

# CAROTENOIDS AS FOOD COLOURANTS

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## INTRODUCTION

Carotenoids are one of the most important groups of natural pigments. It has been estimated that nature produces about 100 million tons of these pigments per year. They give brilliant yellow and red colours to many fruits, vegetables, roots, flowers and autumn leaves; they produce the colour of the egg yolk, of many algae, yeasts and mushrooms, Crustaceae as well as of the feathers and skins of many birds.

The carotenoids have attracted the curiosity of scientists since the beginning of organic chemistry, actually since 1818. Numerous outstanding chemists made valuable contributions and many tools and methods have been introduced into organic chemistry via the carotenoids<sup>1</sup>. I mention the early analyses (by Willstätter and Zechmeister), the rediscovery of column chromatography by Kuhn and Karrer and of the thin-layer chromatography by Stahl<sup>2</sup>, the elucidation of the isoprene rule by Ruzicka and of the symmetrical structures of squalene,  $\beta$ -carotene and lycopene by Karrer, the studies on comparative biochemistry by Goodwin<sup>3</sup>, the first rules on u.v.-absorption of polyenes by Richard Kuhn, the investigation of *cis-trans* isomerism (Pauling and Zechmeister<sup>4</sup>) and the first syntheses by Karrer and Inhoffen. The application of n.m.r. spectroscopy by Jackman and Weedon<sup>5</sup> proved to be a valuable tool for the identification of carotenoids, the synthesis of which was especially advanced by the development of condensation reactions for the buildup of the conjugated chain (Wittig<sup>6</sup>, Horner<sup>7</sup>).

We aimed at the development of commercial syntheses of some selected carotenoids and the investigation of their use as food colourants. By substituting natural colouring matters for artificial dyes we fulfil a physiological desideratum that good food should not contain unnatural pigments.

## PRODUCTION OF CAROTENOIDS FROM NATURAL SOURCES

The classical method for producing  $\beta$ -carotene and other carotenoids is solvent extraction of the plant material. *Table 1* gives a survey of the main carotenoid extracts used as yellow and red colourants. The natural source, the main pigments, possible provitamin A activity of the extract, and the degree of pigmentation of eggs and broilers, after feeding, are indicated.

Carrots, palm oil, alfalfa, dried grass and leaves are the starting materials for practically all preparations of natural carotene with provitamin A activity. The extracts from alfalfa, grass, leaves, *Tagetes* and yellow maize, containing either lutein or zeaxanthin, are valuable supplements to chicken

Table 1. Carotenoid preparations used as yellow and red colourants

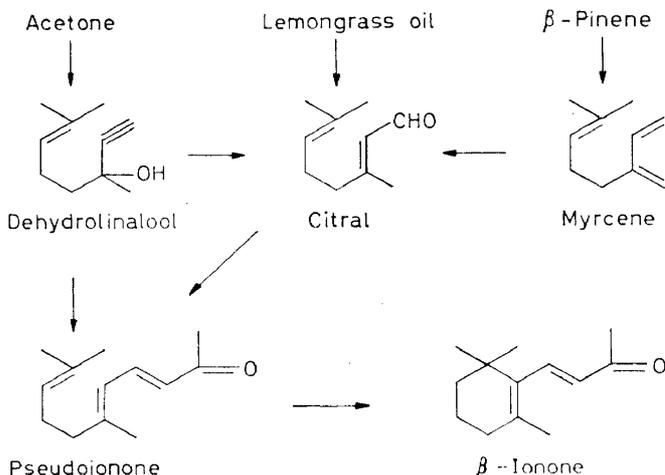
Colour	Natural source	Main pigments	Vitamin A activity	Pigmentation of eggs and broiler
Yellow	Carrots	$\beta$ -Carotene, $\alpha$ -Carotene	++	
	Palm oil	Carotenes, Lutein	++	+
	Alfalfa, grass meal	Lutein, $\beta$ -Carotene	+	++
	Leaves	Lutein, $\beta$ -Carotene	+	++
	Tagetes	Lutein, $\beta$ -Carotene	(+)	++
	Yellow maize	Cryptoxanthin, Zeaxanthin	(+)	++
	Saffron	Crocetin, $\beta$ -Carotene, Zeaxanthin	+	+
	Seeds of <i>Bixa orellana</i>	Bixin and decomposition products		++
Red	Paprika (red pepper)	Capsanthin, Capsorubin		++
	Rhodotorula rubra (yeast)	Torularhodin, $\beta$ -Carotene, Torulene	+	++

feed because all xanthophylls colour the egg yolk in contrast to the carotenes. Besides  $\beta$ -carotene, annatto—which is an extract of the seeds of *Bixa orellana*—is also used for colouring dairy products. For red carotenoids large quantities of paprika are extracted. Torula yeast and certain algae are other sources of red polyene pigments used as colourants for oil and cheese.

The market for natural carotenes has declined since the introduction of synthetic  $\beta$ -carotene. Today, only one crystalline  $\beta$ -carotene preparation extracted from dehydrated carrots is still on the market. Recently it was announced that  $\beta$ -carotene and further carotenoids will be produced in Brazil by fermentation from mated strains of *Blakeslea trispora*<sup>8</sup>.

### PRODUCTION OF CAROTENOIDS BY SYNTHESIS

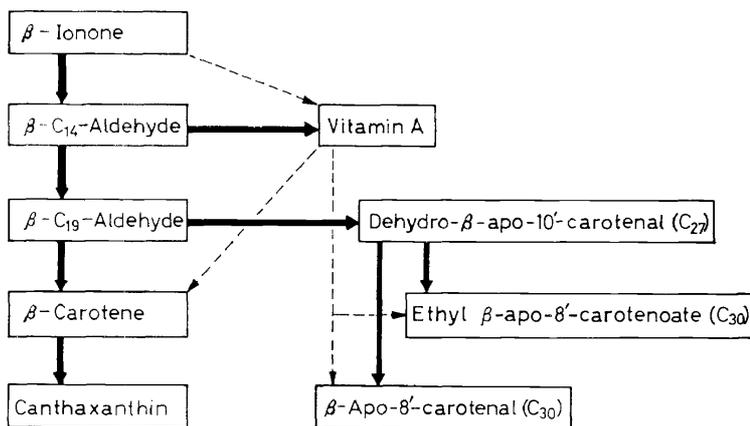
Up to now all industrial syntheses<sup>9</sup> have been based on  $\beta$ -ionone, which is a key product of the perfumery industry and the starting material for all

Figure 1. Syntheses of  $\beta$ -ionone

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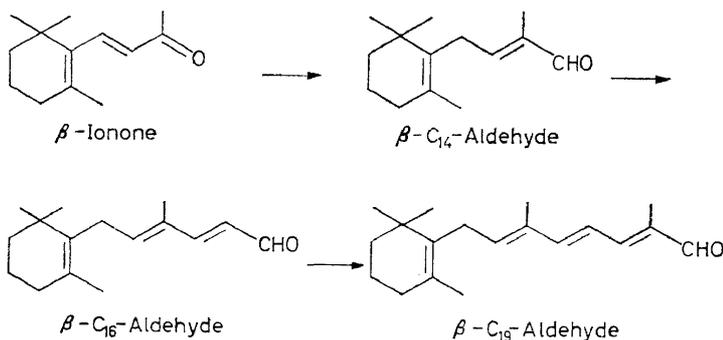
vitamin A manufacturing processes. The various methods of preparation of this monocyclic C<sub>13</sub>-ketone are summarized in *Figure 1*.

$\beta$ -Ionone can be manufactured by total synthesis from acetone via dehydrolinalool and pseudoionone. The latter can also be prepared from citral by condensation with acetone. Citral is produced in three ways: (i) by total synthesis from dehydrolinalool, (ii) by isolation from lemon grass oil, and (iii) via myrcene, by transformation of  $\beta$ -pinene, a constituent of turpentine oil.



*Figure 2.* Methods for the manufacture of carotenoids at the works of F. Hoffmann-La Roche & Co., Basle

The manufacture of the carotenoids at Roche is summarized in *Figure 2*.  $\beta$ -Ionone is transformed to the  $\beta$ -C<sub>14</sub>-aldehyde, an intermediate of the Roche vitamin A production, and  $\beta$ -C<sub>19</sub>-aldehyde, another key substance in our carotenoid syntheses. We use it for the manufacture of  $\beta$ -carotene and subsequently for canthaxanthin and astaxene. Dehydro- $\beta$ -apo-10'-carotenal (C<sub>27</sub>) can also be prepared and from it ethyl  $\beta$ -apo-8'-carotenoate and  $\beta$ -apo-8'-carotenal (C<sub>30</sub>).  $\beta$ -C<sub>19</sub>-Aldehyde is prepared as outlined in *Figure 3*.



*Figure 3.* Synthesis of  $\beta$ -C<sub>19</sub>-aldehyde

$\beta$ -Ionone is lengthened to the  $\beta$ -C<sub>14</sub>-aldehyde by glycidic ester synthesis followed by alkali treatment. The side-chain of this aldehyde is linked to the ring by a CH<sub>2</sub>-group, thus interrupting the conjugation with the ring double bond. For chain lengthening the  $\beta$ -C<sub>14</sub>-aldehyde is converted into its acetal which is condensed with vinyl ether under the catalytic influence of acid. Subsequent hydrolysis gives the crystalline  $\beta$ -C<sub>16</sub>-aldehyde. This is converted by an analogous procedure with propenyl ether to the crystalline  $\beta$ -C<sub>19</sub>-aldehyde, which also has a CH<sub>2</sub>-group attached to the ring.

In collaboration with Professor Inhoffen we developed the synthesis of

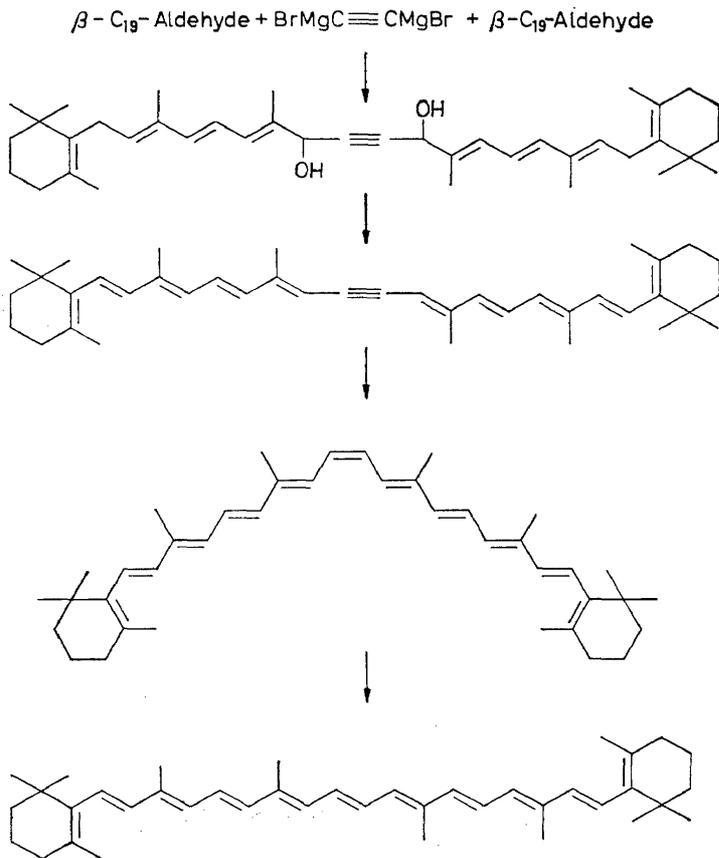


Figure 4. Synthesis of  $\beta$ -carotene

$\beta$ -carotene (Figure 4). Two moles of  $\beta$ -C<sub>19</sub>-aldehyde are condensed with acetylene in a Grignard reaction to give a  $\beta$ -C<sub>40</sub>-diol. This is transformed into  $\beta$ -carotene with a central triple bond by elimination of two molecules of water with simultaneous allylic rearrangement. Partial hydrogenation with Lindlar's catalyst gives 15,15'-*cis*- $\beta$ -carotene, which is isomerized in high boiling petroleum ether to crystalline all-*trans*- $\beta$ -carotene. Synthetic  $\beta$ -carotene was first marketed in 1954.

The commercial synthesis of canthaxanthin is based on Karrer's work and

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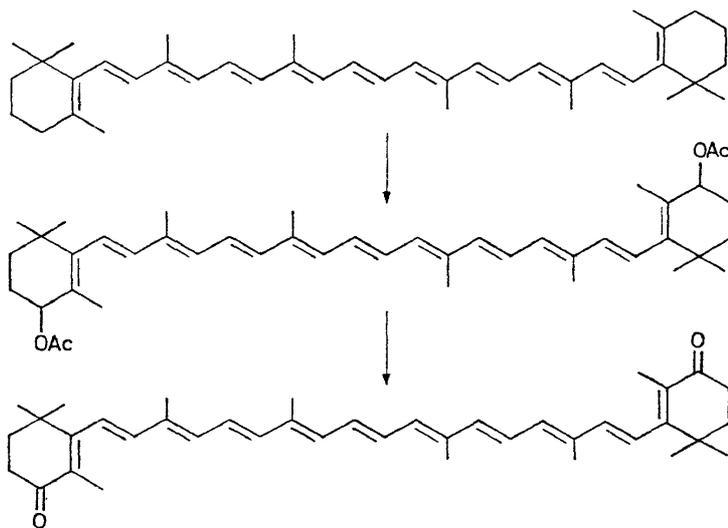


Figure 5. Commercial synthesis of canthaxanthin

starts with  $\beta$ -carotene (Figure 5). Treatment with *N*-bromosuccinimide in acetic acid and chloroform gives isozeaxanthin diacetate which is saponified and subsequently subjected to an Oppenauer oxidation.

Dehydro- $\beta$ -C<sub>27</sub>-apocarotenal is prepared by the condensation of  $\beta$ -C<sub>19</sub>-aldehyde with a C<sub>6</sub>-acetal which is obtained from acetylene and the enol ether of methylmalonaldehyde (Figure 6). Condensation with lithium in liquid ammonia, followed by acid treatment of the resulting hydroxyacetal

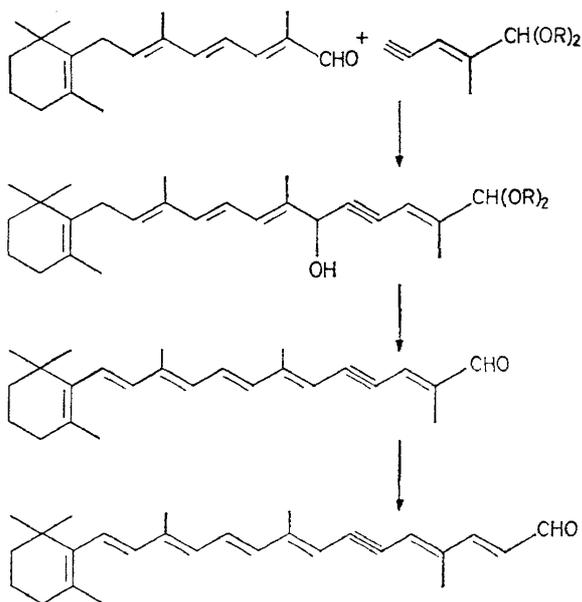


Figure 6. Synthesis of dehydro- $\beta$ -C<sub>27</sub>-apocarotenal

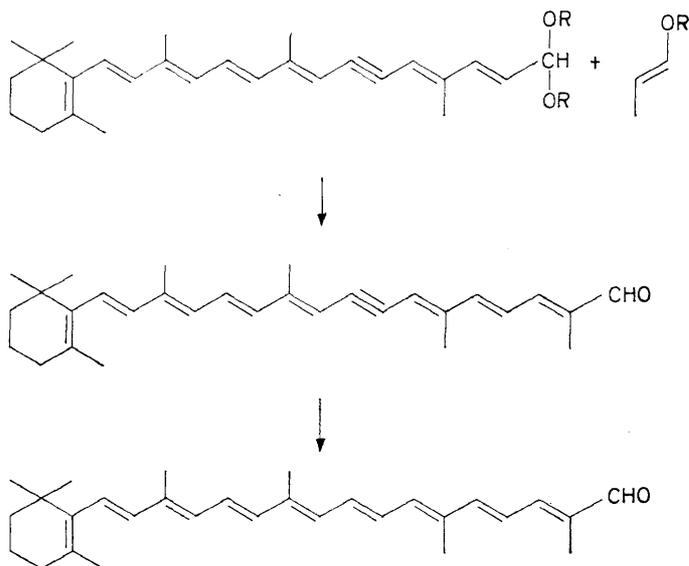


Figure 7. Synthesis of  $\beta$ -C<sub>30</sub>-apocarotenal

leads to dehydro- $\beta$ -C<sub>25</sub>-aldehyde, which is lengthened with vinyl ether by two carbon atoms to dehydro- $\beta$ -C<sub>27</sub>-aldehyde.

$\beta$ -C<sub>30</sub>-Apocarotenal is synthesized from dehydro- $\beta$ -C<sub>27</sub>-apocarotenal by extension with propenyl ether followed by partial hydrogenation of the triple bond and isomerization (Figure 7).

Ethyl  $\beta$ -apo-8'-carotenoate is synthesized from dehydro- $\beta$ -C<sub>27</sub>-apocarotenal by condensation with the Wittig-compound of  $\alpha$ -bromopropionate

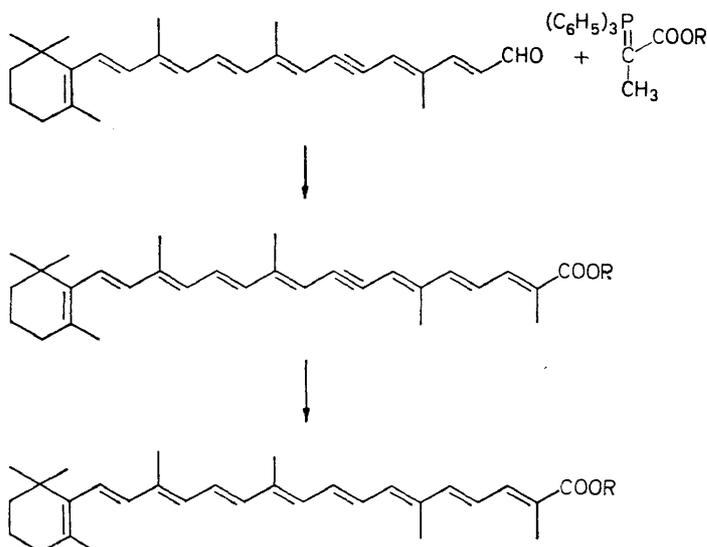
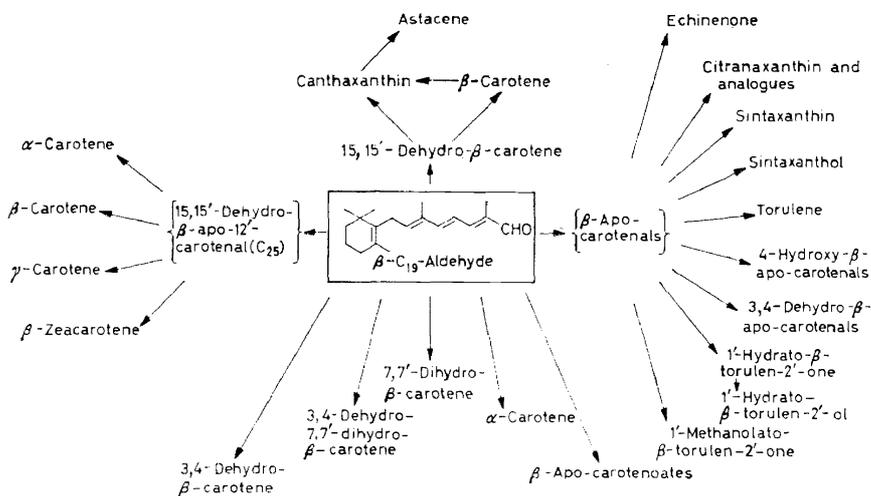


Figure 8. Synthesis of ethyl  $\beta$ -apo-8'-carotenoate (R = C<sub>2</sub>H<sub>5</sub>)

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followed by partial hydrogenation and isomerization (*Figure 8*). The  $\beta$ -C<sub>30</sub>-apocarotenoids were introduced in the market in 1960 and 1962, and canthaxanthin in 1964.

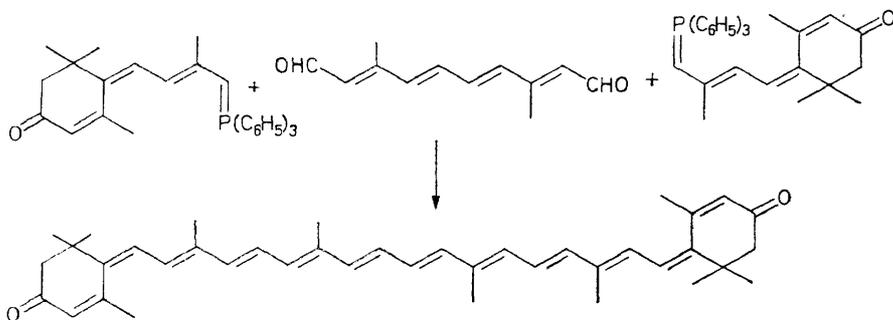
A comprehensive survey on all syntheses and all methods used in the carotenoid field was published by us 3 years ago in *Advances in Organic*



*Figure 9.* Carotenoids from  $\beta$ -C<sub>19</sub>-aldehyde

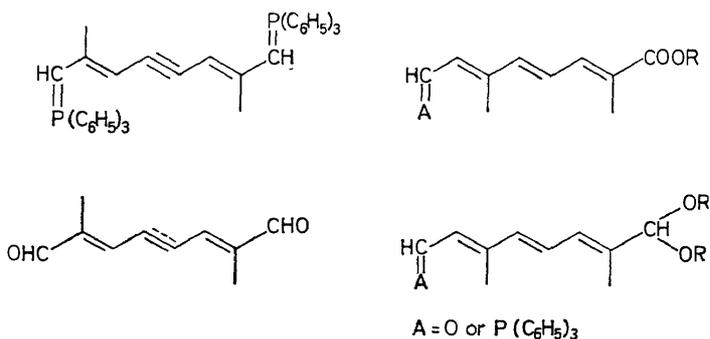
*Chemistry*<sup>10</sup>. More than 20 naturally occurring carotenoids prepared from  $\beta$ -C<sub>19</sub>-aldehyde are given in *Figure 9*.

The syntheses of rhodoxanthin and of diketospirilloxanthin are our latest contributions. In the synthesis of rhodoxanthin<sup>11</sup> (*Figure 10*) two moles of an oxo-C<sub>14</sub>-Wittig salt are condensed with a C<sub>12</sub>-retro-dialdehyde.



*Figure 10.* Synthesis of rhodoxanthin

The latter is obtained from methylpentynol, the cheap C<sub>6</sub>-building unit of our vitamin A process by the following reaction sequence: dimerization, oxidation, and partial hydrogenation. Rhodoxanthin has very good qualities as a red colourant; but its synthesis is not yet economical.

Figure 11. C<sub>10</sub>-Building units

C<sub>10</sub>-Building units (Figure 11) proved to be valuable tools in many of our syntheses<sup>12</sup>. The symmetrical C<sub>10</sub>-di-Wittig compound and the C<sub>10</sub>-dialdehyde represent the central 10 carbon atoms in the synthesis of carotenoids. The asymmetric C<sub>10</sub>-esters and acetals in which the additional functional group can be an aldehyde, a phosphorane or an equivalent group to perform Wittig-type reactions are components to build both ends of aliphatic carotenoids.

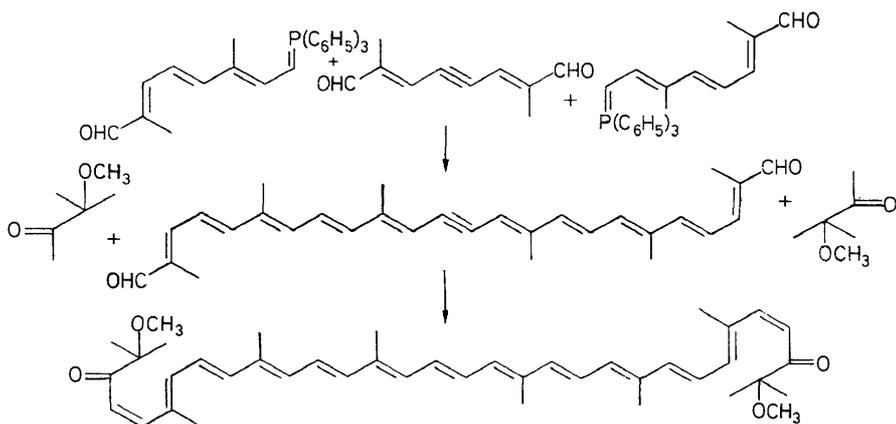


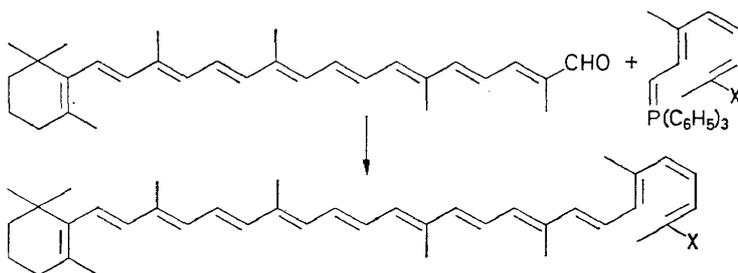
Figure 12. Synthesis of diketospirilloxanthin

The application of these C<sub>10</sub>-building units was demonstrated in the synthesis of diketospirilloxanthin<sup>13</sup> (Figure 12), which has a beautiful red of Bordeaux colour. Two asymmetric C<sub>10</sub>-units are linked by a Wittig reaction to the symmetrical C<sub>10</sub>-dialdehyde. The C<sub>30</sub>-dialdehyde obtained is condensed on both sides in a Claisen reaction with an appropriate C<sub>5</sub>-unit.

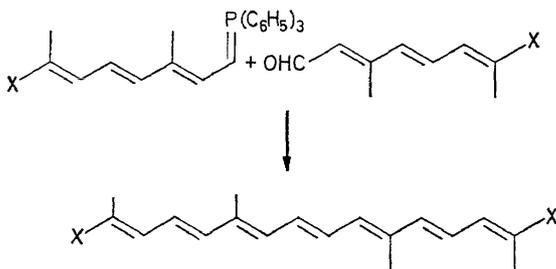
Another example is the synthesis of torularhodinaldehyde (Figure 13) and the corresponding ester from  $\beta$ -C<sub>30</sub>-apocarotenal by a Wittig-type reaction with the asymmetric C<sub>10</sub>-building units.

Similarly crocetin dialdehyde and crocetin diesters are synthesized by

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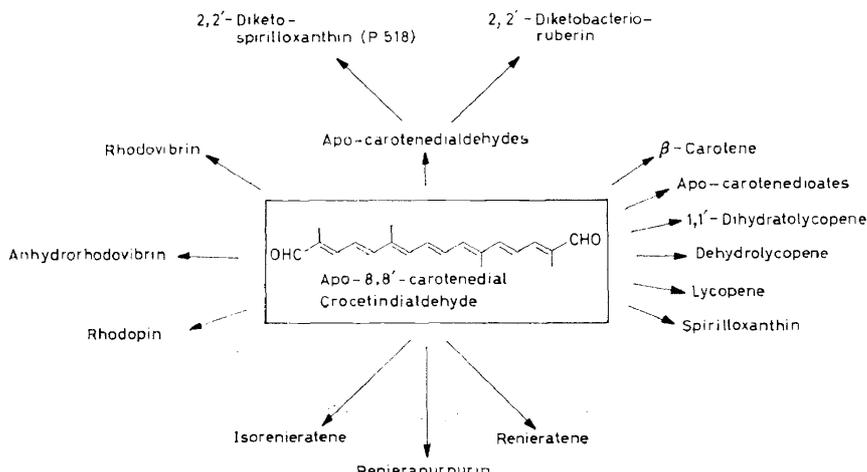
*Figure 13.* Synthesis of torularhodinaldehyde



*Figure 14.* Synthesis of crocetindialdehyde and crocetin diesters

linking two  $\text{C}_{10}$ -units by a Wittig reaction (*Figure 14*). Alternatively crocetindialdehyde has been made by chain extension of the symmetrical  $\text{C}_{10}$ -dialdehyde at both ends with vinyl and propenyl ether.

Crocetindialdehyde and its dehydro compound are important intermediates representing the central 20 carbon atoms of carotenoid molecules. Compounds which have been synthesized from these units are listed in



*Figure 15.* Carotenoids from crocetindialdehyde

Figure 15, including the important vinylogous series of symmetrical C<sub>24</sub>-, C<sub>30</sub>-, C<sub>34</sub>- and C<sub>40</sub>-dialdehydes and diesters.

In our synthesis<sup>14</sup> of lycopene in 1955 crocetindialdehyde with a central triple bond was condensed at both ends with geranylidene-triphenylphosphorane to give 15,15'-dehydrolycopene. This is partially hydrogenated and isomerized to all-*trans*-lycopene (Figure 16). This simple synthesis was not further developed because of difficulties in obtaining a stabilized preparation.

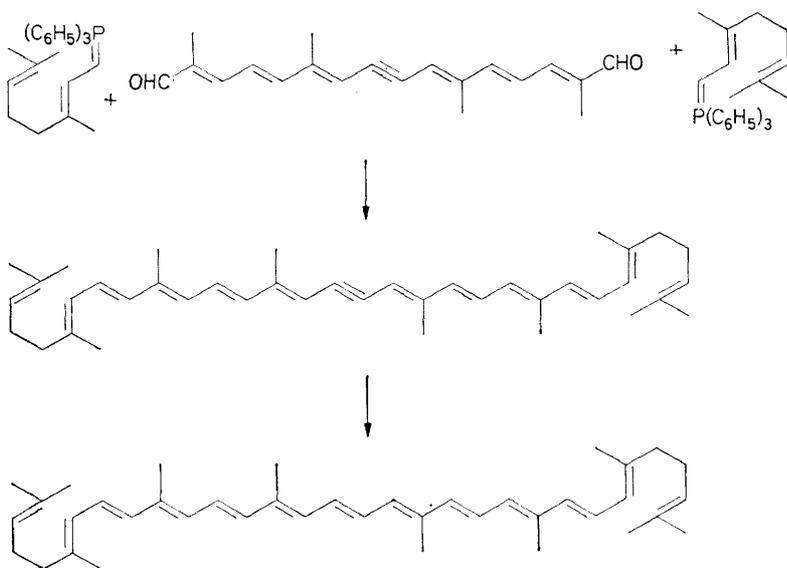


Figure 16. Synthesis of lycopene

According to Pommer<sup>15</sup> vitamin A acetate forms a retinylphosphonium salt on treatment with triphenylphosphine and acid. This crystalline compound can easily be obtained from any vitamin A mother-liquor by counter-current distribution. Its condensation with vitamin A aldehyde leads to  $\beta$ -carotene (Figure 17).

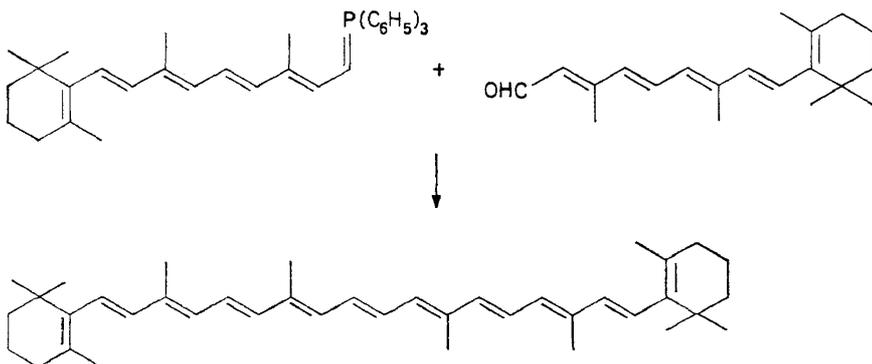
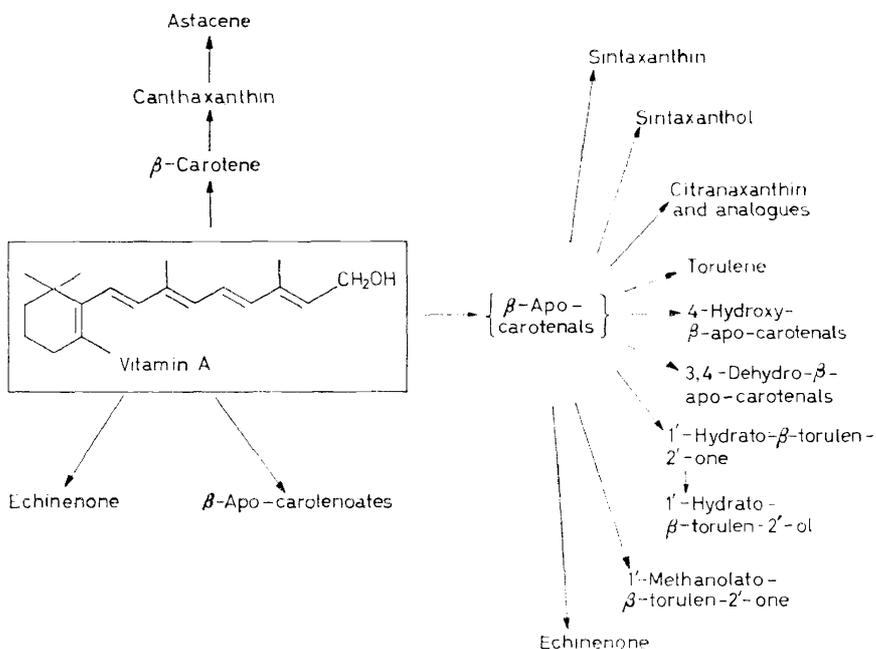


Figure 17. Synthesis of  $\beta$ -carotene

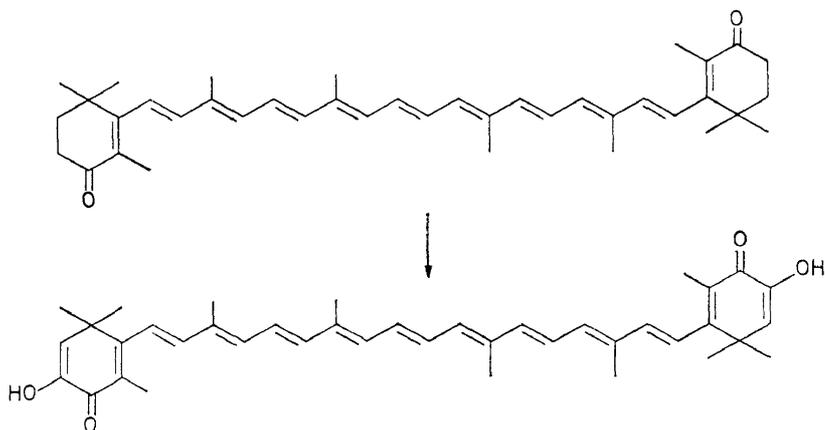
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Most syntheses of provitamin A compounds in which  $\beta$ -C<sub>19</sub>-aldehyde was used could also be accomplished starting with vitamin A. The carotenoids which were actually prepared from vitamin A are given in *Figure 18*.



*Figure 18.* Carotenoids from vitamin A

A product which has been carefully examined in many tests is astacene. It can be synthesized from canthaxanthin (*Figure 19*). According to Weedon and Barton<sup>16</sup> the additional oxo groups are introduced by treatment with



*Figure 19.* Synthesis of astacene

oxygen in potassium *t*-butoxide solution. Unfortunately the compound is relatively unstable in food and feed and its formulations do not have any brilliant colour.

### INTERRELATION BETWEEN COLOUR AND STRUCTURE

The examination of carotenoids as food colourants included the evaluation and comparison of several series of vinylogous apocarotenoids. These mono- and dialdehydes or esters are important degradation products of the carotenoid metabolism. The synthetic compounds are used for the identification of metabolites of labelled carotenoids. The interrelationship between colour and structure can best be demonstrated in these series.

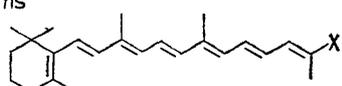
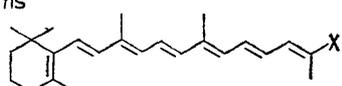
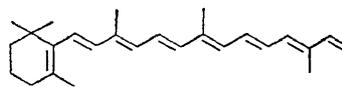
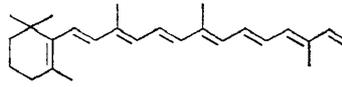
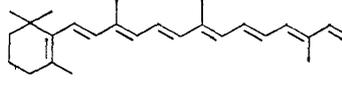
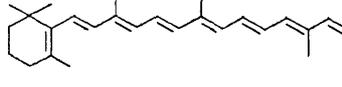
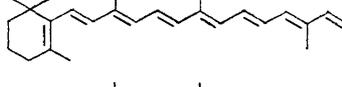
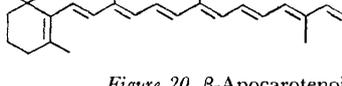
C atoms		$\lambda_{\max}$ (petroleum ether), nm	
		X=CHO	X=COOCH <sub>3</sub>
C <sub>25</sub>		414	—
C <sub>27</sub>		437	426
C <sub>30</sub>		457	445
C <sub>32</sub>		473	464
C <sub>35</sub>		485	476
C <sub>37</sub>		498	488
C <sub>40</sub>		508	497

Figure 20.  $\beta$ -Apocarotenoids and their u.v. absorption data

The main absorption maxima in petroleum ether of the  $\beta$ -apocarotenal- and the  $\beta$ -apocarotenoate series are listed in Figure 20. The C<sub>25</sub>-aldehyde has the maximum at 414 nm and the C<sub>40</sub>- or torularhodinaldehyde at 508 nm. The difference between the lowest members is 23 nm, whereas that of the highest is only 10 nm. A similar decline is also seen in the apocarotenoate series.

Citranaxanthin occurs in great quantities in certain Citrus fruits. Its vinylogues with absorption maxima ranging from 432 to 494 nm have been obtained by condensation of  $\beta$ -apocarotenals with acetone (Figure 21).

The absorption maxima of symmetrical diesters of the crocetin type with

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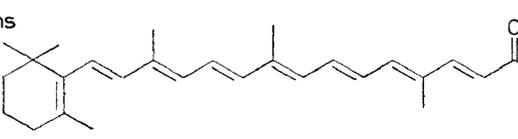
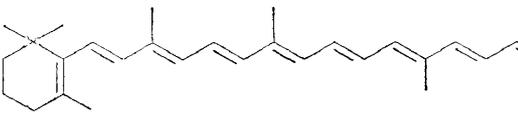
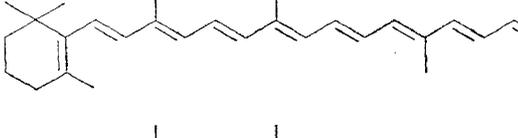
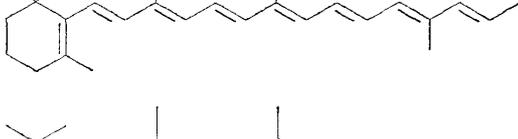
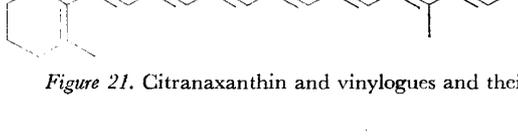
C atoms		$\lambda$ max, nm (petroleum ether)
C <sub>28</sub>		432
C <sub>30</sub>		451
C <sub>33</sub>		466
C <sub>35</sub>		481
C <sub>38</sub>		494

Figure 21. Citranaxanthin and vinylogues and their u.v. absorption data

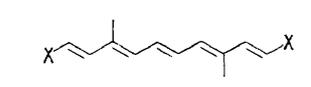
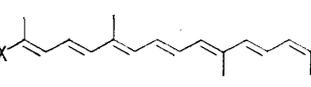
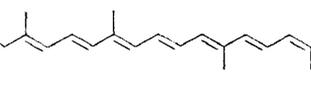
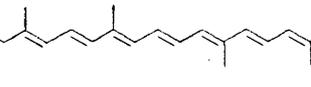
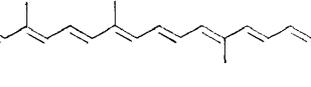
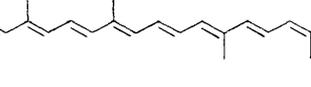
C atoms		$\lambda$ max (CHCl <sub>3</sub> ), nm	
		X=CHO	X=COOC <sub>2</sub> H <sub>5</sub>
C <sub>14</sub>		417	—
C <sub>20</sub>		455	434
C <sub>24</sub>		492	477
C <sub>30</sub>		520	502
C <sub>34</sub>		541	530
C <sub>40</sub>		556	545

Figure 22. Symmetrical apocarotenoids and their u.v. absorption data

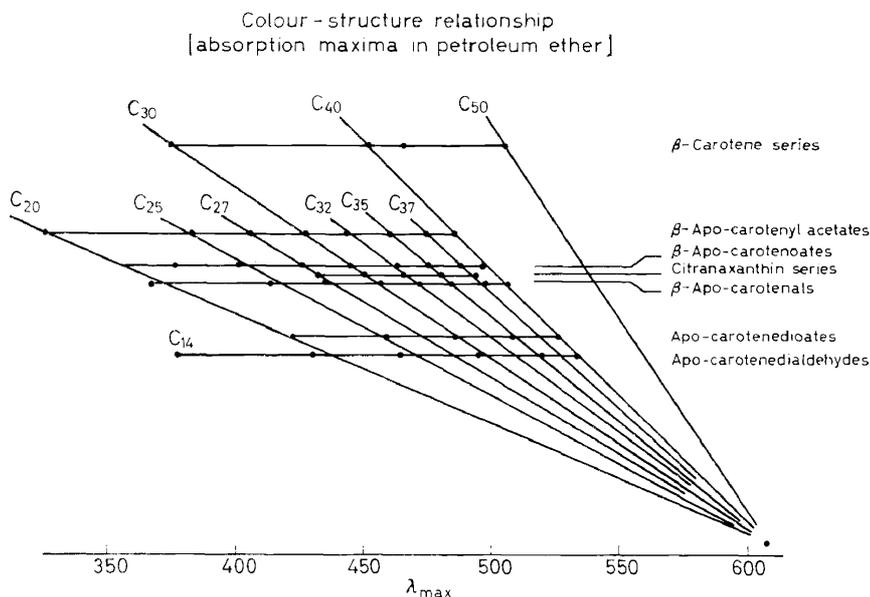
20, 24, 30, 34 and 40 carbon atoms and of the corresponding series of symmetrical dialdehydes are given in *Figure 22*.

The isoprenologous series of  $\beta$ -carotene includes the analogues with 30, 50 and 60 carbon atoms (*Figure 23*). The absorption range is between 374 and 537 nm. These values correspond to a yellow and a deep red solution.

If the main absorption maxima of polyenes of vinylogous series are arranged on lines parallel to the abscissa and the different members with the equal number of carbon atoms in the conjugated chain are joined by straight lines (*Figure 24*), they have a common point of intersection at about

C atoms	$\lambda_{\max}$ , nm (Petroleum ether)
C <sub>30</sub>	374
C <sub>40</sub>	452
C <sub>50</sub>	504
C <sub>60</sub>	537

*Figure 23.*  $\beta$ -Carotene and isoprenologues and their u.v. absorption data

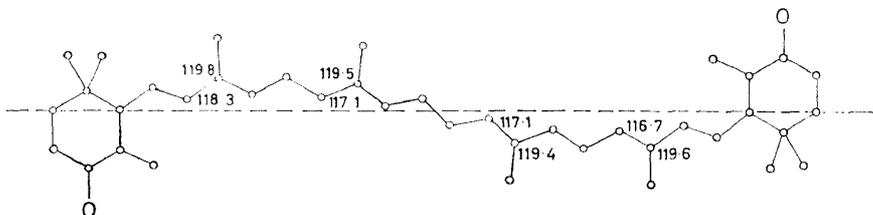


*Figure 24.* Colour-structure relationship of polyenes of vinylogous series from u.v. absorption spectral data

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610 nm, a wavelength that has been calculated for infinite conjugation of polyenes<sup>17</sup>.

Recent x-ray studies by MacGillavry<sup>18</sup> reveal that the polyene chain of carotenoids is almost planar with a S-shaped bending. This is demonstrated in the reproduction of the canthaxanthin molecule by drawing a straight line from the carbon atoms 6 to 6' (*Figure 25*).



*Figure 25.* Canthaxanthin molecule—Demonstration of the almost planar nature of the polyene chain in carotenoids

The bending is due to the steric interference of the methyl groups at the carbon atoms 9 and 13 next to the hydrogen atoms. This 1,3-interaction causes abnormal valency angles at the methyl bearing carbon atoms.

So far all crystalline cyclic carotenoids have a 6,7 *s-cis* conformation of ring and conjugated chain with a certain degree of deviation. In addition there might also be a difference between the structure in the crystalline and the dissolved state. The shape of the molecule probably has an influence on colour and absorption, but at present allowance for this factor in any calculations can only be made on an empirical basis.

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Due to their lipophilic character and poor solubility characteristics special formulations had to be developed for the use of carotenoids as food colourants<sup>19</sup>. Twenty to thirty per cent oily suspensions of microcrystals, particularly of  $\beta$ -carotene, are used for the colouring of margarine, fats and oils, shortenings and other fat containing food, galenic<sup>20</sup> and cosmetic products. Water-dispersible forms, which contain 10 per cent of the pure carotenoid, serve for the colouring of water-base foods such as beverages, particularly carbonated orange drinks, candies, ice-cream, jellies, etc. Similar preparations of apocarotenoids and of canthaxanthin find more and more use as feed additives<sup>21</sup> for improving and standardizing the colour of egg yolk and poultry meat.

The colour range of aqueous solutions obtainable with carotenoids varies from a greenish yellow to a deep bluish red (*Picture 1*). The colour of the oily solutions is in most cases identical with the one obtained in organic solvents while the corresponding aqueous solutions can differ considerably from it.

Different types of candies and frosting are presented with *Pictures 2 and 3*. Gelatine desserts and milk-base products are also very suitable for colouring. Puddings, jellies and ice-cream are shown in *Pictures 4–6*. The confectionery

industry is a more promising consumer of carotenoids because the carotenoids are very stable in these formulations. The *Pictures 7-9* show examples of different formulations coloured with the same carotenoid.

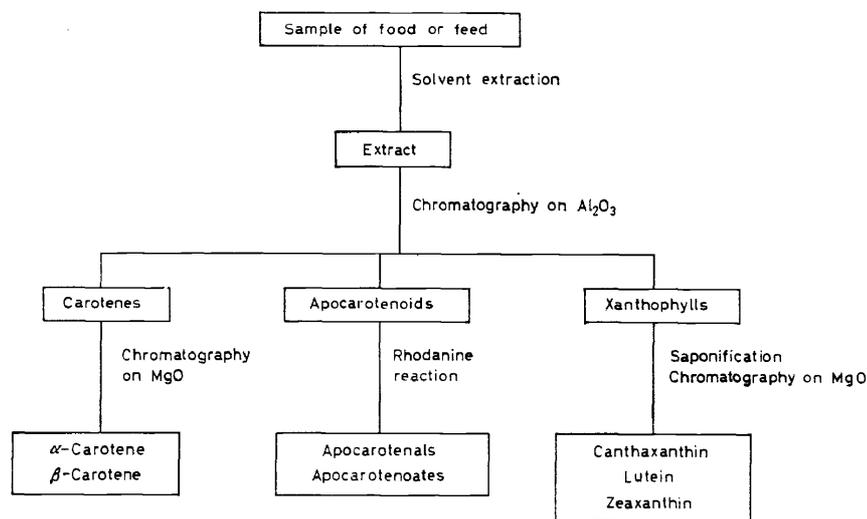
The products in *Picture 7* have been coloured by the addition of 3-10 mg of pure  $\beta$ -carotene per kg of food.  $\beta$ -Carotene is commercially available.

The next two pictures show carotenoids which are not yet available on a commercial basis. They are suitable for the broadening of the present colour range, which covers only yellow-orange to orange-red tinges. More-or-less lemon yellow colours are obtained with crocetin diethyl ester (*Picture 8*), whereas cherry red colours result with torularhodinaldehyde (*Picture 9*).

Typical examples of the colouring of galenic and cosmetic preparations are shown in *Pictures 10-12* comprising sugar-coated tablets, suppositories and tooth-paste.

### Analysis of carotenoids in foods

The analysis of carotenoids in food and feed is extremely complex. The analytical procedure used in our laboratories<sup>22</sup> is shown in *Figure 26*.



*Figure 26.* Analytical procedure used for carotenoids in food and feed at the Roche laboratories

Extraction with solvent and chromatography on standardized alumina gives a separation into carotenes, apocarotenoids and xanthophylls. By a second chromatography on magnesium oxide the carotenes can be separated into  $\alpha$ - and  $\beta$ -carotene fractions, and the xanthophylls into canthaxanthin-, lutein-, and zeaxanthin fractions. The apocarotenoids can be differentiated by means of the rhodanine reaction. It is easier to analyse food and feed products enriched with pure synthetic carotenoids than products enriched with crude extracts.

It can generally be said, that the most useful criteria of purity are provided by chromatography and absorption spectroscopy. The presence of

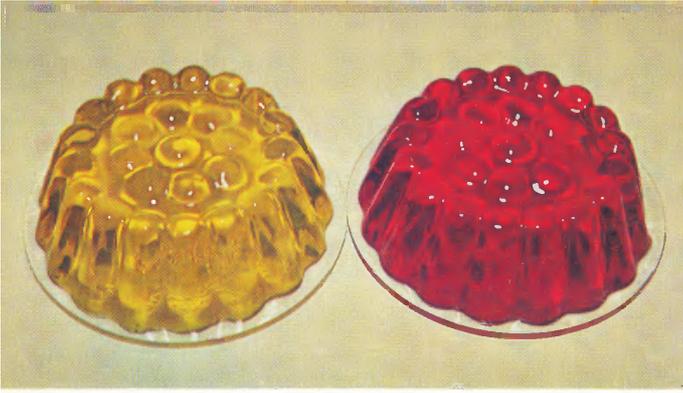


1

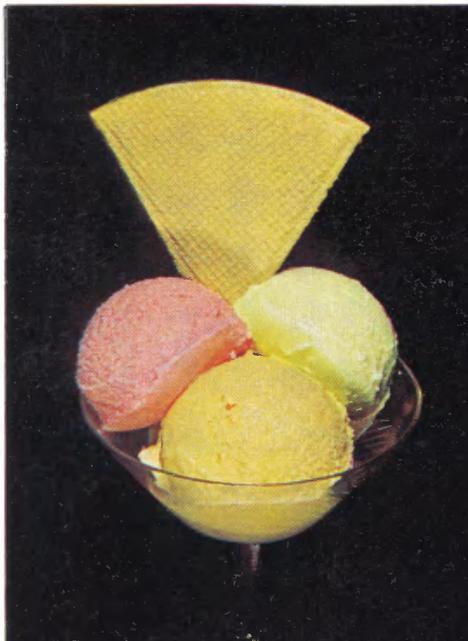


2





5



4

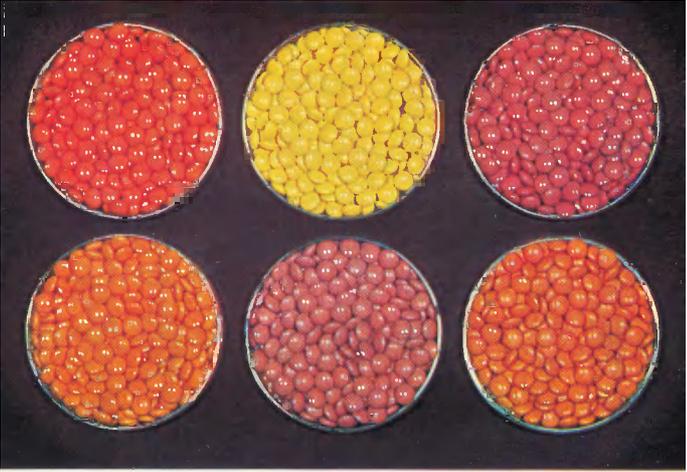


8

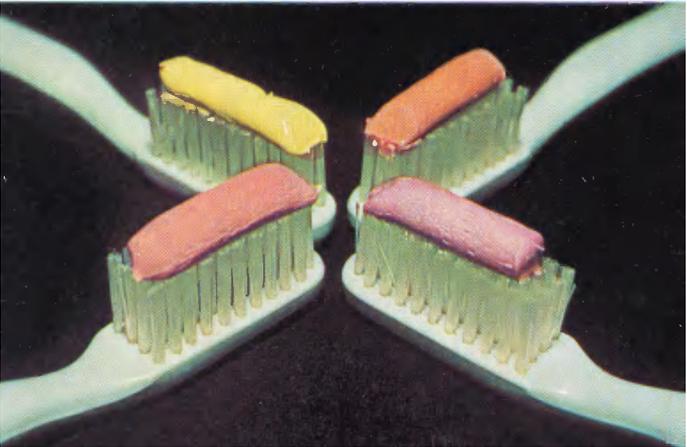


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10



11

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*cis* isomers, a typical feature in carotenoid chemistry, may be detected by additional spots on the thin-layer or paper chromatogram and by a “*cis* peak” in the absorption spectrum.

An American subcommittee under the auspices of the National Academy of Sciences and headed by Porter will publish specifications and criteria of purity for 15 carotenoids in the near future and intends to add an additional 15 by summer of 1967.

### ANIMAL TOLERANCE OF CAROTENOIDS

The whole class of carotenoids is well tolerated.  $\beta$ -Carotene, the most important precursor of vitamin A, as well as many other carotenoids have always been present in the diet of man. This seems to be a much more decisive demonstration of tolerance than toxicity tests with pigments carried out on a few generations of small laboratory animals.

A joint committee of FAO and WHO experts is investigating food colourants<sup>23</sup>. This committee decided to abstain from classifying food colours obtained from natural sources due to the lack of knowledge of compositions and because insufficient toxicity data are available. This decision is in line with the tendency to admit the use of chemically well defined food additives only.

Our synthetic carotenoids fulfil the requirements of high purity and controlled tolerance and toxicity tests as well as being members of a class of non-toxic compounds. Many of them have also been ingested in foods for thousands of years.

Large quantities of selected carotenoids have been applied without any undesirable symptoms. This is illustrated by the chronic toxicity studies on rats with canthaxanthin as a typical example. *Table 2* shows the amount of

*Table 2. Chronic toxicity studies of canthaxanthin on rats*

Feed (%)	Generation of rats	Number		Trials in weeks	Canthaxanthin consumed (g/kg)
		♂	♀		
0.1	1st	20	20	104	30
0.1	2nd	16	14	104	30
0.1	3rd	11	13	52	15
0.5		25	25	95-98	240-280
2.0		25	25		1000-1300
5.0		15	15		2600-3300

substance consumed within a given time. The upper part of the table deals with a tolerance test in three consecutive generations, the lower part with a separate study in which excessively high doses have been used for almost two years. In the highest dose group each animal consumed a total of about 3 kg of canthaxanthin per kg of body weight, enough for the pigmentation of 1500 tons of chicken feed.

*Figure 27* shows that the weight development of the animals treated with the highest doses differs in no way from the controls.

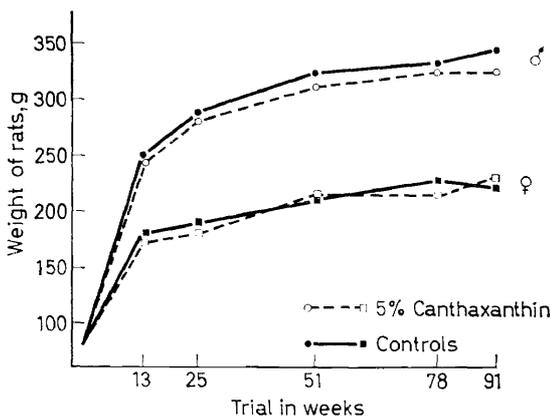


Figure 27. Weight development of rats fed with 5 per cent canthaxanthin

Extensive haematological and histopathological examinations failed to reveal any evidence of a toxic effect.

### CONCLUSION

Research on carotenoids which began 150 years ago and has included all branches of natural sciences has led the way to pure natural food colouring matters. It is my firm belief that for food colouring it is desirable to substitute artificial dyes by pure natural pigments. Furthermore I believe that pure synthetic carotenoids will gradually replace the natural extracts in the same way as the pure synthetic vitamins have practically eliminated the impure vitamin preparations obtained from natural sources.

The aim of our present work is the selection of a carotenoid with the shade of deep red and one of a bright yellow in order to extend our present colour range from orange ( $\beta$ -apocarotenal) to tomato red (canthaxanthin).

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