Chapter 13
Red Seaweeds: Their Use in Formulation of Nutraceutical Food Products

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Abbreviations

FAO	Food and Agriculture Organization
PC	Protein concentrate
PUFAs	Polyunsaturated fatty acids

1 Introduction

Seaweeds are currently seen as promising species for providing new biologically active compounds to produce novel foods due to the large variety of compounds they contain, thus contributing to the development of nutraceutical food products (Kim 2011; Villanueva et al. 2014; Shama et al. 2019). Previous studies have shown that several seaweed-based compounds can improve human health by reducing symptoms of several diseases like cancer, asthma, diabetes, autoimmune, ocular, or cardiovascular (Lopes et al. 2013; Alves et al. 2018; Tanna and Mishra 2018). Seaweeds have been seen as a feedstock for bioactive molecules that can be incorporated in the daily diet as a supplement to promote human health, thus being considered nutraceutical food products (Alwaleed 2019; Shama et al. 2019).

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A. Ranga Rao, G. A. Ravishankar (eds.), *Sustainable Global Resources of Seaweeds Volume 2*, https://doi.org/10.1007/978-3-030-92174-3_13

Among the algal phyla or classes, Chlorophyta (green), Phaeophyceae (brown) and Rhodophyta (red), the red seaweeds group contains great biodiversity (Torres et al. 2019). Red seaweeds contain pigments (i.e., phycoerythrin) that can be employed in food industry, as a natural substitute of synthetic food colorants, with antioxidant bioactivity (Ganesan and Shanmugam 2020). Besides that, these seaweeds present a rich nutritional profile, providing several important molecules, such as fatty acids, vitamins, essential amino acids, and minerals, through their direct incorporation in the daily diet. For instance, red seaweeds can contain up to 26 mg kg^{-1} of Vitamin E (Irene et al. 2018); and among the three phyla, Rhodophyta algal species exhibits the highest protein content (Černá 2011). Moreover, red seaweeds present several essential amino acids, exhibiting almost the same amount of plant-based protein sources (Barbier et al. 2019). For example, the species *Pyropia*/*Porphyra* has a score of 0.91 (on a scale between 0 and 1, whereas egg protein has a score of 1) (Murata and Nakazoe 2001). Furthermore, seaweeds lipidic profile, composed essentially by polyunsaturated fatty acids (ω-6 and ω-3), makes them an important source of these compounds, which humans acquire only through the daily diet (Belattmania et al. 2018).

However, their nutritional profile varies according to the harvest season, geolocation, and other biotic (i.e., temperature, salinity, light intensity, nutrients availability, and pollutants concentration) and abiotic parameters (i.e., predators). So, it is a current challenge to guarantee the safety and quality of seaweeds traded (Tanna and Mishra 2019; Cho and Rhee 2020; Rosa et al. 2020). For this reason, aquaculture techniques and technologies have evolved to tackle this need (Campbell et al. 2020). Currently, the most industrially exploited red seaweeds species are *Gracilaria* spp., *Kappaphycus alvarezii, Porphyra/Pyropia* spp. and *Eucheuma denticulatum*, being cultivated in several coastal countries.

Red seaweeds are pivotal for phycocolloids industry, for agar and carrageenan extraction, being widely employed in the food industry as thickener or emulsifier agent (Kraan 2012; Garcia-Vaquero et al. 2017). Furthermore, their physical capacity to emulsify and preserve water improves their technological functionality as food ingredients (Ruocco et al. 2016). The direct addition of seaweeds or their polysaccharides to meat and plant-based food products will improve nutritional, structural, antimicrobial, organoleptic, and shelf-life characteristics of these food products (Shannon and Abu-Ghannam 2019). Moreover, these phycocolloids can help to reduce glucose levels (BNF 2016). Besides the mentioned sulfated polysaccharides, porphyran can also be founded in some red seaweeds species, such *as Porphyra*/*Pyropia* sp., promoting health benefits, such as the reduction of cholesterol levels (Tsuge et al. 2004).

These polysaccharides, such as agar and carrageenan present several biological activities as it was forementioned, however their bioactivity varies according to their molecular weight, sulphation level and the quantity of sulphate esters groups present in the molecule (Tsuge et al. 2004; Cunha and Grenha 2016). Moreover, different seaweed species produce chemically distinct polysaccharides, and this can also be affected by the extraction method selected. Commonly, carrageenophytes contains a higher concentration of sulphate groups, in comparison to the agarophytes (Zhong et al. 2020). Still, carrageenan chemical structure is very heterogeneous, being the most economically important the carrageenan iota, lambda and kappa (Necas and Bartosikova 2013). So, what distinguish these different types of carrageenan is mainly their sulphate esters content and their position in the molecule (Sangha et al. 2015).

The goal of this book chapter is to highlight the role of red seaweeds for food industry as a key element for the development of innovative products with nutraceutical properties for the food industry as human health promoters.

2 Red Seaweed Nutritional Characteristics

The red seaweeds nutritional values are very dispersed due to a high number of species, and due to the variation of abiotic factors (salinity, nutrients, pH, luminosity, water temperature, profundity). However, these seaweeds can have an internal ratio of the nutrient composition (Table 13.1). Several eastern countries traditionally consume seaweeds as food (mainly Japan, China and Korea) (Dawes 1995), due to its high nutritional value as a source of proteins, carbohydrates, vitamins and minerals (Pereira 2011; Leandro et al. 2020a). Moreover, the seaweeds have interesting secondary metabolites with nutraceutical properties (Table 13.2).

These bioactivities are observed in the most cultivated species of red seaweeds, according to Food and Agriculture Organization (FAO) data (FAO 2020): *Gracilaria* spp., *Kappaphycus alvarezii*, *Porphyra* spp./*Porphyra tenera* and *Eucheuma denticulatum*. Moreover, in 2018 32.4 million tons of seaweeds were produced. In 2016, the volume of aquatic plants collected or produced was 31.2 million tons, where practically all this production was related to seaweeds, with growth from 13.5 million tons in 1995 to over 30 million tons in 2016 (FAO 2018). Also, according to FAO (Ferdouse et al. 2018), some red seaweed species, such as *Porphyra*/*Pyropia* spp. (Rhodophyta) were produced in the East and Southeast Asia, are produced almost exclusively for direct human food consumption. Indonesia increased seaweed production from less than four million tons in 2010 to more than 11 million tons in 2015 and 2016, mainly in red seaweed species (FAO 2018). This exponential growth in the production of tropical red seaweeds species, such as *Kappaphycus alvarezii* and *Eucheuma* spp. was due to their commercial

Table 13.1 Red seaweed nutritional values (Pereira 2011)

Nutrient	Concentration range (% of dry weight)
Protein	6.9–47
Lipid	0.3–3.3
Carbohydrates	43–68
Dietary fiber	10–46
Ash	7.8–37

Table 13.2 Secondary metabolites with nutraceutical properties, based in (Sonani 2016; Cotas et al. 2020a, b; Leandro et al. 2020a, b)

Compound	Bioactivity
Vitamins A, B_{12}, C, E, K	Immunological and human development
Carotenoids	Antioxidative, anti-inflammatory, antitumor
Allophycocyanin	Antioxidative, anti-inflammatory, antitumor, anti-enterovirus, hepatoprotective
Phycocyanin	Antitumor, anti-inflammatory, anti-oxidative, anti-irradiative
Phycoerythrin	Antioxidant, antitumor, neuroprotective, anti-inflammatory, hepatoprotective, hypocholesterolemic
Mycosporine-like amino acid	Anti-inflammatory, immunomodulatory
Phenolic terpenoids	Antioxidant, anti-inflammatory
Flavonoids	Antioxidant
Bromophenols	Antioxidant, antitumor, anti-angiogenesis, anti-diabetic, anti-obesity, antimicrobial, anti-fungal, anti-viral, neuroprotective

exploitation for carrageenan extraction and direct food consumption, which has been the main contributor to the growth in seaweed cultivation in recent years. The high economic interest is also justified by the growing demand for phycocolloids for different uses in the pharmaceutical, food, and cosmetics industries (Smit 2004; Leandro et al. 2020b; Morais et al. 2021), which has led several countries to cultivate seaweed (García-Poza et al. 2020).

2.1 Gracilaria *sp. Nutritional Profile*

Gracilaria sp. is a red seaweed that produces agar as main structural polysaccharide, and their content have interesting values for direct food consumption, due to high content in protein (10.86%) and carbohydrates (63.13%) (Rasyid et al. 2019).

The study of Kazir et al. (2019) aimed to study *Gracilaria* sp. protein content for the development of food products, obtaining interesting protein levels (25% dry weight (DW)). The authors also obtained, in the highest concentrations, the amino acids: glutamic acid (13.01%), aspartic acid (12.81%), arginine (10.32%) and alanine (10.03%). In order to develop a seaweed protein-based product, the authors employed the ion exchange technique, enabling a high protein yield (70%) and a reduced co-extraction of carbohydrates (1%) in the seaweed protein extract. Showing a potential of *Gracilaria* sp. as protein food alternative source as a raw or processed ingredient.

This potential is also demonstrated in lipidic profile (Table 13.3), where the content of lipids and polyunsaturated fatty acids (PUFAs) in several *Gracilaria* species exhibited a high content of PUFAs, mainly *G. corticata* and *G. dura* (Kumari et al. 2013).

Table 13.3 Lipidic profile in *Gracilaria* sp. (Kumari et al. 2013)

Species	Lipids (%)	PUFAs (%)
Gracilaria dura	6.3 ± 0.3	62.8 ± 1.2
Gracilaria salicornia	7.6 ± 0.5	11.5 ± 0.8
Gracilaria textorii	7.3 ± 1.2	28.6 ± 2.9
Gracilaria corticata	8 ± 2.0	65.6 ± 2.5
Gracilaria corticata var. *cylindrica*	5.2 ± 1.1	29.8 ± 2.8
Gracilaria debilis	2.9 ± 0.2	48.4 ± 3.4

Khan et al. (2019) studied the polysaccharides of *Gracilaria chouae* and found the presence of a heteropolysaccharide (agar). Agar contained a sulphate content of 7.9%, in addition to 52.63% total sugar (mainly galactose) and 9.62% galacturonic acid. Galactose and 3,6-anhydrogalactose were found in a molar ratio of 1.0: 0.6. On further analysis, this polysaccharide exhibited jellification and melting points at 41.3 and 71.7 °C, respectively, which makes it a suitable candidate for industrial processing where further heating is required and/or where the end product needs to have an extended shelf life in hot climate.

2.2 **K. alvarezii** ***Nutritional Profile***

K. alvarezii is a red seaweed that produces kappa-carrageenan as a main polysaccharide, and its nutritional profile has interesting values of minerals (58%) and carbohydrates (38%) and lower content in lipids and proteins (Wanyonyi et al. 2017), which is similar to other *Kappaphycus* species (Adharini et al. 2019). Moreover, these seaweeds can have an interesting prebiotic effect as a food supplement (Wanyonyi et al. 2017).

Kumar et al. (2014) analyzed the protein content of *K. alvarezii*, grown on the west coast of India, and found that this species contained 62.3 ± 1.62%. To further exploit this high yield in the food industry, this protein content can be transformed into a concentrate (PC), by the increase of the pH up to 12 and adding a solution of NaCl (0.5 M in the final solution). The emulsifier and foaming properties of this PC varied with time and pH. Thus, the results obtained in this study suggest the possibility of this seaweed and their based PC as an inexpensive source of protein; thus, this PC could be incorporated into several value-added food products.

2.3 **Euchema** ***sp. Nutritional Profile***

Eucheuma sp. is a red seaweed that produces iota-carrageenan as main polysaccharide, which is mainly exploited from these species (Naseri et al. 2020). From an industrial perspective, the seaweed powder can be added into the food products to preserve and add nutritional value (Huang and Yang 2019). However, there is a lack of nutritional studies in this genus.

The red macroalgae *Eucheuma denticulatum*, also known by the common name "Spinosum", develops naturally in coral reefs with moderately strong currents in tropical and subtropical regions. This species has a high commercial value, as it contains iota-carrageenan, a compound widely used in the nutraceutical and manufacturing industries. Due to the high demand, the cultivation of *Eucheuma denticulatum* has significantly expanded (Othman et al. 2019).

Balasubramaniam et al. (2020) studied *E. denticulatum* carotenoids (mg/100 g of DW extract) and detected in various samples maximum content of each of the pigments viz. lutein 87.7, zeaxanthin 21.3, coxanthin 4.0, β-cryptoxanthin 3.6, canthaxanthin <0.001, astaxanthin 3.0, and β-carotene 4.7. These results indicate that *E. denticulatum* has an excellent carotenoid profile (as vitamin A) composition and hence rich in antioxidant potential.

De Corato et al. (2017) evaluated *E. denticulatum* composition in terms of concentration of fatty acids, polysaccharides and phenolic compounds. *E. denticulatum* presented in its composition 20.5 ± 0.5% of lipids, water-soluble polysaccharides 16 ± 0.6% and phenolic compounds 0.2 ± 0.001%, demonstrating that the species presents a good percentage of fatty acids and polysaccharides, with potential in several applications as direct food source and as ingredient for food industry.

2.4 Porphyra/Pyropia/Neopyropia/Neoporphyra *Nutritional Profile*

The genus *Porphyra* is evolving and modified/divided into four different genera due to the genetic analysis (Yang et al. 2020; Kavale et al. 2021).

Porphyra/*Pyropia*/*Neopyropia*/*Neoporphyra* sp. is a red seaweed that produces porphyran, as main polysaccharide, and actually is the seaweed most consumed in the world, due to their presence in the Japanese cuisine as "nori" (Levine and Sahoo 2010; Bito et al. 2017) Nori can ameliorate the deficiency of iron and vitamin B_{12} in vegan diet. Thus, *Porphyra*/*Pyropia*/*Neopyropia*/*Neoporphyra* sp. are one of the most economically important species, as it has functional bioactivities such as porphyrans, dietary fibers, PUFAs, minerals, phycoerythrin, mycosporine-like Amino Acids and vitamins (Bito et al. 2017). Porphyran and oligo-porphyran have a range of biological functions, such as antioxidant, anticancer, anti-aging, anti-allergic, immunomodulatory, hypoglycemic and hypolipemic effects. Consequently, these species' demonstrate several potential applications in the food, medicinal and cosmetic fields (Qiu et al. 2021). The most consumed and cultivated seaweeds are *Porphyra tenera*, *Neopyropia tenera*, *Neopyropia yezoensis*, *Neoporphyra dentata* and *Neoporphyra haitanensis* (Levine and Sahoo 2010; Niu et al. 2010). In fact, for these genera cultivation was of the value US Dollar 0.9 billion (Kim et al. 2017) mainly for direct food consumption.

Table 13.4 Macro and trace elements in *Porphyra* commercial samples from different European and Asian countries based in Larrea-Marín et al. (2010)

Element (mg g^{-1} DM)	France	Spain	Korea	Japan
Ca	7.06 ± 0.30a	6.04 ± 0.47^{b}	7.26 ± 0.11^{a}	2.90 ± 0.22^{c}
Mg	7.94 ± 0.11b	7.10 ± 0.16^{b}	3.73 ± 0.08^{d}	4.24 ± 0.20^{c}
P	1.49 ± 0.07c	5.60 ± 0.43^{b}	8.59 ± 0.15^{a}	8.47 ± 0.38^{a}
Na	43.7 ± 0.57a	41.4 ± 5.41^{a}	6.54 ± 0.16^{b}	2.34 ± 0.38^{c}
K	23.6 ± 0.60b	23.1 ± 0.67^{b}	29.8 ± 0.10^{a}	29.8 ± 1.91^{a}
Sr	0.12 ± 0.02b	0.13 ± 0.02^{b}	0.22 ± 0.02^{a}	0.06 ± 0.01^{c}
Al	21.5 ± 0.37c	15.0 ± 2.55^{c}	220.8 ± 7.95^{a}	94.0 ± 5.43^{b}
Ba	0.53 ± 0.05c	0.85 ± 0.05^{c}	3.97 ± 0.16^{a}	2.5 ± 0.29^{b}
Cu	9.98 ± 0.59c	20.2 ± 2.40^{b}	19.7 ± 0.91^{b}	37.0 ± 5.00^{a}
Fe	149.2 ± 9.83d	201.2 ± 6.30^{b}	285.9 ± 12.20^{a}	165.8 ± 3.90^{c}
Mn	23.0 ± 0.50b	32.5 ± 2.60^{a}	34.3 ± 2.41^{a}	32.0 ± 3.54^{a}
Zn	82.4 ± 2.88b	52.5 ± 1.80^{c}	85.4 ± 3.65^{b}	94.2 ± 5.31^{a}

[*] Values in the same row bearing different superscript letters are significantly different ($p < 0.05$)

Kim et al. (2018), studied *Neopyropia tenera*, determining the composition of carbohydrates, lipids, and proteins of *N. tenera* procured from a local market. The composition ratio (% DW) of carbohydrates, lipids, and proteins in *N. tenera* was 41.4%, 1.7% and 39.6%, respectively were determined. The study showed similar levels of carbohydrates and proteins, but with a low lipid content.

Holdt and Kraan (2011) and Rioux and Turgeon (2015), evaluated several seaweed species of the genus *Porphyra*/*Pyropia*/*Neopyropia*/*Neoporphyra*, and studied their bioactive compounds with economic importance. Among the determined compounds, the total polysaccharides had higher concentrations, with 40 and 76%, while the lipid content was 0.12 and 2.8% and protein of 7 and 50%. The results demonstrate that the *Porphyra*/*Pyropia*/*Neopyropia*/*Neoporphyra* genus, due to its higher concentration of polysaccharides, namely the hybrid porphyran/carrageenan/agar, are essential compounds in the food industry, as they are characterized by their solubility, gelation, viscosity, stability, reactivity with proteins and thixotropy properties (Hongfeng et al. 1993; Sasuga et al. 2017; Wahlström et al. 2018).

Larrea-Marín et al. (2010), evaluated the macro and trace elements in commercially grown *Porphyra* from four different countries (Table 13.4). The 12 elements determined were Al, Ba, Ca, Cu, Fe, K, Mg, Mn, Na, P, Sr and Zn, in the seaweed used as human food. However, differential compositions were due to the origin of the seaweeds, and impact of seawater mineral composition.

Although, these four genera are being cultivated and consumed, there is a lack of nutritional values of these seaweeds, which are understandable, due to the variation and influence of extrinsic factor that make seaweed composition fluctuate (García-Poza et al. 2020; Leandro et al. 2020b). However, the principal traits are normally identical as demonstrated above. Still, *Porphyra*/*Pyropia*/*Neopyropia*/*Neoporphyra* are the most exploited seaweeds for food and not for polysaccharide extraction, mainly due to the presence of a hybrid polysaccharide.

3 Red Seaweeds Consumption and Commercial Based Products

Seaweeds and their components already hold a market positioning worldwide (Ścieszka and Klewicka 2019; Rahikainen and Yang 2020). Still, several seaweeds remain as undiscovered resources, showing a very promising potential for the food industry, with nutraceutical properties (Pereira et al. 2020; John et al. 2020).

For instance, the red seaweeds dulse (*Palmaria palmata*) and nori (*Porphyra/Pyropia/Neopyropia/Neoporphyra*) are the major commercial products in the nutraceutical industry, as a food ingredient. These can be marketed fresh or dried, in a form of sheet, powder or capsule (Griffiths et al. 2016). The incorporation of milled seaweeds, such as *Porphyra umbilicalis* in meat products can indeed enrich these products in phenolic compounds and other nutrients likewise manganese, calcium and magnesium, which are pivotal for the homeostasis of the human organism (López-López et al. 2009). Besides, the bioactive and nutritional components of this seaweed species are associated with several health benefits, such as anticancer, cardiovascular disease prevention, antioxidant and anti-inflammatory (Cho and Rhee 2020). Moreover, the enrichment of cereal-based products (i.e., bread or pasta) with dried and milled seaweeds, such as *Kappaphycus alvarezii* was found to improve the nutritional profile of commercial noodles (Kumoro et al. 2016). However, heavy metals, toxic isotopes, dioxins, or pesticides are all risks associated with the whole seaweed intake. To address these drawbacks, thorough testing of seaweed for food application is needed prior to its use (Garcia-Vaquero and Hayes 2016).

In counterpart, industrial phycocolloids are under strict regulation, and several analyses are required for their incorporation as food additives in commercially available products (Mortensen et al. 2016; Younes et al. 2018). Thus, red seaweeds phycocolloids are already exploited and employed in several commercial products in food and nutraceutical industries. For instance, WavePure is a product based on *Gracilaria* sp., whereas the phycocolloid (agar) is extracted in order to be commercialized for food proposes as a gelling and thickening agent for desserts confection (Cargill 2021a). While carrageenan is a key element of the products Satiagel™, Satiagum™, Aubygel™ and Seabrid™, which can be used in a wide range of food products, such as dairy, fruit meat, ice-creams, powder products, pharmaceuticals and nutraceuticals (Cargill 2021b). Moreover, the vegetable jelly sold by Condi (based on carrageenan), shown to be also a nutraceutical promoter, due to its anticholesterolemic properties (Valado et al. 2020).

4 Conclusions and Future Perspectives

As novel foods and nutraceutical products demand for red seaweeds has risen. From the seaweeds belonging to the phylum Rhodophyta, only a few of them are industrially exploited. Thus, red seaweeds constitute a pool of unexplored biodiversity in several areas; for food and nutraceutical implying that a wide range of innovative products can be developed with these seaweeds.

Acknowledgments This work is financed by national funds through FCT—Foundation for Science and Technology, I.P., within the scope of the projects UIDB/04292/2020 granted to MARE—Marine and Environmental Sciences Centre and UIDP/50017/2020 + UIDB/50017/2020 (by FCT/MTCES) granted to CESAM—Centre for Environmental and Marine Studies. João Cotas thanks to the European Regional Development Fund through the Interreg Atlantic Area Program, under the project NASPA (EAPA_451/2016). Diana Pacheco thanks to PTDC/BIA-CBI/31144/2017-POCI-01 project-0145-FEDER-031144-MARINE INVADERS, co-financed by the ERDF through POCI (Operational Program Competitiveness and Internationalization) and by the Foundation for Science and Technology (FCT, IP). Ana M.M. Gonçalves acknowledges University of Coimbra for the contract IT057-18-7253, and also thanks to the project MENU—Marine Macroalgae: Alternative recipes for a daily nutritional diet (FA_05_2017_011), funded by the Blue Fund under Public Notice No. 5—Blue Biotechnology, which partially financed this research.

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