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Structures of Carotenoids Determined by Our Research Group During 2009 to 2019

Takashi Maoka*

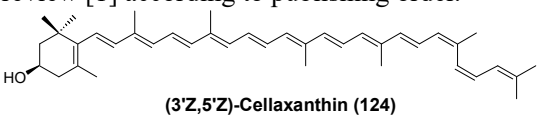
Research Institute for Production Development, 15 Shimogamo, Morimoto Cho, Sakyoku, Kyoto 606-0805, Japan

*Correspondence should be addressed. Tel:+81-75-481-1107, FAX: +81-75-791-7659
E-mail: maoka@mbox.kyoto-inet.or.jp

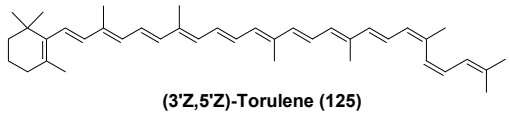
Abstract : Our research group determined 123 structures of carotenoids during 1978 to 2008. Since then, structures of 78 carotenoids were newly determined. They were 43 natural products of carotenoids, 22 reaction products of carotenoids with reactive oxygen species, and 13 carotenoids produced by pathway engineering. In this review, structures of 78 carotenoids determined by our research group during this decade were described.

Key Words: structure, new carotenoids

Since 1978, I have contributed structural studies of various carotenoids. In 2009, I described the list of 123 carotenoids determined by our research group during 1978 to 2008 [1]. The next decade, our research group determined structure of 78 carotenoids, including 43 naturally occurring compounds, 22 reaction products of carotenoids with reactive oxygen species, and 13 carotenoids produced by pathway engineering. In the present review, structures of these 78 carotenoids were described. The compounds numbers are described continuously previous review [1] according to publishing order.

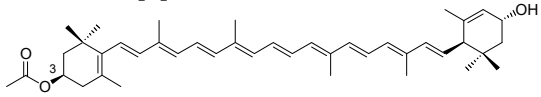


(3'Z,5'Z)-Cellaxanthin (124)



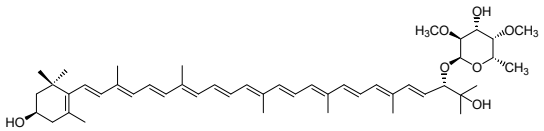
(3'Z,5'Z)-Torulene (125)

Carotenoids (**124**) and (**125**) were isolated from the seeds of oriental bitter sweet *Celastrus orbiculatus* [2].

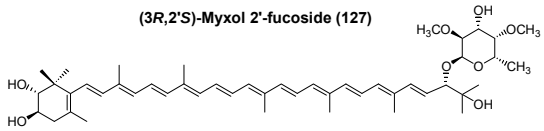


Lutein 3-acetate (126)

Carotenoid (**126**) was found in senescent leaves of rice [3].

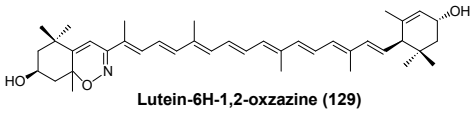


(3*R*,2'S)-Myxol 2'-fucoside (127)

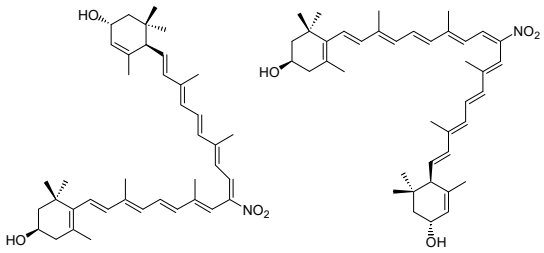


(2R,3R,2'S)-2-hydroxymyxol 2'-fucoside (128)

Carotenoids (**127**) and (**128**) are isolated from cyanobacterium *Nostoc commune* NIES-24 [4].



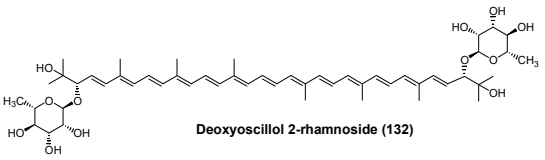
Lutein-6H-1,2-oxzazine (129)



14-s-*cis*-15-nitro-lutein (130)

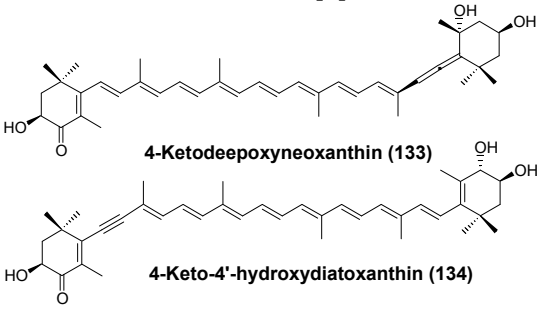
14'-s-*cis*-15'-nitro-lutein (131)

Carotenoids (**129**) ~ (**131**) was obtained as reaction products of lutein with peroxynitrite [5].



Deoxyoscillol 2-rhamnoside (132)

Carotenoid (**132**) was isolated from *Gemmatimonas aurantiaca* [6].



4-Ketodeepoxyneoxanthin (133)

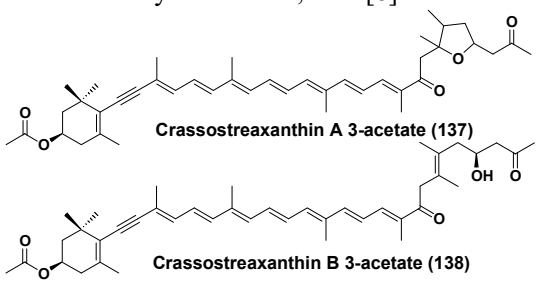
4-Keto-4'-hydroxydiatoxanthin (134)

Epigobiusxanthin (135)

Stereostructure was revised by Yamano et al. (2015)

7,8-Dihydrodiadinoxanthin (136)

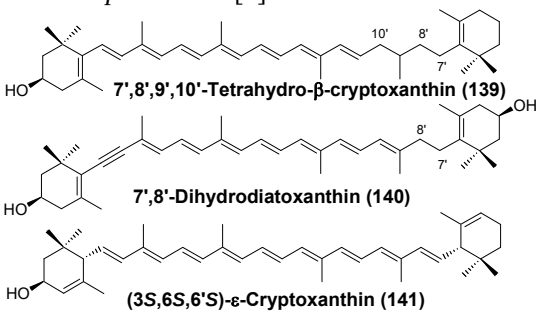
Carotenoids (**133**) ~ (**136**) were isolated from the crown-of-thorns starfish *Acanthaster planci* [7]. Stereostructure of epigobiusxanthin (**135**) was revised by Y. Yamano, et al [8].



Crassostreaxanthin A 3-acetate (137)

Crassostreaxanthin B 3-acetate (138)

Carotenoids (**137**) and (**138**) were isolated from clams, *Ruditapes philippinarum* and *Meretrix petechialis* [9].

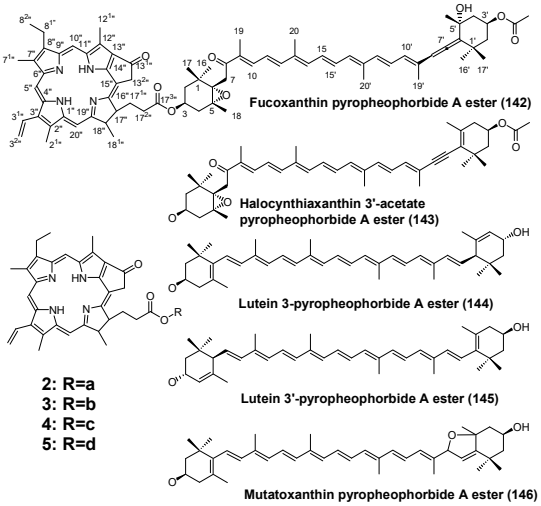


7',8',9',10'-Tetrahydro-β-cryptoxanthin (139)

7',8'-Dihydrodiatoxanthin (140)

(3*S*,6*S*,6'*S*)-ε-Cryptoxanthin (141)

Catotenoids (**139**) ~ (**141**) were isolated from the Japanese common catfish *Silurus asotus* [10].



Fucoxanthin pyropheophorbide A ester (142)

Halocynthiaxanthin 3'-acetate pyropheophorbide A ester (143)

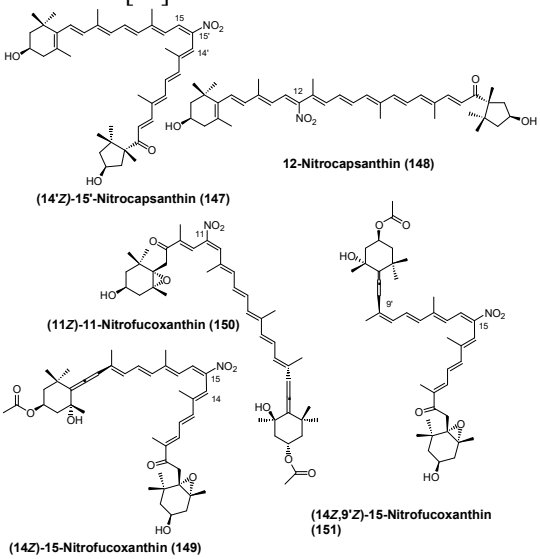
Lutein 3-pyropheophorbide A ester (144)

Lutein 3'-pyropheophorbide A ester (145)

2: R=a
3: R=b
4: R=c
5: R=d

Mutatoxanthin pyropheophorbide A ester (146)

Novel carotenoids and pyropheophorbide A esters (**142**) ~ (**146**) were isolated from viscera of abalone [11].



12-Nitrocapsanthin (148)

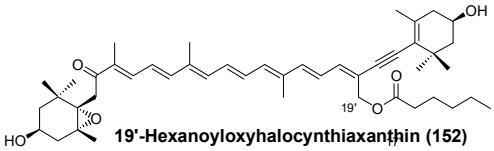
(14'*Z*)-15'-Nitrocapsanthin (147)

(11*Z*)-11-Nitrofucoxanthin (150)

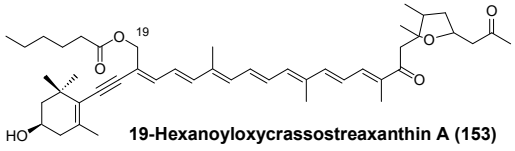
(14*Z*)-15-Nitrofucoxanthin (149)

(14*Z*,9'*Z*)-15-Nitrofucoxanthin (151)

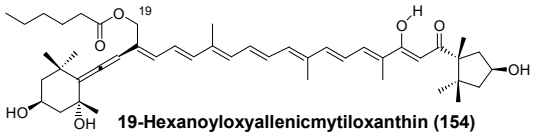
Carotenoids (**147**) ~ (**151**) were obtained as products of fucoxanthin with peroxynitrite [12].



19'-Hexanoyloxyhalocynthiaxanthin (152)

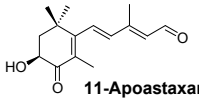


19-Hexanoyloxycrassostreaxanthin A (153)

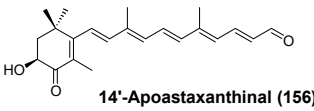


19-Hexanoyloxyallenicmytiloxanthin (154)

Carotenoids (**152**) ~ (**154**) were from the sea mussel *Mytilus galloprovincialis*, grown in the Black Sea [13].

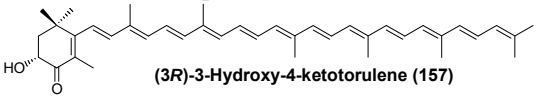


11-Apoastaxanthinal (155)

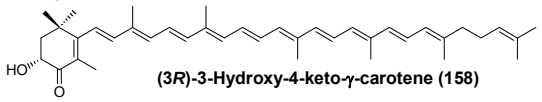


14'-Apoastaxanthinal (156)

Carotenoids (**155**) and (**156**) were obtained as auto-oxidation products of astaxanthin [14].

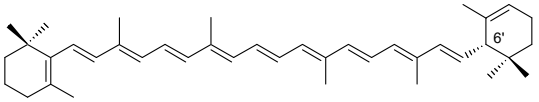


(3*R*)-3-Hydroxy-4-ketotorulene (157)



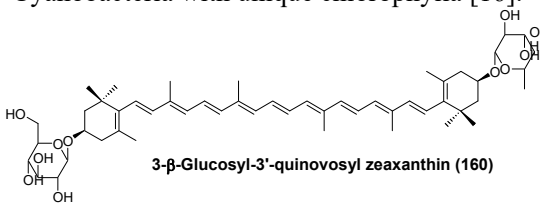
(3*R*)-3-Hydroxy-4-keto-γ-carotene (158)

Carotenoids (**157**) and (**158**) were isolated from the yeast *Xanthophyllomyces dendrorhrous* [15].



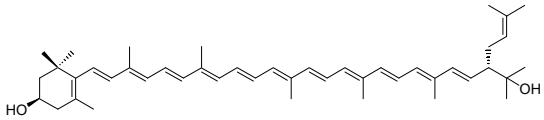
(6'*S*)-α-Carotene (159)

Carotenoid (**159**) was isolated from unusual Cyanobacteria with unique chlorophylla [16].



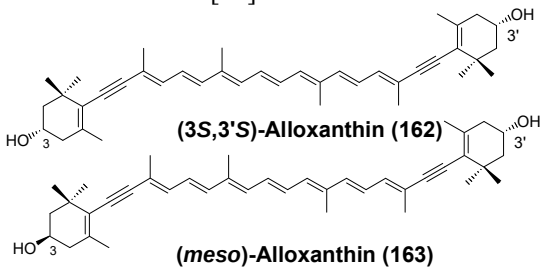
3-β-Glucosyl-3'-quinovosyl zeaxanthin (160)

Carotenoid (**169**) was obtained by *Escherichia coli* cells expressing the *Pantoea ananatis* carotenoid biosynthesis gene cluster [17].



(3*R*,2'*S*)-2-Isopentenylsaproxanthin (161)

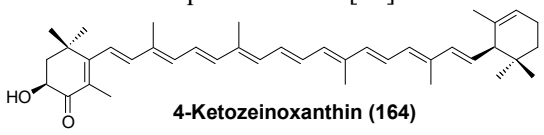
Carotenoid (**161**) was isolated from yellow-orange bacterium Jejuia pallidilutea strain 11shimoA1 [18].



(3S,3'*S*)-Alloxanthin (162)

(*meso*)-Alloxanthin (163)

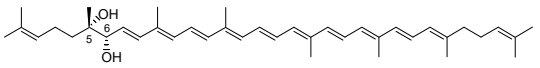
Alloxanthin optical isomers (**162**) and (**163**) were found in aquatic animals [19].



4-Ketozeinoxanthin (164)

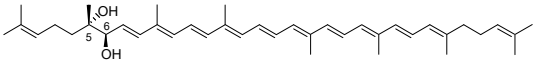
Carotenoid (**164**) was produced in *Escherichia coli* through metabolic engineering using carotenogenic genes of bacterium and liverwort [20].

relative stereostructure was dtermined



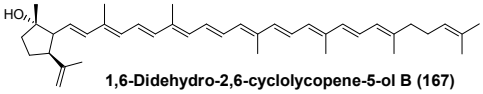
(*threo*)-Lycopene-5,6-diol (165)

relative stereostructure was dtermined

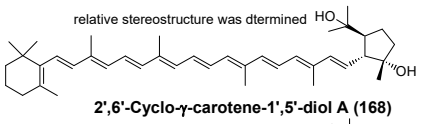


(*erythro*)-Lycopene-5,6-diol (166)

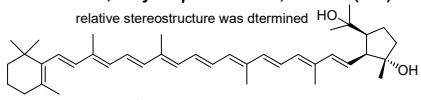
relative stereostructure was dtermined



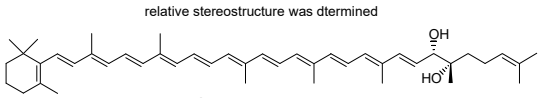
1,6-Didehydro-2,6-cyclolycopene-5-ol B (167)



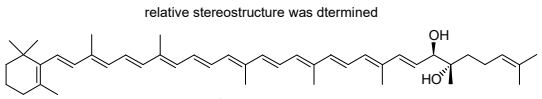
2',6'-Cyclo-γ-carotene-1',5'-diol A (168)



2',6'-Cyclo-γ-carotene-1',5'-diol B (169)

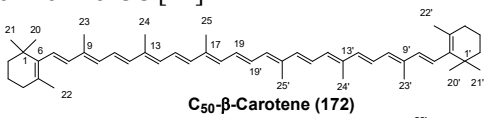


(*threo*)-γ-Carotene-5',6'-diol (170)

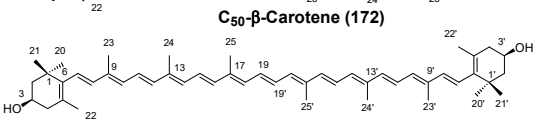


(*erythro*)-γ-Carotene-5',6'-diol (171)

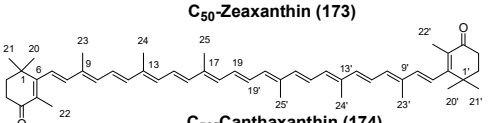
Carotenoids (**165**) to (**171**) were isolated from the frits of gac *Momordica cochinchinensis* [21].



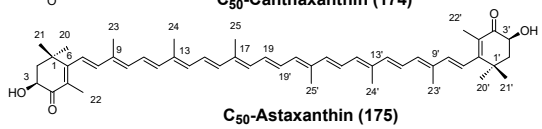
C_{50}-β-Carotene (172)



C_{50}-Zeaxanthin (173)

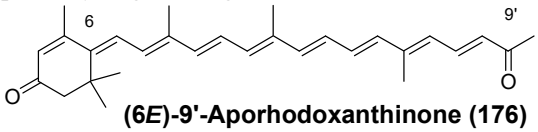


C_{50}-Canthaxanthin (174)

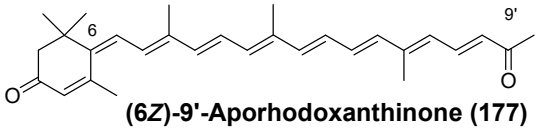


C_{50}-Astaxanthin (175)

Carotenoids (**172**) ~ (**175**) produced by pathway engineering in *Escherichia coli* [22].

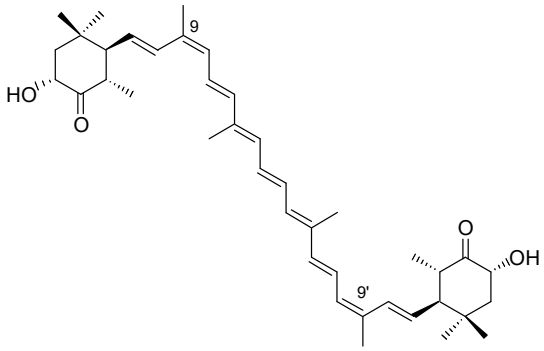


(6*E*)-9'-Aporhodoxanthinone (176)



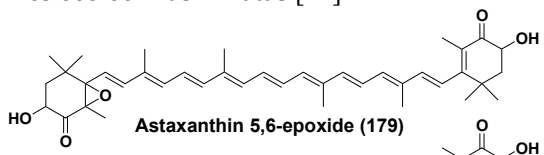
(6*Z*)-9'-Aporhodoxanthinone (177)

Carotenoids (**176**) and (**177**) were obtained in zeaxanthin-synthesizing *Escherichia coli* by redox stress [23].

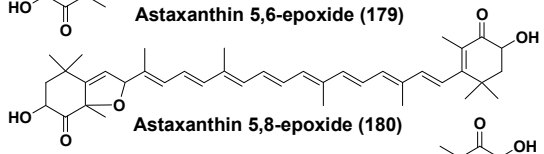


(9Z,9'Z)-Tetrahydroastaxanthin (178)

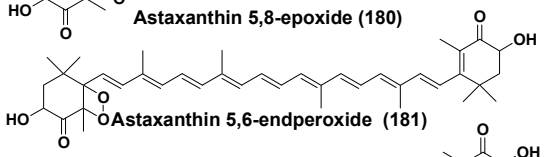
Carotenoid (**178**) from the sea cucumber *Plesiocolochirus minutus* [24].



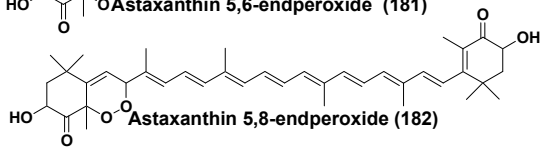
Astaxanthin 5,6-epoxide (179)



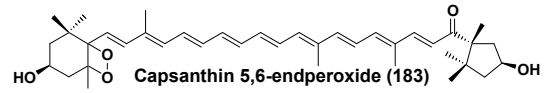
Astaxanthin 5,8-epoxide (180)



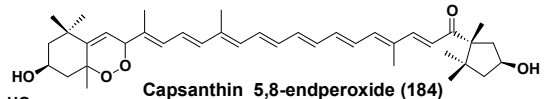
Astaxanthin 5,6-endperoxide (181)



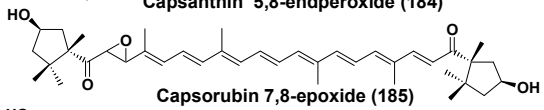
Astaxanthin 5,8-endperoxide (182)



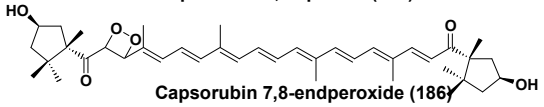
Capsanthin 5,6-endperoxide (183)



Capsanthin 5,8-endperoxide (184)

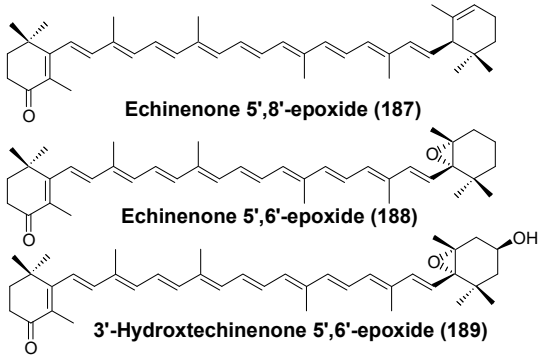


Capsorubin 7,8-epoxide (185)

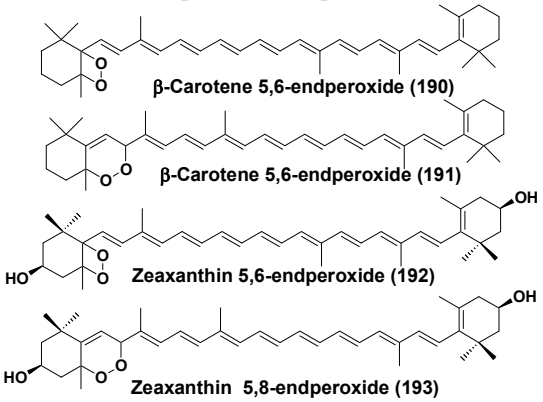


Capsorubin 7,8-endperoxide (186)

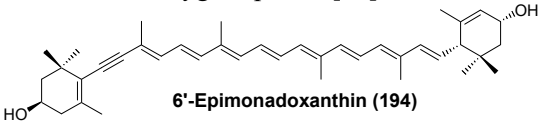
Carotenoids (**179**) ~ (**184**) was obtained as reaction products of astaxanthin with reactive oxygen species [25]. Carotenoids (**185**) and (**186**) were obtained as capsanthin and capsorubin with reactive oxygen species [26] .



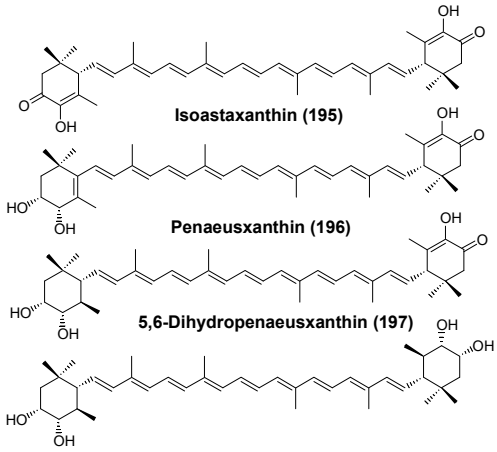
Carotenoids (**187**) ~ (**189**) were obtained by the interaction of the foreign carotenoid ketolase CrtW and endogenous epoxy carotenoids unique to sweet potato tubers [27].

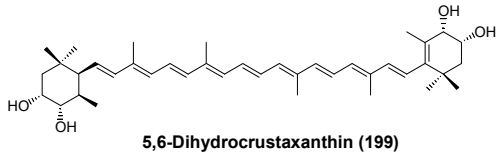


Carotenoids (**190**) ~ (**193**) were obtained as reaction products of β-Carotene and zeaxanthin with reactive oxygen species [28].

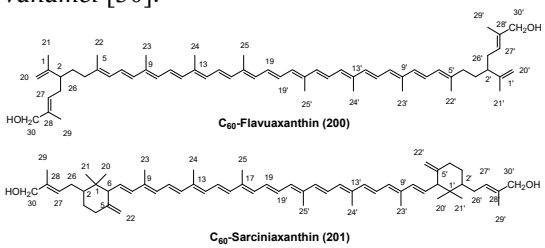


Carotenoid (**194**) was isolated from the rosary goby Gymnogobius castaneus [29].





Carotenoids (**195**) ~ (**199**) were isolated from the prawn *Penaeus japonicus* and *Penaeus vanamei* [30].



Carotenoids (**200**) and (**201**) were obtained genetically engineering biosynthetic product in *Escherichia coli* [31].

Improvements of analytical instruments such as NMR, MS, and HPLC have made it possible to perform the structural elucidation of very minor (**141**, **199**) or complex structures of carotenoids (**142**~**146**) in nature. Determination of complex stereo-structure of carotenoids (**165**~**171**) is needed chemical synthetic approach. Progress of LC/MS, LC/MS/MS methods can be determined unstable compounds such as reaction products of carotenoids with reactive oxygen species (**179**~**184** and **190**~**193**). These results indicated that carotenoids scavenged not only singlet oxygen but also hydroxyradical and superoxiide anion radical through chemical reactions. Furthermore, carotenoids are able to capture peroxynitrite and nitrogen dioxide radicals from their molecules to form

nitro-carotenoids (**129**~**131** and **147**~**151**). Pathway engineering produced several interesting structural carotenoids, which are not found in nature.

In conclusion, I determined total 201 carotenoids during for decade as described above. I acknowledged all of co-authors of my publications.

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