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An overview of algal carotenoids: source, applications and biosynthesis

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ABSTRACT: Algae have significant potential for the large scale production of high value biochemical compounds like Carotenoids. β-carotene, lycopene, astaxanthin, lutein, fucoxanthin, and violaxanthin are some of the common microalgal carotenoids. The basic structure of carotenoid molecules is formed by polene backbone adjoining 40 atoms of carbon having a varying double bond (C=C). Carotenoids are accessory pigments in photosynthetic apparatus primarily in LHC, also known to act as antioxidant (Scavenger for reactive oxygen species). They perform significant roles for humans, such as being precursors of vitamin A, lowering the risk of malignancies, aiding in the prevention of age-related and cardiovascular illnesses, improving skin health, and stimulating and boosting immunity. There have been over 850 different kinds of natural carotenoids known to exist, with an estimated global market $2.1 billion. This review summarizes recent sources, functions and pathways of carotenoids. Modern lifestyle required the inclusion and acceptance of algal based carotenoids, especially for children and women to fight against the malnutrition.

Keywords: ae, Antioxidants, Bioactive, Compounds, Carotenoids

INTRODUCTION

Bacteria, cyanobacteria, algae, plants, fungi and animals have been a natural source of many bioactive compounds such as alkaloids, lipids, proteins, polysaccharides, phenols and various pigments including carotenoids (Kant *et al*., 2005). Carotenoids are a diverse class of naturally occurring colorful molecules ranging orange, yellow, red, dark green color that are fat soluble (lipophilic), formed through the isoprenoid pathway (IPP). Basic structure of carotenoid molecules is formed by polene backbone of adjoining 40 atoms of carbon. This backbone is formed through a series of alternating single and double bonds (C=C), creating a conjugated system (Hou *et al*., 2016; Cheng *et al*., 2020). These bonds are responsible for light absorbing properties of carotenoids, giving them their vibrant colors. Additionally, the polyene chain contributes to the molecule's antioxidant activity by neutralizing reactive oxygen species (Fiedor and Burda, 2014). The structural arrangement of these bonds not only influences the pigment's optical characteristics but also plays a crucial role in its biological functions, including photoprotection and free radical scavenging (Young and Lowe, 2018).

Majorly carotenoids are of 40 carbon skeletons and those having 45-50 carbons are termed as higher carotenoids whereas those with less than 40 carbon skeletons are referred as apocarotenoids which are known to be formed by the enzymatic or non-enzymatic breakdown of parent carotenoid (Harrison, 2022). There are ~40 higher carotenoids from bacteria, more than 100 apocarotenoids from higher plants have been so far reported. The existence of π-electron conjugation in carotenoids structures accounts for their distinctive spectroscopic features. Structurally more than 850 carotenoids have been identified from bacteria, cyanobacteria, algae, fungi, plants and animals (Honda *et al*., 2020). At present, most commercially available carotenoids are produced by chemical synthesis, that incurs high costs and environmental challenges. As a result, there has been a growing interest in natural carotenoid sources, particularly from microorganisms such as algae. In plants as well as in algae, Carotenoids are very crucial for the structural building of photosystems (PSI & PSII), light harvesting complex (LHC), and chemical quenching (Siziya *et al*., 2022). Carotenoids are the well-known precursor of Vitamin A. They are an antioxidising agent for the protection of living cells from negative impacts of reactive oxygen and free radical species (Melendez-Martinez, 2007). Structures of some major carotenoids are shown in figure 1. According to market projections, the global value of the carotenoid industry is anticipated to grow to USD 2.0 billion by 2026 (Miyashita *et al*., 2020). However, algae cultivation remains largely centered in Asia,

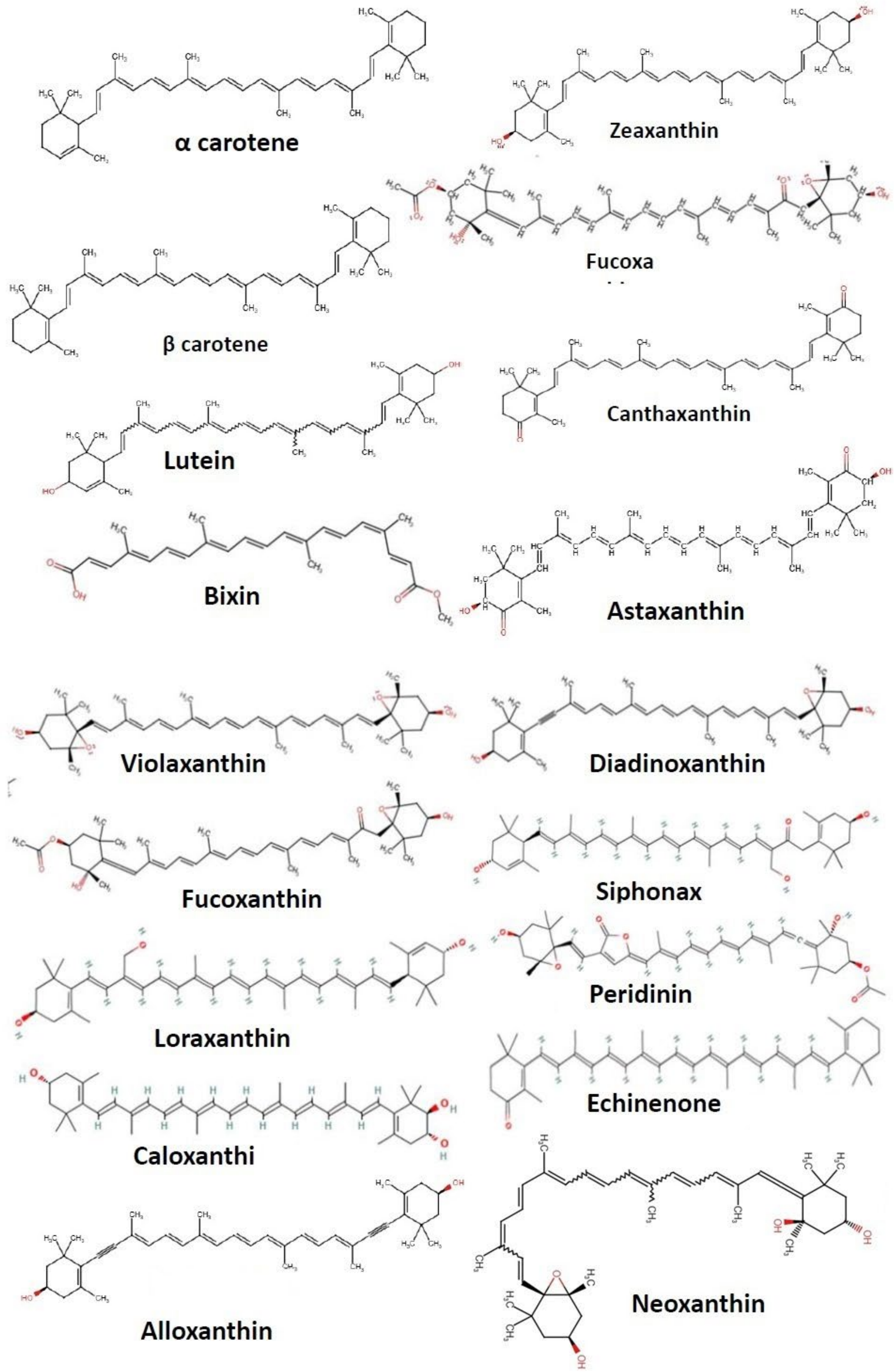

Figure 1. Chemical structures of some carotenoids of different algal species (Redrawn using source-https://pubchem.ncbi.nlm.nih.gov/compound).

with China leading the way-accounting for more than 56% of global aquaculture output (Zhang *et al*., 2022).

As compared to higher plants, very few studies have been done on algal carotenoids at the molecular and gene regulation level (Takaichi, 2011). But due to the advancement in technologies and Transcriptome research, it gave a chance to understand carotenoid evolution as well as their synthesis in various algae. Various types of carotenoids have been reported among the algae species shown in Table 1. In stressful conditions carotenoids, such as astaxanthin and canthaxanthin (keto-carotenoid), are accumulated in significant amounts within cytoplasm in the form of lipid globules. Begum *et al*., (2016) observed that some stressed microalgae show characteristic pink color due to synthesis of carotenoid and formation of a protective layer of carotenoid. Algae have a short life span, high growth rate as compared to the plants (Kant *et al*., 2006), require much less land area for cultivation, making them a better source for commercially important bioactive compounds, including carotenoids at a lower cost (Kant *et al*., 2022). Carotenoids such as β-Carotene can be identified in the majority of photosystem I and PSII (both core of the reaction centre as well as LHC). Whereas in some red algae, zeaxanthin is present in LHC of PSI, also bound the carotenoids in PSII's peripheral LHC vary by class of algae.

As discussed earlier, carotenoids are most prominent accessory pigments in LHC as well as in photosystems, also they act as antioxidants thus providing photoprotection in living green cells. They are proved to be important for human diet, as being a precursor of vitamin A and having antioxidant or anti-aging properties, thus lowering the impact of various malignancies, aiding to overcome skin & age-related issues, cardiovascular diseases, as well boosting immunity (Bjørklund *et al*., 2022). So far, more than 800 types of nature based carotenoid compounds have been documented, with a global market value of around 1.8 billion US dollars (Honda *et al*., 2020). Carotenoids are significant in aesthetic sense also as they are contributing to the beauty of nature by imparting various levels of pigmentation to fruits and flowers and enhancing their flavor and aroma which results in better engagement of pollinators and seed dispersal organisms.

Biosynthesis of Carotenoids in Algae

Carotenoids are synthesized within specific organelles, such as chloroplast and chromoplast in microalgae and higher plants (Pizarro, and Stange, 2009). Some potential algal strains through which carotenoids can be effectively extracted are mentioned in figure 2. In microalgae, the core biosynthetic pathway for carotenoids shares considerable similarity with that of streptophytes (Yao

Table1. Carotenoids reported from different microalgal species.

Algae	Carotenoid	Reference
Haematococcus pluvialis	Astaxanthin	Pansi *et al*.,2016
Chlorella striolata var. *multistriata*	Astaxanthin	Bar *et al*.,1995
C. vulgaris	Astaxanthin, Lutein	Cha, *et al*.,2010; Singh *et al*.,2010
C. zofingiensis	Astaxanthin	Singh *et al*.,2010
Botryococcus braunii	Astaxanthin	Pansi *et al*.,2016
Dunaliella salina	β-carotene	Chiu *et al*., 2017
Dunaliella bardawil	β-carotene	Koller *et al*.,2014
Coelastrella striolata var. *multistriata*	β-carotene	Abe *et al*.,2007
Dunaliella salina	Bixin	Koller *et al*.,2014
Phaeodactylum tricornutum	Fucoxanthin	Ishika *et al*.,2019
Isochrysis galbana	Fucoxanthin	Kim *et al*.,2012
Odentella aurita	Fucoxanthin	Xia *et al*., 2013
Cylindrotheca closterium	Fucoxanthin	Ishika *et al*.,2019
Chlorella prothecoides	Lutein	Sun *et al*., 2016
Chlorella pyrenoidosa	Lutein	Wu *et al*.,2007
Dunaliella salina	Lutein	Gayathri *et al*., 2016
Muriellopsis sp.	Lutein	Del Campo *et al*., 2007
Phormidium sp.	Zeaxanthin, β- carotene	Hertzberg *et al*.,1971
Anabaena flos-aquae	β-Carotene	Hertzberg *et al*.,1971
Synechococcus sp. PCC7002	Cryptoxanthin, Echinenone Myxoxanthophyll, Synechoxanthin, Zeaxanthin,	Zhu *et al*.,2010

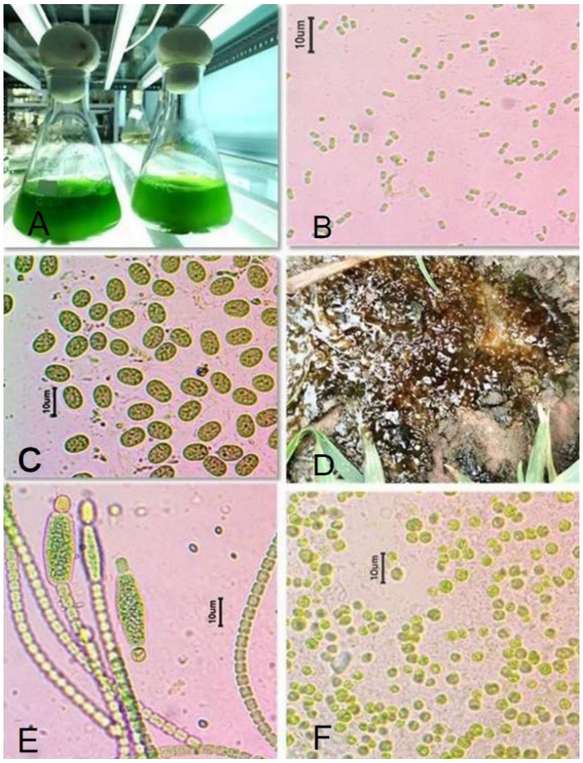

Figure 2. Some potential microalgal strains through which carotenoids could be extracted- A. *Synechococcus* sp. culture in liquid culture in flasks and B. Cells of *Synechococcus* sp.; C. Cells of *Aphanothece* sp., D. Growth in Nature of *Aphanothece* sp., E. Cells of *Cylindrospermum* sp.; F. Cells of *Chlorella* sp. (Our original pictures captured from lab cultures).

et al., 2022). However, the pathway in microalgae exhibits greater complexity compared to terrestrial plants. This increased complexity arises from various evolutionary events, including gene duplications, gene losses, and horizontal gene transfers, which have collectively shaped the diversity of carotenoid biosynthesis in these organisms (Gupta *et al*., 2021). The biosynthesis pathway of carotenoids and its derivatives are shown in figure 3. According to the existing studies the entire carotenoids synthesis can be grouped into following:

- Synthesis of monomer isoprene unit, IPP or DMAPP i.e Five carbon Compound (C_5) via Mevalonate Pathway (MVA pathway) in cytosol or through the MEP pathway (Methylerythritol Pathway) in plastid.
- Synthesis of GGPP (geranylgeranyl diphosphate)- it is a 20 carbon compound formed through the IPP and DMAPP subunits
- Synthesis of Phyotene and Lycopene
- Synthesis of Carotene and Xanthophyll

Applications for carotenoids

Carotenoids derived from algae have emerged as promising natural antioxidants that may help combat obesity and excessive weight gain. Research indicates that obesity is closely related to inflammation and oxidative stress, both of which play a central role in triggering metabolic disorders such as type 2 diabetes, high blood pressure and liver conditions (Generalić *et al*., 2023). Due to their antioxidant properties, carotenoids compounds from marine algae are being explored as alternatives to traditional obesity treatments like medication and surgery. Specifically, algal carotenoids have been linked to the regulation of key biological processes involved in fat cell formation, blood sugar balance and fatty acid metabolism (Ojulari *et al*., 2020).

Algal carotenoids are also being explored as nutrition enhancers in various food products. They can be added in powder or oil form to items like bread, pasta, cookies, soups, and yoghurt, contributing both to their nutrient content and functional properties (Diprat *et al*., 2020) However, determining the ideal amount and formulation type of food remains a challenge. Higher concentrations of these compounds, or of algae themselves, may cause sensory issues-particularly related to taste and color that reduce consumer acceptance. Still, when used at suitable levels, algal carotenoids offer benefits such as improved nutritional value, antioxidant protection, and extended shelf life. Notably, certain pigments like fucoxanthin have also shown potential as natural food colorants, enhancing both the visual appeal and health-promoting qualities of various food and drink products (Din *et al*., 2022).

Carotenoids extracted from algae have also been incorporated into animal feed to enhance the pigmentation of species like salmon, trout, crustaceans, and eggs, which are common components of the human diet (Pangestuti and Siahaan, 2018). Diets enriched with carotenoids are often linked to various health advantages. The specific carotenoid content in these animals largely reflects the composition of their feed (Zaheer, 2017). While carotenoids have long been used as food colorants, the growing availability of natural sources and their compatibility with synthetic alternatives have expanded their use in the animal nutrition sector (Pangestuti and Siahaan, 2018). Researchers have demonstrated that algal pigment extracts rich in carotenoids can improve shrimp immunity against

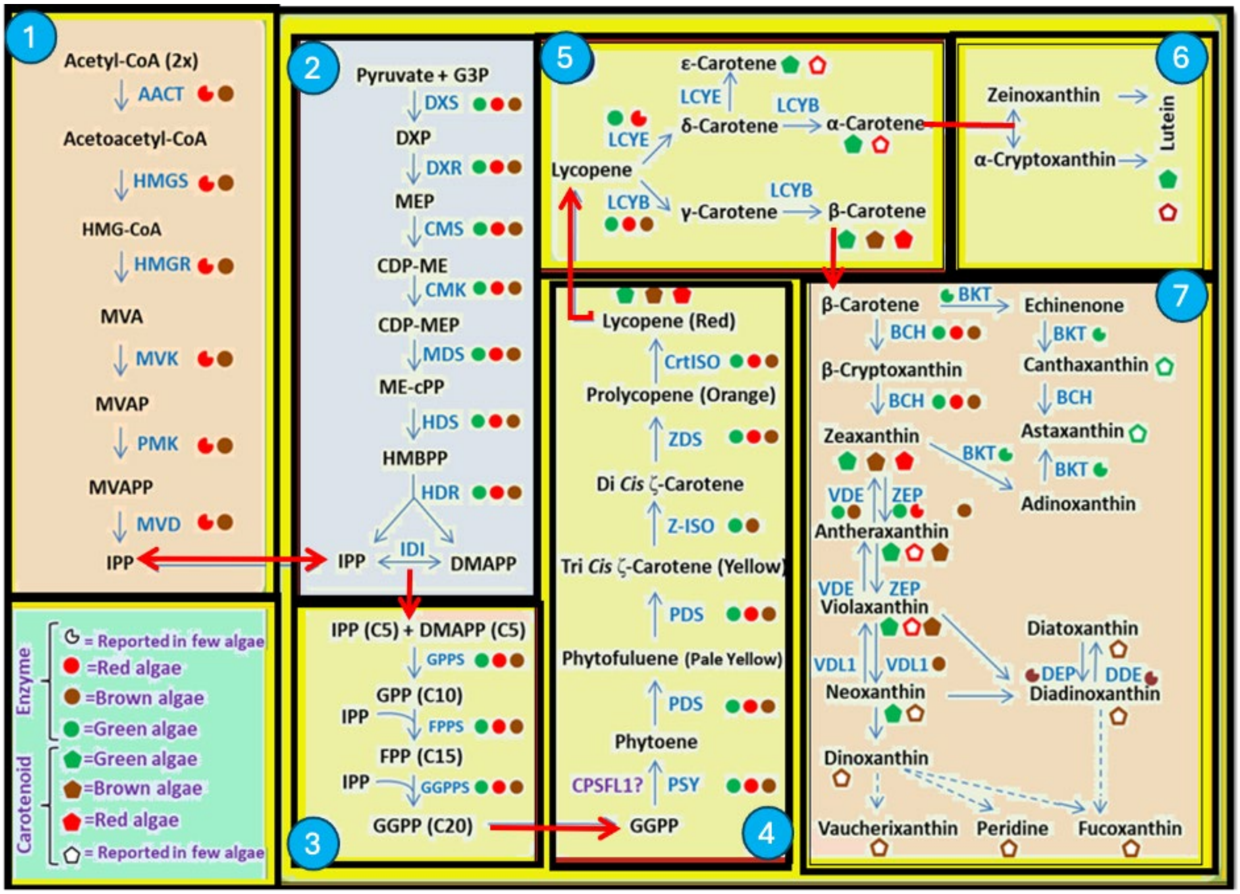

Figure 3. Mechanism for the synthesis of carotenoids in algae. The different phases are represented by (1-7) boxes as follows: (1): MVA Pathway (mevalonate), (2): MEP (methylerythritol phosphate) pathway, (3): GGPP (Geranylgeranyl diphosphate) pathway. (4): Phytoene and Lycopene synthesis, (5): Carotene synthesis. (6): Xanthophyll formation from α-carotene, (7): xanthophylls from β-carotene (Gupta *et al*., 2021).

Vibrio infections and support better growth performance (AftabUddin *et al*., 2021). In another instance, supplementing cattle feed with algae helped reduce methane emissions during digestion, thereby lowering the environmental impact without compromising feed efficiency (Roque *et al*., 2021).

Algal pigments are increasingly utilized as bioactive compounds in cosmetic formulations due to their ability to slow down skin aging and shield the skin from UV radiation, a major contributor to the production of reactive oxygen species (ROS) (Kant, 2011; Jesumani *et al*., 2019). These ROS can damage cellular DNA and are linked to adverse skin effects such as hyperpigmentation, early aging, sunburn, and even skin cancer. Carotenoids present in the skin reach the tissue through two primary pathways: passive diffusion from internal sources like blood plasma and fat tissue, or secretion via sebaceous glands followed by reabsorption into the skin (Darvin *et al*., 2011). The concentration and type of carotenoids found in the skin largely mirror those present in the bloodstream, with key examples including lutein, β-carotene, lycopene, zeaxanthin, β-cryptoxanthin, and the non-colored pigments phytoene and phytofluene. Grether-Beck *et al*., (2017) demonstrated that oral intake of lutein and lycopene provided photoprotective benefits by reducing gene expression triggered by UVA1 and combined UVA/B exposure. Additionally, astaxanthin was found to downregulate matrix metalloproteinases responsible for breaking down collagen and elastin and has been linked to improvements in skin oil balance, wrinkle reduction, elasticity, and hydration.

CONCLUSION

Microalgae have already found commercial success in the production of carotenoids and are gaining attention across various industries. This is largely due to their rapid growth, eco-friendly cultivation, and superior carotenoid yield compared to plants, as well as their strong adaptability to different environmental conditions. They can be cultivated in both saltwater and freshwater environments without the use of harmful chemicals like pesticides, making them an attractive resource for extracting bioactive compound. This underscores the need for continued research and advanced technologies, particularly to enhance the efficiency of processing and extraction processes.

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