the powder photographs more accurately; the unit cell so determined agrees well with that of Taylor.

The dimensions of the resulting unit cells in kX are given in the Table I.

TABLE I.

Compound.	*a*.	*b*.	*c*.	β.	Density: calc. from *X*-ray.	Density: observed (flotation).
β-Carotene	7·745	9·44	25·2	105·5°	1·00	—
Mutatochrome	7·75	9·66	25·2	105·0	0·998	—
Aurochrome	7·64	9·90	26·1	106·5	0·992	0·996
β-Carotenone	7·55	9·31	25·0	105·0	1·16	1·16

The dimensions of the unit cells chosen account for practically all of the observed diffraction lines and for the density, assuming two molecules per unit cell. As, however, the determination of the unit cell from the powder photographs is not as certain as from single crystals, and the determination of the space group is impossible, the data must not be regarded as final. Since β-carotene has a centre of symmetry and mutatochrome (I) cannot have one, it is quite probable that the true unit cells of some compounds are multiples of ours, requiring thus a doubling of one or more of our cell edges. The observed lines are described, however, in terms of the unit cells given.

The results show that on passing from β-carotene to mutatochrome the *b* cell edge increases by 0·22 kX, whereas the other parameters remain practically constant. Similarly, on passing from mutatochrome to aurochrome, the *b* cell edge increases by a further 0·24 kX, whereas the remaining parameters show only small changes. This progressive change of the *b* cell edge can be understood from the chemical evidence; the nuclear oxygen atoms evidently distend the cell dimensions in the direction of the *b* axis, and their action is therefore additive. On the other hand, β-carotenone shows a significant shrinkage in both *a* and *b* cell edges, accompanied by an increase of density. This can be understood from the effect of coiling back of the opened terminal ionone rings.

Interesting qualitative information with regard to oxidation of β-carotene, aurochrome, and β-carotenone by air in the solid crystalline state was obtained by re-examining the specimens which had been kept in the specimen holders at laboratory temperature for periods of 20 days and 3 months. No detectable change in the *X*-ray pattern of β-carotene was observed after 20 days; considerable weakening of the pattern occurred, without appearance of new lines, after 3 months. A similar result, but with less weakening of the pattern after 3 months was observed with aurochrome; again, no new lines were observed indicating the amorphous nature of the oxidation product. With β-carotenone, however, the pattern remained unchanged during the period of 3 months, indicating the higher stability of this carotenoid.

Experimental.—The specimen of β-carotene was freshly recrystallised and stored in carbon dioxide before measurement ($E^{1\%}_{1\ cm.}$ = 2300 at 464 mμ. in benzene).

The specimen of mutatochrome was one of those prepared by oxidation of β-carotene with perbenzoic acid and purified by rechromatography and recrystallisation as already described (Gridgeman, Hunter, and Williams, *J.*, 1947, 131).

Aurochrome, prepared by oxidation of β-carotene with perbenzoic acid and purified by rechromatography and recrystallisation from acetone, had m. p. 184° (abs. max. at 456 and 429 mμ. in carbon disulphide).

β-Carotenone was prepared by Kuhn and Brockmann's method (*Ber.*, 1932, **65**, 894). The recrystallised specimen showed absorption maxima at 538·5, 502, and 470 mμ, in carbon disulphide.

The powder photographs were taken with Ni-filtered Cu-K_α radiation in our 12·5 cm. focusing camera of the Frevel type, which will be described elsewhere. As a source of *X*-rays, a Metrovick "Raymax" demountable tube with aluminium windows was used. The exposures were for 1½ hours at 46 kv. and 20 ma. The specimens were sealed in specimen holders between two single cellophane sheets by means of a pressure-sensitive adhesive, and the first series of photographs taken immediately after sealing. The thickness of the specimens was arranged to be equal to the reciprocal value of the linear absorption coefficient of the specimen.

TABLE II.

d.	Intensity.	Index.	$d_{calc.}$.	*d*.	Intensity.	Index.	$d_{calc.}$.
			β-Carotene.				
8·870	2	011	8·80	3·534	10	$21\bar{3}$	3·525
7·536	10	100	7·47	3·371	10	—	—
6·075	80	013—80% 004—20%	6·14 6·07	3·234	10	—	—
				3·081	5	026	3·073
5·708	60	102	5·72	2·966	5	213	2·944
5·492	10	111	5·48	2·857	8	—	—
5·324	80	$11\bar{3}$	5·30	2·747	2	$20\bar{8}$	2·741
5·050	10	014	5·108	2·621	1	—	—
4·722	100	$11\bar{4}$	4·742	2·528	2	—	—
4·442	10	022	4·399	2·481	2	—	—
4·165	50	104—50% $11\bar{5}$—50%	4·194 4·194	2·436	1	206	2·439
				2·358	1	—	—
4·055	50	023	4·078	2·319	1	—	—
3·843	10	—	—	2·274	1	—	—
3·640	90	016—95% $20\bar{4}$— 5%	3·720 3·623	2·182	2	—	—
				2·030	5	—	—

TABLE II—*continued.*

d.	Intensity.	Probable index.	$d_{calc.}$.	*d*.	Intensity.	Probable index.	$d_{calc.}$.
			Mutatochrome.				
7·645	2	012	7·57	4·324	8	015	4·355
7·153	20	$10\bar{2}$	7·27	4·165	15	—	—
6·720	10	101	6·685	3·679	60	—	—
6·090	40	004	6·086	3·448	10	—	—
5·906	30	110	5·917	3·173	5	—	—
5·708	10	102	5·747	2·950	1	—	—
5·261	80	$11\bar{3}$	5·329	2·255	2	—	—
5·076	20	$\frac{1}{2}0\bar{5}$	5·076	2·020	2	—	—
4·831	100	020	4·831	1·852	1	—	—
4·480	5	022	4·491				
			Aurochrome.				
8·34	60	003	8·32	3·478	1	025	3·515
6·25	5	004	6·24	3·360	1	—	—
6·00	10	$11\bar{1}$	6·038	3·146	5D	—	—
5·557	100	102	5·643	3·096	2D	—	—
5·282	10	014	5·280	3·03—2·97	2D	—	—
5·158	10	?	?	2·902	1	—	—
4·842	20	103, 021	4·847, 4·854	2·82—2·72	2D	—	—
4·588	5	022	4·602	2·570	1	—	—
4·241	20	023	4·255	2·438	1	—	—
4·039	10	120	4·102	2·343	1	—	—
3·880	2	024	3·877	2·227	1	—	—
3·784	1	$20\bar{2}$, $20\bar{1}$	3·808, 3·771	2·110	1D	—	—
3·713	2	122	3·713	2·033	1	—	—
3·614	20	105, 200	3·665, 3·652	1·869	1	—	—
			β-Carotenone.				
7·94	1	003	8·05	3·279	1	—	—
7·17	25	$10\bar{2}$	7·11	3·185	1	—	—
6·41	1	101, $10\bar{3}$	6·53, 6·27	3·140	1	—	—
6·06	2	013, 004	6·09, 6·04	3·048	3	—	—
5·751	25	110	5·741	2·976	5	—	—
5·391	15	$10\bar{4}$	5·382	2·931	1	—	—
5·102	4	014	5·066	2·819	2	—	—
4·975	5	?	?	2·780	2	—	—
4·842	100	103, 112	4·819, 4·819	2·703	1	—	—
4·658	50	020, $11\bar{4}$	4·656, 4·660	2·621	2	—	—
4·386	1	022	4·344	2·570	2	—	—
4·292	15	113	4·281	2·506	1	—	—
4·207	8	104	4·155	2·342	1	—	—
4·122	40	$11\bar{5}$	4·132	2·268	1	—	—
3·877	3	$12\bar{2}$	3·894	2·152	1	—	—
3·731	3	$12\bar{3}$	3·737	2·106	1	—	—
3·656	10	$11\bar{6}$	3·664	2·020	2	—	—
3·460	15	201	3·476	1·987	2	—	—
3·368	8	—	—	1·802	2	—	—

In Table II are given the values of the observed spacings *d* in kX, the relative intensities of the diffraction lines, their probable indices, and the spacings calculated from the assumed cells. The relative intensities * were estimated by eye, taking the intensity of the strongest line as 100.

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RESEARCH DEPARTMENT, LEVER BROTHERS AND UNILEVER LTD., PORT SUNLIGHT. [*Received, March 4th,* 1947.]

* According to our experience, the intensities obtained with our camera are comparable with the intensities obtained with cameras usually used.