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Chapter 2

A REVIEW OF THE NUTRIENT COMPOSITION OF SELECTED EDIBLE SEAWEEDS

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ABSTRACT

Currently, our society lives under a misleading apprehension of there being food abundance.....etc, etc..... Many people of the west are surrounded by fast food rich in calories and unsaturated fats, high powered advertising and over-consumption. The mass market has actually become accustomed to the expression of "junk food" to designate such offerings, but yet this highly processed "food" is consumed in large amounts. The consequences of consumption of these offerings for the mass (western) the lack of essential nutrients, obesity and diseases related to excessive intake of sugars (diabetes) and fat (arteriosclerosis), among others. It is worrying that the fast food trends of the west are being adopted seemingly without concern in developing countries as they become more prosperous, hence rates of associated disease are increasing.

What roles have the seaweeds in this picture?

Represent exactly the opposite: a natural food that gives us a highly nutritious but low in calories. Algae are therefore the best way to address the nutritional deficiencies of the current food, due to its wide range of constituents: minerals (iron and calcium), protein (with all essential amino acids), vitamins and fiber [1,2].

Contrary to what happens in East Asia, the West is more involved with use of seaweed as a source in thickeners and gelling properties of hydrocolloids extracted from seaweeds: carrageenan, agar and alginate (E407, E406 and E400, respectively), which are widely used in food industry, especially in desserts, ice cream, the fresh vegetable gelatin. Perhaps in most cases, the consuming public are blissfully unaware they are consuming seaweed derived products.

However attitudes are quite different in Asian cultures where seaweeds are highly valued and regarded for their appearance, texture, flavour and in a number of cases, beneficial health properties.

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Some seaweeds can be rich in polysaccharides which, in the absence of appropriate enzymes, due to their long chain molecules, they are not broken down, nor absorbed by the digestive system and behave as soluble fiber, with no calories, having a positive impact on the regulation of intestinal transit.

From the composition of seaweed highlight: Presence of minerals with values about ten times higher than found in traditional vegetables, such as iron in *Himanthalia elongata* (Sea spaghetti) in comparison with that of *Lens esculenta* (lentils) or in the case of calcium present in *Undaria pinnatifida* (Wakame) and *Chondrus crispus* (Irish Moss), in comparison with milk; presence of proteins containing all essential amino acids, constituting a type of protein of high biological value, comparable in quality to the egg; presence of vitamins in significant quantities, in particular the presence of B₁₂ (*Porphyra* spp.), absent in higher plants; *Palmaria palmata* and *Himanthalia elongata* are rich in potassium and, together with the algae of the genus *Porphyra* and *Laminaria*, have a ratio of sodium/potassium ratio considered optimal for human health.

This review aims to describe some of the key nutritional characteristics of the main algae used as human food and their potential in the nutraceuticals industry.

1. INTRODUCTION

Seaweeds are used in many maritime countries as a source of food, for industrial applications and as a fertilizer. The major utilization of these plants as food is in Asia, particularly Japan, Korea and China, where seaweed cultivation has become a major industry. In most western countries, food and animal consumption is restricted and there has not been any major pressure to develop seaweed cultivation techniques. Industrial utilization is at present largely confined to extraction for phycocolloids and, to a much lesser extent, certain fine biochemical. Fermentation and pyrolysis are not been carried out on an industrial scale at present but are possible options for the 21st century.

The present uses of seaweeds are as human foods, cosmetics, fertilizers, and for the extraction of industrial gums and chemicals. They have the potential to be used as a source of long- and short-chain chemicals with medicinal and industrial uses [3].

Worldwide only about 221 species of algae: 125 Rhodophyta (Red algae), 64 Phaeophyceae (Brown algae) and 32 Chlorophyta (Green algae) are used. Of these, about 145 species are used (66%) directly in food: 79 Rhodophyta, 38 Phaeophyceae and 28 Chlorophyta. In phycocolloid industry, 101 species are used: 41 alginophytes (algae that produce alginic acid), 33 agarophytes (algae producing agar) and 27 carrageenophytes (algae producing carrageenan). Other activities will use: 24 species in traditional medicine, 25 species in agriculture, animal feed and fertilizers and about 12 species are cultivated in "marine agronomy" [4,5].

The species *Alaria esculenta* (Linnaeus) Greville, *Codium fragile* (Suhr) Hariot, *Caulerpa lentillifera* J.Agardh, *Caulerpa racemosa* (Forsskål) J.Agardh, *Dilsea carnosa* (Schmidel) Kuntze, *Eisenia bicyclis* (Kjellman) Setchell, *Fucus vesiculosus* Linnaeus, *Fucus spiralis* Linnaeus, *Gelidium* spp., *Gracilaria changii* (B.M.Xia and I.A.Abbott) I.A.Abbott, J.Zhang and B.M.Xia, *Gracilaria chilensis* C.J.Bird, McLachlan and E.C.Oliveira, *Laminaria digitata* (Hudson) J.V.Lamouroux, *Laminaria ochroleuca* Bachelot de la Pylaie, *Porphyra leucosticta* Thuret, *Porphyra tenera* Kjellman, *Porphyra umbilicalis* Kützting, *Porphyra yezoensis* Ueda, *Saccharina japonica* (Areschoug) C.E.Lane, C.Mayes, Druehl and G.W.Saunders, *Saccharina latissima* (Linnaeus) C.E.Lane, C.Mayes, Druehl and

G.W.Saunders, *Sargassum fusiformes* (Harvey) Setchell, *Ulva compressa* Linnaeus, *Ulva lactuca* Linnaeus, *Ulva pertusa* Kjellman, *Ulva rigida* C.Agardh and *Ulva rotundata* Bliding are analyzed in this chapter.

2. WORLD PRODUCTION OF SEAWEED

The world seaweed production reached in 2000 around 10 millions tons including wild and maricultured. The top 12 main producing countries are: China, France, UK, Japan, Chile, Philippines, Korea, Indonesia, Norway, USA, Canada and Ireland. The wild seaweed harvesting did not change much the last 12 years but aquaculture (including integrated mariculture) is increasing incessantly [3,6].

3. USE OF VARIOUS SEAWEEDS AS HUMAN FOOD

Seaweed as a staple item of diet has been used in Japan, Korea and China since prehistoric times. In 600 BC, *Sze Teu* wrote in China, "Some algae are a delicacy fit for the most honored guests, even for the King himself." Some 21 species are used in everyday cookery in Japan, six of them since the 8th century. Seaweed (Kaiso) accounted for more than 10% of the Japanese diet until relatively recently, and seaweed consumption reached an average of 3.5 kg per household in 1973, a 20% increase in 10 years [1,7]. Although there is little tradition of using seaweed in Western cuisine, there is now renewed interest in Western countries in the use of seaweed as sea vegetables [2,8,9].

In recent years, there has been a growing interest in so-called functional food groups, amongst which seaweeds would seem to be able to play an important role since they can provide physiological benefits, additional to nutritional as, for instance, anti-hypertensive, anti-oxidant or anti-inflammatory [10,11]. A functional food can be defined as a food that produces a beneficial effect in one or more physiological functions, increases the welfare and or decreases the risk of suffering from the onset or development of a particular disease. The functionalities are far more preventative than curative. Furthermore, new types of products, derived from food, often referred to as nutraceuticals have recently been developed and marketed extensively. These products are usually employed as food supplements, rather than whole foods and are marketed as tablets and pills and can provide important health benefits. Frequently, functional foods are obtained from traditional foods enriched with an ingredient which is able to provide or promote a beneficial action for human health. These are the so-called functional ingredients. According Madhusudan et al. [11], many biologically active compounds are present in seaweed, which can be used as therapeutic agents (see Table 4) in dietary supplements.

4. EXAMPLES OF SEAWEEDS USED AS HUMAN FOOD

4.1. Chlorophyta (Green Algae)

Dichotomous sponge tang or shui-sung (*Codium fragile*, Bryopsidophyceae) – The marine green alga *Codium fragile* is a invasive species (in particular the subspecies *tomentosoides*), widely distributed in temperate areas throughout the world and is eaten in Korea, China and Japan [1, 12, 13]. This alga is an additive of Kinchi, a traditional fermented vegetable [14]. The nutrient composition and vitamin content of this species [15,16] are shown in Table 1 and 3, respectively.

Table 1. Nutrient composition of selected edible seaweed (% dry weight)

Species	Protein	Ash	Dietary fiber	Carbohydrate	Lipid	Reference
Chlorophyta (Green seaweed)						
<i>Caulerpa lentillifera</i>	10 - 13	24 - 37	33	38 - 59	0.86 - 1.11	[18,19,20]
<i>C. racemosa</i>	17.8 - 18.4	7 -19	64.9	33 - 41	9.8	[95,96,97,98]
<i>Codium fragile</i>	8 - 11	21 - 39	5.1	39 - 67	0.5 - 1.5	[15,16]
<i>Ulva compressa</i>	21 - 32	17 - 19	29 – 45	48.2	0.3 - 4.2	[21,23,28,29]
<i>U. lactuca</i>	10 - 25	12.9	29 – 55	36 - 43	0.6 - 1.6	[21,22,24,26,56,99]
<i>U. pertusa</i>	20 - 26	-	-	47.0	-	[22,27]
<i>U. rigida</i>	18 - 19	28.6	38 – 41	43 - 56	0.9 - 2.0	[31,56,97,100]
<i>U. reticulata</i>	17 - 20	-	65.7	50 - 58	1.7 - 2.3	[100,101]
Phaeophyceae (Brown seaweed)						
<i>Alaria esculenta</i>	9 - 20	-	42.86	46 - 51	1 - 2	[26,12]
<i>Eisenia bicyclis</i>	7.5	9.72	10 – 75	60.6	0.1	[21,35,103]
<i>Fucus spiralis</i>	10.77	-	63.88	-	-	[29]
<i>F. vesiculosus</i>	3 - 14	14 - 30	45-59	46.8	1.9	[8,22,37,102,104,105]
<i>Himanthalia elongata</i>	5 - 15	27 - 36	33 – 37	44 - 61	0.5 - 1.1	[8,21, 23,62,106,107]
<i>Laminaria digitata</i>	8 - 15	38	36 – 37	48	1.0	[21,22,23,26,37]
<i>L. ochroleuca</i>	7.49	29.47	-	-	0.92	[21]
<i>Saccharina japonica</i>	7 - 8	27 - 33	10 – 41	51.9	1.0 – 1.9	[21,34,35,103]
<i>S. latissima</i>	6 - 26	34.78	30	52 - 61	0.5 - 1.1	[8,26,107]
<i>Sargassum fusiforme</i>	11.6	19.77	17 – 69	30.6	1.4	[21,34,35,103]
<i>Undaria pinnatifida</i>	12 - 23	26 - 40	16 – 51	45 - 51	1,05 - 4.5	[8,23,34,35,37,39,62, 103,108]
Rhodophyta (Red seaweed)						
<i>Chondrus crispus</i>	11 - 21	21	10 – 34	55 - 68	1.0 - 3.0	[8,21,26,37,39,51]
<i>Gracilaria changii</i>	6.9	22.7	24.7		3.3	[21]
<i>G. chilensis</i>	13.7	18.9	-	66.1	1.3	[15]
<i>Palmaria palmata</i>	8 - 35	12 - 37	29 – 46	46 - 56	0.7 - 3	[8,21,22,26,39,51]
<i>Porphyra tenera</i>	28 - 47	8 - 21	12 – 35	44.3	0.7 - 1.3	[21,22,23,35,37,103]
<i>P. umbilicalis</i>	29 - 39	12	29 – 35	43	0.3	[8,62]
<i>P.yezoensis</i>	31 - 44	7.8	30 – 59	44.4	2.1	[21,34,51,63]

Sea grapes or Green caviar (*Caulerpa* spp., Bryopsidophyceae) – There are many species of the genus *Caulerpa*, but *Caulerpa lentillifera* and *C. racemosa* are the two most popular edible ones. Both have a grape-like appearance and due to their grass-green in color, soft and succulent texture, are usually consumed in the form of fresh vegetable or salad. They are commonly found on sandy or muddy sea bottoms in shallow protected, sub-tropical areas.

Table 2. Mineral composition of some edible seaweeds (mg.100 g⁻¹ DW)

Species	Na	K	P	Ca	Mg	Fe	Zn	Mn	Cu	I	Reference
Chlorophyta (Green seaweed)											
<i>Caulerpa lentillifera</i>	8917	700 - 1142	103 0	780 - 1874	630 - 1650	9.3 - 21.4	2.6 - 3.5	7.9	0.1 - 2.2	-	[18,19,21]
<i>C. racemosa</i>	2574	318	29.7 1	1852	384 - 1610	30 - 81	1 - 7	4.91	0.6 - 0.8	-	[97,100]
<i>Ulva lactuca</i>	-	-	140	840	-	66	-	-	-	-	[25]
<i>U. rigida</i>	1595	1561	210	524	2094	283	0.6	1.6	0.5	-	[31]
Phaeophyceae (Brown seaweed)											
<i>Fucus vesiculosus</i>	2450 - 5469	2500 - 4322	315	725 - 938	670 - 994	4 - 11	3.71	5.50	<0.5	14.5	[8,37]
<i>Himanthalia elongata</i>	4100	8250	240	720	435	59	-	-	-	14.7	[8]
<i>Laminaria digitata</i>	3818	11,5 79	-	1005	659	3.2 9	1.77	<0.5	<0.5	-	[37]
<i>Saccharina japonica</i>	2532 - 3260	4350 - 5951	150 - 300	225 - 910	550 - 757	1.1 - 43	0.89 - 1.63	0.13 - 0.65	0.2 - 0.4	130 - 690	[44,109,110]
<i>S. latissima</i>	2620	4330	165	810	715	-	-	-	-	15.9	[8]
<i>Sargassum fusiforme</i>	-	-	-	1860	687	88, 6	1.35	-	-	43.6	[21,42]
<i>Undaria pinnatifida</i>	1600 - 7000	5500 - 6810	235 - 450	680 - 1380	405 - 680	1.5 - 30	0.94 - 4	0.33 - 2	0.1 - 85	22 - 30	[8,21,44]
Rhodophyta (Red seaweed)											
<i>Chondrus crispus</i>	1200 - 4270	1350 - 3184	135	420 - 1120	600 - 732	4 - 17	7.14	1.32	<0.5	24.5	[8,37]
<i>Gracilaria</i> spp.	5465	3417	-	402	565	3.6 5	4.35	-	-	-	[111]
<i>Palmaria palmata</i>	1600 - 2500	7000 - 9000	235	560 - 1200	170 - 610	50	2.86	1.14	0.3 - 76	10 - 100	[8,21]
<i>Porphyra tenera</i>	3627	3500	-	390	565	10 - 11	2 - 3	3	<0.63	1.7	[21,37]
<i>P. umbilicalis</i>	940	2030	235	330	370	23	-	-	-	17.3	[8]
<i>P. yezoensis</i>	570	2400	-	440	650	13	10	2	1.4 7	-	[63]

The pond cultivation of *C. lentillifera* has been very successful on Mactan Island, Cebu, in the central Philippines, with markets in Cebu and Manila and some exports to Japan [1,17,18]. Compared to those reported in other seaweeds, the protein content of *C. lentillifera* (12.49%) was comparable to the red algae *Palmaria* sp. (13.87%), and was notably higher than some other brown algae tested, e.g. *Himanthalia elongata* (7.49%) and *Laminaria ochroleuca* (7.49%) (see Table 1) [19,20]. Apart from iodine, *C. lentillifera* is also rich in phosphorus, calcium, copper and magnesium (Table 2) [19,21]. This species is also rich in vitamin E with moderate amount of vitamin B1, vitamin B2 and niacin (Table 3) [18].

Sea lettuce or Ao-Nori (*Ulva* spp., Ulvophyceae) – The sea lettuces comprise the genus *Ulva*, a group of edible green algae that are widely distributed along the coasts of the world's oceans. The type species within the genus *Ulva* is *Ulva lactuca* (see <http://macoi.ci.uc.pt/imagem.php?id=247andtp=7>), “lactuca” meaning lettuce. Sea lettuce as a food for humans is eaten raw in salads and cooked in soups. It is high in protein (level between 10 and 25% of dry mass; see Table 1) [22-24], soluble dietary fibers, and a variety of vitamins and minerals, especially iron (Table 2 and 3) [25,26].

The species *Ulva pertusa* (see http://www.algaebase.org/_mediafiles/algaebase/5B7BE95A076ca2C19Dsxv2CAFF8E/k857fWdJXeJD.jpg), which is frequently consumed under the name of “ao-nori” by the Japanese people, has a high protein level between 20 and 26% (dry product) (see Table 1) [22,27,159]. According Pengzhan et al. [159] the sulfated polysaccharide (ulvan) extracted from this species has antilipidemic effects.

The species *Ulva compressa* (formerly *Enteromorpha compressa*) (see <http://macoi.ci.uc.pt/imagem.php?id=940andtp=7>) is used dried in cooking, particularly with eggs [3]. Is used to as an ingredient in the preparation of a high fibre snack, namely Pakoda, a common Indian product made from chickpea flour [28] and their crude protein levels ranging from 21 and 32% (see Table 1) [21,28,29].

The level of aspartic and glutamic acids can represent up to 26 and 32% of the total amino acids of the edible species *Ulva rigida* (see <http://macoi.ci.uc.pt/imagem.php?id=1508andtp=7>) and *Ulva rotundata* (see http://www.algaebase.org/_mediafiles/algaebase/3EE735B10772e14708IjI34FDB98/dgduKPpgE9Zn.jpg), respectively [30,31].

4.2. Phaeophyceae (Brown Algae)

Arame (*Eisenia bicyclis*, Lessoniaceae) – Is a brown alga or kelp (see http://www.algaebase.org/_mediafiles/algaebase/5B7BE95A076ca284FAXLt2BF7E95/x7Zsjf19i3Bh.jpg) that is also known as “sea oak” because of the shape of its leaves. It grows wild attached to stable on rock at a depth of a few meters on many coasts of the Pacific Ocean. This alga is one of the most nutritious of all plants [32]. It is a species of kelp best known for its use in many Japanese dishes. Arame is high in calcium, iodine, iron, magnesium, and vitamin A as well as being a good dietary source for many other minerals. It also is harvested for alginate. It contains the storage polysaccharide laminarin and the tripeptide eisenin, a peptide with immunological activity [33-35], and phlorotannins with antioxidant activity [134] (see Table 4).

Table 3. Vitamin content of some edible seaweeds (mg/100 g edible portion)

Species	A	B ₁ (Thiamin)	B ₂ (Riboflavin)	B ₃ (Niacin)	B ₅ (Panthoic Acid)	B ₆ (Pyridoxine)	B ₈ (Biotin)	B ₉ (Cobalamin)	C (Ascorbic Acid)	E	Folic acid	Reference
Chlorophyta (Green seaweed)												
<i>Caulerpa lentillifera</i>	-	0.05	0.02	1.09	-	-	-	-	1.00	2.2	-	[18]
<i>Codium fragile</i>	0.52 7	0.223	0.559	-	-	-	-	-	<0.2 23	-	-	[56]
<i>Ulva lactuca</i>	0.01 7	<0.02 4	0.533	98*	-	-	-	6*	<0.2 42	-	-	[26,5 6]
<i>Ulva pertusa</i>	-	-	-	-	-	-	-	-	30 - 241**	-	-	[112]
<i>Ulva rigida</i>	9581	0.47	0.199	<0.5	1.70	<0.1	0.01 2	6	9.42	19. 70	0.1 08	[31]
Phaeophyceae (Brown seaweed)												
<i>Alaria esculenta</i>	-	-	0.3 - 1*	5*	-	0.1*	-	-	100 - 500†	-	-	[26]
<i>Fucus vesiculosus</i>	0.30 7	0.02	0.035	-	-	-	-	-	14.1 24	-	-	[8,56]
<i>Himantalia elongata</i>	0.07 9	0.020	0.020	-	-	-	-	-	28.5 6	-	0. 176 - 0.2 58	[8,47 ,56]
<i>Laminaria digitata</i>	-	1.250	0.138	61.2	-	6.41	6.41	0.0005	35.5	3.4 3	-	[113]
<i>Laminaria ochroleuca</i>	0.04 1	0.058	0.212	-	-	-	-	-	0.35 3	-	0.4 79	[47,5 6]
<i>Saccharina japonica</i>	0.48 1	0.2	0.85	1.58	-	0.09	-	-	-	-	-	[44]
<i>Saccharina latissima</i>	0.04	0.05	0.21	-	-	-	-	0.0003	0.35	1.6	-	[8]
<i>Undaria pinnatifida</i>	0.04 - 0.22	0.17 - 0.30	0.23 - 1.4	2.56	-	0.18	-	0.0036	5.29	1.4 - 2.5	0.4 79	[44,4 7,56]
Rhodophyta (Red seaweed)												
<i>Chondrus crispus</i>	-	-	-	-	-	-	-	0.6 -4*	10 - 13*	-	-	[26,3 7]
<i>Gracilaria spp.</i>	-	-	-	-	-	-	-	-	16 - 149**	-	-	[112]
<i>Gracilaria changii</i>	-	-	-	-	-	-	-	-	28.5	-	-	[21]
<i>Palmaria palmata</i>	1.59	0.073 - 1.56	0.51 - 1.91	1.89	-	8.99	-	0.009	6.34 - 34.5	2.2 13. 9	0.2 67	[8,26 ,47]
<i>Porphyra umbilicalis</i>	3.65	0.144	0.36	-	-	-	-	0.029	4.21 4	-	0.3 63	[47,5 6]
<i>Porphyra yezoensis</i>	1600 0***	0.129	0.382	11.0	-	-	-	0.052	-	-	-	[63,1 14]

* expressed as ppm; ** expressed as mg%; *** expressed as I.U.

Fucus (*Fucus vesiculosus* and *F. spiralis*, Fucaceae) – Members of this genus (see <http://macoi.ci.uc.pt/imagem.php?id=242andtp=7> for *F. vesiculosus* photo and <http://macoi.ci.uc.pt/imagem.php?id=2493andtp=7> for *F. spiralis* photo) are not commonly used as food, but their extracts are reported to be useful as anti-inflammatory and anti-cellulite and weight loss treatments. Fucus species has are reported to contain (see Table 1, 2 and 3): polysaccharides mucilage with algin, fucoidan and laminarin; polyphenols, trace elements and minerals (iodine in the form of salts and attached to proteins and lipids), potassium, bromine, chlorine, magnesium, calcium, iron and silicon, mannitol, vitamins and pro-vitamins A and D, ascorbic acid and lipids (glycosylglycerides) [36-39].

Hiziki or Hijiki (*Sargassum fusiforme*, Sargassaceae) – The species *Sargassum fusiforme* (formerly *Hizikia fusiformis*) (see http://www.algaebase.org/_mediafiles/algaebase/5B7BE95A076ca2541CiyH2B27FDF/mmQhPonex6Cw.jpg) is a common, edible alga which is widely consumed and used as a medicinal herb in China, Japan, Korea and Southeast Asia [22,40]. It is collected from the wild in Japan and cultivated in the Republic of Korea. The alga naturally grows at the bottom of the eulittoral and top of the sublittoral zones, and is found on the southern shore of Hokkaido, all around Honshu, on the Korean peninsula and most coasts of the China Sea. About 90 percent of the Republic of Korea production is processed and exported to Japan [17].

Hiziki contains potential and intensively investigated bioactive compounds especially fucoxanthin pigments and phlorotannins, a polyphenolic secondary metabolite (see Table 4) [34,41]. The protein, fat, carbohydrate and vitamin contents (see Table 1 and 3) are similar to those found in Kombu (formerly *Laminaria japonica*), although most of the vitamins are destroyed in the processing of the raw seaweed. The iron, copper and manganese contents (Table 2) are relatively high, certainly higher than in Kombu [21, 42]. Like most brown seaweeds, its fat content is low (1.5%) but 20-25% of the fatty acid is eicosapentaenoic acid (EPA) [17,35].

According to the Canadian Food Inspection Agency (CFIA) reports, this seaweed contains inorganic arsenic that can exceed the tolerable daily intake levels considered safe for safe human consumption. Even though, inorganic arsenic has been linked with gastrointestinal effects, anemia and liver damage, no evidence of such health complications reported to date due to direct consumption of Hiziki [41].

Kombu or Haidai (*Laminaria* spp. and *Saccharina* spp., Laminariaceae) – *Saccharina japonica* (formerly *Laminaria japonica*) (see http://www.algaebase.org/_mediafiles/algaebase/3EE735B10772e11C1FMvk34536ED/YSqPfyD87qHw.jpg) is perhaps the best known species of kelp. It has broad, shiny leaves and flourishes in cool waters off the coasts of Japan and Korea. It has been cultivated in Japan for about 300 years and elsewhere on a large scale for about forty years. A rich stock (Dashi) can be prepared from kelp because of its concentration of the flavor-enhancer glutamic acid. It is considered that the best varieties of Kombu grow in the cool coastal waters of the northern-most Japanese island of Hokkaido [32]. Haidai is the Chinese name for *Saccharina japonica*, seaweed that was introduced to China accidentally from Japan in the late 1920s. Previously, China had imported all of its requirements from Japan and the Republic of Korea. This alga is now cultivated on a large scale in China. *Saccharina japonica* grows naturally in the Republic of Korea and is also cultivated, but on a much smaller scale; the demand is lower because Koreans prefer Wakame (*Undaria pinnatifida*) [17].

The species *Saccharina latissima* (formerly *Laminaria saccharina*), despite being a deep seaweed (see <http://macoi.ci.uc.pt/imagem.php?id=1506andtp=7>), prefers areas with calm waters, being present in the North Atlantic from Norway to northern Portugal. Commercially this seaweed is called "Royal Kombu" and its composition is very similar to that of *Laminaria ochroleuca* (see <http://macoi.ci.uc.pt/imagem.php?id=1638andtp=7>), known commercially as "Atlantic Kombu" and of *L. digitata* (see http://www.algaebase.org/_mediafiles/algaebase/3EE735B10772e033A6jpH30F0391/2rgkFQ1L8AyP.jpg), known commercially as "Kombu Breton". The Atlantic Kombu is a rather tougher than the Kombu from Japan and is distributed in Iberian Peninsula from Santander, in Cantabria (Spain), to Cape Mondego in Portugal [8,38,43].

Kombu stands out for its high mineral content (particularly magnesium, calcium and iodine). Calcium and magnesium regulate together many functions, including the nervous system and muscles. The various species of the genera *Laminaria* and *Saccharina* have been used as a source of iodine in the industry, mineral with a role in thyroid function, as noted above (see Table 2 and 4). The alginic acid present in these algae has shown preventive effects against contamination by heavy metals and radioactive substances, especially Strontium 90. Among the properties of these seaweeds, we highlight the following: anti-rheumatic, anti-inflammatory, regulators of body weight and blood pressure (due to the presence of laminarin and laminin). These Laminariaceae also prevent atherosclerosis and other vascular problems due to its bloodstream fluidifying effects [8,34,39].

Sea spaghetti or Haricot vert de mer (*Himantalia elongata*, Himantaliaceae) - Is long, dark (see <http://macoi.ci.uc.pt/imagem.php?id=276andtp=7>), and rich in trace elements and vitamins. It is successfully cultivated in Brittany, France, and increasingly exported fresh for the Japanese restaurant trade. The long strands must first have its furry layer removed by hand under cold running water before it is prepared for eating [32].

Little known in Asian countries, it is increasingly valued in Europe, both in restaurants and in specialty bakeries. For several years they have manufactured specialty pies, pizzas, pastas, pates, breads, and snacks, since its taste is reminiscent of some cephalopods (squid and cuttlefish) [8].

This species is characterized in particular by its high iron content (59 mg per 100 g of algae) and the simultaneous presence of vitamin C, which facilitates the absorption of this trace element (see Table 2 and 3) [47]. Sea spaghetti is rich in phosphorus, a mineral known to enhance brain function, helping to preserve memory, concentration and mental agility [8,38].

Wakame or Quandai-cai (*Undaria pinnatifida*, Alariaceae) – Is a invasive brown seaweed (see <http://macoi.ci.uc.pt/imagem.php?id=1146andtp=7>) originating from the Pacific, which lives in deep waters (up to 25 m) and can reach 1.5 m in length and is one of the most important species of commercial seaweed, next to nori, on the Japanese menu and is eaten both dried and fresh [8, 38].

The nutritional value is high, as the leaves consist of 13% protein, as well as containing substantial amounts of calcium (see Table 1 and 2) [21,44]. Traditionally Wakame is harvested from wild populations by boats by means of long hooks and then sold fresh or sun dried. Since this seaweed is salted for transport, certain cleansing must take place before eating. Wakame must be thoroughly rinsed under running water, then placed in boiling water for thirty seconds, then rinsed in ice water. The leaves are then spread out and the hard midrib is removed [32]. Wakame has relatively high total dietary fibre content; it is higher than Nori

or Kombu (see Table 1). Consumption of dietary fibre has a positive influence on several aspects related to health such as reducing the risk of suffering from colon cancer, constipation, hypercholesterolemia, obesity and diabetes. Besides, many constituents of dietary fibre show antioxidant activity as well as immunological activity [45]. In this sense, *U. pinnatifida* (Wakame) showed some positive effect on cardiovascular diseases (hypertension and hypercholesterolemia) [46]; this alga contains basically dietetic fibre, being its principal component alginate. This alginic acid has demonstrated to reduce hypertension in hypertensive rates [46].

Like other brown seaweeds, the fat content is quite low (see Table 1). Air-dried Wakame has a similar vitamin content to the wet seaweed and is relatively rich in the vitamin B group, especially niacin (see Table 3) [44,47]; however, processed Wakame products lose most of their vitamins. Wakame contains appreciable amounts of essential trace elements (see Table 2) such as manganese, copper, cobalt, iron, nickel and zinc, similar to Kombu and Hiziki [8,7,44].

Wakame is one of the most popular edible seaweed in Japan and has been found to contain 5–10% fucoxanthin [48] apart from containing polar lipids such as glycolipids. Health benefits of fucoxanthin are anticancer effect — it is evaluated that neoxanthin and fucoxanthin were reported to cause a remarkable reduction in growth of prostate cancer cells, and also demonstrated anti-obesity activity and anti-inflammatory activity [49]. Fucoxanthin (see Table 4) is other major biofunctional pigment of brown seaweeds and the content in various edible seaweeds including *U. pinnatifida* has been reviewed by Hosakawa et al. [50].

Winged kelp, Edible kelp or Atlantic wakame (*Alaria esculenta*, Alariaceae) – This is a large brown kelp (see <http://macoi.ci.uc.pt/imagem.php?id=2115andtp=7>) which grows in the upper limit of the sublittoral zone. It has a wide distribution in cold waters and does not survive above 16°C. It is found in areas such as Ireland, Scotland (United Kingdom), Iceland, Brittany (France), Norway, Nova Scotia (Canada), Sakhalin (Russia) and northern Hokkaido (Japan). The seaweed is eaten in Ireland, Scotland (United Kingdom) and Iceland either fresh or cooked, and it is said to have the best protein among the kelps and is also rich in trace metals and vitamins (see Table 1 and 3), especially niacin and contains up to 42% alginic acid [17,26,51,52]. The species is used for a cultivar of purposes from value-added sea-vegetables to fodder and body care products. Recently, it has become of economic interest as a foodstuff in aquaculture for herbivorous mollusks, urchins, shrimp and fish [53].

4.3. Rhodophyta (Red Algae)

Kanten (Japan) or Agar-Agar, Dai choy goh (China), Gulaman (Philippines) (Agarophytes, Florideophyceae) – *Ahnfeltia*, *Gelidiella*, *Gelidium*, *Gracilaria* and *Pterocladia* are the major sources of raw materials used for the commercial extraction. Agar-Agar is the Malay name for a gum discovered in Japan that had been extracted from a red seaweed of the genus *Eucheuma* (see Phycocolloid “Agar”).

With common names such as Kanten (see http://www.mitoku.com/products/seavegetables/img/kanten001_s.jpg) in Japan, but can also be referred to by many names including 'Grass jelly', 'Seaweed jelly', and 'Vegetable gelatin' (true gelatin is an animal by-product and as such can be unacceptable on account of dietary or religious preferences).

Table 4. Summary of nutraceutical value of some seaweed compounds

Category	Compounds	Seaweed source	Potential health benefit	Reference
Lipids and fatty acids	Omega 3 and omega 6 acids	<i>Porphyra</i> spp. Brown algae	Prevention of cardio-vascular diseases, osteoarthritis and diabetes	[8,23,39]
Carotenoids	β -carotene, lutein	<i>Chondrus crispus</i> <i>Porphyra yezoensis</i> Red algae	Antimutagenic; protective against breast cancer	[94,115,116,117,118,119]
	β -carotene, lycopene	<i>Porphyra</i> spp. Red algae	Recent studies have shown the correlation between a diet rich in carotenoids and a diminishing risk of cardio-vascular disease, cancers	[39,120,121,161]
	Lutein, zeaxanthin	Red algae Brown algae	Diminishing risk of ophthalmological diseases	
	Fucoxanthin	<i>Undaria pinnatifida</i> Brown algae	Antiangiogenic; protective effects against retinol deficiency; anticancer effect; anti-obesity and anti-inflammatory activity	[39,120,121,122] [1,48,123,124,125,126]
Minerals	Iodine	<i>Fucus vesiculosus</i> <i>Laminaria</i> spp. <i>Undaria pinnatifida</i>	The brown seaweeds have traditionally been used for treating thyroid goiter.	[8,39,127]
	Calcium	<i>Undaria pinnatifida</i> <i>Laminaria</i> spp. <i>Saccharina</i> spp.	Seaweed consumption may thus be useful in the case of expectant mothers, adolescents and elderly that all exposed to a risk of calcium deficiency.	[8,23]
Phycobilin pigments	Phycoerythrin , Phycocyanin	Red algae	Antioxidant properties, which could be beneficial in the prevention or treatment of neuro-degenerative diseases caused by oxidative stress (Alzheimer's and Parkinson's) as well as in the cases of gastric ulcers and cancers Amelioration of diabetic complications	[39,128,129,130]
	Phycoerythrin	Red algae		[131]

Table 4. (Continued).

Category	Compounds	Seaweed source	Potential health benefit	Reference
Polyphenols	Flavonoids	<i>Palmaria palmata</i>	At high experimental concentrations that would not exist <i>in vivo</i> , the antioxidant abilities of flavonoids <i>in vitro</i> are stronger than those of vitamin C and E	[132,133]
	Phlorotannins	Brown algae	Antioxidant activity of polyphenols extracted from brown and red seaweeds has already been demonstrated by <i>in vitro</i> assays; anti-inflammatory effect Algicidal and bactericidal effect	[134,135,136,137,138] [138,139,140]
Polysaccharides and dietary fibers	Agars, carrageenans, ulvans and fucoidans	Red, green and brown algae	These polysaccharides are not digested by humans and therefore can be regarded as dietary fibers.	[141,142,143]
		<i>Ulva pertusa</i>	Antihyperlipidemic effects	[27,159]
	Ulvans	Red algae (carrageenophytes),	Antitumor and anti-viral	[1,138,144,145,146,147,148]
	Carrageenan, fucoidan	<i>Undaria pinnatifida</i> , brown algae	Anti-viral, anti-HSV and anti-HIV	[60,71,149]
		Red algae (carrageenophytes)	Anticoagulant and antithrombotic activity	[60,138,150]
	Carrageenan (lambda, iota and nu variants)	Brown algae	Antitumor and immunomodulatory activity	[146,150,151]
	Fucoidan		Antiviral and anti-HIV	[60,94,150,152,153,154,155]
	Fucoidan	<i>Fucus vesiculosus</i> <i>Saccharina japonica</i>	Hypolipidemic effect	[156,157]

Category	Compounds	Seaweed source	Potential health benefit	Reference
Proteins and amino acids	Proteins	<i>Palmaria palmata</i> <i>Porphyra tenera</i>	Higher protein contents are recorded in green and red seaweeds (on average 10-30 % of the dry weight). In some red seaweed, such as <i>Palmaria palmata</i> (dulse) and <i>Porphyra tenera</i> (nori), proteins can represent up to 35 and 47% of the dry matter, respectively.	[23]
	Proteins, amino acids	<i>Undaria pinnatifida</i>	<i>Undaria pinnatifida</i> (wakame) has a high balance between the essential amino acids, which gives a high biological value to their proteins. Proteins, in addition, with a high bioavailability (85-90%)	[8,39]
Vitamins	Vitamin B ₁₂	<i>Porphyra</i> spp.	Is particularly recommended in the treatment of the effects of ageing, of CFS and anemia.	[114]
	Vitamin C	<i>Himanthalia elongata</i> <i>Palmaria palmata</i>	Strengthens the immune defense system, activates the intestinal absorption of iron, controls the formation of conjunctive tissue and the protidic matrix of bony tissue, and also acts in trapping free radicals and regenerates Vitamin E.	[8,23]
	Vitamin E	<i>Fucus</i> spp.	Due to its antioxidant activity, vitamin E inhibits the oxidation of the low-density lipoproteins. It also plays an important part in the arachidonic acid chain by inhibiting the formation of prostaglandins and thromboxan.	[23]

Abbreviations: CFS - Chronic fatigue syndrome; HIV - Human immunodeficiency virus; HSV - Herpes simplex virus.

Agar-agar is a powerful gel-forming of all gums because of the unusual length of its carbohydrate molecules. It is also unique in its ability to withstand near boiling-point temperatures, making it ideal for use in jellied confections in tropical countries since the ingredients can be treated at high temperatures and then cooled [32,54,55].

The agarophytes, from which this gum is extracted, are gathered and left on the beach to dry and bleach before being sold to a factory where it is cleaned, washed, and boiled to extract the gum. Traditionally the, water soluble extract is it is frozen and thawed. More

recently precipitation methods have been developed, which alternative process relies on syneresis [17]. As the water runs out of it, so do any of the impurities, leaving the purified gum to be dried. This method of purifying (freezing and thawing) is said to have been discovered accidentally by a Japanese innkeeper during a frosty winter of 1658. Since then, the product has gained in popularity in Japanese cuisine, not only for making jellies, but also as a general thickener for soups and sauces [32,38,54].

A popular Japanese sweet dish is mitsumame; this consists of cubes of agar gel containing fruit and added colors. It can be canned and sterilized without the cubes melting. Agar is also used in gelled meat and fish products, and is preferred to gelatin because of its higher melting temperature and gel strength. In combination with other gums, agar has been used to stabilize sherbets and ices. It improves the texture of dairy products such as cream cheese and yoghurt. Agar has been used to clarify wines, especially plum wine, which can prove difficult by traditional methods. Unlike starch, agar is not readily digested and so adds little calorific value to food. It is used in vegetarian foods such as meat substitutes. There is an increased recent interest in agar as used in dedicated Kanten restaurants catering for modern weight conscious Japanese consumers [17].

Dulse or Dilisk (*Palmaria palmata*, Florideophyceae) – Is a relatively common Atlantic seaweed (see <http://macoi.ci.uc.pt/imagem.php?id=854andtp=7>). It is comparatively small (up to 50 cm long), and can occupy a wide range of habitats from the intertidal, with brief exposure to relatively deep niches, in cold and turbulent waters. The name "dulse" comes from the Irish vocabulary (dils = edible seaweed) and has little to do with the Latin dulce meaning tasting good or sugary or sweet. In fact eating dried dulse may be described as being an acquired taste which can be quite strong and distinctive [38]. Dulse was prized by the Celts and the Vikings and has been harvested on beaches at low tide, air-dried, and boiled in soups from Ireland to Iceland well into the 20th century. The people of Scotland, Ireland, and Iceland have been using Dulse for centuries, and collect it off their coasts. Many consider it to be the most delectable of all seaweeds [32,56]. Today, this species is successfully cultivated along the coast of Brittany in France, Ireland and northern Spanish coast [57,58,59].

Dilsea carnosa is another type of edible seaweed (<http://macoi.ci.uc.pt/imagem.php?id=370andtp=7>), unrelated to the regular Dulse, but identical in taste, appearance, and nutritional value. Dried Dulse is a popular food in Canada, where much of the world's current supply is harvested in New Brunswick and Nova Scotia. From there, it is exported to Scotland, Ireland and the US. Dulse is extremely rich in iodine, phosphorus, calcium, and contains more potassium than any other food. In Canada, Dulse is available in many major coastal food outlets and supermarkets and can be served in a variety of ways: as a side dish, in soups and salads, as a sandwich ingredient or in powdered form to be used as a spice or condiment flavoring [17,32].

About 30% of the dry weight of dulse comprises minerals (e.g. iron, iodine and potassium) and proteins of high nutritive value (18%). *Palmaria palmata* also has relatively high amounts of vitamin C, which facilitates the absorption of iron (see Table 2 and 3). This seaweed is ideal as a restorative in states of anemia and asthenia (weakness). Strengthens vision (vitamin A) and is recommended for treatment of gastric and intestinal problems and for regeneration of the mucous membranes (respiratory, gastric, and vaginal). Like other few red algae [60], *Palmaria palmata* has anthelmintic effect and acts as an antiseptic and parasites control, cleaning up the gut [8,56].

Irish moss or Carrageen moss (*Chondrus crispus*, Florideophyceae) – This species (see <http://macoi.ci.uc.pt/imagem.php?id=305andtp=7> for hand harvest photo, <http://macoi.ci.uc.pt/imagem.php?id=1522andtp=7> for Irish moss pudding photo and <http://macoi.ci.uc.pt/imagem.php?id=1020andtp=7> for habit photo) is found along the coasts of the North Atlantic in both Europe and North America [61]. It can either be reddish-purple or green in color. Ireland is a major source of the world's supply and where this vegetable is steamed and eaten with potatoes or cabbage. Its most common use outside of Ireland is in the making of rennet-free gelatin (carrageen). This is preferred by full vegetarians and on certain religious grounds since true gelatin is a product of animal processing. One example of its traditional use is in the production of blancmange (literally white jelly), a traditional vanilla-flavoured pudding. In eastern Canada, a company is cultivating a strain of *Chondrus crispus* in on land tanks and marketing it as Hana Tsunomata, for seaweed salad (see www.acadianseaplants.com), a yellow variant that resembles traditional Japanese seaweed that is in limited supply from natural resources [17,38,56].

Mastocarpus stellatus is frequently collected with *C. crispus* and sold as a mixture under the name Carrageen or Irish moss [17].

Carrageenan is extensively used in the manufacture of various soft cheeses, ice cream, aspics and jellies (see “Phycocolloids” and Table 6).

Nori or Purple laver (a large number of species including *Porphyra yezoensis*, *P. tenera*, *P. umbilicalis* and *Porphyra* spp., Bangiophyceae) – The original and traditional Nori is produced from *Porphyra yezoensis* (see http://upload.wikimedia.org/wikipedia/commons/5/5f/Porphyra_yezoensis.jpg) and *P. tenera* cultivated in Japan. The word “nori” originally means “all seaweed”; however the modern application of the word is taken to include the purplish-black seaweed sheets often seen wrapped around rice in sushi cuisine. Nori sheets come largely from cultivation in Japan, the Republic of Korea and China. In Japan's list of products from marine culture, Nori has the highest production volume, followed by oysters, yellowtails and Wakame, the last being another seaweed used as food. In traditional way, to obtain Nori, freshly harvested fronds of *Porphyra* are chopped, pressed between bamboo mats, and dried either in drying rooms or in the sun. Good quality Nori is mild-tasting and black in color, but having a purple sheen. It should be packed airtight since it is very hygroscopic. However, today the production of Nori is more mechanical [17,38].

There is an Atlantic Nori (see <http://macoi.ci.uc.pt/imagem.php?id=569andtp=7>), which is produced from wild algae of the genus *Porphyra* (e.g. *P. umbilicalis*, *P. leucosticta* and others), which is traditionally consumed in Celtic countries and in the Azores archipelago. In Wales and Ireland it is still used in preparing the dish called “laverbread” [8,38].

Many species of the genus *Porphyra* are rich in amino acids. Nori is exceptionally rich in provitamin A (see Table 3), surpassing the vegetables and also seafood and fish. Nori has a low percentage of fats and these are of great nutritional value because more than 60% of them are polyunsaturated fatty acids omega 3 and 6. This dried seaweed contains large amounts of protein, ash, vitamins and carbohydrate (see Table 1) [21,62]. The levels of taurine (> 1.2%) are notable as this compound aids enterohepatic circulation of bile acid, thus preventing gallstone through controlling blood-cholesterol levels. Relatively high levels of eicosapentanoic acid, choline, inositol and other B-group vitamins are regarded as beneficial to health. The occurrence of porphyrins and betaines that prevent respectively, gastric ulcers and lower blood-cholesterol levels are particular interest (see Table 4) [8,38,63].

Ogo, Ogonori or Sea moss (*Gracilaria* spp., Florideophyceae) – Fresh *Gracilaria* species have been collected and sold as a salad vegetable in Hawaii (United States of America) for several decades. The mixture of ethnic groups in Hawaii (Hawaiians, Filipinos, Koreans, Japanese and Chinese) creates an unusual demand and supply has, at times, been limited by the availability of stocks natural sources. The alga is being successfully cultivated in Hawaii using an aerated tank system, producing up to 6 tones fresh weight per week. In Indonesia, Malaysia, the Philippines and Vietnam, species of *Gracilaria* are collected by coastal people for food [64]. In southern Thailand, an education program was undertaken to show people how it could be used to make jellies by boiling and making use of the extracted agar (See Phycocolloid “Agar” and Table 6). In the West Indies, *Gracilaria* is sold in markets as “Sea moss” and in some locations is marketed also as “Irish moss”; it is reputed to have aphrodisiac properties and is also used as a base for a non-alcoholic drink. It has been successfully cultivated for this purpose in St Lucia and adjacent islands. *Gracilaria changii* (see <http://www.naturia.per.sg/cjsurvey/vegetative/text/gracilaria%20changii.htm>) is consumed in certain coastal areas especially along the east coast of Peninsula Malaysia and in East Malaysia, where it is occasionally eaten as a salad dish [17,65].

The red alga *Gracilaria chilensis* (see http://www.algaebase.org/_mediafiles/algaebase/3EE735B1076ca33F0Bquh2E9B16C/f8jBtU6jjj4V.jpg), belonging to the Gracilariaceae, is known as “Pelillo” in Chile, on account of its appearance [15]. It has a long and filamentous thallus. It is a reddish brown alga, with variable branching reaching 2 m. It grows in bunches or isolated, in habitats with solid substrates [66]. This alga is almost entirely used in the domestic and foreign industry for the development of agar, and is one of the most exported (126,000 tones/year) [15].

5. PHYCOCOLLOIDS

What Are Phycocolloids?

Colloids are compounds that form colloidal solutions, an intermediate state between a solution and a suspension, and are used as thickeners, gelling agents, and stabilizers for suspensions and emulsions (see Table 6). Hydrocolloids are carbohydrates that when dissolved in water form viscous solutions. The phycocolloids are hydrocolloids extracted from algae and represent a growing industry, with more than 1 million tons of seaweeds extracted annually for hydrocolloid production [67-69].

Many seaweeds produce hydrocolloids, associated with the cell wall and intercellular spaces. Members of the red algae (Rhodophyta) produce galactans (e.g. carrageenans and agars) and the brown algae (Heterokontophyta, Phaeophyceae) produce uronates (alginates) [68,70-72].

The different phycocolloids used in food industry as natural additives are (European codes of phycocolloids):

- Alginic acid – E400
- Sodium alginate – E401
- Potassium alginate – E402

- Ammonium alginate – E403
- Calcium alginate – E404
- Propylene glycol alginate – E405
- Agar – E406
- Carrageenan – E407
- Semi-refined carrageenan or processed eucheuma seaweed – E407A

Agar (Agarophytes, Rhodophyta) – Most Agar is extracted from species of *Gelidium* and *Gracilaria*. Closely related to *Gelidium* are species of *Pterocladia* (see <http://macoi.ci.uc.pt/imagem.php?id=571andtp=7>), and small quantities of these are collected, mainly in the Azores (Portugal) and New Zealand. *Gelidiella acerosa* is the main source of agar in India. *Ahnfeltia* species have been used in both Russia and Japan, one source being the island of Sakhalin (Russia) [17, 38]. *Gelidium* spp. and *Gracilaria* spp. are collected in Morocco and Tunisia and Chile for Agar production [15,73-76].

Agar is a phycocolloid the name of which comes from Malaysia and means “red alga” in general and has traditionally been applied to what we now know taxonomically as – *Eucheuma* (see “Agar-Agar”). Ironically we now know this to be the commercial source of iota carrageenan. Agar is composed of two polysaccharides: namely agarose and agarpectin. The first is responsible for gelling, while the latter has thickening properties [77].

Agar is a relatively mature industry in terms of manufacturing methods and applications. Today most processors are using press/syneresis technology; although some still favor freeze/thaw technology or a mixture of these technologies. While the basic processes may not have changed, improvements in presses and freezing equipment must be noted. High-pressure membrane presses have greatly improved dewatering of agar and thereby reducing energy requirements for final drying before powder milling. Average prices of this phycocolloid were US\$ 18 kg⁻¹ and global sales in 2009 were US\$ 173 million [70].

The origin of agar as a food ingredient is in Asia where it has been consumed for several centuries. Its extraordinary qualities as a thickening, stabilizing and gelling agent make it an essential ingredient for preparing processed food products. Furthermore, its satiating and gut regulating characteristics make it an ideal fiber ingredient in the preparation of low calorie food products. The principal applications of agar food grade are (see Table 6): fruit jellies, milk products, fruit pastilles, caramels, chewing gum, canned meat, soups, confectionery and baked goods, icing, frozen and salted fish [77].

About 80 percent of the agar produced globally is for food applications (see Table 5 and 6), the remaining 10 percent is used for bacteriological plates and other biotechnology uses (in particular agarose electrophoresis). Agar has been classified as GRAS (Generally Recognized as Safe) by the United States of America Food and Drug Administration, which has set maximum usage levels depending on particular applications. In the baked goods industry, the ability of agar gels to withstand high temperatures allows for its use as a stabilizer and thickener in pie fillings, icings and meringues. Cakes, buns, etc., are often pre-packed in various kinds of modern wrapping materials and often stick to them, especially in hot weather; by reducing the quantity of water and adding some agar, a more stable, smoother, non-stick icing may be obtained [17,68]. Some agars, especially those extracted from *Gracilaria chilensis*, can be used in confectionery with very high sugar content, such as fruit candies. These agars are said to be “sugar reactive” because the sugar (sucrose) increases

the strength of the gel. Since agar is tasteless, it does not interfere with the flavors of foodstuffs; this is in contrast to some of its competitive gums which require the addition of calcium or potassium salts to form gels. In Asian countries, it is a popular component of jellies; this has its origin in the early practice of boiling seaweed, straining it and adding flavors to the liquid before it cooled and formed a jelly [17].

Table 5. Agar grades depending on their final use (Adapted from Armisen [78])

	Agar type	Source
Natural agar	Strip	Only <i>Gelidium</i> by old traditional methods
	Square	
Industrial agar	Food grade	<i>Gelidium</i> , <i>Gracilaria</i> , <i>Pterocladia</i> , <i>Gelidiella</i> , <i>Ahnfeltia</i>
	Pharmacological grade	Only <i>Gelidium</i>
	Clonic plants production grade	<i>Gelidium</i> , <i>Pterocladia</i>
	Bacteriological agar	Only <i>Gelidium</i> , <i>Pterocladia</i>
	Purified agar	<i>Gelidium</i>

The remaining 20 percent is accounted for biotechnological applications [77]. A list of different uses and the corresponding type of algae required can be found in Table 5 [78]. Agar is fundamental in biotechnology studies, and is used in the preparation of inert, solidified culture media for bacteria, microalgae, fungi, tissue culture. It is also used to obtain monoclonal antibodies, interferons, steroids and alkaloids. The biotechnological applications of agar are increasing – it essential for the separation of macromolecules by electrophoresis, chromatography and DNA sequencing [38,69].

Alginate (Alginophytes, Phaeophyceae) – "Alginate" is the term usually used for the salts of alginic acid, but it can also refer to all the derivatives of alginic acid and alginic acid itself; in some publications the term "algin" is used instead of alginate. Alginate is a linear copolymer of β -D-mannuronic acid (M) and α -L-guluronic acid (G) (1→4)-linked residues, arranged either in heteropolymeric (MG) and/or homopolymeric (M or G) blocks [54,79,80].

Alginic acid is present in the cell walls of brown seaweeds, and it is partly responsible for the flexibility of the seaweed. Consequently, brown seaweeds that grow in more turbulent conditions usually have higher alginate content than those in calmer waters. While any brown seaweed could be used as a source of alginate, the actual chemical structure of the alginate varies from one genus to another, and similar variability is found in the properties of the alginate that is extracted from the seaweed. Since the main applications of alginate are in thickening aqueous solutions and forming gels, its quality is judged on how well it performs in these uses [17].

Twenty-five to 30 years ago almost all extraction of alginates took place in Europe, USA, and Japan. The major change in the alginates industry over the last decade has been the emergence of producers in China in the 1980s. Initially, production was limited to low cost, low quality alginate for the internal, industrial markets produced from the locally cultivated *Saccharina japonica*. By the 1990s, Chinese producers were competing in western industrial markets to sell alginates, primarily based on low cost. Average prices of alginates were 12 US\$ kg⁻¹ and global sales in 2009 were 318 million US\$ [70].

Table 6. Applications of seaweed phycocolloids as food additives (Adapted from van de Velde and de Ruiter [86], Dhargalkar and Pereira [158] and Pereira [38])

Use	Phycocolloid	Function
Baked food	Agar, Kappa, Iota, Lambda	Improving quality and controlling moisture
Beer and wine	Alginate, Kappa	Promotes flocculation and sedimentation of suspended solids
Canned and processed meat	Alginate, Kappa	Hold the liquid inside the meat and texturing
Cheese	Kappa	Texturing
Chocolate milk	Kappa, lambda	Keep the cocoa in suspension
Cold preparation puddings	Kappa, Iota, Lambda	Thicken and gelling
Condensed milk	Iota, lambda	Emulsify
Dairy Creams	Kappa, iota	Stabilize the emulsion
Fillings for pies and cakes	Kappa	Give body and texture
Frozen fish	Alginate	Adhesion and moisture retention
Gelled water-based desserts	Kappa + Iota Kappa + Iota + CF	Gelling
Gums and sweets	Agar, Iota	Gelling, texturing
Hot preparation flans	Kappa, Kappa + Iota	Gelling and improve the mouth-feel
Jelly tarts	Kappa	Gelling
Juices	Agar, Kappa, Lambda	Viscosity, emulsifier
Low calorie gelatins	Kappa + Iota	Gelling
Milk ice-cream	Kappa + GG, CF, X	Stabilize the emulsion and prevent ice crystals formation
Milkshakes	Lambda	Stabilize the emulsion
Salad dressings	Iota	Stabilize the suspension
Sauces and condiments	Agar, Kappa	Thicken
Soy milk	Kappa + iota	Stabilize the emulsion and improve the mouth-feel

Non-seaweed colloids: CF - Carob flour; GG - Guar gum; X - Xanthan.

A high quality alginate forms strong gels and gives thick, aqueous solutions. A good raw material for alginate extraction should also give a high yield of alginate. Brown seaweeds that fulfill the above criteria are species of *Ascophyllum*, *Durvillaea*, *Ecklonia*, *Fucus*, *Laminaria*, *Lessonia*, *Macrocystis* and *Sargassum*. However, *Sargassum*, is only used when nothing else is available: its alginate is usually borderline quality and the yield usually low [38, 81].

The goal of the extraction process is to obtain dry, powdered, sodium alginate. The calcium and magnesium salts do not dissolve in water; the sodium salt does. The rationale behind the extraction of alginate from the seaweed is to convert all the alginate salts to the sodium salt, dissolve this in water, and remove the seaweed residue by filtration [17].

Water-in-oil emulsions such as mayonnaise and salad dressings are less likely to separate into their original oil and water phases if thickened with alginate. Sodium alginate is not useful when the emulsion is acidic, because insoluble alginic acid forms; for these applications propylene glycol alginate (PGA) is used since this is stable in mild acid conditions. Alginate improves the texture, body and sheen of yoghurt, but PGA is also used in the stabilization of milk proteins under acidic conditions, as found in some yoghurts. Some fruit drinks have fruit pulp added and it is preferable to keep this in suspension; addition of sodium alginate, or PGA in acidic conditions, can prevent sedimentation of the pulp and to

create foams. In chocolate milk, the cocoa can be kept in suspension by an alginate/phosphate mixture, although in this application it faces strong competition from carrageenan (see Table 6). Small amounts of alginate can thicken and stabilize whipped cream [82,83].

Carrageenan (Carrageenophytes, Rhodophyta) – Carrageenans represent one of the major texturising ingredients used by the food industry; they are natural ingredients, which have been used for decades in food applications and are generally regarded as safe (GRAS). The phycocolloid “carrageenin”, as it was first called, was discovered by the British pharmacist, Stanford in 1862 who extracted it from Irish moss (*Chondrus crispus*). The name was later changed to “carrageenan” so as to comply with the ‘-an’ suffix for the names of polysaccharides. The modern carrageenan industry dates from the 1940s, receiving its impetus from the dairy applications (see the carrageenan applications in Table 6) where carrageenan was found to be the ideal stabilizer for the suspension of cocoa in milk chocolate [68].

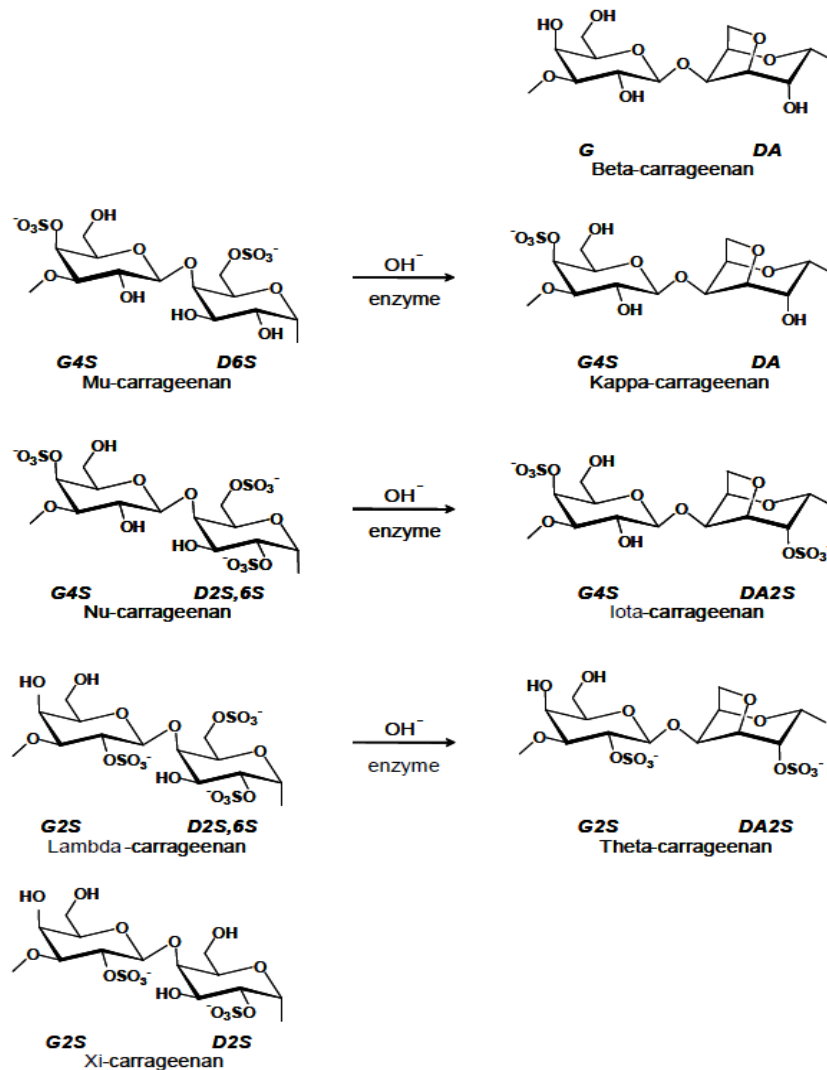


Figure 1. Idealized units of the main carrageenan types (After Pereira et al. [68]).

The commercial carrageenans are normally divided into three main types: kappa-, iota- and lambda-carrageenan. The idealized disaccharide repeating units of these carrageenans are given in Figure 1. Generally, seaweeds do not produce these idealized and pure carrageenans, but more likely a range of hybrid structures and or precursors (see Table 7). Several other carrageenan repeating units exist: e.g. xi, theta, beta, mu and nu (Figure 1). The precursors (mu and nu), when exposed to alkali conditions, are modified into kappa and iota, respectively, through formation of the 3,6-anhydrogalactose bridge [68,72,84,85]. This is a feature used extensively in extraction and industrial modification.

Carrageenans are the third most important hydrocolloid in the food industry, after gelatin (animal origin) and starch (plant origin) [86]. The most commonly used, commercial carrageenans are extracted from *Kappaphycus alvarezii* and *Eucheuma denticulatum* [17].

Primarily, wild-harvested genera such as *Chondrus*, *Furcellaria*, *Gigartina*, *Chondracanthus*, *Sarcothalia*, *Mazzaella*, *Iridaea*, *Mastocarpus*, and *Tichocarpus* are also mainly cultivated as carrageenan raw materials and producing countries include Argentina, Canada, Chile, Denmark, France, Japan, Mexico, Morocco, Portugal, North Korea, South Korea, Spain, Russia, and the USA [4,70].

The original source of carrageenans was from the red seaweed *Chondrus crispus*, which continues to be used, but in limited quantities. *Betaphycus gelatinum* is used for the extraction of beta (β) carrageenan. Some South American red algae used previously only in minor quantities have, more recently, received attention from carrageenan producers, as they seek to increase diversification of raw materials in order to provide for the extraction of new carrageenan types with different physical functionalities and therefore increased product development, which in turn stimulates demand [17]. *Gigartina skottsbergii*, *Sarcothalia crispata*, and *Mazzaella laminaroides* are currently the most valuable species and all are harvested from natural populations in Chile and Peru. We can not let to mention the recent earthquake in Chile (February 27th, 2010), which caused the elevation of intertidal areas and the consequent large losses of harvestable biomass. Small quantities of *Gigartina canaliculata* are harvested in Mexico and *Hypnea musciformis* has been used in Brazil [87]. The use of high value carrageenophytes as a dissolved organic nutrient sink to boost economic viability of integrated multitrophic aquaculture (IMTA) operations has been considered [88,160].

Large carrageenan processors have fuelled the development of *Kappaphycus alvarezii* (which goes by the name “cottonii” to the trade) and *Eucheuma denticulatum* (commonly referred to as “spinosum” in the trade) farming in several countries including the Philippines, Indonesia, Malaysia, Tanzania, Kiribati, Fiji, Kenya, and Madagascar [17]. Indonesia has recently overtaken the Phils as the world’s largest producer of dried carrageenophyte biomass.

Shortages of carrageenan-producing seaweeds suddenly appeared in mid-2007, resulting in doubling of the price of carrageenan; some of this price increase was due to increased fuel costs and a weak US dollar (most seaweed polysaccharides are traded in US dollars). The reasons for shortages of the raw materials for processing are less certain: perhaps it is a combination of environmental factors, sudden increases in demand, particularly from China, and some market manipulation by farmers and traders. Most hydrocolloids are experiencing severe price movements. Average prices of carrageenans were 10.5 US\$ kg⁻¹ and the global sales in 2009 were 527 million US\$ [4,70].

Table 7. Industrial carrageenophytes: composition as determined by FTIR-ATR and FT-Raman (After Pereira et al. [4])

Family	Species	Lifecycle phase	Harvest Season	Origin	Carrageenan			
					Yield ⁽¹⁾	Alkali-extracted	Iota/kappa ratio	Native ⁽²⁾
Gigartinales	Chondracanthus chamissoi	NF	Summer	Chile (W)	13.5	kappa/iota	0.77	kappa/iota (mu/nu)
	C. chamissoi	T	Late Spring	Chile (W)	24.6	xi/theta	-	xi/theta
	C. chamissoi	FG	Summer	Chile (W)	14.2	kappa/iota	0.79	kappa/iota (mu/nu)
	Chondrus crispus	G + T	Late Spring	Canada (W)	33.8	kappa/iota lambda	-	kappa/iota (mu/nu) lambda/alpha
	Sarcothalia crispata	NF	Late Winter	Chile (W)	14.6	kappa/iota	0.81	kappa/iota (mu/nu)
	S. crispata	NF	Spring	Chile (W)	16.7	kappa/iota	0.79	kappa/iota (mu/nu)
	S. crispata	FG	Late Winter	Chile (W)	5.4	kappa/iota	0.81	kappa/iota (mu/nu)
Petrocelidaceae	Mastocarpus papillatus	G	Winter	Chile (W)	5.4	kappa/iota	0.83	kappa/iota (mu/nu)
Solieriaceae	Betaphycus gelatinum	-	June - October	Philippines (W)	71.0	kappa/beta	1.004 (4)	kappa/beta (mu/gamma)
	Eucheuma denticulatum	-	October - February	Philippines (F)	39.7	iota	0.92	iota (nu)
	E. denticulatum	-	Late Spring	Madagascar (F)	35.3	iota	0.93	iota (nu)
	E. denticulatum	-	Spring	Tanzania (F)	31.5	iota/kappa	0.88	iota/kappa (nu)
	Eucheuma isiforme	-	Late Summer	Colombia (F)	20.4	kappa/iota	0.71	kappa/iota (mu)
	Kappaphycus alvarezii	-	October - February	Indonesia (F)	20.0	kappa/iota	0.64	kappa/iota (mu)
	K. alvarezii (Ph)	-	October - February	Philippines (F)	30.4	kappa/iota	0.72	kappa/iota (mu)
	K. alvarezii	-	June-October	Philippines (F)	68.0	kappa/iota	0.70	kappa/iota (mu)
	K. alvarezii (Tz)	-	Winter	Tanzania (F)	18.7	kappa/iota	0.69	kappa/iota (mu)
	K. alvarezii (M1)	-	2 weeks ⁽³⁾	Mexico (C)	58.1	kappa/iota	0.80	kappa/iota (mu/nu)

Family	Species	Lifecycle phase	Harvest Season	Origin	Carrageenan			
					Yield ⁽¹⁾	Alkali-extracted	Iota/kappa ratio	Native ⁽²⁾
	K. alvarezii (M2)	-	4 weeks ⁽³⁾	Mexico (C)	60.2	kappa/iota	0.75	kappa/iota (mu)
	K. alvarezii (M3)	-	6 weeks ⁽³⁾	Mexico (C)	62.4	kappa/iota	0.76	kappa/iota (mu)
	K. alvarezii (M4)	-	8 weeks ⁽³⁾	Mexico (C)	48.0	kappa/iota	0.80	kappa/iota (mu/nu)
	K. alvarezii (P1)	-	2 weeks ⁽³⁾	Panama (C)	-	-	0.59	kappa/iota (mu)
	K. alvarezii (P2)	-	3 weeks ⁽³⁾	Panama (C)	-	-	0.66	kappa/iota (mu)
	K. alvarezii (P3)	-	4 weeks ⁽³⁾	Panama (C)	-	-	0.65	kappa/iota (mu)
	K. alvarezii (P4)	-	5 weeks ⁽³⁾	Panama (C)	-	-	0.70	kappa/iota (mu)
	K. alvarezii (P5)	-	6 weeks ⁽³⁾	Panama (C)	-	-	0.67	kappa/iota (mu)
	K. alvarezii (P6)	-	7 weeks ⁽³⁾	Panama (C)	-	-	0.71	kappa/iota (mu)
	K. alvarezii (P7)	-	8 weeks ⁽³⁾	Panama (C)	-	-	0.60	kappa/iota (mu)
	Kappaphycus striatum	-	Late Spring	Madagascar (F)	75.6	kappa/iota	0.66	kappa/iota (mu)

Ph – the Philippines; Tz – Tanzania; M – Mexico; P – Panama; C – Experimental Cultivation; F – Farmed; W – Wild; T – Tetrasporophyte; FG – Female Gametophyte; G – Gametophyte; NF – Non-fructified thalli; 1 – Yield expressed as percentage of dry weight; 2 – Composition determined by FTIR-ATR and FT-Raman analysis of native carrageenan or ground seaweed samples; the carrageenans are identified according to the Greek lettering system; the letters between parentheses () correspond to the biological precursors of the carrageenans, present in native samples (or ground seaweed); 3 – Carrageenophytes subjected to increasing duration of culture; 4 – The ratio between 845 and 890 cm^{-1} absorption bands in FTIR spectra was calculated and used as a parameter to determine the degree of the kappa/beta hybridization.

However, the monocultures of some carrageenophytes (namely *Kappaphycus alvarezii*) have several problems due to environmental change and also diseases. The problems with ice-ice and epiphytes have resulted in large scale crop losses [89-91].

CONCLUSION

In addition to their ecological importance, seaweeds exhibit original and interesting nutritional properties. From a nutritional standpoint, the main properties of seaweeds are their high mineral (iodine, calcium) and soluble dietary fibre contents, the occurrence of vitamin B₁₂ and specific components such as fucoxanthin, fucosterol, phlorotannin. If more research is needed to evaluate the nutritional value of other marine algae (e.g. *Grateloupia* spp., *Bonnemaisonia* spp., *Delesseria* spp., etc.) seaweeds can be regarded as an under-exploited source of health benefit molecules for food processing and nutraceuticals industry.

The potential for commercialization of seaweed based, antioxidant compounds as food supplements or nutraceuticals ensures continued dedicated efforts to eventually develop

functional, condition-specific, antioxidant products. Seaweeds are indeed suitable natural agents for producing and delivering these products based on the multi-functional aspects of secondary seaweed metabolites and the presence of a wide variety of associated non-toxic antioxidants [60, 92]. Such relatively non-toxic associations can enhance the synergistic effects of multiple antioxidants and provide buffering capacity if necessary for those compounds which may have been intentionally increased. Algae are efficient harvesters and proficient managers of electromagnetic energy and as highly nutritional foodstuffs, can be regularly consumed without fear of metabolic toxicities. As part of a balanced diet, seaweeds can provide fibre, protein, minerals, vitamins and low fat carbohydrate content [93]. The versatility of algae as food allows consumption in fresh, dried, pickled or cooked forms and as a component in a wide assortment of other products. Cornish and Garbary [94], in the review “Antioxidants from macroalgae: potential applications in human health and nutrition”, advocates the regular consumption of a variety of marine algae, primarily for their anticipated *in vivo* antioxidant capacities and associated synergistic effects.

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