CHAPTER 23

Impact of Marine Micro- and Macroalgal Consumption on Photoprotection

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Abstract

The enormousness of species diversity of oceans leads to the isolation and development of health- and beauty-enhancing components from various marine organisms. The significance of these marine-derived compounds or substances has been scientifically well implied for various biological and biomedical parameters. One such important parameter is photoprotectivity, which is the major concern nowadays because of the depletion in ozone layer and the possible high risk of UV irradiation to humans. The marine macro- as well as microalgae and their food products, knowingly and unknowingly, have been used since hundreds of years. These foods possess tremendous implications in defending the highly hazardous UV radiation, thereby facilitating photoprotection to humans. In addition, based on the recent studies, many of the UV-protecting algal species is directed for the use as medicinally

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valuable foods and food ingredients. This chapter describes certain micro- and macroalgal species along with their photoprotective importance.

I. INTRODUCTION

Marine environment possesses a diverse cluster of plants and animals of biomedical, pharmacological, and nutritional importance. The exploration and exploitation of marine micro- and macroorganisms toward various health benefits are increasing day by day via the fundamental and biotechnological approaches. One of such organisms of marine habitat are the algae, which have been proved to possess tremendous health benefits from ancient times. In fact, the terms ''seaweeds'' or ''sea-vegetables'' are used interchangeably for the large and visible macroalgae, whereas microalgae have been recognized as the microscopic producers of some highly bioactive compounds of chemical and pharmacological diversity. Moreover, microalgae are considered as the actual producers of biomedical substances found in marine resources.

Algae can provide sustainable and affordable food and fuel, as well as ecological and novel solutions. Any food, fibers, or materials that can be achieved from land-based crops can be made from algae because land plants evolved from algae 500 million years ago (Edwards, 2010). Seaweeds are majorly consumed in the oriental countries, such as Japan, China, and Korea, and nowadays, in the United States and Europe (NAAS, 2003). The earliest recorded use of seaweeds dates back to 2700 BC in ''Chinese Herbs'' compiled by the Emperor Shen Nung. Humans are dependent on micro- and macroalgae, which have been utilized for hundreds of years as food, fodder, medicine, cosmetics, etc., and hence, consumption of algae is recommended for best health and medicinal prospects worldwide. A market-based survey at Arizona State University found that nearly 70% of medicinal and cosmetic products commonly depend on algal components. Most people do not consume algae directly as food but enjoy the products made from algal components that include algal flour in lieu of wheat, corn, or soy flour; algal oils that are healthier and less fattening than corn oil; and algal nutrients such as ω-3 fatty acids, etc. Several species of macroalgae, belonging to Rhodophyceae (red), Phaeophyceae (brown), and Chlorophyceae (green algae), are also used as foods and food ingredients/components in Asian, Pacific, Canadian, and Icelandic traditions (Yuan, 2008).

Photoprotection is a group of mechanisms that nature has developed to minimize the damages that an organism encounters, when exposed to UV radiation (UVR). These mechanisms can be controlled or organized by certain organic and inorganic compounds or substances (e.g., melanin) produced by different terrestrial and aquatic sources. A number of photoprotective compounds such as scytonemins (exclusively in cyanobacteria), mycosporines (in fungi), mycosporine-like amino acids (MAAs; in cyanobacteria, algae, and animals), phenyl propanoids and flavonoids (in higher plants), melanins (in humans and other animals and even some bacteria), and several other UV-absorbing substances of unknown chemical structures from different organisms have been developed to counteract the photodamage. Besides the nutritional value, many algal species that are commonly exposed to elevated solar radiation synthesize and accumulate high concentrations of UV-absorbing compounds (Rastogi *et al.*, 2010). This principle of photoprotection has been taken into consideration by the researchers to develop and isolate various photoprotecting and antiaging compounds/formulations from marine algae, and basing the fundamentals of photoprotective consequences by these macro- and microalgal species, certain species of algae are well recommended as various foods and nutritional supplements. Although majority of research is pending with regard to the identification of certain algal species of photoprotective importance, ancient people have used a variety of these organisms in their regular diet and noticed the medicinal value of them; for example, previous reports show that seaweeds have been a part of the Japanese diet since 300 BC. It was reported earlier that more than 10 million algal species presumed to exist all over the world and around 90% of all their bioactive and therapeutic compounds remain to be discovered (Edwards, 2010; Singleton, 2011).

In spite of possessing photoprotecting principle, algae are believed to have iodine, which is responsible for low rates of goiters in areas where algae are consumed frequently. In addition, the Memorial Sloan Kettering Cancer Center (MSKCC) notes that the protein and vitamin combination in algae may help decrease fatigue.

II. UV-INDUCED PHOTODAMAGE AND PHOTOPROTECTION

UVR is the main etiological agent for most of the skin cancer incidence and a key factor responsible for photoaging and photodamage (González *et al.*, 2008). UV spectrum reaching earth's surface has been classified as UVB (290–320 nm) and UVA (320–400 nm). UVB causes acute sunburn, DNA mutation, or even cancer by its absorbance in the epidermis, whereas the longer wavelengths of UVA region can penetrate much deeper into the skin.

Continuous exposure to UV irradiation (both UVA and UVB) leads to skin cancer and other photoaging complications, which are typically mediated by the reactive oxygen species (ROS), generated in the oxidative pathways (Dummermuth *et al.*, 2003; Pallela *et al.*, 2010). Normal skin cells generate ROS such as superoxide anion (O^{2-}) and hydrogen peroxide (H_2O_2) as a result of normal metabolism in minute concentrations. Both O^{2-} and H_2O_2 may be converted to the highly reactive hydroxyl radical (OH^-) by iron (Fe^{2+})-catalyzed Haber–Weiss and Fenton reactions. Similarly, reactive nitrogen species (RNS) are generated as a result of sequential reactions that begin with nitric oxide synthase (NOS)-mediated conversion of arginine to citrulline. In this reaction, NO is generated, which reacts with O^{2-} to produce peroxynitrite ($ONOO^-$). Similarly, ROS and RNS can be formed as a result of exposure to environmental agents including chemicals (xenobiotics) and solar UVA and UVB. Many xenobiotics are converted to toxic quinones by the family of functionally related enzymes known as cytochrome P450 (CYP). These quinones are redox-sensitive agents and are reversibly reduced to semihydroquinones/hydroquinones, which generate O^{2-}. Both UVA and UVB produce similar free radicals and/or singlet oxygen ($^1O_2$) either directly following interaction with cellular components or in the presence of chemical agents known as photosensitizers. These photoactive chemicals while in their lowest energy or ground state absorb incident radiation (including UVA/UVB), within their absorption spectrum. The energy of the absorbed photon creates an excited state molecule, which is highly unstable under ambient conditions. In returning to the ground state, excited species transfer energy to adjacent intracellular chemical moieties particularly molecular oxygen (O_2) and thereby convert it into ROS. These ROS interact with lipid-rich plasma membranes and initiate a reaction known as lipid peroxidation. Numerous intracellular enzymes serve to degrade these reactive species. Some of these enzymes are specific such as SODs, which dismute O^{2-} to H_2O_2, whereas others have overlapping substrate affinities such as catalase and glutathione peroxidases, both of which can degrade H_2O_2 to water and O_2 but glutathione peroxidases also degrade organic peroxides to relatively nontoxic alcoholic species. These enzymes also require GSH during the course of peroxide degradation and convert GSH into its oxidized form, which is recycled by the enzyme glutathione reductase. Similarly, toxic quinones are converted to relatively less toxic hydroquinones by quinone reductases (QR).

As a result of UVA/UVB-mediated ROS generation during the pathogenesis of various skin diseases, a number of signaling pathways are activated. ROS drive activation of MAPKs, the most important of which are ERK, JNK, and p38 kinases. ERK and JNK are important in recruiting c-Fos and c-Jun to the nucleus where they activate the transcription factor AP-1, whereas activation of p38 and inhibitory kappa kinases (IKK) is important in the transcriptional activation of NF-κB. Both of these factors are important in regulating the diverse array of genes, which play key roles in the pathogenesis of inflammation (such as iNOS, COX-2) and in regulation of cell cycle, proliferation, and apoptosis (cyclin D1, Bcl2, Bclx, IAP, p21, p53, etc.).

Hence, photoprotection is a critical and crucial concern to avoid these undesired effects. The increase in solar UVR on the earth's surface due to the deterioration in the stratospheric ozone layer has increased the interest for searching natural, photoprotective compounds from various sources (Rastogi *et al.*, 2010). Stratospheric ozone depletion leads to an increase in the short wavelengths of UVR and in consequence to an increase in H_2O_2 formation in surface waters. In such cases, algae undergo oxidative stress, where UVR induces the formation of H_2O_2 by photoactivation of dissolved organic material (DOM), photochemical degradation, and liberation of exited electrons, which initiate reduction of molecular oxygen (Dummermuth *et al.*, 2003). Hence, photoprotective processes prevent or minimize generation of oxidizing molecules, scavenge ROS efficiently, and repair damage that inevitably occurs (Niyogi, 1999). Micronutrients such as carotenoids, tocopherols, ascorbates, flavonoids, or ω-3 fatty acids can act as UV absorbers or antioxidants, or can modulate signaling pathways elicited upon UV exposure. In addition, protection depends on the topical applications as well as the algal consumption, which constitute many of the UV absorbers as mentioned above. Hence, algae are the richest source for these photoprotecting constituents and can be recommended as highly nutritional supplements, which can bring resilience to human body.

III. PHOTOPROTECTIVE ROLE OF VARIOUS ALGAL FOODS

Knowingly or unknowingly, algae are well consumed by most of the Asian countries, which is the gateway to understand the potentiality of the algal foods. As human beings are health as well as beauty cautious, several nutritional supplements containing algae have entered the food markets. Below are such microalgal and macroalgal foods that are very important in terms of health and photoprotection. As per a published article on Web, pleasant taste, minerals, and vitamin and bioactive compounds are just some of the reasons for the applications of seaweed in the kitchen, stall, and health products.

A. Microalgal foods

Microalgae have been used in various foods because of their ubiquitous availability in oceans and also due to their tremendous medicinal values. Earlier, as many as 206 strains of 152 marine microalgal species with UVA- and UVB-absorbing compounds were identified (Jeffrey *et al.*, 1999). *Arthrospira platensis* or *Spirulina platensis* (commonly called as nutraceutical spirulina) is a blue-green microalgae with a long history as a food source in East Africa and precolonial Mexico (Wikipedia).

Spirulina is high in protein and other nutrients, finding use as a food supplement and for malnutrition. Previous studies of the photoprotection of various pigments in *S. platensis* were carried out in the presence and the absence of biopterin-a-glucoside to evaluate the photostability of these photosynthetic pigments in the photosynthetic vesicles that undergo UV irradiation (Noguchi *et al.*, 1999).

Another popular microalga, *Chlorella*, has similar nutritional values as that of spirulina and is majorly popular in Japan. It is also used as a nutritional supplement with possible effects on human metabolic rate, and few researchers reported that *Chlorella* can reduce mercury levels in humans via the chelation of mercury to the cell wall of the organism.

The abundance of diatoms in the oceans makes them an important food source for many of the macroorganisms. These microscopic organisms tend to live in diverse climates and are able to attain resistance against aberrant conditions. One such important stress condition is the photostress caused by the extra radiation that enters the planet earth. The xanthophyll cycle pigments and the content of α-tocopherol in *Phaeodactylum tricornutum* were previously studied to get molecular information about the physiological reasons of light-stress resistance (Müller and Wilhelm, 1997). According to these studies, it was clearly understood that under natural conditions when the light is fluctuating between optimal, sub-, and supraoptimal intensities, the photostress resistance is much higher than under conditions of the absence of light stress. These principles of photoacclimation, photoadaptation, and photoinhibition/photoproduction direct these microorganisms as potential sources for antiphotoaging foods.

B. Macroalgal foods

Several species of algae are raised for food; for example, purple laver (*Porphyra umbilicalis*) is the most widely domesticated marine algae. It is used as nori and gim in most of the Asian countries. In addition to the Asian countries, in Wales, it is used as a traditional food called laver bread, and in Ireland, it is collected and made into a jelly by stewing or boiling. Preparation also can involve frying or heating the fronds with a little water and beating with a fork to produce a pinkish jelly. Harvesting also occurs along the west coast of North America and in Hawaii and New Zealand. Dulse (*Palmaria palmata*) is a red species sold in Ireland and Atlantic Canada. It is eaten raw, fresh, dried, or cooked like spinach.

Macroalgal extracts possess various proteins and peptides which play an important role in the formulation of new collagen as well as increased skin hydration. In addition, marine red algae increases skin hydration significantly because of the enzymes and minerals present in the algae which are prominent in Hawaiian Islands. French seaweeds are other important algae that play effective role in photoprotection and this principle is used even to formulate certain shaving gels (Somersets).

In addition, extracts and oils from algae, for example, ω-3 and ω-6 fatty acids, are also used as additives in various food products. *Sargassum* species are an important group of seaweeds with photoprotecting principle. These algae have many phlorotannins that involve in various biological activities including photoprotection.

It has been well demonstrated previously that seaweeds and seaweed extracts can help to protect skin from UVR (Bulteau *et al*., 2006; Ryu *et al*., 2009). Methanolic extracts of *Corallina pilulifera* (CPM) possess high phenolic content, which reduces the expression of UV-induced MMP-2 and -9 in human dermal fibroblasts, which is an indication of photoprotection to use this algae as food. Phlorotannins from *Ecklonia cava* are gaining tremendous interest for endeavoring novel photoprotecting mechanisms in various skin oriented *in vitro* and *in vivo* experiments (Kim *et al*., 2006). These kelps are highly recommended to use as food sources by many Asian countries, and in fact, few of the beauty products have already entered the cosmetic markets, with strong photoprotecting and antiphotoaging principle. For example, Edicos, Fibroboost (contains Seanol-F), are naturally occurring substances that act as antioxidative as well as anti-inflammatory material from seaweeds. Along with other species of this genus, *E. cava* has been used as a traditional food from ancient times toward various health benefits and other biomedical applications (Wijesekara *et al*., 2010, 2011).

The most active natural UV-absorbing substances are the MAAs that are produced by algae and possess tremendous implications for being used as medicinal foods. A human study showed that a cream containing MAAs from the red alga *P. umbilicalis* efficiently protects the skin against UVA exposure on a typical working day (Schmid *et al*., 2003).

In addition, blue-green algae contain all essential amino acids as well as most of the nonessential amino acids, making these foods a complete protein supplement in regular diets.

Irish moss (*Chondrus crispus*) is a good source of carrageenan, which is used as a stiffening agent in instant puddings, sauces, and dairy products such as ice cream. *C. crispus* can be directed to be a UVB-protecting food source because of the presence of carrageenan; especially κ-carrageenan oligosaccharides with molecular weight of about 3 kDa (κ-ca3000) are proven to be the strong antioxidants when they are tagged with some peptides (Heo and Jeon, 2008).

Lettuce species like *Ulva lactuca* have been used in Scotland and other provinces where it is added to soups and salads. Similar species, *Ulva thalli*, contain only two cell layers; however, it can withstand the higher levels of both visible and UVR (Figueroa *et al*., 2009). This is achieved with the involvement of UVB in the protection from UV damage, which has already been reported in another macroalgae, *Dictyota dichotoma*, and in the blue-green algae, *Ulva pertusa* (Flores-Moya *et al*., 1999; Han and Han, 2005).

The functional significance of phlorotannins from the spores of Arctic Laminariales as UVR screens has been presented before (Roleda *et al*., 2006). *Alaria esculenta* and *Laminaria digitata* showed strong absorption in the UV waveband, characteristic of several phlorotannins. *A. esculenta* is commonly known as dabberlocks or badderlocks, eaten either fresh or cooked in Greenland, Iceland, Scotland, and Ireland.

IV. CONCLUSIONS

Marine algae hold immense potential to be utilized as photoprotective elements. Proper utilization of this resource would pave a pay for future detonation in the cosmeceutics and medicinal food market. Advanced biotechnological approaches need to be implied to ocean sciences to explore the vast prospective of these photoprotective agents. Strategies need to be formulated for the appropriate usage of the marine algal photoprotective compounds as an answer to the photodamage caused by UVA/UVB or even the xenobiotics.

REFERENCES

Bulteau, A., Moreau, M., Saunois, A., Nizard, C., and Friguet, B. (2006). Algae extract-mediated stimulation and protection of proteasome activity within human keratinocytes exposed to UVA and UVB irradiation. *Antioxid. Redox Signal.* **8**, 136–143.

Dummermuth, A. L., Karsten, U., Fisch, K. M., König, G. M., and Wiencke, G. M. C. (2003). Responses of marine macroalgae to hydrogen-peroxide stress. *J. Exp. Mar. Biol. Ecol.* **289**, 103–112.

Edwards, M. (2010). Algae 101, part 2. What's it all about algae? Algae industry magazine. http://www.algaeindustrymagazine.com/algae-101-part-two-what%E2%80%99s-it-all-about-algae/.

Flores-Moya, A., Hanelt, D., Figueroa, F. L., Altamirano, M., Viñegla, B., and Salles, S. (1999). Involvement of solar UV-B radiation in recovery of inhibited photosynthesis in the brown alga *Dictyota dichotoma* (Hudson) Lamoroux. *J. Photochem. Photobio. B* **49**, 129–135.

Figueroa, F. L., Israel, A., Amir, N., Brezo, M., Erik-jan, M., Put, A., Jr., Sven, I., Ronny, M., and Nathalie, K. (2009). Effects of nutrient supply on photosynthesis and pigmentation in *Ulva lactuca* (Chlorophyta): Responses to short-term stress. *Aquat. Biol.* **7**, 173–183.

González, S., Fernández-Lorente, M., and Gilaberte-Calzada, Y. (2008). The latest on skin photoprotection. *Clin. Dermatol.* **26**, 614–626.

Han, Y. S. and Han, T. (2005). UV-B induction of UV-B protection in *Ulva pertusa* (Chlorophyta). *J. Phycol.* **41**, 523–530.

Heo, S.-J. and Jeon, Y.-J. (2008). Radical scavenging capacity and cytoprotective effect of enzymatic digests of *Ishige okamurae*. *J. Appl. Phycol.* **20**, 1087–1095.

Jeffrey, S. W., MacTavish, H. S., Dunlap, W. C., Vesk, M., and Groenewoud, K. (1999). Occurrence of UVA- and UVB-absorbing compounds in 152 species (206 strains) of marine microalgae. *Mar. Ecol. Prog. Ser.* **189**, 35–51.

Kim, M. M., Quang, V.-T., Mendis, E., Rajapakse, N., Jung, W.-K., Byun, H.-G., Jeon, Y.-J., and Kim, S.-K. (2006). Phlorotannins in *Ecklonia cava* extract inhibit matrix metalloproteinase activity. *Life Sci.* **79**, 1436–1443.

Müller, A.-M. and Wilhelm, C. (1997). Light adaptation of the phytoplankton diatom *Phaeodactylum tricornutum* under conditions of natural light climate. *Int. Rev. Hydrobiol.* **82**(3), 315–328.

NAAS (2003). National Academy of Agricultural Sciences. Policy Paper.

Niyogi, K. K. (1999). Photoprotection revisited: Genetic and Molecular Approaches. *Annu. Rev. Plant Physiol. Plant Mol. Biol.* **50**, 333–359.

Noguchi, Y., Ishii, A., Matsushima, A., Haishi, D., Yasumuro, K.-i., Moriguchi, T., Wada, T., Kodera, Y., Hiroto, M., Nishimura, H., Sekine, M., and Inada, Y. (1999). Isolation of biopterin-a-glucoside from *Spirulina* (Arthrospira) *platensis* and its physiologic function. *Mar. Biotechnol.* **1**, 207–210.

Pallela, R., Yoon, N.-Y., and Kim, S.-K. (2010). Anti-photoaging and photoprotective compounds derived from marine organisms. *Mar. Drugs* **8**, 1189–1202.

Rastogi, R. P., Richa, Sinha, R. P., Singh, S. P., and Häder, D.-P. (2010). Photoprotective compounds from marine organisms. *J. Industr. Microbiol. Biotechnol.* **37**, 537–558.

Roleda, M. Y., Clayton, M. N., and Wiencke, C. (2006). Screening capacity of UV-absorbing compounds in spores of Arctic Laminariales. *J. Exp. Mar. Biol. Ecol.* **338**, 123–133.

Ryu, B., Qian, Z. J., Kim, M. M., Nam, K. W., and Kim, S.-K. (2009). Anti-photoaging activity and inhibition of matrix metalloproteinase (MMP) by marine red alga, *Corallina pilulifera* methanol extract. *Radiat. Phys. Chem.* **78**, 98–105.

Schmid, D., Schürch, C., Zülli, F., Nissen, H.-P., and Prieur, H. (2003). Mycosporine-like amino acids: Natural UV-screening compounds from red algae to protect the skin against photoaging. *SÖFW J. (Int. J. Appl. Sci.)* **129**, 1–5.

Somersets http://www.somersets.com/products/shave-gel-original.php.

Singleton, B. (2011). Algae as a food source for humans. http://www.livestrong.com/article/458681-algae-as-a-food-source-for-humans/.

Wijesekara, I., Yoon, N.-Y., and Kim, S.-K. (2010). Phlorotannins from *Ecklonia cava* (Phaeophyceae): Biological activities and potential health benefits. *Biofactors* **36**, 408–414.

Wijesekara, I., Senevirathne, M., Li, Y.-X., and Kim, S.-K. (2011). Functional ingredients from marine algae as potential antioxidants in the food industry. *In* ''Handbook of Marine Macroalgae: Biotechnology and Applied Phycology'', (S.-K. Kim, Ed.), pp. 398–402. Elsevier, Academic Press, USA.

Wikipedia. http://en.wikipedia.org/wiki/Algaculture#Food.

Yuan, Y. V. (2008). Marine algal constituents. *In* ''Marine Nutraceuticals and Functional Foods'', (C. Barrow and F. Shahidi, Eds), pp. 259–296. Taylor and Francis, Boca Raton.