Commercial Products from Algae

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Abstract The growing interest in algae is associated with current commercial products and future potential biofuel developments. The focus of this chapter is on commercial products from microalgae and macroalgae. This market is estimated to be of the order of billions of dollars per year with more than 20 different commercial products. The largest market is food products, including nutraceuticals and functional foods. There are many refined products; in some cases, there are multiple product streams associated with the separation process. Production occurs in fresh water for some microalgae such as Spirulina. Many macroalgae are grown in salt water environments; there are both managed production systems and harvests from natural areas of seas and oceans. Because of the diversity of growth environments and species, many more potential products are possible, and additional research is to be encouraged. There are many additional locations in the world that can be used to produce beneficial products.

Keywords Macroalgae · Microalgae · Nutraceuticals · Products · Seaweeds

Acronyms

N Nutraceut
P Pharmaceut

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1 Introduction

Algae grow rapidly, produce useful products, and provide environmental benefits. This vast collection of diverse aquatic organisms has received increased attention the past few decades, and for good reason: algae have potential as future biofuels, foods, and other valuable commercial products. Furthermore, algal products can be produced sustainably. This chapter focuses on socioeconomic and environmental considerations of algae while emphasizing the organisms' commercial value.

Algae can create commodity products such as biofuels and foods. While the byproducts of biofuel production do hold potential for future products, this work focuses more on products currently on the commercial market. Items such as nutraceuticals and functional foods created with algae have grown in importance since the year 2000 and there are now significant markets for these products. With the great diversity of algae, there is great promise that algal features may serve to enhance a large variety of current products, and produce new ones. As the currently expanding market for algae-based goods indicates, the future is bright for the research and development of algal products. There are many potential useful products that can be discovered and developed through future research (De Luca et al. 2012).

Concern for the environment and global climate change has increased in recent years, and algae can provide a number of significant environmental benefits. They remove carbon dioxide from the atmosphere, helping to reduce the harmful effects of the gas on climate change and the health of the environment. Algae have also been used to reduce nitrogen and phosphorus concentrations in wastewater before it is fed back to rivers, oceans, or other bodies of water.

In order to produce a commercial product, the algae must be able to be grown at reasonable cost and with appropriate quality control to have a product with sufficient purity to serve customer needs. The processing required to have a consistent product with desired functional properties must be at a cost low enough to compete with other products. Just like any other commercial product, the value of products from algae must exceed the cost of production to have good sales and a growing market.

Algae also contribute to increased sustainable practices. In the last 500 years, agricultural production processes on land have advanced, and there are now new and well-developed approaches to conventional farming operations. Significant progress also stems from the production of commercial products in water. As an aquatic organism, algae can be grown to produce useful products without using very much land. However, commercial operations to grow algae and produce commercial goods must be carried out with appropriate environmental management to avoid degradation of water quality. This work addresses such environmental concerns, demonstrating that algae production is sustainable.

The purpose of this chapter is to bring together information on algal characteristics of commercial value while reviewing progress in the development of algal products.

2 Commercial Products from Algae

One of the largest markets for algae is the food industry. Commercial products include algal powders such as Spirulina that are sold as health foods (Venugopal 2009; Yuan 2008; Henrikson 2009); algal products that contain polyunsaturated fatty acids (Venugopal 2009; Shahidi 2008); polysaccharides from microalgae and seaweeds (macroalgae) that provide beneficial dietary fiber and other health benefits (Venugopal 2009; Fitton et al. 2008); carotenoids that serve as sources of antioxidants and provide Vitamin A (Venugopal 2009; Miyashita and Hosokawa 2008; Olaizola 2008; Capelli et al. 2010); algal products that give color to foods and are marketed as food colorants (Delgado-Vargas and Paredes-Lopez 2003); and seaweeds that are used as foods (Venugopal 2009; Yuan 2008).

Algae are used for animal feed, especially in aquaculture where fish, shrimp, oysters, and other seafood are produced in confined environments (Venugopal 2009; Spolaore et al. 2006).

Hydrocolloids, including agars, alginates, and carrageenans, are marketed for their functional use in foods as well as their use in many industrial products (Bixler and Porse 2011; Venugopal 2009). Many processed foods make use of hydrocolloids to provide desired texture, water holding capacity, and as a preservative (Yuan 2008; Bixler and Porse 2011).

Substances from algae also have many applications in scientific research. For example, many cyanobacteria produce phycobiliproteins which are used in analytical chemistry. Telford et al. (2001) describes their use in antigen detection by flow cytometry.

Products from algae are also used in sunscreen, cosmetics, and pharmaceutical products. Table 11.1 provides a list of refined products from algal sources.

There are many different species of algae and there are significantly different natural environments for development and production. Because of this, there have been many research studies on many different products, and some of these have resulted in products that have commercial value as demonstrated by significant markets and sales. Venugopal (2009) and Barrow and Shahidi (2008) have contributed to the effort to identify important studies and significant markets for products from algae. Sales of products from algae are at the billions of dollars per year level (Venugopal 2009; Bixler and Porse 2011).

2.1 Health Foods, Functional Foods, and Nutraceuticals

One of the major commercial markets for algal products is the food industry. Algae have been consumed as foods for centuries in many parts of the world. In the 1950s, the microalgae Chlorella was considered seriously as a food source in light of rapidly growing populations. Better crop efficiency, however, fed the growing population, and microalgae never became a prominent food source.

Table 11.1 Refined Products from Algae. (Sources: Bixler and Porse 2011; Spolaore et al. 2006; Venugopal 2009; Burja and Radianingtyas 2008; Bhatia et al. 2010; Fitton et al. 2008; Miyashita and Hosokawa 2008)

Carotenoids
Astaxanthin
Beta-carotene
Bixin
Fucoxanthin
Lutein
Lycopene
Polysaccharides
Agar
Alginates
Ascophyllan
Carageenan
Fucoidans
Furcelleran
Polyuronides
Polyunsaturated Fatty Acids
Archidonic acid (AA)
Docosahexaenoic acid (DHA)
Eicosapentaenoic acid (EPA)
Gamma-Linolenic acid (GLA)
Proteins and Amino Acids
Allophycocyanin
Kainic acid
Mycosporine-like amino acids
Phycocyanins
Phycoerythrins
Sterols
Desmosterol
Fucosterol
Isotopically Labeled Compounds
Carbon 13 Isotopes
Nitrogen 15 Isotopes
Hydrogen 2 Isotopes

In the last 50 years, there has been increased interest and understanding of the benefits of many different chemicals in foods. Food science has advanced during this period, and the importance of diet and exercise has been emphasized in public education.

It's clear that the term nutraceutical comes from combining the terms nutrition and pharmaceutical. It's an appropriate term because in terms of health benefits nutraceuticals usually lie somewhere between food and medication. The U.S. Institute of Medicine defined a nutraceutical compound as "any substance that is a food or part of a food which provides medicinal or health benefits including the prevention and treatment of disease, beyond the traditional nutrients it contains" (Burja and Radianingtyas 2008). Functional foods are closely related, defined as "products derived from natural sources, whose consumption is likely to benefit human health and enhance performance" (Burja and Radianingtyas 2008).

Nutraceuticals may be present in a whole food product such as seaweed; they may also be found in dietary supplements in which the nutraceutical providing the health benefit has been concentrated relative to its concentration in a natural product. Spirulina supplements, in powder or tablet form, are an example of a nutraceutical. Spirulina has been shown to provide "medicinal or health benefits…beyond the traditional nutrients it contains." Some nutraceutical substances that come from algae include antioxidants and carotenoids.

The medical benefits of nutraceuticals include the prevention and treatment of disease. The terms health foods, functional foods, and nutraceuticals are all used to describe many of the food products from algae that have health benefits. Weight reduction, promotion of healthy bones and teeth, cholesterol reduction, disease resistance, improved immune system, anti cancer properties, healthier gut and digestive system, blood pressure control and reduction, heart health, antioxidant properties, and antiviral properties are examples of health benefits associated with different algal food products. The increased popularity of health foods, functional foods, and nutraceuticals associated with algae is due to a better understanding of nutrition and health benefits, commercial availability, increased purchasing power, advances in food processing, and globalization of foods from algae (Venugopal 2009).

2.2 Aquaculture and Animal Feed

Algae are used in commercial aquaculture operations for the production of salmon, shrimp, other fish, and mollusks. The algae supply important nutrients such as polyunsaturated fatty acids (PUFAs), carotenoids, and proteins (Venugopal 2009; Becker 2004). The production of algae for use in aquaculture is often on site, which allows the algae to flow into the aquaculture tanks where they are consumed (Zmora and Richmond 2004). Becker (2004) lists more than 30 species of algae that have been used as feed in aquaculture. Some species are selected because they accumulate large quantities of PUFAs (Cryptomonas sp. and Nannochloropsis sp.) (Becker 2004; Venugopal 2009). Zmora and Richmond (2004) describe several different bioreactors that are used to grow algae that are used for animal feed, including flat plate reactors, polyethylene bag reactors, and open tanks.

Seaweed and fish can be polycultured such that both products are produced in the same growth environment. Significantly higher mean net production rates of seaweed have been observed (Venugopal 2009). The effluents from aquaculture have been fed to seaweed farms where they provide needed nutrients (Venugopal 2009). This provides a good environmental management option for the effluents from aquaculture.

Mollusks, such as oysters, clams, and mussels are fed significant quantities of algae. Many different microalgal species have been used as feed for mollusks (Muller-Feuga 2004). Shrimp farming occurs in the United States, Ecuador, Thailand, China, and other countries of South East Asia. Microalgae may be used in specialized production facilities (Muller-Feuga 2004).

Algae can also be incorporated in feed for animals such as pets and farm animals. The species used the most in animal feed are Spirulina, Chlorella, and Scenesdesmus species. Supplementing the feed of cows, horses, pigs, poultry, and even cats and dogs with algal biomass has had positive results on the health of these animals (Spolaore et al. 2006). In poultry feed, up to 5–10 % can be safely replaced with algal biomass as a partial replacement for conventional proteins. Any higher concentrations, however, can result in undesirable effects such as reduced growth rate and changes in color and flavor of chicken eggs (Becker 2004). In pigs, algae can replace conventional proteins such as soybean or fish meal without serious issues. It has been suggested that at least 33 % of the total protein supplied can be replaced without adverse effects (Becker 2004).

2.3 Polyunsaturated Fatty Acids

Polyunsaturated fatty acids (PUFAs) are important for many aspects of human health. Recently, attention has been focused especially on omega-3 fatty acids because of their association with many health benefits. Fish and other seafood are good sources of these substances, but safety issues arise because fish can also accumulate mercury or other toxins, making them less safe for consumption (Spolaore et al. 2006). Due to a growing world population and overfishing, marine fish are not a sustainable source of PUFAs. Marine microalgae are a source of commercial omega-3 PUFAs, and macroalgae have also been shown to be a significant source of PUFAs (Venugopal 2009). Algae, in fact, are the primary producers of basic fatty acids in marine food webs (Bergé and Barnathan 2005). PUFAs from algae also have the advantage of being vegetarian in nature.

Solvent extraction is used to extract PUFAs from algae. Because of concern for preservation of the product, supercritical carbon dioxide has been used in some cases (Peretti et al. 2003; Venugopal 2009).

Many positive health effects have been linked with the consumption of PUFAs, especially the omega-3s. Venugopal (2009) provides a list of nutraceutical potentials of omega-3 fatty acids. Consumption of these PUFAs can possibly prevent atherosclerosis, arrhythmias, and chronic obstructive pulmonary diseases, reduce blood pressure, reduce symptoms in asthma patients, fight against manic-depressive illness, protect against chronic obstructive pulmonary diseases, alleviate symptoms of cystic fibrosis, prevent relapses in patients with Crohn's disease, prevent various cancers, provide bone health, and improve brain functions in children (Venugopal 2009). The omega-3 Docosahexaenoic acid (DHA) is an important component of tissue in the brain, nervous system, and eye (Venugopal 2009). Because of this, DHA is very important in the development of infants, as well as in growing children. A few studies have shown improvement in behavior of children whose diets have been supplemented with fatty acids, including children with attention deficit hyperactivity disorder (ADHD) (Venugopal 2009; Young and Conquer 2008).

Algae-derived PUFAs, such as DHA and Eicopentaenoic acid (EPA), are already commercially available as supplements that can be purchased at many nutrition stores or pharmacies. The microalga *Crypthecodinium cohnii* is a significant heterotrophic producer of DHA. The lipids of *C. cohnii* contain up to 30% DHA (De Swaaf et al. 2003). The alga *Schizochytrium limacinum* has also been reported as an excellent DHA producer (Chi et al. 2007). A study to test the effectiveness of DHA was conducted in 485 subjects over the age of 55 with age-related cognitive decline (ARCD). The study demonstrated that DHA supplementation, using DHA from *Schizochytrium sp*., improved episodic memory and learning in older adults that were healthy apart from mild memory problems (Yurko-Mauro et al. 2010).

One example of how producing commercial products from algae can accompany the production of renewable fuels is demonstrated by Chi et al. (2007). A major byproduct of biodiesel production is crude glycerol, an impure substance of low economic value. Glycerol was shown to be an inexpensive potential substance with which to produce DHA using Schizochytrium sp.

The production of PUFAs by microalgae can be optimized in many ways. Reducing nitrogen concentration can result in higher fatty acid production. Gamma-linolenic acid content has been increased in Spirulina by adding fatty acids and fatty acid precursors to the production media (Kim et al. 2012). Using light and dark two-stage culture was also beneficial.

2.4 Sunscreen Protection of Mycosporine-like Amino Acids

In the search for sun-protective chemicals, Mycosporine-like Amino Acids (MAAs) have been identified as significant due to their ability to absorb harmful UV radiation. MAAs have been found in bacteria, cyanobacteria, microalgae, macroalgae, and some other multicellular organisms. One of these MAAs is Porphyra-334, which has been isolated from *Porphyra vietnamensis* and investigated for its value as a sunscreen (Bhatia et al. 2010). Cyanobacteria also produce MAAs, and several species that have high yields have been studied (Musher and Fatma 2011). Tao et al. (2008) have shown that MAAs have antioxidative activities, and that they can protect against lipid oxidation. Carreto and Carignan (2011) have reviewed the structure and physicochemical properties of MAAs. A commercial product for use as a sunscreen has been developed (Andes Natural Skin Care 2012).

3 Important Species of Microalgae and Cyanobacteria, and their Products

3.1 Spirulina

Arthrospira platensis and *Arthrospira maxima*, both of which go by the common name Spirulina, are two species of cyanobacteria that are grown for their commercial value. Spirulina can grow in alkaline waters where competition with other

Table 11.2 Amino acid composition in protein from Spirulina, cow's milk and whole egg. (Sources include Henrikson 2009, wdatech.free.fr/CSUTECH-t/spirulinafacts.htm, Clement et al. 1967, www.geb.org/food-manufacturers/egg-nutrition-and-trends/nutrient composition#top,www.dairyamerica.com/acid.cfm)

Amino acid	Spirulina	Cow's milk	Whole egg
Alanine	7.5	3.3	5.6
Arginine	7.7	3.4	6.0
Aspartic + Asparagine	11.7	7.2	10.0
Cystine	0.9	0.9	2.3
Glutamic + Glutamine	13.6	19.9	13.1
Glycine	5.1	2.0	3.4
Histidine	2.4	2.6	2.4
Isoleucine	5.2	5.7	5.5
Leucine	7.9	9.3	8.5
Lysine	4.2	7.6	7.2
Methionine	2.1	2.4	3.1
Phenylalanine	4.2	4.5	5.3
Proline	4.0	9.3	4.0
Serine	4.3	5.2	7.4
Threonine	4.5	4.3	4.8
Tryptophan	1.4	1.3	1.2
Tyrosine	3.8	4.6	4.1
Valine	6.0	6.4	6.1

Note that because of rounding, columns do not sum to exactly 100 %. Values reported by different sources may vary by a relative concentration of 10–20 % for any amino acid. There are few primary literature sources for spirulina, most are secondary and of uncertain reliability

organisms is reduced. Productivities of about 12 metric tons/hectare per year can be obtained in open pond systems (Henrikson 2009). Spirulina are high in protein and there are many other nutraceutical and functional food products associated with Spirulina. A representative amino acid distribution in Spirulina is shown in Table 11.2. Values for cow's milk and whole egg are shown for comparison. Spirulina powder is marketed in grocery stores and health food stores, as are Spirulina tablets. It is grown in the United States, Mexico, Japan, Thailand, China, Taiwan, and India (Henrikson 2009). It is also harvested from naturally occurring sources such as Lake Chad (Fitton et al. 2008; Henrikson 2009).

Spirulina is rich in Vitamin A (beta carotene), Vitamin K, and Vitamin B_{12}. It also contains an antioxidant rich mixture of at least 10 carotenoids and essential polyunsaturated fatty acids such as linoleic acid (Henrikson 2009). The mineral content of Spirulina depends on the water in which it was grown, but iron, calcium, and magnesium are some of the important minerals that are usually present and give the Spirulina high nutritional value.

Sulfated polysaccharides that are produced by Spirulina have medicinal value as antiviral agents. Viruses to be treated with extracts of sulfate- and phosphate-bound polysaccharides include the herpes group of viruses and HIV viruses (Burja and Radianingtyas 2008). A dietary supplement for promoting health hormonal balance has been developed using a blend of Spirulina platensis powder with powders of other organisms (Burja and Radianingtyas 2008).

Spirulina and extracts from Spirulina have exhibited therapeutic properties such as cancer prevention, reduction of blood cholesterol levels, and stimulation of the immunological system. Phycocyanins, carotenoids, organic acids, polyunsaturated fatty acids, and sulfated polysaccharides have been identified as substances that may have therapeutic value. Some of these substances act as antioxidants and free radical scavengers that reduce the oxidative stress associated with reactive oxygen species (El-Baky et al. 2008). Supercritical carbon dioxide can be used to extract antioxidants from algae (Mendiola et al. 2008). Spirulina boosts the immune system, which is important in preventing viral infection and cancer (Kralovec and Barrow 2008). A beneficial effect of Spirulina on asthma has been reported (Kralovec and Barrow 2008).

3.2 Astaxanthin from Haematococcus pluvialis

Astaxanthin (3,3'-dihydroxy-ß-carotene-4,4'-dione) is a red-colored pigment carotenoid that is produced commercially for use for aquaculture feeds for salmon and trout as well as for human uses. The green alga, *Haematococcus pluvialis*, produces significant concentrations up to about 3 % dry weight and as much as 390 mg/L of broth. However, one of the challenges of production is contamination. Thus, pure culture photobioreactors have been used for the growth of this organism (Olaizola 2008; Venugopal 2009). Cyanotech Corporation in Hawaii uses a combination of closed photobioreactors and open culture ponds to produce Astaxanthin in Haematococcus. The production process involves growing the algae in the photobioreactors. This is followed by deprivation of nitrate and phosphate, and increased temperature and light intensity. Haematocysts form and Astaxanthin accumulates (Lorenz and Cysewski 2000). The cells appear as shown in Fig. 11.1 when they are growing; their color then changes when the haematocysts form and the Astaxanthin accumulates as shown in Fig. 11.2. The Astaxanthin is separated by crushing the algae and extracting the Astaxanthin; supercritical carbon dioxide has been used for extraction (Venugopal 2009). Ranjbar et al. (2008) have reported good results with a bubble column photobioreactor. Because the commercial market is in millions of dollars per year (Valensa 2009), research to find new strains is continuing (Dragos et al. 2011). While the production using Haematococcus is the most widely used process for human use; for animal feeds, synthetic processes have been developed. A recent economic assessment study reports that the production cost is estimated to be $ 718/kg of Astaxanthin and $ 18/kg of Haematococcus, which is less than the estimated cost of synthesis by the chemical process (Li et al. 2011).

Astaxanthin is used in human health because of its antioxidant activity (Ranjbar et al. 2008; Valensa 2009). Valensa (2009) has a patent in relation to oxidative

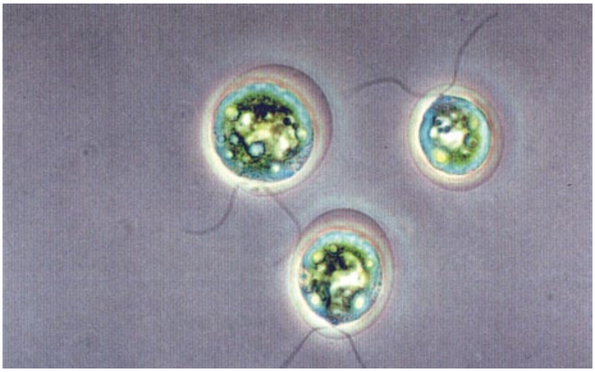

Fig. 11.1 Green Growing Haematococcus; courtesy of Cyanotech Corporation

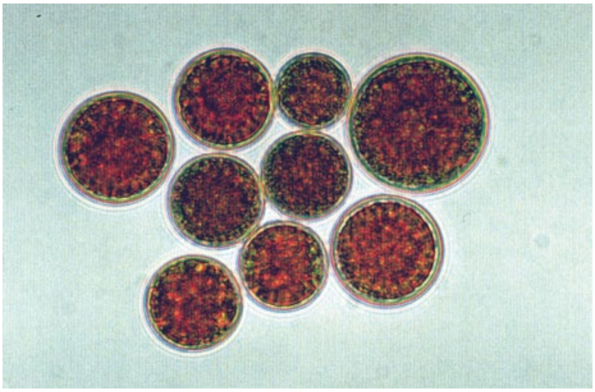

Fig. 11.2 Red Haematocysts; courtesy of Cyanotech Corporation

stress-related eye health conditions. The antioxidant properties of Astaxanthin protect against oxidative stress, protein degradation, macular degeneration, and reduced visual function in eye health studies (Nakajima et al. 2008; Parisi et al. 2008; Wu et al. 2006; Nagaki et al. 2002). Astaxanthin is also of interest because of its cancer prevention properties (Valensa 2009).

The antioxidant properties of Astaxanthin may provide protective effects which are beneficial with respect to management of neurodegenerative disorders associated with Parkinson's disease (Ikeda et al. 2008). These antioxidant properties of Astaxanthin inhibit the production of inflammatory compounds. Thus, Astaxanthin has anti-inflammatory properties that are of interest in cardiovascular disease and rheumatoid arthritis (Capelli et al. 2010; Choi et al. 2008; Pashkow et al. 2008).

Olaizola (2008) has reviewed the beneficial properties of Astaxanthin as a nutraceutical and functional food. Photoprotective properties associated with skin and eye health, immunomodulating capability, cardiovascular health benefits, and anticancer activity are included. The health benefits are related to the antioxidant properties of Astaxanthin.

3.3 Chlorella

Chlorella species are single-celled green alga. Chlorella has been produced commercially since the first pilot project in 1953 (Iwamoto 2004), and is still widely used as a dietary supplement as well as for aquaculture and animal feed (Kralovec and Barrow 2008). It has been grown commercially in photobioreactors and in open ponds, and is produced by more than 70 companies (Spolaore et al. 2006; Iwamoto 2004). The size of the market for Chlorella is of the order of billions of dollars per year (Spolaore et al. 2006).

An important substance in Chlorella is β-1,3-glucan, which is a free-radical scavenger that stimulates immune response. Biological studies have focused on antitumor effects associated with polysaccharides that have immunostimulating activity (Kralovec and Barrow 2008). The conclusion of several studies is that Chlorella is beneficial in suppressing several forms of cancer. Resistance to pathogen invasion has also been observed (Kralovec and Barrow 2008).

Chlorella extracts can lower blood sugar levels, reduce the concentration of blood lipids, increase hemoglobin concentration, and act as a hepatoprotective agent (Burja and Radianingtyas 2008; Iwamoto 2004). The cell wall of Chlorella needs to be disrupted mechanically in order for the beneficial compounds in Chlorella to be available when Chlorella powder is used as a health food.

3.4 Dunaliella

Dunaliella species are flagellate green microalgae, and are found in many marine and freshwater habitats. Dunaliella are marketed for their value as a functional food product. The commercial value is due to the high concentration of vitamin A, β-carotene, and the presence of other carotenoids that have value as antioxidants. Products from Dunaliella are also used as colorants in foods (Ben-Amotz 2004; Venugopal 2009; Delgado-Vargas and Paredes-Lopez 2003). Ben-Amotz (2004) has reviewed production methods for Dunaliella. Using intensive cultivation in ponds with constructed raceways with paddle wheels, 200 mg/m^2 per day of β-carotene can be produced. Salt concentration and intense solar radiation contribute to successful production of the biomass and β-carotene. Nitrogen deficiency is also used to stimulate carotenoid production.

One of the natural environments where Dunaliella is found is the Dead Sea. The high salt concentration and high solar radiation are beneficial to carotenoid production by Dunaliella in the Dead Sea (AbuSara et al. 2011). Many cosmetic products are available that include minerals and algae from the dead sea.

One of the characteristics of Dunaliella is the thin elastic plasma membrane that encloses the cell. This is easily disrupted for recovery of the carotenoids (Pisal and Lele 2005). The ability to accumulate carotenoids to about 12 % of dry weight is another important characteristic. Since Dunaliella has been used as a food for many years, it is recognized as safe for consumption (Venugopal 2009). This is important for industrial exploitation of the products from Dunaliella.

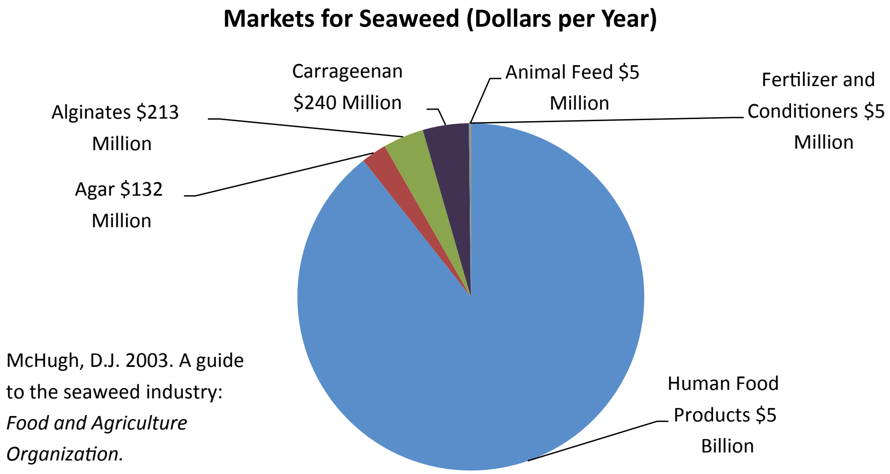

Fig. 11.3 Global value of seaweed products per year

β-carotene is a precursor of vitamin A which prevents some eye disorders and some cancers. Results of experiments show a positive effect of extracts from Dunaliella with antioxidant properties on health of diabetics, though more study may be needed (Ruperez et al. 2009).

4 Important Macroalgae and their Products

Seaweeds are marine macroalgae that produce edible products, industrial hydrocolloids, and nutraceuticals. There are Chlorophyceae (green), Rhodophyceae (red), and Phaeophyceae (brown) seaweeds. The market for seaweed products is worth billions of dollars per year, and the scale of the different markets for seaweed products is shown in Fig. 11.3, using data from McHugh (2003).

The hydrocolloids agar, alginates, and carrageenans have major applications in processed food products such as yogurt, soymilk, and deli meats, to name just a few. Agar has applications as thermally reversible gel in pastry fillings and in bacteriological laboratories. Alginates are used in restructured meats and in pharmaceutical products. Carrageenan has applications as a toothpaste binder, in dairy foods, and water gels (Bixler and Porse 2011). Seaweed hydrocolloid sales exceeded 80,000 metric tons in 2009, with prices in the range from $10–$20 per kg (Bixler and Porse 2011).

Gracilaria and Gelidium are the principal seaweeds for the commercial production of agar. Gracilaria is commercially cultivated in Chile, Indonesia, Thailand, and several other countries. Gelidium is harvested from natural sources in Spain, Portugal, Morocco, Japan, and Mexico (Bixler and Porse 2011). Gracilaria and Gelidium are red macroalgae or Rhodophyceae. Gracilaria has significant amounts of polyunsaturated fatty acids, which have nutraceutical benefits (Yuan 2008).

Table 11.3 Amino acid composition in protein from Palmaria palmate and Porphyra tenera (Percent of total). (Source: Yuan 2008)

Amino Acid	Palmaria	Porphyra
Histidine	0.5	1.52
Isoleucine	3.7	4.34
Leucine	7.1	9.44
Lysine	3.3	4.88
Methionine	2.7	1.19
Phenylalanine	5.1	4.23
Threonine	3.6	4.34
Tryptophan	3.4	2.60
Valine	6.9	6.94
Aspartic acid	18.5	7.59
Glutamic acid	9.9	7.81
Hydroxy Proline	2.3	0.0
Proline	1.8	6.94
Serine	6.3	3.14
Glycine	13.3	7.81
Alanine	6.7	8.03
Arginine	5.1	17.79

Alginates are produced by Laminaria japonica and Lessonia nigrescens, brown macroalgae, or Phaeophyceae.

Carrageenan is produced by red macroalgae, or Rhodophyceae, including Gigartina, Sarcothalia, Kappaphycus alvarezii, and Eucheuma denticulatum. Recently farmed Kappaphycus and farmed Eucheuma have been important sources of carageenans (Bixler and Porse 2011).

The interest in seaweeds as sources of nutraceuticals and functional foods was enhanced by epidemiological data that showed that people who consumed seaweeds regularly had greatly reduced mortality rates for coronary heart disease and reduced cholesterol levels (Yuan 2008). Epidemiological studies also showed reduced incidences of breast and prostate cancers among populations that consumed seaweeds regularly (Yuan 2008). Research with animal populations has provided supporting data that show that seaweeds have health benefits. (Yuan 2008).

The seaweeds Palmaria and Porphyra have a long history of being consumed in Japan and other Asian countries, as well as in some European countries and North America. The amino acid composition for these Rhodophyceae is shown in Table 11.3. The amount of protein and the amino acid profile both vary with the growth environment, including the nitrogen concentration, the geographical location, and time of year (Yuan 2008).

Fitzgerald et al. (2011) have reviewed the literature on proteins and peptides from macroalgae and their applications as nutraceuticals and medicinal products. Several bioactive peptides have been isolated from macroalgae, and their functional properties have been reported. Lectins have been isolated from Rhodophyta and used for clinical blood typing. Lectins have been used as analgesics, anti-inflammatory products, antibacterial agents, and in anticancer therapies (Fitzgerald et al.

Table 11.4 Total carotenoid, fucoxanthin, and fucoxanthinol content (mg/g) in selected Phaeophyceae, brown seaweeds. (Source: Miyashita and Hosokawa (2008). Values are mg/g dry weight.)

Species	Total Carotenoid	Fucoxanthin	Fucoxanthinol
Ecklonia radiate	6.85	1.65	0.24
Carphophyllum maschalocarpum	6.21	1.17	–
C. plumosum	5.68	1.44	0.41
Cystophora retroflexa	4.71	0.46	0.62
Sargassum sinclairii	9.79	0.54	–

2011). Phycobiliproteins have been used as a label on antibodies and other biological molecules. They also have value because of their antioxidant, anti-diabetic, and anticancer properties (Fitzgerald et al. 2011). The investigation of the properties of these proteins provides greater understanding of the benefits associated with a diet in which these proteins are present in algal foods such as seaweed. Fitzgerald et al. (2011) review algal food products with bioactive peptides, including beverages and bakery products.

Seaweeds have significant amounts of dietary fiber, and this is beneficial because of reductions in plasma cholesterol and glucose concentrations (Yuan 2008). The water holding capacity of algal polysaccharides is also beneficial.

The mineral content of seaweeds varies with the growth environment and the season of the year. Seaweeds are considered to be a good source of minerals such as iodine, iron, calcium, and magnesium. There is also the potential for bioaccumulation of lead, cadmium, mercury, and arsenic in seaweed. Thus, the growth environment, especially water quality, is important.

There are important carotenoids in seaweeds. Flucoxanthin is the characteristic pigment of Phaeophyceae. Brown macroalgae produce significant amounts of flucoxanthin and flucoxanthinol (Miyashita and Hosokawa 2008). The concentration varies with the season and the life cycle of these algae. Some representative data is shown in Table 11.4. Flucoxanthin is of interest because of its ability to inhibit the proliferation of cancer cells and its beneficial value as an antiobesity compound (Miyashita and Hosokakawa 2008). Since the brown kelps are grown for their hydrocolloid content, the fucoxanthin has the potential to be recovered as a valuable byproduct.

Pressurized liquid extraction has been used with ethanol to extract fucoxanthin from Eisenia bicyclis, a common edible brown macroalgae (Shang et al. 2011). The optimal conditions of 90% ethanol in water at 110°C, and 2500 psi, were reported for extraction effectiveness. Mise et al. (2011) investigated extraction and drying to obtain a fucoxanthin-rich product of high purity. They reported that the instability of fucoxanthin because of oxidation and heat was a consideration in developing effective commercial products. The effectiveness of the products was evaluated using a DPPH (2,2-diphenyl-1-picrylhydrazyl) assay to evaluate the radical scavenging activity of each product. Comparison of drying methods showed that freeze-dried powder was best when evaluated using the DPPH assay (Mise et al. 2011).

The dietary fiber in seaweeds has antiobesity value in the diets of obese individuals (Venugopal 2009). The seaweed polysaccharides have a higher water holding

Fig. 11.4 Fucus vesiculosus; courtesy of Irish Seaweed Research Group. Copyright Michael D. Guiry, Algaebase

capacity than cellulosic fibers. They can be added to foods that are low in fiber to improve functional properties, such as viscosity, texture, and water binding (Venugopal 2009).

Because of their antibacterial and antiviral activities, the carrageenans are used as effective preservatives in processed foods. Venugopal (2009) has reviewed research on the effectiveness of several algal compounds for control of human pathogens. Alginate dietary fibers stimulate the immune system. Alginates and carrageenans can be used in place of lipids in formulated products to reduce caloric intake in the diet (Venugopal 2009).

4.1 Fucus Vesiculosus

Figure 11.4 is a photograph of the seaweed *Fucus vesiculosus*, which belongs to the group Phaeophyceae, or brown algae, and is more commonly known as bladderwrack. It is high in iodine, and it contains fucoidans and antioxidants. It is used in cosmetics because of anti-aging properties (Fujimura et al. 2002). Dietary fibers from this seaweed, including sulfated polysaccharides, fucans, and alginic acid derivatives, have value for their anticoagulant, anti-inflammatory, antiviral, and antitumoral properties (Ruperez et al. 2002). Polyphenols appear to be important contributors to the antioxidant capacity of powders of Fucus and commercial fucoidans (Diaz-Rubio et al. 2009). Autohydrolysis is a method used to extract fucoidan from the Fucus (Rodriquez-Jasso et al. 2013). The antioxidant activities of brown algae have many applications in the food and cosmetic industries (Tutour et al. 1998).

4.2 Chondrus Crispus

Figure 11.5 is a photo of the red alga *Chondrus crispus*, also known as Irish Moss. This Rhodophycea has a long history as a source of carrageenan. Carageenan from

Fig. 11.5 Chondrus crispus; courtesy of Irish Seaweed Research Group. Copyright Michael D. Guiry, Algaebase

Irish Moss is a mixture of kappa carrageenan, which forms strong opaque gels with potassium salts, and lambda carrageenan, which creates viscosity suitable for suspensions (Fitton et al. 2008).

Chondrus crispus produces compounds for protection from solar radiation. Mycosporine amino acids are UV-absorbing compounds from Irish Moss that can be incorporated into sunscreens (Burja and Radianingtyas 2008). Irish Moss is used on skin and in foods. It is used in ice creams and yogurt as a stabilizer, and in tooth pastes as a binding agent.

5 Commercial Production of Algae

5.1 Farming of Seaweed

The commercial production of seaweeds occurs in sea coasts of Korea, Japan, China, the Philippines, Taiwan, Indonesia, Russia, Italy, France, the United States, and Chile (Venugopal 2009). More than 200 species are utilized for useful products. One vegetative propagation method starts with small quantities of the species attached to bamboo poles fixed to the subsurface ground. The macroalgae grow for 60–75 days, with a harvestable yield of 2–8 dry tons per hectare. Specific growth rates are of the order of 0.38/day under early growth conditions (Venugopal 2009). Attached seaweeds generally have higher yields than floating species.

About 60–70 % of the 16 million tons of seaweed produced per year was used for human consumption in 2005 (Venugopal 2009). The hydrocolloids produced from seaweeds account for about 10–15 % of the market. The largest fraction of the production is brown seaweeds. The quantity of seaweed from farmed areas exceeds that harvested from natural production.

Fig. 11.6 Raceway ponds for growing Spirulina; courtesy of Robert Henrikson; from Earth Food Spirulina. (Henrikson 2009)

5.2 Production of Microalgae

The commercial production of microalgae has been accomplished in several different environments and bioreactor systems. The commercial production of Spirulina has been continuing since 1982 at Earth Rise Farms in California (Henrikson 2009). Ponds with liners, like those shown in Fig. 11.6, are used to grow Spirulina at a high pH, with carbon dioxide bubbled into the water to supply carbon that is needed for growth. In order to avoid contamination, nitrogen, potassium, and other needed nutrients are supplied from sterilized sources. Hu (2004) points out that when Spirulina are cultured at pH 9.5 to 9.8, this enables Spirulina to have a competitive growth advantage that leads to good quality products. Paddle wheels are used to provide mixing and water flow in raceway ponds (Hu 2004; Henrikson 2009).

Spirulina grow optimally at 35–38°C; however, temperature is not controlled in the open ponds. Commercial operations have been set up in the sunny California desert, in Hawaii, and in other locations where sun and temperature are appropriate for good production. At Earth Rise Farms, Colorado River water is used as the source of fresh water.

Filtration is used to separate the Spirulina from the water. Spray drying is one of the more common forms of drying, as it is a quick process and preserves heat sensitive nutrients (Hu 2004; Henrikson 2009).

Dunaliella commercial production with beta-carotene as the product of interest occurs in environments with excellent solar radiation, in brine water with high levels of magnesium (Ben-Amotz 2004). Most production occurs in open ponds or raceways near a good source of sea water. By operating at high brine concentrations, contamination problems are reduced. The use of evaporated concentrated sea water or augmentation by adding salt to achieve the desired salinity has been reported, as has the reuse of the production brine water after harvest (Ben-Amotz 2004). With raceways, productivity can reach 200 mg of beta carotene per square meter per day (Ben-Amotz 2004). Seawater with 1.5 M NaCl, more than 0.4 M $MgSO_4$, and 0.1 M $CaCl_2$ and pH control have been recommended for good growth of Dunaliella. High pH and nitrogen deficiency are both used to enhance beta-carotene production.

Harvesting and separation of the beta-carotene is not well described in the literature for established commercial processes. It is known that extraction has been used to separate the beta-carotene from the other substances which are present (Ben-Amotz 2004). In some cases, the product may contain other carotenoids, including lutein, neoxanthin, zeaxanthin, violaxanthin, and cryptoxanthin (Ben-Amotz 2004).

Chlorella have been produced commercially using mixotrophic production with acetic acid as a source of carbon for growth and product formation. Bacterial contamination is one of the challenges faced by Chlorella producers. With light and carbon sources such as acetic acid, the biomass production is 1.5–2 times higher than for photoautotrophic growth (Iwamoto 2004). The yield of biomass for mixotrophic growth has been analyzed by Lee et al. (1985) and Lee and Erickson (1987). Energetic yields are often higher for mixotrophic growth compared to photoautotrophic growth. Most of the Chlorella production is by mixotrophic mass cultivation (Iwamoto 2004).

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