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*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

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## 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 Willstäter 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, $^{13}$C, $^{14}$C) [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., **11Cl-15Cl** [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⦿S, ⦿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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## 6. List of Xenobiotic Carotenoids

### *6.1. Halogen-Carotenoids*

6.1.1. Fluorine **F**

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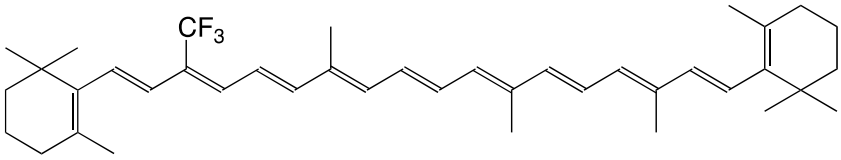
1F 9-trifluoromethyl-β,β-carotene $C_{40}H_{53}F_3$




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

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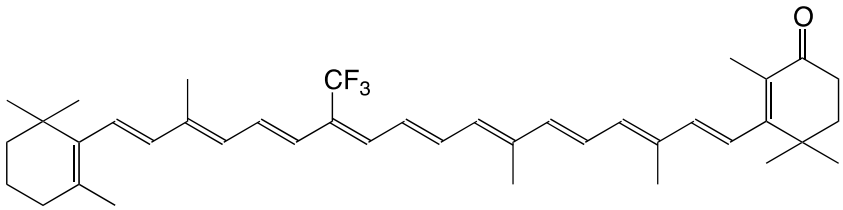
2F 13-trifluoromethyl-β,β-carotene $C_{40}H_{53}F_3$




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

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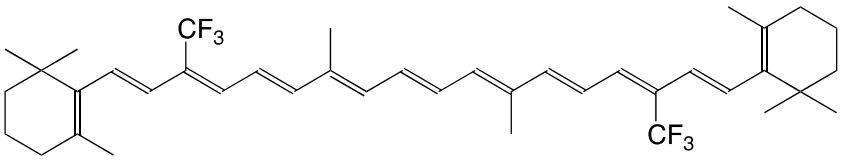
3F 9,9'-bis(trifluoromethyl)-β-carotene $C_{40}H_{50}F_6$




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

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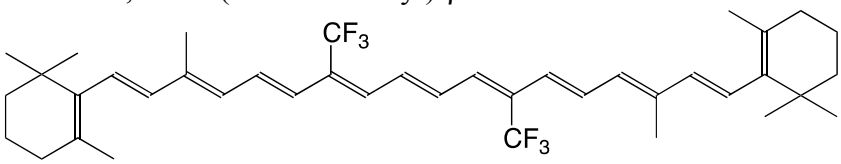
4F 13,13'-bis(trifluoromethyl)-β-carotene $C_{40}H_{50}F_6$




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

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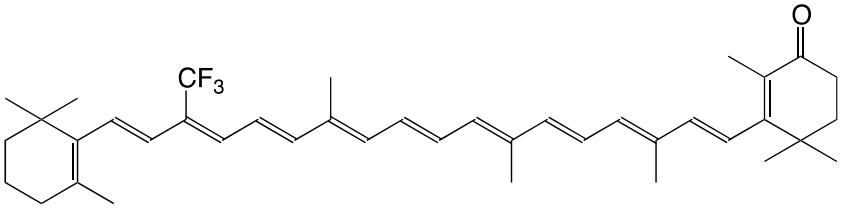
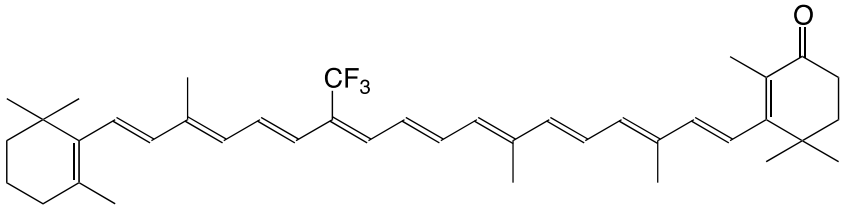
5F 9-trifluoromethyl echinenone $C_{40}H_{51}F_3O$



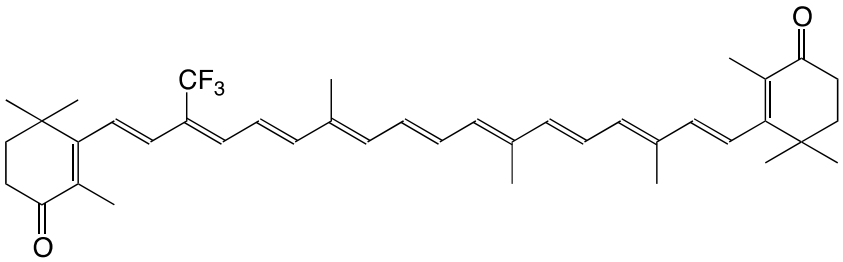

D. Hoischen, L.U. Colmenares, I. Koukhareva, M. Ho, R.S.H. Liu, *J. Fluorine Chem*. **1999**, *97*, 165

6F 13-trifluoromethyl echinenone $C_{40}H_{51}F_3O$



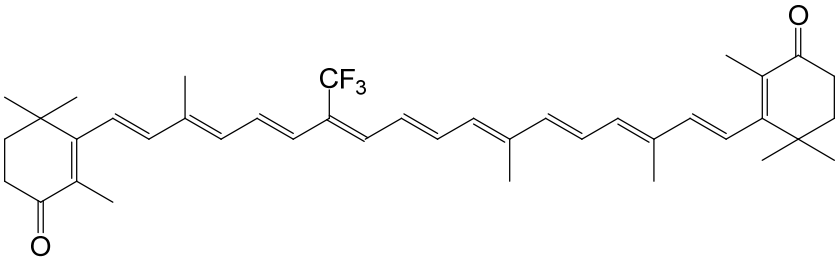

D. Hoischen, L.U. Colmenares, I. Koukhareva, M. Ho, R.S.H. Liu, *J. Fluorine Chem*. **1999**, *97*, 165

7F 9-trifluoromethyl canthaxanthin $C_{40}H_{49}F_3O_2$



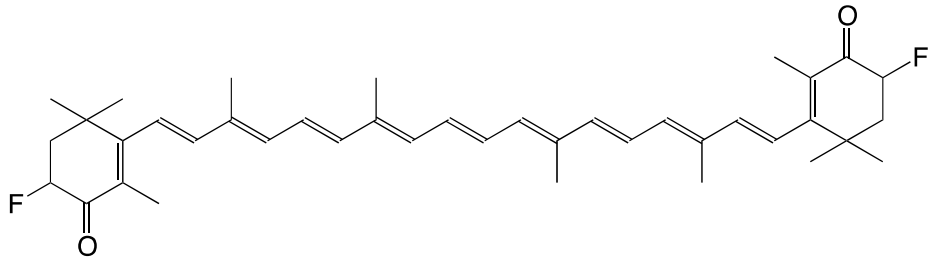

D. Hoischen, L.U. Colmenares, I. Koukhareva, M. Ho, R.S.H. Liu, *J. Fluorine Chem*. **1999**, *97*, 165

8F 13-trifluoromethyl canthaxanthin $C_{40}H_{49}F_3O_2$



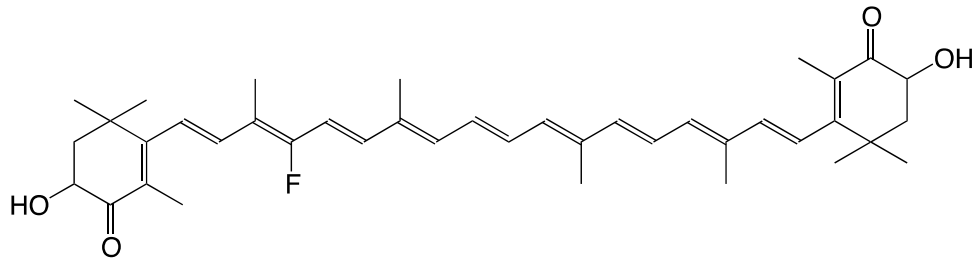

D. Hoischen, L.U. Colmenares, I. Koukhareva, M. Ho, R.S.H. Liu, *J. Fluorine Chem*. **1999**, *97*, 165

9F 3,3'-difluoro-canthaxanthin $C_{40}H_{50}F_2O_2$



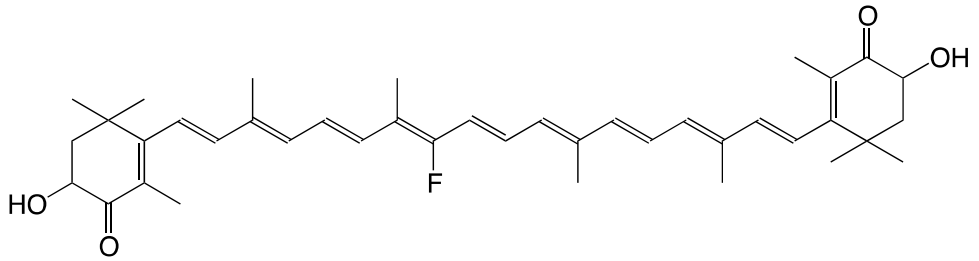

R.S.H. Liu, J. Liu, *J. Nat. Prod.* **2011**, *74*, 512

10F 10-fluoro-astaxanthin $C_{40}H_{51}FO_4$



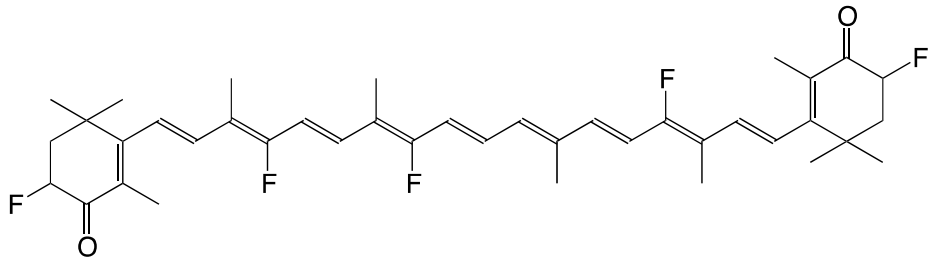

R.S.H. Liu, J. Liu, *J. Nat. Prod.* **2011**, *74*, 512

11F 14-fluoro-astaxanthin $C_{40}H_{51}FO_4$




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

12F 3,3',10,10',14-pentafluoro-canthaxanthin $C_{40}H_{47}F_5O_2$




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

ϕ-carotenoids

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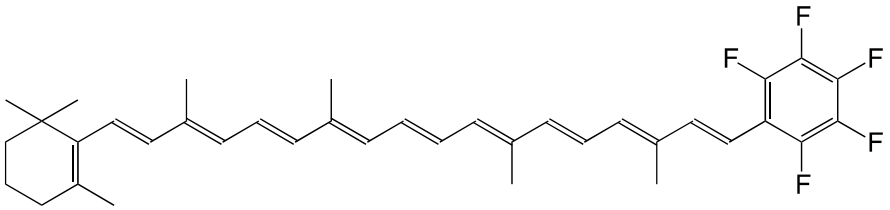
13F 1',2',3',4',5'-pentafluoro-β,ϕ-carotene $C_{37}H_{41}F_5$




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

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6.1.2. Chlorine **Cl**

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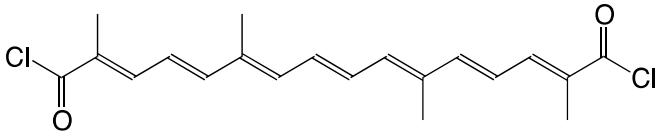
1Cl crocetin dichloride $C_{20}H_{22}Cl_2O_2$




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

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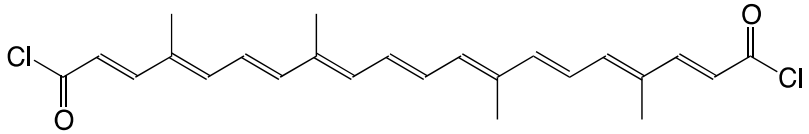
2Cl norbixin dichloride $C_{24}H_{26}Cl_2O_2$




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

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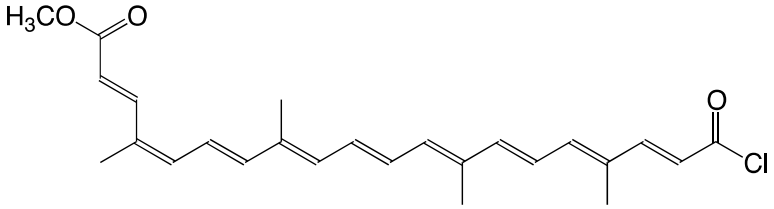
3Cl bixin chloride $C_{25}H_{29}ClO_3$




G. Ferrari, V. Vecchietti, *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

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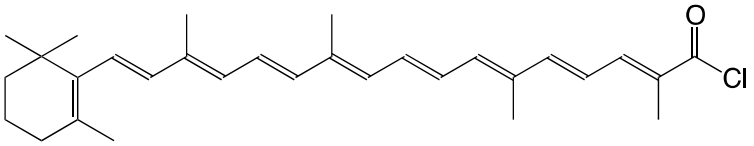
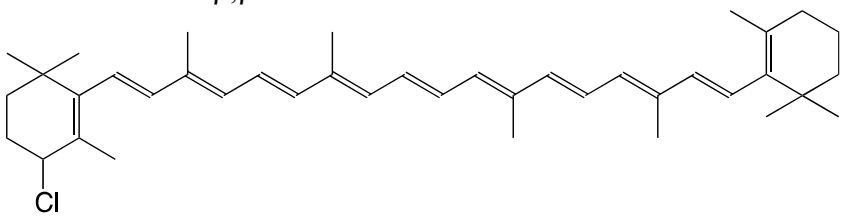
4Cl β-apo-8'-carotenoyl chloride, C30-acid chloride $C_{30}H_{39}ClO$



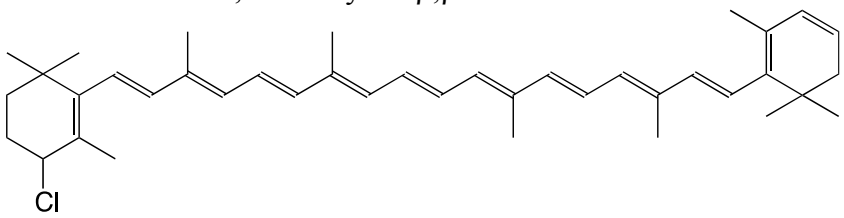

T. Naalsund, K.E. Malterrud, V. Partali, H.R. Sliwka, *Chem. Phys. Lipids* **2001**, *112*, 59
L. Levy, R. H. Binnington, A. Tabatnik, *WO 02/068385*, **2002**

5Cl 4-chloro-β,β-carotene $C_{40}H_{55}Cl$



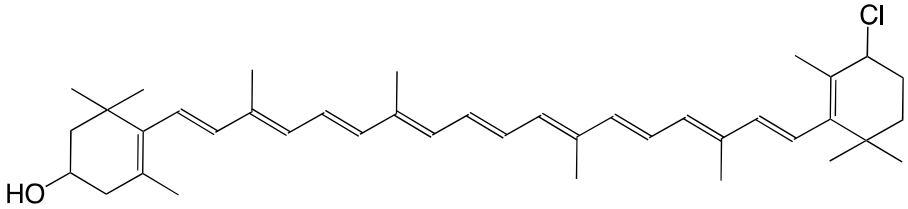

H. Pfander, U. Leuenberger, *Chimia* **1976**, *30*, 71

6Cl 4-chloro-3',4'-didehydro-β,β-carotene $C_{40}H_{53}Cl$



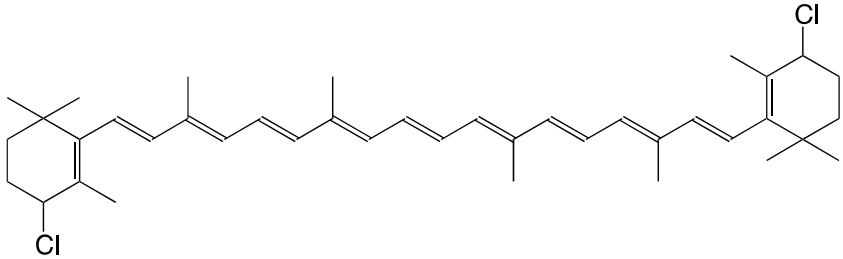

H. Pfander, U. Leuenberger, *Chimia* **1976**, *30*, 71

7Cl 4'-chloro-β,β-caroten-3-ol $C_{40}H_{55}ClO$



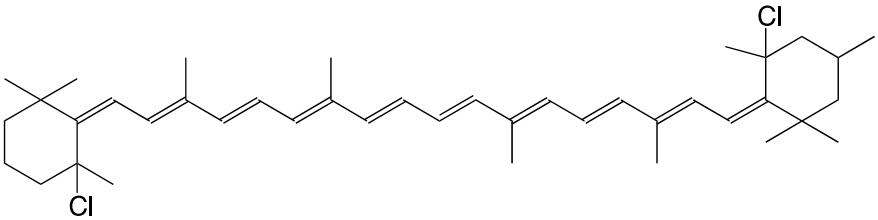

H. Pfander, U. Leuenberger, *Chimia* **1976**, *30*, 71

8Cl 4,4'-dichloro-β,β-carotene $C_{40}H_{54}Cl_2$



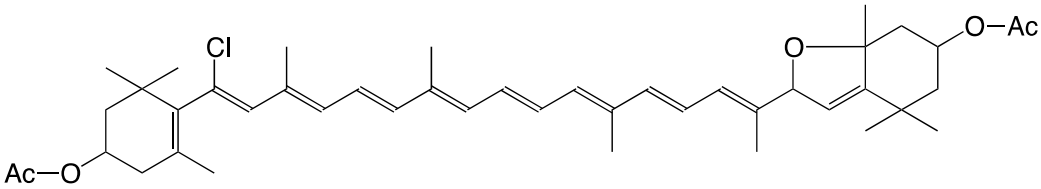

H. Pfander, U. Leuenberger, *Chimia* **1976**, *30*, 71

9Cl 5,5'-dichloro-4,5,4',5'-tetrahydroisocarotene $C_{41}H_{58}Cl_2$



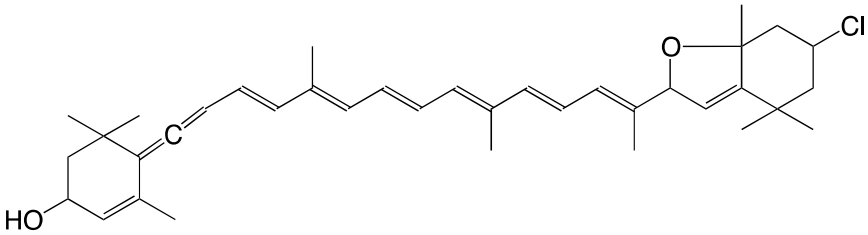

C. Bodea, E. Nicoara, *Acad. rep. populare Romîne, Filiala Cluj, Studii Cercetâri Chim*. **1959**, *10*, 1959

10Cl 7-chloro-mutatoxanthin-3,3'-diacetate $C_{44}H_{59}ClO_5$



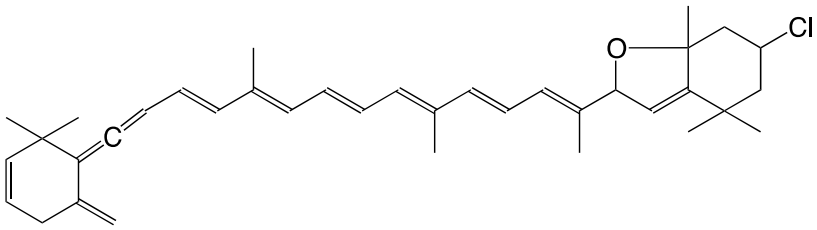

J.E. Johansen, S. Liaaen-Jensen, *Acta Chem. Scand*. **1974**, *B28*, 949
R. Buchecker, S. Liaaen-Jensen, *Helv. Chim. Acta* **1975**, *58*, 89

11Cl 3'-chloro-4,5-dehydro-5-dehydroxy-neochrome $C_{37}H_{49}ClO_2$



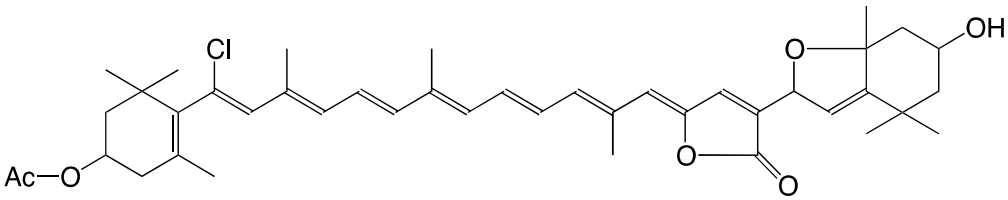

R. Buchecker, S. Liaaen-Jensen, *Helv. Chim. Acta* **1975**, *58*, 89

12Cl 3'-chloro-2,3-didehydro-5,18-dehydro-5-dehydroxy-neochrome $C_{37}H_{47}ClO$



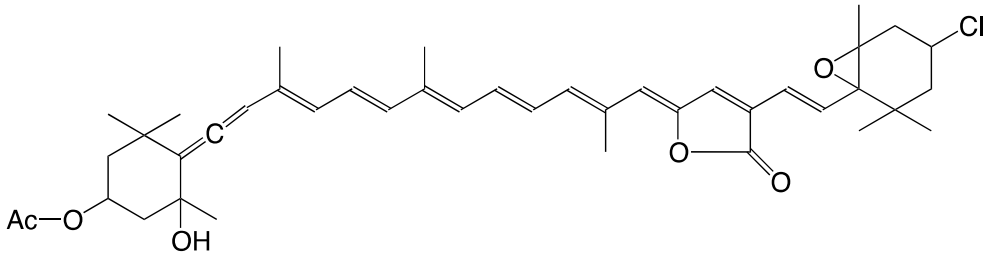

R. Buchecker, S. Liaaen-Jensen, *Helv. Chim. Acta* **1975**, *58*, 89

13Cl 7-chloro-mutatoxanthin-19',11'-olide 3-acetate $C_{42}H_{53}ClO_6$



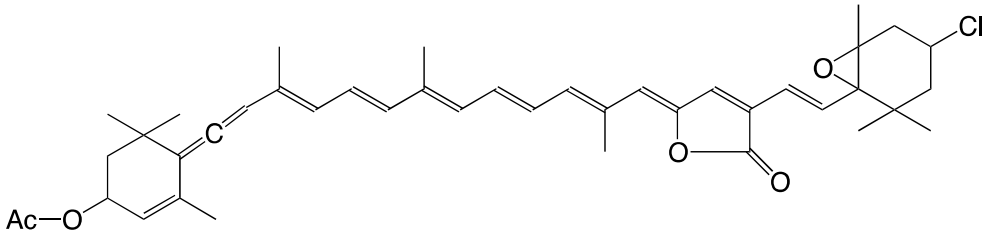

J.E. Johansen, S. Liaaen-Jensen, *Acta Chem. Scand*. **1974**, *B28*, 949

14Cl 3'-chloro-6,7-didehydro-peridinol-3-acetate $C_{42}H_{53}ClO_6$




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

15Cl 4,5-didehydro-5-dehydroxy-3'-chloro-peridinin-3-acetate $C_{42}H_{51}ClO_5$




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

6.1.3. Bromine **Br**

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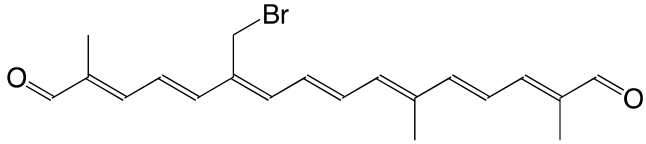
1Br 20-bromo-crocetindial $C_{20}H_{23}BrO_2$




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

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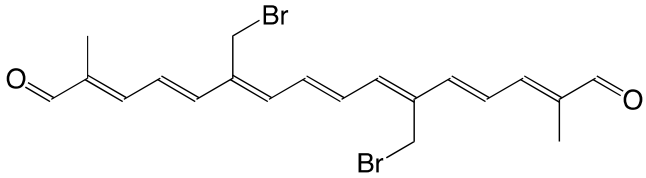
2Br 20,20'-dibromo-crocetindial $C_{20}H_{22}Br_2O_2$




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

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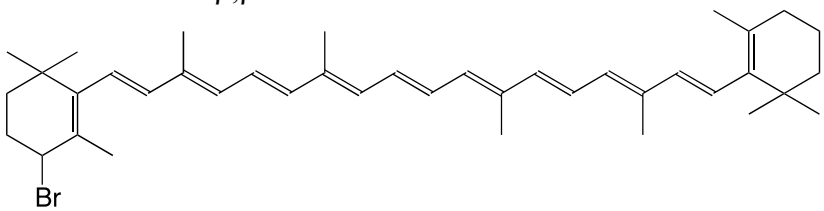
3Br 4-bromo-β,β-carotene $C_{40}H_{55}Br$




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

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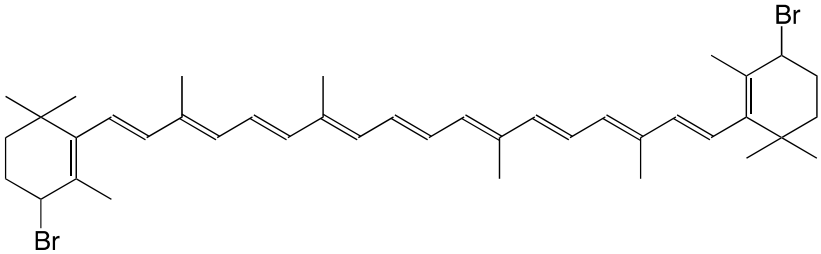
4 Br 4,4'-dibromo-β,β-carotene $C_{40}H_{58}Br_2$




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

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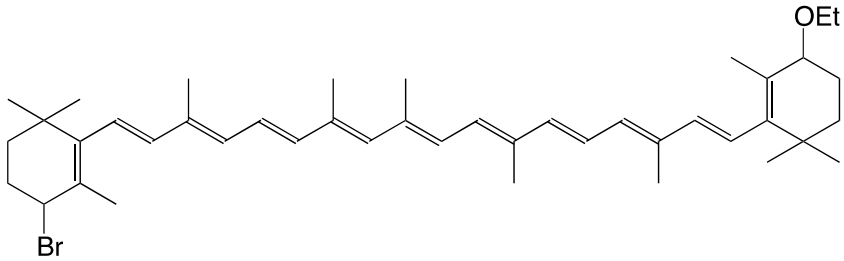
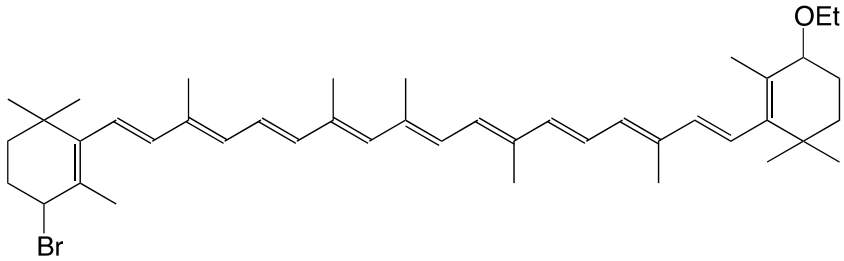
5Br 4-bromo-4'-ethoxy-β,β-carotene $C_{42}H_{59}BrO$



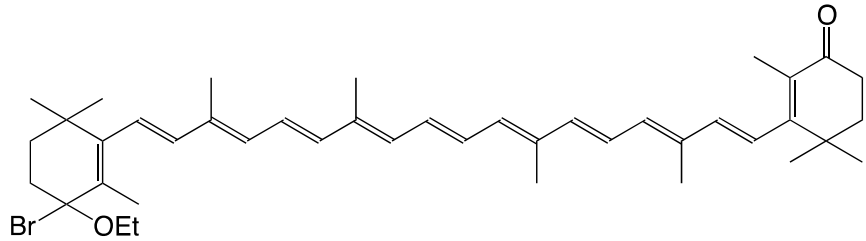

R. Entschel, P. Karrer, *Helv. Chim. Acta* **1958**, *41*, 402

6Br 4-bromo-4'-ethoxy-β,β-carotene $C_{44}H_{63}BrO_2$



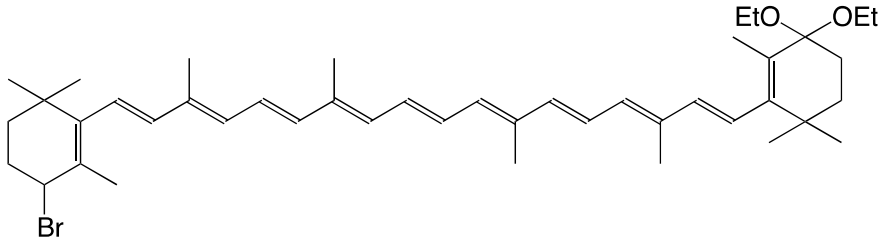

R. Entschel, P. Karrer, *Helv. Chim. Acta* **1958**, *41*, 402

7Br 4-bromo-4-ethoxy echinenone $C_{42}H_{57}BrO_2$



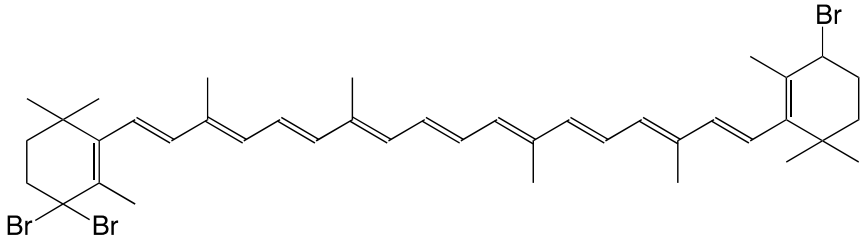

R. Entschel, P. Karrer, *Helv. Chim. Acta* **1958**, *41*, 402

8Br 4 bromo-4',4'-diethoxy-β,β-carotene $C_{44}H_{63}BrO_2$



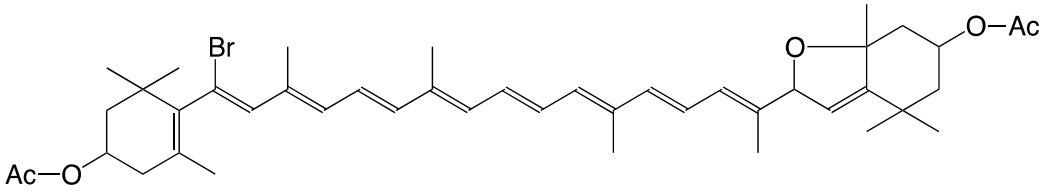

F.J. Petracek, L. Zechmeister, *J. Am. Chem. Soc*. **1956**, *78*, 1427

9Br 4,4,4'-tribromo-β,β-carotene $C_{40}H_{53}Br_3$




F.J. Petracek, L. Zechmeister, *J. Am. Chem. Soc*. **1956**, *78*, 1427

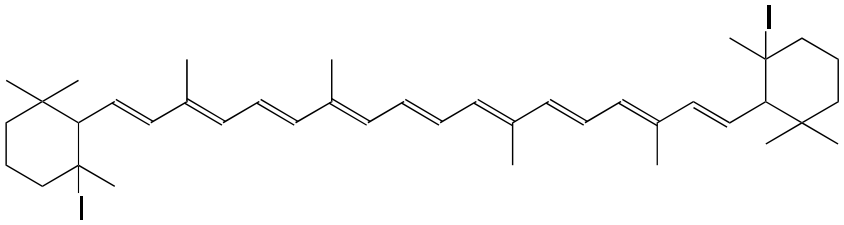
10Br 7-bromo-mutatoxanthin-diacetate $C_{44}H_{59}BrO_5$




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

6.1.4. Iodine **I**

1I 5,5'-diiodo-5,6,5',6'-didehydro-β,β-carotene $C_{40}H_{58}I_2$




unconfirmed structure
B.G. Savinov, G.S. Tretyakova, *Vitaminy 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**

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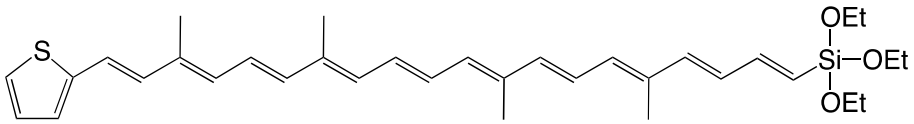
1Si (= 2⊙S) 7,5'-diapo-7-thienyl-carotene-5'-triethoxysilane $C_{34}H_{46}O_3SSi$




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

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6.3. *Nitrogen-Carotenoids* **N**

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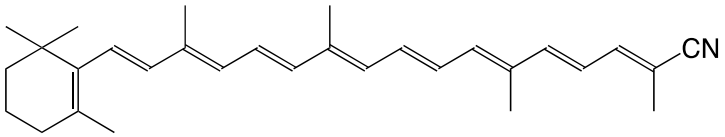
1N 8'-apo-β-carotene-8'-nitrile $C_{30}H_{39}N$




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

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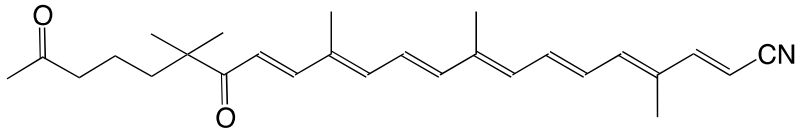
2N 10'-apo-5,6-seco-β-carotene-10'-nitrile $C_{27}H_{35}NO_2$




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

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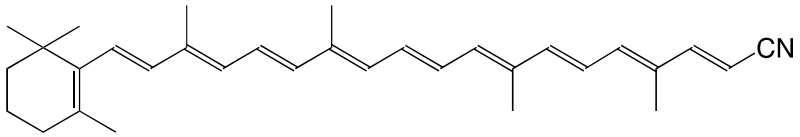
3N 6'-apo-β-carotene-6'-nitrile $C_{32}H_{41}N$




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

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

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

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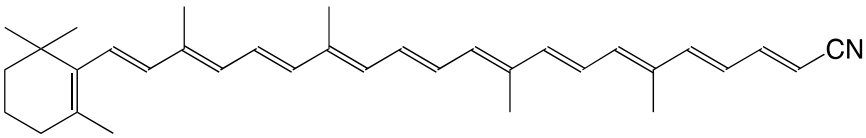
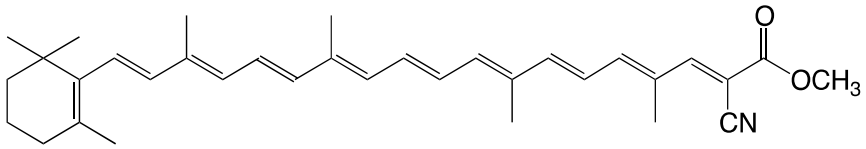
4N 4'-apo-β-carotene-4'-nitrile $C_{34}H_{43}N$



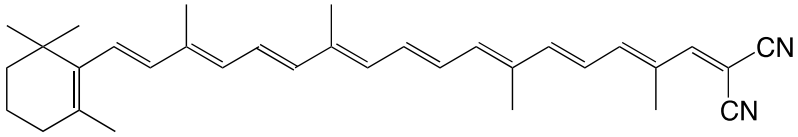

Z. He, D. Gosztola, Y. Deng, G. Gao, M.R. Wasielewski, L.D. Kispert, *J. Phys. Chem. B* **2000**, *104*, 6668

5N 7'-cyano-β-apo-7'-carotenoic acid methyl ester $C_{34}H_{43}NO_2$




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

6N 7'-apo-7',7'-dicyano-β–carotene $C_{33}H_{40}N_2$

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H. Ikeda, T. Sakai, Y. Kawabe, *JP 2-2534*, **1990**
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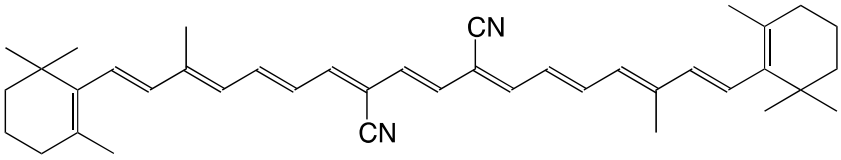
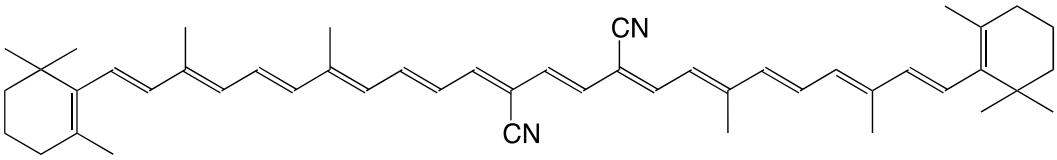
A.J. Cruz, K. Siam, D.P. Rillema, *J. Phys. Chem*. **2011**, *115*, 1108

7N 4,14'-dicyano-20,20'-dinor-β,β-carotene- $C_{40}H_{50}N_2$



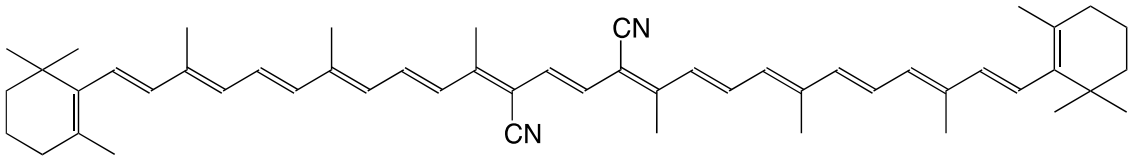

H.H. Haeck, T. Kralt, *Rec. Trav. Chim. Pays-Bas* **1966**, *85*, 343
P.B. Braun, J. Hornstra, J.I. Leenhouts, *Acta Cryst*. **1971**, *B27*, 90

8N dicyano-C44:14 $C_{48}H_{60}N_2$



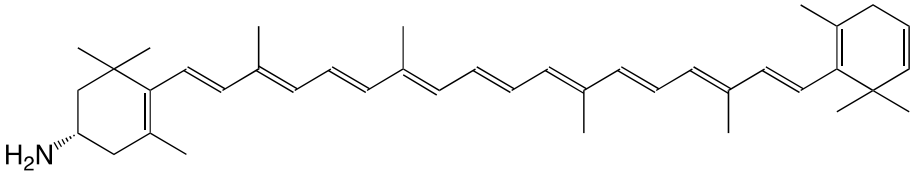

H.H. Haeck, T. Kralt, *Rec. Trav. Chim. Pays-Bas* **1966**, *85*, 343

9N dicyano-C48:15 $C_{52}H_{66}N_2$



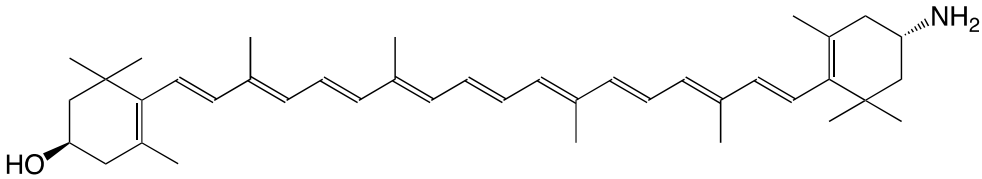

H.H. Haeck, T. Kralt, *Rec. Trav. Chim. Pays-Bas* **1966**, *85*, 343

10N (3*S*)-2',3'-didehydro-β,β-carotene-3-amine $C_{40}H_{55}N$



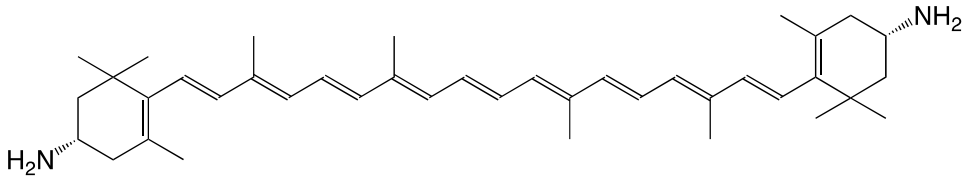

H.R. Sliwka, S. Liaaen-Jensen, *Tetrahedron Asym*. **1993**, *4*, 2377

11N (3*R*,3′*S*)-3'-amino-β,β-carotene-3-ol $C_{40}H_{57}NO$



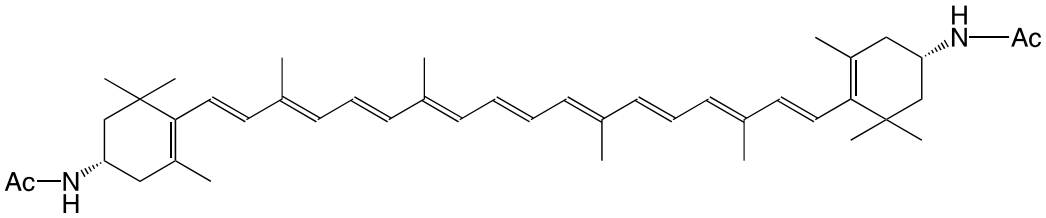

H.R. Sliwka, S. Liaaen-Jensen, *Tetrahedron Asym*. **1993**, *4*, 2377

12N (3*S*,3′*S*)-β,β-carotene-3,3'-amine $C_{40}H_{58}N_2$



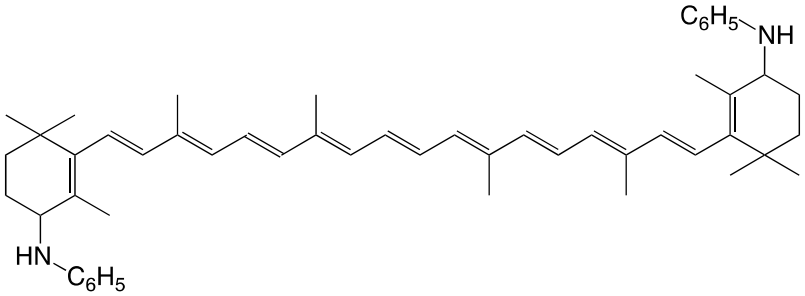

H.R. Sliwka, S. Liaaen-Jensen, *Tetrahedron Asym*. **1993**, *4*, 2377
J. Inananga, M. Yamaguchi, *Mem. Fac. Sci. Kyushi Univ. Ser. C*, **1989**, *17*, 109

13N (3*S*,3′*S*)-β,β-carotene-3,3'-diacetamide $C_{44}H_{62}N_2O_2$



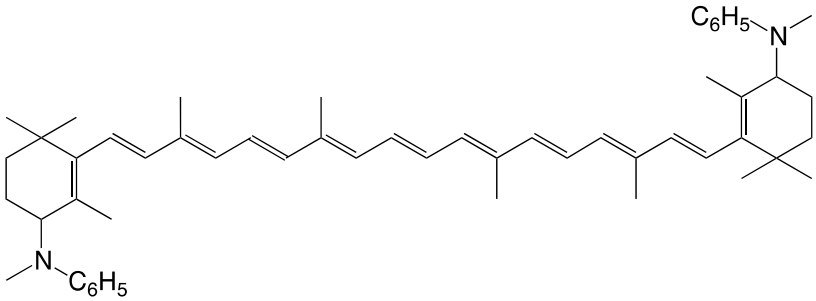

J. Inananga, M. Yamaguchi, *Mem. Fac. Sci. Kyushi Univ. Ser. C*, **1989**, *17*, 109

14N 4,4'-dianilino-β,β-carotene $C_{52}H_{66}N_2$



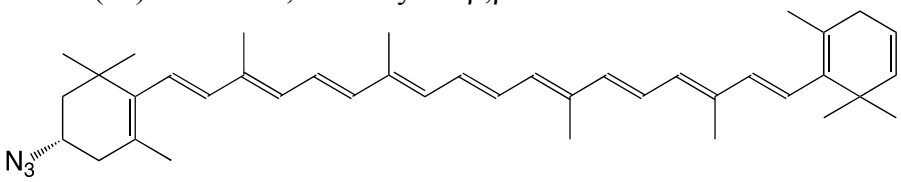

C. Martin, P. Karrer, *Helv. Chim. Acta* **1959**, *42*, 464
H. Budzikiewicz, H.Brzezinka, B. Johannes, *Monatshefte* **1970**, *101*, 579

15N 4,4'-bis(*N*-methyl-anilino)-β,β-carotene $C_{54}H_{70}N_2$



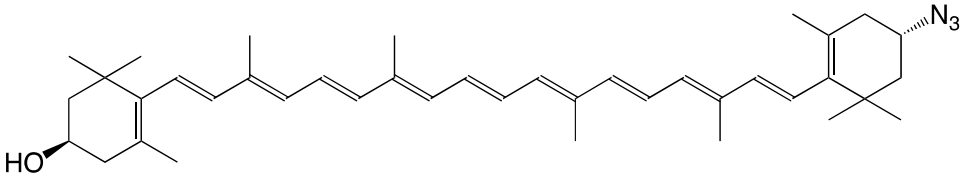

C. Martin, P. Karrer, *Helv. Chim. Acta* **1959**, *42*, 464

16N (3*S*)-3-azido-2',3'-didehydro-β,β-carotene $C_{40}H_{53}N_3$



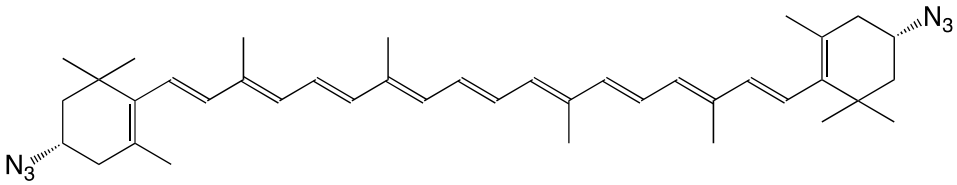

H.R. Sliwka, S. Liaaen-Jensen, *Tetrahedron Asym*. **1993**, *4*, 2377
H.R. Sliwka, *Helv. Chim. Acta* **1999**, *82*, 161

17N (3*R*,3'*S*)-3'-azido-β,β-carotene-3-ol $C_{40}H_{55}N_3O$



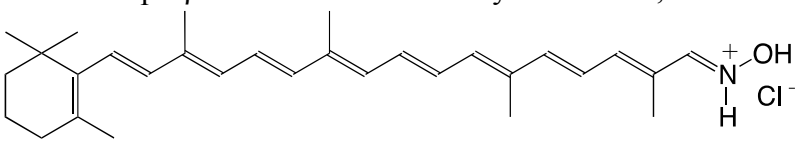

H.R. Sliwka, S. Liaaen-Jensen, *Tetrahedron Asym*. **1993**, *4*, 2377
H.R. Sliwka, *Helv. Chim. Acta* **1999**, *82*, 161

18N (3*S*,3′*S*)-diazido-β,β-carotene $C_{40}H_{54}N_6$




H.R. Sliwka, S. Liaaen-Jensen, *Tetrahedron Asym*. **1993**, *4*, 2377
J. Inananga, M. Yamaguchi, *Mem. Fac. Sci. Kyushi Univ. Ser. C*, **1989**, *17*, 109
H.R. Sliwka, *Helv. Chim. Acta* **1999**, *82*, 161

19N 8'-apo-β-caroten-8'-aldoxime hydrochloride, C30-aldoxime hydrochloride $C_{30}H_{42}ClNO$

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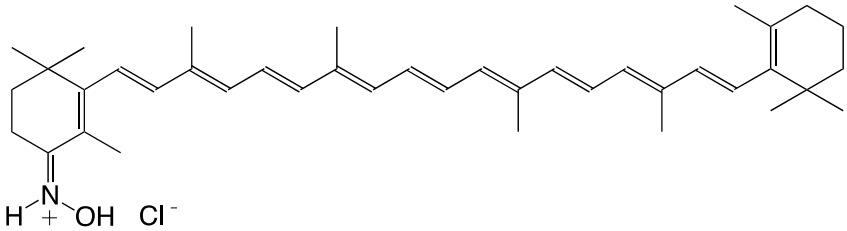
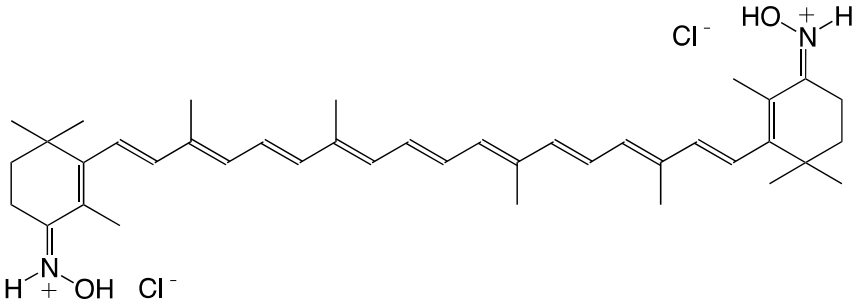
H.R. Sliwka, V. Partali, S.F. Lockwood, in *Carotenoids*, ed. J.T. Landrum, CRC Press, Boca Raton, USA, **2010**, chpt. 3

20N echinenenon oxime hydrochloride $C_{40}H_{56}ClNO$



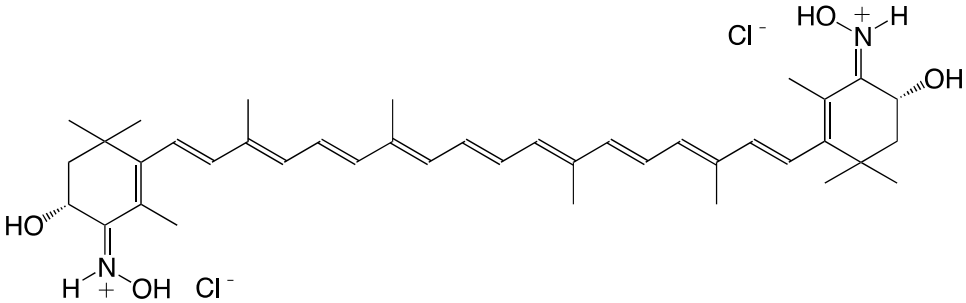

J. Willibald, S. Rennebaum, S. Breukers, S.H. Abdel Hafez, A. Patel, C.L. Øpstad, R. Schmid, S. Nalum Naess, H.R. Sliwka, V. Partali, *Chem. Phys. Lipids* **2009**, *161*, 32
H.R. Sliwka, V. Partali, S.F. Lockwood, in *Carotenoids*, ed. J.T. Landrum, CRC Press, Boca Raton, USA, **2010**, chpt. 3

21N canthaxanthin dioxime hydrochloride $C_{40}H_{56}Cl_2N_2O_2$



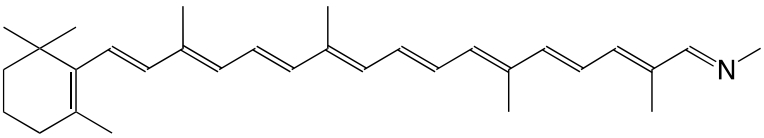

J. Willibald, S. Rennebaum, S. Breukers, S.H. Abdel Hafez, A. Patel, C.L. Øpstad, R. Schmid, S. Nalum Naess, H.R. Sliwka, V. Partali, *Chem. Phys. Lipids* **2009**, *161*, 32
H.R. Sliwka, V. Partali, S.F. Lockwood, in *Carotenoids*, ed. J.T. Landrum, CRC Press, Boca Raton, USA, **2010**, chpt. 3

22N astaxanthin dioxime hydrochloride $C_{40}H_{56}Cl_2N_2O_4$



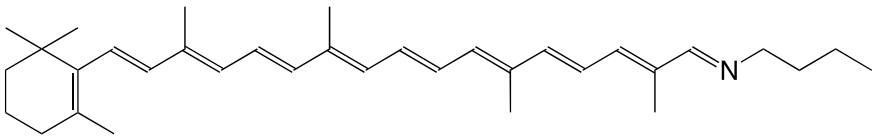

J. Willibald, S. Rennebaum, S. Breukers, S.H. Abdel Hafez, A. Patel, C.L. Øpstad, R. Schmid, S. Nalum Naess, H.R. Sliwka, V. Partali, *Chem. Phys. Lipids* **2009**, *161*, 32
H.R. Sliwka, V. Partali, S.F. Lockwood, in *Carotenoids*, ed. J.T. Landrum, CRC Press, Boca Raton, USA, **2010**, chpt. 3

23N 7'-aza-7'-methyl-7'-apo-β-carotene $C_{31}H_{43}N$



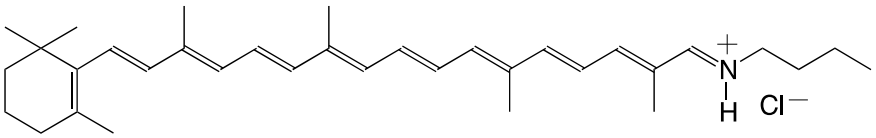

G.A.J. Pitt, F.D. Collins, R.A. Morton, P. Stok, *Biochem. J.* **1955**, *59*, 122

24N 7'-aza-7'-butyl-7'-apo-β-carotene $C_{34}H_{49}N$



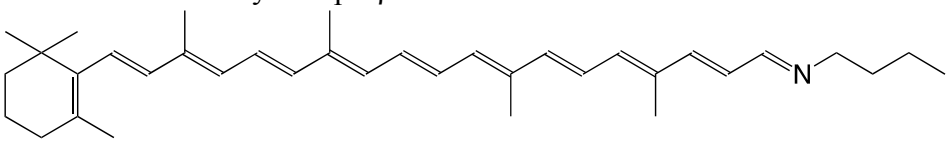

T.A. Moore, P.S. Song, *J. Mol. Spec*. **1974**, *52*, 224

25N 7'-aza-7'-butyl-7'-apo-β-carotene hydrochloride $C_{35}H_{52}ClN$



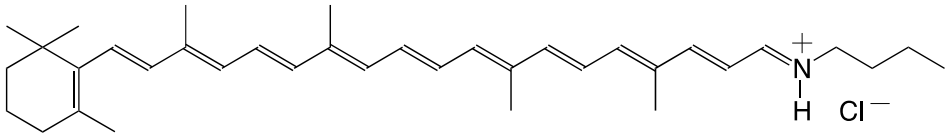

T.A. Moore, P.S. Song, *J. Mol. Spec*. **1974**, *52*, 224

26N 5'-aza-5'-butyl-5'-apo-β-carotene $C_{37}H_{53}N$



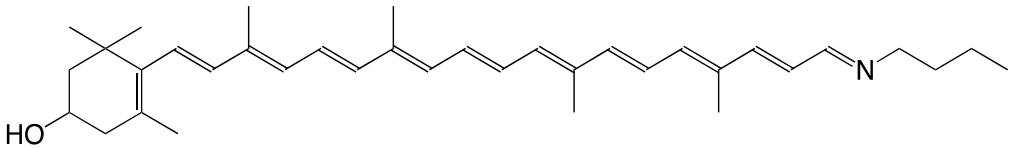

T.A. Moore, P.S. Song, *J. Mol. Spec*. **1974**, *52*, 224

27N 5'-aza-5'-butyl-5'-apo-β-carotene hydrochloride $C_{37}H_{54}ClN$



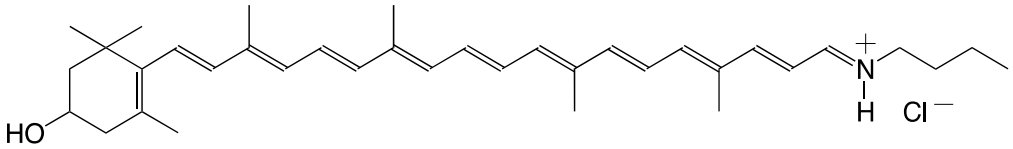

T.A. Moore, P.S. Song, *J. Mol. Spec*. **1974**, *52*, 224

28N 5'-aza-5'-butyl-5'-apo-β-caroten-3-ol $C_{36}H_{51}NO$



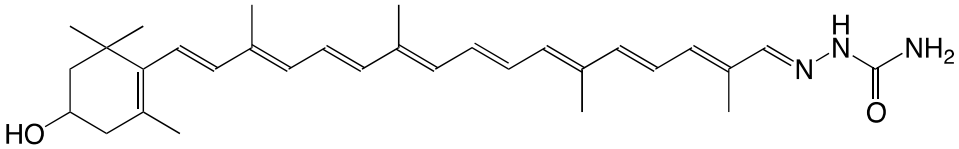

T.A. Moore, P.S. Song, *J. Mol. Spec*. **1974**, *52*, 224

29N 5'-aza-5'-butyl-5'-apo-β-caroten-3-ol hydrochloride $C_{36}H_{52}ClNO$



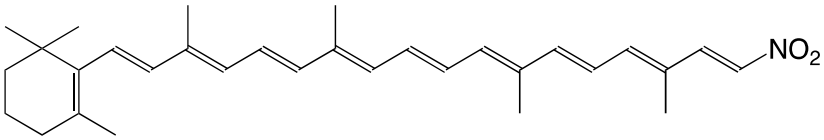

T.A. Moore, P.S. Song, *J. Mol. Spec*. **1974**, *52*, 224

30N 7'-aza-7'-ureido-7'-apo-β-caroten-3-ol, β-citraurin semicarbazone $C_{31}H_{43}N_3O_2$



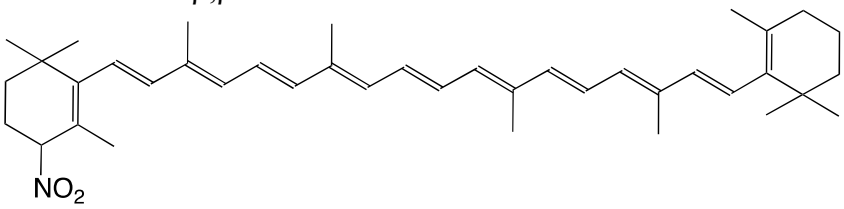

L. Zechmeister, L. von Cholnoky, *Liebigs Ann*. **1937**, *530*, 291

31N 7'-nitro-7'-apo-β-carotene $C_{31}H_{41}NO_2$



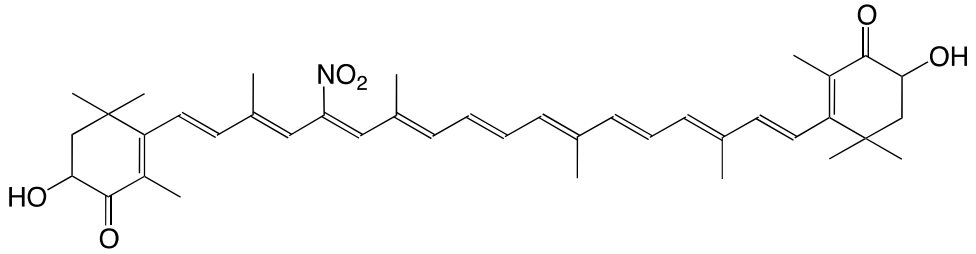

H. Ikeda, T. Sakai, Y. Kawabe, *JP 2-2534*, **1990**

32N 4-nitro-β,β-carotene $C_{40}H_{55}NO_2$



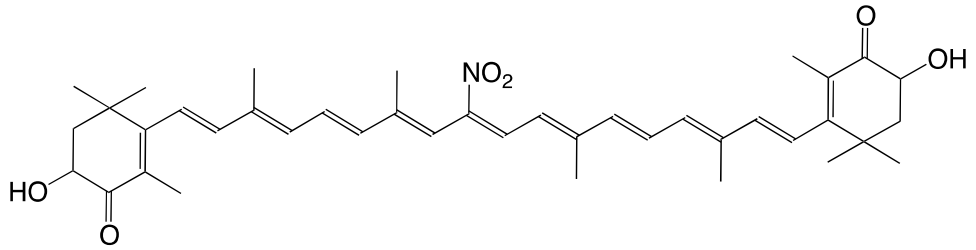

D.L. Baker, E.S. Kroll, N. Jacobsen, D.C. Liebler, *Chem. Res. Toxicol.* **1999**, *12*, 535

33N 11-nitroastaxanthin $C_{40}H_{51}NO_6$



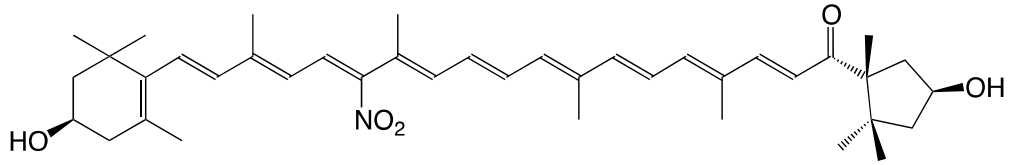

R. Yoshioka, T. Hayakawa, K. Ishuzuka, A. Kulkarni, Y. Terada, T. Maoka, H. Etoh, *Tetrahedron Lett*. **2006**, *47*, 3637 (*cis*-isomer)

34N 15-nitroastaxanthin $C_{40}H_{51}NO_6$



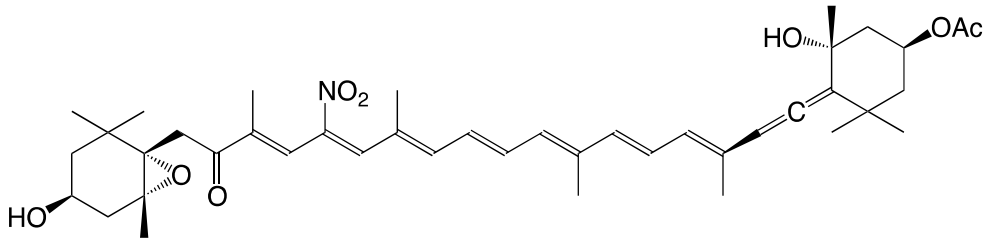

R. Yoshioka, T. Hayakawa, K. Ishuzuka, A. Kulkarni, Y. Terada, T. Maoka, H. Etoh, *Tetrahedron Lett*. **2006**, *47*, 3637 (*cis*-isomer)

35N 12-nitrocapsanthin $C_{40}H_{55}NO_5$



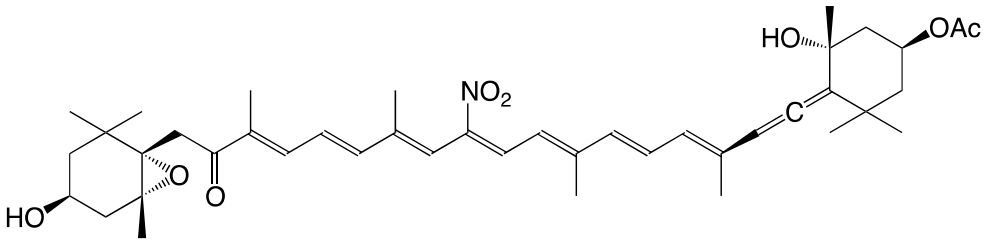

M. Tsuboi, H. Etoh, K. Kato, H. Nakatugawa, H. Kato, Y. Maejima, G. Matsumoto, H. Mori, M. Hosokawa, K. Miyashita, H. Tokuda, N. Suzui, T. Maoka, *J. Agric. Food Chem*. **2011**, *59*, 10572

36N 11-nitrofucoxanthin $C_{42}H_{57}NO_8$



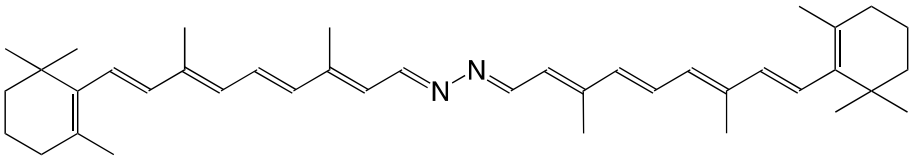

M. Tsuboi, H. Etoh, K. Kato, H. Nakatugawa, H. Kato, Y. Maejima, G. Matsumoto, H. Mori, M. Hosokawa, K. Miyashita, H. Tokuda, N. Suzui, T. Maoka, *J. Agric. Food Chem*. **2011**, *59*, 10572

37N 15-nitrofucoxanthin $C_{42}H_{57}NO_8$



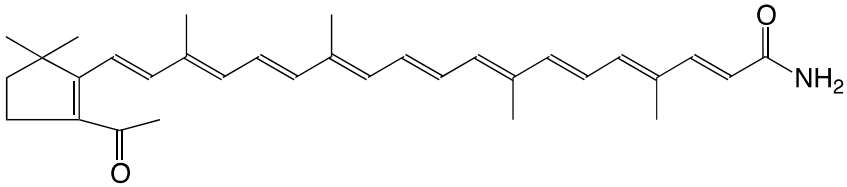

M. Tsuboi, H. Etoh, K. Kato, H. Nakatugawa, H. Kato, Y. Maejima, G. Matsumoto, H. Mori, M. Hosokawa, K. Miyashita, H. Tokuda, N. Suzui, T. Maoka, *J. Agric. Food Chem*. **2011**, *59*, 10572

38N "16,16'-diaza-carotene" (diretinyliden hydrazine) $C_{40}H_{56}N_2$



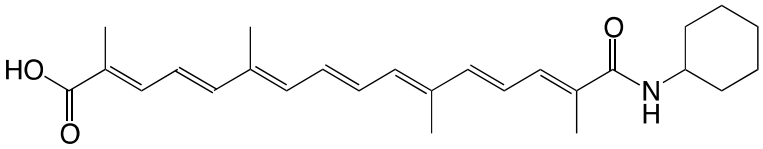

T. Miki, Y. Hara, *JP 34-002118*, **1959**
T. Miki, Y. Hara, *Chem. Pharm. Bull*. **1962**, *10*, 922

39N 5-acetyl-2-nor-β-apo-7'-carotenoic acid amide $C_{32}H_{41}NO_2$



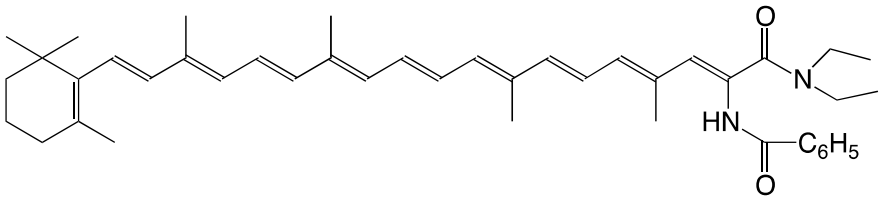

R. Kuhn, H. Brockmann, *Chem. Ber*. **1934**, *67*, 885

40N *N*-hexyl crocetinamide $C_{26}H_{35}NO_3$



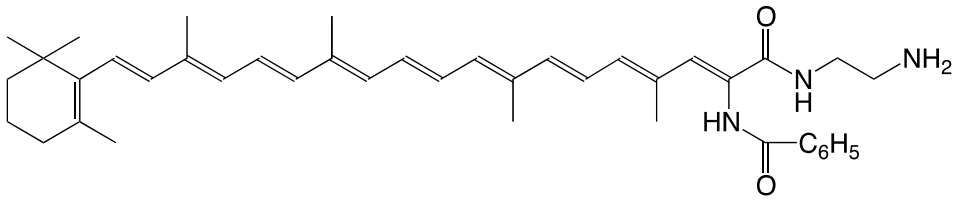

G. Quinkert, K.R. Schmieder, G. Dürner, K. Hache, A. Stegk, D.H.R. Barton, *Chem. Ber*. **1977**, *110*, 3582

41N β-apo-7'-benzoylamino-7'-carotenoic acid *N,N*-diethylamide $C_{43}H_{56}N_2O_2$



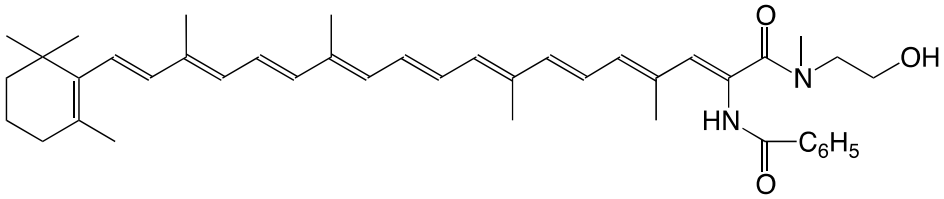

M. Tomoaia-Cotisel, J. Zsako, E. Chifu, D.A. Ladenhead, *Langmuir* **1990,** *6*,191. The authors list several related amides.

42N β-apo-7'-benzoylamido-7'-carotenoic acid *N*-aminoethylamide $C_{41}H_{53}N_3O_2$



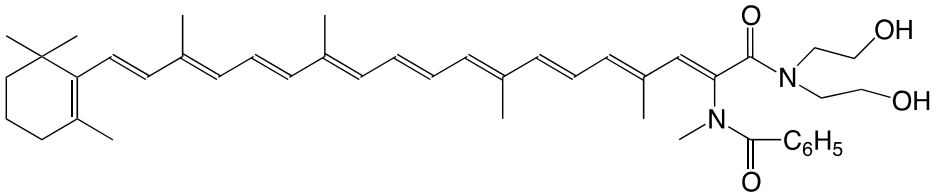

M. Tomoaia-Cotisel, J. Zsako, E. Chifu, D.A. Ladenhead, *Langmuir* **1990,** *6*,191

43N β-apo-7'-benzoylamido-7'-carotenoic acid *N*-methyl-N-(2-hydroxyethyl)-amide $C_{42}H_{54}N_2O_3$



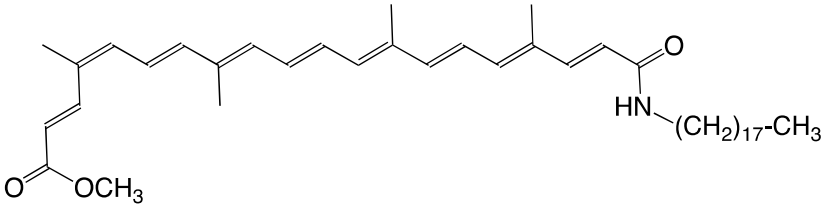

M. Tomoaia-Cotisel, J. Zsako, E. Chifu, D.A. Ladenhead, *Langmuir* **1990,** *6*,191

44N β-apo-7'-benzoylamido-7'-carotenoic acid *N,N*-(bis(2-hydroxyethyl)-amide $C_{43}H_{56}N_2O_4$



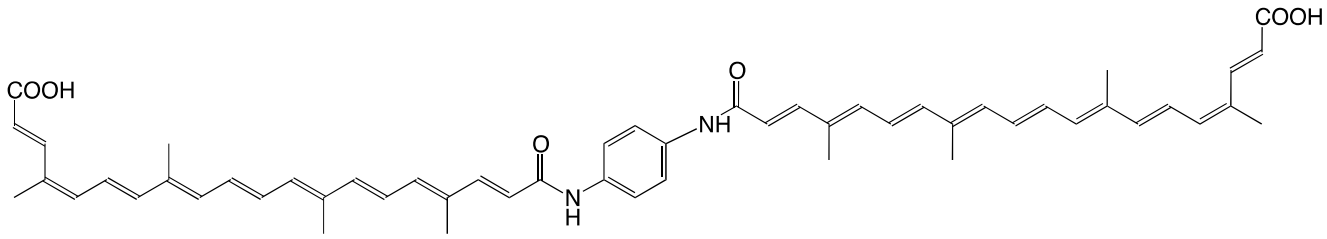

M. Tomoaia-Cotisel, J. Zsako, E. Chifu, D.A. Ladenhead, *Langmuir* **1990,** *6*,191

45N *N*-octadecyl bixinamide $C_{42}H_{65}NO_3$



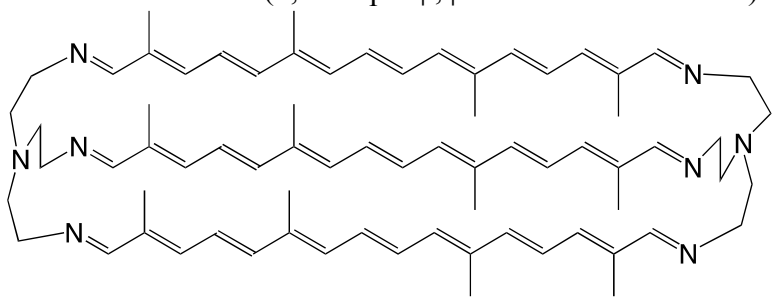

J.H. Fuhrhop, M. Krull, A. Schulz, D. Möbius, *Langmuir* **1990**, *6*,497. The authors list several related bixin amides.
G. Ferrari, V. Vecchietti, *EP 030009*, **1980** describe numerous bixin amides.

46N dibixine diphenylenediamid $C_{54}H_{60}N_2O_6$




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) $C_{72}H_{96}N_8$




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

ϕ-carotenoids

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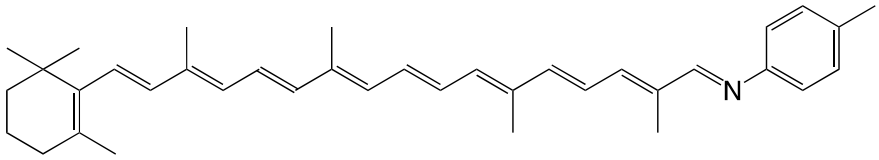
48N 7'-aza-3'-methyl-β,ϕ-carotene $C_{37}H_{47}N$




H. Kamogawa, *Polym. Lett. Ed.* **1972**, *10*, 929

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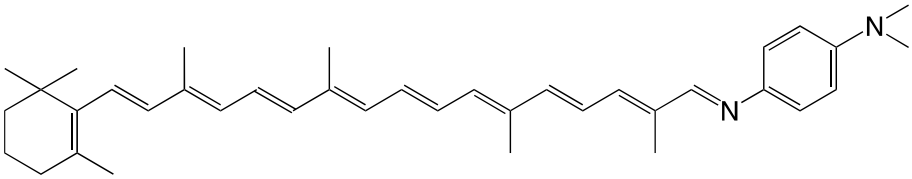
49N 7'-aza-3'-dimethylamino-β,ϕ-carotene $C_{36}H_{46}N_2$




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

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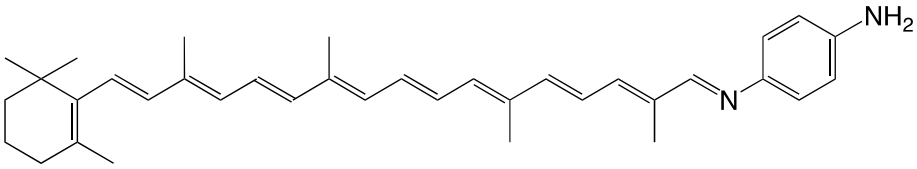
50N 7'-aza-β,ϕ-caroten-3'-amine $C_{36}H_{46}N_2$




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

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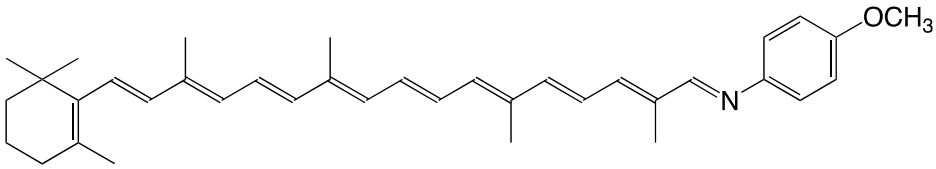
51N 7'-aza-3'-methoxy-β,ϕ-carotene $C_{37}H_{47}NO$




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

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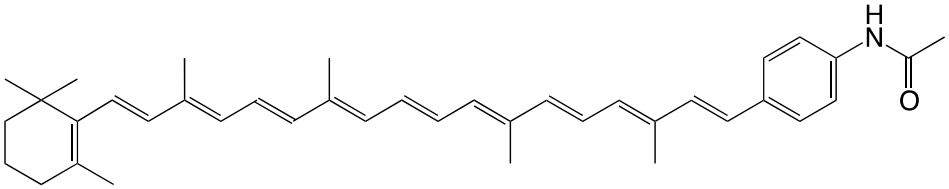
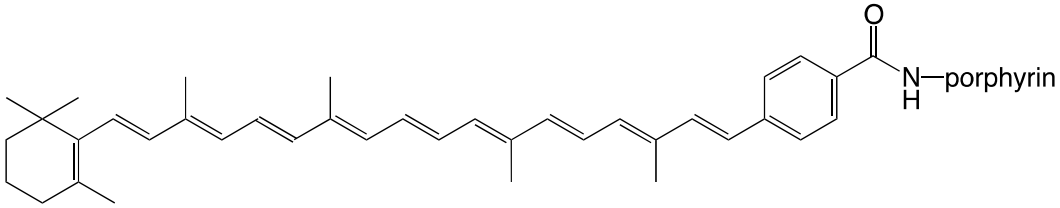
52N β,ϕ-carotene-3'-acetamide $C_{39}H_{49}NO$



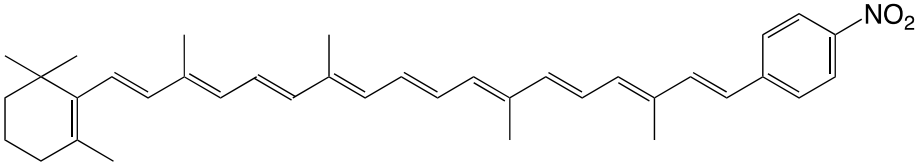

M.R. Wasielewski, P.A. Liddel, D. Barrett, T.A. Moore, D. Gust, *Nature* **1986**, *322*, 570

53N β,ϕ-carotene-3'-porphyrinamide



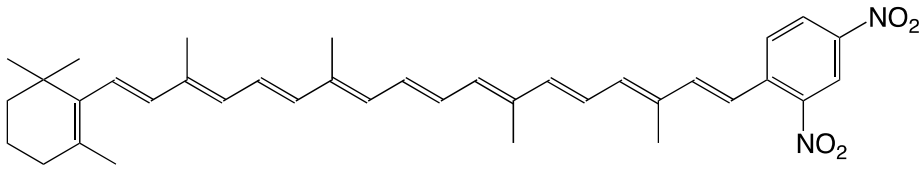

D. Gust, T.A. Moore, P.A. Liddell, G.A. Nemeth, L.R. Makings, A.L. Moore, D. Barrett, P.J. Pessiki, R.V. Bemasson, M. Rougiée, C. Chachaty, F.C. De Schryver, M. Van der Auweraer, A.R. Holzwarth, J. S. Connolly, *J. Am. Chem. Soc*. **1987**, *109*, 846

54N 3'-nitro-β,ϕ-carotene $C_{37}H_{45}NO_2$



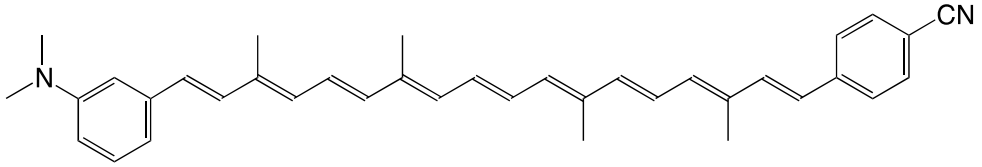

H. Ikeda, T. Sakai, Y. Kawabe, *JP 2-2534*, **1990**
S. Gilmour, S.R. Marder, B.G. Tiemann, L.T. Cheng, *J. Chem. Soc. Chem. Commun*. **1993**, 432
E.S. Hand, K.A. Belmore, L.D. Kispert, *Helv. Chim. Acta* **1993**, *76*, 1928

55N 1',3'-dinitro-β,ϕ-carotene $C_{37}H_{44}N_2O_4$



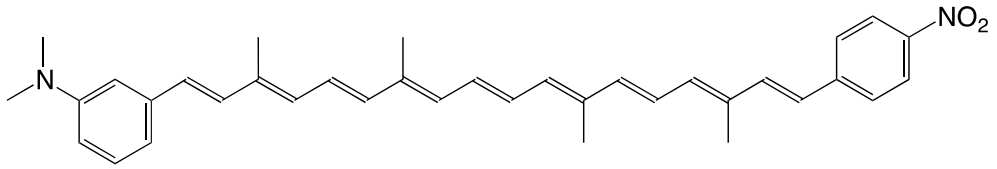

H. Ikeda, T. Sakai, Y. Kawabe, *JP 2-2534*, **1990**

56N 2-dimethylamino-ϕ,ϕ-carotene-3'-nitrile $C_{37}H_{40}N_2$



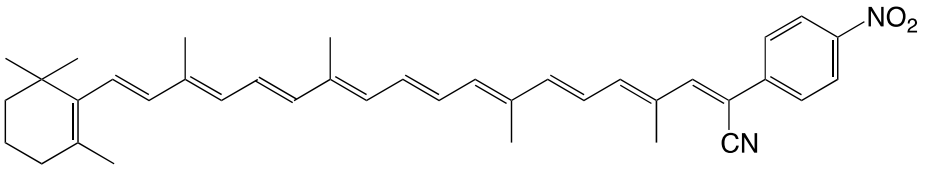

A. Slama-Schwok, M. Blanchard-Desce, J.M Lehn, *J. Phys. Chem*. **1990**, *94*, 3894

57N 3'-nitro-ϕ,ϕ-carotene-2-dimethylamine $C_{36}H_{40}N_2O_2$



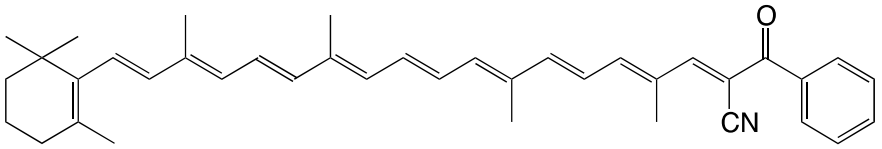

A. Slama-Schwok, M. Blanchard-Desce, J.M Lehn, *J. Phys. Chem*. **1990**, *94*, 3894

58N 7'-cyano-3'-nitro-β,ϕ-carotene $C_{38}H_{44}N_2O_2$



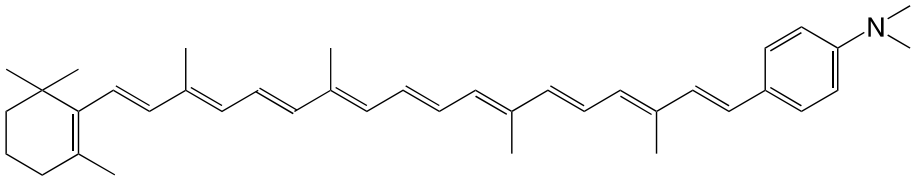

H. Ikeda, T. Sakai, Y. Kawabe, *JP 2-2534*, **1990**

59N 7'-cyano-7'-benzoxo-β-carotene $C_{39}H_{45}NO$



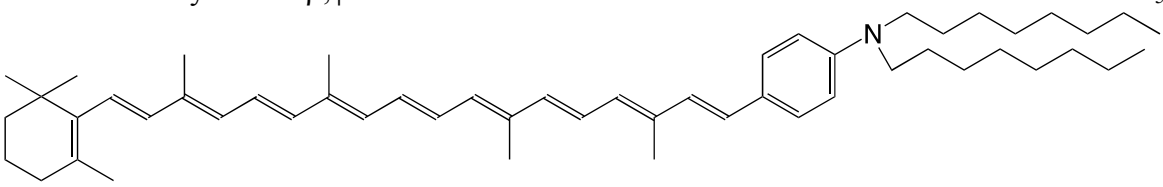

H. Ikeda, T. Sakai, Y. Kawabe, *JP 2-2534*, **1990**

60N 3'-dimethylamino-β,ϕ-carotene $C_{39}H_{51}N$



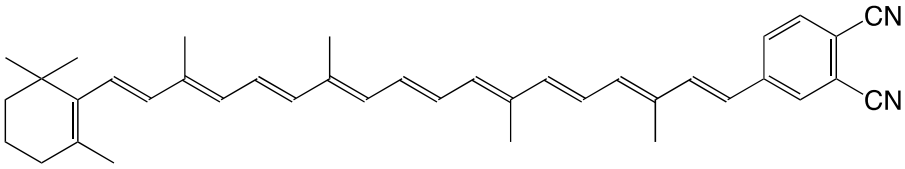

H. Ikeda, T. Sakai, Y. Kawabe, *JP 2-2534*, **1990**

61N 3'-dioctylamino-β,ϕ-carotene $C_{53}H_{79}N$




T. Wagner, S. Roth, *Synth. Metals* **1993**, *54*, 307

62N 2',3'-dicyano-β,ϕ-carotene $C_{39}H_{44}N_2$

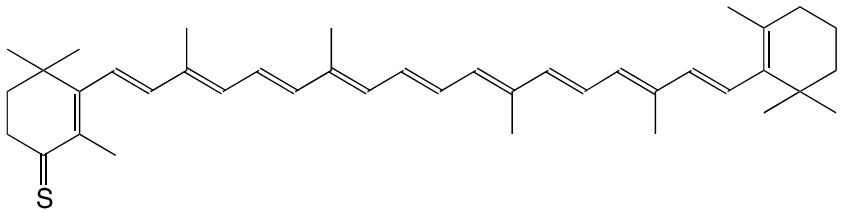



H. Ikeda, T. Sakai, Y. Kawabe, *JP 2-2534*, **1990**

*6.3. Chalcogen-Carotenoids*

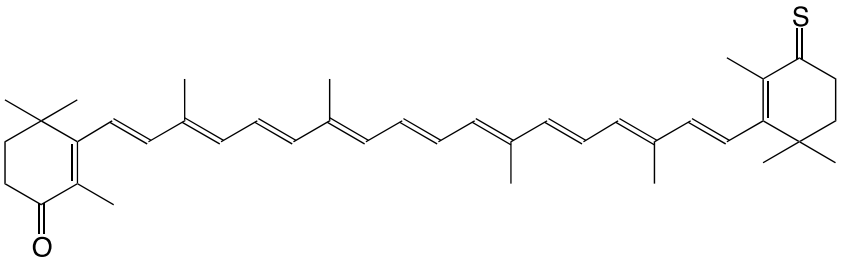
6.3.1. Sulfur **S**

1S echinenone thione $C_{40}H_{54}S$



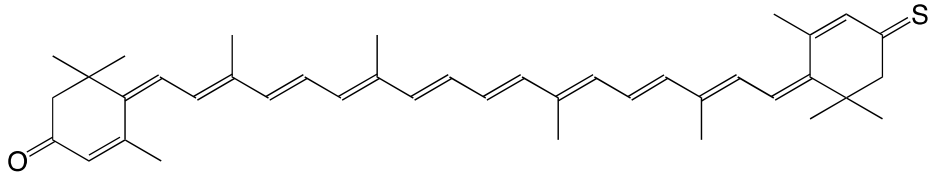

H.R. Sliwka, S. Liaaen-Jensen, *Acta Chem. Scand*. **1994**, *48*, 679

2S canthaxanthin thione $C_{40}H_{52}OS$



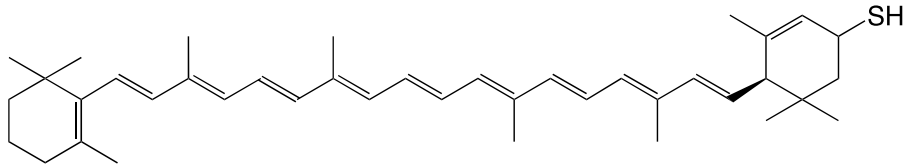

H.R. Sliwka, S. Liaaen-Jensen, *Acta Chem. Scand*. **1994**, *48*, 679

3S rhodoxanthin thione $C_{40}H_{50}OS$



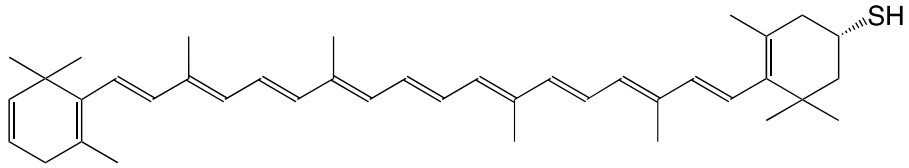

H.R. Sliwka, S. Liaaen-Jensen, *Acta Chem. Scand*. **1994**, *48*, 679

4S 3'-thiolutein $C_{40}H_{56}OS$



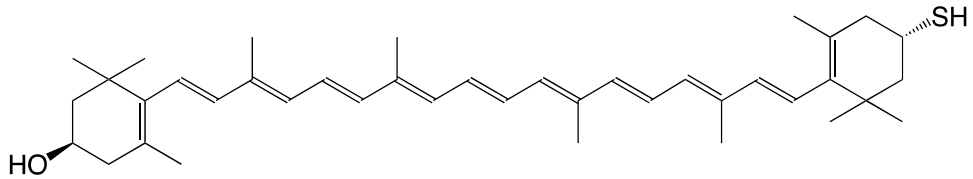

H.R. Sliwka, S. Liaaen-Jensen, *Acta Chem. Scand*. **1990**, *44*, 61

5S (3*S*)-2',3'-didehydro-β,β-carotene-3-thiol $C_{40}H_{54}S$



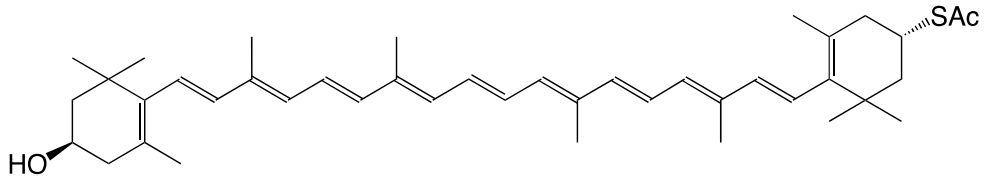

H.R. Sliwka, S. Liaaen-Jensen, *Tetrahdron Asym.* **1993**, *4*, 361
H.R. Sliwka, *Helv. Chim. Acta* **1999**, *82*, 161

6S (3*R*,3′*S*)-3'-sulfanyl-β,β-caroten-3-ol $C_{40}H_{56}OS$



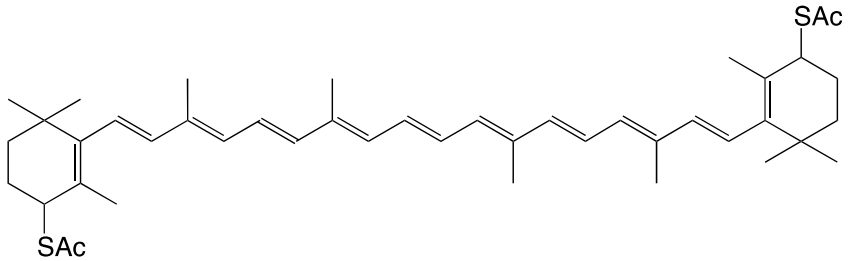

H.R. Sliwka, S. Liaaen-Jensen, *Tetrahdron Asym.* **1993**, *4*, 361
H.R. Sliwka, *Helv. Chim. Acta* **1999**, *82*, 161

7S 3'-thioacetyl lutein $C_{42}H_{58}O_2S$



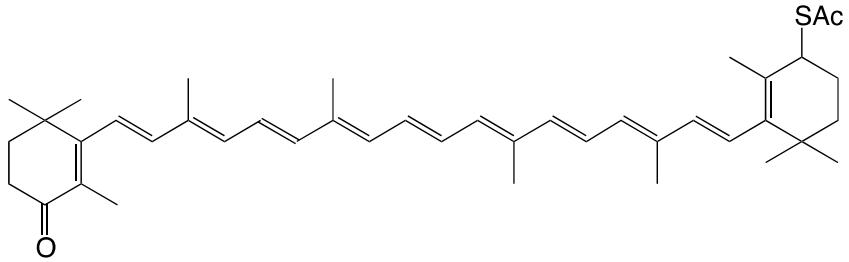

H.R. Sliwka, S. Liaaen-Jensen, *Acta Chem. Scand*. **1990**, *44*, 61

8S 4,4'-dithioacetyl-β,β-carotene $C_{44}H_{60}O_2S_2$



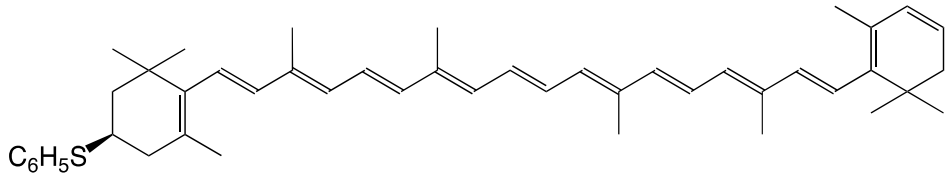

H.R. Sliwka, *Helv. Chim. Acta* **1999**, *82*, 161

9S 4'-thioacethyl-β,β-caroten-4-one $C_{42}H_{56}O_2S$



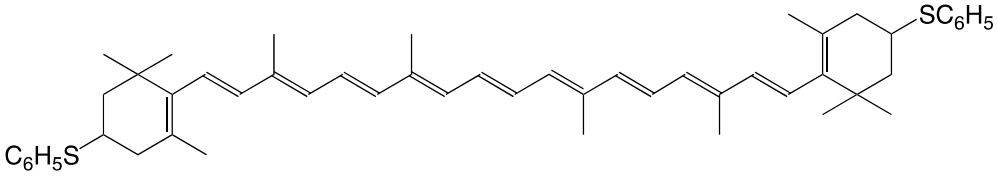

H.R. Sliwka, S. Liaaen-Jensen, *Acta Chem. Scand*. **1990**, *44*, 61

10S (3*R*)-3',4'-didehydro-3-phenylsulfanyl-β,β-carotene $C_{46}H_{58}S$



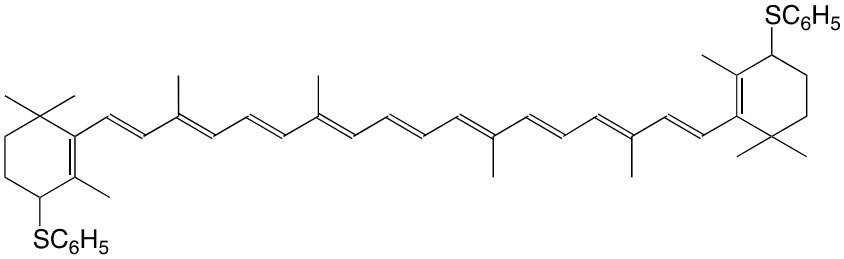

J. Inananga, M. Yamaguchi, *Mem. Fac. Sci. Kyushi Univ. Ser. C*, **1989**, *17*, 109

11S 3,3'-diphenylsulfanyl-β,β-carotene $C_{52}H_{64}S_2$



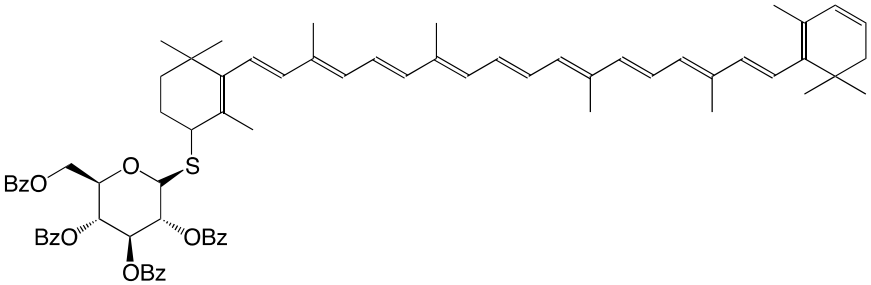

J. Inananga, M. Yamaguchi, *Mem. Fac. Sci. Kyushi Univ. Ser. C*, **1989**, *17*, 109

12S 4,4'-diphenylsulfanyl-β,β-carotene $C_{52}H_{64}S_2$



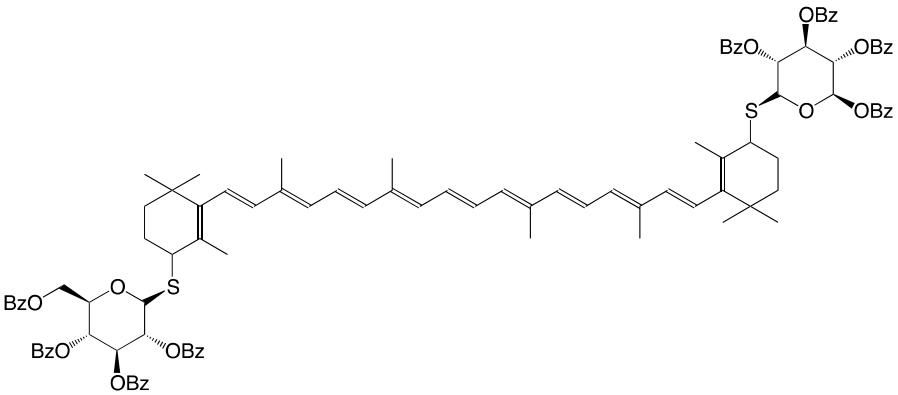

C. Martin, P. Karrer, *Helv. Chim. Acta* **1959**, *42*, 464

13S 3,4'-dehydro-β,β-carotene-4-thioglucopyranoside $C_{74}H_{80}O_9S$



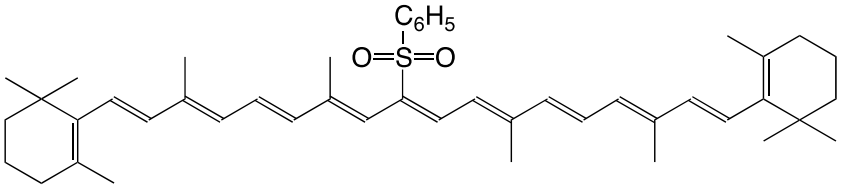

V. Nagy, A. Agócs, E. Turcsi, J. Deli, Tetrahedron Lett. **2010**, *52*, 1020

14S β,β-carotene-4,4'-bisthioglucopyranoside $C_{107}H_{106}O_{18}S_2$




V. Nagy, A. Agócs, E. Turcsi, J. Deli, Tetrahedron Lett. **2010**, *52*, 1020

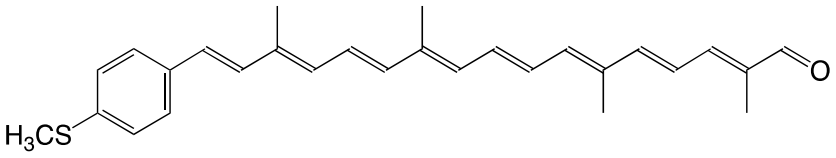
15S β,β-carotene-15-yl-phenylsulfone $C_{46}H_{60}O_2S$




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

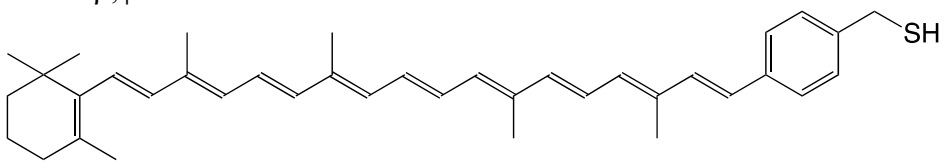
ϕ-carotenoids

16S 3-methylsulfanyl-8'-apo-ϕ-carotenal $C_{28}H_{32}OS$



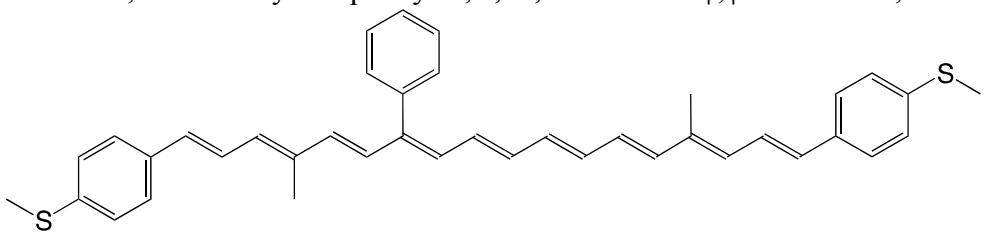

Y.Q. Shen, W. Göhring, S. Hagen, S. Roth, *J. Mol. Electron*. **1990**, *6*, 31

17S β,ϕ-carotene-3'-methanethiol $C_{38}H_{48}S$




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'-dimethanethiol $C_{40}H_{40}S_2$




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**

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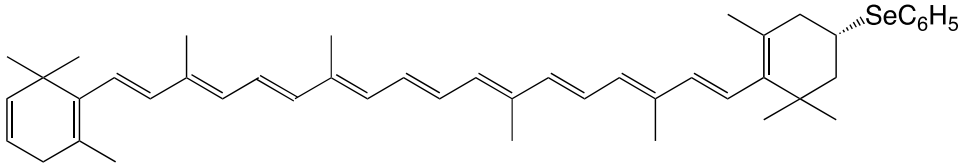
1Se (*3S*)-2',3'-didehydro-β,β-carotene-3-phenylselenide $C_{46}H_{58}Se$




H.R. Sliwka, S. Liaaen-Jensen, *Acta Chem. Scand*. 1**995**, *49*, 428
E. Oliveros, A.M. Braun, T. Aminian-Saghafi, H.R. Sliwka, *New J. Chem*. **1994**, *18*, 535
H.R. Sliwka, *Helv. Chim. Acta* **1999**, *82*, 161

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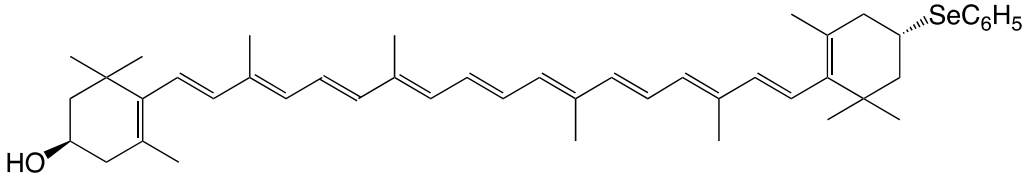
2Se zeaxanthin phenylselenide, (3*R,*3'*S*)-3'-phenylseleno-β,β-caroten-3-ol $C_{46}H_{60}OSe$




H.R. Sliwka, S. Liaaen-Jensen, *Acta Chem. Scand*. 1**995**, *49*, 428
H.R. Sliwka, *Helv. Chim. Acta* **1999**, *82*, 161

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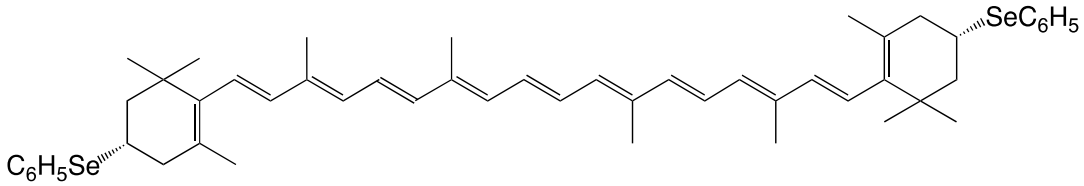
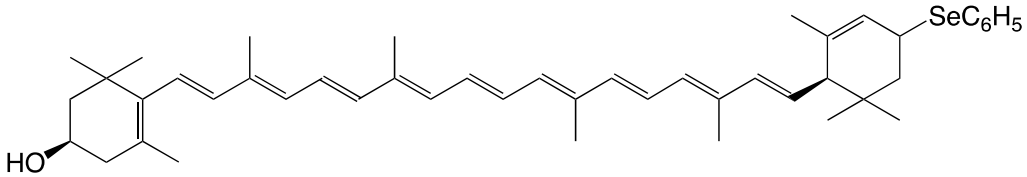
3Se zeaxanthin diphenylselenide, (3*S,*3'*S*)-β,β-carotene-3,3'-diphenylselenide $C_{52}H_{64}Se_2$




H.R. Sliwka, S. Liaaen-Jensen, *Acta Chem. Scand*. 1**995**, *49*, 428
H.R. Sliwka, *Helv. Chim. Acta* **1999**, *82*, 161

---

4Se lutein phenylselenide, (3*R,*3'*R,S,*6'*R*)-3'-phenyleleno-β,ε-caroten-3-ol $C_{46}H_{60}OSe$




H.R. Sliwka, S. Liaaen-Jensen, *Acta Chem. Scand*. 1**995**, *49*, 428

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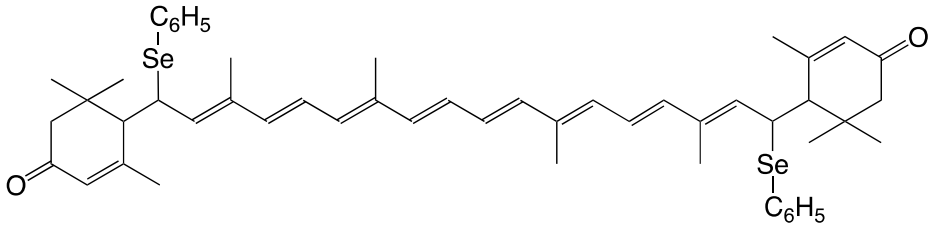
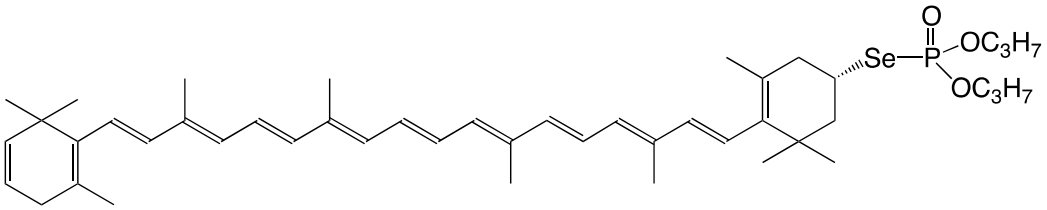
5Se rhodoxanthin diphenylselenide, 7,7'-di(phenylseleno)-7,8,7',8'-dihydro-*retro*-ε,ε-carotene-3,3'-dione $C_{52}H_{62}O_2Se_2$




postulated unstable intermediate

H.R. Sliwka, S. Liaaen-Jensen, *Acta Chem. Scand*. 1**995**, *49*, 856

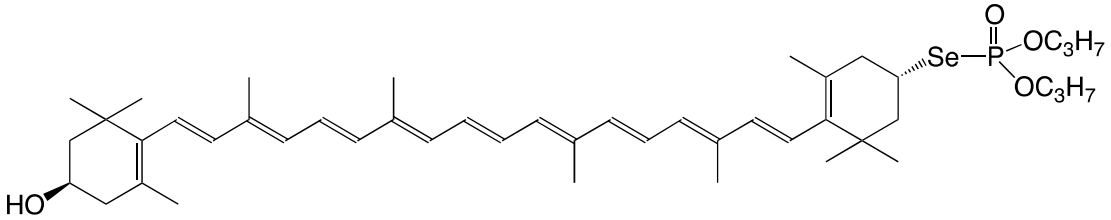
6Se (3*S*)-2',3'-didehydro-β,β-caroten-3-yl-di-O,O-propylselenophosphate $C_{46}H_{67}O_3PSe$




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**

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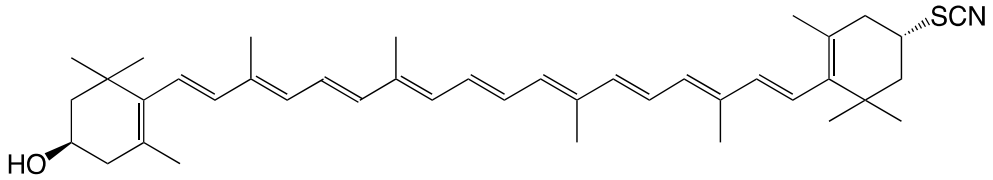
1NS zeaxanthin thiocyanate, (3*S*)-3'-thiocyano-β,β-caroten-3-ol $C_{41}H_{55}NOS$




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

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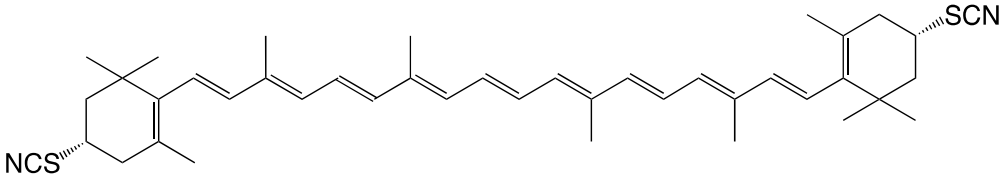
2NS zeaxanthin dithiocyanat, (3*S*,3'*S*)-β,β-carotene-3,3'-dithiocyanate $C_{42}H_{54}N_2S_2$




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

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*6.5. Iron* **Fe**

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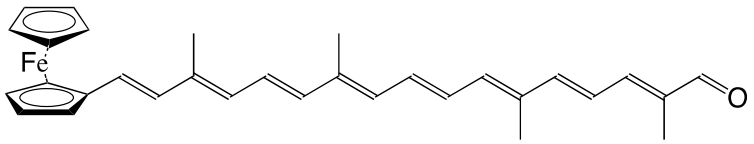
1Fe ferrocenyl-C21 aldehyde, 7-ferrocenyl-7,8'-diapocaroten-8'-al $C_{31}H_{35}FeO$




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

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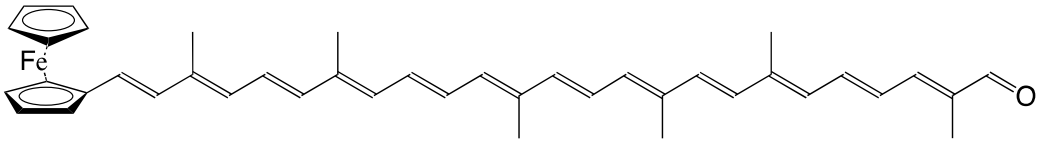
2Fe ferrocenyl-C31 aldehyde $C_{41}H_{47}FeO$




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

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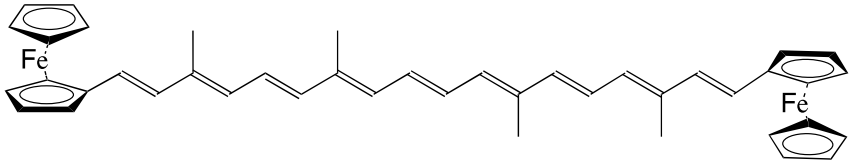
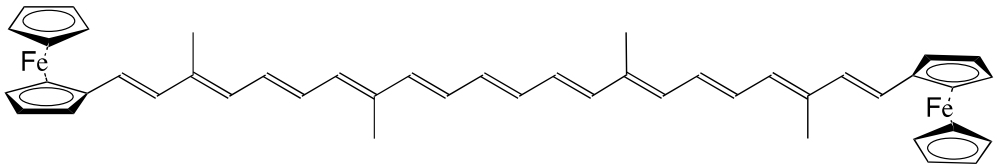
3Fe C22 bis(ferrocenyl), 7,7'-bis(ferrocenyl)-7,7'-diapocarotene $C_{42}H_{48}Fe$



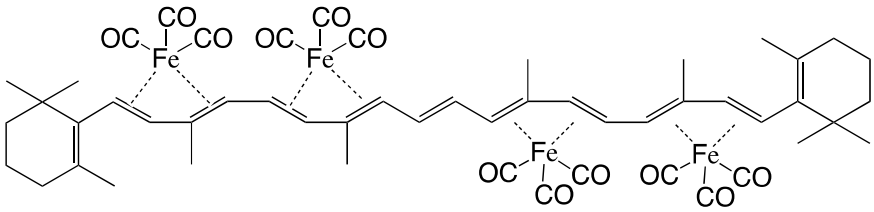

F. Effenberger, H. Schlosser, *Synthesis* **1990**, 1085

4Fe C26 bis(ferrocenyl) $C_{46}H_{52}Fe_2$



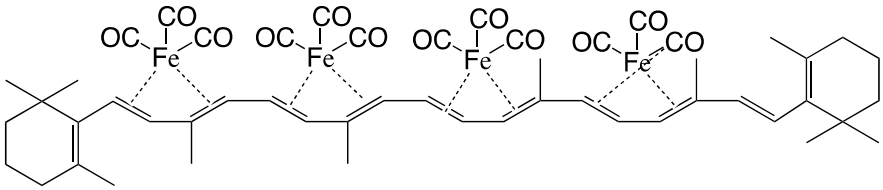

J.M. Lehn, *Angew. Chem. Int. Ed.* **1990**, *29*, 1304

5Fe tetrakis(iron tricarbonyl)-β,β-carotene $C_{52}H_{56}Fe_4O_{12}$



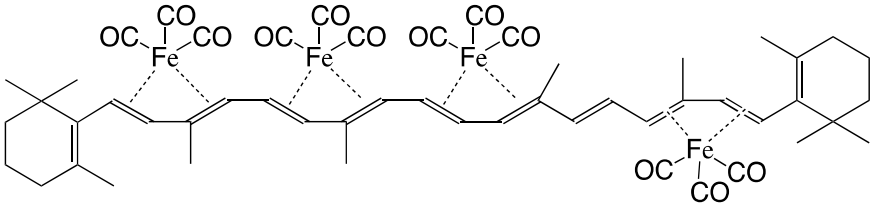

M. Ichikawa, M. Tsutsui, F. Vohwinkel, *Z. Naturforschg*. **1967**, *22b*, 376

6Fe tetrakis(iron tricarbonyl)-β,β-carotene $C_{52}H_{56}Fe_4O_{12}$




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

7Fe tetrakis(iron tricarbonyl)-β,β-carotene $C_{52}H_{56}Fe_4O_{12}$

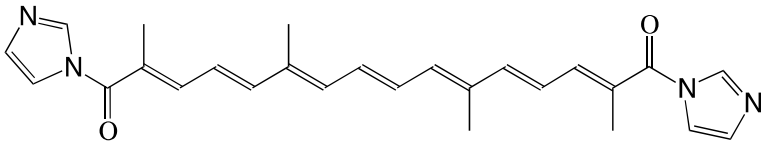



M. Ichikawa, M. Tsutsui, F. Vohwinkel, *Z. Naturforschg*. **1967**, *22b*, 376

*6.6. Heterocycle Carotenoids*

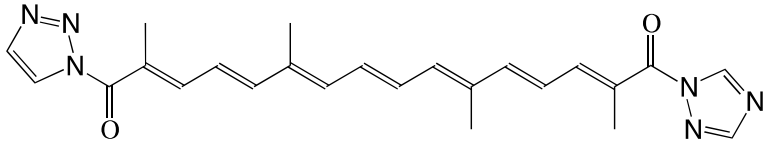
6.6.1. N-heterocycle ⊙N

1⊙N crocetin-di-imidazolide $C_{26}H_{30}N_4O_2$



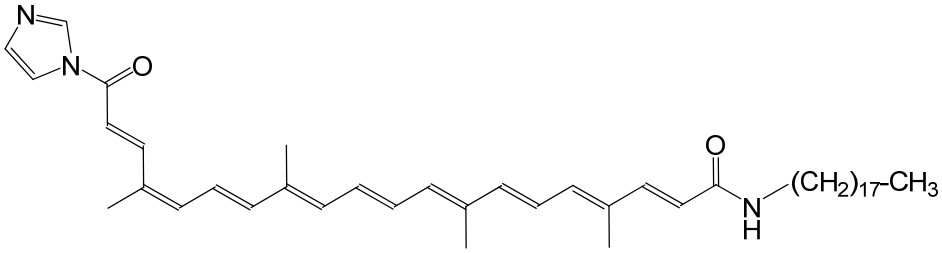

H. Pfander, F. Wittwer, *Helv. Chim. Acta* **1979**, *62*, 1944

2⊙N crocetin-bis(1,2,4-triazolide) $C_{26}H_{30}N_4O_2$



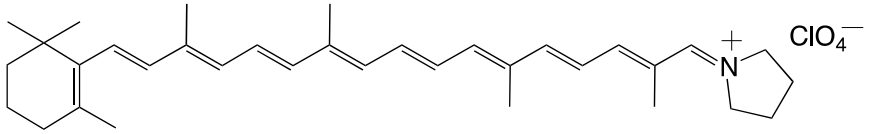

H. Pfander, F. Wittwer, *Helv. Chim. Acta* **1979**, *62*, 1944

3⊙N octadexylbixin imidazolide $C_{45}H_{67}N_3O_2$



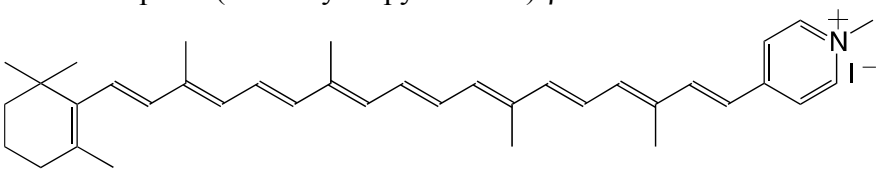

J.H. Fuhrhop, M. Krull, A. Schulz, D. Möbius, *Langmuir* **1990**, *6*,497

4⊙N *N*-(8'-apo-β-carotene-8-ylidene)-pyrrolidium perchlorate $C_{34}H_{48}ClNO_4$



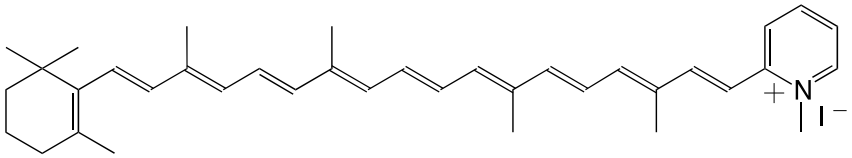

D.L. Coffen, E. Ho, C. Nocka, G. Sasso, V. Toome, T.R. Wagler, T.H. Williams, *J. Prakt. Chem.* **1993**, *335*, 135

5⊙N 7'-apo-7'-(*N*-methyl-4-pyridinium)-β-carotene iodide $C_{37}H_{48}IN$



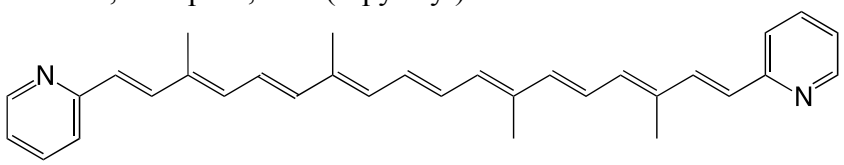

H. Ikeda, T. Sakai, Y. Kawabe, *JP 2-2534*, **1990**

6⊙N 7'-apo-7'-(*N*-methyl-2-pyridinium)-β-carotene iodide $C_{37}H_{48}IN$



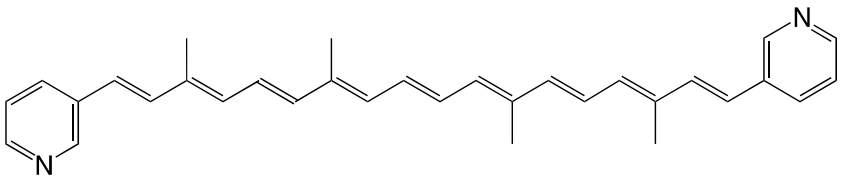

H. Ikeda, T. Sakai, Y. Kawabe, *JP 2-2534*, **1990**

7⊙N 7,7'-diapo-7,7'-bis(2-pyridyl)-carotene $C_{32}H_{34}N_2$



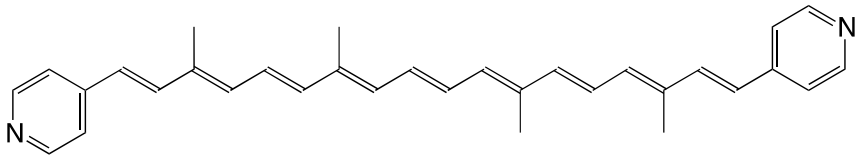

H.R. Brahmana, K. Katsuyama, J. Inaga, T. Katsuki, M. Yamaguchi, *Tetrahedron Lett.* **1981**, *22*, 1695

8⊙N 7,7'-diapo-7,7'-bis(3-pyridyl)-carotene $C_{32}H_{34}N_2$



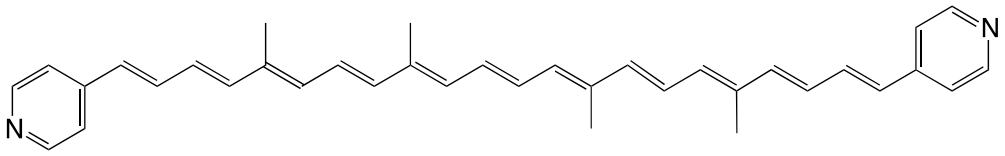

H.R. Brahmana, K. Katsuyama, J. Inaga, T. Katsuki, M. Yamaguchi, *Tetrahedron Lett.* **1981**, *22*, 1695
T.S. Arrhenius, M. Blanchard-Desce, M. Dvolaitzky, J.M. Lehn, J. Malthête, *Proc. Natl. Acad. Sci. USA* **1986**, *83*, 5355

9⊙N 7,7'-diapo-7,7'-bis(4-pyridyl)-carotene $C_{32}H_{34}N_2$



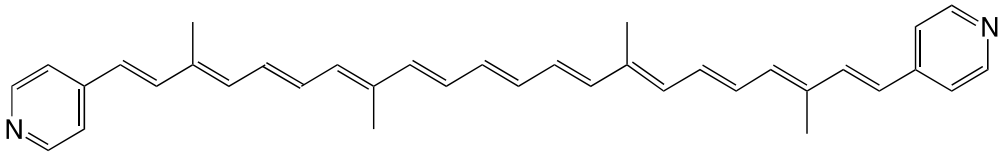
I. Visoly-Fisher, K. Daie, Y. Terazono, C. Herrero, F. Fungo, L. Otero, E. Durantini, J.J. Silber, L. Sereno, D. Gust, T.A. Moore, A.L. Morre, S.M. Lindsay, *PNAS* **2006**, *103*, 8686

10⊙N bis(4-pyridyl)-C26:11-carotene $C_{36}H_{38}N_2$



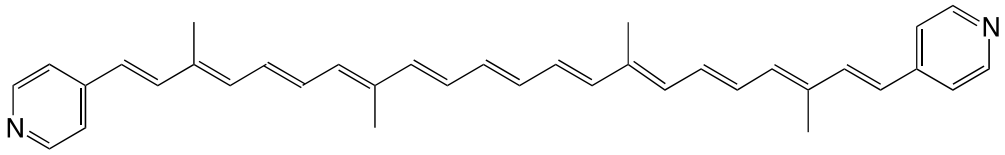
I. Visoly-Fisher, K. Daie, Y. Terazono, C. Herrero, F. Fungo, L. Otero, E. Durantini, J.J. Silber, L. Sereno, D. Gust, T.A. Moore, A.L. Morre, S.M. Lindsay, *PNAS* **2006**, *103*, 8686

11⊙N bis(4-pyridyl)-C26:11-carotene $C_{36}H_{38}N_2$



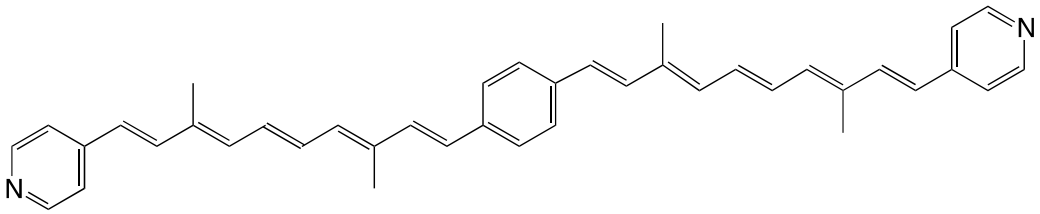
T.S. Arrhenius, M. Blanchard-Desce, M. Dvolaitzky, J.M. Lehn, J. Malthête, *Proc. Natl. Acad. Sci. USA* **1986**, *83*, 5355

12⊙N bis(4-pyridyl)-C34:15-carotene $C_{36}H_{38}N_2$



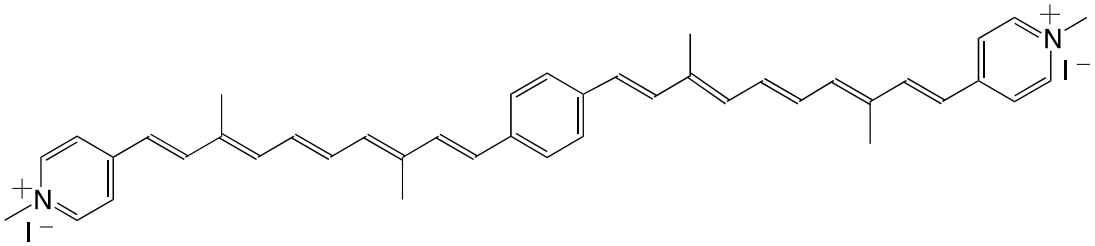
T.S. Arrhenius, M. Blanchard-Desce, M. Dvolaitzky, J.M. Lehn, J. Malthête, *Proc. Natl. Acad. Sci. USA* **1986**, *83*, 5355

13⊙N 1,4-bis(4-pyridyl-C12:5)-benzene $C_{40}H_{40}N_2$



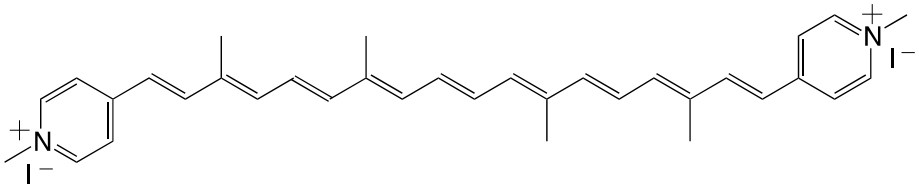

T.S. Arrhenius, M. Blanchard-Desce, M. Dvolaitzky, J.M. Lehn, J. Malthête, *Proc. Natl. Acad. Sci. USA* **1986**, *83*, 5355

14⊙N 1,4-bis(4-pyridinium-C12:5)-benzene diiodide $C_{42}H_{46}I_2N_2$



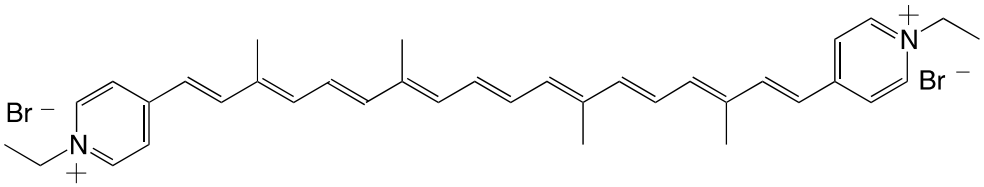

T.S. Arrhenius, M. Blanchard-Desce, M. Dvolaitzky, J.M. Lehn, J. Malthête, *Proc. Natl. Acad. Sci. USA* **1986**, *83*, 5355

15⊙N 7,7'-diapo-7,7'-bis(4-methylpyridinium)-carotene diiodide $C_{34}H_{40}I_2N_2$



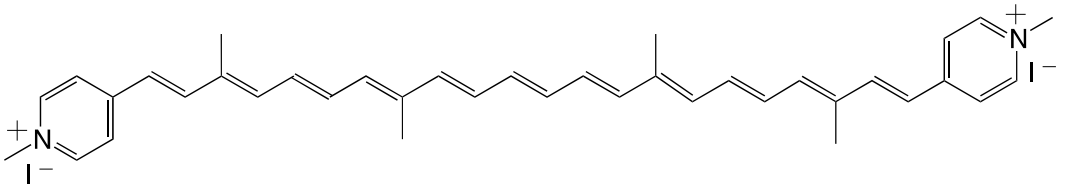

T.S. Arrhenius, M. Blanchard-Desce, M. Dvolaitzky, J.M. Lehn, J. Malthête, *Proc. Natl. Acad. Sci. USA* **1986**, *83*, 5355

16⊙N 7,7'-diapo-7,7'-bis(4-ethylpyridinium)-carotene dibromide $C_{36}H_{44}Br_2N_2$



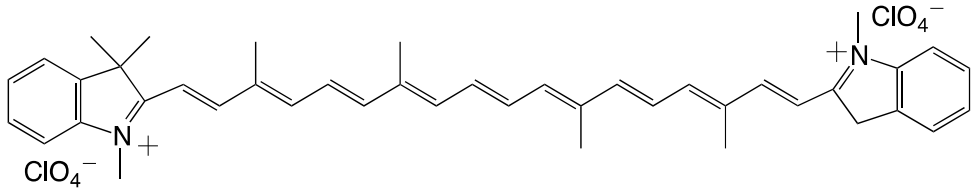

T. Okumoto, N. Morita, I. Nakamura, M. Konishi, M. Yamaguchi, *J. Cancer Res.. Clin. Oncol*. **1985**, *109*, 257

17⊙N bis(4-pyridinium)-C34:15-carotene diiodide $C_{38}H_{44}I_2N_2$



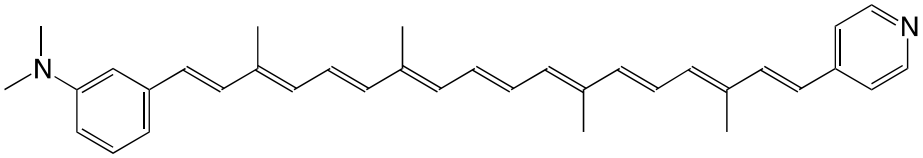
T.S. Arrhenius, M. Blanchard-Desce, M. Dvolaitzky, J.M. Lehn, J. Malthête, *Proc. Natl. Acad. Sci. USA* **1986**, *83*, 5355

18⊙N 7,7'-diapo-7,7'-bis(1,3,3 trimethylindolenium)-carotene dichlorate $C_{42}H_{48}Cl_2N_2O_8$



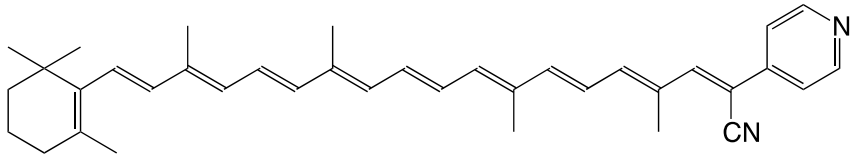
S. Hünig, F. Linhart, D. Scheutzow, *Liebigs Ann.* **1975**, 2089

19⊙N 7,7'-diapo-7'-(4-pyridyl)-ϕ-carotene-2-dimethylamine $C_{35}H_{40}N_2$



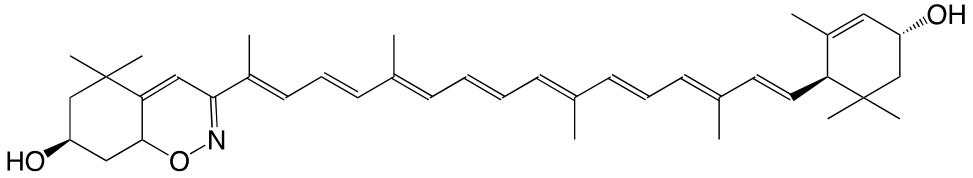
M. Blanchard-Desce, J.M. Lehn, I. Ledoux, J. Zyss, *Special Publication - Royal Society of Chemistry* (Org. Mater. Non-linear Opt.) **1989**, *69*, 170

20⊙N 7'-cyano-7'-(4-pyridyl)-β,ϕ-carotene $C_{37}H_{44}N_2$



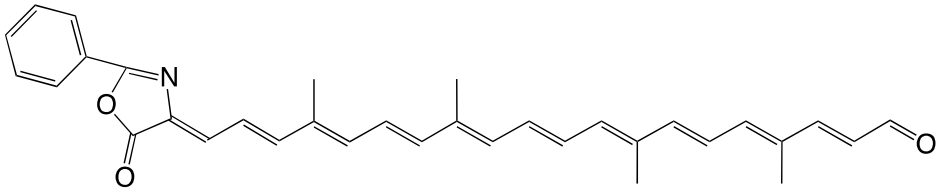
A.J. Cruz, K. Siam, D.P. Rillema, *J. Phys. Chem*. **2011**, *115*, 1108

21⊙N lutein-6*H*-1,2-oxazine $C_{39}H_{53}NO_3$



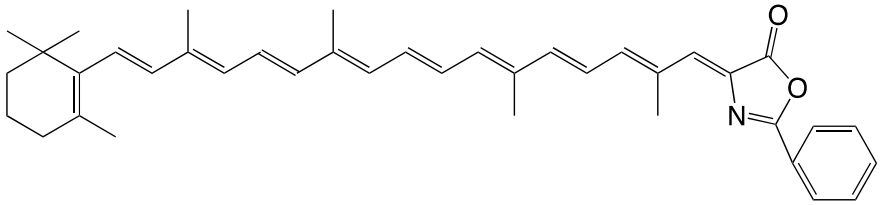

M. Tsuboi, H. Etoh, Y. Yomoda, K. Kato, H. Kato, A. Kulkarni, Y. terada, T. Maoka, H. Mori, T. Inakuma, *Tetrahedron Lett*. **2010**, *521*, 676

22⊙N 6,6'-diapocarotenal-6'-(2-phenyl-azlactone) $C_{33}H_{33}NO_3$



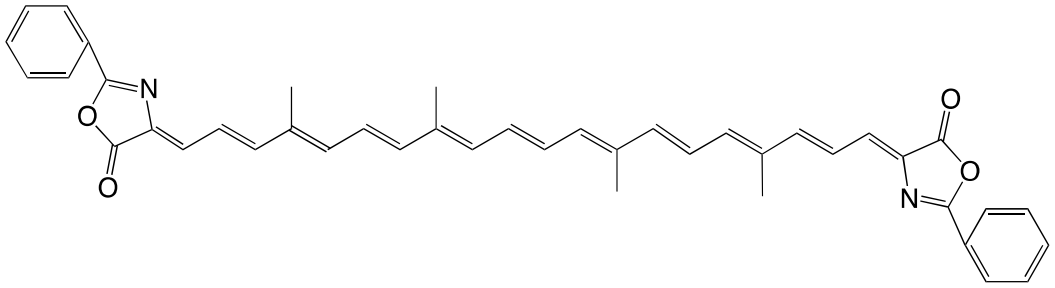

J. Zsako, M. Tomoaia-Cotisel, V. Tamas, C. Coman, E. Chifu, *Rev. Roum. Chim*. **1987**, *32*, 1193. The authors describe several other azlactones.

23⊙N β-apo-6'-carotenal-2-phenyl-azlactone $C_{39}H_{45}NO_2$



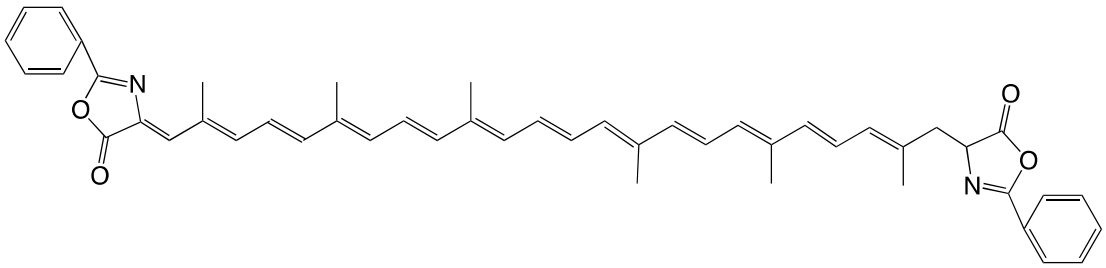

V. Tamas, V. Ciurdaru, C. Bodea, *Rev. Roum. Chim*. **1973**, *18*, 1409

24⊙N β-apo-6'-carotendial bis-2-phenyl diazlactone, C24:11 diazlactone $C_{42}H_{38}N_2O_4$



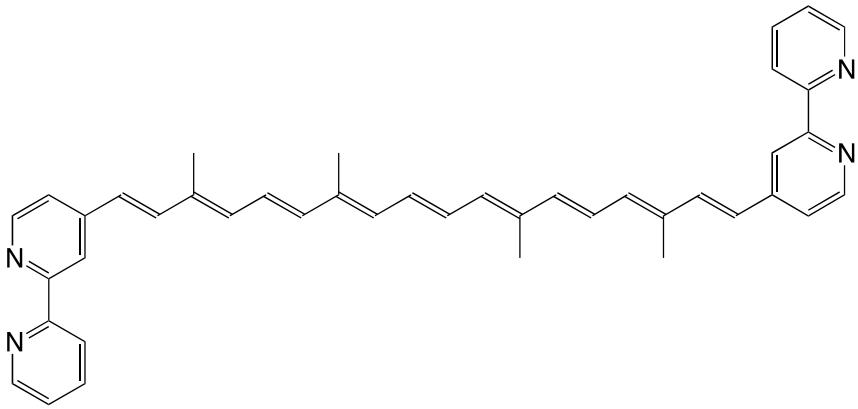

V. Tamas, V. Ciurdaru, C. Bodea, *Rev. Roum. Chim*. **1973**, *18*, 1409

25⊙N C30:13-diazlactone $C_{48}H_{48}N_2O_4$



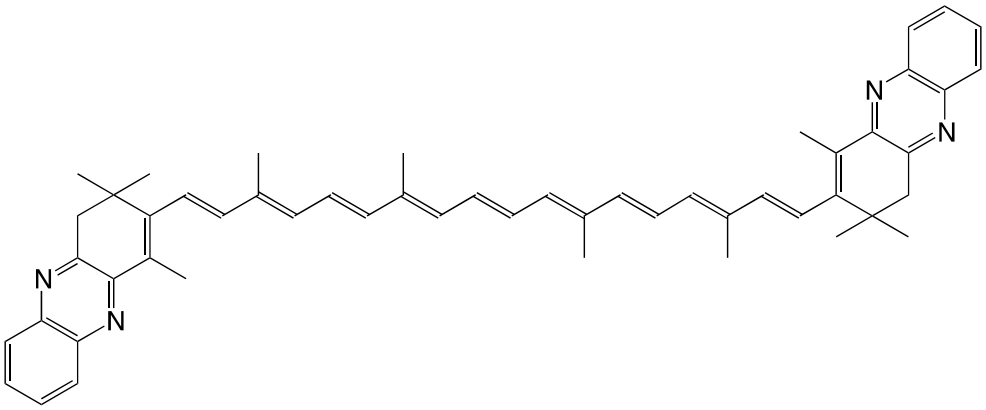
V. Tamas, V. Ciurdaru, C. Bodea, *Rev. Roum. Chim*. **1973**, *18*, 1409. The authors describe several other azlactones.

26⊙N bis(2,2'-bipyridine-4-yl)-carotene $C_{42}H_{40}N_4$



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

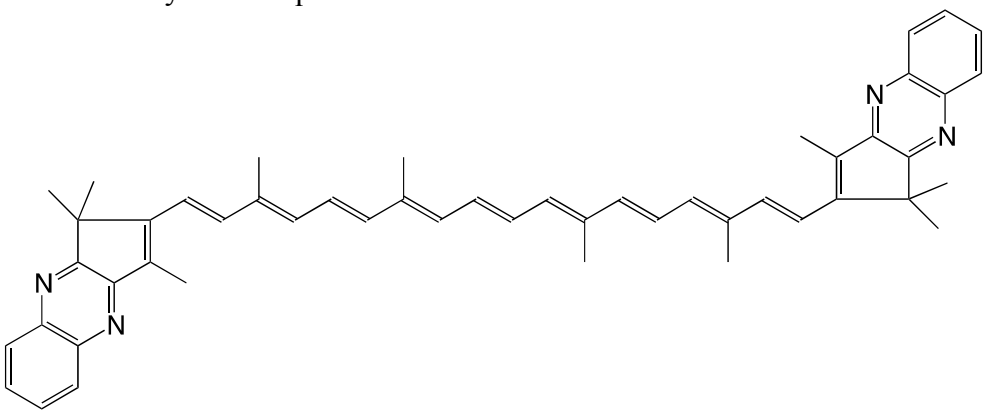
27⊙N astacene bisphenazine $C_{52}H_{56}N_4$



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

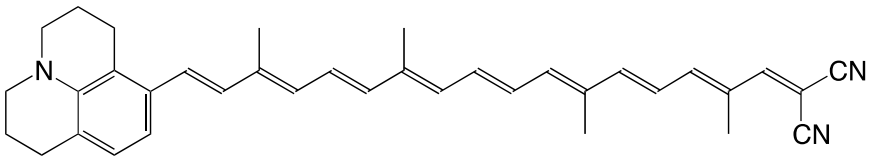
S. Hertzberg, S. Liaaen-Jensen, C.R. Enzell, G.W. Francis, *Acta Chem. Scand*. **1969**, *23*, 3290

28⊙N violerythrin bisquinoxaline $C_{50}H_{52}N_4$



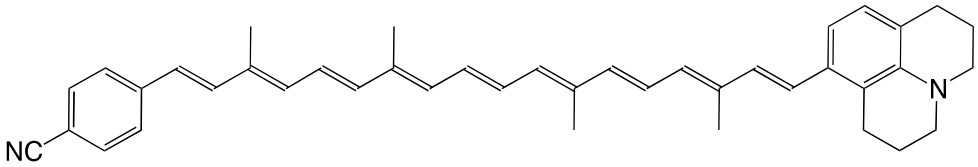

S. Hertzberg, S. Liaaen-Jensen, C.R. Enzell, G.W. Francis, *Acta Chem. Scand*. **1969**, *23*, 3290

29⊙N 7,7'-diapo-7',7'-dicyano-7-julolidinyl-carotene $C_{36}H_{39}N_3$



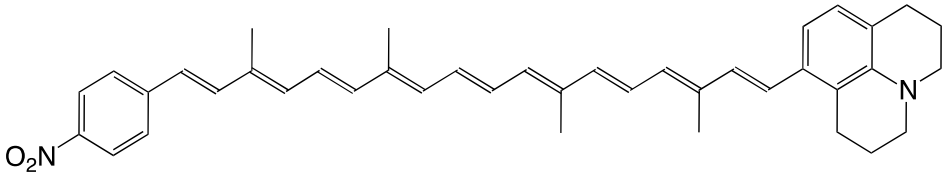

M. Blanchard-Desce, J.M. Lehn, M. Barzoukas, I. Ledoux, J. Zyss, *Chem. Phys*. **1994**, *181*, 281

30⊙ 7'-apo-3-cyano-7'-julolidinyl-ϕ–carotene $C_{41}H_{44}N_2$



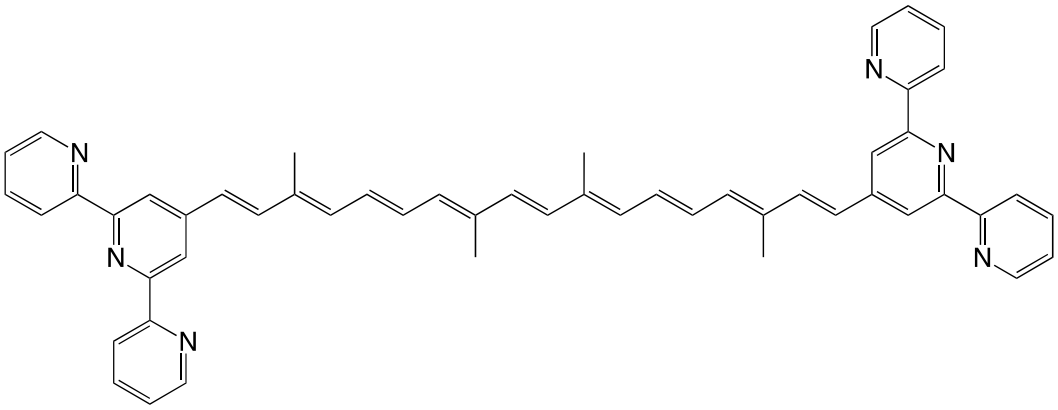

M. Blanchard-Desce, J.M. Lehn, M. Barzoukas, I. Ledoux, J. Zyss, *Chem. Phys*. **1994**, 181, 281

31⊙N 7'-apo-7'-julolidinyl-3-nitro-ϕ-carotene $C_{40}H_{44}N_2O_2$




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

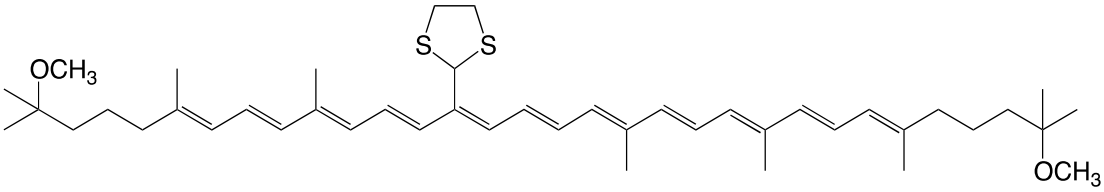
32⊙N diterpyridine carotenoid $C_{52}H_{46}N_6$




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

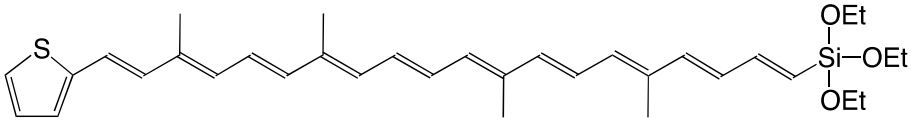
6.6.2. S-heterocycle **⊙S**

1⊙S 3,4,3',4',-tetrahydrospirilloxanthin-20-(1,3-dithiolane) $C_{44}H_{66}O_2S_2$



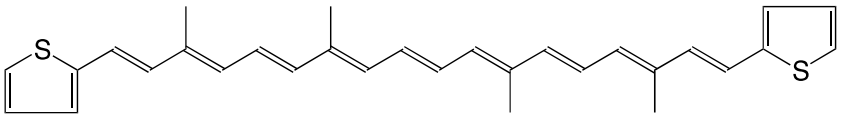

A.J. Aasen, S. Liaaen Jensen, *Acta Chem. Scand*. **1967**, *21*, 2185

2⊙S (= 1Si) 7,5'-diapo-7-thienyl-carotene-5'-triethoxysilane $C_{34}H_{46}O_3SSi$



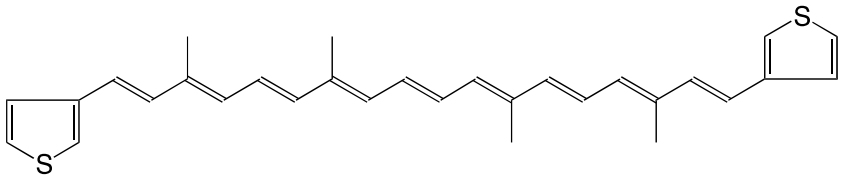

F. Effenberger, M. Wezstein, *Synthesis* **2001**, 1368

3⊙S 7,7'-diapo-bis(2-thienyl)-carotene $C_{30}H_{32}S_2$



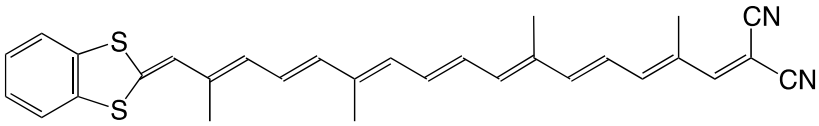

H.R. Brahmana, K. Katsuyama, J. Inaga, T. Katsuki, M. Yamaguchi, *Tetrahedron Lett*. **1981**, *22*, 1695
F. Effenberger, M. Wezstein, *Synthesis* **2001**, 1368

4⊙S 7,7'-diapo-bis(3-thienyl)-carotene $C_{30}H_{32}S_2$



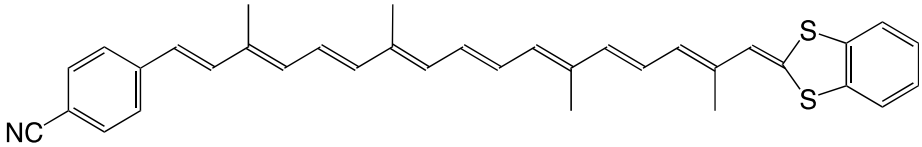

H.R. Brahmana, K. Katsuyama, J. Inaga, T. Katsuki, M. Yamaguchi, *Tetrahedron Lett*. **1981**, *22*, 1695

5⊙S 7',8-diapo-7',7'-dicyano-8-(benzodithiol-2-ylidene)-carotene $C_{30}H_{28}N_2S_2$



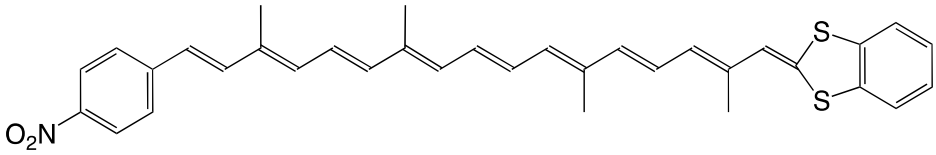

M. Blanchard-Desce, I. Ledoux, J. Malthête, J. Zyss, *J. Chem. Soc., Chem. Commun*. **1988**, 737

6⊙S 8'-apo-8'-(benzodithiol-2-ylidene)-3-cyano-ϕ–carotene $C_{35}H_{33}NS_2$




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

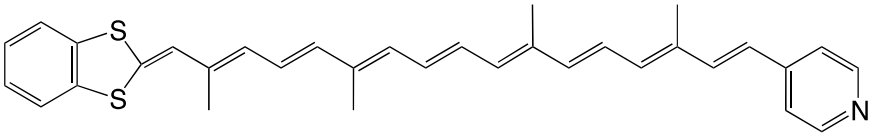
7⊙S 8'-apo-8'-(benzodithiol-2-ylidene)-3-nitro-ϕ-carotene $C_{34}H_{33}NO_2S_2$




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

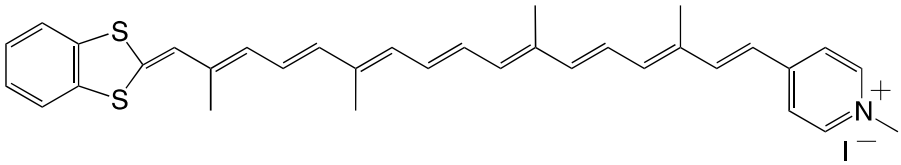
6.6.3. N,S-heterocycle **⊙N,S**

1⊙N,S 7,8'-diapo-8'-(benzodithiol-2-ylidene)-7-(4-pyridyl)-carotene $C_{33}H_{33}NS_2$



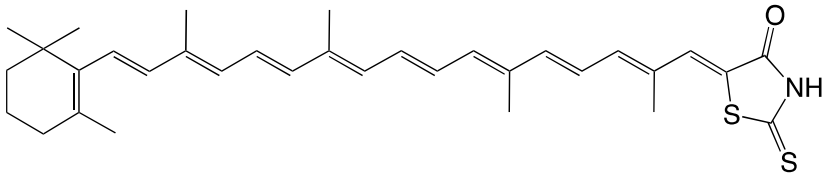

M. Blanchard-Desce, I. Ledoux, J. Malthête, J. Zyss, *J. Chem. Soc., Chem. Commun*. **1988**, 737

2⊙N,S 7,8'-diapo-8'-(benzodithiol-2-ylidene)-7-(4-pyridinium)-carotene iodide $C_{34}H_{36}INS_2$




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 $C_{33}H_{41}NOS_2$




H. Hegedus, *US3071583*, **1963**
H. Thommen, *Int. Z. Vitaminforsch*. **1967**, *37*, 175

*Sample Availability*: Not available.

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