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Research review paper

Carotenoids from microalgae: A review of recent developments

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ABSTRACT

Carotenoids have been receiving increasing attention due to their potential health benefits. Microalgae are recognized as a natural source of carotenoids and other beneficial byproducts. However, the production of micro-algal carotenoids is not yet sufficiently cost-effective to compete with traditional chemical synthetic methods and other technologies such as extraction from plant based sources. This review presents the recent biotechnological developments in microalgal carotenoid production. The current technologies involved in their bioprocessing including cultivation, harvesting, extraction, and purification are discussed with a specific focus on downstream processing. The recent advances in chemical and biochemical synthesis of carotenoids are also reviewed for a better understanding of suitable and economically feasible biotechnological strategies. Some possible future directions are also proposed.

Contents

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1. Introduction

Microalgae play a fundamental role in ecosystems (Guedes et al., 2011a, 2011b). Recently, microalgae are gaining attention as a source of useful products such as carotenoid pigments, polyunsaturated fatty acids, vitamins, lipids and proteins. Some of the specific advantages microalgae cultivation offers, compared to traditional plant-based sources, include a faster cultivation, processing and harvesting cycle and the ability to be cultured on waste materials. The anti-oxidants astaxanthin, β-carotene, lutein, lycopene, and canthaxanthin are the major carotenoids of commercial value found in microalgae. In spite of the perceived advantages, the large scale and cost-effective manufacture of the carotenoids from algae is currently quite challenging both in terms of production and downstream extraction and purification. An integrated bioprocessing approach using microalgae thus needs to consider both the upstream production of microalgae and the downstream harvesting and extraction of carotenoids. The existence of rigid cell walls in many algal species poses difficulties as this prevents full recovery of bioactive compounds. This is, therefore, a significant bottleneck in the overall bioprocess.

Many recent reviews have previously discussed microalgae and their products and applications (Guedes et al., 2011a, 2011b; Markou and Nerantzis, 2013; Mata et al., 2010); however, there has been less focus on the downstream processing aspects. In this review, an attempt has been made to emphasize the extraction and downstream processing steps as a critical component for the overall bioprocessing. First the chemistry and biochemistry is described for a better understanding of the carotenoid production. Next the biotechnology, engineering and downstream approaches are discussed.

2. Chemistry and biochemistry of carotenoids

Carotenoids are lipophilic compounds and are usually colored yellow, orange or red and are the most diverse and wide spread pigments found in nature (Sasso et al., 2012; Varela et al., 2015). Most carotenoids share a common C40 backbone structure of isoprene units (termed terpenoid), and are divided into two groups: carotenes and xanthophylls. Some common carotenoids structure are shown in Fig. 1. Each of the carotenoids consists of different *trans* and *cis* isomers. Xanthophylls, the oxygenated derivatives of carotenes (which are hydrocarbon only), are relatively hydrophilic compounds due to the presence of hydroxyl groups and keto-groups at the end rings. As antioxidants, carotenoids are in general sensitive to light, oxygen and heat, which can lead to difficulties in storage and handling.

In spite of the diversity of the carotenoid family, less than 30 carotenoids play important roles in photosynthesis (Varela et al., 2015). Most of these are located in the thylakoid membranes, and are bound with the Light Harvesting Complexes (LHCs) (Nisar et al., 2015). The carotenoids function to absorb light and quench excess energy in photosynthetic metabolism. Some primary carotenoids like lutein serve as accessory pigments which can transfer absorbed energy to chlorophylls (Ye et al., 2008), therefore expanding the light absorbing spectrum of algae or plants.

Secondary carotenoids like astaxanthin and canthaxanthin play a role in cell protective mechanisms. Unlike primary carotenoids which are tightly associated with structural and functional components in the cellular photosynthetic apparatus, the secondary carotenoids are produced to high levels and are dispensed in oily droplets. They function to form a protective layer when the cells are exposed to stressed conditions, and provide the characteristic pink/red color of some stressed algae (Begum et al., 2015; Wang et al., 2015). Most carotenoids are found in ester or di-ester form, therefore saponification is needed after the extraction of pigments (Rebecca et al., 2011).

Due to their anti-oxidant property, carotenoids can protect cells from reactive radicals, prevent lipid peroxidation, and promote the stability and functionality of the photosynthetic apparatus (Grossman et al., 2004). The integrity of membranes, which is essential for cell survival, can also be promoted by carotenoids. In particular, they improve the cell membrane fluidity under high temperature or high light conditions (Camejo et al., 2006). Similar stabilization effects were reported for low temperature as well when the lipids became more unsaturated (Ramel et al., 2012). In addition, the excess energy generated inside the cell can be dissipated as heat by non-photosynthetic quenching (NPQ). The energy dissipation is to protect cell damage from chemical reactive species ($^1O_2^{+}$, $^3Chl^*$), and is achieved by intersystem crossing from triplet state carotenoids to the ground state (Musser et al., 2015; Niyogi et al., 1997; Velikova et al., 2005).

2.1. Biosynthesis of carotenoids

The biosynthesis of carotenoids differs from species to species; however, almost all photosynthetic microalgae or plant species share the common primary metabolic pathway as shown in Fig. 2. All pathways initiate from the same C5 building block, isopentenyl pyrophosphate (IPP) or its isomer, dimethylallyl diphosphate (DMAPP), produced from either Acetyl-CoA (the cytosolic mevalonic acid pathway (MVA) pathway) or pyruvate and G3P (the plastidic methylerythritol 4-phosphate (MEP) pathway). Although both pathways lead to the same end-product, it was suggested that the carotenoid synthesis uses IPP or DMAPP derived from the MEP pathway (Barredo, 2012). Then the intermediate C15 farnesyl diphosphate (FPP) or C20 geranylgeranyl diphosphate (GGPP) is synthesized by successive chain elongation in the

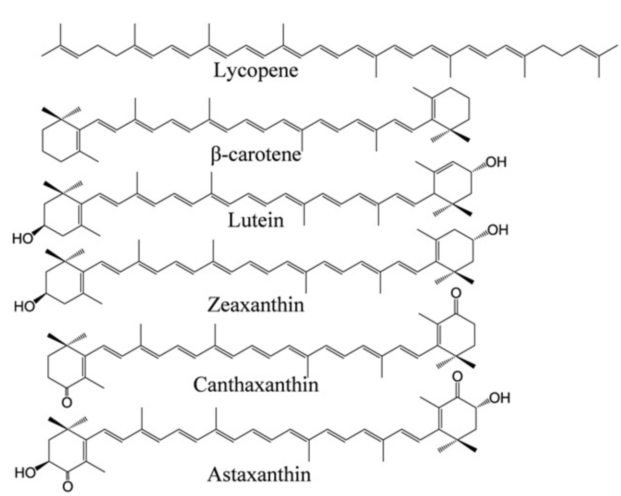

Fig. 1. Chemical structure of some common carotenoids found in microalgae.