

Review

Key to Xenobiotic Carotenoids

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Abstract: A listing of carotenoids with heteroatoms (X = F, Cl, Br, I, Si, N, S, Se, Fe) directly attached to the carotenoid carbon skeleton has been compiled. The 178 listed carotenoids with C,H,X atoms demonstrate that the classical division of carotenoids into hydrocarbon carotenoids (C,H) and xanthophylls (C,H,O) has become obsolete.

Keywords: carotenoids; xanthophylls; fluorocarotenoids; chlorocarotenoids; bromocarotenoids; iodocarotenoids; silicon carotenoids; nitrogen carotenoids; sulfur carotenoids; selenium carotenoids; iron carotenoids

1. Introduction

The number of natural occurring carotenoids registered in the relevant books on the topic has increased continuously: 19 carotenoids in 1934, 67 in 1948, 273 in 1971, 563 in 1987, 750 in 2004 [1–5]. The importance of the Carotenoids Handbook is evident for all those working frequently or occasionally with carotenoids. However, the extensive compilation of natural occurring carotenoids has ignored the existence of the numerous xenobiotic carotenoids [6]. The impact of the Carotenoids Handbook is overwhelming insofar that carotenoids with atoms other than C,H,O are barely thinkable. Carotenoids are still classified in two groups: *carotenes* (polyenes containing C,H) and *xanthophylls* (polyenes with C,H,O), and the occurrence of carotenoids with other atoms was not contemplated by the existing nomenclature rules. In contrast, the Natural Product Reports dedicate a specific chapter to steroids with heteroelements, sulfur flavonoids and heteroatom-substituted carbohydrates have been reviewed. [7–10]. Admittedly, no hetero-carotenoids have been detected so far in Nature, but

nonetheless, it is not incongruous to expect carotenoids from sea organisms to incorporate Cl (compounds **5Cl-8Cl** in the list) [11]; the interactions between selenium and carotenoids support speculations about the existence of combination products [12–14]. After all, heterocarotenoids may not keep forever their status as xenobiotic compounds, though by then, xenophobia towards xenobiotic carotenoids may be encountered. In a historical review on the “Development of Carotenoid Chemistry 1922–1991” the first Br-, N- and S-carotenoids (**4Br-9Br**, **2N**, **12S**) were ignored [15]. When the author’s first manuscript on carotenoid thioketones (**1S-3S**) was rejected by the referees, the honorary co-author commented the rejection as the logical consequence of working with bizarre compounds. The syntheses of selenium carotenoids (**1Se-7Se**) were regarded by some of the author’s colleagues as a completely useless, ill-famed and ill-smelling occupation. Strangely enough, the summarizing speaker at the end of a carotenoid conference intentionally omitted to mention the author’s presentation on S, N and Se carotenoids. Fortunately, these narrow-minded discriminatory prejudices have now tended to cease; heterocarotenoids have found applications impossible to achieve with “normal” carotenoids, e.g., **2S**, **15S**, **3Se**, **12N**, **46N** [16–19].

Despite the increasing interest in xenobiotic carotenoids, searching the databases for these compounds often results in zero hits. The unawareness of heterocarotenoids may perhaps be the reason for avoidable syntheses. The molecular wire carotenoid thiol **15S** was prepared in several steps [16]. Carotenoid thione **2S**, synthesized previously from a commercial carotenoid in a one-step synthesis, could probably have been more appropriate for the investigation [20]. Even an author sensitized to xenobiotic carotenoids witnessed ignorance; compounds **25N**, **27N**, **29N** were not cited in a paper on carotenoid oxime hydrochlorides **19N-22N** [21,22]. Unfamiliarity with heterocarotenoids is possibly the cause for further lack of mention, e.g., nitrile carotenoid **6N** was patented in 1990 and published in 2011 without referring to previous work from 1988; thienyl carotenoid **3⊙S**, first reported in 1981, was not cited when the compound was resynthesized 20 years later (for an explanation of the designation **3⊙S** see Section 4: Nomenclature).

This thematic issue of *Molecules* on “Carotenoids” now offers the opportunity to compile a systematic listing of xenobiotic carotenoids. This inventory is a first attempt to take these carotenoids out of their obscurity.

2. Historical Remarks

Carotenoids became eye-catching in 1906 with the invention of chromatography by Tswett and got scientific consecration with the first determination of their molecular formula by Willstätter in 1907 [23,24]. During the period of structure determination the first nitrogen carotenoids were prepared as analytical derivatives (oxime, semicarbazone) [25,26]. Bromo and sulfur carotenoids were synthesized in 1958 and 1959 and chloro carotenoids in 1976 [27–29]. The synthesis of carotenoid amines was not successful until 1990 [30–32]. The most heterogenic carotenoids are probably iron carbonyl compounds **5Fe-7Fe**. The common Greek-letter termed cyclic end groups are now increasingly being replaced by heterocycles.

3. Selection Criteria

Polyenes with a branched polyene chain >C20 capped with different cyclic or acyclic end groups and with heteroatoms covalently bound to the carbon carotenoid were considered. Thus, compounds with a heteroatom linked via oxygen to the carotenoid scaffold were omitted (e.g., phosphates). Adhering strictly to the isoprenoid nature of carotenoids would not allow including the interesting aza compound **37N** [33]. This compound has been perceived as an azine of retinal, but is much more attractive when viewed as a diazapolyene. Various carotenoid derivatives prepared for analytical purposes (oximes, hydrazones amides *etc.*) are not mentioned [34,35], unless the derivative has also found an application extending characterization, e.g., canthaxanthin oxime was skipped, canthaxanthin oxime hydrochloride **21N** as a surface active hydrophilic carotenoid was included [22]. Some carotenoids are drawn in the concise all-*trans* form, since the dimension of the actual *cis*-isomers would be too space demanding, e.g., **32N** and **33N**. The main concern of the recording, the heteroatom character of the compound, is not affected by this presentation.

In a departure from *Molecules*' normal style, reference registration in the compound list follows the example of the handbooks excluding article title and search-irrelevant data on the length of a paper. The references for the individual compounds are not exhaustive. A reader interested in a particular compound should perform a structural search in a database to receive complete and updated citations.

There certainly exist more xenobiotic carotenoids than presented in the list. Many hetero-carotenoids, especially from the patent literature, are not recorded owing to search problems or involuntary neglect. Such compounds ought to be included in a forthcoming extended register. Enlarging the selection criteria to <C20 chains, to xenobiotic C,H,O carotenoids, considering heteroatoms outside the carotenoid carbon skeleton sphere and taking into account ionic bounded heteroatoms is desirable for future compilation [36,37]. It would furthermore be valuable to have at hand a complete directory of isotope-substituted carotenoids (D, T, ¹³C, ¹⁴C) [38–40]. A catalog of modified carotenoids (e.g., long chain carotenoids, carotenoid dimers, carotenoids with deviated conjugation, hydrophilic carotenoids) and of compounds where carotenoids are part of other molecule classes (e.g., carotenoid lipids, antioxidant combinations) would likewise be desirable [41–51].

4. Nomenclature

The designation “xenobiotic carotenoids” is synonymously used with the term “heterocarotenoids”. Whereas “heterocarotenoids” may appear more precise, the prefix hetero- is too strongly linked with heterocyclic chemistry and could create confusing expressions such as heterocyclic heterocarotenoids. Xenobiotic is, at present, the more explanatory designation.

Applying the nomenclature rules to xenobiotic carotenoids can lead to unintelligible descriptions; consequently, many authors have avoided naming their products, e.g., **11CI-15CI** [52]. Keeping in mind that a short trivial name engenders more associative information than a (semi)systematic designation, some names in the list may appear randomly chosen or meaningless. A name search in a database will, therefore, often be unsuccessful, e.g., the name dicyano-C48:15 for **9N** is certainly not canonical, but articulates the essential information: a dicyano substituted carotenoid of 48 C with 15 conjugated double bonds. The exact name would hide this evidence. In any case, the interested

reader should certainly scrutinize the carotenoids visually and not by their appellation, and a structure search in a database is, therefore, recommended. The structures are approximately listed according to increasing structural complexity; however, the relation to a parent compound was considered more important than complexity ranking.

Aryl carotenoids have been recorded separately within a heteroatom section. Natural occurring aryl carotenoids display trimethylbenzene ϕ - or χ - end groups. Phenyl end groups without methyl are identified as either 16,17,18-trinor- ϕ - or 16,17,18-trinor- χ -; nevertheless, the letter ϕ is preferred, in analogy to the widely used short form of ϕ for phenyl [53]. Thus, all carotenoids with a benzene ring are termed ϕ -carotenoids; the ϕ -ring positions are indicated as recommended by the nomenclature rule.

The compounds were arbitrarily numbered; the numbers are not intended to reflect the appointed personal identification digits used in the Key to Carotenoids and the Carotenoids Handbook [4,5]. Carotenoids with heterocycles were, for example, enumerated as x \odot S, \odot S indicating a cycle with sulfur.

The catalog of xenobiotic carotenoids definitely proves that the term *xanthophyll* has become obsolete [54]. Applying the classical two level differentiation – hydrocarbon carotenoids (C, H) and xanthophylls (C,H,O)—simply implies denying the existence of the listed 178 carotenoids. The use of *xanthophyll* is therefore discouraged and should be replaced by *oxygen carotenoids*; such a designation is unequivocally extendable to *sulfur (nitrogen, halogen...) carotenoids*.

5. Conclusions

Xenobiotic carotenoids have been synthesized for a long time but have remained largely unnoticed by carotenoid chemists. Many of those who work with these compounds may not consider themselves carotenoid chemists. Heteroatoms have helped carotenoids to leave their terrain of origin: xenobiotic carotenoids merit the same appreciation as biotic carotenoids.

Acknowledgement

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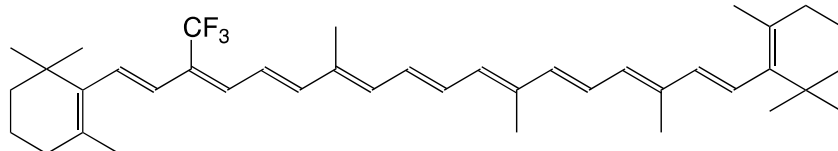
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6. List of Xenobiotic Carotenoids

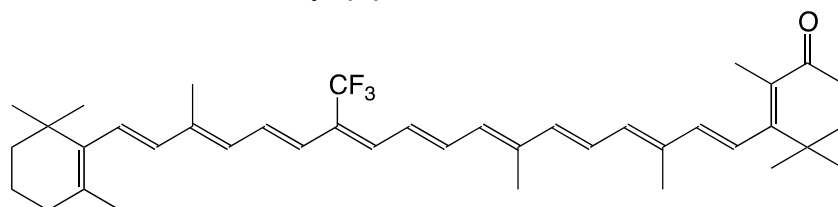
6.1. Halogen-Carotenoids

6.1.1. Fluorine

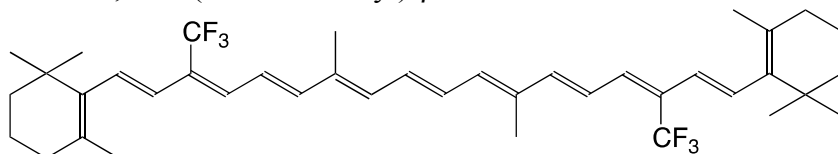
F

1F 9-trifluoromethyl- β,β -carotene $C_{40}H_{53}F_3$ 

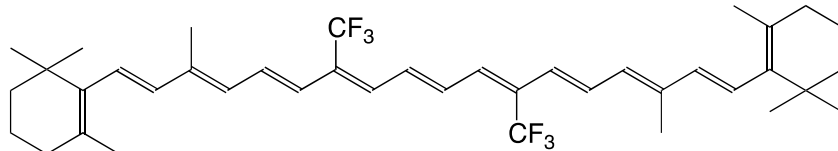
D. Hoischen, L.U. Colmenares, I. Koukhareva, M. Ho, R.S.H. Liu, *J. Fluorine Chem.* **1999**, *97*, 165

2F 13-trifluoromethyl- β,β -carotene $C_{40}H_{53}F_3$ 

D. Hoischen, L.U. Colmenares, I. Koukhareva, M. Ho, R.S.H. Liu, *J. Fluorine Chem.* **1999**, *97*, 165

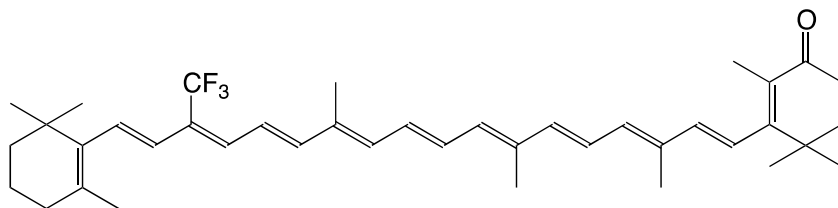
3F 9,9'-bis(trifluoromethyl)- β -carotene $C_{40}H_{50}F_6$ 

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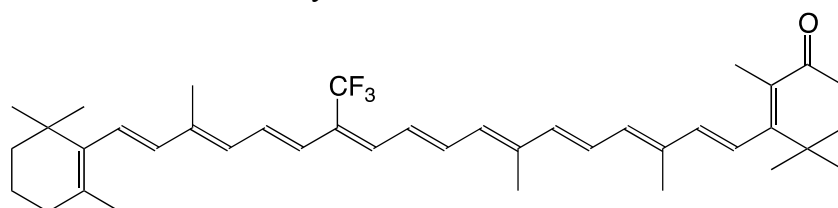
4F 13,13'-bis(trifluoromethyl)- β -carotene $C_{40}H_{50}F_6$ 

D. Hoischen, L.U. Colmenares, I. Koukhareva, M. Ho, R.S.H. Liu, *J. Fluorine Chem.* **1999**, *97*, 165

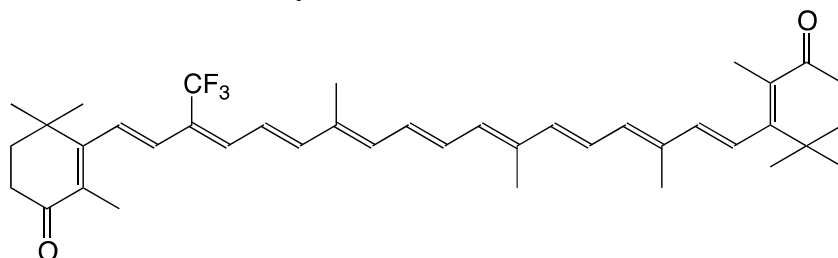
5F 9-trifluoromethyl echinenone

C₄₀H₅₁F₃OD. Hoischen, L.U. Colmenares, I. Koukhareva, M. Ho, R.S.H. Liu, *J. Fluorine Chem.* **1999**, *97*, 165

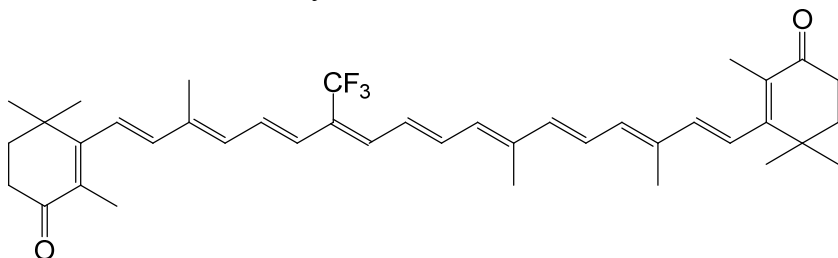
6F 13-trifluoromethyl echinenone

C₄₀H₅₁F₃OD. Hoischen, L.U. Colmenares, I. Koukhareva, M. Ho, R.S.H. Liu, *J. Fluorine Chem.* **1999**, *97*, 165

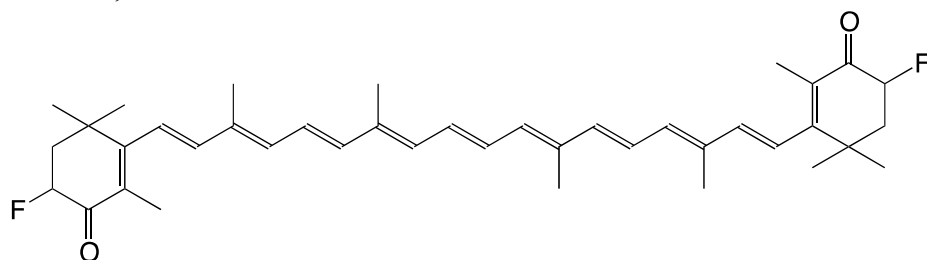
7F 9-trifluoromethyl canthaxanthin

C₄₀H₄₉F₃O₂D. Hoischen, L.U. Colmenares, I. Koukhareva, M. Ho, R.S.H. Liu, *J. Fluorine Chem.* **1999**, *97*, 165

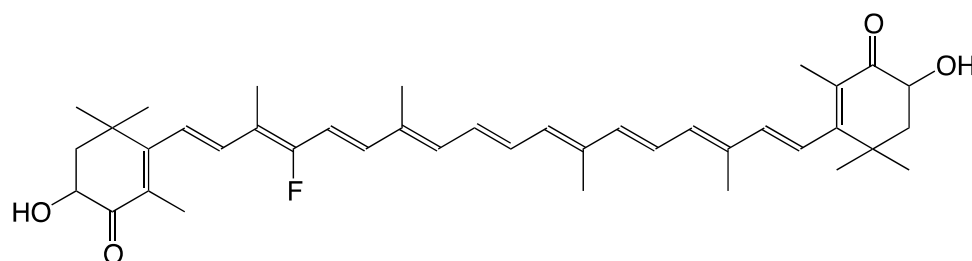
8F 13-trifluoromethyl canthaxanthin

C₄₀H₄₉F₃O₂D. Hoischen, L.U. Colmenares, I. Koukhareva, M. Ho, R.S.H. Liu, *J. Fluorine Chem.* **1999**, *97*, 165

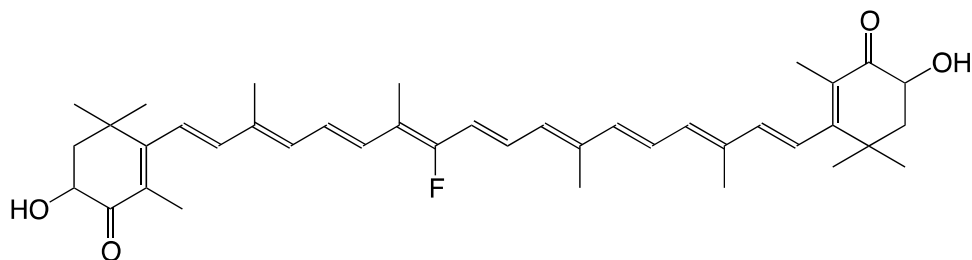
9F 3,3'-difluoro-canthaxanthin

C₄₀H₅₀F₂O₂R.S.H. Liu, J. Liu, *J. Nat. Prod.* **2011**, 74, 512

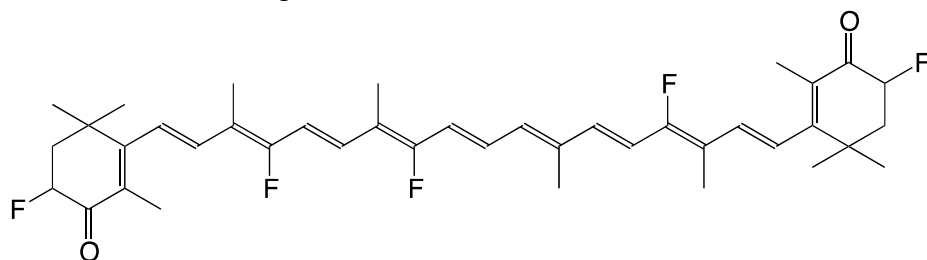
10F 10-fluoro-astaxanthin

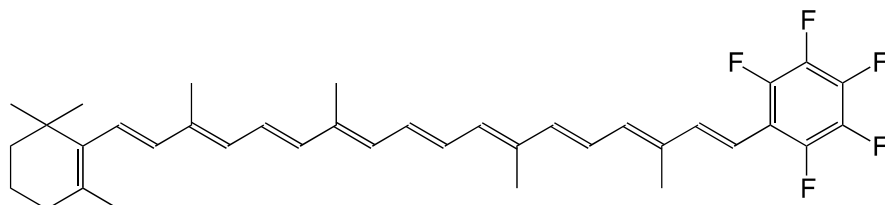
C₄₀H₅₁FO₄R.S.H. Liu, J. Liu, *J. Nat. Prod.* **2011**, 74, 512

11F 14-fluoro-astaxanthin

C₄₀H₅₁FO₄R.S.H. Liu, J. Liu, *J. Nat. Prod.* **2011**, 74, 512

12F 3,3',10,10',14-pentafluoro-canthaxanthin

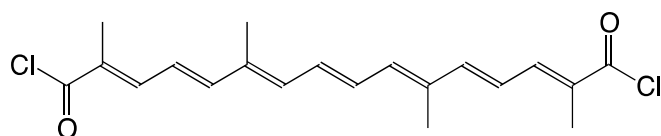
C₄₀H₄₇F₅O₂R.S.H. Liu, J. Liu, *J. Nat. Prod.* **2011**, 74, 512

ϕ -carotenoids13F 1',2',3',4',5'-pentafluoro- β , ϕ -caroteneC₃₇H₄₁F₅E. Hand, K.A. Belmore, L.D. Kispert, *Helv. Chim. Acta* **1993**, 76, 1928

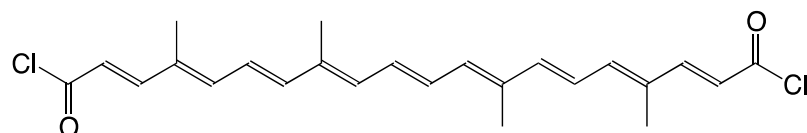
6.1.2. Chlorine

Cl

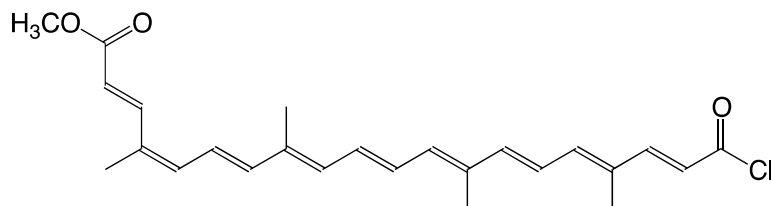
1Cl crocetin dichloride

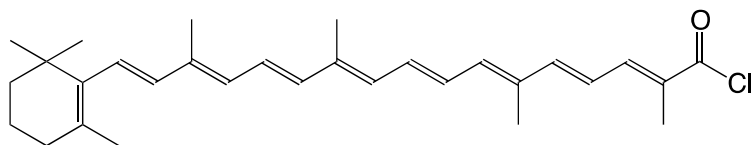
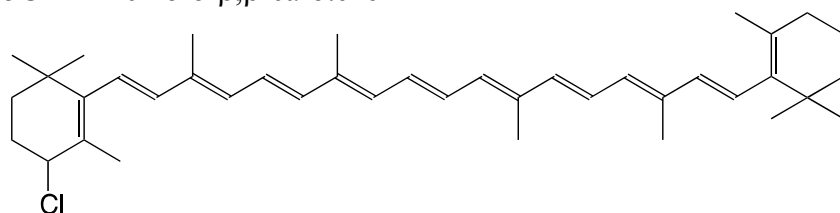
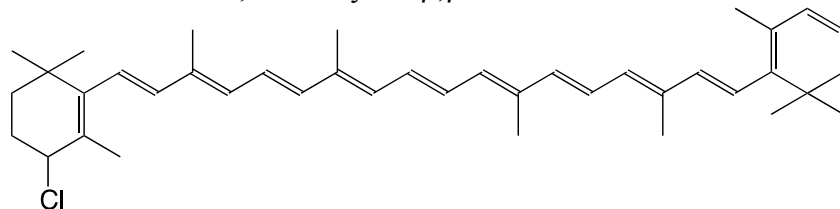
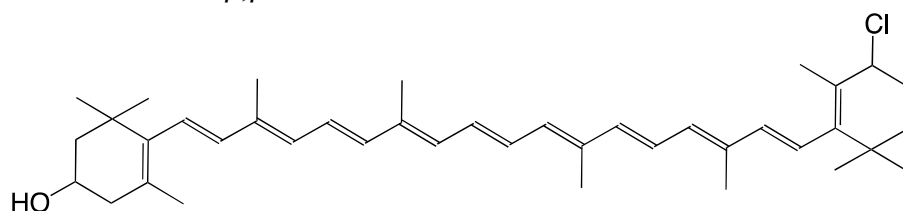
C₂₀H₂₂Cl₂O₂H. Pfander, F. Wittwer, *Helv. Chim. Acta* **1979**, 62, 1944

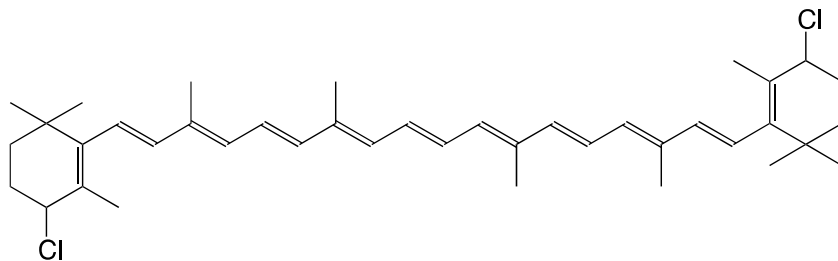
2Cl norbixin dichloride

C₂₄H₂₆Cl₂O₂L. Levy, R.H. Binnington, A. Tabatnik, *WO 02/068385*, **2002**

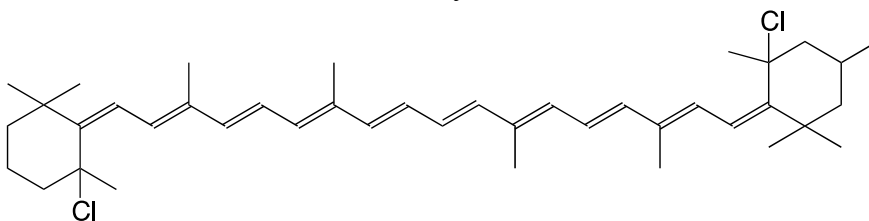
3Cl bixin chloride

C₂₅H₂₉ClO₃G. Ferrari, V. Vecchiotti, *EP 30009*, **1981**T. Komatsu, E. Tsuchia, C. Böttcher, D. Donner, C. Messerschmidt, U. Siggel, W. Stocker, J.P. Rabe, J.H. Fuhrhop, *J. Am. Chem. Soc.* **1997**, 119, 11660

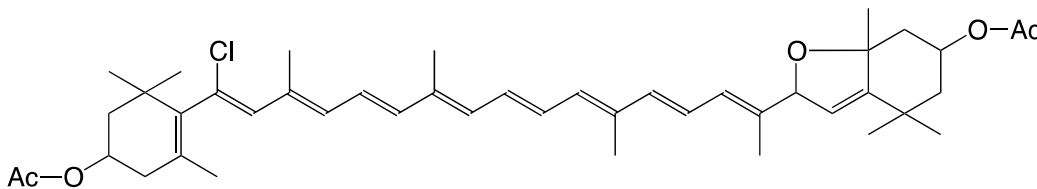
4Cl β -apo-8'-carotenoyl chloride, C30-acid chlorideC₃₀H₃₉ClOT. Naalsund, K.E. Malterrud, V. Partali, H.R. Sliwka, *Chem. Phys. Lipids* **2001**, *112*, 59L. Levy, R. H. Binnington, A. Tabatnik, *WO 02/068385*, **2002**5Cl 4-chloro- β , β -caroteneC₄₀H₅₅ClH. Pfander, U. Leuenberger, *Chimia* **1976**, *30*, 716Cl 4-chloro-3',4'-didehydro- β , β -caroteneC₄₀H₅₃ClH. Pfander, U. Leuenberger, *Chimia* **1976**, *30*, 717Cl 4'-chloro- β , β -caroten-3-olC₄₀H₅₅ClOH. Pfander, U. Leuenberger, *Chimia* **1976**, *30*, 71

8Cl 4,4'-dichloro- β,β -caroteneC₄₀H₅₄Cl₂H. Pfander, U. Leuenberger, *Chimia* **1976**, *30*, 71

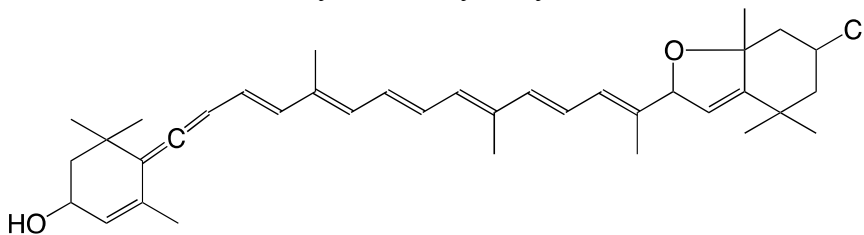
9Cl 5,5'-dichloro-4,5,4',5'-tetrahydroisocarotene

C₄₁H₅₈Cl₂C. Bodea, E. Nicoara, *Acad. rep. populare Romîne, Filiala Cluj, Studii Cercetâri Chim.* **1959**, *10*, 1959

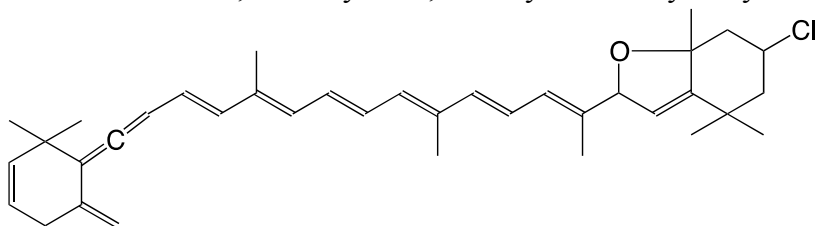
10Cl 7-chloro-mutatoxanthin-3,3'-diacetate

C₄₄H₅₉ClO₅J.E. Johansen, S. Liaaen-Jensen, *Acta Chem. Scand.* **1974**, *B28*, 949R. Buchecker, S. Liaaen-Jensen, *Helv. Chim. Acta* **1975**, *58*, 89

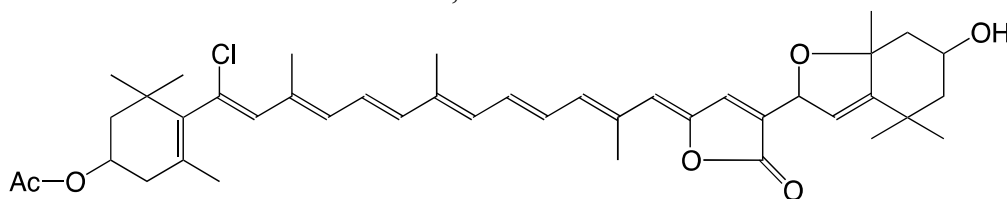
11Cl 3'-chloro-4,5-dehydro-5-dehydroxy-neochrome

C₃₇H₄₉ClO₂R. Buchecker, S. Liaaen-Jensen, *Helv. Chim. Acta* **1975**, *58*, 89

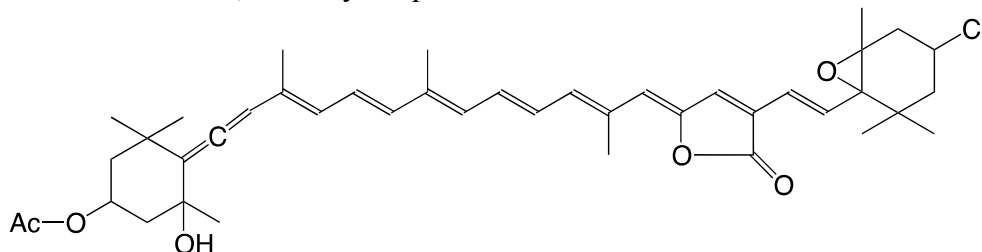
12Cl 3'-chloro-2,3-didehydro-5,18-dehydro-5-dehydroxy-neochrome

C₃₇H₄₇ClOR. Buchecker, S. Liaaen-Jensen, *Helv. Chim. Acta* **1975**, *58*, 89

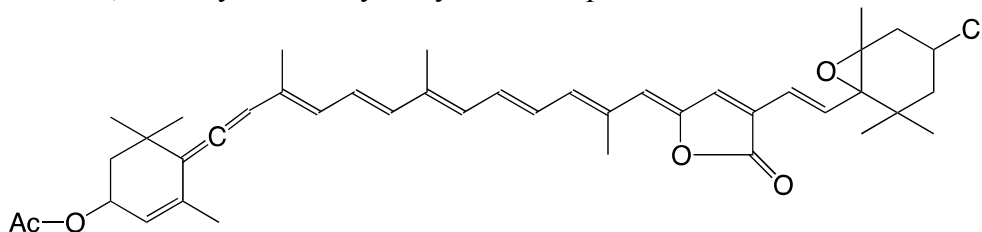
13Cl 7-chloro-mutatoxanthin-19',11'-olide 3-acetate

C₄₂H₅₃ClO₆J.E. Johansen, S. Liaaen-Jensen, *Acta Chem. Scand.* **1974**, *B28*, 949

14Cl 3'-chloro-6,7-didehydro-peridinol-3-acetate

C₄₂H₅₃ClO₆J.E. Johansen, S. Liaaen-Jensen, *Acta Chem. Scand.* **1974**, *B28*, 949

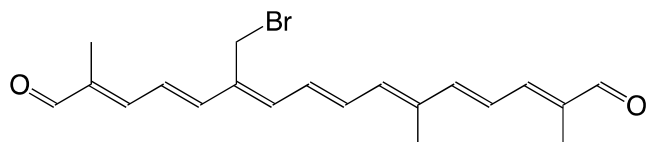
15Cl 4,5-didehydro-5-dehydroxy-3'-chloro-peridin-3-acetate

C₄₂H₅₁ClO₅J.E. Johansen, S. Liaaen-Jensen, *Acta Chem. Scand.* **1974**, *B28*, 949

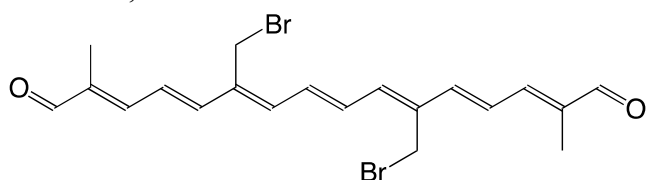
6.1.3. Bromine

Br

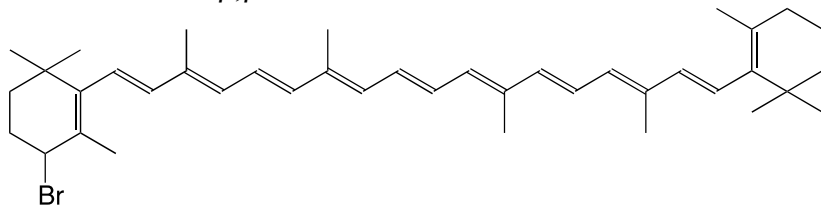
1Br 20-bromo-crocetindial

C₂₀H₂₃BrO₂J.E. Johansen, S. Liaaen-Jensen, *Acta Chem. Scand.* **1975**, B29, 315

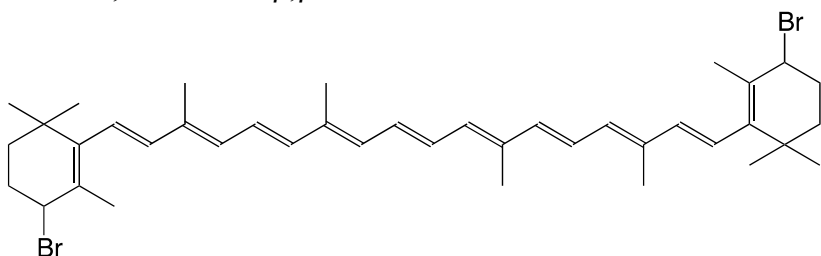
2Br 20,20'-dibromo-crocetindial

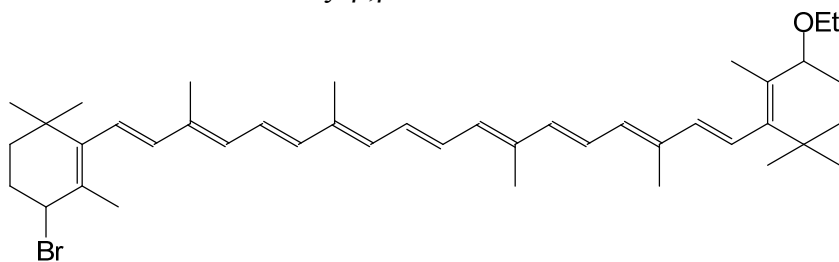
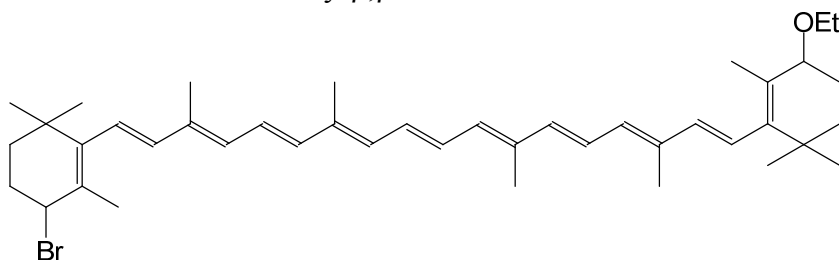
C₂₀H₂₂Br₂O₂J.E. Johansen, S. Liaaen-Jensen, *Acta Chem. Scand.* **1975**, B29, 315

3Br 4-bromo-β,β-carotene

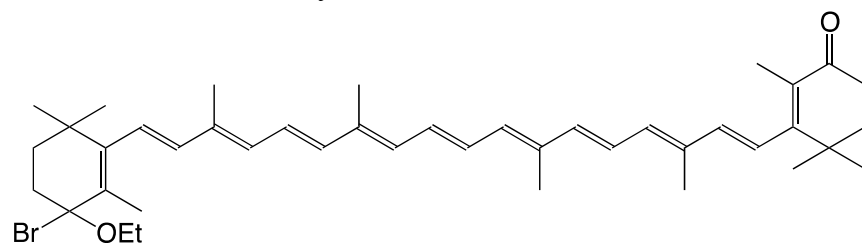
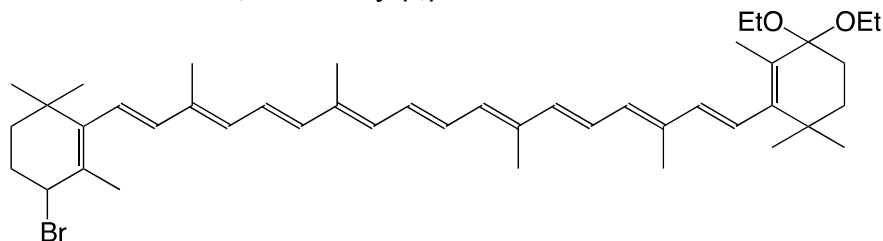
C₄₀H₅₅BrR. Entschel, P. Karrer, *Helv. Chim. Acta* **1958**, 41, 983J. Morel, *DE2001957*, **1970**

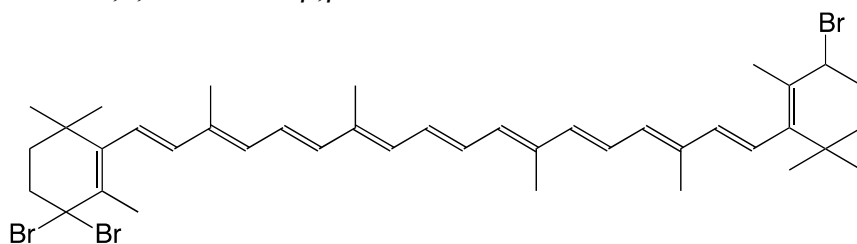
4 Br 4,4'-dibromo-β,β-carotene

C₄₀H₅₈Br₂R. Entschel, P. Karrer, *Helv. Chim. Acta* **1958**, 41, 402C. Martin, P. Karrer, *Helv. Chim. Acta* **1959**, 42, 464

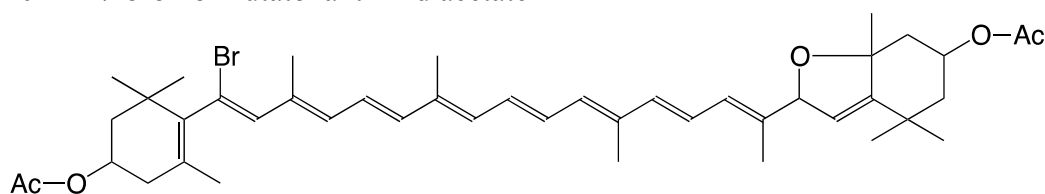
5Br 4-bromo-4'-ethoxy- β,β -caroteneC₄₂H₅₉BrOR. Entschel, P. Karrer, *Helv. Chim. Acta* **1958**, 41, 4026Br 4-bromo-4'-ethoxy- β,β -caroteneC₄₄H₆₃BrO₂R. Entschel, P. Karrer, *Helv. Chim. Acta* **1958**, 41, 402

7Br 4-bromo-4-ethoxy echinenone

C₄₂H₅₇BrO₂R. Entschel, P. Karrer, *Helv. Chim. Acta* **1958**, 41, 4028Br 4 bromo-4',4'-diethoxy- β,β -caroteneC₄₄H₆₃BrO₂F.J. Petracek, L. Zechmeister, *J. Am. Chem. Soc.* **1956**, 78, 1427

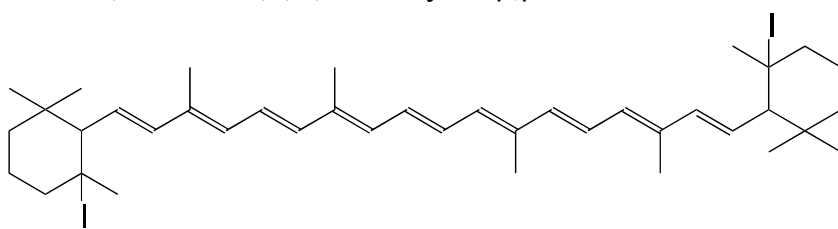
9Br 4,4,4'-tribromo- β,β -caroteneC₄₀H₅₃Br₃F.J. Petracek, L. Zechmeister, *J. Am. Chem. Soc.* **1956**, *78*, 1427

10Br 7-bromo-mutatoxanthin-diacetate

C₄₄H₅₉BrO₅R. Buchecker, S. Liaaen-Jensen, *Helv. Chim. Acta* **1975**, *58*, 89

6.1.4. Iodine

I

II 5,5'-diiodo-5,6,5',6'-didehydro- β,β -caroteneC₄₀H₅₈I₂

unconfirmed structure

B.G. Savinov, G.S. Tretyakova, *Vitamins Akad. Nauk Ukr. S.S.R* **1953**, *1*, 137

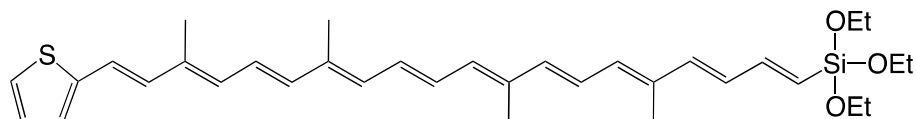
Other carotenoid-iodine compounds are formulated as ionic complexes:

B.F. Lutnaes, J. Krane, S. Liaaen-Jensen, *Org. Biomol. Chem.* **2004**, *2*, 2821

6.2. Silicon-Carotenoids

Si

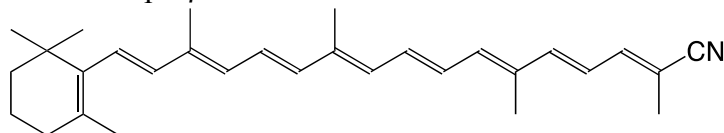
1Si (= 2⊙S) 7,5'-diapo-7-thienyl-carotene-5'-triethoxysilane

C₃₄H₄₆O₃SSiF. Effenberger, M. Wezstein, *Synthesis* **2001**, 1368

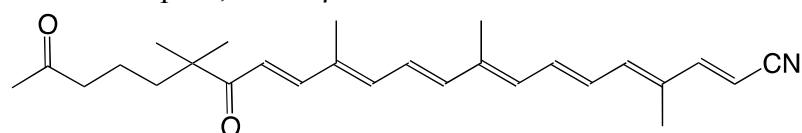
6.3. Nitrogen-Carotenoids

N

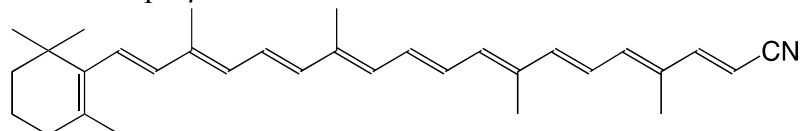
1N 8'-apo-β-carotene-8'-nitrile

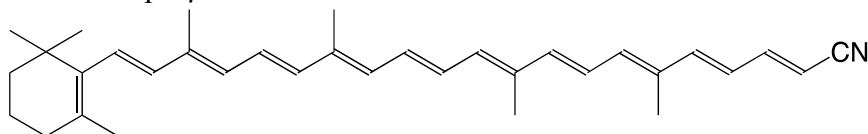
C₃₀H₃₉NZ. He, D. Gosztola, Y. Deng, G. Gao, M.R. Wasielewski, L.D. Kispert, *J. Phys. Chem. B* **2000**, *104*, 6668

2N 10'-apo-5,6-seco-β-carotene-10'-nitrile

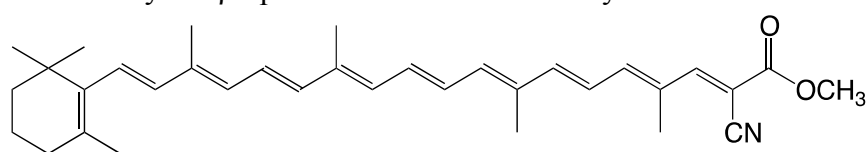
C₂₇H₃₅NO₂R. Kuhn, H. Brockmann, *Chem. Ber.* **1934**, *67*, 885

3N 6'-apo-β-carotene-6'-nitrile

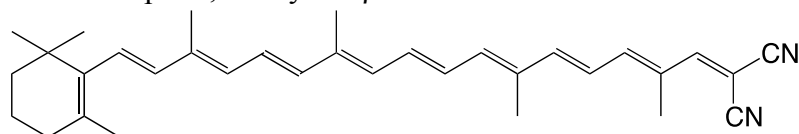
C₃₂H₄₁NZ. He, D. Gosztola, Y. Deng, G. Gao, M.R. Wasielewski, L.D. Kispert, *J. Phys. Chem. B* **2000**, *104*, 6668S. Tretiak, V. Chernyak, S. Mukamel, *J. Am. Chem. Soc.* **1997**, *119*, 11408S. Gilmour, S.R. Marder, B.G. Tiemann, L.T. Cheng, *J. Chem. Soc. Chem. Commun.* **1993**, 432

4N 4'-apo- β -carotene-4'-nitrileC₃₄H₄₃N

Z. He, D. Gosztola, Y. Deng, G. Gao, M.R. Wasielewski, L.D. Kispert, *J. Phys. Chem. B* **2000**, *104*, 6668

5N 7'-cyano- β -apo-7'-carotenoic acid methyl esterC₃₄H₄₃NO₂

H. Ikeda, T. Sakai, Y. Kawabe, *JP 2-2534*, **1990**

6N 7'-apo-7',7'-dicyano- β -caroteneC₃₃H₄₀N₂

M. Blanchard-Desce, I. Ledoux, J.M. Lehn, J. Malthête, J. Zyss, *J. Chem. Soc. Chem. Commun.* **1988**, 737

H. Ikeda, T. Sakai, Y. Kawabe, *JP 2-2534*, **1990**

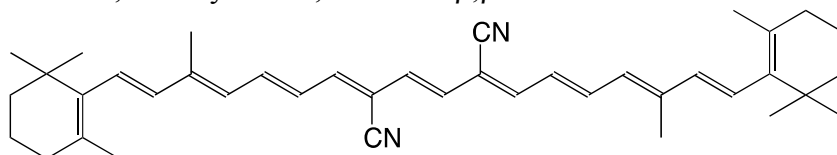
M.P. O'Neil, M.R. Nasielewski, M.M. Khaled, L.D. Kispert, *J. Chem. Phys. B*, **1991**, *95*, 7212

S. Gilmour, S.R. Marder, B.G. Tiemann, L.T. Cheng, *J. Chem. Soc. Chem. Commun.* **1993**, 432

E.S. Hand, K.A. Belmore, L.D. Kispert, *J. Chem. Soc. Perkin Trans 2*, **1993**, 659

S. Tretiak, V. Chernyak, S. Mukamel, *J. Am. Chem. Soc.* **1997**, *119*, 11408

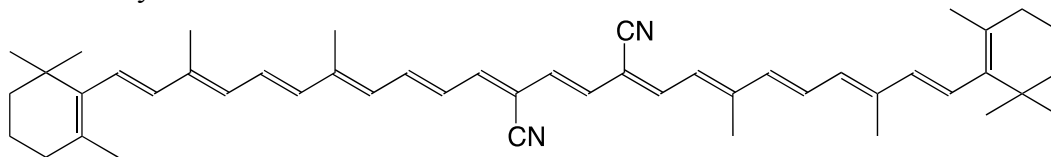
A.J. Cruz, K. Siam, D.P. Rillema, *J. Phys. Chem.* **2011**, *115*, 1108

7N 4,14'-dicyano-20,20'-dinor- β,β -carotene-C₄₀H₅₀N₂

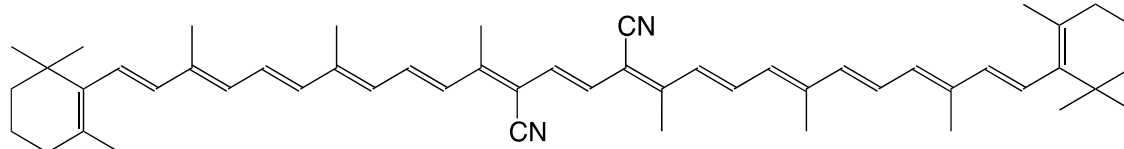
H.H. Haack, T. Kralt, *Rec. Trav. Chim. Pays-Bas* **1966**, *85*, 343

P.B. Braun, J. Hornstra, J.I. Leenhouts, *Acta Cryst.* **1971**, *B27*, 90

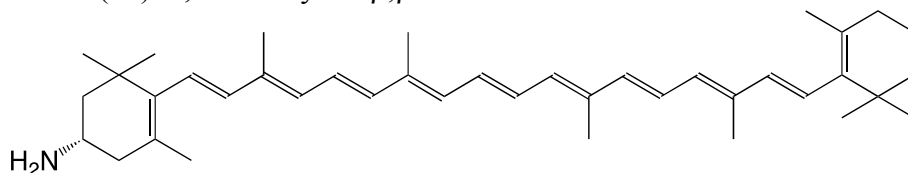
8N dicyano-C44:14

C₄₈H₆₀N₂H.H. Haeck, T. Kralt, *Rec. Trav. Chim. Pays-Bas* **1966**, 85, 343

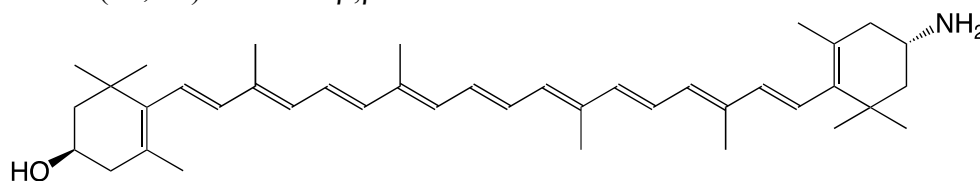
9N dicyano-C48:15

C₅₂H₆₆N₂H.H. Haeck, T. Kralt, *Rec. Trav. Chim. Pays-Bas* **1966**, 85, 343

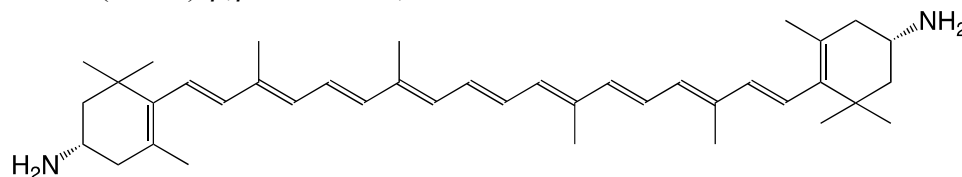
10N (3S)-2',3'-didehydro-β,β-carotene-3-amine

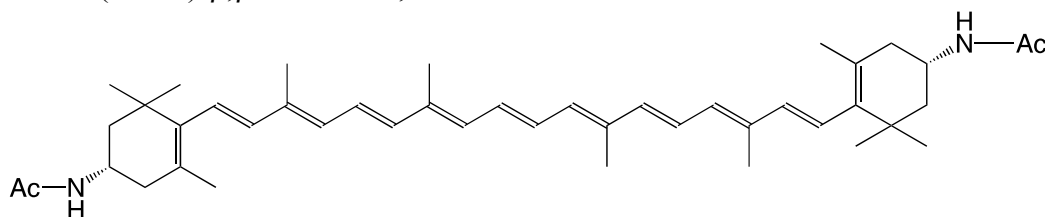
C₄₀H₅₅NH.R. Sliwka, S. Liaaen-Jensen, *Tetrahedron Asym.* **1993**, 4, 2377

11N (3R,3'S)-3'-amino-β,β-carotene-3-ol

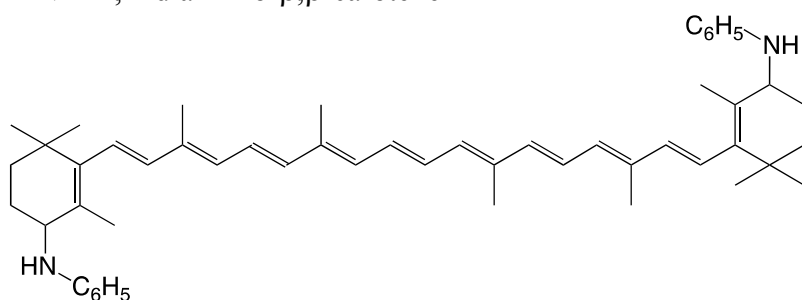
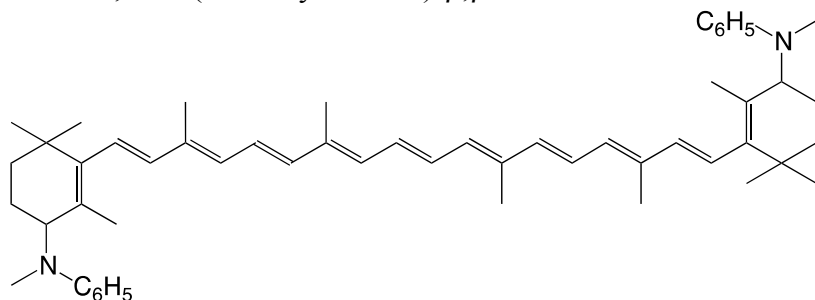
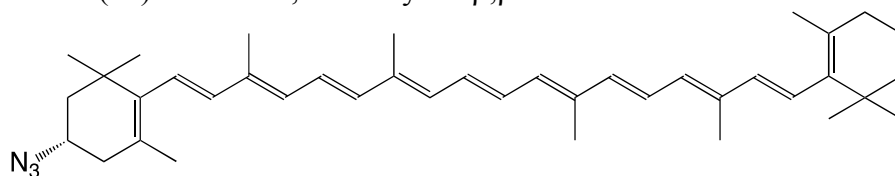
C₄₀H₅₇NOH.R. Sliwka, S. Liaaen-Jensen, *Tetrahedron Asym.* **1993**, 4, 2377

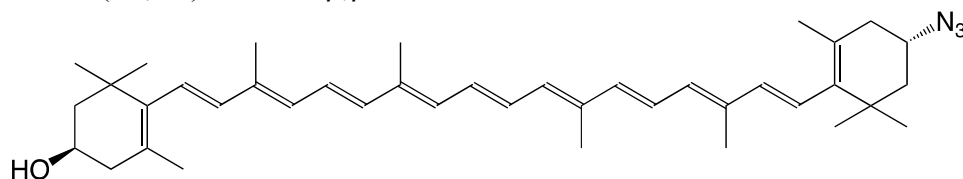
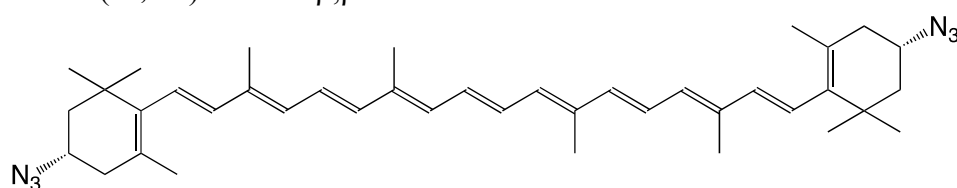
12N (3S,3'S)-β,β-carotene-3,3'-amine

C₄₀H₅₈N₂H.R. Sliwka, S. Liaaen-Jensen, *Tetrahedron Asym.* **1993**, 4, 2377J. Inananga, M. Yamaguchi, *Mem. Fac. Sci. Kyushi Univ. Ser. C*, **1989**, 17, 109

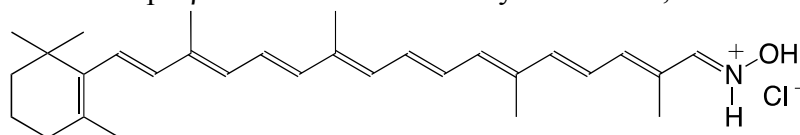
13N (3*S*,3'*S*)-β,β-carotene-3,3'-diacetamideC₄₄H₆₂N₂O₂J. Inananga, M. Yamaguchi, *Mem. Fac. Sci. Kyushi Univ. Ser. C*, **1989**, 17, 109

14N 4,4'-dianilino-β,β-carotene

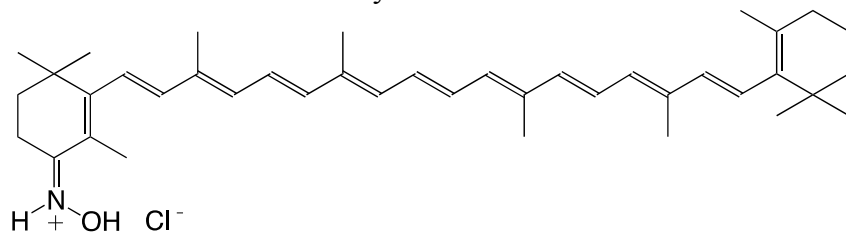
C₅₂H₆₆N₂C. Martin, P. Karrer, *Helv. Chim. Acta* **1959**, 42, 464H. Budzikiewicz, H. Brzezinka, B. Johannes, *Monatshefte* **1970**, 101, 57915N 4,4'-bis(*N*-methyl-anilino)-β,β-caroteneC₅₄H₇₀N₂C. Martin, P. Karrer, *Helv. Chim. Acta* **1959**, 42, 46416N (3*S*)-3-azido-2',3'-didehydro-β,β-caroteneC₄₀H₅₃N₃H.R. Sliwka, S. Liaaen-Jensen, *Tetrahedron Asym.* **1993**, 4, 2377H.R. Sliwka, *Helv. Chim. Acta* **1999**, 82, 161

17N (3*R*,3'*S*)-3'-azido-β,β-carotene-3-olC₄₀H₅₅N₃OH.R. Sliwka, S. Liaaen-Jensen, *Tetrahedron Asym.* **1993**, *4*, 2377H.R. Sliwka, *Helv. Chim. Acta* **1999**, *82*, 16118N (3*S*,3'*S*)-diazido-β,β-caroteneC₄₀H₅₄N₆H.R. Sliwka, S. Liaaen-Jensen, *Tetrahedron Asym.* **1993**, *4*, 2377J. Inananga, M. Yamaguchi, *Mem. Fac. Sci. Kyushi Univ. Ser. C*, **1989**, *17*, 109H.R. Sliwka, *Helv. Chim. Acta* **1999**, *82*, 161

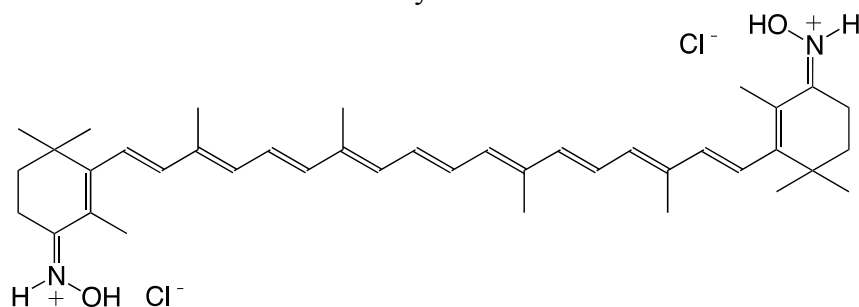
19N 8'-apo-β-caroten-8'-aldoxime hydrochloride, C30-aldoxime hydrochloride

C₃₀H₄₂ClNOJ. Willibald, S. Rennebaum, S. Breukers, S.H. Abdel Hafez, A. Patel, C.L. Øpstad, R. Schmid, S. Nalum Naess, H.R. Sliwka, V. Partali, *Chem. Phys. Lipids* **2009**, *161*, 32H.R. Sliwka, V. Partali, S.F. Lockwood, in *Carotenoids*, ed. J.T. Landrum, CRC Press, Boca Raton, USA, **2010**, chpt. 3

20N echinenenon oxime hydrochloride

C₄₀H₅₆ClNOJ. Willibald, S. Rennebaum, S. Breukers, S.H. Abdel Hafez, A. Patel, C.L. Øpstad, R. Schmid, S. Nalum Naess, H.R. Sliwka, V. Partali, *Chem. Phys. Lipids* **2009**, *161*, 32H.R. Sliwka, V. Partali, S.F. Lockwood, in *Carotenoids*, ed. J.T. Landrum, CRC Press, Boca Raton, USA, **2010**, chpt. 3

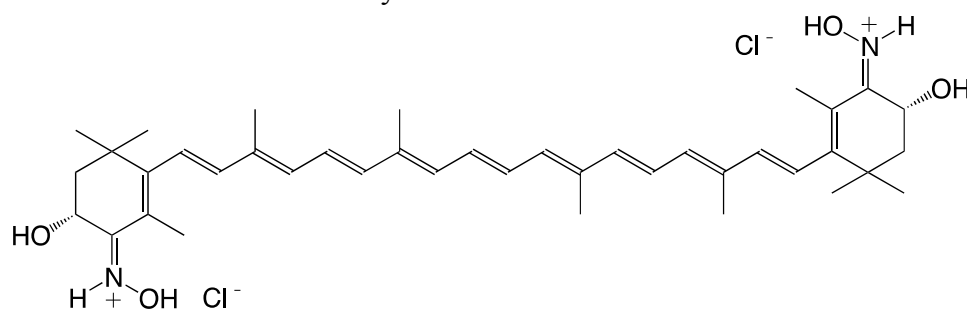
21N canthaxanthin dioxime hydrochloride



J. Willibald, S. Rennebaum, S. Breukers, S.H. Abdel Hafez, A. Patel, C.L. Øpstad, R. Schmid, S. Nalum Naess, H.R. Sliwka, V. Partali, *Chem. Phys. Lipids* **2009**, *161*, 32

H.R. Sliwka, V. Partali, S.F. Lockwood, in *Carotenoids*, ed. J.T. Landrum, CRC Press, Boca Raton, USA, **2010**, chpt. 3

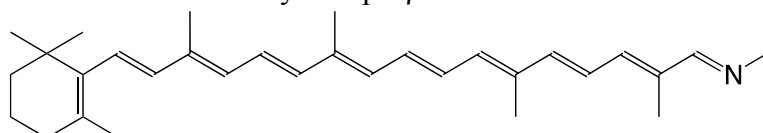
22N astaxanthin dioxime hydrochloride



J. Willibald, S. Rennebaum, S. Breukers, S.H. Abdel Hafez, A. Patel, C.L. Øpstad, R. Schmid, S. Nalum Naess, H.R. Sliwka, V. Partali, *Chem. Phys. Lipids* **2009**, *161*, 32

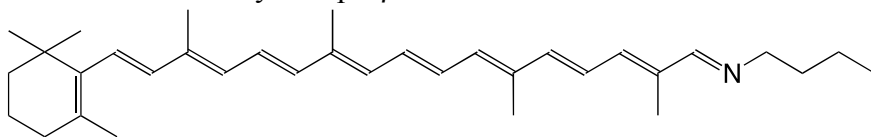
H.R. Sliwka, V. Partali, S.F. Lockwood, in *Carotenoids*, ed. J.T. Landrum, CRC Press, Boca Raton, USA, **2010**, chpt. 3

23N 7'-aza-7'-methyl-7'-apo-β-carotene

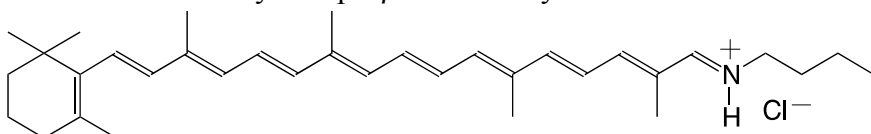


G.A.J. Pitt, F.D. Collins, R.A. Morton, P. Stok, *Biochem. J.* **1955**, *59*, 122

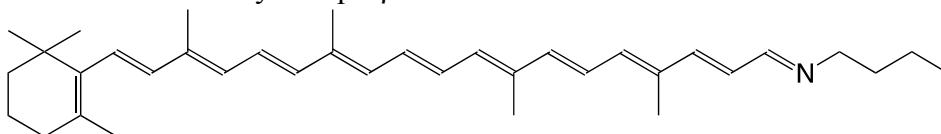
24N 7'-aza-7'-butyl-7'-apo-β-carotene

C₃₄H₄₉NT.A. Moore, P.S. Song, *J. Mol. Spec.* **1974**, *52*, 224

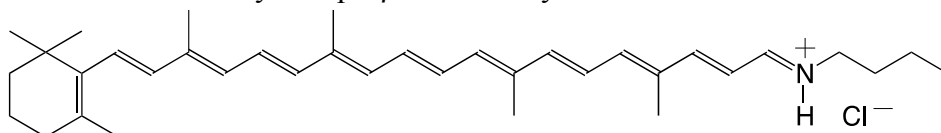
25N 7'-aza-7'-butyl-7'-apo-β-carotene hydrochloride

C₃₅H₅₂ClNT.A. Moore, P.S. Song, *J. Mol. Spec.* **1974**, *52*, 224

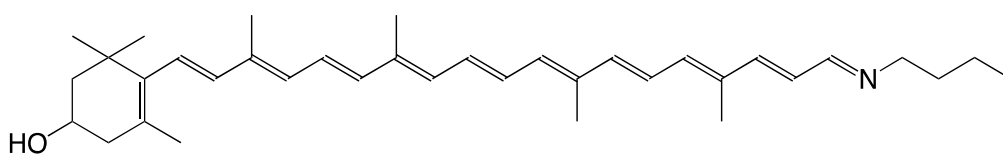
26N 5'-aza-5'-butyl-5'-apo-β-carotene

C₃₇H₅₃NT.A. Moore, P.S. Song, *J. Mol. Spec.* **1974**, *52*, 224

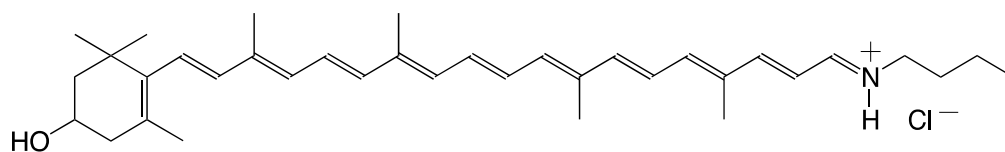
27N 5'-aza-5'-butyl-5'-apo-β-carotene hydrochloride

C₃₇H₅₄ClNT.A. Moore, P.S. Song, *J. Mol. Spec.* **1974**, *52*, 224

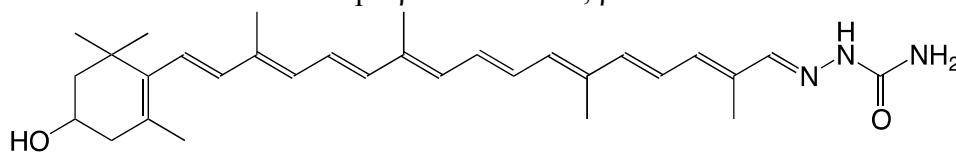
28N 5'-aza-5'-butyl-5'-apo-β-caroten-3-ol

C₃₆H₅₁NOT.A. Moore, P.S. Song, *J. Mol. Spec.* **1974**, *52*, 224

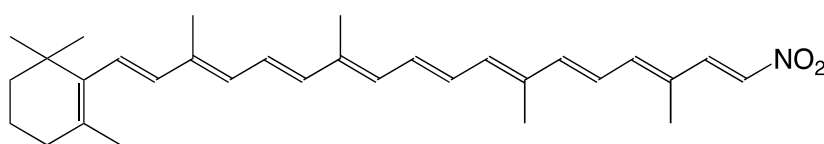
29N 5'-aza-5'-butyl-5'-apo-β-caroten-3-ol hydrochloride

C₃₆H₅₂ClNOT.A. Moore, P.S. Song, *J. Mol. Spec.* **1974**, 52, 224

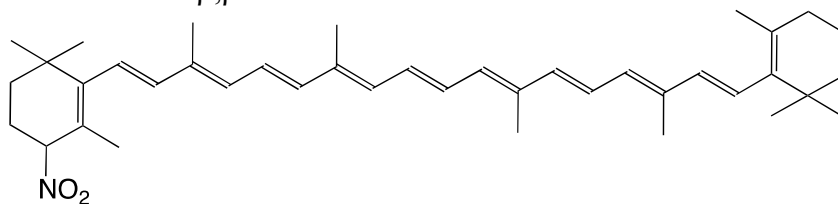
30N 7'-aza-7'-ureido-7'-apo-β-caroten-3-ol, β-citraurin semicarbazone

C₃₁H₄₃N₃O₂L. Zechmeister, L. von Cholnoky, *Liebigs Ann.* **1937**, 530, 291

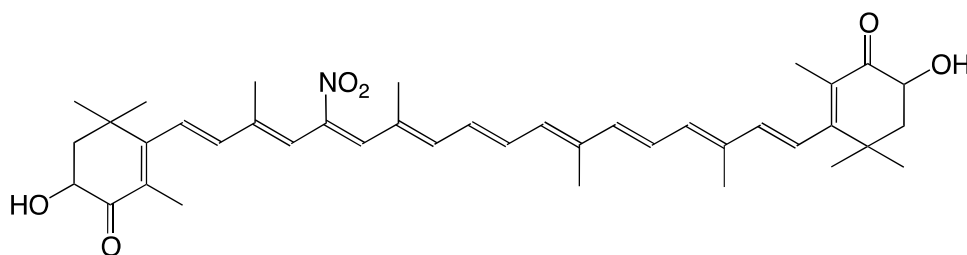
31N 7'-nitro-7'-apo-β-carotene

C₃₁H₄₁NO₂H. Ikeda, T. Sakai, Y. Kawabe, *JP 2-2534*, **1990**

32N 4-nitro-β,β-carotene

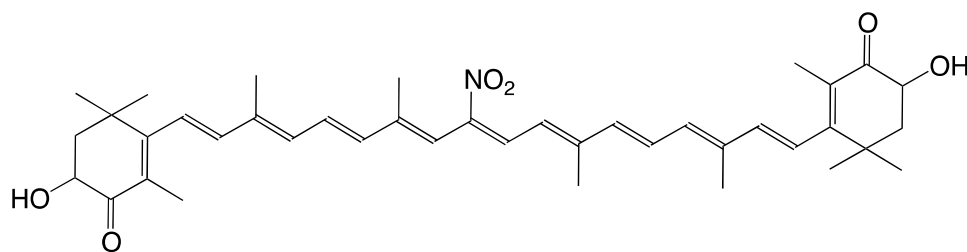
C₄₀H₅₅NO₂D.L. Baker, E.S. Kroll, N. Jacobsen, D.C. Liebler, *Chem. Res. Toxicol.* **1999**, 12, 535

33N 11-nitroastaxanthin

C₄₀H₅₁NO₆

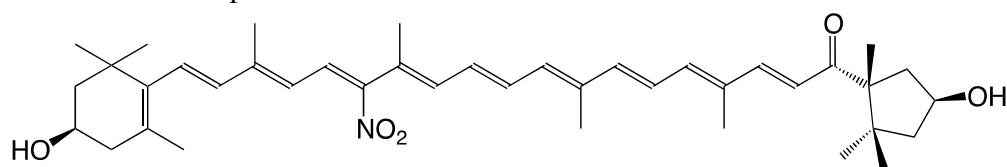
R. Yoshioka, T. Hayakawa, K. Ishuzuka, A. Kulkarni, Y. Terada, T. Maoka, H. Etoh, *Tetrahedron Lett.* **2006**, 47, 3637 (*cis*-isomer)

34N 15-nitroastaxanthin

C₄₀H₅₁NO₆

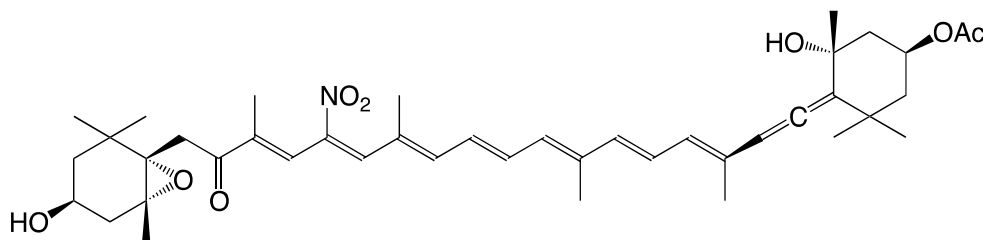
R. Yoshioka, T. Hayakawa, K. Ishuzuka, A. Kulkarni, Y. Terada, T. Maoka, H. Etoh, *Tetrahedron Lett.* **2006**, 47, 3637 (*cis*-isomer)

35N 12-nitrocapsanthin

C₄₀H₅₅NO₅

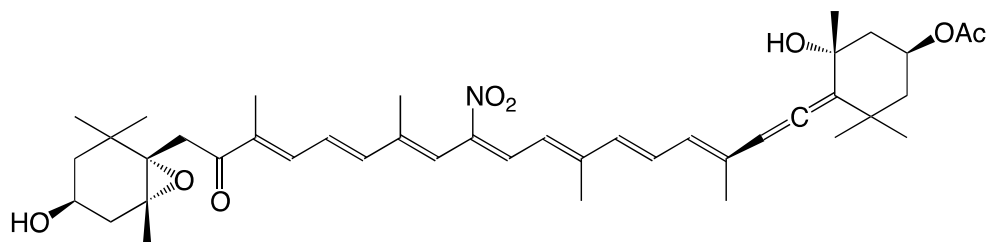
M. Tsuboi, H. Etoh, K. Kato, H. Nakatugawa, H. Kato, Y. Maejima, G. Matsumoto, H. Mori, M. Hosokawa, K. Miyashita, H. Tokuda, N. Suzui, T. Maoka, *J. Agric. Food Chem.* **2011**, 59, 10572

36N 11-nitrofucoxanthin

C₄₂H₅₇NO₈

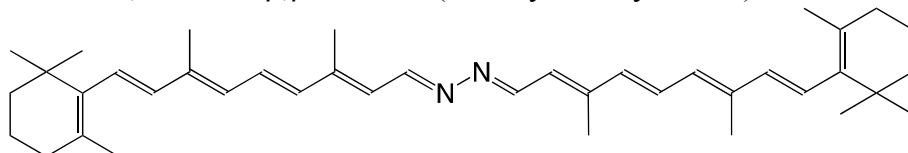
M. Tsuboi, H. Etoh, K. Kato, H. Nakatugawa, H. Kato, Y. Maejima, G. Matsumoto, H. Mori, M. Hosokawa, K. Miyashita, H. Tokuda, N. Suzui, T. Maoka, *J. Agric. Food Chem.* **2011**, 59, 10572

37N 15-nitrofucoxanthin

C₄₂H₅₇NO₈

M. Tsuboi, H. Etoh, K. Kato, H. Nakatugawa, H. Kato, Y. Maejima, G. Matsumoto, H. Mori, M. Hosokawa, K. Miyashita, H. Tokuda, N. Suzui, T. Maoka, *J. Agric. Food Chem.* **2011**, *59*, 10572

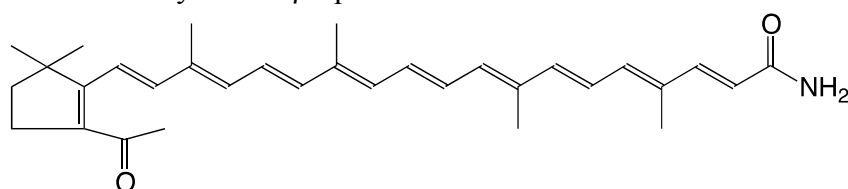
38N 16,16'-diazabeta,beta-carotene (direzinylyden hydrazine)

C₄₀H₅₆N₂

T. Miki, Y. Hara, *JP 34-002118*, **1959**

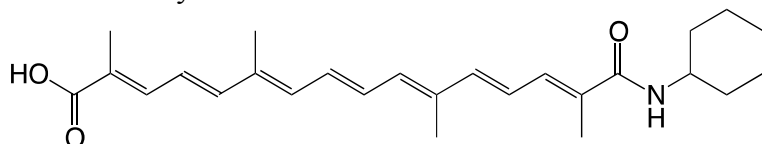
T. Miki, Y. Hara, *Chem. Pharm. Bull.* **1962**, *10*, 922

39N 5-acetyl-2-nor-beta-apo-7'-carotenoic acid amide

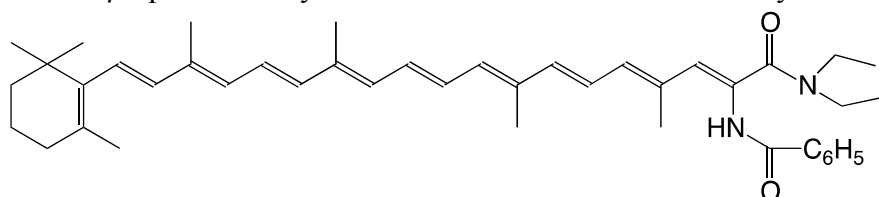
C₃₂H₄₁NO₂

R. Kuhn, H. Brockmann, *Chem. Ber.* **1934**, *67*, 885

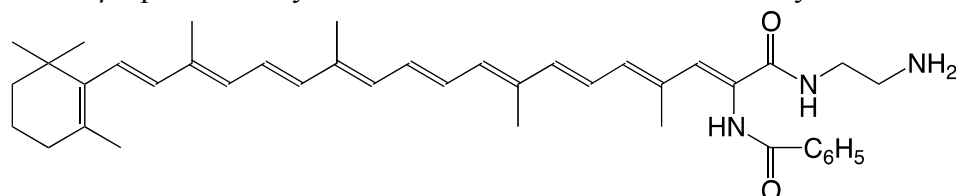
40N N-hexyl crocetinamide

C₂₆H₃₅NO₃

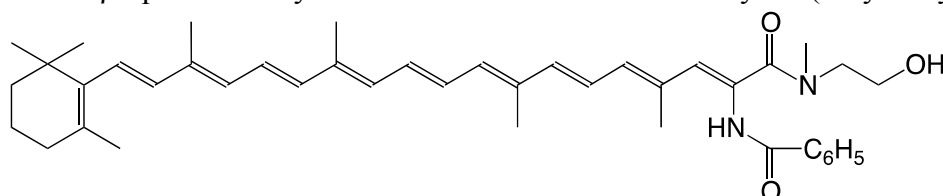
G. Quinkert, K.R. Schmieder, G. Dürner, K. Hache, A. Stegk, D.H.R. Barton, *Chem. Ber.* **1977**, *110*, 3582

41N β -apo-7'-benzoylamino-7'-carotenoic acid *N,N*-diethylamideC₄₃H₅₆N₂O₂

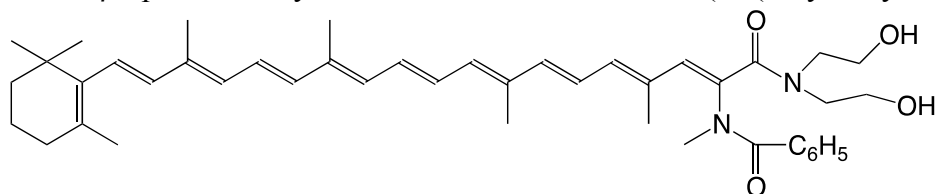
M. Tomoaia-Cotisel, J. Zsako, E. Chifu, D.A. Ladenhead, *Langmuir* **1990**, 6,191. The authors list several related amides.

42N β -apo-7'-benzoylamido-7'-carotenoic acid *N*-aminoethylamideC₄₁H₅₃N₃O₂

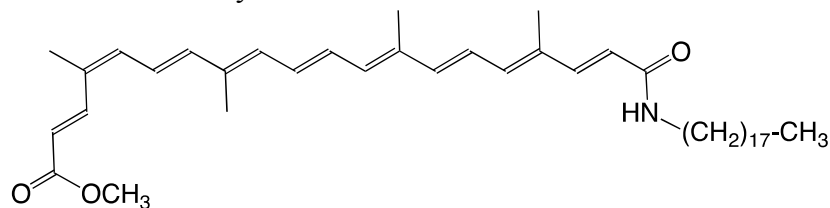
M. Tomoaia-Cotisel, J. Zsako, E. Chifu, D.A. Ladenhead, *Langmuir* **1990**, 6,191

43N β -apo-7'-benzoylamido-7'-carotenoic acid *N*-methyl-*N*-(2-hydroxyethyl)-amideC₄₂H₅₄N₂O₃

M. Tomoaia-Cotisel, J. Zsako, E. Chifu, D.A. Ladenhead, *Langmuir* **1990**, 6,191

44N β -apo-7'-benzoylamido-7'-carotenoic acid *N,N*-(bis(2-hydroxyethyl)-amideC₄₃H₅₆N₂O₄

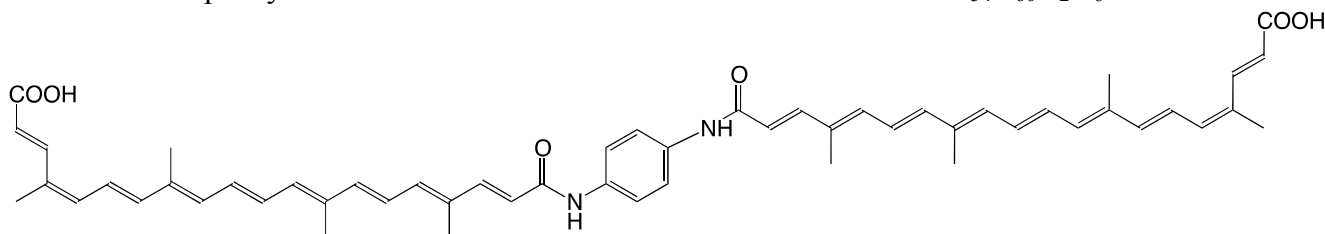
M. Tomoaia-Cotisel, J. Zsako, E. Chifu, D.A. Ladenhead, *Langmuir* **1990**, 6,191

45N *N*-octadecyl bixinamideC₄₂H₆₅NO₃

J.H. Fuhrhop, M. Krull, A. Schulz, D. Möbius, *Langmuir* **1990**, 6,497. The authors list several related bixin amides.

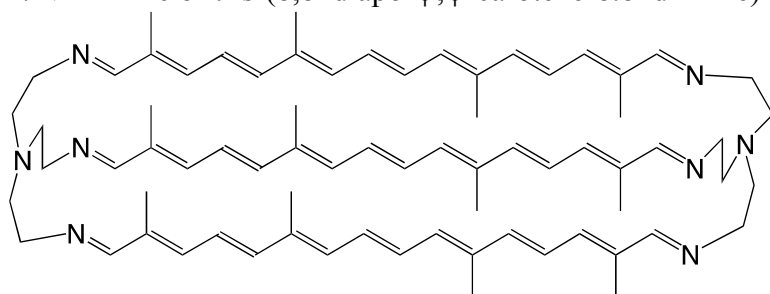
G. Ferrari, V. Vecchiotti, *EP 030009*, **1980** describe numerous bixin amides.

46N dibixine diphenylenediamid

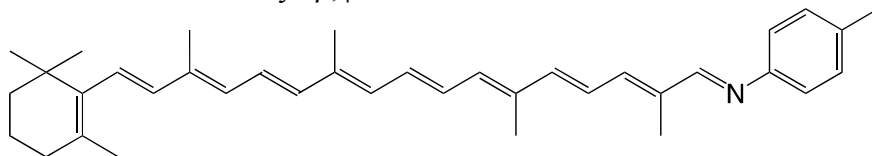
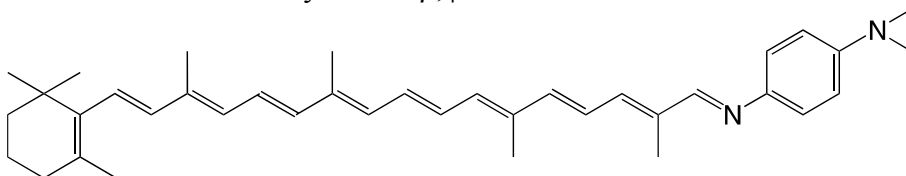
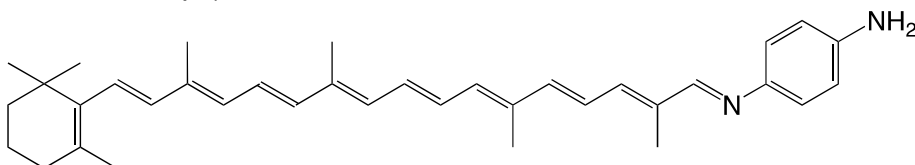
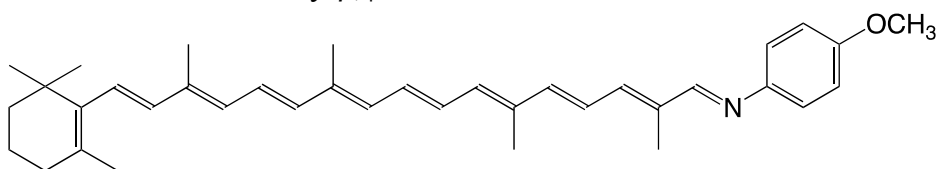
C₅₄H₆₀N₂O₆

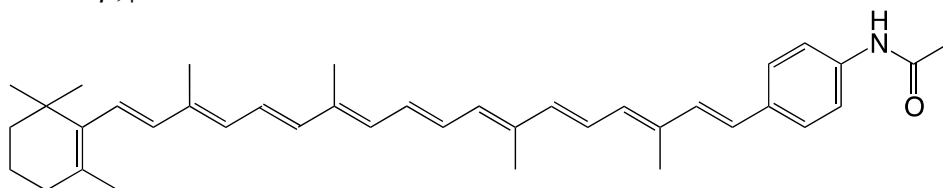
J.H. Fuhrhop, M. Krull, A. Schulz, D. Möbius, *Langmuir* **1990**, 6, 497

47N imine of tris-(8,8'-diapo-ψ,ψ-carotene-8,8'-diimine)

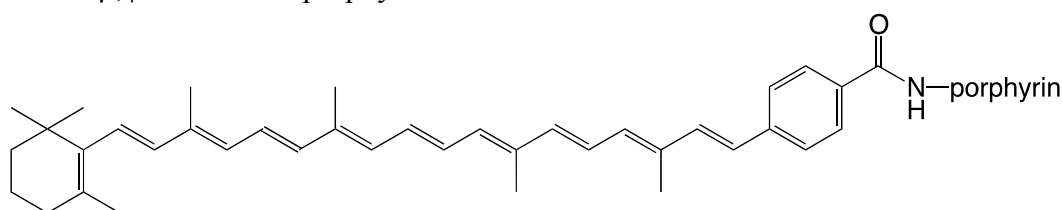
C₇₂H₉₆N₈

J.M. Lehn, J.P. Vigneron, I. Bkouhe-Waksman, J. Guilhem, C. Pascal, *Helv. Chim. Acta* **1992**, 75, 1069

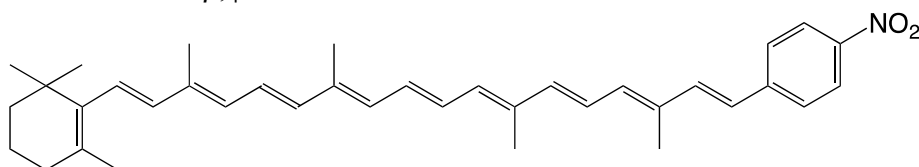
ϕ -carotenoids48N 7'-aza-3'-methyl- β,ϕ -caroteneC₃₇H₄₇NH. Kamogawa, *Polym. Lett. Ed.* **1972**, *10*, 92949N 7'-aza-3'-dimethylamino- β,ϕ -caroteneC₃₆H₄₆N₂H. Ikeda, T. Sakai, Y. Kawabe, *JP 2-2534*, **1990**50N 7'-aza- β,ϕ -caroten-3'-amineC₃₆H₄₆N₂H. Ikeda, T. Sakai, Y. Kawabe, *JP 2-2534*, **1990**51N 7'-aza-3'-methoxy- β,ϕ -caroteneC₃₇H₄₇NOH. Ikeda, T. Sakai, Y. Kawabe, *JP 2-2534*, **1990**

52N β,ϕ -carotene-3'-acetamideC₃₉H₄₉NO

M.R. Wasielewski, P.A. Liddel, D. Barrett, T.A. Moore, D. Gust, *Nature* **1986**, 322, 570

53N β,ϕ -carotene-3'-porphyrinamide

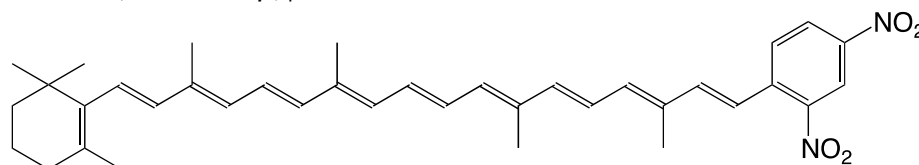
D. Gust, T.A. Moore, P.A. Liddell, G.A. Nemeth, L.R. Makings, A.L. Moore, D. Barrett, P.J. Pessiki, R.V. Bemasson, M. Rougiée, C. Chachaty, F.C. De Schryver, M. Van der Auweraer, A.R. Holzwarth, J. S. Connolly, *J. Am. Chem. Soc.* **1987**, 109, 846

54N 3'-nitro- β,ϕ -caroteneC₃₇H₄₅NO₂

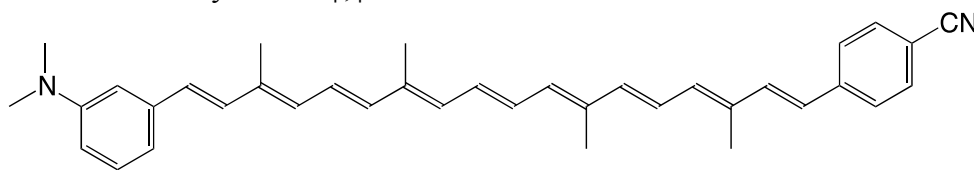
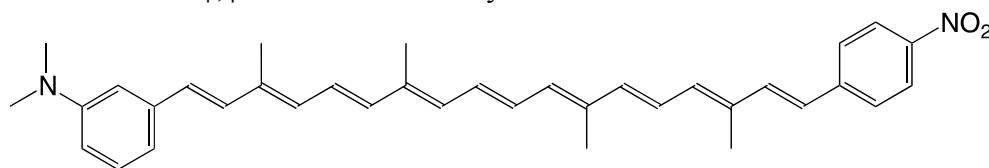
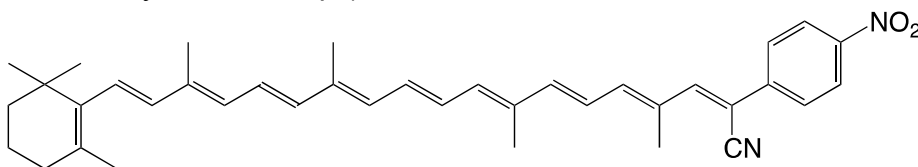
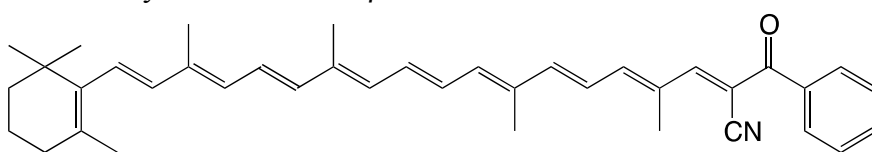
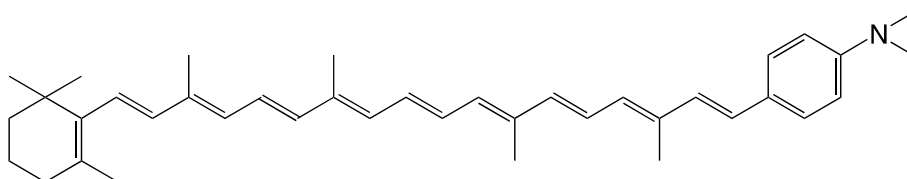
H. Ikeda, T. Sakai, Y. Kawabe, *JP 2-2534*, **1990**

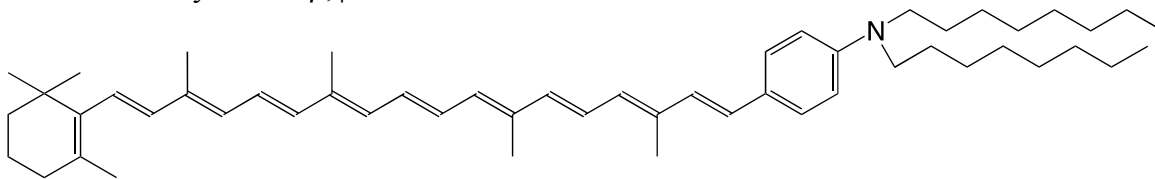
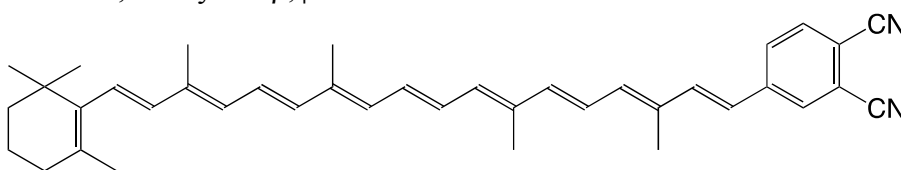
S. Gilmour, S.R. Marder, B.G. Tiemann, L.T. Cheng, *J. Chem. Soc. Chem. Commun.* **1993**, 432

E.S. Hand, K.A. Belmore, L.D. Kispert, *Helv. Chim. Acta* **1993**, 76, 1928

55N 1',3'-dinitro- β,ϕ -caroteneC₃₇H₄₄N₂O₄

H. Ikeda, T. Sakai, Y. Kawabe, *JP 2-2534*, **1990**

56N 2-dimethylamino- ϕ,ϕ -carotene-3'-nitrileC₃₇H₄₀N₂A. Slama-Schwok, M. Blanchard-Desce, J.M Lehn, *J. Phys. Chem.* **1990**, *94*, 389457N 3'-nitro- ϕ,ϕ -carotene-2-dimethylamineC₃₆H₄₀N₂O₂A. Slama-Schwok, M. Blanchard-Desce, J.M Lehn, *J. Phys. Chem.* **1990**, *94*, 389458N 7'-cyano-3'-nitro- β,ϕ -caroteneC₃₈H₄₄N₂O₂H. Ikeda, T. Sakai, Y. Kawabe, *JP 2-2534*, **1990**59N 7'-cyano-7'-benzoxo- β -caroteneC₃₉H₄₅NOH. Ikeda, T. Sakai, Y. Kawabe, *JP 2-2534*, **1990**60N 3'-dimethylamino- β,ϕ -caroteneC₃₉H₅₁NH. Ikeda, T. Sakai, Y. Kawabe, *JP 2-2534*, **1990**

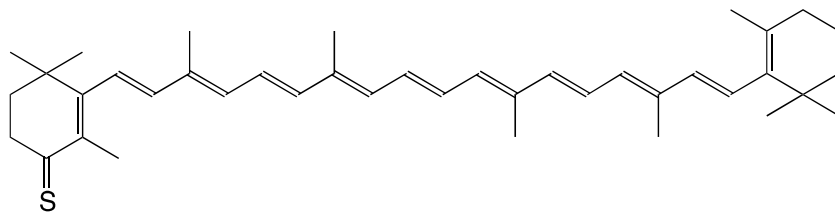
61N 3'-dioctylamino- β,ϕ -caroteneC₅₃H₇₉NT. Wagner, S. Roth, *Synth. Metals* **1993**, *54*, 30762N 2',3'-dicyano- β,ϕ -caroteneC₃₉H₄₄N₂H. Ikeda, T. Sakai, Y. Kawabe, *JP 2-2534*, **1990**

6.3. Chalcogen-Carotenoids

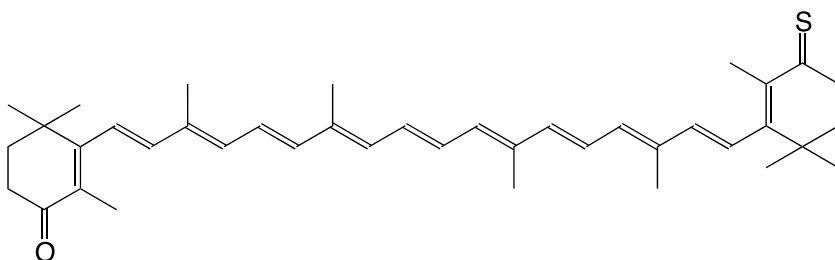
6.3.1. Sulfur

S

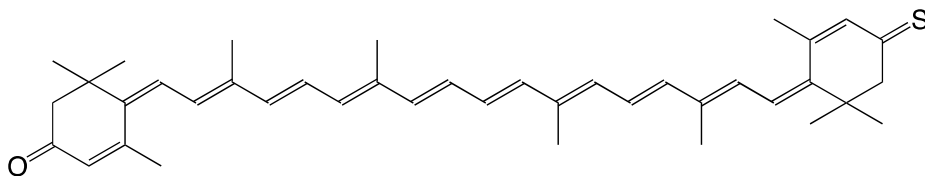
1S echinenone thione

C₄₀H₅₄SH.R. Sliwka, S. Liaaen-Jensen, *Acta Chem. Scand.* **1994**, *48*, 679

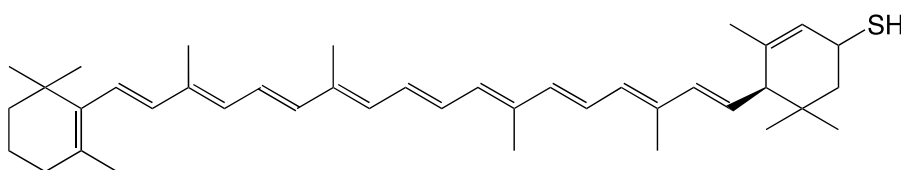
2S canthaxanthin thione

C₄₀H₅₂OSH.R. Sliwka, S. Liaaen-Jensen, *Acta Chem. Scand.* **1994**, *48*, 679

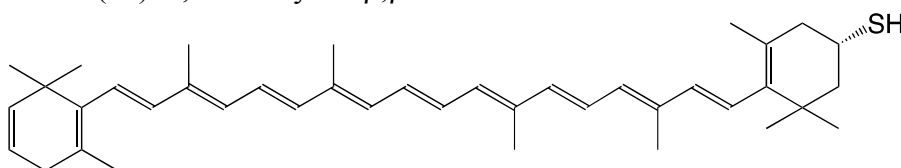
3S rhodoxanthin thione

C₄₀H₅₀OSH.R. Sliwka, S. Liaaen-Jensen, *Acta Chem. Scand.* **1994**, *48*, 679

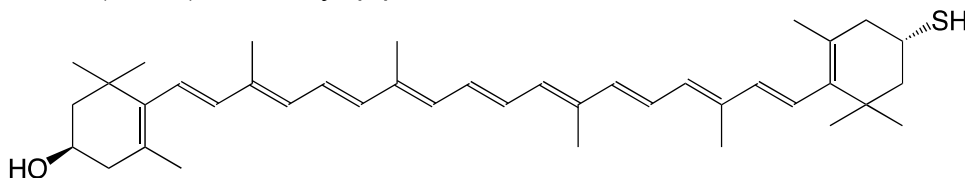
4S 3'-thiolutein

C₄₀H₅₆OSH.R. Sliwka, S. Liaaen-Jensen, *Acta Chem. Scand.* **1990**, *44*, 61

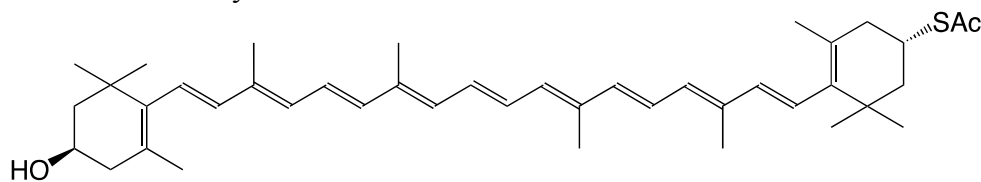
5S (3S)-2',3'-didehydro-β,β-carotene-3-thiol

C₄₀H₅₄SH.R. Sliwka, S. Liaaen-Jensen, *Tetrahedron Asym.* **1993**, *4*, 361H.R. Sliwka, *Helv. Chim. Acta* **1999**, *82*, 161

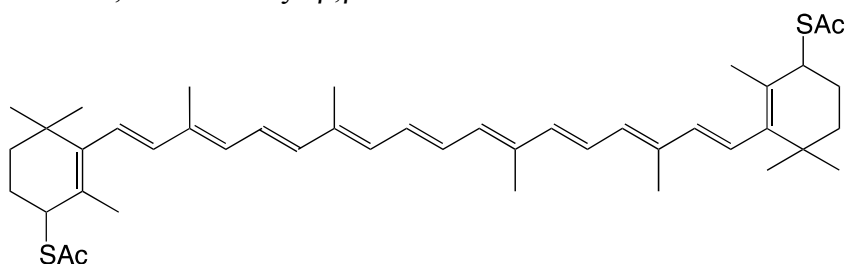
6S (3R,3'S)-3'-sulfanyl-β,β-caroten-3-ol

C₄₀H₅₆OSH.R. Sliwka, S. Liaaen-Jensen, *Tetrahedron Asym.* **1993**, *4*, 361H.R. Sliwka, *Helv. Chim. Acta* **1999**, *82*, 161

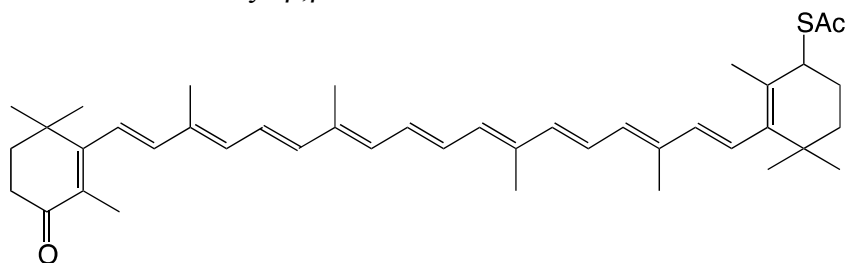
7S 3'-thioacetyl lutein

C₄₂H₅₈O₂SH.R. Sliwka, S. Liaaen-Jensen, *Acta Chem. Scand.* **1990**, *44*, 61

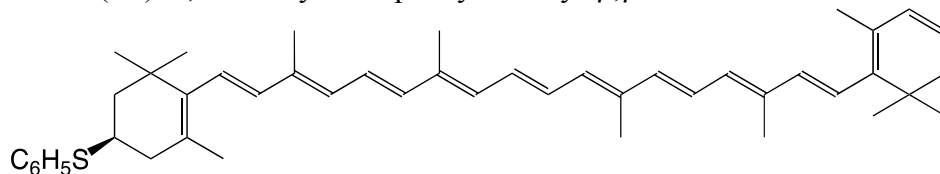
8S 4,4'-dithioacetyl-β,β-carotene

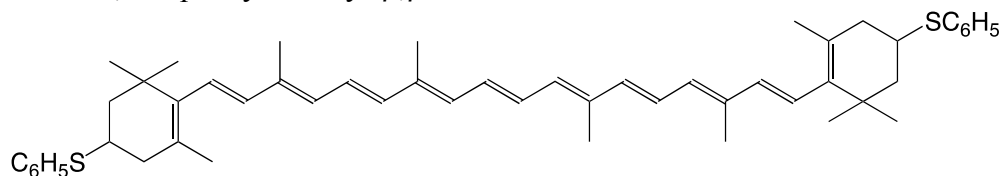
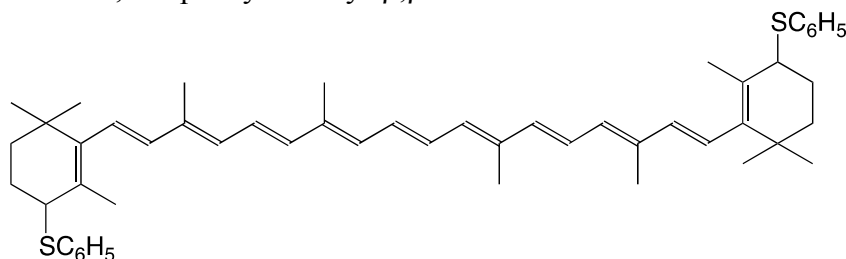
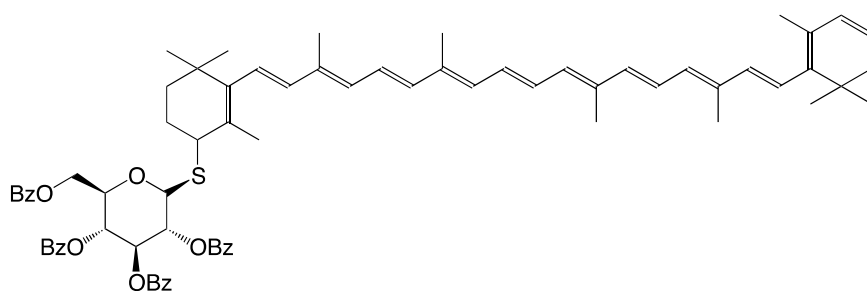
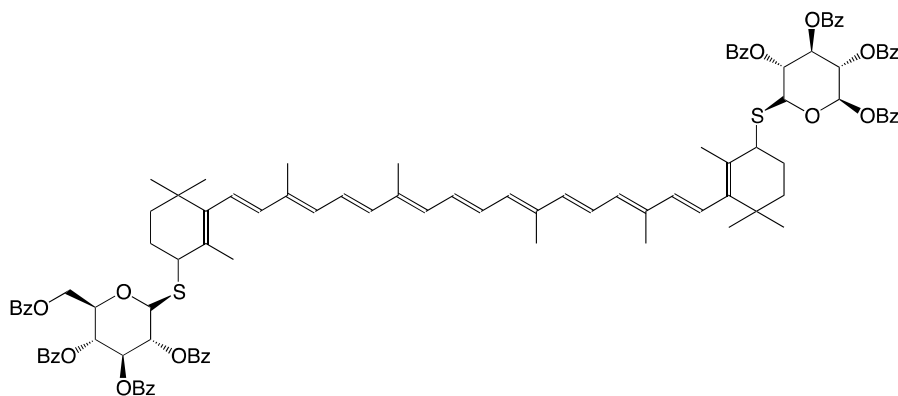
C₄₄H₆₀O₂S₂H.R. Sliwka, *Helv. Chim. Acta* **1999**, *82*, 161

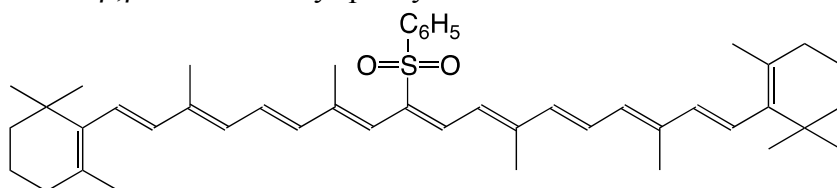
9S 4'-thioacetyl-β,β-caroten-4-one

C₄₂H₅₆O₂SH.R. Sliwka, S. Liaaen-Jensen, *Acta Chem. Scand.* **1990**, *44*, 61

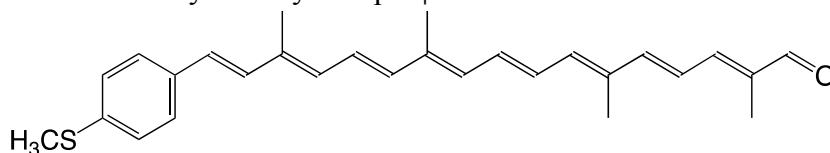
10S (3R)-3',4'-didehydro-3-phenylsulfanyl-β,β-carotene

C₄₆H₅₈SJ. Inananga, M. Yamaguchi, *Mem. Fac. Sci. Kyushi Univ. Ser. C*, **1989**, *17*, 109

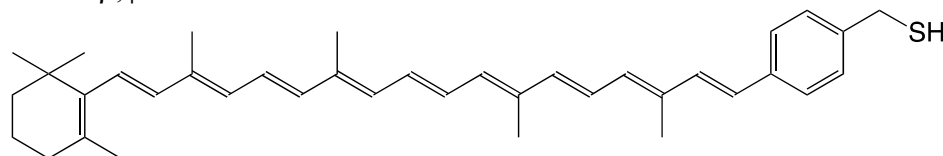
11S 3,3'-diphenylsulfanyl- β,β -caroteneC₅₂H₆₄S₂J. Inananga, M. Yamaguchi, *Mem. Fac. Sci. Kyushi Univ. Ser. C*, **1989**, 17, 10912S 4,4'-diphenylsulfanyl- β,β -caroteneC₅₂H₆₄S₂C. Martin, P. Karrer, *Helv. Chim. Acta* **1959**, 42, 46413S 3,4'-dehydro- β,β -carotene-4-thioglucopyranosideC₇₄H₈₀O₉SV. Nagy, A. Agócs, E. Turcsi, J. Deli, *Tetrahedron Lett.* **2010**, 52, 102014S β,β -carotene-4,4'-bisthioglucopyranosideC₁₀₇H₁₀₆O₁₈S₂V. Nagy, A. Agócs, E. Turcsi, J. Deli, *Tetrahedron Lett.* **2010**, 52, 1020

15S β,β -carotene-15-yl-phenylsulfoneC₄₆H₆₀O₂S

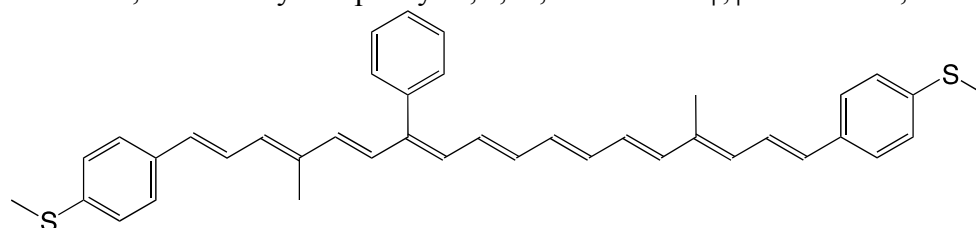
K. Berhard, S. Jäggi, P. Kreienbühl, U. Schwieter, *EU298404*, **1989**. The patent lists numerous other phenylsulfones and *p*-chlorophenylsulfones as synthetic intermediates.

 ϕ -carotenoids16S 3-methylsulfanyl-8'-apo- ϕ -carotenalC₂₈H₃₂OS

Y.Q. Shen, W. Göhring, S. Hagen, S. Roth, *J. Mol. Electron.* **1990**, 6, 31

17S β,ϕ -carotene-3'-methanethiolC₃₈H₄₈S

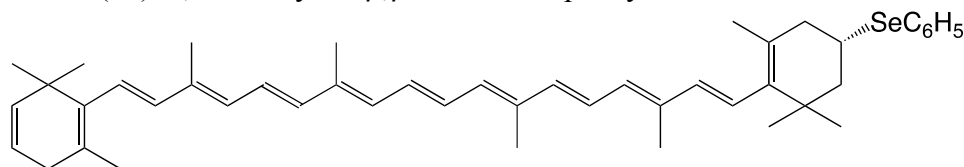
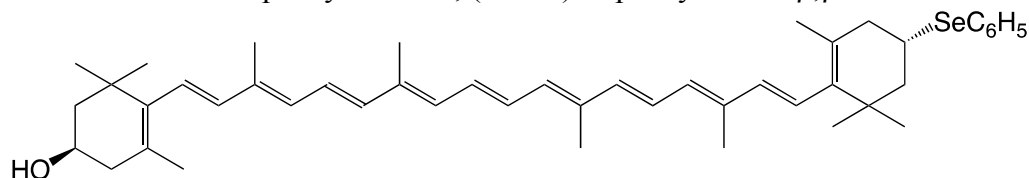
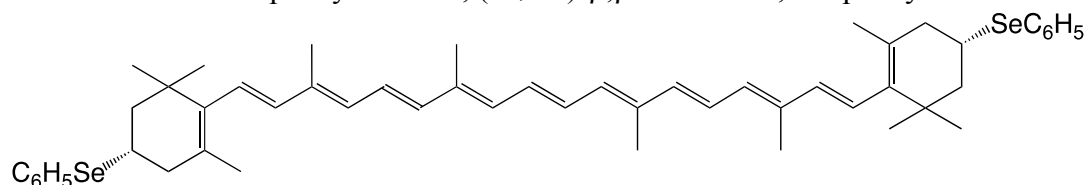
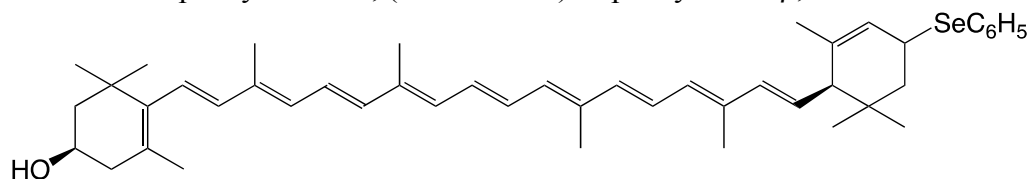
G. Leatherman, E.N. Duranti, D. Gust, T.A. Moore, A.L. Moore, S. Stone, Z. Zhou, P. Rez, Y.Z. Liu, S.M. Lindsay, *J. Phys. Chem. B* **1999**, 103, 4006

18S 10,10'-dimethyl-13-phenyl-9,9',13,13'-tetranor- ϕ,ϕ -carotene-3,3'-dimethanethiolC₄₀H₄₀S₂

J. Maeng, S.B. Kim, N.J. Lee, E. Choi, S.Y. Jung, I. Hong, S.H. Bae, J.T. Oh, B. Lim, J.W. Kim, C.J. Kang, S. Koo, *Chem. Eur. J.* **2010**, 16, 7395. The authors list other similar compounds.

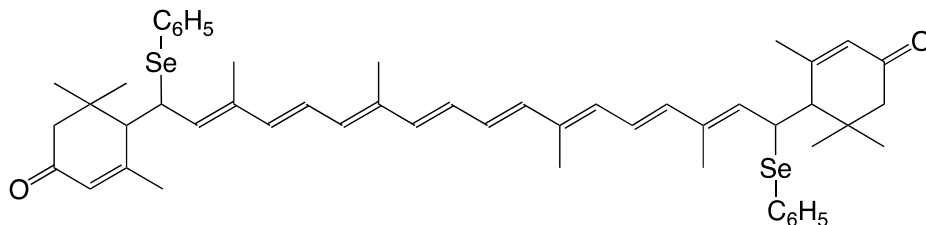
6.3.1. Selenium

Se

1Se (3S)-2',3'-didehydro- β,β -carotene-3-phenylselenide $C_{46}H_{58}Se$ H.R. Sliwka, S. Liaaen-Jensen, *Acta Chem. Scand.* **1995**, *49*, 428E. Oliveros, A.M. Braun, T. Aminian-Saghafi, H.R. Sliwka, *New J. Chem.* **1994**, *18*, 535H.R. Sliwka, *Helv. Chim. Acta* **1999**, *82*, 1612Se zeaxanthin phenylselenide, (3R,3'S)-3'-phenylseleno- β,β -caroten-3-ol $C_{46}H_{60}OSe$ H.R. Sliwka, S. Liaaen-Jensen, *Acta Chem. Scand.* **1995**, *49*, 428H.R. Sliwka, *Helv. Chim. Acta* **1999**, *82*, 1613Se zeaxanthin diphenylselenide, (3S,3'S)- β,β -carotene-3,3'-diphenylselenide $C_{52}H_{64}Se_2$ H.R. Sliwka, S. Liaaen-Jensen, *Acta Chem. Scand.* **1995**, *49*, 428H.R. Sliwka, *Helv. Chim. Acta* **1999**, *82*, 1614Se lutein phenylselenide, (3R,3'R,S,6'R)-3'-phenylseleno- β,ϵ -caroten-3-ol $C_{46}H_{60}OSe$ H.R. Sliwka, S. Liaaen-Jensen, *Acta Chem. Scand.* **1995**, *49*, 428

5Se rhodoxanthin diphenylselenide, 7,7'-di(phenylseleno)-7,8,7',8'-dihydro-*retro*- ϵ,ϵ -carotene-3,3'-dione

$C_{52}H_{62}O_2Se_2$

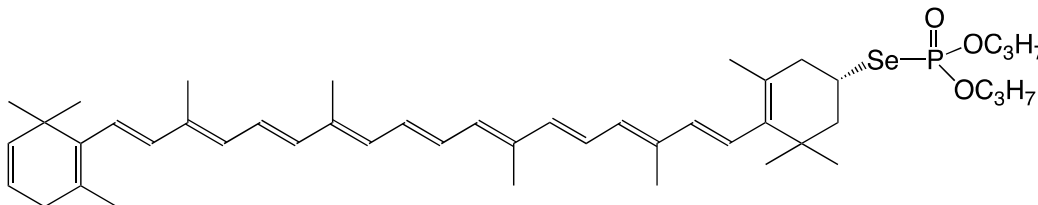


postulated unstable intermediate

H.R. Sliwka, S. Liaaen-Jensen, *Acta Chem. Scand.* **1995**, 49, 856

6Se (3*S*)-2',3'-didehydro- β,β -caroten-3-yl-di-O,O-propylselenophosphate

$C_{46}H_{67}O_3PSe$

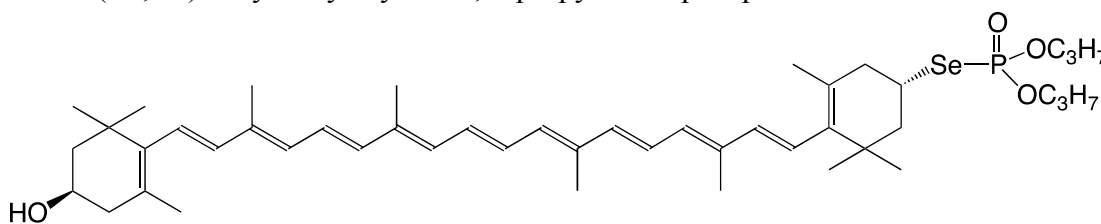


H.R. Sliwka, *Acta Chem. Scand.* 1997, 51, 345

H.R. Sliwka, *Helv. Chim. Acta* **1999**, 82, 161

7Se (3*R*,3'*S*)-3-hydroxy-3-yl-di-O,O-propylselenophosphate

$C_{46}H_{69}O_4PSe$



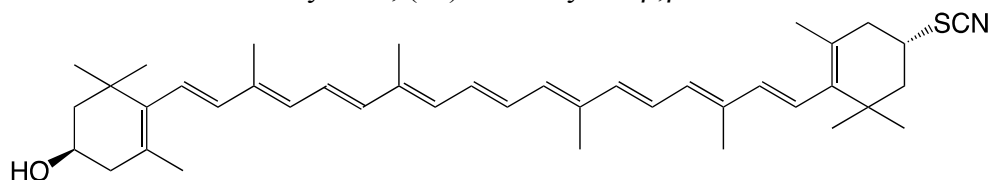
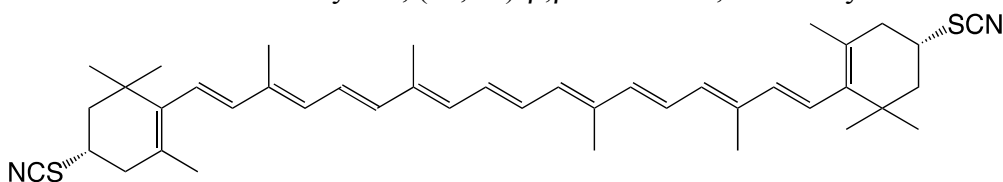
H.R. Sliwka, *Acta Chem. Scand.* 1997, 51, 345

H.R. Sliwka, *Helv. Chim. Acta* **1999**, 82, 161

6.4. Combinations

6.4.1. Nitrogen, Sulfur

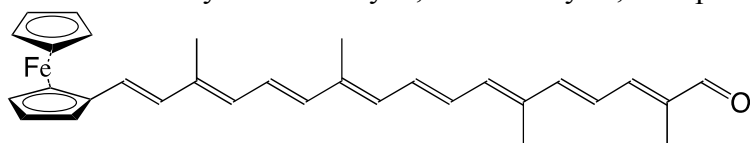
N,S

1NS zeaxanthin thiocyanate, (3*S*)-3'-thiocyano-β,β-caroten-3-olC₄₁H₅₅NOSH.R. Sliwka, S. Liaaen-Jensen, *Tetrahedron Asym.* **1993**, 4, 23772NS zeaxanthin dithiocyanat, (3*S*,3'*S*)-β,β-carotene-3,3'-dithiocyanateC₄₂H₅₄N₂S₂H.R. Sliwka, S. Liaaen-Jensen, *Tetrahedron Asym.* **1993**, 4, 2377

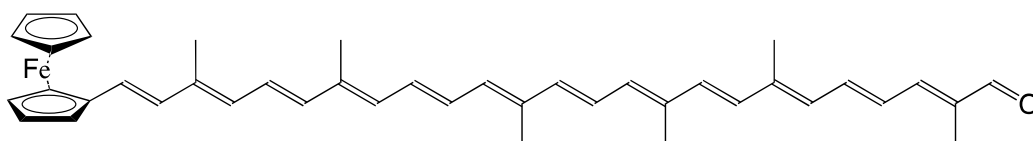
6.5. Iron

Fe

1Fe ferrocenyl-C21 aldehyde, 7-ferrocenyl-7,8'-diapocaroten-8'-al

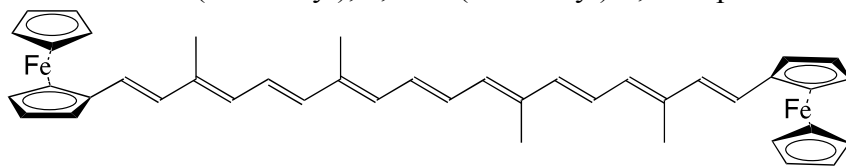
C₃₁H₃₅FeOF. Effenberger, H. Schlosser, *Synthesis* **1990**, 1085

2Fe ferrocenyl-C31 aldehyde

C₄₁H₄₇FeOF. Effenberger, H. Schlosser, *Synthesis* **1990**, 1085

3Fe C22 bis(ferrocenyl), 7,7'-bis(ferrocenyl)-7,7'-diapocarotene

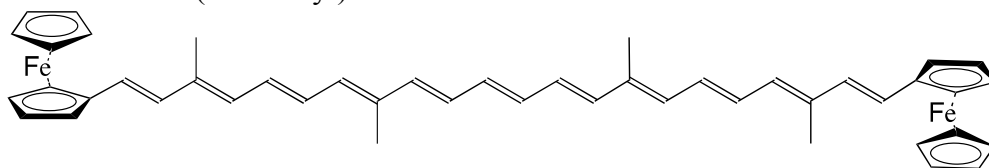
C₄₂H₄₈Fe₂



F. Effenberger, H. Schlosser, *Synthesis* **1990**, 1085

4Fe C26 bis(ferrocenyl)

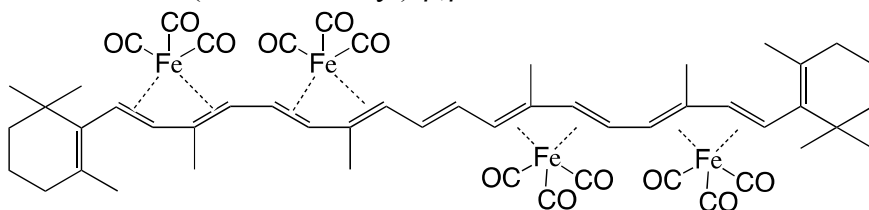
C₄₆H₅₂Fe₂



J.M. Lehn, *Angew. Chem. Int. Ed.* **1990**, 29, 1304

5Fe tetrakis(iron tricarbonyl)-β,β-carotene

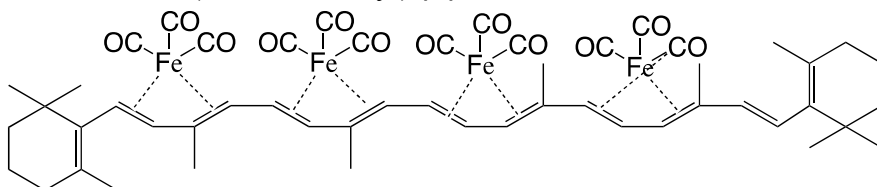
C₅₂H₅₆Fe₄O₁₂



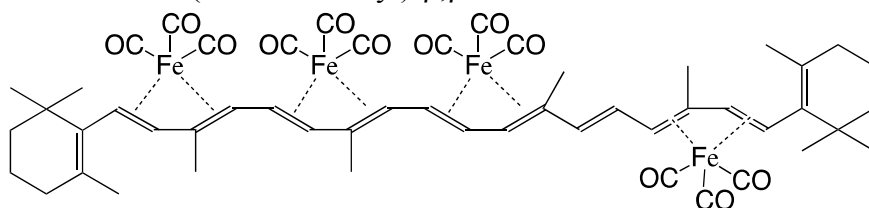
M. Ichikawa, M. Tsutsui, F. Vohwinkel, *Z. Naturforschg.* **1967**, 22b, 376

6Fe tetrakis(iron tricarbonyl)-β,β-carotene

C₅₂H₅₆Fe₄O₁₂



M. Ichikawa, M. Tsutsui, F. Vohwinkel, *Z. Naturforschg.* **1967**, 22b, 376

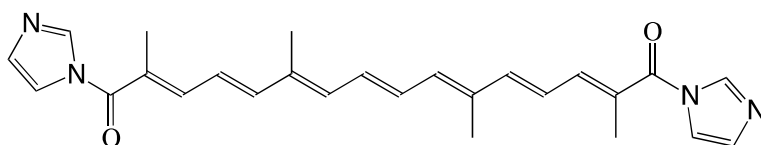
7Fe tetrakis(iron tricarbonyl)- β,β -carotene $C_{52}H_{56}Fe_4O_{12}$ M. Ichikawa, M. Tsutsui, F. Vohwinkel, *Z. Naturforschg.* **1967**, 22b, 376

6.6. Heterocycle Carotenoids

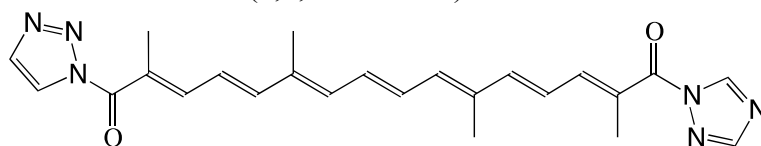
6.6.1. N-heterocycle

⊙N

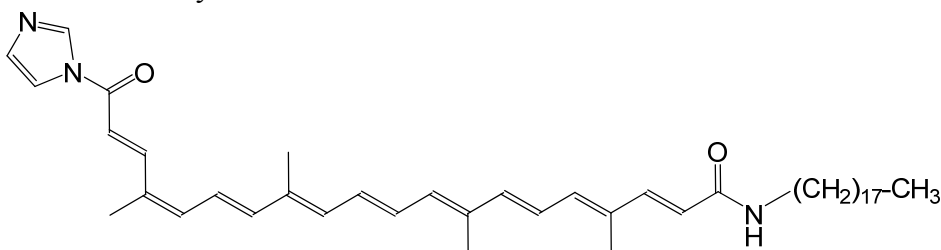
1⊙N crocetin-di-imidazolide

 $C_{26}H_{30}N_4O_2$ H. Pfander, F. Wittwer, *Helv. Chim. Acta* **1979**, 62, 1944

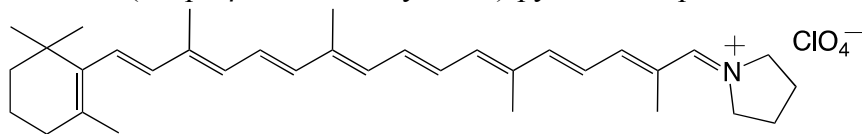
2⊙N crocetin-bis(1,2,4-triazolide)

 $C_{26}H_{30}N_4O_2$ H. Pfander, F. Wittwer, *Helv. Chim. Acta* **1979**, 62, 1944

3⊙N octadexylbixin imidazolide

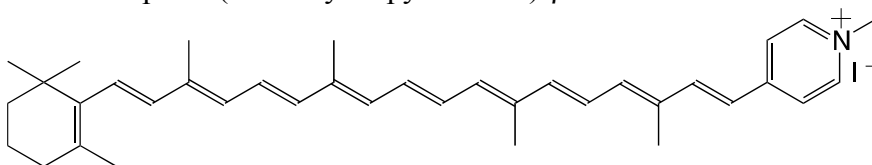
 $C_{45}H_{67}N_3O_2$ J.H. Fuhrhop, M. Krull, A. Schulz, D. Möbius, *Langmuir* **1990**, 6,497

4⊙N N-(8'-apo-β-carotene-8-ylidene)-pyrrolidinium perchlorate

C₃₄H₄₈ClNO₄

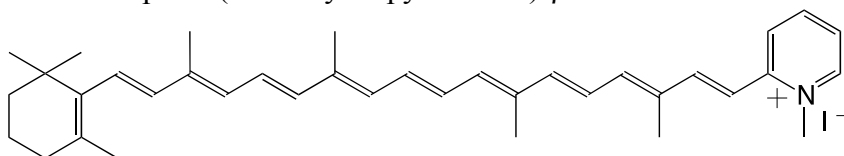
D.L. Coffen, E. Ho, C. Nocka, G. Sasso, V. Toome, T.R. Wagler, T.H. Williams, *J. Prakt. Chem.* **1993**, 335, 135

5⊙N 7'-apo-7'-(N-methyl-4-pyridinium)-β-carotene iodide

C₃₇H₄₈IN

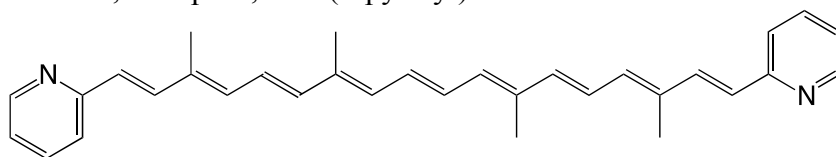
H. Ikeda, T. Sakai, Y. Kawabe, *JP 2-2534*, **1990**

6⊙N 7'-apo-7'-(N-methyl-2-pyridinium)-β-carotene iodide

C₃₇H₄₈IN

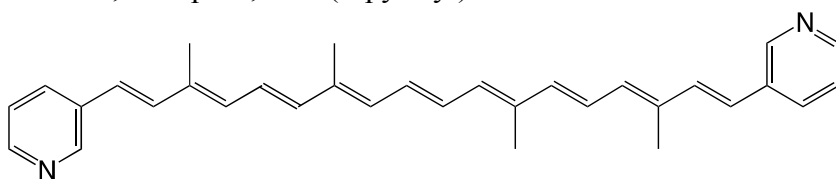
H. Ikeda, T. Sakai, Y. Kawabe, *JP 2-2534*, **1990**

7⊙N 7,7'-diapo-7,7'-bis(2-pyridyl)-carotene

C₃₂H₃₄N₂

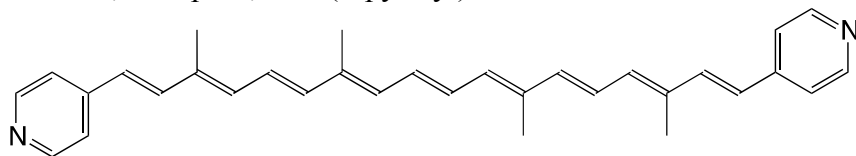
H.R. Brahmna, K. Katsuyama, J. Inaga, T. Katsuki, M. Yamaguchi, *Tetrahedron Lett.* **1981**, 22, 1695

8⊙N 7,7'-diapo-7,7'-bis(3-pyridyl)-carotene

C₃₂H₃₄N₂

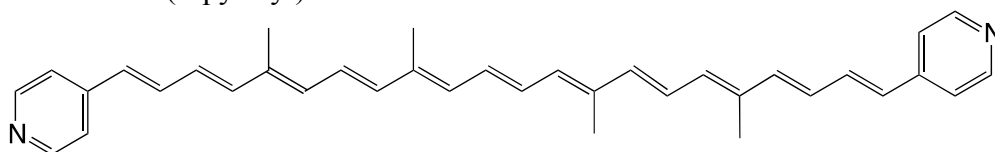
H.R. Brahmna, K. Katsuyama, J. Inaga, T. Katsuki, M. Yamaguchi, *Tetrahedron Lett.* **1981**, 22, 1695
 T.S. Arrhenius, M. Blanchard-Desce, M. Dvolaitzky, J.M. Lehn, J. Malthête, *Proc. Natl. Acad. Sci. USA* **1986**, 83, 5355

9⊙N 7,7'-diapo-7,7'-bis(4-pyridyl)-carotene

C₃₂H₃₄N₂

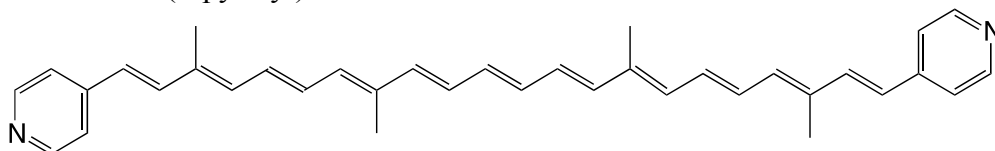
I. Visoly-Fisher, K. Daie, Y. Terazono, C. Herrero, F. Fungo, L. Otero, E. Durantini, J.J. Silber, L. Sereno, D. Gust, T.A. Moore, A.L. Morre, S.M. Lindsay, *PNAS* **2006**, *103*, 8686

10⊙N bis(4-pyridyl)-C26:11-carotene

C₃₆H₃₈N₂

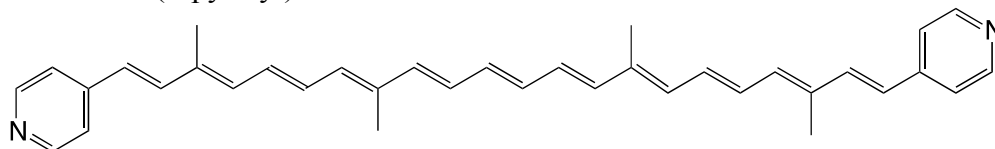
I. Visoly-Fisher, K. Daie, Y. Terazono, C. Herrero, F. Fungo, L. Otero, E. Durantini, J.J. Silber, L. Sereno, D. Gust, T.A. Moore, A.L. Morre, S.M. Lindsay, *PNAS* **2006**, *103*, 8686

11⊙N bis(4-pyridyl)-C26:11-carotene

C₃₆H₃₈N₂

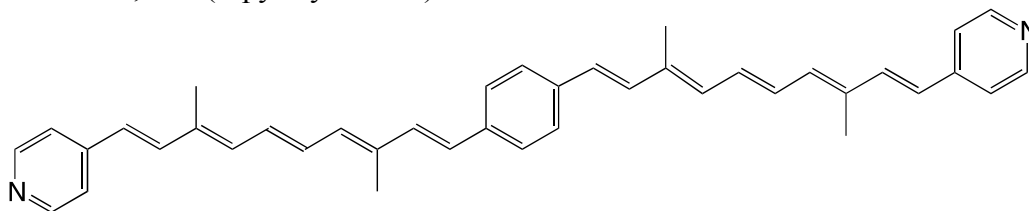
T.S. Arrhenius, M. Blanchard-Desce, M. Dvolaitzky, J.M. Lehn, J. Malthête, *Proc. Natl. Acad. Sci. USA* **1986**, *83*, 5355

12⊙N bis(4-pyridyl)-C34:15-carotene

C₃₆H₃₈N₂

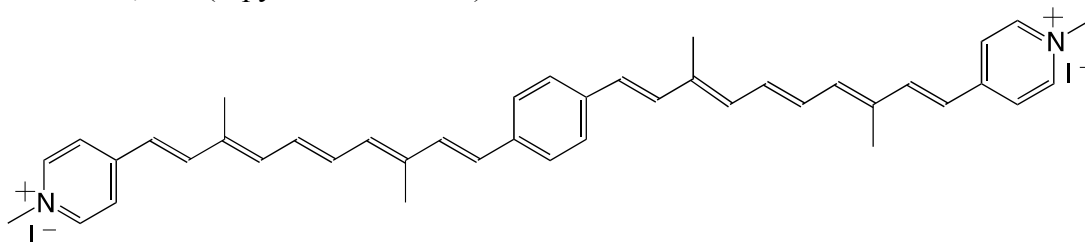
T.S. Arrhenius, M. Blanchard-Desce, M. Dvolaitzky, J.M. Lehn, J. Malthête, *Proc. Natl. Acad. Sci. USA* **1986**, *83*, 5355

13⊙N 1,4-bis(4-pyridyl-C12:5)-benzene

C₄₀H₄₀N₂

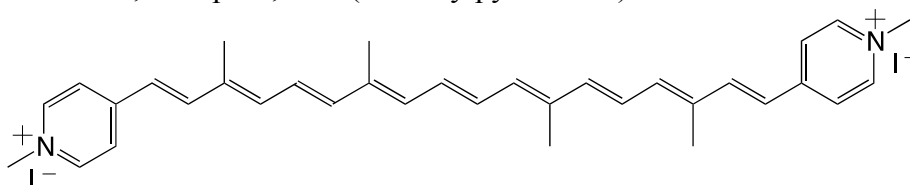
T.S. Arrhenius, M. Blanchard-Desce, M. Dvolaitzky, J.M. Lehn, J. Malthête, *Proc. Natl. Acad. Sci. USA* **1986**, *83*, 5355

14⊙N 1,4-bis(4-pyridinium-C12:5)-benzene diiodide

C₄₂H₄₆I₂N₂

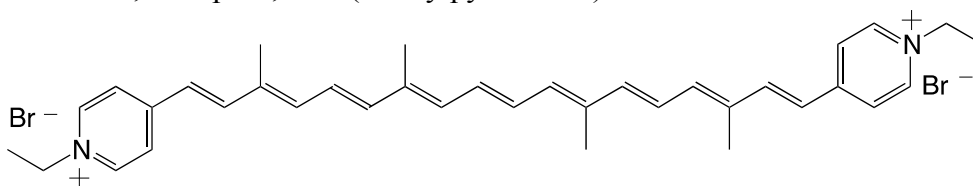
T.S. Arrhenius, M. Blanchard-Desce, M. Dvolaitzky, J.M. Lehn, J. Malthête, *Proc. Natl. Acad. Sci. USA* **1986**, *83*, 5355

15⊙N 7,7'-diapo-7,7'-bis(4-methylpyridinium)-carotene diiodide

C₃₄H₄₀I₂N₂

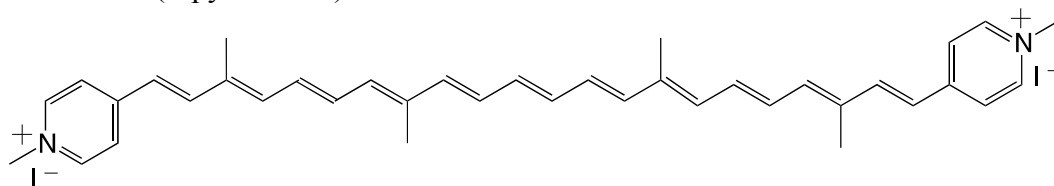
T.S. Arrhenius, M. Blanchard-Desce, M. Dvolaitzky, J.M. Lehn, J. Malthête, *Proc. Natl. Acad. Sci. USA* **1986**, *83*, 5355

16⊙N 7,7'-diapo-7,7'-bis(4-ethylpyridinium)-carotene dibromide

C₃₆H₄₄Br₂N₂

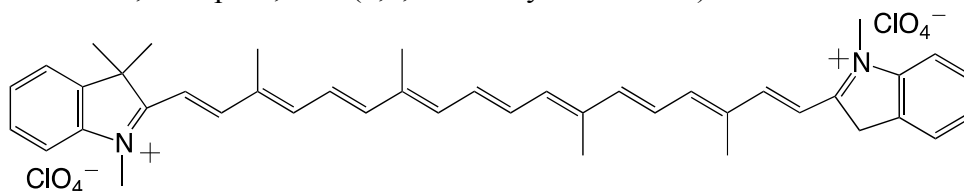
T. Okumoto, N. Morita, I. Nakamura, M. Konishi, M. Yamaguchi, *J. Cancer Res.. Clin. Oncol.* **1985**, *109*, 257

17⊙N bis(4-pyridinium)-C34:15-carotene diiodide

C₃₈H₄₄I₂N₂

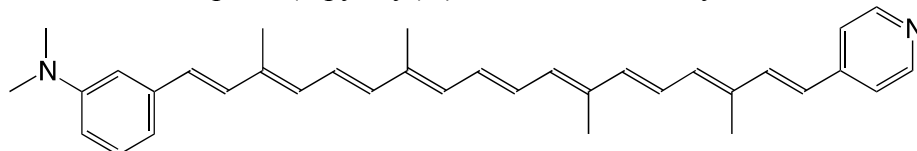
T.S. Arrhenius, M. Blanchard-Desce, M. Dvolaitzky, J.M. Lehn, J. Malthête, *Proc. Natl. Acad. Sci. USA* **1986**, *83*, 5355

18⊙N 7,7'-diapo-7,7'-bis(1,3,3 trimethylindolenium)-carotene dichlorate

C₄₂H₄₈Cl₂N₂O₈

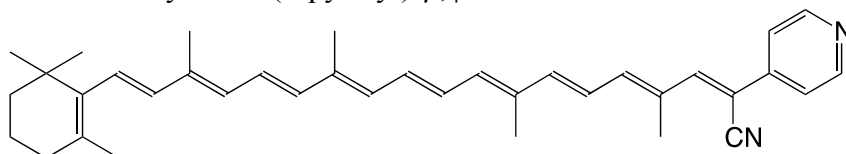
S. Hünig, F. Linhart, D. Scheutzow, *Liebigs Ann.* **1975**, 2089

19⊙N 7,7'-diapo-7'-(4-pyridyl)-ϕ-carotene-2-dimethylamine

C₃₅H₄₀N₂

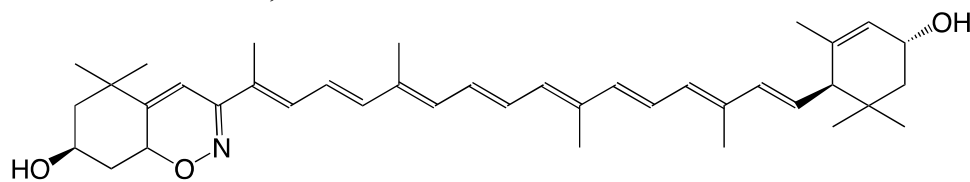
M. Blanchard-Desce, J.M. Lehn, I. Ledoux, J. Zyss, *Special Publication - Royal Society of Chemistry (Org. Mater. Non-linear Opt.)* **1989**, *69*, 170

20⊙N 7'-cyano-7'-(4-pyridyl)-β,ϕ-carotene

C₃₇H₄₄N₂

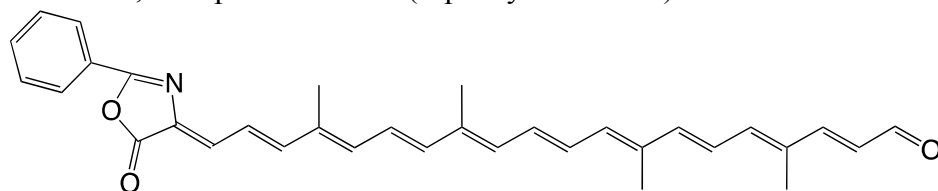
A.J. Cruz, K. Siam, D.P. Rillema, *J. Phys. Chem.* **2011**, *115*, 1108

21⊙N lutein-6H-1,2-oxazine

C₃₉H₅₃NO₃

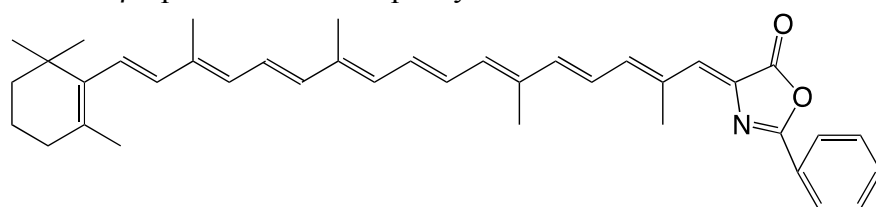
M. Tsuboi, H. Etoh, Y. Yomoda, K. Kato, H. Kato, A. Kulkarni, Y. terada, T. Maoka, H. Mori, T. Inakuma, *Tetrahedron Lett.* **2010**, 521, 676

22⊙N 6,6'-diapocarotenal-6'-(2-phenyl-azlactone)

C₃₃H₃₃NO₃

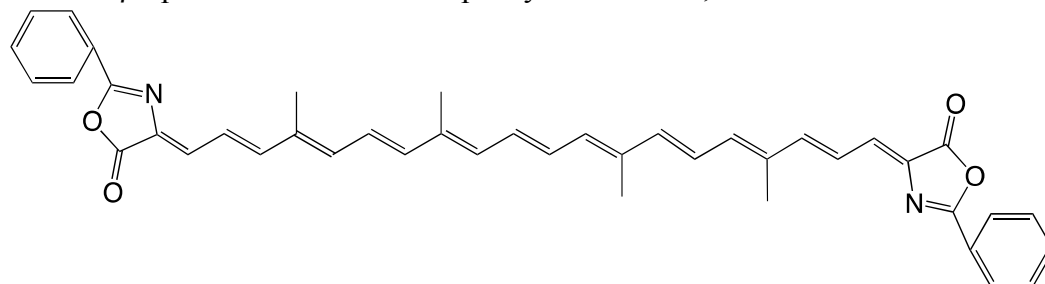
J. Zsako, M. Tomoaia-Cotisel, V. Tamas, C. Coman, E. Chifu, *Rev. Roum. Chim.* **1987**, 32, 1193.
The authors describe several other azlactones.

23⊙N β-apo-6'-carotenal-2-phenyl-azlactone

C₃₉H₄₅NO₂

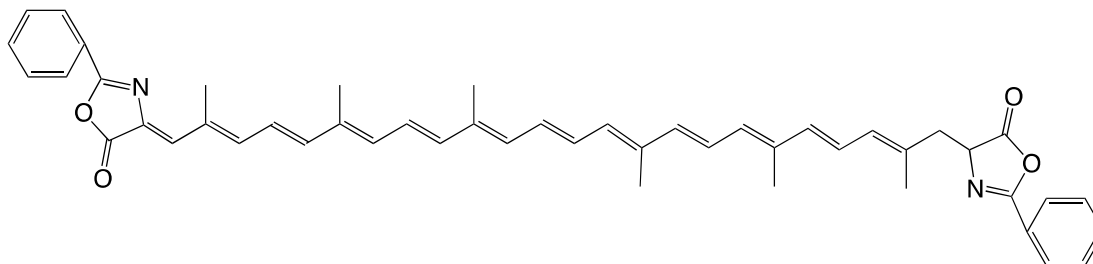
V. Tamas, V. Ciurdu, C. Bodea, *Rev. Roum. Chim.* **1973**, 18, 1409

24⊙N β-apo-6'-carotendial bis-2-phenyl diazlactone, C24:11 diazlactone

C₄₂H₃₈N₂O₄

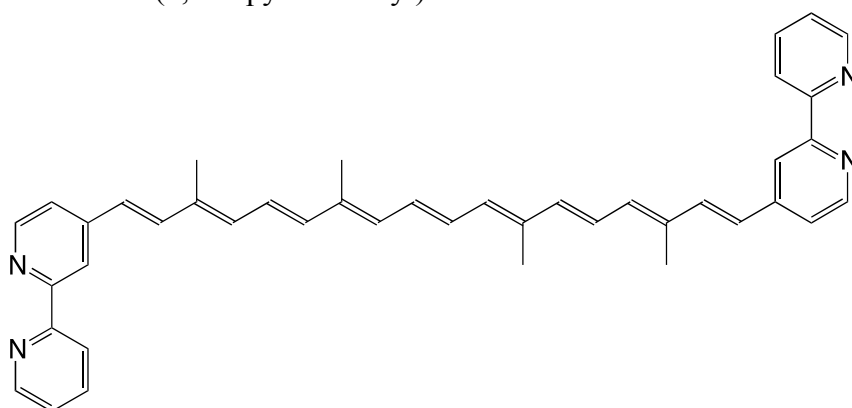
V. Tamas, V. Ciurdu, C. Bodea, *Rev. Roum. Chim.* **1973**, 18, 1409

25⊙N C30:13-diazlactone

C₄₈H₄₈N₂O₄

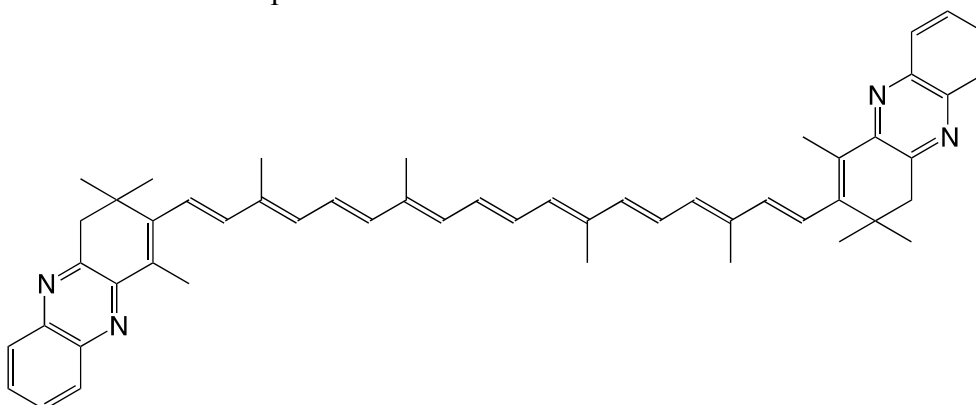
V. Tamas, V. Ciurdaru, C. Bodea, *Rev. Roum. Chim.* **1973**, *18*, 1409. The authors describe several other azlactones.

26⊙N bis(2,2'-bipyridine-4-yl)-carotene

C₄₂H₄₀N₄

F. Effenberger, M. Wezstein, *Synthesis* **2001**, 1368

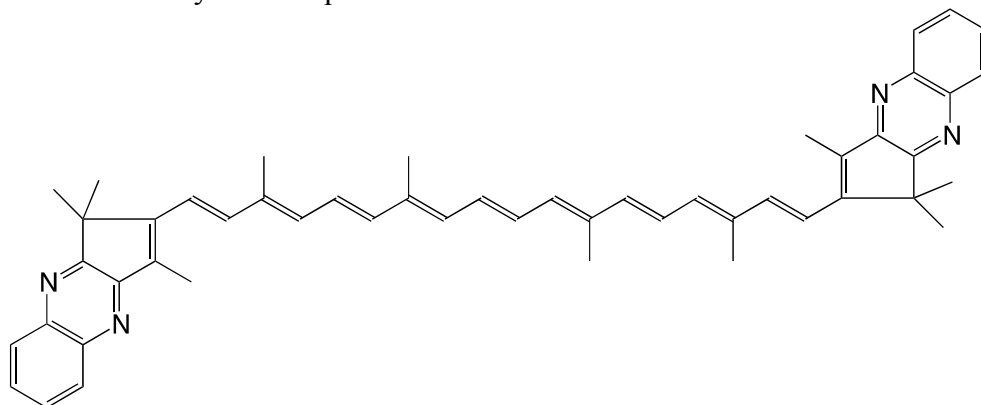
27⊙N astacene bisphenazine

C₅₂H₅₆N₄

P. Karrer, L. Loewe, *Helv. Chim. Acta* **1934**, *17*, 745

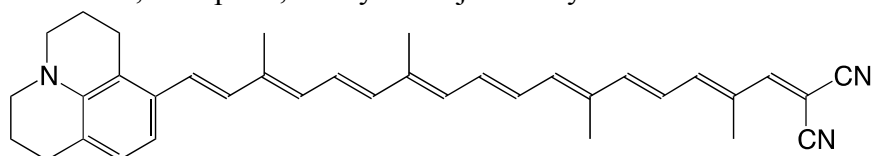
S. Hertzberg, S. Liaaen-Jensen, C.R. Enzell, G.W. Francis, *Acta Chem. Scand.* **1969**, *23*, 3290

28⊙N violerythrin bisquinoxaline

C₅₀H₅₂N₄

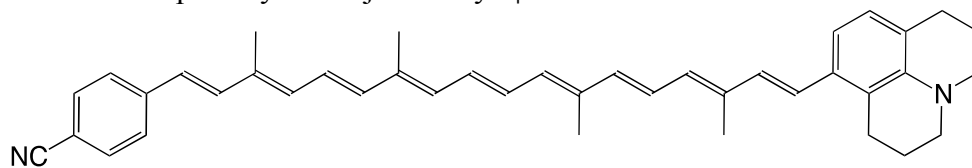
S. Hertzberg, S. Liaen-Jensen, C.R. Enzell, G.W. Francis, *Acta Chem. Scand.* **1969**, 23, 3290

29⊙N 7,7'-diapo-7,7'-dicyano-7-julolidinyl-carotene

C₃₆H₃₉N₃

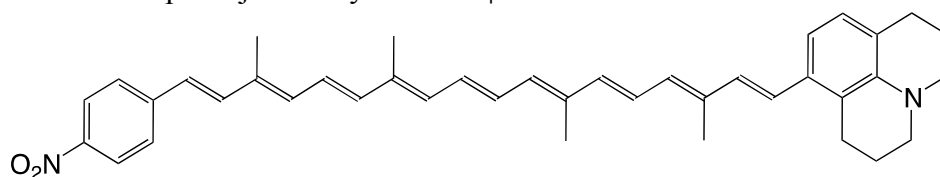
M. Blanchard-Desce, J.M. Lehn, M. Barzoukas, I. Ledoux, J. Zyss, *Chem. Phys.* **1994**, 181, 281

30⊙N 7'-apo-3-cyano-7'-julolidinyl-φ-carotene

C₄₁H₄₄N₂

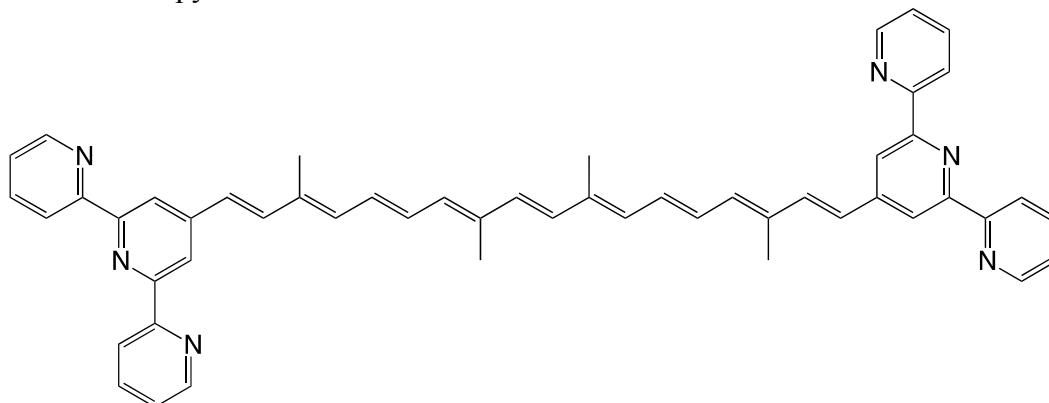
M. Blanchard-Desce, J.M. Lehn, M. Barzoukas, I. Ledoux, J. Zyss, *Chem. Phys.* **1994**, 181, 281

31⊙N 7'-apo-7'-julolidinyl-3-nitro-φ-carotene

C₄₀H₄₄N₂O₂

M. Blanchard-Desce, J.M. Lehn, M. Barzoukas, I. Ledoux, J. Zyss, *Chem. Phys.* **1994**, 181, 281

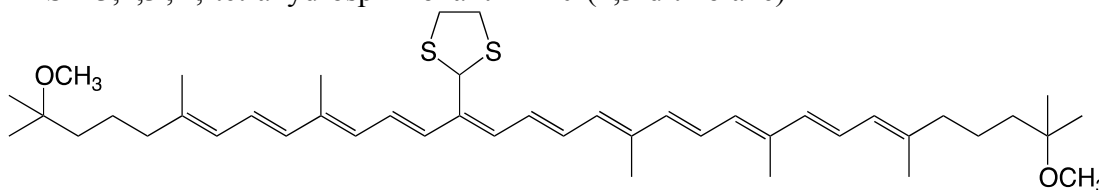
32⊙N diterpyridine carotenoid

C₅₂H₄₆N₆G. Pickaert, R. Ziessel, *Tetrahedron Lett.* **1998**, *39*, 3497

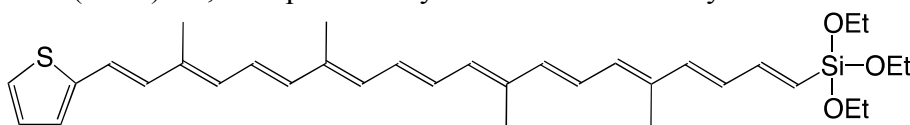
6.6.2. S-heterocycle

⊙S

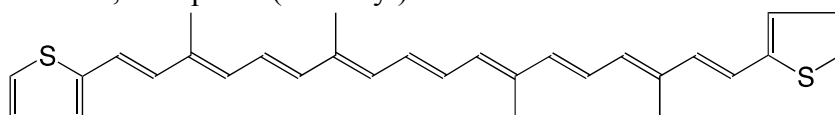
1⊙S 3,4,3',4',-tetrahydrospirilloxanthin-20-(1,3-dithiolane)

C₄₄H₆₆O₂S₂A.J. Aasen, S. Liaaen Jensen, *Acta Chem. Scand.* **1967**, *21*, 2185

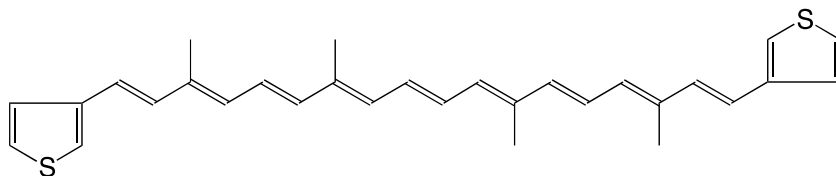
2⊙S (= 1Si) 7,5'-diapo-7-thienyl-carotene-5'-triethoxysilane

C₃₄H₄₆O₃SSiF. Effenberger, M. Wezstein, *Synthesis* **2001**, 1368

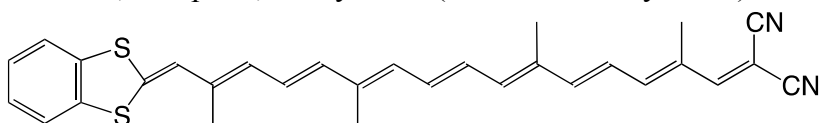
3⊙S 7,7'-diapo-bis(2-thienyl)-carotene

C₃₀H₃₂S₂H.R. Brahmna, K. Katsuyama, J. Inaga, T. Katsuki, M. Yamaguchi, *Tetrahedron Lett.* **1981**, *22*, 1695F. Effenberger, M. Wezstein, *Synthesis* **2001**, 1368

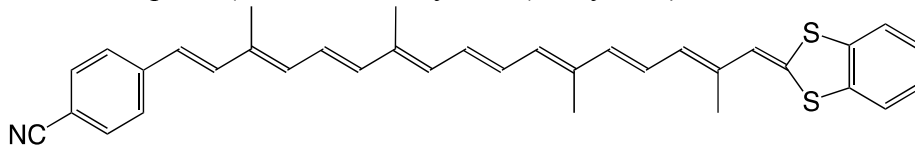
4⊙S 7,7'-diapo-bis(3-thienyl)-carotene

C₃₀H₃₂S₂H.R. Brahmna, K. Katsuyama, J. Inaga, T. Katsuki, M. Yamaguchi, *Tetrahedron Lett.* **1981**, 22, 1695

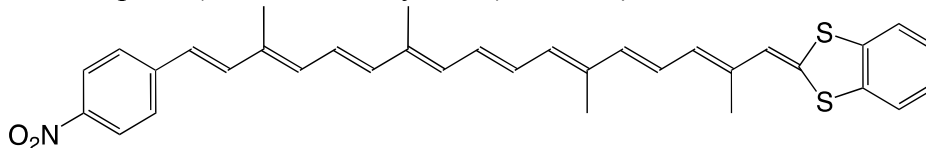
5⊙S 7,8-diapo-7',7'-dicyano-8-(benzodithiol-2-ylidene)-carotene

C₃₀H₂₈N₂S₂M. Blanchard-Desce, I. Ledoux, J. Malthête, J. Zyss, *J. Chem. Soc., Chem. Commun.* **1988**, 737

6⊙S 8'-apo-8'-(benzodithiol-2-ylidene)-3-cyano-φ-carotene

C₃₅H₃₃NS₂M. Blanchard-Desce, I. Ledoux, J. Malthête, J. Zyss, *J. Chem. Soc., Chem. Commun.* **1988**, 737

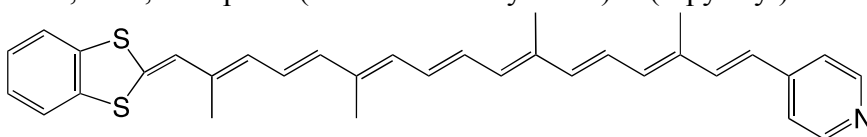
7⊙S 8'-apo-8'-(benzodithiol-2-ylidene)-3-nitro-φ-carotene

C₃₄H₃₃NO₂S₂M. Blanchard-Desce, I. Ledoux, J. Malthête, J. Zyss, *J. Chem. Soc., Chem. Commun.* **1988**, 737

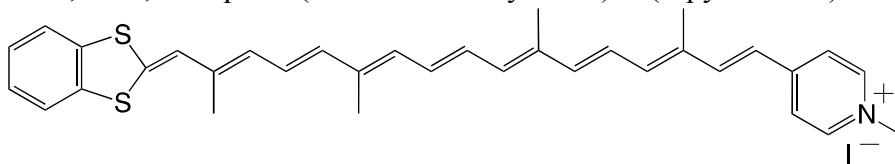
6.6.3. N,S-heterocycle

⊙N,S

1⊙N,S 7,8'-diapo-8'-(benzodithiol-2-ylidene)-7-(4-pyridyl)-carotene

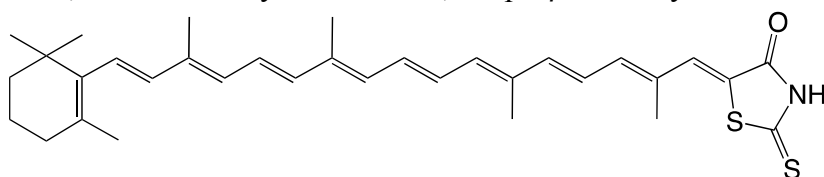
C₃₃H₃₃NS₂M. Blanchard-Desce, I. Ledoux, J. Malthête, J. Zyss, *J. Chem. Soc., Chem. Commun.* **1988**, 737

2⊙N,S 7,8'-diapo-8'-(benzodithiol-2-ylidene)-7-(4-pyridinium)-carotene iodide C₃₄H₃₆INS₂



M. Blanchard-Desce, I. Ledoux, J. Malthête, J. Zyss, *J. Chem. Soc., Chem. Commun.* **1988**, 737

3⊙N,S C30-aldehyde rhodanine, 8'-apo-β-carotenyliden-rhodanine C₃₃H₄₁NOS₂



H. Hegedus, *US3071583*, **1963**

H. Thommen, *Int. Z. Vitaminforsch.* **1967**, 37, 175

Sample Availability: Not available.

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