

Blue carotenoids

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This paper is dedicated to an old friend and colleague, Professor Torbjörn Norin, who has contributed also to the chemistry of isoprenoid compounds

Abstract

A review on the chemistry of blue carotenoids, emphasizing own contributions, is presented. Treated are violerythrin, carotenoid oxonium ions, preparation and characterization of carotenoid cations ($< C_{40}$, C_{40} , $> C_{40}$ -skeletal analogs), the Carr-Price Vitamin A blue colour reaction, carotenoid-iodine complexes and blue carotenoproteins.

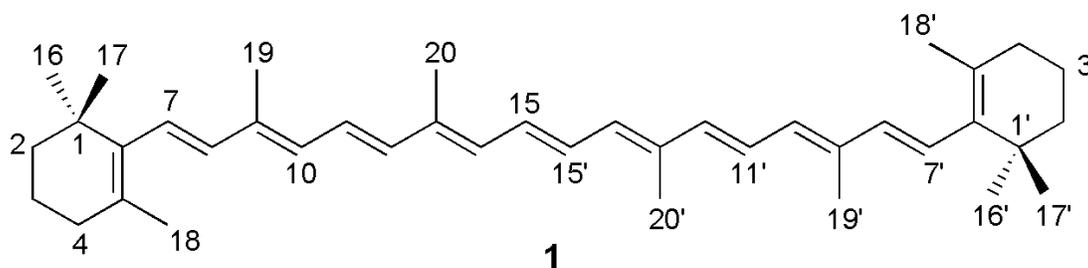
Keywords: Polyenyl cations, preparation, characterization, retinoids, carotenoproteins

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1. Introduction

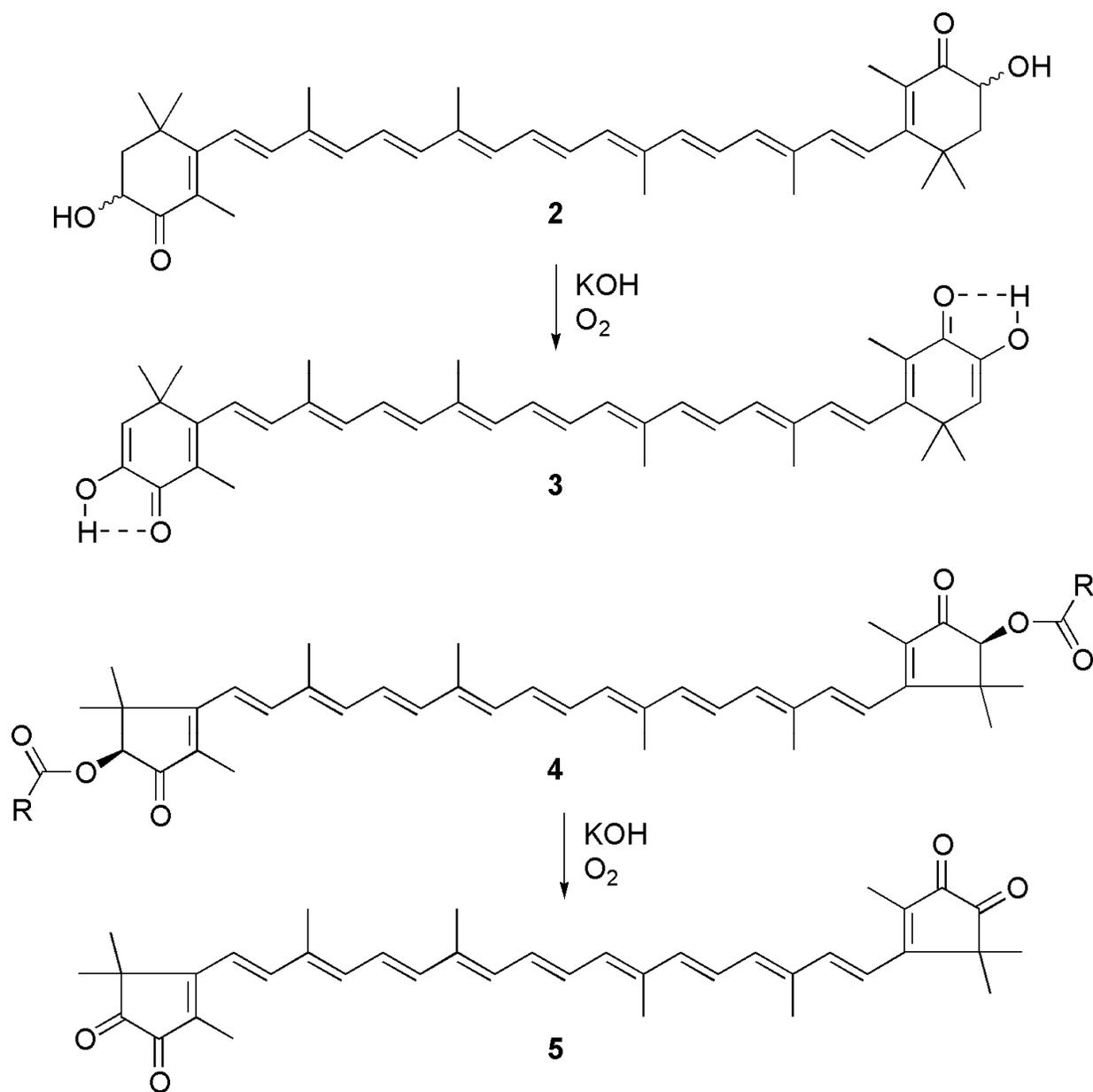
Amongst the isoprenoids the carotenoids constitute a class of coloured polyenes, mainly with C₄₀-skeletons, as illustrated by β,β -carotene (**1**).¹ Whereas a few colourless representatives are known, the majority are yellow-orange-red pigments widely distributed in Nature.² No blue carotenoids are naturally occurring in an uncomplexed state. However, various carotenoids may be derivatized to blue products, and the chemistry of these reactions has been revealed mainly within the last two decades. The blue products comprise conjugated cyclopentenediones, oxonium ions, carbocations, iodine complexes and carotenoproteins. Their chemistry is briefly reviewed in this account, emphasizing own contributions.



2. Violerythrin

Astaxanthin (**2**), the typical red carotenoid of salmon and boiled lobster,² is known to undergo facile oxidation in the presence of bases and oxygen to the enolized diketone astacene (**3**) with closely similar absorption maximum.³ The C₃₈ skeletal 2,2'-dinor carotenoid diester actinioerythrin (**4**) from sea anemones reacts in a similar way to provide the blue cyclopentenedione violerythrin (**5**, λ_{\max} 549 nm in acetone), unable to enolize, Scheme 1.^{4,5}

Violerythrin (**5**) was later prepared by total synthesis.⁶ As a curiosity it may be mentioned that the industrial application of the blue product **5** as an eye cosmetics was once considered.

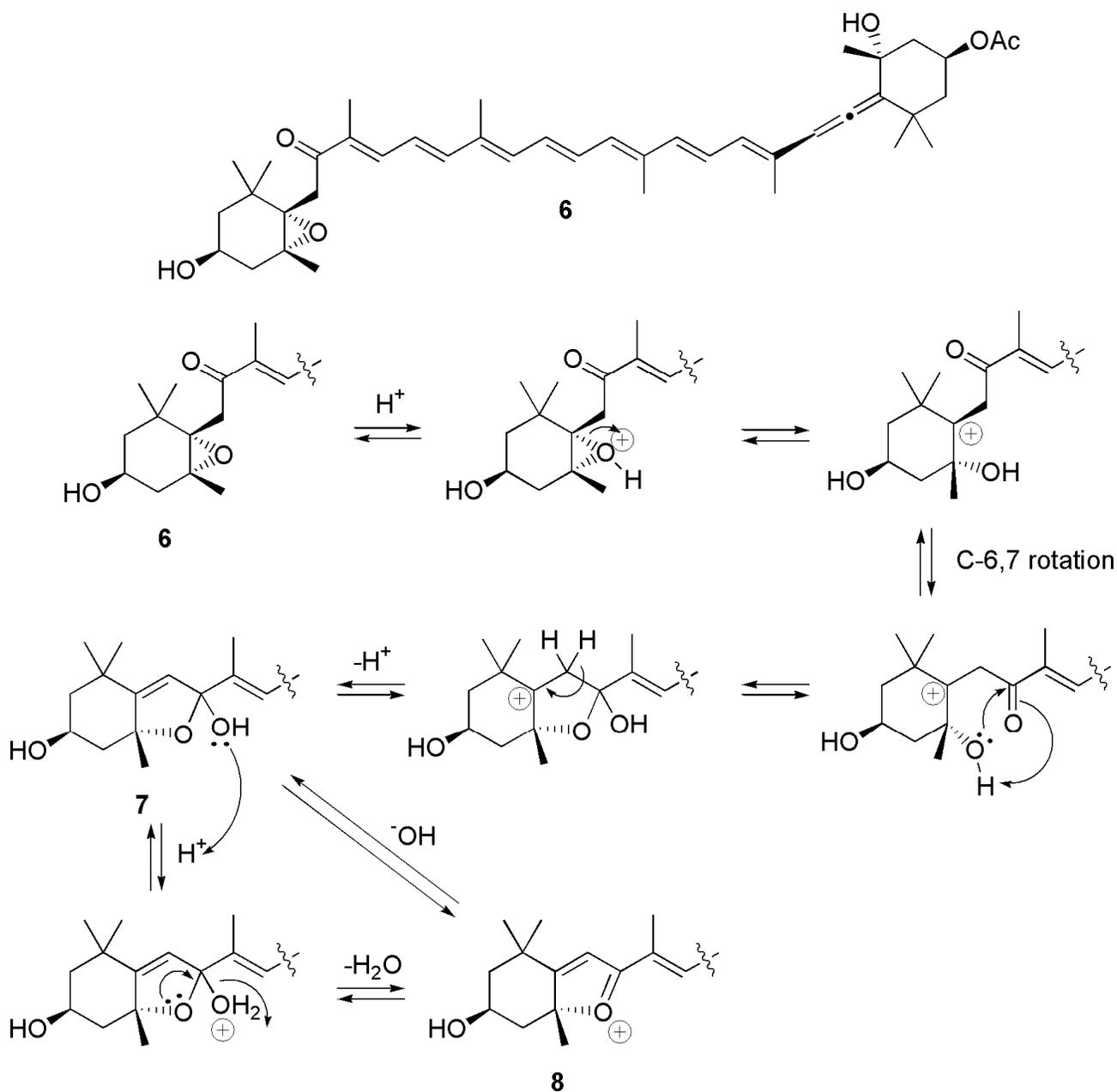


Scheme 1

3. Oxonium Ions

Since Karrer's work in the forties it has been known that carotenoid 5,6-epoxides undergo epoxide-furanoxide rearrangement with weak Brønsted acid and subsequently transferred to blue products by treatment with concentrated acid.^{7,8} The chemistry of the blue colour reaction was revealed in the early nineties.^{9,10} Examples are given below for carotenoid mono- and diepoxides. Fucoxanthin (6), with the 5,6-epoxy group close to the carbonyl function, is converted by HCl via the hemiketal 7 to

the blue oxonium ion **8**, which is readily transformed to the yellow hemiketal **7** with base, Scheme 2.⁹



Scheme 2

The colour changes occurring during the final steps in this reaction scheme is illustrated in Figure 1. The orange fucoxanthin (**6**) is converted to the yellow hemiketal (**7**) by weak acid and by stronger acid to the blue oxonium ion (**8**). Like an indicator in an acid-base reaction is the blue oxonium ion (**8**) reconverted to the stable yellow hemiketal (**7**) with base. Back reaction to the blue oxonium ion occurs spontaneously with strong acid.⁹

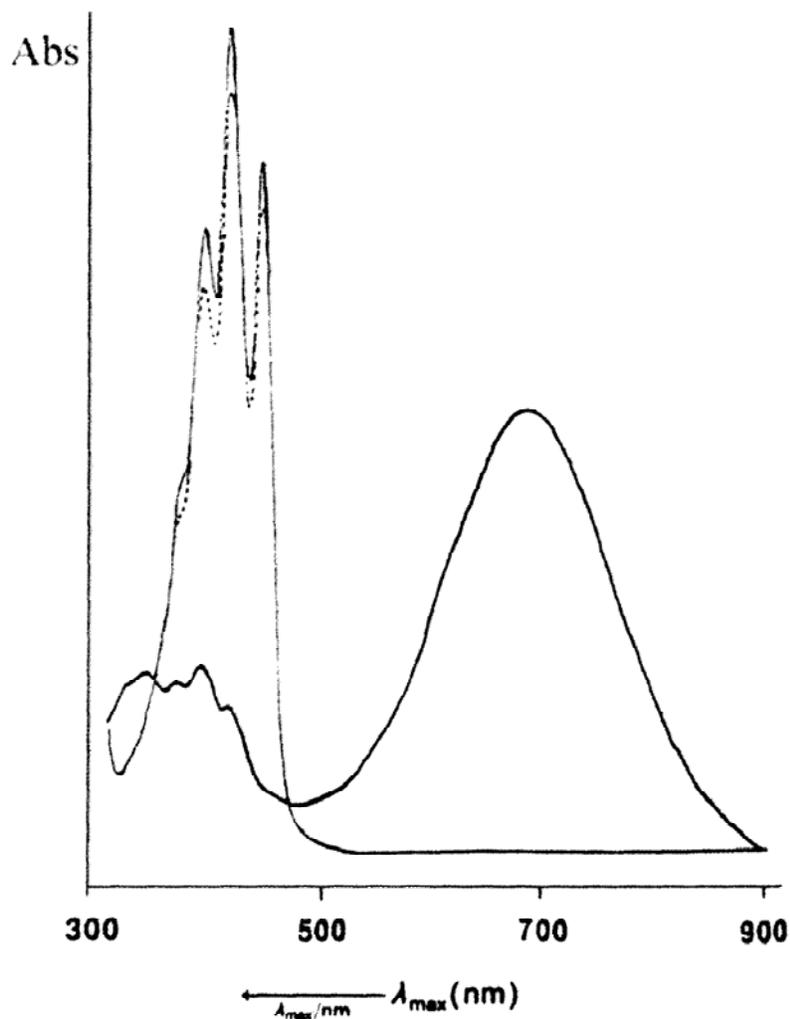
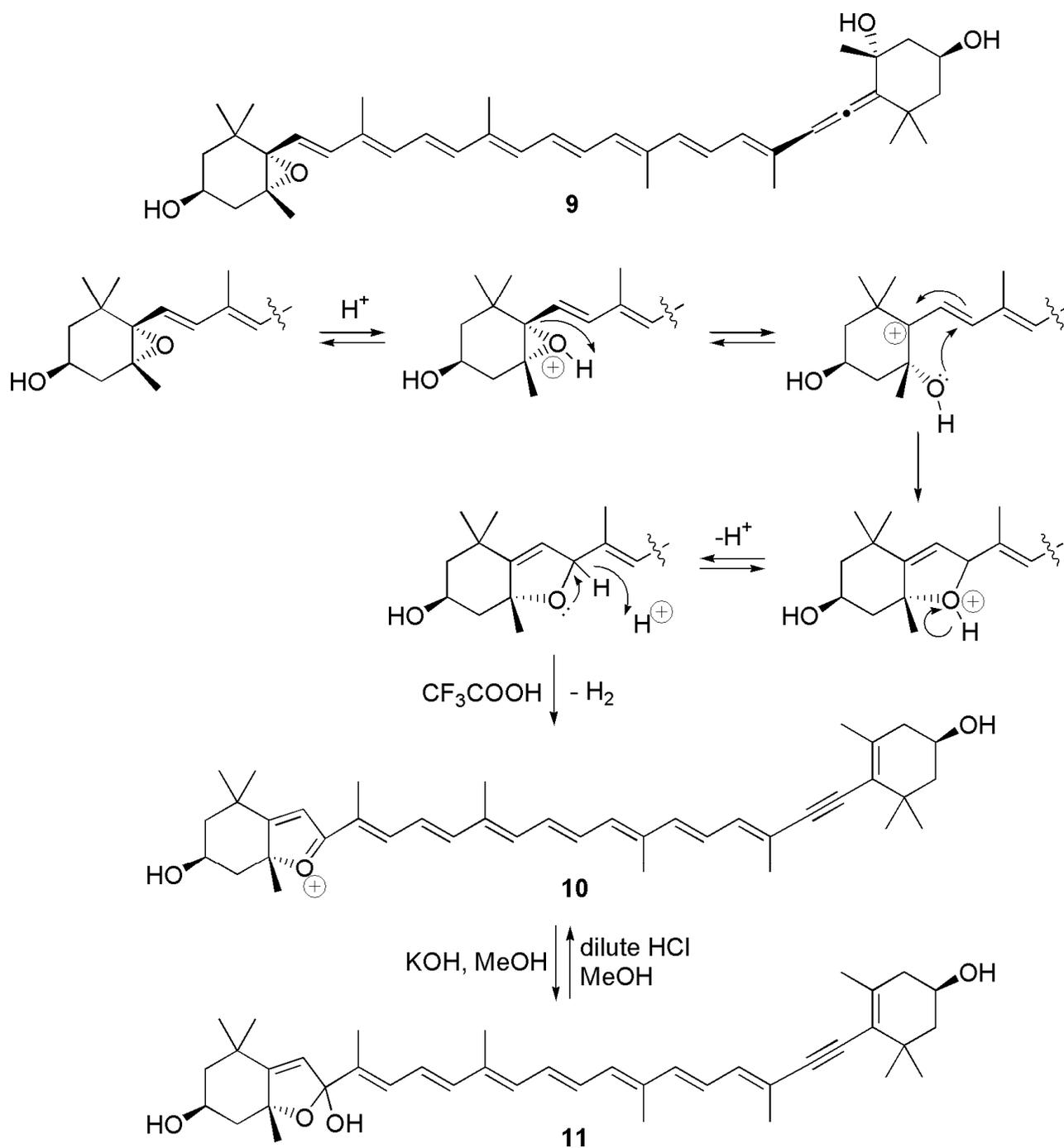


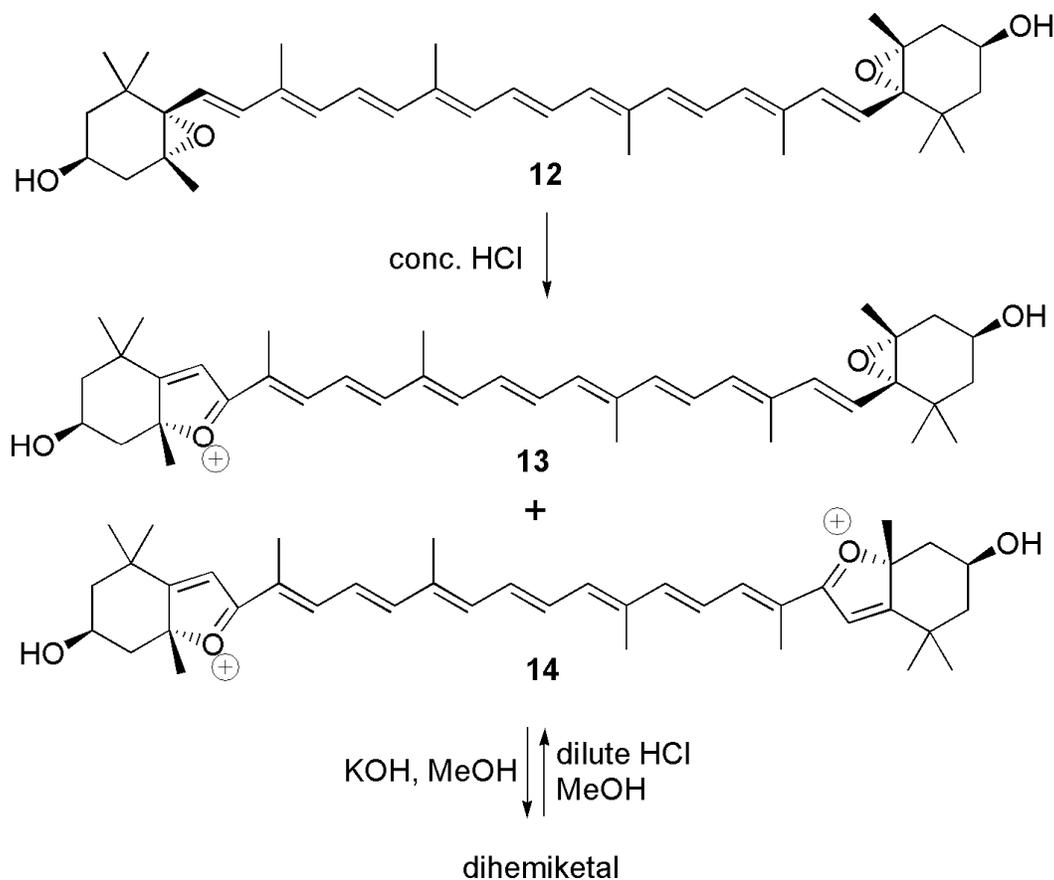
Figure 1. Absorption spectra of fucoxanthin hemiketal (**7**, solid line), the blue oxonium ion produced by treatment with acid (**8**, λ_{max} 690 nm), fucoxanthinol hemiketal formed by subsequent treatment with base (dotted line).⁹

The simpler 5,6-epoxide neoxanthin (**9**) is converted to the furanoxide by weak acid and by concentrated trifluoroacetic acid to the blue oxonium ion **10**, Scheme 3, which again may be reacted with base to the stable yellow hemiketal **11**, Scheme 3.¹⁰ During these transformations the allenic end group in neoxanthin (**9**) was converted to the acetylenic end group in product **11**.



Scheme 3

The diepoxide violaxanthin (**12**) was in similar manner transformed to the blue mono- (**13**) and dioxonium ions (**14**), Scheme 4, which could be converted to the respective, stable mono- and dihemiketals.¹⁰



Scheme 4

The identification of the oxonium ions studied above was mainly based on their VIS/NIR absorption and conversion to characterized hemiketals. Detailed NMR spectra could not be achieved, albeit downfield shift of olefinic protons is consistent with the positive charge. Less extensive charge delocalization than for the carotenoid cations treated later, and preference for the oxonium ion structure, are assumed.

4. Carotenoid Carbocations

4.1 Preparation and characterization

Convenient methods for the preparation of carotenoid carbocations are:^{11,12}

- From carotenes with the Lewis acid BF_3 -etherate as reagent, where BF_3 serves as a strong electrophile, removing electrons from the polyene chain.
- From allylic carotenols with CF_3COOH or $\text{CF}_3\text{SO}_3\text{H}$ in CH_2Cl_2 for selective protonation of hydroxy groups, rather than protonation of the polyene chain. The protonated hydroxy group is a good leaving group.

The carbocations are formed in quantitative yield and exhibit considerable stability at room temperature due to charge delocalization.

The blue colour is caused by absorption in the VIS-NIR region (λ_{\max} around 900 nm) and the stability is monitored by NIR measurements. Carotenoid radical cations exhibit closely similar NIR spectra in comparison with the diamagnetic cation, but may be distinguished by EPR spectra and lower stability.

NMR spectroscopy has been successfully adapted for detailed structural analyses of diamagnetic carotenoid carbocations. High field 2D NMR spectra, including ^1H - ^1H COSY, ROESY, ^1H - ^{13}C HSQC and ^1H - ^{13}C HMBC, recorded at $-10\text{ }^\circ\text{C}$ – $-20\text{ }^\circ\text{C}$, provide the following key information:

(i) total downfield shifts for all carbon atoms is *ca.* 250 ppm for monocations and 500 ppm for dications.

(ii) the charge distribution may be estimated by comparison of the ^{13}C shift of individual carbons relative to a relevant, neutral model. Relative charge is conveniently illustrated by the size of filled circles, *vide infra*.

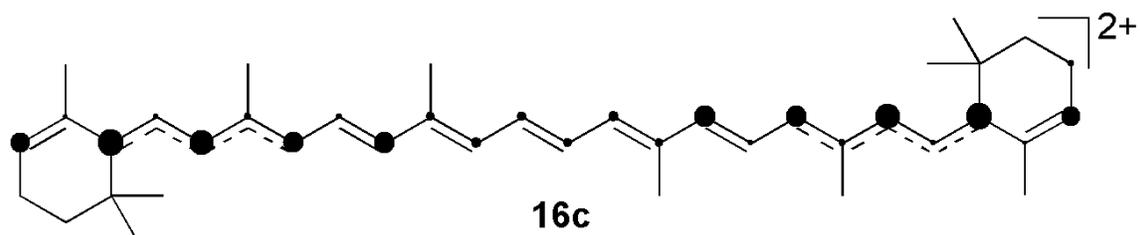
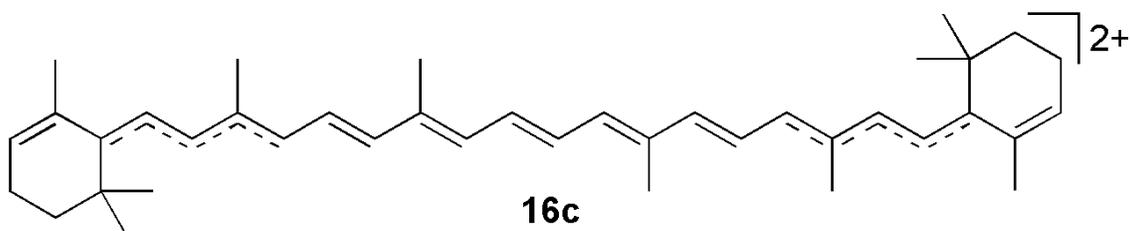
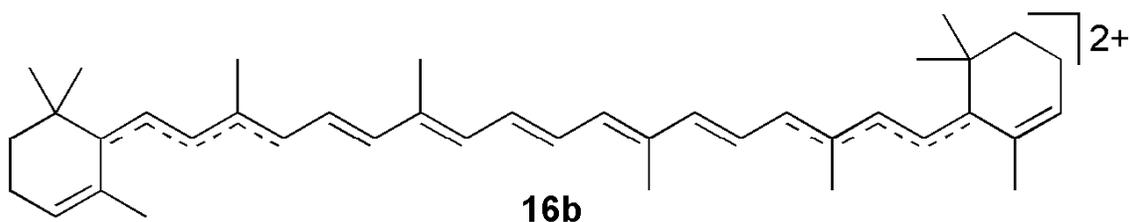
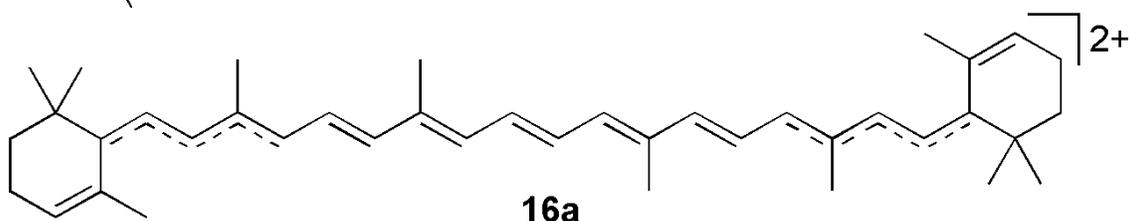
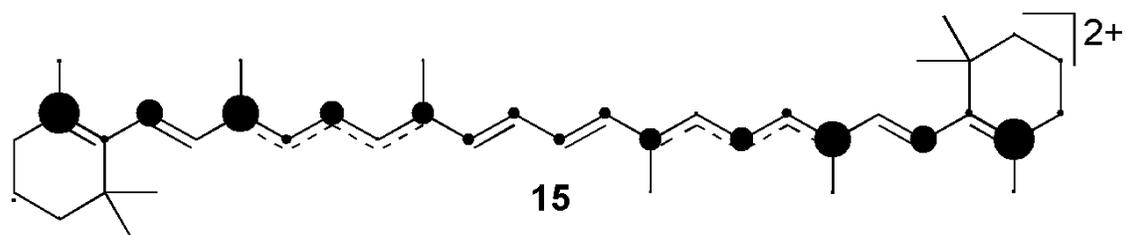
(iii) bond order (single, intermediate, double) may be estimated from ^1H - ^1H coupling constants in comparison with known coupling constants across single and double bonds in appropriate models. Intermediate bonds are illustrated by dotted bonds.

Quenching reactions provide additional information. Carotenoid cations react with various O-, N- and S-nucleophiles to neutral products that may be isolated and identified (VIS, MS, ^1H NMR), the structure of which may support the structure assigned to the parent carbocation by NIR and NMR spectroscopy.¹³⁻¹⁵

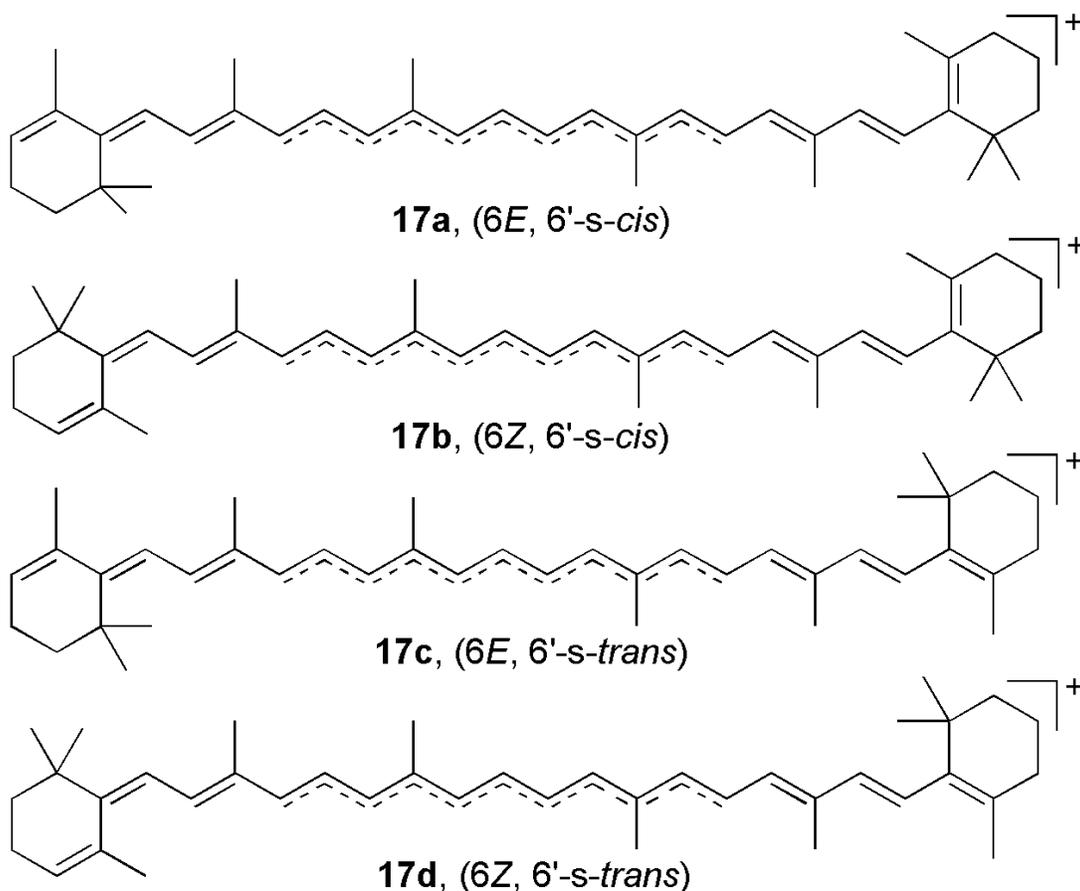
4.2 C₄₀-carotenoid cations

Several mono- and dications have been prepared and characterized. Representative examples are given. β,β -Carotene dication (**15**) was prepared from β,β -carotene (**1**) reacted with BF_3 -dimethyl etherate. Radical species were shown to be present by EPR, supporting a reaction mechanism with two successive one-electron oxidations via the radical cation. This blue cation (λ_{\max} 985 nm in the NIR region) had considerable stability. The estimated charge distribution, compatible with charge repulsion, bond reversal and regions of intermediate bonds should be noted, as well as the conformation of the C-6,7 (C-6',7') single bonds.¹³

The dication **16a-c**, prepared by allylic elimination of β,β -carotene-4,4'-diol, occurred as three stereoisomers according to NMR data. Estimated charge distribution for the all-*E*-isocarotene dication (**16c**) shows similar structural features as the dication **15**.¹⁶



The monocations **17a-d**, prepared by allylic elimination of β,β -caroten-4-ol, consisted of four stereoisomers with end group modifications. The charge distribution for **17a,b** differ from that of the dications with central location in a region of intermediate bonds.^{16,17}



4.3 Cations of carotene analogs with extended polyene chain

The 4-dehydro- β,β -carotenyl monocation (**17**) is the longest delocalized cation fully characterized by NMR spectroscopy, including charge distribution. By regression analysis a soliton half width of $l = 7.8$ was calculated. A soliton is described in the SSH (Su-Schrieffer-Heeger) theory by a charge density wave, with a width defined by the soliton half-width l .

Polyenyl cations with longer polyene systems were prepared from C_{50} -, C_{54} - and C_{60} -carotene analogs, aiming at determining the maximum soliton half width. However, detailed charge distribution data could not be obtained, compatible with the mobility of the free soliton and NMR signal averaging in dynamic systems.¹⁴ The absorption maxima plotted against the number of sp^2 hybridised carbons of shorter polyenyl cations,¹⁸ together with the maxima recorded for the C_{40} monocation, Part 4.2, and the longer polyenyl cations are shown in Figure 2.

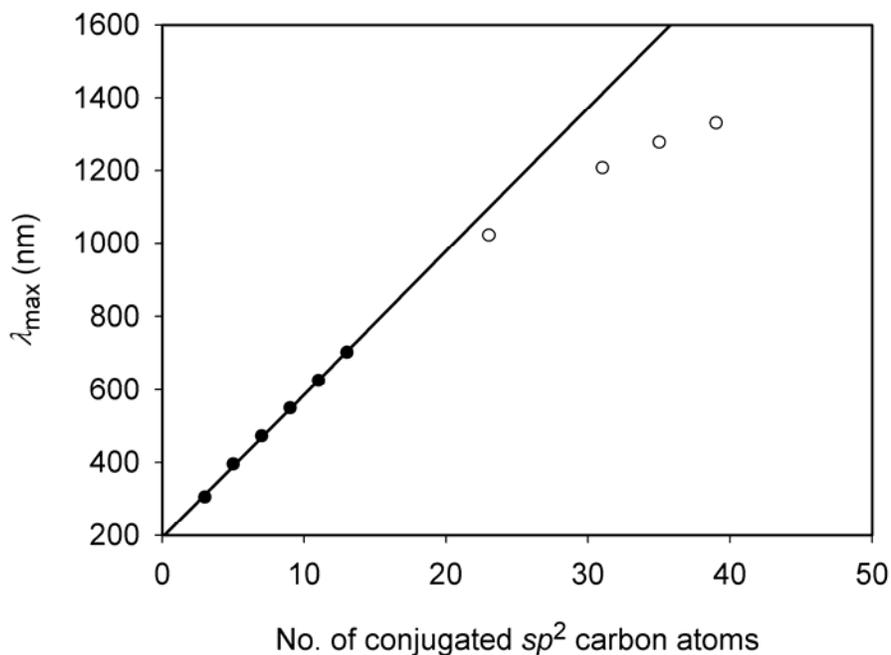
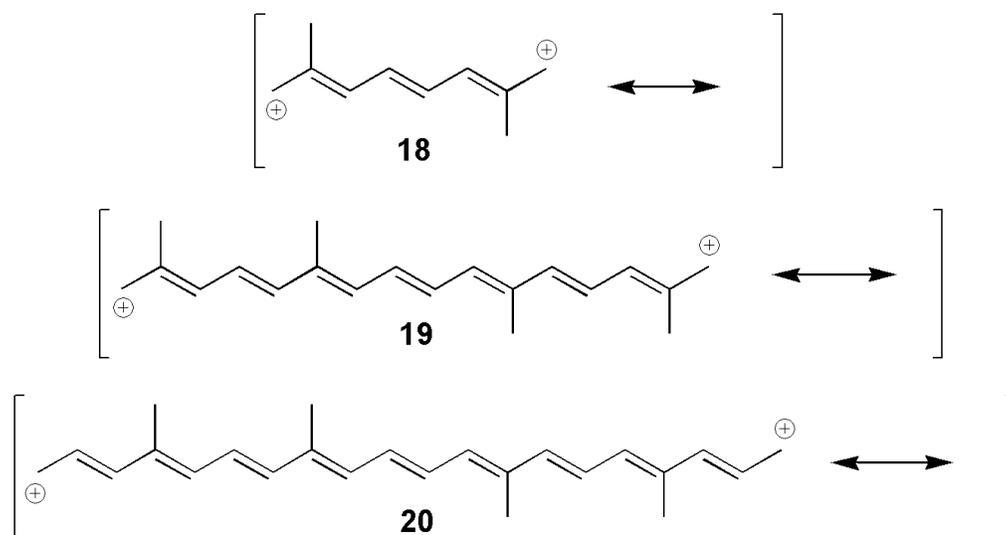


Figure 2. Absorption maxima at room temperature as function of the number of conjugated sp^2 hybridised carbon atoms in polyenyl monocations. ● From ref.¹⁸, in 80-96% sulfuric acid. ○ Polyenes **1**, **14-16**, dissolved in 0.013 M trifluoroacetic acid in CH_2Cl_2 .

Deviations from the linearity of the free electron model^{18,19} is seen already for the monocation **17** with 23 sp^2 carbon atoms. This may be taken as evidence for the manifestation of free solitons in these longer polyenes.

4.4 Shorter polyenylic dications

Carotenoids absorb light below *ca.* 550 nm, blue carotenoproteins, *vide infra*, around *ca.* 600 nm and carotenoid cations have λ_{\max} above 870 nm. In order to fill the gap in the VIS-NIR absorption of carotenoid related compound in the 700-900 nm region, shorter polyenylic dications were synthesized, **18** (C_{10}^+), **19** (C_{20}^+) and **20** (C_{24}^+) and characterized by λ_{\max} 438, 735 and 850 nm, respectively.²⁰



An empirical correlation for λ_{max} and polyene length was developed, where m is the number of sp^2 hybridized carbon atoms.²⁰

Monocations: $\lambda_{\text{max}} = (204.8 + 38.3m)$ nm

Dications: $\lambda_{\text{max}} = (156.0 + 35.4m)$ nm

The wide spectral UV-VIS-NIR absorption covered by carotenoids is illustrated in Figure 3.

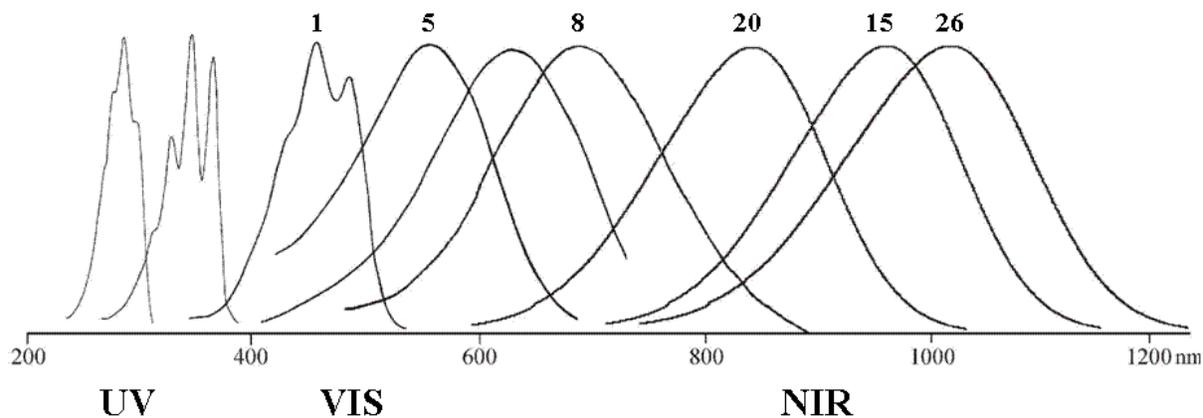
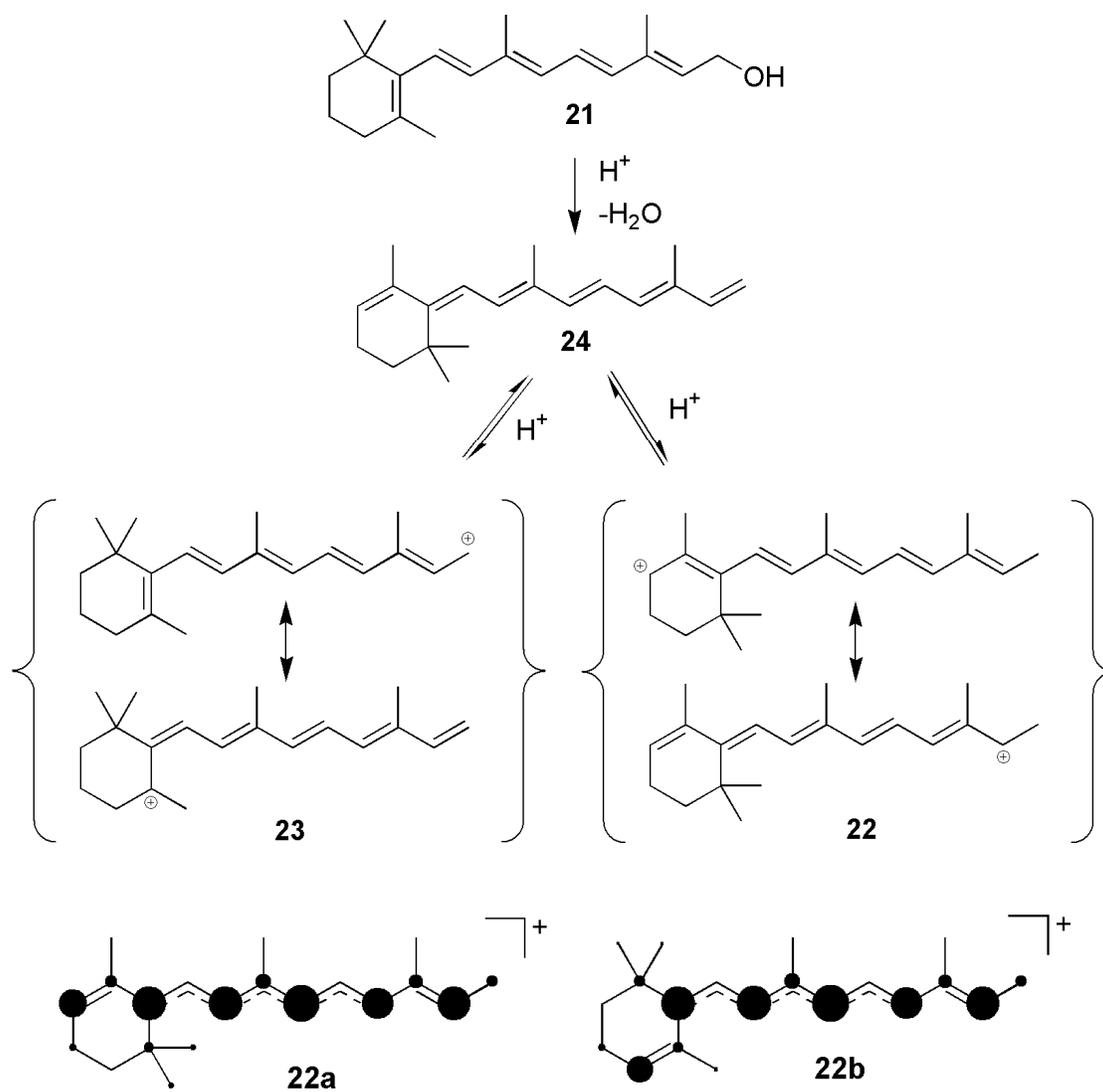


Figure 3. UV/VIS/NIR absorption spectra of selected carotenoids, from left the colorless phytoene (conjugated triene) and phytofluene (conjugated pentaene), β,β -carotene (**1**), violerythrin (**5**), crustacyanin (carotenoprotein), fucoxanthin oxonium ion (**8**), C_{24} -dication (**20**), β,β -carotene dication (**15**), and β,β -carotene-iodine solvent complex (**26**).

5. The Carr-Price Vitamin A Blue Colour Reaction

The classical Carr-Price blue colour reaction for the quantitative determination of Vitamin A content has recently been reinvestigated.²¹⁻²⁴ When Vitamin A (retinol, **21**) is reacted with SbCl_3 (a Lewis acid) in CHCl_3 , an unstable blue colour is developed, which may be quantified spectrometrically (λ_{max} 620 nm). A more stable product with closely similar λ_{max} (622 nm) is obtained upon treatment with Brønsted acid.

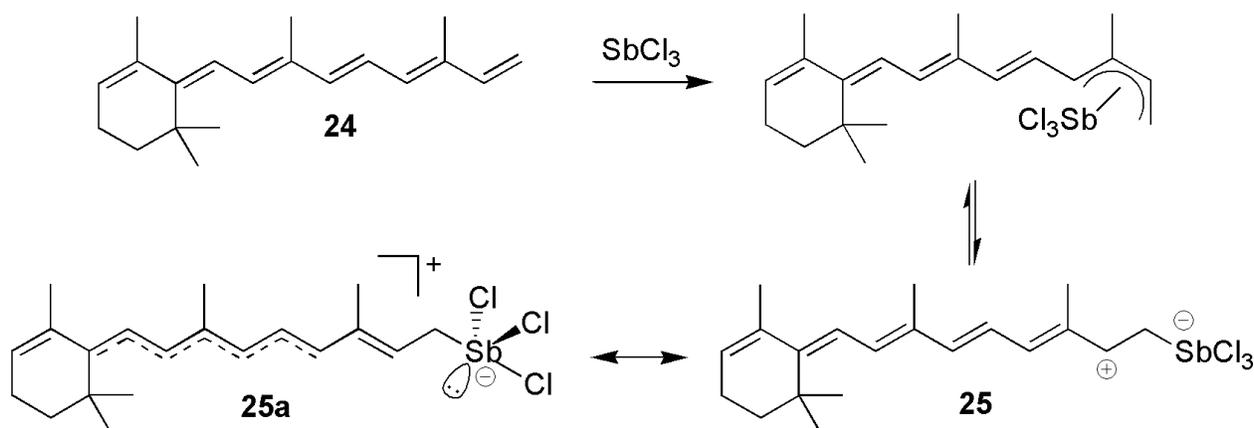
It is now confirmed by NMR data that the product obtained with the protic acid $\text{CF}_3\text{SO}_3\text{H}$ is the anhydroretinyl cation **22** and not the retinyl cation **23**, compatible with a reaction *via* anhydroretinol (**24**),²⁵ Scheme 5. The anhydroretinyl cation consisted of two stereoisomers **22a** and **22b**, differing in the conformation of the C-6,7 bond (carotenoid numbering) with rather even charge distribution in the short polyene system.



Scheme 5

Due to the instability and unsuccessful NMR spectra it was suspected that the Carr-Price product might be a radical cation. However, separate studies showed that retinol (**21**), in contrast to carotenoids, did not readily form radical cations, and it was revealed by light scattering data that strong aggregation could rationalize the results. Addition of sodium methoxide as a nucleophile to the Carr-Price product provided dimeric products, supporting intermolecular retinoid reactions as a major decay pathway for the blue product, rationalizing its observed instability.

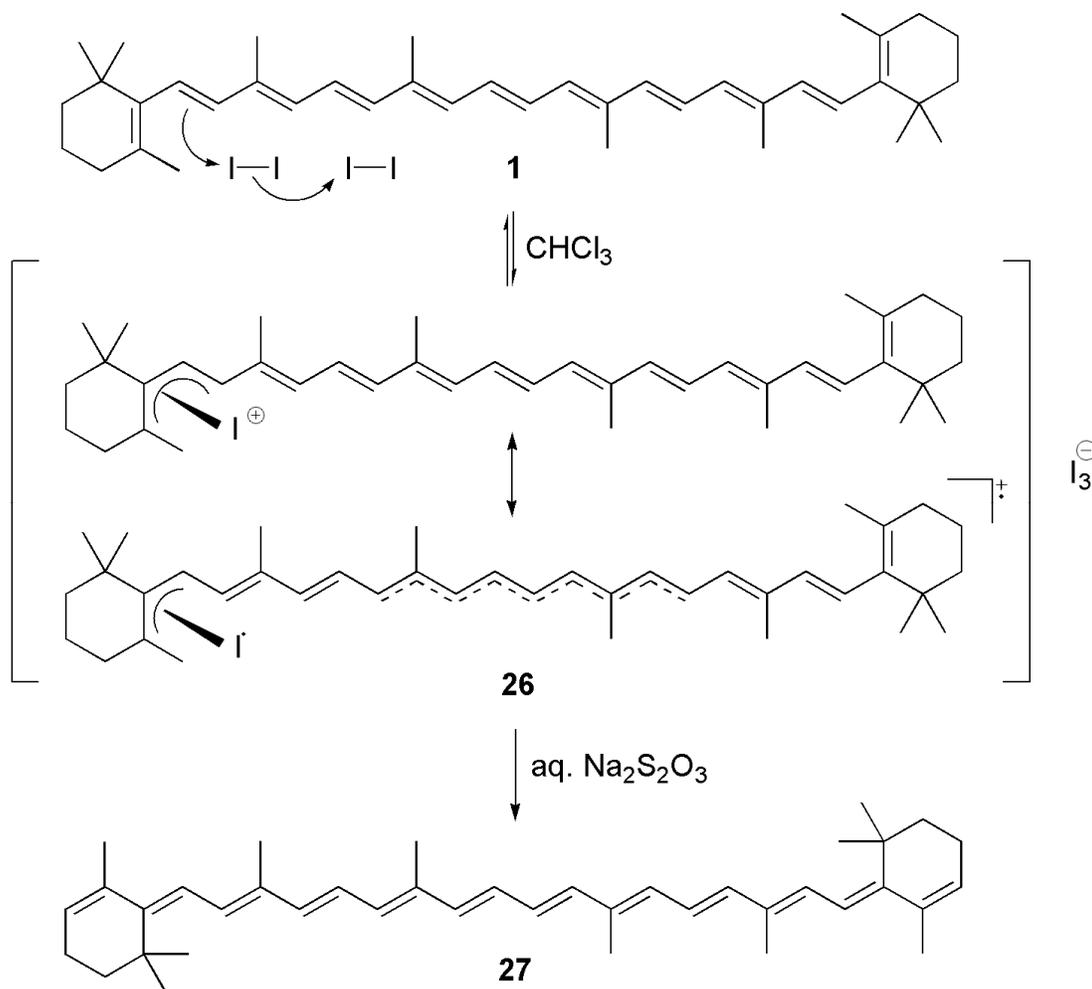
Structure **25a** is suggested for the monomeric form of the Carr-Price blue product, with a trigonal bipyramidal geometry around the antimony atom, including the stereochemically active lone pair, Scheme 6.



Scheme 6

6. Carotenoid Iodine Complexes

Carotenoid iodine complexes have been studied since 1886, and their history was recently reviewed.²⁶ A black solid complex ($\text{C}_{40}\text{H}_{56}\text{I}_4$) from heptane, as well as a blue solvent complex of β,β -carotene (**1**) with iodine in CHCl_3 (λ_{max} 1010 nm) and of β,β -carotene-3,3'-diol have been reexamined by modern methods, including UV/VIS/NIR, IR, MS, EPR, ENDOR and NMR (^1H , ^1H - ^1H COSY, TOCSY, 2D ROESY, ^1H - ^{13}C HSQC and ^1H - ^{13}C HMBC) spectroscopy and chemical reactions monitored by HPLC, TLC and spectral analysis (VIS, MS, ^1H NMR). Iodine is not covalently bound to the carotenoid, and spectroscopic and chemical evidence is rationalized by a β,β -carotene-iodine complex with cationic / radical cationic properties, containing iodine in a π -complex (**26**), Scheme 7.



Scheme 7

The solid complex is considered as the alkane insoluble salt with the same structure **26** as the solvent complex formed in chlorinated solvents.

The major quenching product of the solvent complex with thiosulfite is isocarotene (**27**). All quenching products obtained from the iodine complexes are strongly *E/Z* isomerized, consistent with cationic intermediates.

7. Blue Carotenoproteins

Protein-bound carotenoids are responsible for the mauve-blue-black colour of several tissues in invertebrate animals.²⁷ The carotenoprotein of the lobster carapace has been extensively studied.^{27,28} Two molecules of astaxanthin (**2**; all three optical isomers (3*R*,3'*R*)-, (3*R*,3'*S*, meso)- and (3*S*,3'*S*)-**2** are involved)²⁹ are non-covalently bound to two apoproteins in β-crustacyanin (λ_{max} 587 nm in phosphate buffer), significantly bathochromically shifted relative to astaxanthin (**2**, λ_{max} 480 nm in

acetone). Aggregation of eight β -crustacyanin units provided α -crustacyanin, with further bathochromically shifted λ_{max} (632 nm).²⁷

X-ray studies of β -crustacyanin have established the structure of the apoproteins and the amino acid residues binding to the astaxanthin (**2**) molecule, Figure 4. Water molecules are also involved.^{30,31}

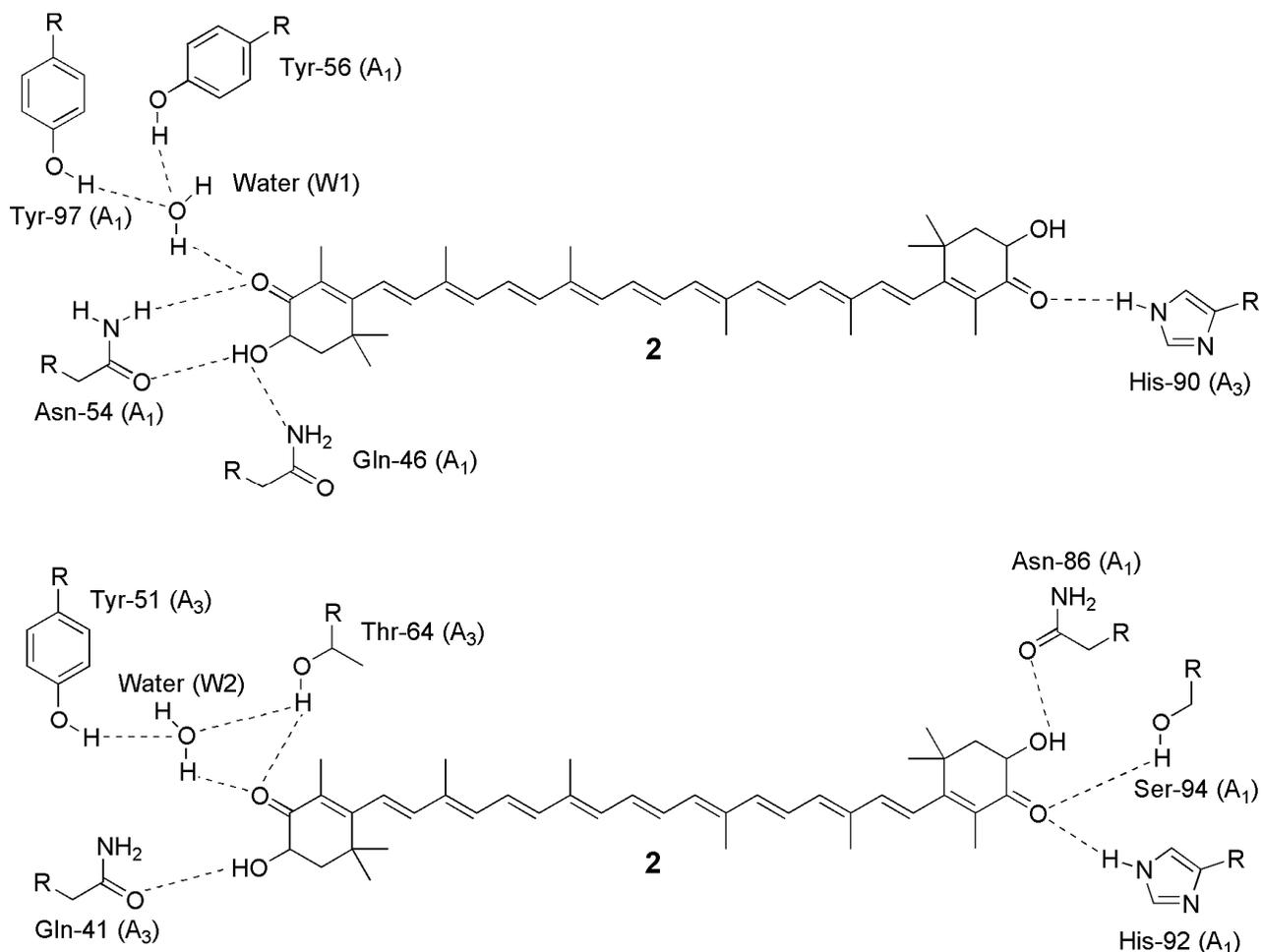


Figure 4. Astaxanthin (**2**) binding in β -crustacyanin. Adapted from X-ray data.³⁰

Prior to the results of the X-ray analysis, the colouration mechanism was believed to occur by protonation of the keto-groups in astaxanthin (**2**), or by a polarisation.^{28,32} From the amino acid environment and pH consideration, the polarisation mechanism was not confirmed. For comparison with the ^{13}C solid state NMR shifts observed for selectively enriched astaxanthin (**2**) bound in recombinated α -crustacyanin,³³ we have investigated by NMR the protonated products obtained by treatment of the simpler model canthaxanthin (**28**) by various Brønsted acids.³⁴ The diprotonated product **29** was not achieved, but ^{13}C chemical shift data could indirectly be estimated from other

protonated products, Figure 5. However, the ^{13}C shifts observed in the recombined α -crustacyanin were not compatible with C=O-protonation,³⁴ consistent with X-ray data for β -crustacyanin.³⁰

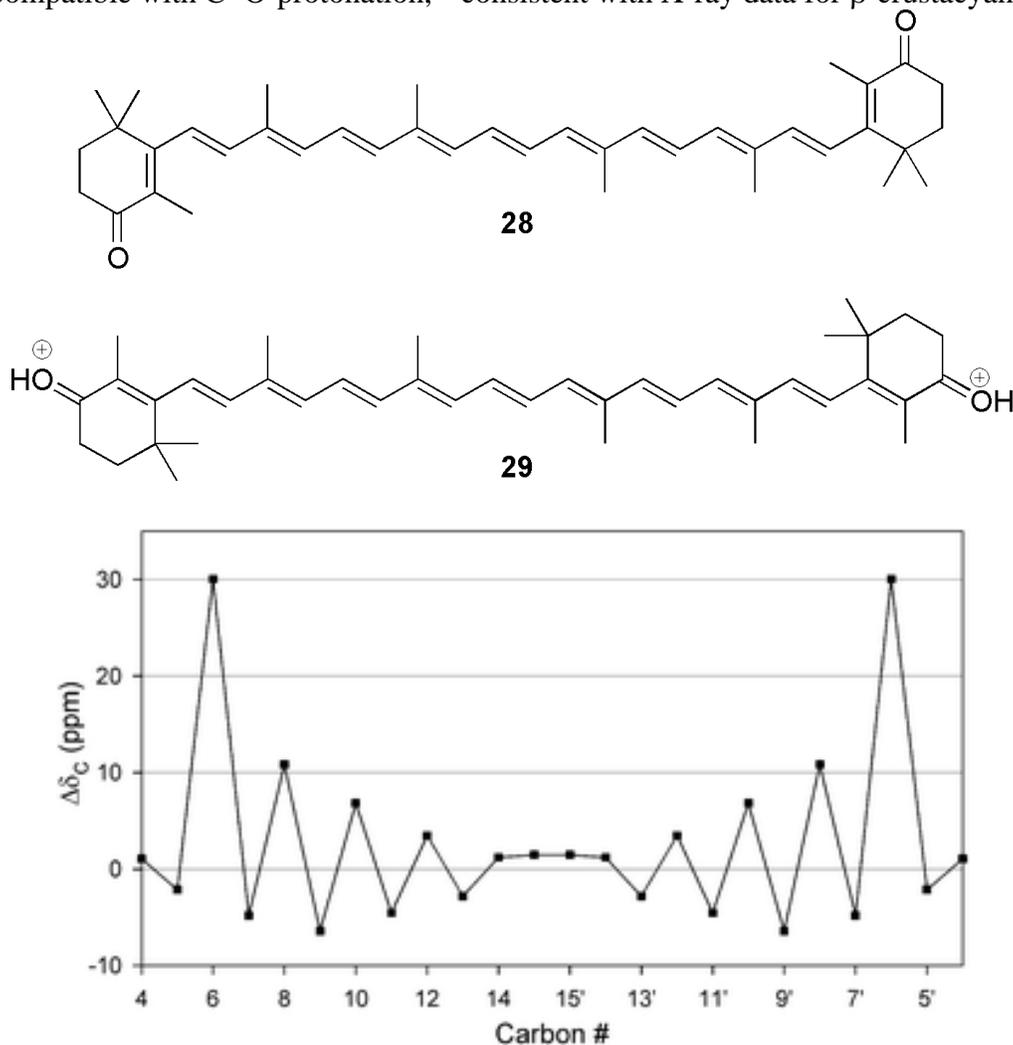
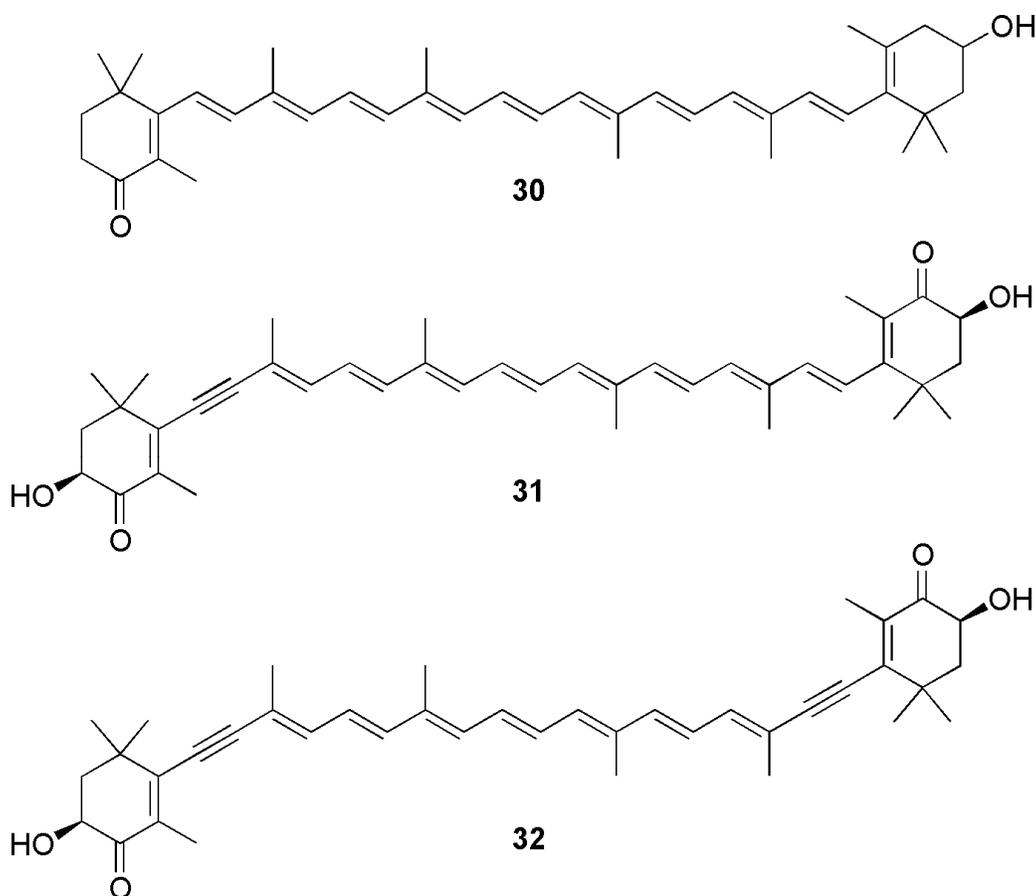


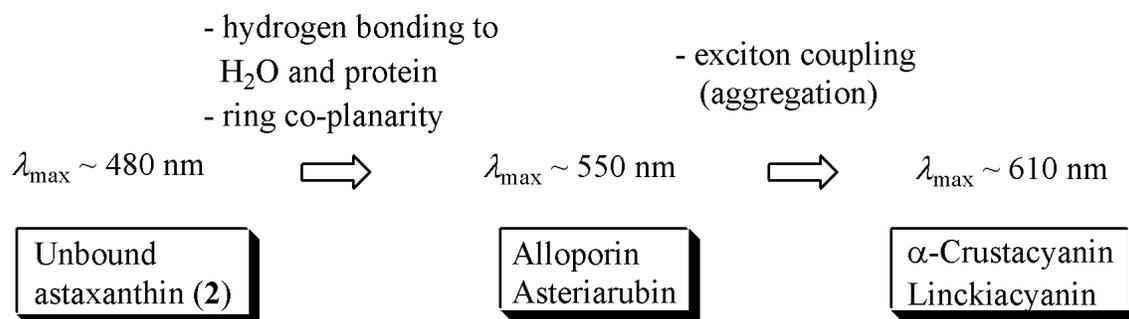
Figure 5. Expected downfield ^{13}C chemical shifts of the hypothetical O-4,4' diprotonated canthaxanthin (29) relative to canthaxanthin (28).

Based on calculations, the co-planarity of the rings with the aliphatic polyene chain should account for about a third of the bathochromic colour shift.³³ However, the major contribution to the bathochromic shift of astaxanthin (2) in the absorption spectra of crustacyanins was explained by an exciton coupling effect. Bathochromic shifts are observed in exciton coupling systems if the angle between two electronic transition moments is larger than 90° .^{35,36} In β -crustacyanin, the two astaxanthin molecules are at a close distance, 7 Å, and form an exciton coupling system with an angle of 120° . Combined with the elongation of the conjugation of the π -system caused by co-planarity of the cyclic end group, illustrated in Figure 4, and the effect of hydrogen bonding of the keto-groups, a calculated value for λ_{max} in β -crustacyanin of 650 nm was found.³³ Further proof of

the importance of aggregation effects for the colour in lobster may be found in the additional bathochromic shift of 45 nm going from β -crustacyanin subunits to α -crustacyanin. Experimental data from femtosecond time-resolved spectroscopic studies on α -crustacyanin were found to be in agreement with dimerisation of astaxanthin (**2**) as the main cause of the bathochromic shift.³⁷ X-ray data for another carotenoprotein, present in the cyanobacterium *Arthrospira maxima*, has revealed the incorporation of monomeric 3'-hydroxyechinenone (**30**). The smaller bathochromic shift (55 nm) of λ_{\max} observed in this carotenoprotein (λ_{\max} 505 nm) is compatible with hydrogen bonding and extended π -conjugation by ring co-planarity, and with exciton effects absent.³⁸ The blue (λ_{\max} 554 nm) carotenoprotein asteriarubin from starfish (*Asterias rubens*) has a single mono- (**31**) or diacetylenic astaxanthin (**32**) molecule per protein oligomer,³⁹ where excitation interaction also may be disregarded.



Also the blue alloporin (λ_{\max} 545 nm) of coral origin contains only one astaxanthin (**2**) molecule per protein monomer.⁴⁰ On the other hand in linckiacyanin (λ_{\max} 612 nm) from the blue starfish *Linckia laevigata*, (3S,3'S)-astaxanthin ((3S,3'S)-**2**) is the dominant carotenoid and excitation interaction between carotenoids has been suggested.⁴¹ A simple hypothesis is advanced here in Scheme 8.



Scheme 8

As pointed out in a recent computational study, the protonation state of the histidine residues shown in Figure 4 is not known from the X-ray analysis, and protonation of astaxanthin (2) by these residues may give rise to bathochromic shifts of the same magnitude as the ones observed. Furthermore, only small bathochromic shifts (5 nm or less in organic solvents) was observed in a study of chiral carotenoid dimers.⁴² Both because of the commercial need for a stable blue colorant, and the remaining uncertainty regarding the colouration mechanism in blue carotenoproteins, efforts should be made to prepare synthetic carotenoid dimers mimicking the stereochemical relationships between the two carotenoid molecules present in β -crustacyanin.

8. Conclusions

The UV/VIS/NIR absorption range of carotenoids has been expanded in recent years, from yellow-orange-red, Figure 3, now including colourless and blue carotenoids. Only the cyclopentenedione derivative violerythrin (5) is a blue, neutral, stable carotenoid, besides a series of blue carotenoproteins. The blue carotenoid oxonium ions, delocalized cations and radical cations (as in the iodine complex) investigated have restricted lifetimes, but offer interesting structural chemistry.

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