Biochemistry

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IUPAC Commission on the Nomenclature of Organic Chemistry and IUPAC–IUB Commission on Biochemical Nomenclature: Tentative Rules for the Nomenclature of Carotenoids

INTRODUCTION: *Definitive Rules for the Nomenclature of Carotenoids* were approved at the IUPAC 14th Conference (London, 1947; *Comptes Rendus*, pp 142–143) and the 16th Conference (New York, 1951; *Comptes Rendus*, p 110). Many recent developments in the carotenoid field have resulted in situations that are not covered adequately by the existing rules; since these rules were adopted, the number of known naturally occurring carotenoids has increased from some 80 to about 300. In 1965, the IUPAC Commission on the Nomenclature of Organic Chemistry and the IUPAC–IUB Commission on Biochemical Nomenclature approved the formation of a Subcommission to revise the carotenoid rules. The subcommission consisted of Professor W. Klyne (representative of CBN; and Chairman), Professor S. Veibel (representative of CNOC), Professor C. Bodea, Professor T. W. Goodwin, Dr. F. Haxo, Dr. O. Isler, Dr. S. Liaaen-Jensen, Dr. W. Powell, Dr. W. Quackenbush, Professor N. A. Sørensen, and Professor B. C. L. Weedon.

The subcommission met in Trondheim in 1966 and considered a number of approaches to the naming of carotenoids.

Subsequently the set of proposals selected by the Trondheim subcommission was refined by an *ad hoc* "working party" (S. Liaaen-Jensen, B. C. L. Weedon, W. Klyne, and L. C. Cross) to give a set of tentative rules for the nomenclature of this group of naturally occurring chemical compounds that is in accord with both the general traditions of biochemical usage and the principles of organic chemical nomenclature.

These rules are now issued jointly by the IUPAC Commission for the Nomenclature of Organic Chemistry[1] and the IUPAC–IUB Commission on Biochemical Nomenclature.[2] Comments are invited; they should be sent to one or other of the commission chairmen or secretaries.[3]

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Rule Carotenoid 1. Class of Compound

Carotenoids are a class of hydrocarbons (carotenes) and their oxygenated derivatives (xanthophylls) consisting of eight isoprenoid units joined in such a manner that the arrangement of isoprenoid units is reversed at the center of the molecule so that the two central methyl groups are in a 1,6 positional relationship and the remaining nonterminal

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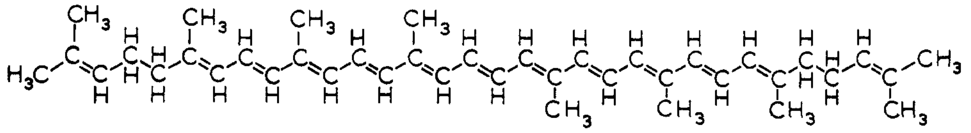
[1] Those who have served on the Commission on the Nomenclature of Organic Chemistry for varying periods during 1967–1971 are the following (present members are shown by an asterisk): P. E. Verkade (Chairman to 1971), N. Lozac'h* (Chairman from 1971), K. Bláha*, L. C. Cross*, G. M. Dyson, S. P. Klesney*, W. Klyne*, K. L. Loening*, H. S. Nutting, J. Rigaudy*, S. Veibel*. Associate members: R. S. Cahn, H. Grünewald*, K. Hirayama*. Observer: K. A. Jensen.

[2] Those who have served on the Commission on Biochemical Nomenclature for varying periods during 1967–1971 are the following (present members are shown by an asterisk): O. Hoffmann-Ostenhof (Chairman), A. E. Braunstein*, W. E. Cohn*, J. S. Fruton, B. L. Horecker*, P. Karlson*, B. Keil*, W. Klyne*, C. Liébecq*, E. C. Slater, B. C. Webb*, W. J. Whelan*. Observer: S. Veibel*.

[3] Chairman (CNOC): Professor N. Lozac'h, Ecole nationale supérieure de Chimie, 5 Avenue d'Edimbourg, F-14 Caen, France; Secretary: S. P. Klesney, Central Report Index, 566 Building, The Dow Chemical Company, Midland, Michigan 48640, U. S. A. Chairman (CBN): Professor O. Hoffman-Ostenhof, Lehrkanzel für Biochemie, Universität Wien, Währingerstrasse 38, A1090 Vienna, Austria; Secretary: Dr. Waldo E. Cohn, Oak Ridge National Laboratory, Post Office Box Y, Oak Ridge, Tennessee 37830, U. S. A.

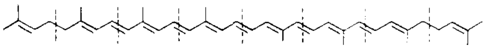
methyl groups are in a 1,5 positional relationship. All carotenoids may be formally derived from the acyclic $C_{40}H_{56}$ structure (I below), having a long central chain of conjugated double bonds, by (i) hydrogenation, (ii) dehydrogenation, (iii) cyclization, or (iv) oxidation, or any combination of these processes.



(I)

The class also includes certain compounds that arise from certain rearrangements or degradations of the carbon skeleton (I) provided that the two central methyl groups are retained. This excludes retinol (vitamin A) and related C_{20} compounds.

For convenience carotenoid formulae are often written in a shorthand form as

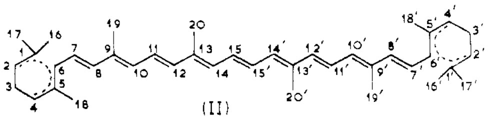


(IA)

(General formula; broken lines indicate formal division into isoprenoid units)

Rule Carotenoid 2. The Stem Name

All specific names are based on the stem name "carotene," which corresponds to the structure and numbering shown in II, where the broken lines at the two terminations are intended only to represent two "double-bond equivalents." Individual compounds may have C_9 acyclic end groups with two double bonds at positions 1,2 and 5,6 (*e.g.*, III) or cyclic end groups (such as IV, V, VI, VII, and VIII).



(II)

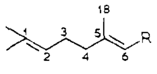
Rule Carotenoid 3. Specific Names; End-Group Designations

3.1. The name of a specific carotenoid hydrocarbon is constructed by adding two Greek letters as prefixes to the stem name "carotene" (defined in Rule Carotenoid 2), these prefixes being characteristic of the two C_9 end groups.

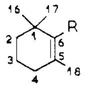
3.2. The prefixes are

Type	Prefix	Formula	Structure
Acyclic	ψ	C_9H_{15}	III
Cyclohexene	β, ε	C_9H_{15}	IV, V
Cyclopentane	κ	C_9H_{17}	VI
Aryl	φ, χ	C_9H_{11}	VII, VIII

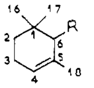
and correspond to the following end-group modifications



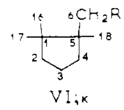
III;ψ



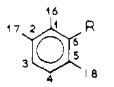
IV;β



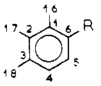
V;ε



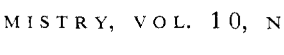
VI;κ



VII;φ



VIII;χ

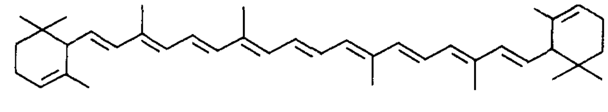


Note: The choice of locants 16 and 17 for the two methyl groups at C-1 is considered in connection with stereochemistry in Rule Carotenoid 12.4.

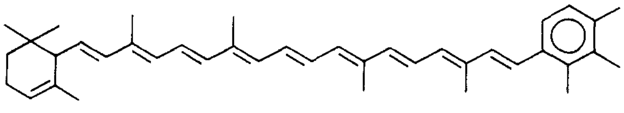
3.3. The Greek-letter prefixes are cited in alphabetical order; the first is separated from the second by a comma, and the second is connected to the stem name by a hyphen.

Note: The Greek-letter alphabetical order is β (beta), ε (epsilon), κ (kappa), φ (phi), χ (chi), ψ (psi).

Examples:



ε,ε-Carotene

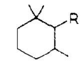


ε,χ-Carotene

Notes: (i) The Greek-letter prefixes are derived: β and ε from the symmetrical carotenoids with the trivial names "β-carotene" and ε-carotene," κ from the symmetrical capsorubin, ψ from ψ-ionone, φ for phenyl, and χ, the next Greek letter after φ. (ii) α, γ, and δ, from the trivial names α-, γ-, and δ-carotene, are not used.

3.4. When, in a modified or degraded carotenoid, an end group can be derived from more than one specific end group, the end group chosen as the basis of the name is that occurring earliest in the alphabetical order (see Rule Carotenoid 3.3).

Example:



is a derivative of the β end group, not the ε end group.

Rule Carotenoid 4. Numbering of Carotenoid Hydrocarbons

The basic system of numbering is that shown in structure II of Rule Carotenoid 2; the end groups are numbered as indicated in Rule Carotenoid 3. If the two end groups are dissimilar, lower (unprimed) numbers are given to that end of the molecule which is associated with the Greek-letter prefix cited first in the name. (All unprimed locants are cited before primed locants.[4])

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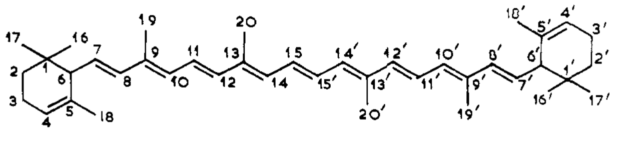
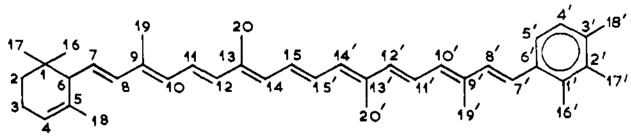
[4] IUPAC Nomenclature of Organic Chemistry (*Pure Appl. Chem. 11*, No. 1 and 2 (1965); Sections A, B, and C published by Butterworths, London, 1971) indicates that, in ranking locants for priority, a primed numeral ranks immediately after the same numeral unprimed. In general organic nomenclature the common practice is therefore to cite locants in the order $x,x,(x+n),(x+n)'$. The established sequence in the carotenoid field is, however, to cite all unprimed numerals before any primed numerals, and this practice is followed in these rules.

Examples:



ε,ε-Carotene



ε,χ-Carotene

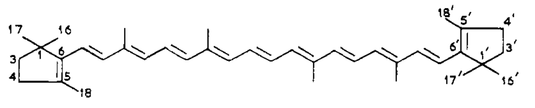
Note: It is recommended that formulae be drawn so that unprimed numbers are on the left-hand side.

Rule Carotenoid 5. Nor Carotenoids and Seco Carotenoids

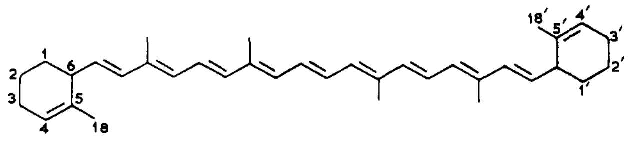
(*a*) *Nor Carotenoids*

Elimination of a CH_3, CH_2, or CH group from a carotenoid is indicated by the prefix "nor," which in all cases is preceded by the locant of the carbon atom that has been eliminated. The prefix is nondetachable. When alternatives are possible, the locant attached to nor is the lowest possible.[5] The basic numbering of the carotenoid is retained in the nor carotenoid.

Examples:



2,2′-Dinor-β,β-carotene

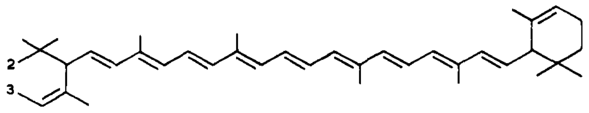


16, 17, 16′, 17′-Tetranor-ε,ε-carotene

(*b*) *Seco Carotenoids*

Fission of the bond between two adjacent carbon atoms (other than carbon atoms 1 and 6) of a cyclic end group), with addition of one or more hydrogen atoms at each terminal group thus created, is indicated by the prefix "seco," the original carotenoid numbering being retained.

Example:



2, 3-Seco-ε, ε-carotene

Rule Carotenoid 6. Changes in Hydrogenation Level

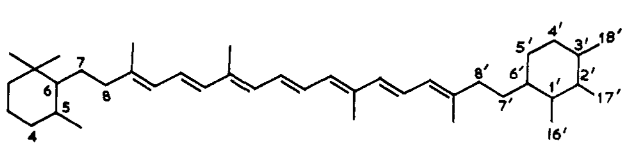
Carotenoid hydrocarbons, including carotenoid acetylenes and allenes, that differ in hydrogenation level from the corresponding carotenoid hydrocarbon defined by Rule Carotenoid 3, are named from the latter by use of the prefixes "hydro" and "dehydro" together with the locants specifying the carbon atoms at which hydrogen atoms have been added or removed.

These prefixes are nondetachable[6] and immediately precede the Greek-letter prefixes denoting the end groups, and, if both occur in one name, are cited in the order: dehydro *before* hydro (multipliers do not affect the order).

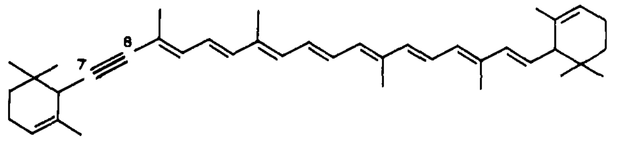
Example: tetradehydrodihydro.

Note: Since, to maintain valency requirements, hydrogen atoms are, formally, always added or removed in pairs these prefixes will always be used with an even-number multiplier, *e.g.*, tetrahydro, didehydro.

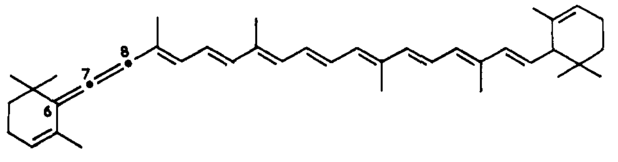
Examples:



5, 6, 7, 8, 1′, 2′, 3′, 4′, 5′, 6′, 7′, 8′-Dodecahydro-β, χ-carotene



7, 8-Didehydro-ε, ε-carotene



6, 7-Didehydro-ε, ε-carotene

Rule Carotenoid 7. Oxygenated Derivatives

7.1. Oxygenated (and other) derivatives of carotenoid hydrocarbons are named by use of suffixes and prefixes according to the rules of general organic chemical nomenclature.[7]

Of the oxygen-containing characteristic groups present, that occurring earliest in the sequence carboxylic acid, ester of carotenoid acid, aldehyde, ketone, alcohol, ester of carotenoid alcohol, is chosen as principal group (following IUPAC Rule C-10.3) and is cited by use of a suffix; all other groups are cited as prefixes.

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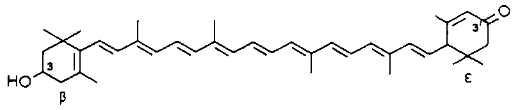
[5] The contrast with steroid usage (IUPAC–IUB 1967 Revised Rules for Nomenclature of Steroids, IUPAC Information Bulletin No. 33, Rule 2S-6; also in *Biochemistry 8*, 2227 (1969), and elsewhere, where the prefix "nor" is associated with the highest permissible number, is to be noted.

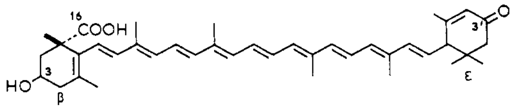
[6] IUPAC Nomenclature of Organic Chemistry (reference in footnote 4), Rule C-16.1, allows the prefix "hydro" to be detachable or nondetachable and the former has become the established usage in general organic chemistry. However, the common practice in carotenoid names is now to use this prefix as nondetachable, a practice that is followed in this set of rules.

[7] IUPAC Rules, Nomenclature of Organic Chemistry (reference in footnote 4), Subsections C-2 to C-4.

Examples:

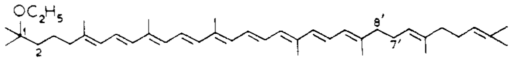


3-Hydroxy-β,ε-caroten-3′-one



3-Hydroxy-3′-oxo-β,ε-caroten-16-oic acid

7.2. A nonbridging ether group is named by use of the appropriate alkoxy or aryloxy prefix (Rule C-211.2).

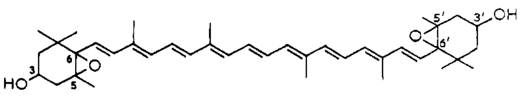


1-Ethoxy-1,2,7′,8′-tetrahydro-ψ,ψ-carotene

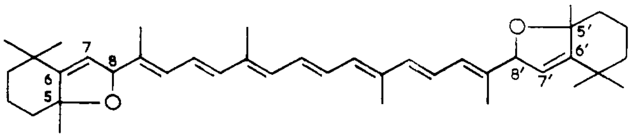
7.3. Oxygen bridges are indicated by use of the prefix "epoxy"; this prefix is preceded by the locants of the two carbon atoms that form the bridgeheads of the oxygen bridge.

Note: The prefix "epoxy" denotes replacement, by an oxygen bridge, of a hydrogen atom at each of two carbon atoms already otherwise connected to one another. An epoxide, notionally formed by adding an oxygen atom to a double bond, is therefore an epoxydihydro derivative of the original compound.

Examples:



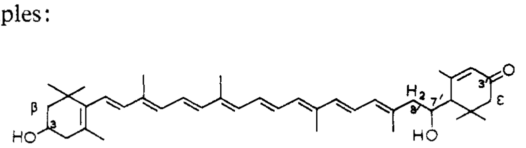
5,6:5′,6′-Diepoxy-5,6,5′,6′-tetrahydro-β,β-carotene-3,3′-diol



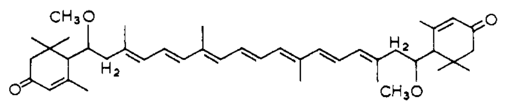
5,8:5′,8′-Diepoxy-5,8,5′,8′-tetrahydro-β,β-carotene

7.4. Compounds that may be formally derived from a carotenoid hydrocarbon by the addition of the elements of water (H, OH) or of methanol (H, OCH_3) to a double bond are named as "hydroxydihydro" or "methoxydihydro" derivatives.

Examples:



3,7′-Dihydroxy-7′,8′-dihydro-β,ε-caroten-3′-one

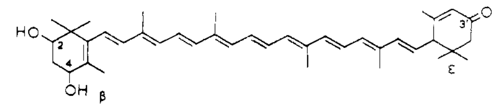


7,7′-Dimethoxy-7,8,7′,8′-tetrahydro-ε,ε-carotene-3,3′-dione

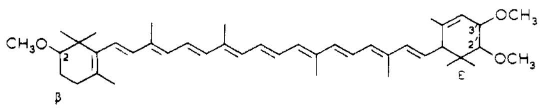
Rule Carotenoid 8. Numbering of Oxygenated Derivatives

8.1. If the two C_9 end groups of the parent carotenoid hydrocarbon are dissimilar, their oxygenated derivatives are numbered according to Rule Carotenoid 4, *i.e.*, the end group designated by the Greek letter occurring earlier in the Greek alphabet receives unprimed locants.

Examples:



2,4-Dihydroxy-β,ε-caroten-3′-one



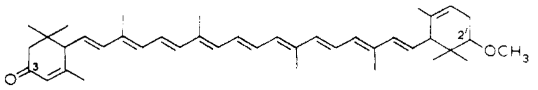
2,2′,3′-Trimethoxy-β,ε-carotene

8.2. (a) If the two C_9 end groups of the parent carotenoid hydrocarbon are identical, then the lowest* locant possible is assigned to the principal group, cited as suffix.

(b) If more than one of the group chosen to be cited as suffix is present, the numbering is determined by the principle of lowest locants** applied to the suffixes.

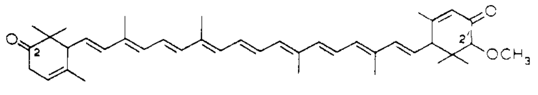
(c) If no group qualifies to be cited as suffix, then the numbering is determined by the principle of lowest locants* for all groups cited as prefixes.

Examples:
(a)



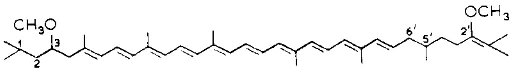
2′-Methoxy-ε,ε-caroten-3-one
(not 2-Methoxy-ε,ε-caroten-3′-one)

(b)



2′-Methoxy-ε,ε-carotene-2,3′-dione
[not 2-Methoxy-ε,ε-carotene-3,2′-dione; see para (b)]

(c)



3,2′-Dimethoxy-1,2,5′,6′-tetrahydro-ψ,ψ-carotene
[not 2,3′-Dimethoxy-1′,2′,5,6-tetrahdro-ψ,ψ-carotene,
1,2,3,2′,5′,6′ having priority over 2,5,6,1′,2′,3′; see para (c)]

Notes: * In the carotenoid series *all* unprimed numbers are cited *before* primed numbers and the former are therefore considered as "lower than" primed numbers, *e.g.*, 2,6,6,1′,2′,6′, etc. ** When series of locants containing the same number of terms are compared term by term, that series is "lowest" which contains the lowest number on the occasion of the first difference [IUPAC Rule C-13.11(e), footnote].

Rule Carotenoid 9. *retro* Nomenclature

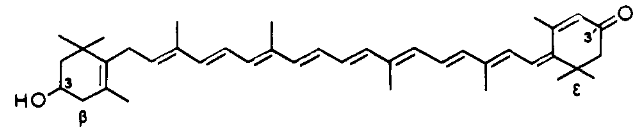
9.1. The prefix "*retro*" (printed in italics) and a pair of locants are used to indicate a shift, by one position, of *all* single and double bonds of the conjugated polyene system delineated by the pair of locants.

9.2. The pair of locants precedes the prefix *retro*. The first locant is that of the carbon atom that has lost a proton, the second that of the carbon atom that has gained one.

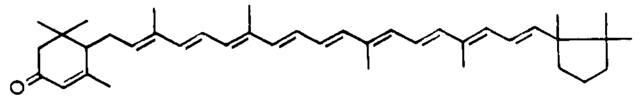
9.3. The prefix and its accompanying locants are placed immediately before, and hyphenated to, the Greek-letter prefixes of the name defined according to Rule Carotenoid 3.

9.4. The prefix and its associated locants are not detachable from the names defined according to Rule Carotenoid 3.

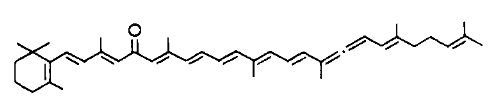
Examples:



3-Hydroxy-6′,7-*retro*-β,ε-caroten-3′-one



6′,7-*retro*-ε,κ-Caroten-3-one



8′,11-*retro*-β,ψ-Caroten-11-one

Rule Carotenoid 10. Apo Nomenclature

It is often necessary to designate derivatives in which the carbon skeleton has been shortened by the formal removal of fragments from one or both ends of a carotenoid.

10.1. The unitalicized prefix "apo," preceded by a locant, is used to indicate that all of the molecule beyond the carbon atom corresponding to that locant has been replaced by hydrogen atoms. A side-chain methyl group is not considered to be "beyond" the carbon atom to which it is attached.

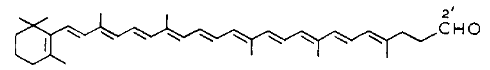
10.2. The prefix and its locant immediately precede the specific name (Rule Carotenoid 3) unless the locant associated with the prefix "apo" is greater than 5, in which case there is no need to give a Greek-letter end-group designation for that end of the molecule.

10.3. For purposes of numbering, etc., an end that has been shortened by 5 or less skeletal carbon atoms is considered a ψ (acyclic) end group.

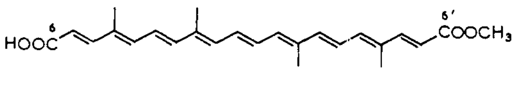
10.4. The prefix diapo, preceded by two locants, is used to indicate removal of fragments from both ends of the molecule.

10.5. If, in a diapo compound, the two ends of the carotenoid skeleton have been shortened unequally, the lower locant associated with the prefix "diapo" is unprimed.

Examples:



2′-Apo-β,ψ-caroten-2′-al

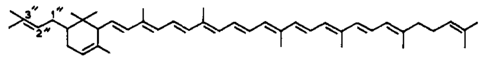


Methyl hydrogen 6,6′-diapocarotene-6,6′-dioate (*trans*-Bixin)

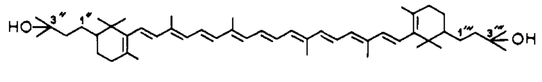
Rule Carotenoid 11. Higher Carotenoids

The higher carotenoids are a class of hydrocarbons and their oxygenated derivatives consisting of *more than* eight isoprenoid units joined in a manner similar to that of the C_{40} carotenoids. They are named as mono- or disubstituted C_{40} carotenoids. The numbering of the normal carotenoid is retained.

Examples:



2-(3-Methyl-2-butenyl)-ε,ψ-carotene

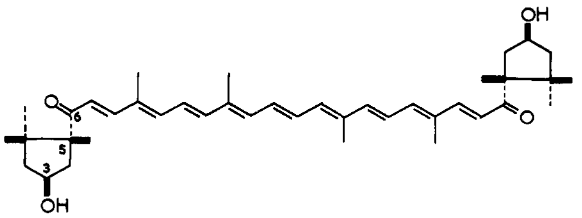


2,2′-Bis(3-methylbutyl)-β,β-carotene-3″,3‴-diol
or
2,2′-Bis(3-hydroxy-3-methylbutyl)-β,β-carotene

Rule Carotenoid 12. Stereochemistry

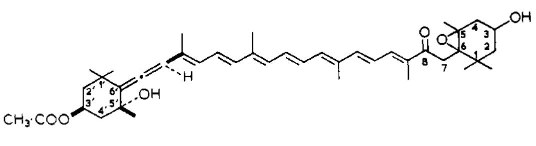
12.1. *Absolute Configuration at Chiral Centers.* The absolute configuration at chiral centers is designated by use of the *RS* convention,[8] the symbols being placed, with the corresponding locants, before the carotenoid name.

Example:



(3*S*,5*R*,3′*S*,5′*R*)-3,3′-Dihydroxy-κ,κ-carotene-6,6′-dione
(Capsorubin)

12.2. *Absolute Configuration of Allenic Compounds.* The absolute configuration around allene groups will be similarly designated, when known.



(3′*S*,5′*R*,6′*R*)-3′-Acetoxy-5,6-epoxy-3,5′-dihydroxy-6′,7′-didehydro-5,6,7,8,5′,6′-hexahydro-β,β-caroten-8-one (Fucoxanthin)

12.3. *Geometrical Configuration around Double Bonds.* The stem name "carotene" implies trans configuration about all double bonds unless the contrary is indicated. Following the designation of absolute configuration (if any), geometrical configuration is indicated by citing the double bond or bonds with a cis configuration.

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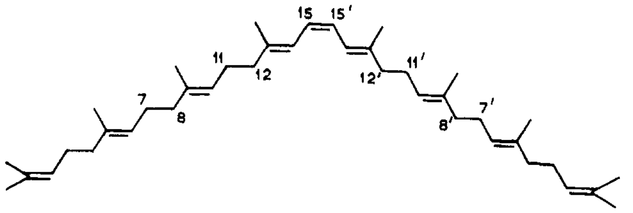
[8] For a discussion on the *RS* convention and the use of thickened lines, broken lines, wavy lines, and wedges in displayed formulae, see IUPAC Tentative Rules for the Nomenclature of Organic Chemistry, Section E, Fundamental Stereochemistry, IUPAC Information Bulletin No. 35, p 68; also published in *J. Org. Chem. 35*, 2849 (1970), and elsewhere.

Example:



Natural phytoene = 15-*cis*-7,8,11,12,7',8',11',12'-octahydro-ψ,ψ-carotene

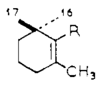
At trisubstituted double bonds the term cis refers to the relative position of the two substituents forming parts of the main chain of carbon atoms.

Example: natural bixin = methyl hydrogen 9'-*cis*-6,6'-diapocarotene-6, 6'-dioate.

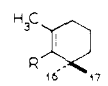
In the absence of definite information on geometrical configuration, cis isomers may be distinguished by prefixes such as neo A, neo U, etc. (*cf.* Zechmeister, "Cis–Trans Isomeric Carotenoids, Vitamins A and Arylpolyenes," Springer-Verlag, Vienna, 1962).

The stereochemical prefixes *E* and *Z* (see footnote to Rule 12.1 and *J. Amer. Chem. Soc. 90*, 509 (1968)) may be used, especially when the prefixes cis and trans might lead to ambiguity.

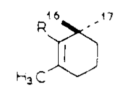
12.4. *Numbering of gem-Dimethyl Groups at C-*1. In an end group of β or ε type, the two methyl groups attached to C-1 are distinguished as follows: when the potential chirality is as shown in formula A, *i.e.*, with the polyene chain (R) to the right of C-1, the methyl groups *below* and *above* the plane of the paper are numbered 16 and 17, respectively; if, with the polyene chain (R) to the left, the end group is as shown in B¹, then these designations are unaltered; if the end group is as shown in B², then they are reversed.



(A)

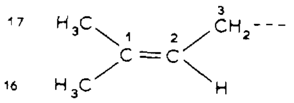


(B¹)



(B²)

In an acyclic end group, the methyl group that is trans to the main skeletal chain is numbered 16 and the methyl group that is cis is numbered 17, as shown in C.



(C)

Rule Carotenoid 13. Trivial Names

The preceding rules are designed to define precisely the structure of a given carotenoid by its name. Use of the semisystematic names derived from these rules will greatly assist communication between scientists and enable work to be more readily retrieved from the literature.

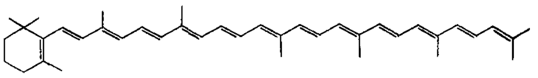
The appendix contains a list of some trival names currently in use for naturally occurring carotenoids; it also gives their semisystematic names and structures. These trival names will be of value in natural-product and biochemical work, but their use in systematic organic work should be restricted. If trivial names are used in a paper, the semisystematic name should always be given, in parentheses or in a footnote at the first mention.

While the need to coin a new trivial name must occasionally arise (*e.g.*, because the structure of the compound is unknown), the list in the appendix should not be unnecessarily enlarged, nor should simple derivatives of known carotenoids be named by use of the trivial name or given a new one.

APPENDIX: Some Naturally Occurring Carotenoids Having Trivial Names (the examples in this appendix are based on an exhaustive list of naturally occurring carotenoids prepared by Dr. O. Straub, which forms Chapter XII of a book "Carotenoids," O. Isler, Ed., Birkhäuser, Basel and Stuttgart, 1971. The two commissions are greatly indebted to Dr. Isler, Dr. Straub, and their colleagues of F. Hoffmann-La Roche Co. Ltd., Basel, for providing this list of compounds. The list includes a few compounds whose natural occurrence or structure is doubtful, but whose systematic names illustrate particular points of nomenclature).

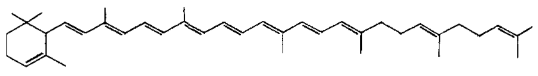
Hydrocarbons

3',4'-Didehydro-β,ψ-carotene



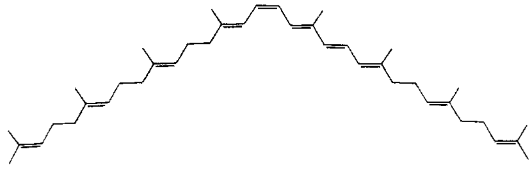
Torulene

7',8'-Dihydro-ε,ψ-carotene



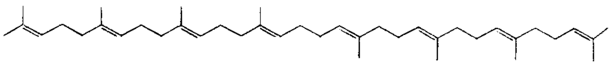
α-Zeacarotene

15-*cis*-7,8,11,12,7',8'-Hexahydro-ψ,ψ-carotene



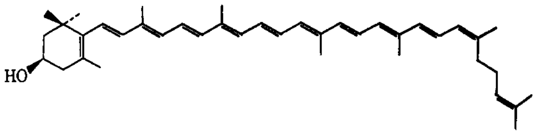
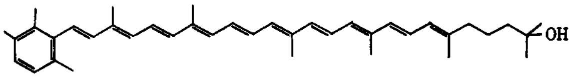
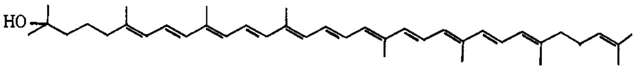
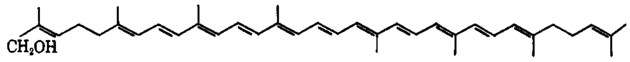
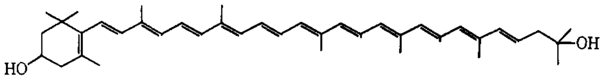
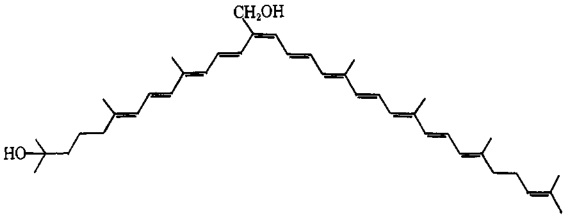
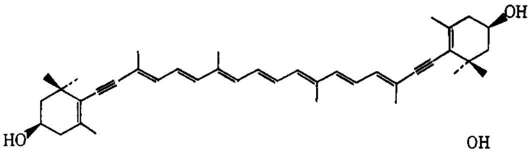
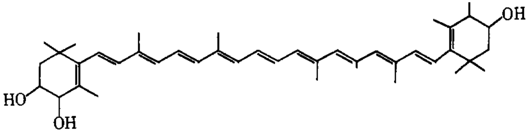
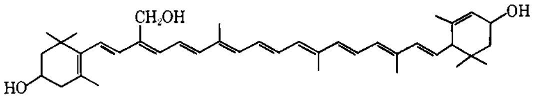
Phytofluene
Hexahydrolycopene

7,8,11,12,15,7',8',11',12',15'-Decahydro-ψ,ψ-carotene

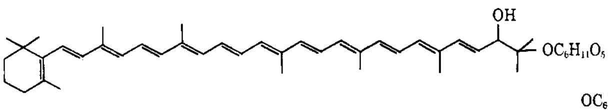
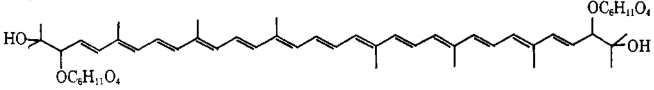


Lycopersene

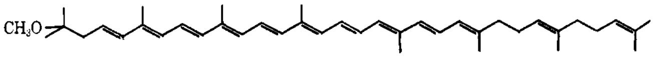
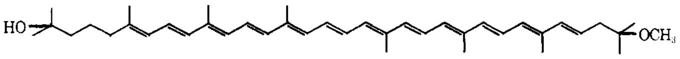
Alcohols

(3*R*)-5′-*cis*-β,ψ-Caroten-3-ol		Gazaniaxanthin
1′,2′-Dihydro-φ,ψ-caroten-1′-ol		OH-Chlorobactene
1,2-Dihydro-ψ,ψ-caroten-1-ol		Rhodopin
ψ,ψ-Caroten-16-ol		Lycoxanthin
3′,4′-Didehydro-1′,2′-dihydro-β,ψ-carotene-3,1′-diol		Saproxanthin
13-*cis*-1,2-Dihydro-ψ,ψ-carotene-1,20-diol		Rhodopinol Warmingol
(3*R*,3′*R*)-7,8,7′,8′-Tetradehydro-β,β-carotene-3,3′-diol		Alloxanthin Cynthiaxanthin Pectenoxanthin Cryptomonaxanthin
β,β-Carotene-3,4,3′,4′-tetrol		Crustaxanthin
β,ε-Carotene-3,19,3′-triol		Loroxanthin

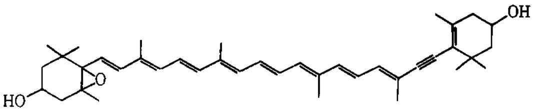
Glycosides

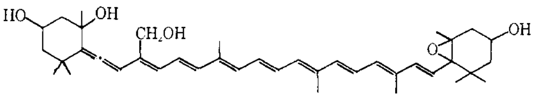
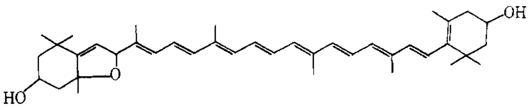
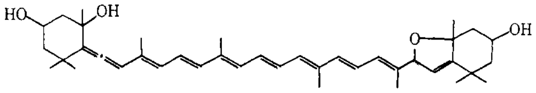
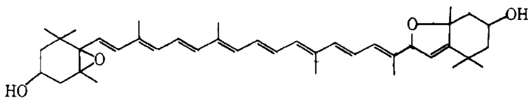
1′-(β-D-Glucopyranosyloxy)-3′,4′-didehydro-1′,2′-dihydro-β,ψ-caroten-2′-ol		Phleixanthophyll
2,2′-Bis(β-L-rhamnopyranosyloxy)-3,4,3′,4′-tetradehydro-1,2,1′,2′-tetrahydro-ψ,ψ-carotene-1,1′-diol		Oscillaxanthin

Ethers

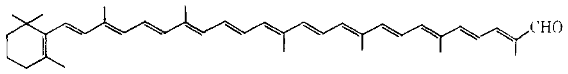
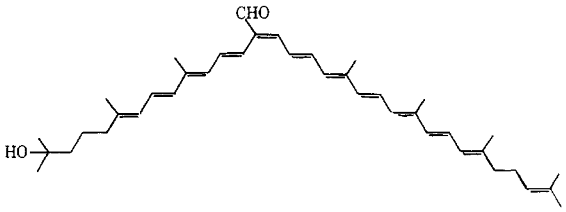
1-Methoxy-3,4-didehydro-1,2,7′,8′-tetrahydro-ψ,ψ-carotene		Spheroidene
1′-Methoxy-3′,4′-didehydro-1,2,1′,2′-tetrahydro-ψ,ψ-caroten-1-ol		Rhodovibrin

Epoxides

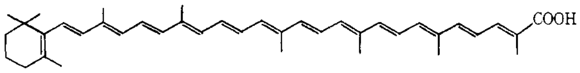
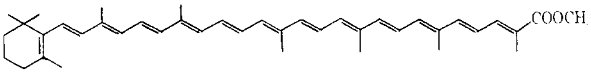
5,6-Epoxy-7′,8′-didehydro-5,6-dihydro-β,β-carotene-3,3′-diol		Diadinoxanthin

5′,6′-Epoxy-6,7-didehydro-5,6,5′,6′-tetrahydro-β,β-carotene-3,5,19,3′-tetrol		Vaucheriaxanthin
5,8-Epoxy-5,8-dihydro-β,β-carotene-3,3′-diol		Mutatoxanthin Citroxanthin Zeaxanthin furanoxide
5′,8′-Epoxy-6,7-didehydro-5,6,5′,8′-tetrahydro-β,β-carotene-3,5,3′-triol		Neochrome Foliachrome Trollichrome
5,6:5′,8′-Diepoxy-5,6,5′,8′-tetrahydro-β,β-carotene-3,3′-diol		Luteoxanthin

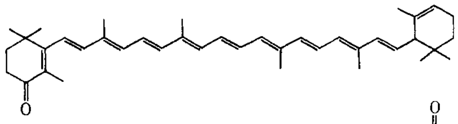
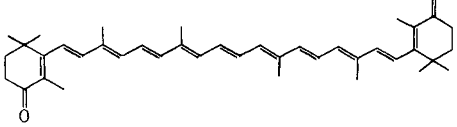
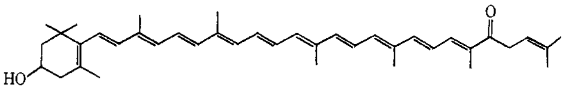
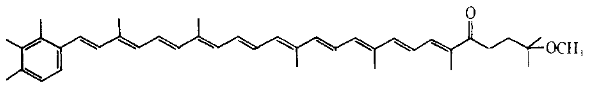
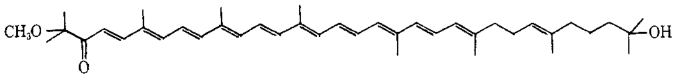
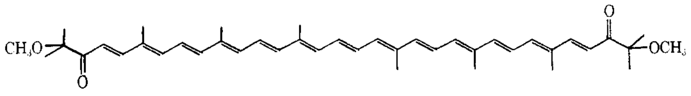
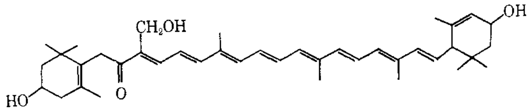
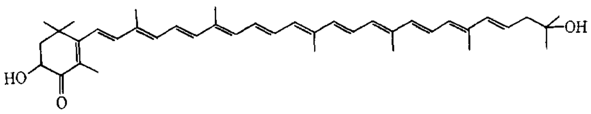
Aldehydes

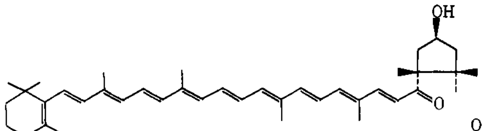
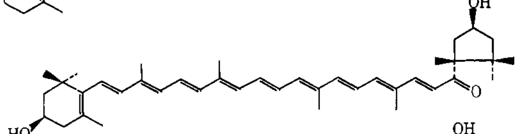
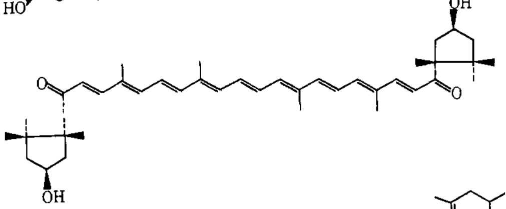
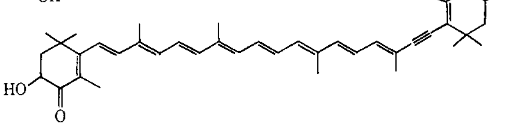
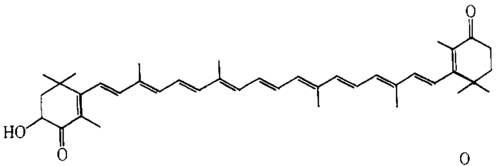
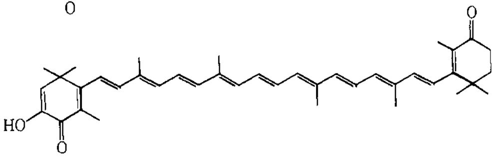
3′,4′-Didehydro-β,ψ-caroten-16′-al		Torularhodinaldehyde
13-*cis*-1-Hydroxy-1,2-dihydro-ψ,ψ-caroten-20-al		Rhodopinal Warmingone

Acids and Acid Esters

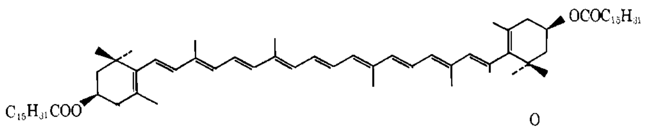
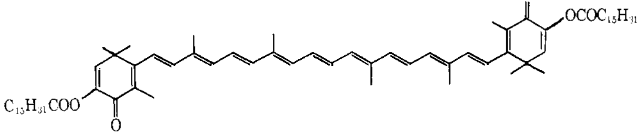
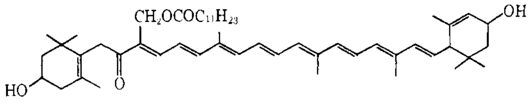
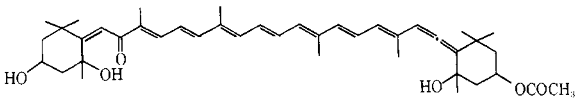
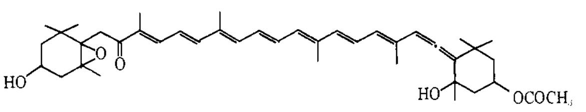
3′,4′-Didehydro-β,ψ-caroten-16′-oic acid		Torularhodin
Methyl 3′,4′-didehydro-β,ψ-caroten-16′-oate		Torularhodin methyl ester

Ketones

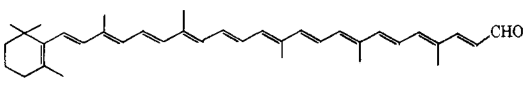
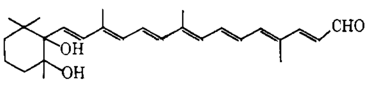
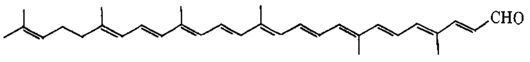
β,ε-Caroten-4-one		Phoenicopterone
β,β-Carotene-4,4′-dione		Canthaxanthin Aphanicin Chlorellaxanthin
3-Hydroxy-β,ψ-caroten-4′-one		Rubixanthone
1′-Methoxy-1′,2′-dihydro-χ,ψ-caroten-4′-one		Okenone
1′-Hydroxy-1-methoxy-3,4-didehydro-1,2,-1′,2′,7′,8′-hexahydro-ψ,ψ-caroten-2-one		Hydroxyspheriodenone
1,1′-Dimethoxy-3,4,3′,4′-tetradehydro-1,2,1′,2′-tetrahydro-ψ,ψ-carotene-2,2′-dione		2,2′-Diketospirilloxanthin
3,19,3′-Trihydroxy-7,8-dihydro-β,ε-caroten-8-one		Siphonaxanthin
3,1′-Dihydroxy-3′,4′-didehydro-1′,2′-dihydro-β,ψ-caroten-4-one		Flexixanthin

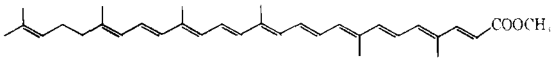
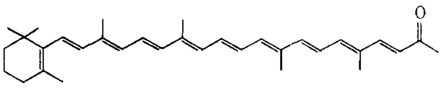
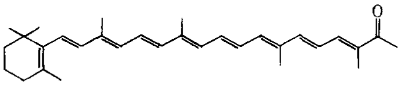
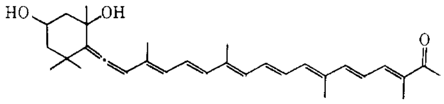
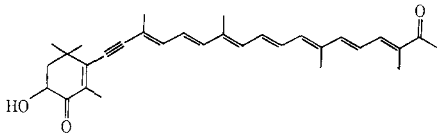
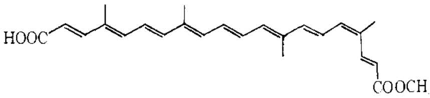
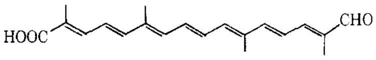
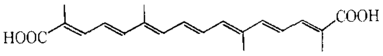
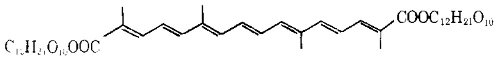
(3′*S*,5′*R*)-3′-Hydroxy-β,κ-caroten-6′-one		Cryptocapsin
(3*R*,3′*S*,5′*R*)-3,3′-Dihydroxy-β,κ-caroten-6′-one		Capsanthin
(3*S*,5*R*,3′*S*,5′*R*)-3,3′-Dihydroxy-κ,κ-carotene-6,6′-dione		Capsorubin
3,3′-Dihydroxy-7′,8′-didehydro-β,β-caroten-4-one		Pectenolone
3-Hydroxy-β,β-carotene-4,4′-dione		Adonirubin Phoenicoxanthin 3-OH-Canthaxanthin
3-Hydroxy-2,3-didehydro-β,β-carotene-4,4′-dione		Phoeniconone Dehydroadonirubin

Esters of Alcohols

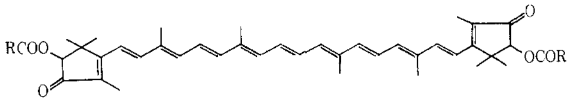
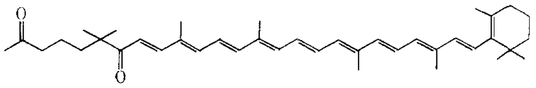
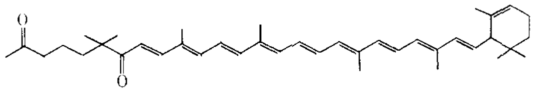
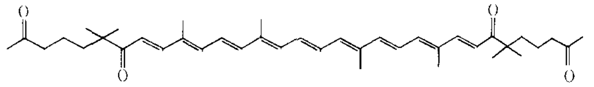
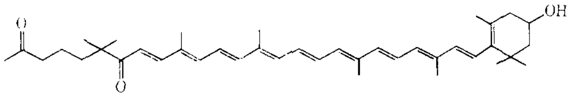
(3*R*,3′*R*)-3,3′-Bispalmitoyloxy-β,β-carotene or (3*R*,3′*R*)-β,β-carotene-3,3′-diol dipalmitate		Zeaxanthin dipalmitate Physalien
3,3′-Bispalmitoyloxy-2,3,2′,3′-tetradehydro-β,β-carotene-4,4′-dione or 3,3′-dihydroxy-2,3,2′,3′-tetradehydro-β,β-carotene-4,4′-dione dipalmitate		Astacein
3,3′-Dihydroxy-19-lauroyloxy-7,8-dihydro-β,ε-caroten-8-one or 3,19,3′-trihydroxy-7,8-dihydro-β,ε-caroten-8-one 19-laurate		Siphonein
3′-Acetoxy-3,5,5′-trihydroxy-6′,7′-didehydro-5,8,5′,6′-tetrahydro-β,β-caroten-8-one		Isofucoxanthin
3′-Acetoxy-5,6-epoxy-3,5′-dihydroxy-6′,7′-didehydro-5,6,7,8,5′,6′-hexahydro-β,β-caroten-8-one		Fucoxanthin

Apo Carotenoids

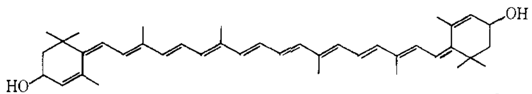
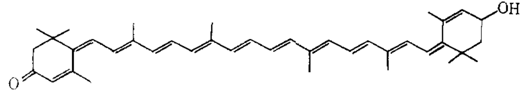
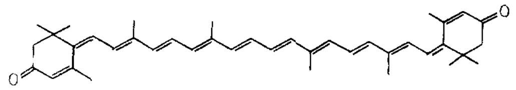
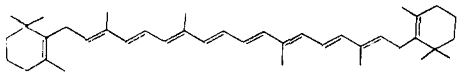
3′,4′-Didehydro-2′-apo-β-caroten-2′-al		β-Apo-2′-carotenal
5,6-Dihydroxy-5,6-dihydro-10′-apo-β-caroten-10′-al		Azafrinaldehyde
6′-Apo-ψ-caroten-6′-al		Apo-2-lycopenal Apo-6′-lycopenal

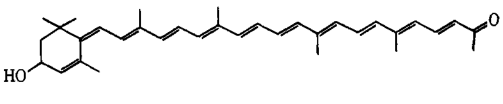
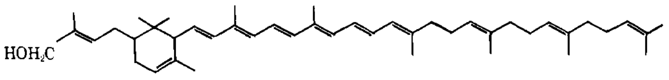
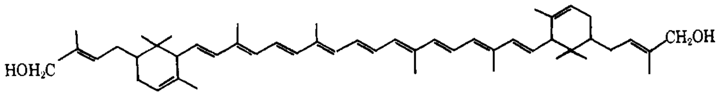
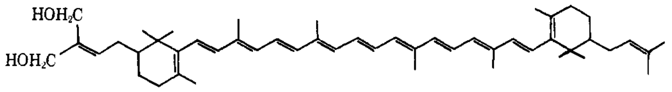
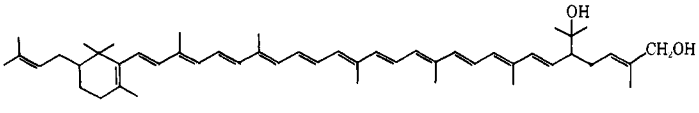
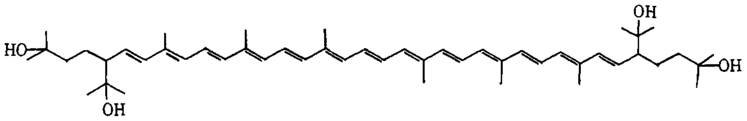
Methyl 6′-apo-ψ-caroten-6′-oate		Methyl apo-6′-lycopenoate
5′,6′-Dihydro-5′-apo-β-caroten-6′-one or 5′,6′-dihydro-5′-apo-18′-nor-β-caroten-6′-one or 6′-methyl-6′-apo-β-caroten-6′-one		Citranaxanthin
7′,8′-Dihydro-7′-apo-β-caroten-8′-one or 8′-methyl-8′-apo-β-caroten-8′-one		Sintaxanthin
3,5-Dihydroxy-6,7-didehydro-5,6,7′,8′-tetrahydro-7′-apo-β-caroten-8′-one or 3,5-dihydroxy-8′-methyl-6,7-didehydro-5,6-dihydro-8′-apo-β-caroten-8′-one		Paracentrone
3-Hydroxy-7,8-didehydro-7′,8′-dihydro-7′-apo-β-carotene-4,8′-dione or 3-hydroxy-8′-methyl-7,8-didehydro-8′-apo-β-carotene-4,8′-dione		Hopkinsiaxanthin
6′-Methyl hydrogen 9′-*cis*-6,6′-diapocarotene-6,6′-dioate		Bixin
8′-Oxo-8,8′-diapo-8-carotenoic acid		Crocetinsemialdehyde
8,8′-Diapo-8,8′-carotenedioic acid		Crocetin
Digentiobiosyl 8,8′-diapo-8,8′-carotenedioate		Crocin

Nor and Seco Carotenoids

3,3′-Bisacyloxy-2,2′-dinor-β,β-carotene-4,4′-dione		Actinioerythrin
5,6-Seco-β,β-carotene-5,6-dione or 5′,6′-seco-β,β-carotene-5′,6′-dione		Semi-β-carotenone
5,6-Seco-β,ε-carotene-5,6-dione		Semi-α-carotenone
5,6:5′,6′-Diseco-β,β-carotene-5,6,5′,6′-tetrone		β-Carotenone
3′-Hydroxy-5,6-seco-β,β-carotene-5,6-dione or 3-hydroxy-5′,6′-seco-β,β-carotene-5′,6′-dione		Triphasiaxanthin 3-Hydroxysemi-β-carotenone

retro Carotenoids and *retro* Apo Carotenoids

4′,5′-Didehydro-4,5′-*retro*-β,β-carotene-3,3′-diol		Eschscholtzxanthin
3′-Hydroxy-4′,5′-didehydro-4,5′-*retro*-β,β-caroten-3-one		Eschscholtzxanthone
4′,5′-Didehydro-4,5′-*retro*-β,β-carotene-3,3′-dione		Rhodoxanthin
7,8-Dihydro-8,7′-*retro*-β,β-carotene or 7,7′-dihydro-β,β-carotene		No trivial name

3-Hydroxy-5′-methyl-4,5′-*retro*-5′-apo-β-caroten-5′-one or 3-hydroxy-4,5′-*retro*-5′-apo-β-caroten-5′-one		Tangeraxanthin
	Higher Carotenoids	
2-(4-Hydroxy-3-methyl-2-butenyl)-7′,8′,11′,12′-tetrahydro-ε,ψ-carotene		Nonaprenoxanthin
2,2′-Bis(4-hydroxy-3-methyl-2-butenyl)-ε,ε-carotene		Decaprenoxanthin
2-[4-Hydroxy-3-(hydroxymethyl)-2-butenyl]-2′-(3-methyl-2-butenyl)-β,β-carotene		C.p. 450
2′-(4-Hydroxy-3-methyl-2-butenyl)-2-(3-methyl-2-butenyl)-3′,4′-didehydro-1′,2′-dihydro-β,ψ-caroten-1′-ol		C.p. 473
2,2′-Bis(3-hydroxy-3-methylbutyl)-3,4,3′,4′-tetradehydro-1,2,1′,2′-tetrahydro-ψ,ψ-carotene-1,1′-diol		Bacterioruberin

Pyridoxal 5′-Phosphate as a Site-Specific Protein Reagent for a Catalytically Critical Lysine Residue in Rabbit Muscle Phosphoglucose Isomerase*

Klaus D. Schnackerz† and Ernst A. Noltmann‡

ABSTRACT: Rabbit muscle phosphoglucose isomerase has been found to be inhibited by pyridoxal 5′-phosphate at concentrations as low as 0.2 mM. When tested in the presence of substrate, this inhibition is competitive, with a K_i of 2.4 mM. The inhibition can be changed to an irreversible inactivation by reduction of the enzyme–pyridoxal 5′-phosphate complex with sodium borohydride. Both a substrate equilibrium mixture and 6-phosphogluconate (a competitive inhibitor of phosphoglucose isomerase) protect the enzyme against this inactivation. The reaction of pyridoxal 5′-phosphate with phosphoglucose isomerase is highly specific since free pyridoxal, 5-deoxypyridoxal, and other aldehydes showed an inhibitory effect only at concentrations up to several 100-fold higher than required for pyridoxal 5′-phosphate. The unreduced phosphoglucose isomerase–pyridoxal 5′-phosphate complex displays a difference spectrum with a maximum near 430 nm, typical for Schiff base formation that accompanies pyridoxal 5′-phosphate–protein interaction. Also, after reduction by sodium borohydride, the absorption spectrum shows a maximum at 325 nm characteristic for ε-aminophosphopyridoxyllysine. Finally, N^6-pyridoxyllysine has been identified in acid hydrolysates of the reduced phosphoglucose isomerase–pyridoxal 5′-phosphate complex. The high degree of specificity permitted the use of pyridoxal 5′-phosphate, in combination with reduction by sodium borohydride, as a stoichiometric inhibition titrant. This approach yielded a stoichiometry of 2 mole equiv of pyridoxal 5′-phosphate bound per mole of enzyme, extrapolating to 100% loss of enzymatic activity. The results are interpreted as lending strong support to the previously proposed involvement of a critical ε-aminolysyl group in the phosphoglucose isomerase reaction.

Studies dealing with the effect of pH and temperature on the kinetic parameters of rabbit muscle phosphoglucose isomerase have recently led to a proposal for the reaction mechanism of this enzyme in which both a histidine and a lysine residue participate in the catalytic process (Dyson and Noltmann, 1968). Ultraviolet difference spectroscopy, performed

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* From the Department of Biochemistry, University of California, Riverside, California 92502, and from the Physiologisch-Chemisches Institut der Universität Würzberg, Germany. *Received July 16, 1970.* This is paper 15 in a series dealing with studies on phosphohexose isomerases. The work was supported in part by U. S. Public Health Service Research Grant AM 07203 and by Cancer Research Funds of the University of California.

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