

# RECENT ADVANCES IN THE CHEMISTRY OF NATURAL CAROTENOIDS

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## INTRODUCTION

One may regard the first epoch in the structural studies of naturally occurring carotenoids as terminated with the authoritative monograph by Karrer and Jucker<sup>1</sup> in 1948.

In the classical period structural determinations of carotenoids, derived mainly from plant sources, were carried out by semi-micro methods by means of chemical degradation. Useful methods such as various types of oxidative degradation, catalytic hydrogenation, determination of side-methyl, etc. were adapted or developed, and the common C<sub>40</sub>-skeleton of carotenoids was established. At that time physical methods were only partly in use. The many correct structures arrived at, without doubt reflect the great ability of the schools, in particular those of Paul Karrer in Zürich and Richard Kuhn in Heidelberg, which devoted their efforts to this field and greatly contributed to making the subject attractive to other research workers.

The subsequent period has been characterized by the development of improved micro techniques and new methods, particularly spectroscopic ones.

## SPECTROSCOPIC METHODS FOR STRUCTURE ELUCIDATION

### Electronic spectra

Whilst electronic spectra have been a useful tool in the structural elucidation of carotenoids since the early thirties, the exact relationship between electronic spectra and chromophoric systems was not initially well understood. This connection has since been clarified on an empirical and theoretical basis<sup>2-5</sup>. Nowadays inspection of the electronic spectrum of a new carotenoid in most cases allows the assignment of a restricted number of possible chromophoric systems. Thus the relationship between the middle main absorption maximum measured in petroleum ether and the number of carbon-carbon double bonds in an aliphatic polyene chain is given by the curve in *Figure 1*. Moreover, it is known that a conjugated double bond in the 5,6-position in a so-called  $\beta$ -ring [1,1,5-trimethylcyclohexene(4,5)], is equivalent to only 0.3 aliphatic (spectroscopically efficient) double bonds, owing to the non-planarity of such a trimethyl substituted cyclohexene ring and the polyene chain, and that a double bond in the 4,5-position in a

similar ring in a *retro* system corresponds to 0.5 spectroscopically efficient double bonds. Although Nature tried to prevent the detection of aryl-carotenoids by making the spectral contribution of a 1,2,5-trimethylphenyl

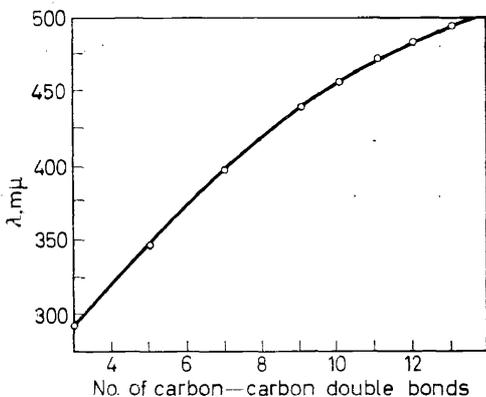


Figure 1. Relationship between the middle main absorption maximum measured in petroleum ether and the number of spectroscopically efficient carbon-carbon double bonds in the polyene chain of carotenoids.

end-group identical to that of a  $\beta$ -ring and that of a 1,2,3-trimethylphenyl group indistinguishable from that of an aliphatic carbon-carbon double bond in the same position, the new class of aryl-carotenoids has not escaped discovery. These data are shown in *Table 1*. The size of the spectral con-

Table 1. The contribution of some common carotenoid end-groups to the electronic spectrum.

End-groups	Equivalence in spectroscopically efficient double bonds
	0.3
	0.5
	1.0

tribution of a conjugated carbonyl group, depending on the location of this group, is also known (*Table 2*), as is the solvent effect on the spectrum of conjugated carbonyl compounds<sup>6, 7</sup>. Finally the degree of fine-structure of the spectrum and the molar extinction coefficient give useful information about the chromophoric system present. This topic has recently been reviewed<sup>6</sup>.

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Table 2. The contribution of keto-groups in various positions to the electronic spectra of carotenoids measured in petroleum ether.

Structure surrounding the conjugated keto groups	$\Delta$ in $m\mu$
	6
	9
	11
	18

### Infrared spectroscopy

Infrared spectroscopy was introduced into the field about 1950, and has contributed as much to the determination of functional groups in carotenoids as to that of other types of natural products. This topic, too, has been recently reviewed<sup>6</sup>. Although the length of the polyene chain is not revealed, and the presence of epoxidic oxygen or aryl end-groups may be difficult to detect, different types of carbonyl groups, methoxyl, various types of hydroxyl groups and the presence of *retro* systems are easily determined by infrared spectroscopy. Some characteristic frequencies are compiled in Table 3.

Table 3. Characteristic frequencies of some common functional groups in carotenoids, measured in KBr-pellet.

Functional group	$cm^{-1}$
Acetate	1730
Keto $\alpha$ , $\beta$ -conjugated	1680-1650
Aldehyde $\alpha$ , $\beta$ -conjugated	1675
Carboxyl $\alpha$ , $\beta$ -conjugated	1675
Methyl ester $\alpha$ , $\beta$ -conjugated	1700
Methoxyl	1080
Hydroxyl <i>tert</i> (1-position)	1140, 905
Hydroxyl <i>sec</i> non-allylic in $\beta$ -ring	1040
Hydroxyl <i>sec</i> allylic in $\beta$ -ring	1025
<i>Trans</i> disubstituted double bond	c. 960 <sup>†</sup>

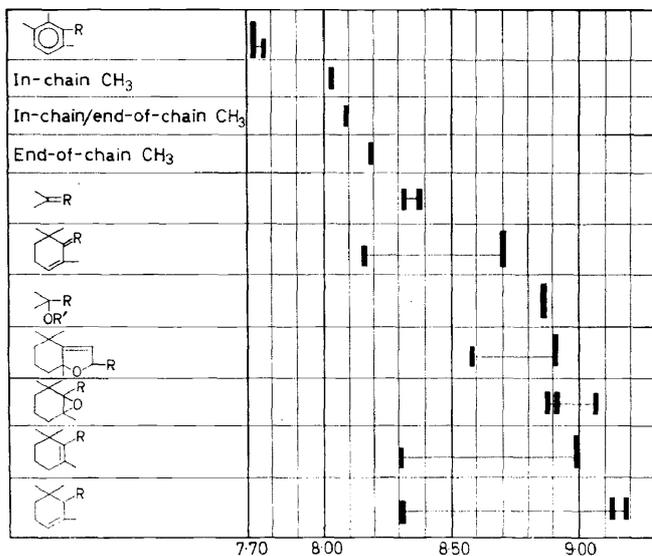
<sup>†</sup> splitted for: (a) *retro* carotenoids; (b) aliphatic conjugated keto carotenoids.

### Proton magnetic resonance spectroscopy

Proton magnetic resonance spectroscopy was introduced to the field of

carotenoids in 1959 by Jackman, Weedon and coworkers<sup>8</sup>, and has since been an invaluable method for the determination of the number and type of methyl groups present. The signals of some methyl groups characteristic of carotenoids, based on the data of Barber *et al.*<sup>8</sup>, are listed in Table 4.

Table 4. Signals (in  $\tau$ -value) of various methyl groups characteristic of carotenoids, recorded in deuteriochloroform.



It may be seen that analysis of the proton magnetic resonance spectra gives valuable indications of the type of end-group present. Moreover, establishment of the location of the polyene chain is now chiefly based on this method. Methoxyl groups, aldehydic and aromatic protons are also readily revealed by this technique. At this point I should like to acknowledge the excellent service offered by Varian Associates in running proton magnetic resonance spectra for institutions lacking suitable facilities.

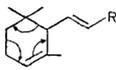
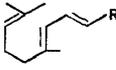
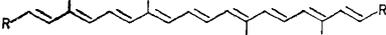
### Mass spectrometry

The latest spectroscopic method to be employed is mass spectrometry, applicable even to unstable compounds with low volatility, such as carotenoids, since the construction of high precision mass spectrometers with direct inlet systems. Here the fundamental study was made at Hoffmann-La Roche by Isler and his group<sup>9</sup>. The possibility of exact molecular weight measurements and unequivocal determination of elementary composition of carotenoids is now finally open to the carotenoid chemists, and some understanding of the fragmentation pattern characteristic of various types of carotenoids is also beginning to emerge. Most carotenoids tend to form stable molecular ions. Compounds with  $\alpha$ -end-groups give an M-56 peak caused by a *retro* Diels-Alder rearrangement of the  $\alpha$ -cyclogeranylidene residue, and carotenoids with isopropylidene end-groups give an M-69

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peak. Carotenoids in general give M-92 (toluene) and M-106 (xylene) peaks by a *cis*-oid rearrangement of the polyene chain (Table 5). It might be mentioned that McCormick (cf. ref. 10) has determined the elementary composition of a carotenoid derivative with a molecular weight as high as 940, and that the first C<sub>50</sub>-carotenoid<sup>11</sup> would not have been recognized as such were it not for mass spectrometry.

Table 5. Some characteristic fragments obtained by mass spectrometry of carotenoids

Original structural element	Fragment obtained
	 M-56
	 M-69
	<div style="display: flex; align-items: center;"> <div style="font-size: 3em; margin-right: 10px;">}</div> <div style="display: flex; flex-direction: column; gap: 10px;"> <div style="display: flex; align-items: center;">  M-92         </div> <div style="display: flex; align-items: center;">  M-106         </div> </div> </div>

Combined use of the four types of spectroscopic methods discussed may sometimes give the complete structure of a carotenoid<sup>12</sup>. However, in most cases further chemical studies are required, particularly for the establishment of the location of hydroxyl substituents.

## CHEMICAL METHODS FOR STRUCTURE ELUCIDATION

### Purification

Although modern spectroscopic methods have greatly minimized the sample requirements in structural determinations, the need for pure samples is maintained. Some progress has been made in the development of chromatographic separation methods for preparative scale work. Adsorbents such as cellulose powder and magnesium silicate have been successfully employed for polar carotenoids, and a few systems based on partition chromatography have been described<sup>13, 14</sup>. Petracek and Zechmeister<sup>15</sup> have determined the partition ratio of a number of carotenoids and provided some of the information necessary to set up solvent systems for Craig-distribution of carotenoids, and counter-current distribution techniques have been developed and refined by Curl<sup>16-18</sup>. Iso-distributive pigments must in most cases be separated into single components by subsequent adsorption chromatography. However, the greatest improvements in efficient and rapid separation techniques have been obtained on a micro scale by the introduction of thin-layer chromatography<sup>19-21</sup> and various types of paper chromatography, generally based on impregnated papers<sup>22</sup>, papers with suitable fillers<sup>23, 24</sup> or reversed phase partition systems<sup>25</sup>. Most of these methods allow a reliable check of the purity of samples and have

proved very helpful for following chemical reactions. However, a warning should be given against the isolated use of  $R_f$ -values in structural assignments.

## Synthesis

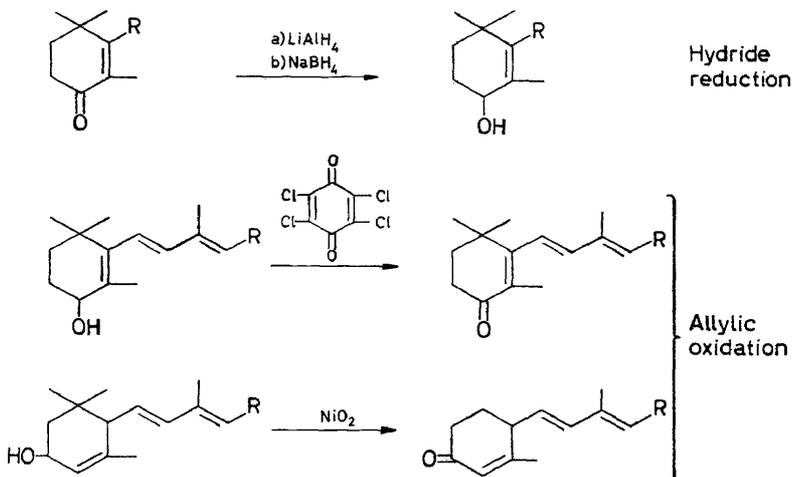
The striking achievements in the field of total synthesis of carotenoids, an explosive development since 1950, have meant an enormous contribution to the establishment of chemical structures for new carotenoids. By providing synthetic model substances of definite structure and particularly by synthesis via defined routes, unequivocal proof of the structures of new, naturally occurring carotenoids, often occurring in trace amounts, has been obtained. In this respect pleasant and fruitful co-operation has developed between scientists engaged in total synthesis and the natural product chemists in the field. A most significant contribution to the general scientific development of the field has been made by the firm Hoffmann-La Roche.

## New reactions

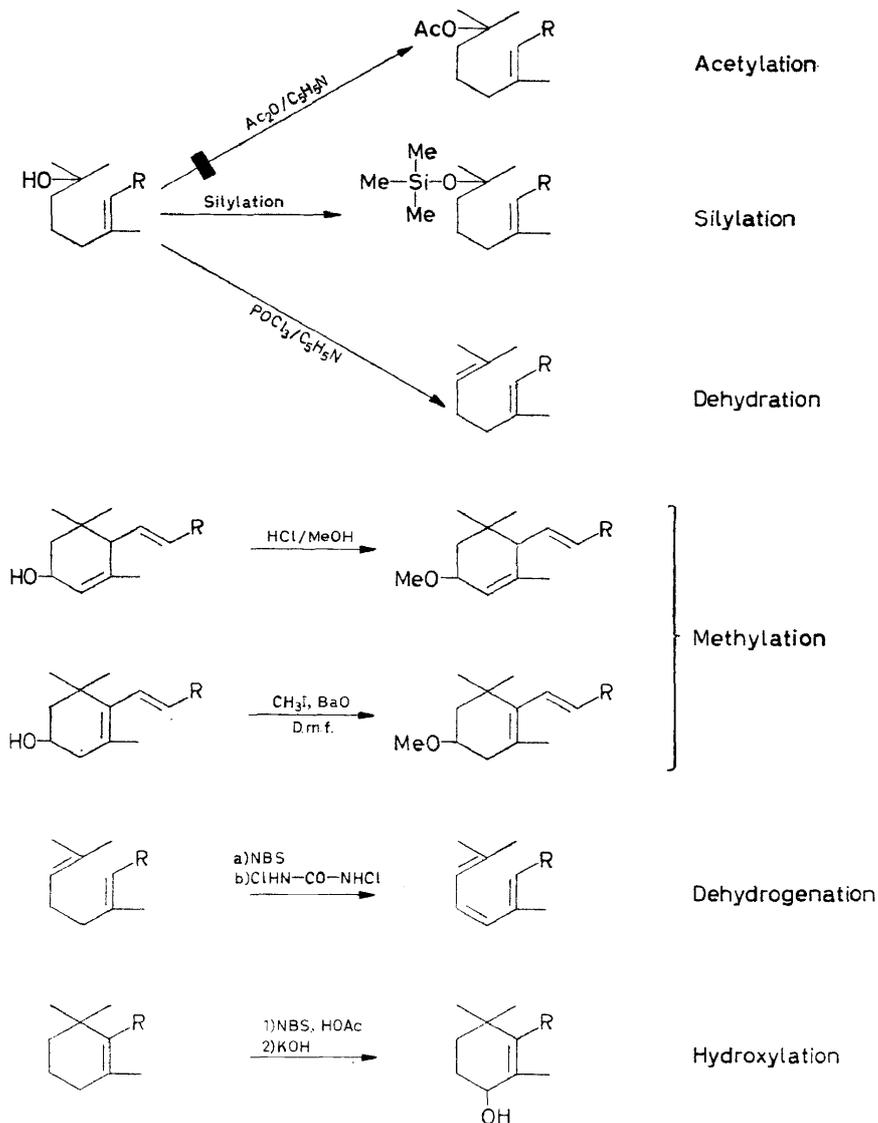
The carotenoid field has benefited from the recent general development in organic chemistry. Thus many new reactions and reagents have proved adaptable to structural studies on this class of natural products many of which are unstable towards acid, heat, light and oxygen. Moreover, new reactions have been developed particularly with regard to carotenoids. Some examples of new reagents and reaction types employed in the structural studies of naturally occurring carotenoids are illustrated below.

Reduction of carbonyl groups with lithium aluminium hydride or sodium borohydride was a great improvement on the previously used Meerwein-Ponndorf reduction.

Useful reagents for the selective oxidation of allylic hydroxyl groups have also been developed. Provided the hydroxyl group is in the allylic position to a long polyene chain, oxidation with  $\beta$ -chloranil is successfully carried



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out<sup>26, 27</sup>. It might be mentioned that  $\alpha$ -glycol arrangements in some cases seem to prevent the reaction<sup>28</sup>. The stronger oxidizing agent nickel peroxide<sup>29</sup> is another new reagent for the selective oxidation of allylic hydroxyls and does not require activation from a long polyene chain<sup>30</sup>.

Whereas chemical criteria for the presence of *tertiary* hydroxyl groups in carotenoids were based for a long time on negative acetylation evidence, trimethylsilyl ethers can now be formed in quantitative yield from most *tertiary* carotenoids<sup>31</sup>. Moreover, phosphorus oxychloride in pyridine has proved to be a suitable reagent for dehydration of *tertiary* alcohols, leading to the introduction of a double bond<sup>32, 33</sup>.

Specific methylation of 3-hydroxylated  $\alpha$ - rings may be readily accomplished by treatment with acid methanol<sup>30, 34</sup>, and, in general, improved yields of methyl ethers are obtained by methylation with methyl iodide and barium oxide in dimethylformamide<sup>35</sup> according to an original procedure of Kuhn and coworkers<sup>36, 37</sup>.

New dehydrogenating agents have recently been reported by Rumanian workers<sup>38</sup>, and modification of the *N*-bromosuccinimide dehydrogenation reaction has led to a useful method for introduction of allylic hydroxyl, ester, or ether groups<sup>39</sup>.

A specific reaction for carotenoids that has found very wide application

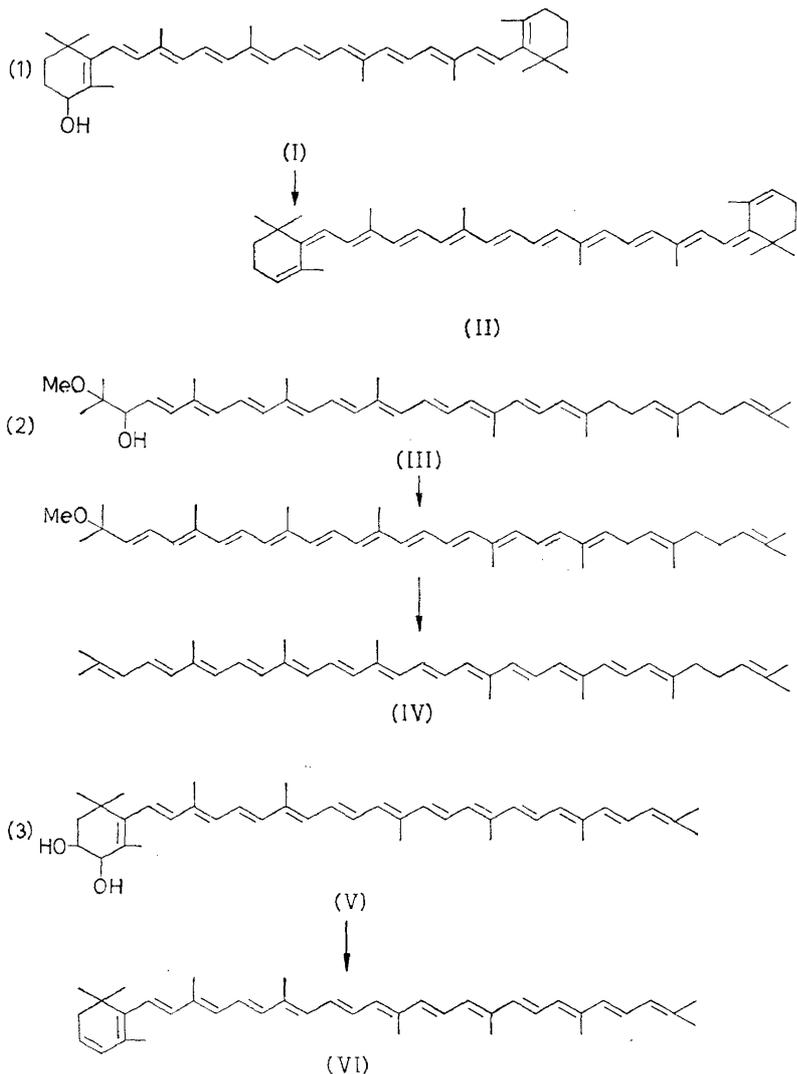


Figure 2. The results of treatment of various carotenoids containing allylic hydroxyl and methoxyl groups with hydrogen chloride in chloroform.

in structural studies is allylic dehydration with hydrochloric acid (*c.* 0.03 N) in chloroform carried out according to the method of Karrer and Leumann<sup>40</sup>. The reaction works also for carotenoids carrying allylic ether groups and leads to products with extended chromophoric systems and lower polarity. When one allylic hydroxyl or ether group only is present, the course of the reaction may be predicted. However, strongly hydroxylated xanthophylls often give related elimination products by unknown mechanisms. A few examples are given in *Figure 2*. In the first example the dehydration of isozeaxanthin (I) to *retro*-dehydrocarotene (II) is depicted<sup>41</sup>. Whenever possible *retro* products seem to be favoured. In the second example the reaction leading from hydride-reduced spheroidenone (III) to 3,4-dehydrolycopene (IV) is formulated as a straight dehydration-de-“methanolation” reaction<sup>42</sup>. The elimination of 3,4-dihydroxytorulene to 3,4-dehydrotorulene<sup>28</sup> in the third example is of a different type.

### RECENTLY DISCOVERED CAROTENOIDS

Having now defended the view that the second period in the study of naturally occurring carotenoids began some fifteen years ago because of the improvements in available methods, one may ask what results have been obtained during this period.

The number of known naturally occurring carotenoids has increased roughly by one hundred from about 80 to about 180. In early times, when the famous schools of Karrer and Kuhn made their fundamental and remarkable contribution to the field, it was mainly the carotenoids of higher plants that were studied. Such studies have been continued, particularly with the successful investigations of fruit carotenoids. In addition, carotenoids from many new sources such as various types of microorganisms, algae, and animals have been studied, and many new structural features have been added to the chemistry of the carotenoids.

A fairly detailed review of the structural investigations carried out during this period has recently been published<sup>6</sup>. At this point I should like to draw the readers attention to some selected examples of new structural types.

The previous definition of carotenoids<sup>43</sup> comprised only coloured representatives. However, the comparatively saturated members of the so-called Porter-Lincoln series, which are considered as biosynthetic precursors of the coloured carotenoids<sup>44, 45</sup>, and which undoubtedly should also be classified as carotenoids, have now been structurally elucidated. The structures of phytoene (VII), phytofluene (VIII),  $\zeta$ -carotene (IX) and neurosporene (X), given in *Figure 3*, are based on dehydrogenation studies by Zechmeister and Koe<sup>46</sup>, thorough degradation studies by Rabourn and Quackenbush<sup>47-49</sup> and finally proved by proton magnetic resonance and synthetic work performed by Weedon's group<sup>50</sup>. Phytoene and phytofluene are oils and were particularly difficult to purify. The discovery of the many isolated double bonds and the non-symmetrical structures of phytofluene (VIII) and neurosporene (X) was rather surprising, but does reflect the biosynthetic pathway leading to coloured carotenoids.

Similar structural features were later found, for instance, in various carotenoids isolated from photosynthetic bacteria. These are mainly

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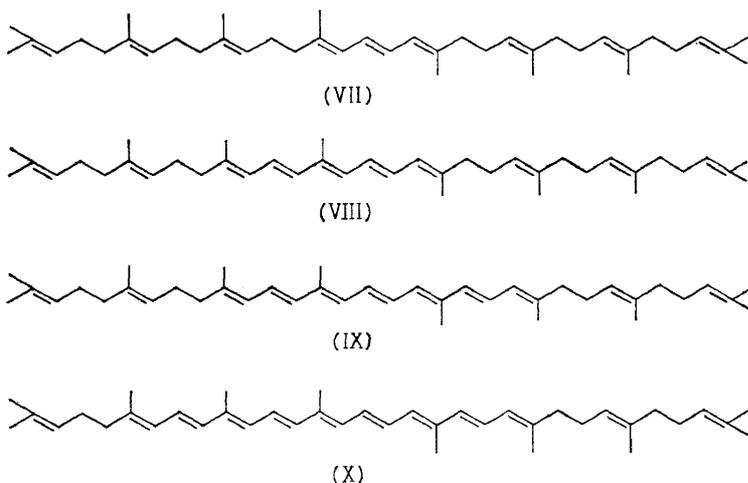


Figure 3. The chemical structures of members of the Porter-Lincoln series.

aliphatic carotenoids, often containing *tertiary* hydroxyl or methoxyl groups in the 1- and 1'-positions or conjugated keto groups in the 2-position. As examples the structures of OH-spheroidenone (XI)<sup>51</sup> and spirilloxanthin (XII)<sup>32, 51, 52</sup> are given in Figure 4.

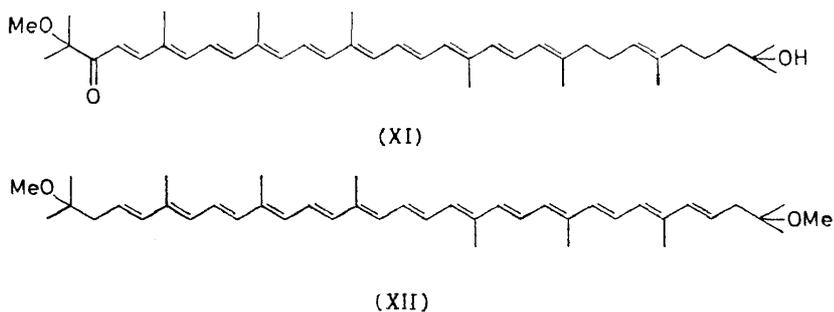


Figure 4. Representatives of aliphatic carotenoids typical of photosynthetic bacteria.

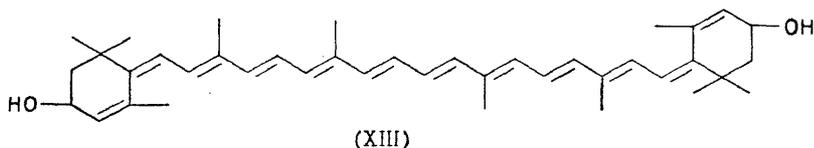
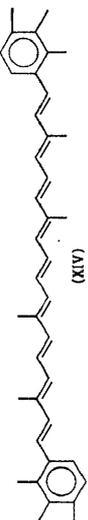
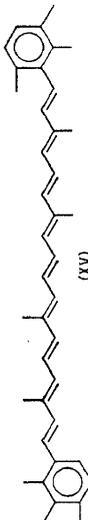
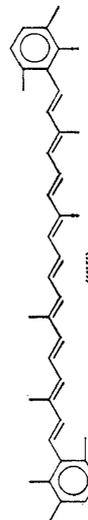
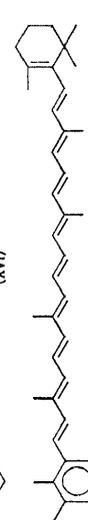
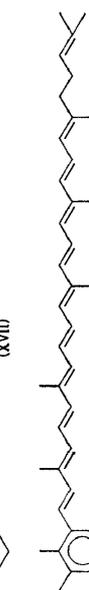
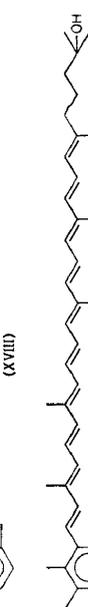
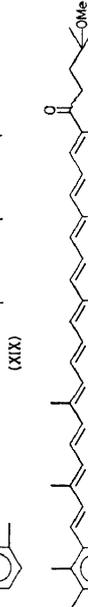


Figure 5. Eschschoitzxanthin.

*Retro* carotenoids are rare in Nature, and besides rhodoxanthin, eschschoitzxanthin (XIII, Figure 5) from Californian poppies represents the second known naturally occurring *retro* carotenoid. The structure was elucidated by Strain<sup>53</sup>, and Karrer and Leumann<sup>40</sup>.

Table 6. The natural distribution of aryl carotenoids<sup>54</sup>.

Structure	Designation	Natural occurrence
 (XIV)	Renierapurpurin	<i>Reniera japonica</i>
 (XV)	Renieratene	<i>Reniera japonica</i>
 (XVI)	Isorenieratene-leptotene	<i>Reniera japonica</i> <i>Mycobacterium</i> spp. <i>Phaeobium</i> spp.
 (XVII)	$\beta$ -Isorenieratene	<i>Phaeobium</i> spp.
 (XVIII)	Chlorobactene	<i>Chlorobacteriaceae</i> <i>Phaeobium</i> spp.
 (XIX)	OH-Chlorobactene	<i>Chlorobacteriaceae</i>
 (XX)	Okenone	<i>Thiorhodaceae</i>

The class of aryl-carotenoids (Table 6) was first detected in 1956 by Yamaguchi in a sea sponge, *Reniera japonica*, shown to contain renierapurpurin (XIV), renieratene (XV) and isorenieratene (XVI) with 1,2,5- and 1,2,3-trimethylphenyl end-groups. The structures were well established by classical degradation studies and synthetic work<sup>55-62</sup>. Later the aryl-carotenoids  $\beta$ -isorenieratene (XVII)<sup>63</sup>, chlorobactene (XVIII)<sup>33</sup>, OH-chlorobactene (XIX)<sup>33</sup> and okenone (probably XX)<sup>54, 64</sup> were isolated from photosynthetic sulphur bacteria. The three first mentioned have also been synthesized<sup>62, 65</sup>. We know at present seven representatives of natural aryl-carotenoids. Leprotene, first isolated from a strain of *Mycobacterium phlei* in 1938<sup>66</sup>, and since stored in the desk of Richard Kuhn together with his synthetic aryl-polyenes, has since actually proved to be an aryl-carotene identical with isorenieratene (XVI).

The elucidation of the structures of the paprika ketones were problems left from the classical period, which have been successfully solved by the schools of Chohnoky<sup>67-70</sup>, Karrer<sup>71-74</sup>, and Weedon<sup>70, 75, 76</sup>. Capsanthin (XXI), capsorubin (XXII) and cryptocapsin (XXIII) contain cyclopentane end-groups (Figure 6). Cooper, Jackman and Weedon<sup>76</sup> have recently carried out a total synthesis of capsorubin (XXII).

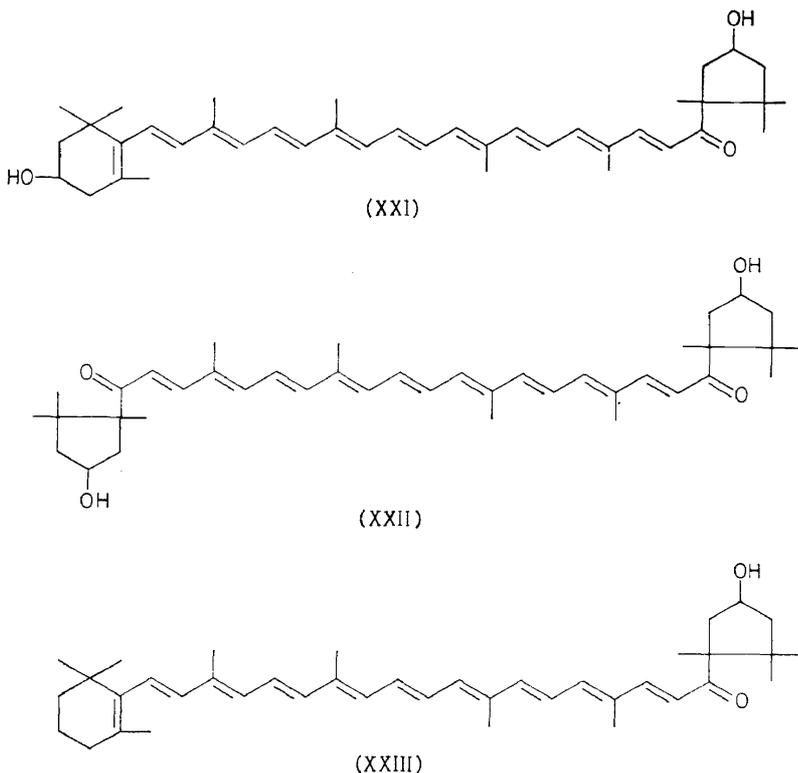


Figure 6. The structures of the paprika ketones.

## RECENT ADVANCES IN CHEMISTRY OF NATURAL CAROTENOIDS

Another old problem, now approaching its solution, is the structure of fucoxanthin, the characteristic carotenoid of brown algae. Its complicated structure has mainly been investigated by Weedon and coworkers<sup>77, 78</sup> and Jensen<sup>79-82</sup>. This structurally very interesting carotenoid possesses an allenic group<sup>77, 83</sup> and is a natural acetate<sup>81</sup>. Structure (XXIV) was first proposed by Jensen<sup>82</sup>, and later independently structure (XXV), whose elementary composition is in agreement with mass-spectrometric data, was suggested by Weedon's group<sup>78</sup> (Figure 7). However, the unequivocal structural proof is still lacking.

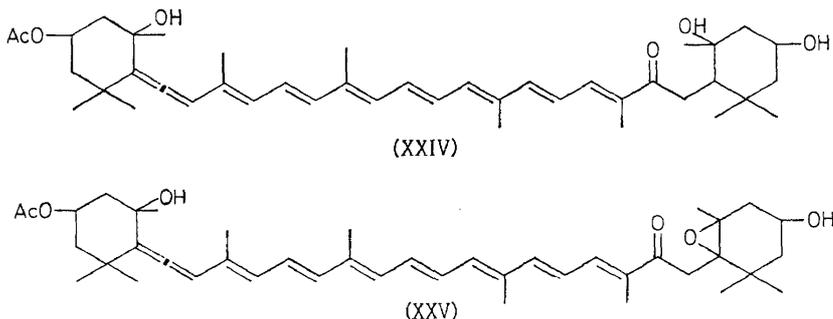


Figure 7. Recent structures proposed for fucoxanthin.

Many representatives among apo-carotenoids with varying numbers of carbon atoms in the skeleton, have been found in Nature recently. From this collection of aldehydes, acids and methyl ketones, the interesting citrus methyl ketones citranaxanthin (XXVI)<sup>84</sup>, reticulataxanthin (XXVII)<sup>85-87</sup> and sintanaxanthin (XXVIII)<sup>88</sup> might be mentioned (Figure 8). The final structures were worked out by Yokoyama and White. The acid yeast carotenoid neurosporaxanthin has been shown to be  $\beta$ -apo-4'-carotenoic acid (C<sub>35</sub>) (XXIX)<sup>7</sup>, whereas torularhodin has turned out to be a C<sub>40</sub>-acid, namely torulene carboxylic (16') acid<sup>89</sup>.

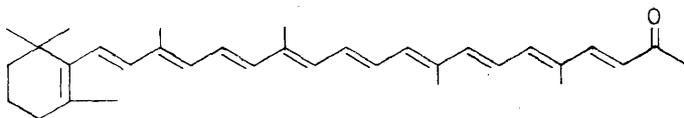
Until very recently, known keto-carotenoids invariably contained conjugated keto groups. Pirardixanthin, isolated by Krinsky and Lenhoff<sup>90</sup> from hydra, and still of unknown structure, appears to contain unconjugated keto groups.

The structures of the majority of highly oxygenated carotenoids are still unsolved. The pentaols phlei-xanthophyll and 4-ketophlei-xanthophyll, synthesized by a particular strain of *Mycobacterium phlei*, have proved to be tertiary glucosides (XXX and XXXI)<sup>10</sup> (Figure 9) and represent, together with crocin (XXXII), the digentiobiose ester of crocetin, the first crystalline glycosides with carotenoid aglycones. Tertiary glycosides in general appear to be very rare in Nature.

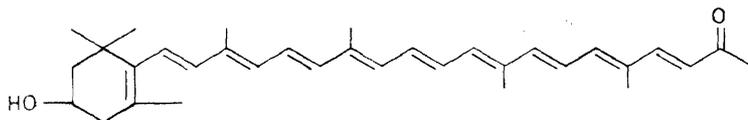
Finally a novel carotenoid, isolated from a bacterial source and provisionally termed P439 might be mentioned. This compound is a C<sub>50</sub>-carotenoid with two primary hydroxyl groups, thus possessing two unusual structural features<sup>11</sup>.

From the examples given here it appears that the previous definition of

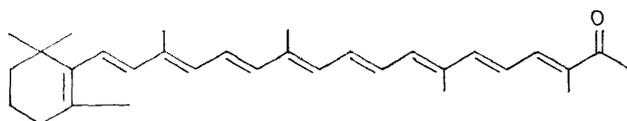
carotenoids<sup>43</sup> needs some revision in order to include the new structural types discovered in recent years. Moreover, the nomenclature of this class of natural pigments is not satisfactory, and it is fortunate that a subcommittee for the revision of the nomenclature of carotenoids is in operation under the auspices of IUPAC.



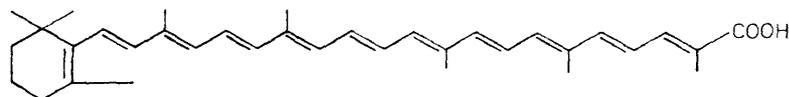
(XXVI)



(XXVII)

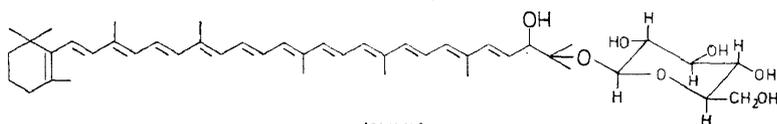


(XXVIII)

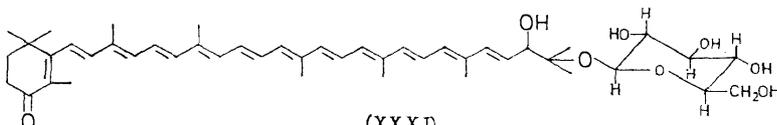


(XXIX)

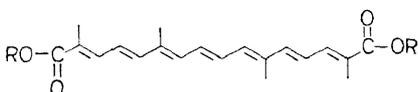
Figure 8. Examples of new apo-carotenoids.



(XXX)



(XXXI)



(XXXII) R=Gentiobiosyl

Figure 9. Carotenoid glycosides.

## UNSOLVED PROBLEMS IN CAROTENOID CHEMISTRY

Having now summarized recent advances in the field, it might be worthwhile to consider some of the unsolved problems.

Regarding the stereochemistry, much effort was made by the school of Zechmeister in clarifying the *cis-trans* isomerism of this class of polyenes. This has been lucidly summarized in his recent book<sup>91</sup>. However, convenient methods for the determination of the location of *cis* double bonds are still lacking. Although some interest has recently arisen in configuration studies, this is a much neglected field. Whereas the full stereochemistry of capsorubin (XXII) and cryptocapsin (XXIII) has been established by modern methods<sup>74, 76, 92</sup>, and the conformation of crustaxanthin has been discussed at this symposium<sup>93</sup>, the steric arrangement around the frequently occurring 3-hydroxy group in xanthophylls is not established, nor is the stereochemistry of furanoid carotenoids such as flavoxanthin and crysanthemaxanthin known<sup>1</sup>.

New structural types are yet to be expected. For instance, carotenoids

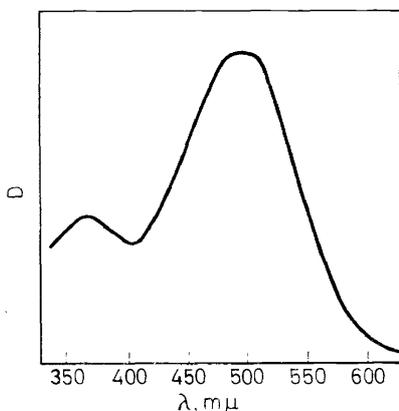


Figure 10. Electronic spectrum of warmingone in acetone.

of the warmingone group<sup>94</sup> with peculiar electronic spectra (Figure 10), contain unknown chromophoric systems. Hetero-atoms other than oxygen have not yet been found in naturally occurring carotenoids, but may still occur. Within the class of aryl-carotenoids phenolic compounds may also be expected.

High precision mass spectrometry will in the future undoubtedly be an indispensable tool for the determination of molecular weight and elementary composition of new carotenoids. By combination of the modern methods available chemists are in a stronger position to solve more complicated problems, including the structures of highly oxygenated carotenoids.

## CHEMOTAXONOMIC CONSIDERATIONS

Finally it might be of some interest to consider the possible use of carotenoids as a taxonomic tool. Chemotaxonomic considerations, based on the distribution of a selected type of accessory or secondary plant substituents have often proved rewarding, although there may be many other factors contributing to biological individualism.

Carotenoids occur in all photosynthetic organisms, where they seem to act as protectors against photodynamic killing<sup>95</sup> and in part as auxiliary light adsorbers for photosynthesis<sup>96</sup>. Furthermore they have a scattered distribution in other types of organisms, where their function is less clear. Micro-organisms and green plants synthesize carotenoids *de novo*. In some higher organisms carotenoids are selectively absorbed from the diet and subsequently somewhat modified structurally.

Since without doubt only a limited selection of carotenoid producing organisms has so far been subjected to carotenoid analysis, it seems premature to judge if carotenoids are chemotaxonomically useful substances. The chemotaxonomic importance of carotenoids, if any, is most likely to be found in organisms producing carotenoids *de novo* where knowledge of biosynthetic pathways, and their function, may give additional support. Moreover, the distribution of structurally rare carotenoids seems most promising for the evaluation of phylogenetic relationships.

Within the photosynthetic organisms there are considerable differences between the carotenoid composition of higher plants, various algal classes and photosynthetic bacteria (*Table 7*). However, in organisms of remote *Table 7*. Simplified presentation of the characteristic carotenoids in some main classes of photosynthetic organisms.

<i>Type of organism</i>	<i>Family</i>	<i>Characteristic carotenoids</i>
Photosynthetic bacteria	Chlorobacteriaceae Athiorhodaceae	Aryl-carotenoids Aliphatic carotenoids with <i>tert</i> -hydroxy or methoxy groups. Occasionally 2-keto-derivatives
	Thiorhodaceae	Similar to those of Athiorhodaceae, not 2-keto-derivatives; aryl-carotenoids
Blue-green algae		Bicyclic carotenes and keto-carotenoids (echinenone and canthaxanthin). Strongly oxygenated carotenoids (myxoxanthophyll)
Brown algae		Fucoxanthin, $\beta$ -carotene, lutein, violaxanthin
Red algae		Require systematic investigation
Green algae		Resembling those of higher plants.
Higher plants		Bicyclic carotenes, lutein, neoxanthin, violaxanthin

systematic position, chemotaxonomic considerations are of restricted value. Within the photosynthetic bacteria differentiation between the green and purple bacteria is also possible on the basis of carotenoids, but further classification within the *Thiorhodaceae* based on carotenoid composition appears at present somewhat doubtful<sup>97</sup>.

Flexibacteria may be classified either as bacteria or as non-photosynthetic blue-green algae. In this case structural determination of the carotenoids produced might be of taxonomic value<sup>98</sup>, and the future will tell if in general a chemotaxonomic approach based on carotenoids might prove rewarding.

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