# Chapter 9
# Prospect of Marine Algae for Production of Industrially Important Chemicals

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## 9.1 Introduction

Marine algae are simple, non-flowering plants with diverse group, consisting of unicellular (3–10 μm) to multicellular forms (kelps up to 70 metres). In the marine environment, they play an important role as a source of food and forming habitats. The origin of alga date back to several million years and becoming the oldest member in the kingdom of plant. As a largest primary producer in the marine environment, they support life in the marine ecosystem through the production of oxygen, by building food webs, and by providing habitats for different organisms. More than 90 % of global photosynthesis is contributed by algae and in the marine ecosystem algae are one of the leading primary producers. They consist of diverse group of large macro and micro algae. Marine microalgae include blue green algae and phytoplanktons. Marine macroalgae (seaweeds) are taxonomically diverse group of plants from which the terrestrial plants diverged over five hundreds millions years ago. As a plant, seaweeds have chlorophyll but do not have real stems, roots, leaves, and vascular tissue. They form an important food source for fishes, invertebrates and also providing breeding ground for several marine organisms. Microalgae are distributed throughout the ocean. Macroalgae mainly grow in the littoral zone, where they are constantly exposed to diverse fluctuating environmental conditions like oxidative stress, temperature and salinity which make them have great adaptations. So, they synthesize numerous valuable antioxidants including carotenoids, tocopherol, ascorbic acid, chlorophyll derivatives, phlorotannins, polyphenols and mycosporine-like amino acids. Marine algae are also a significant source of minerals, vitamins, proteins, fibres and poly unsaturated fatty acids. The beneficial effects

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upon the consumption of marine algae have also been demonstrated in different investigations.

Historically, the people living in coastal area used algae for long time as food, minerals, medicine, insulation, fertilizer and fodder. In Asia, seaweeds are the common ingredients in cuisine, but in western the direct consumption is less common. The food products, including nutraceuticals and functional foods are the largest market. Marine algae used in the human consumption as well as industries are mainly obtained from natural environment and when demand exceeds the availability they are produced through aquaculture. They produce plethora of industrially important chemicals. Now, marine algae have turned into a multibillion dollar industry. The most important industrial chemicals extracted from marine algae include agar, carrageenan, alginates, ulvan, furcellaran, hypnean, funoran, iridophycan, phyllophoran, laminaran, fucoidan and mannitol. Marine algae produce diverse fascinating metabolites with novel structures and biological activities. The isolated marine algal natural products include carotenoids, polyketides, polyphenols, peptides, halogenated compounds, fatty acids, steroids, lectins, etc. These different compounds exhibit diverse biological activities against several disease causing agents. They also become an excellent source of bioenergy as well as biofertilizers. The biofertilizers derived from marine algae form great biofertilizers and improve the soil quality and yields considerably. algae are raw feedstock for different biofuels and bioplastics production. In this chapter, we review the useful applications of marine algae in the production of industrially important chemicals.

## 9.2 Classification of Marine Algae

Marine algae are the photosynthetic organisms living in the marine environments. The photosynthetic mechanism of marine algae is like that of plants in terrestrial environment. The aquatic plants are more effective in the conversion of solar energy into biomass. They receive nutrients directly from the surrounding water through their tissues.

### *9.2.1 Microalgae*

Marine microalgae include diatoms, dinoflagellates, green algae and blue-green algae. They occupy the bottom of the food chain. Even though, the estimated diversity is about 200 to 800 thousand species, only a fraction have been described (35,000). They are one of the important sources of food for various organisms in the marine environment. Marine environment represents the majority of algae classes.

### *9.2.2 Macroalgae*

Macroalgae (seaweeds) can be grouped into three different classes based on their pigmentats as *Chlorophyceae, Phaeophyceae* and *Rhodophyceae*. The phycoerythrin and phycocyanin are responsible for the red colour in Rhodophyta, chlorophyll *a* and *b* present in the higher plants are responsible for the green colour in Chlorophyta, fucoxanthin and xanthophyll carotenoids are responsible for the brown colour in Phaeophyta. In general, brown seaweeds (30 cm to 70 metres) are larger than green and red seaweeds (few cm to about one metre). The Rhodophyceae sometimes appears as purple or brownish red in colour. In marine environment seaweeds are a potential renewable resource and they consist over 6000 species.

## 9.3 Industrial Chemicals

### *9.3.1 Scope of the Marine Algae Chemical Industry*

Marine algae used in the industries are exploited either from natural environment or from cultivated crops. The rapid increase of industrial applications of algae and their products has escalated the aquaculture seaweed production. More than thirty five countries across the world (cold to tropical waters) are involved in commercial algal exploitations. The overall value of the seaweeds have been estimated at US$10 billion per year through the products of direct or indirect human uses (Bixler and Porse, 2011; FAO, 2013). The total production of macroalgae rises every year about 5.7 % and in 2011, from the natural and farming more than eighteen million tons were produced. Of these, over 96 % was produced through aquaculture and Asian countries contributed over 99 % of the total biomass (FAO, 2014). The global production of seaweeds by cultivation constitute around 98 % represented by five major genera including *Saccharina*, *Undaria, Porphyra, Eucheuma/Kappaphycus,* and *Gracilaria*. Marine algae based chemical industry turned into a multibillion industry because of their wide variety of applications (Fig. 9.1).

### *9.3.2 Phycocolloids (Hydrocolloids)*

Phycocolloids are seaweed colloids made up of simple sugars. These gelling and viscous materials have been extracted from marine algae, especially red and brown algae, for centuries and usually used in food preparations. These materials can form colloidal nature in water. These include red algae derivatives agar and carrageenan and brown algae derivative alginates (Table 9.1). These polysaccharides are important as they exhibit high molecular weights, high viscosity and excellent gelling, stabilizing and emulsifying properties. All are water soluble and are extracted with

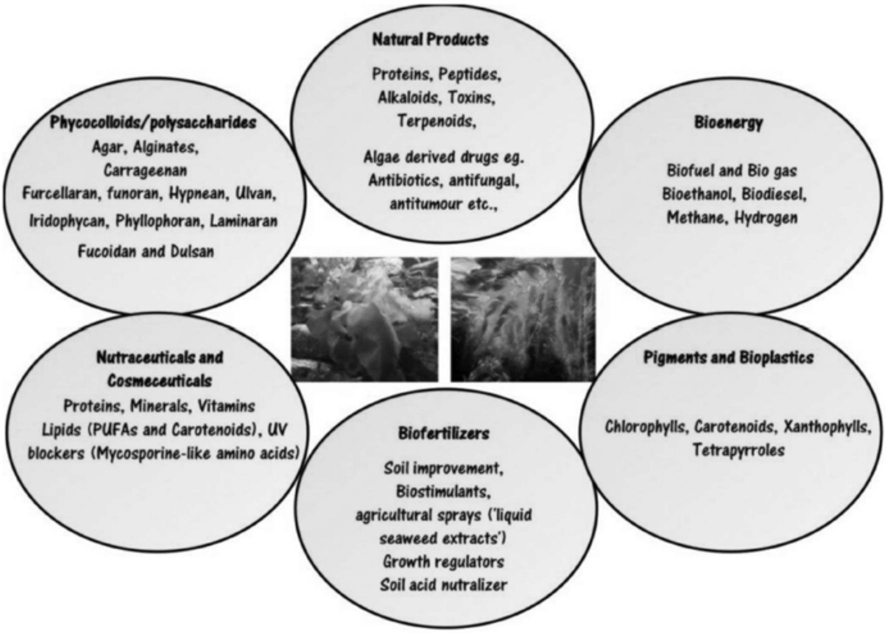


**Fig. 9.1** The applications of marine algae and their chemicals.

**Table 9.1** Marine algae and their hydrocolloids

| Class | Hydrocolloids |
|---|---|
| ***Phaeophyceae*** | |
| *Ascophyllum* | |
| Durvillea | |
| Ecklonia | |
| Eisenia | Alginates |
| Laminaria | |
| Lessonia | |
| Macrocystis | |
| Nereocystis | |
| Sargassum | |
| **Rhodophyceae** | |
| Ahnfeltia | |
| Chondrus | |
| Eucheuma | |
| Furcellaria | Carrageenans |
| Gigartina | |
| Gymnogongrus | |
| Hypnea | |
| Iridaea | |
| Gelidium | |
| Pterocladia | Agar |

hot water or alkaline solution. The four major functions in food applications are thickening, gelling, emulsification and stabilization. The seaweed polysaccharides are economically significant and have diverse applications.

#### 9.3.2.1 Agar

Agar or agar-agar is a gelling hydrocolloid derived from marine algae and is important in the structural features of cell walls in Rhodophyta. Agar producing algae are generally known as agarophytes. The use of agar in culture medium of microbes was the first commercial application other than consumption as food. Seaweeds like *Gelidiales* and *Gracilariales* are important source of agar. Agar is the mixture of agarose and agaropectin (Fig. 9.2). The gelling properties of agar depend on the different factors like molecular weight, type, etc. Seaweeds belonging to the order *Gracilariales* are the largest source of agar. They have broad applications, because of their abundance and chemical characteristics (Abbott, 1996). *Gracilariales* are distributed along the temperate and tropical waters with high efficiency in aquaculture production than *Gelidiales* and at first, it was used to overcome the supply deficiency of *Gelidiales.* The gelling properties of the *Gracilaria* agar is lower than that of the *Gelidium* because of their high sulphate content. In order to increase the gelling ability of this agar it is necessary to remove sulphate groups by alkaline hydrolysis. Mass industrial scale production must have

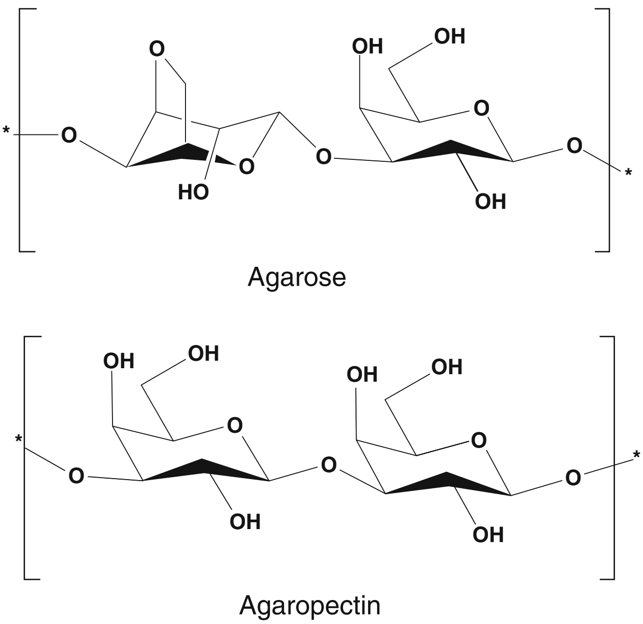


**Fig. 9.2** Structure of agarose and agaropectin.

high attention in the alkali pre-treatment to exclude unwanted contamination through alkaline residues and sodium agaropectinates. In the extraction of the agar from *Gracilaria,* the environmental condition especially temperature and time affect the chemistry of agar. A considerable reduction in the production and the gelling ability are recorded associated to the elevated temperature or long extraction time, which also depends on the species of seaweeds used.

The excellent thickening and gelling properties of this colloid make them industrially important components. It is soluble only in boiling water, but not in cold water. When it is boiled the liquid transforms as a gel having stabilizing and thickening abilities. Among the hydrocolloids it is outstanding because of their gelling strength. The significant properties of agar include great gelling properties at low concentration, great transparency and viscosity in solution etc. Quality of agars are determined based on their gel strength and the international market referred the high quality agar with gelling property greater than 700 g $cm^2$ in a 1.5 % solution (Armisen, 1995). So, the agar with less than this value will be used in traditional applications and also used in some industrial applications like food, cryoprotectants, fat replacer, etc. Generally, in a solution the concentration of agar is directly proportional to its gelling strength. The loss of water and changes in their physical properties are associated with the lowering of agar. To produce gel with reduced loss of water, low gelling agar is important.

Agar is used in biotechnological (electrophoresis, chromatography etc.), medical (as laxative, anticoagulant etc.) and dental (impression materials) applications. It is also used in plant tissue culture, biochemistry, molecular biology and drug industry. Gelling properties of agar at moderate temperatures make it much useful in bakery products, confectionery making, and in puddings, creams, pastries, desserts, salad dressings and jellied products. Agar is used in different food items like milk products, confectionery, sweets, beverages, bakery, meat products, canned meats and fish, and as a clarifying agent in wines and beers. It is also used in the preparation of microbial culture media, tissue culture of plants, therapeutic agents to treat some diseases, medicine carrier, suspension agent of barium sulphate in radiology, stabilizer in cholesterol solutions, moulding, chromatography, electrophoresis, and in several types of emulsions as a suspension agent.

#### 9.3.2.2 Alginate

Alginates (algin) are linear polyuronic acid hydrocolloids. It is a glycuronan of significant commercially important polysaccharide derived from brown seaweeds. The cell wall and in the matrix of the brown algae contain alginates; it gives both mechanical strength and flexibility to the algae. Even though, some bacteria contain polysaccharides similar to the alginates, brown algae are the important source of alginates. About 40 % of the dry weight of brown seaweeds contain alginates. Alginates consist of (1→4) linked β-D-mannuronic acid (M) and α-L-guluronic acid (G) residues (Fig. 9.3) of differing composition and structure. The sequence of monomers widely change with different species.

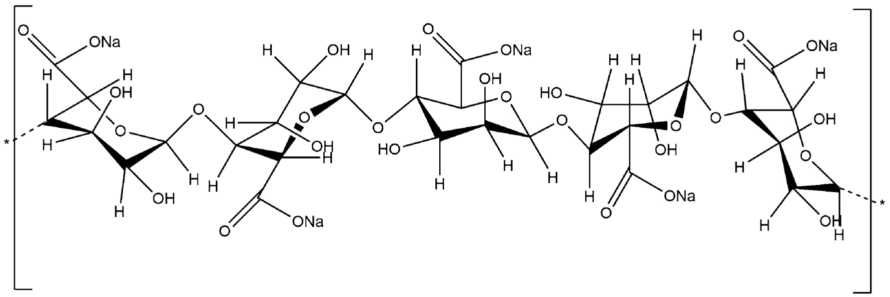

**Fig. 9.3** Bonding of alginate repeating units mannuronate (M) and guluronate (G).

The major seaweeds used in the commercial productions include *Ascophyllum, Laminaria, Lessonia, Ecklonia, Macrocystis* and *Durvillea*, where they reach up to 40 % of the dry weight (Draget et al., 2002; Rinaudo, 2007). In water, they form viscous gel; they are also used as a stabilizer, binder, emulsifier etc. Its molecular weight ranges between 500 and 1000 kDa. The solubility of alginates depends on the different factors like pH, concentration, presence of solution ions and divalent ions. High content of alginates were observed in the seaweeds distributed in turbulent waters when compared to the normal environments. The chemical structure of the alginates varies between brown algae of genus. As the properties of alginate differ between seaweeds, the selection of candidate species for alginates extraction depends on both availability as well as the potential of the alginate production by the species. It is believed that the alginate act as a structure-forming component in brown seaweeds. The gelling strength of alginate depends upon its quality. Brown seaweeds contain alginic acid as calcium salt of alginic acid. The important properties of alginic acids are their high viscosity in solution, gel forming properties in divalent or multivalent cations, biocompatible and adhesive nature. Their capability of water retaining, gelling, viscosifying, and stabilizing properties determine their industrial applications. However, alginates do not have any nutritional value; they are often used as additives to modify and stabilize its texture. They are widely used as stabilizers, viscosifiers, and gelling agents in diverse products such as food, beverages, pharmaceuticals, cosmetics and various biotechnology industries. Moreover, based on their biochemical and biophysical properties several new types of food application are also emerging continuously. The other applications of alginate include pharmaceutical preparations such as Gaviscon, Bisodol, Asilone and in impression-making material in dentistry and prosthetics.

#### 9.3.2.3 Carrageenan

The phycocolloid carrageenan is a linear sulphated polysaccharide derived from red algae of the genus *Gigartina, Hypnea, Eucheuma, Chondrus* and *Iridaea*. The content largely depends on the type of the seaweeds. Carrageenan can be classified in to three types (Fig. 9.4) based on their structure and chemical properties viz., kappa-carrageenan has one sulphate group per disaccharide (rigid and brittle gel, thermo-reversible, high gel strength, showing syneresis), iota-carrageenan has two sulphates per disaccharide (elastic gel, thermo-reversible, no syneresis, thixotropic) and lambda-carrageenan has three sulphates per disaccharide (cold soluble, non-gelling, high viscosity). They are composed of a linear galactose backbone with a varying degree of sulfatation (between 15 % and 40 %). The different carrageenan types vary in composition and conformation, resulting in a wide range of rheological and functional properties.

The carrageenan in industrial seaweeds content varies from 30 % to 60 % of dry weights. It totally depends upon the species of seaweeds and the environmental conditions, such as luminosity, nutrients, water temperature and oxygenation. Some species of seaweeds produce mixed type carrageenan such as kappa/iota, kappa/lambda or iota/lambda. The kappa-type carrageenan are extracted from seaweeds *Hypnea musciformis*, *Gigartina stellata*, *Eucheuma cottonii*, *C. crispus* and *Iridaea*. Seaweed species *G. teedi* and *E. spinosum* produce iota-type carrageenan. The species that produce lambda type carrageenan generally belong to the *Gigartina* class.

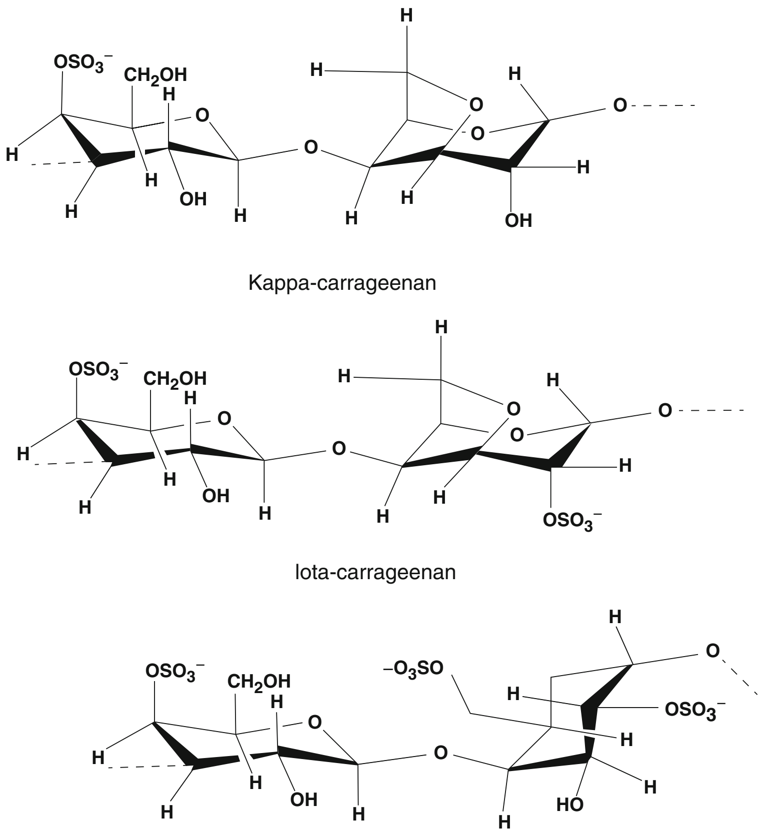


**Fig. 9.4** Different types of carrageenans.

Carrageenans are used in various food items as gelling, thickening, and stabilizing agents. It is also used as a gelling agent to increase viscosity in different foods, clarifier to remove haze-causing proteins in beer and processed meats, stabilizer to prevent constituents separating in toothpaste, ingredient in the encapsulated gel of fruit gushers, thickener to cause foam to become sticky in fire fighting foam, thickener in shampoo, in air freshener gels, in the ancient art of paper and fabric marbling, in shoe polish to increase viscosity, in biotechnology to immobilize cells/enzymes, in pharmaceuticals as an inactive excipient in pills/tablets, plant milks and soy milks used as a thickening agent, in diet sodas as texture and suspend flavours enhancer, pet foods and cosmetics.

## *9.3.3 Other Seaweed Hydrocolloids/Polysaccharides*

### 9.3.3.1 Dulsan

The marine red alga *Rhodymenia palmate* also known as the dulse is the source of Dulsan. Dulsan does not form gels and it is also water soluble and acid hydrolysis gives principally D-xylose, but also galactose and glucose with (1–3) and (1–4) linkages. It is well known as food. It also has been an important source of fibre throughout the centuries.

### 9.3.3.2 Fucoidan

Fucoidan is one of the well studied fucans from brown algae, which was first isolated by Kylin in 1913. These sulphated polysaccharides are composed of a fucose backbone (Fig. 9.5). The total content of fucoidan may vary between 20 and 30 % of algae dry weight, and it depends on the type of seaweed. There are two different forms of fucoidan such as F-fucoidan, which is >95 % composed of sulphated esters of fucose, and U-fucoidan, which is approximately 20 % glucuronic acid. The sulphated polysaccharide in fucoidan consists mainly of L-fucose units; at the same time it can also contain minor amounts of sugars such as galactose, mannose, xylose, or uronic acid and sometimes proteins. This is varying between different species. It has an α-(1,3)-backbone of repeating disaccharide units of α-(1,3)- and α-(1,4)-linked fucose residues. *Fucus vesiculosus* derived commercially available fucoidan is a heterogeneous mixture of more than 15 different fucans with varied properties of industrial monosaccharide moieties. Fucoidan occurs in all brown algae in different ratio and it is in the intercellular tissues and is considered to be a substance used by the weeds to protect themselves against the effects of drying out when exposed. It is extremely viscous after extraction, even in very low concentration, but is highly susceptible to aging, diluted acids and bases. This instability and its quality inconsistency have prevented its commercial significance of fucoidan. It is used as an ingredient in some dietary supplement products. Fucoidan has been consumed for a

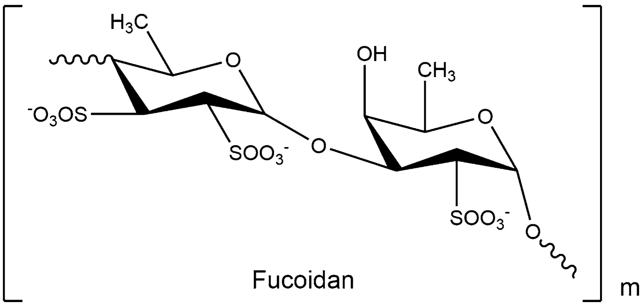


**Fig. 9.5** Structure of fucoidan.

long time in Japan, China, and Korea as part of whole seaweed, and it is used as nutraceuticals in Australia and the United States. The fucoidan materials are also used in cosmetics because their ability to absorb directly by the human skin with the following different effects includes whitening, preserving moisture, removing freckles. It has also significant medical applications and the higher sulphation increases its therapeutic potential. It also acts as modulator of coagulation, as an alternative to the anticoagulant heparin. Fucoidan exhibits many biological activities which include anti-inflammatory, anticell proliferation, antiadhesion, antiviral, anticoagulant, antitumour and antiviral activities.

#### 9.3.3.3 Funoran

Funoran is a sulphated galactans extracted from the red seaweed, *Gloiopeitis* species and distributed along the coasts of Japan, China and Pacific coasts of North America. Funoran isolated from *G. furcata* consists of several components which can be fractionated in terms of the solubility of their quaternary ammonium salts in aqueous potassium chloride. Apart from this main structure, an unfractionated funoran from a closely related species, *G. cervicornis*, has been proposed to possess a precursor moiety that is converted into the agarose sulphate under alkaline conditions. Funoran is marketed in the form of dried condition and not extracted. The mixing of whole seaweed in hot or lukewarm water gives a clear, viscous colloidal solution of excellent adhesive and sizing properties. It is used as an adhesive in several Japanese industries such as pottery and textiles. The major uses of funoran are as a constituent in hair waving and hair dyeing preparations. It is also a paper and textile sizing agent, and has widespread uses as a household adhesive.

#### 9.3.3.4 Furcellaran

Furcellaran also known as Danish agar is an anionic sulphated polysaccharide extracted from the red alga *Furcellaria lumbricalis* and *F. fastigiata*. These species are distributed in the cold waters around Northern Europe and Asia. It is currently considered to be a copolymer of β- and κ-carrageenan and usually represented structurally as a repeating unit of alternating 3-linked β-D-galactopyranose and 4-linked α-D-galactopyranose residues, with part of the latter existing as a 3,6-anhydro derivate. The hydroxyl groups in polysaccharide chain may be substituted (sulphated, methylated, etc.) and other monomer residues such as xylose and glucose may be found. It is a polyelectrolyte that carries sulphate groups and is negatively charged over a wide range of pH. The charge density is usually one sulphate per three or four monomer units. The formation of 3,6-anhydro-α-D-galactose units from α-d-galactose 6-sulphate residues by alkaline treatment is an important and well known reaction of the carrageenans. After alkali treatment of the algae, the polysaccharide is isolated by using hot water. Furcellaran contains significant sulphate (12 to 16 %). It is composed of D-galactose (46 to 53 %), 3,6-anhydro-D-galactose (30 to 35 %), and sulphated portions of both of these sugars (16 to 20 %). It is used commercially to enhance gelation behaviour and, in the laboratory, for the quantitative determination of α-galactose 6-sulphate residues. Furcellaran is also used as a natural colloid, gelling agent, viscosity control agent primarily in food products, pharmaceuticals, in products for diabetics, proprietaries for reducing excess body weight, toothpastes, as carrier for food preservatives, bactericides and in bacteriological culture media.

#### 9.3.3.5 Hypnean

Hypnean is derived from *Hypnea musciformis* and is often considered to be a type of carrageenan. Species of these seaweeds are fairly abundant in tropical waters, notably southern Florida, the Caribbean, the Gulf of Mexico, the northeast coast of Brazil, Australasia, parts of the South China Sea and South Africa and Gulf of Oman. The gel strength is far exceeding that of other phycocolloids. In addition, properties of hypnean are susceptible to a high degree of control and chemical modification. The high commercial importance of this phycocolloid is because of their ability to form, often in combination with other components, gels with great firmness and elasticity. Hypnean is mainly used for their gelling properties for food applications and they are known as a vermifuge in Indonesia, Greece and Turkey.

#### 9.3.3.6 Iridophycan

Iridophycan is extracted from the seaweed species belonging to the genus *Iridea*. These algae are most prevalent in the waters off central California, but also are distributed in the coasts of South Africa, Japan, Chile and the Falkland Islands. It is extracted using boiling water and filtered to isolation. The sulphated galactan gives only D-galactose after hydrolysis. Iridophycan is used as a cold-mix stabilizer, for its adhesive properties, and it prevents the blood coagulation. There are some similarities in properties of funoran and carrageenan. In U.S.A., it has found particularly widespread use as a stabilizer in chocolates and some beverage mixes. It is also used as an excellent multipurpose adhesive and as a paper and textile size. The aqueous extract has pharmaceutical value as an agent to prevent blood coagulation.

#### 9.3.3.7 Laminaran

Laminaran (laminarin) is isolated from species of *Laminaria*, *Ascophyllum* and *Fucus*. The species of *Laminaria* are distributed in the coasts of Norway, Scotland, Ireland, France, Spain and eastern Canada. Laminaran (Fig. 9.6) is a small glucan of 5 kDa with a degree of polymerization (DP) between 20 and 25. Among the two types of Laminaran based on the solubility, the soluble form is completely soluble in cold water and insoluble form only soluble in hot water. It consists of approximately upto 35 % of the dried weight of the algae. The solubility of laminaran increases when the degree of branching increases. There are two types of laminaran described, one with chains that are terminated by D-mannitol residues (M-series) and another type with chains terminated by D-glucose residues (G-series). In *Laminaria* and *Fucus* species, 40–75 % of the reducing end groups are linked to one of the primary hydroxyl groups of D-mannitol. Laminaran does not form gel or any viscous solution and its potential applications are in the medical and pharmaceutical uses. The content of Laminaran varies between species and seasons. The (β1-3,1-6)-linked D-glucans have the ability to enhance and stimulate the immune system of humans. The laminaran from *Alaria praelonga* or *L. coriacea* promotes adhesion of human skin fibroblast cells, and increase proliferation of human osteoblast cells. It was projected as elicitors of phytoalexins and flavonoids in alfalfa cotyledons. It is also used as a safe surgical dusting powder, and may have value as a tumour-inhibiting agent and, in the form of a sulphate ester, as an anti-coagulant. Laminaran

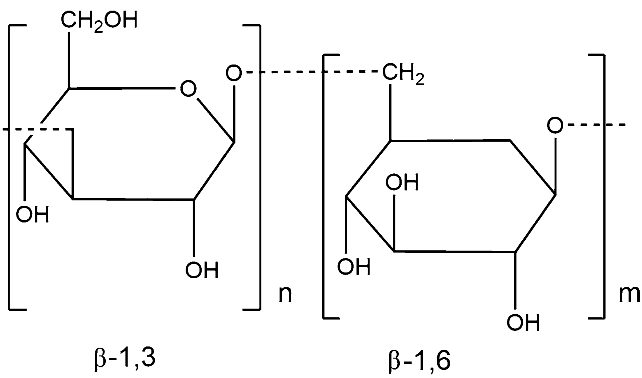


**Fig. 9.6** Structure of laminaran.

has shown various biological activities which include anti-apoptotic and anti-tumoral activities.

#### 9.3.3.8 Phyllophoran

Phyllophoran is extracted from red seaweeds belonging to the genus *Phyllophora*. These species are distributed in coasts of temperate and cold seas, including the eastern and western Atlantic, Baja California and Mexico, but abundant in the Black Sea. The properties of Phyllophoran are intermediate between those of agar and carrageenan.

#### 9.3.3.9 Ulvan

Ulvales (Chlorophyta) are very common seaweeds distributed worldwide. Ulvales (*Ulva* and *Enteromorpha* sp.) are the source for complex sulphated polysaccharide ulvans, which are present in the cell walls, and represent a potential source of new functional biopolymer due to their peculiar composition and structure. The name ulvan is derived from the original terms ulvin and ulvacin introduced by Kylin. They represent 8–29 % of the algae dry weight. The major repeating disaccharide units reported are ulvanobiouronic acid 3-sulphate types containing either glucuronic or iduronic acid (Fig. 9.7). Moreover, minor repeat units have been reported that contain sulphated xylose replacing the uronic acid or glucuronic acid as a branch on *O*-2 of the rhamnose-3-sulphate (Lahaye and Ray, 1996). It contained 23 to 35 % sulphate ester groups, 10 to 15 % uronic acid, and 3.8 to 4.5 % protein. The variation in sugar composition can have methodological, taxonomic, and/or ecophysiological origins. It is an economical value gelling polysaccharide which forms a weak gel at 1.6 % (w/v) in deionized water. Ulvan inhibit the activity of cellulase, which indicates a protective role towards cell wall amorphous α-cellulose, protecting it from marine bacterial attack. It is also used as a nutritional dietary fibre. Ulvan exhibits different pharmacological properties like antiviral, anti-oxidant,

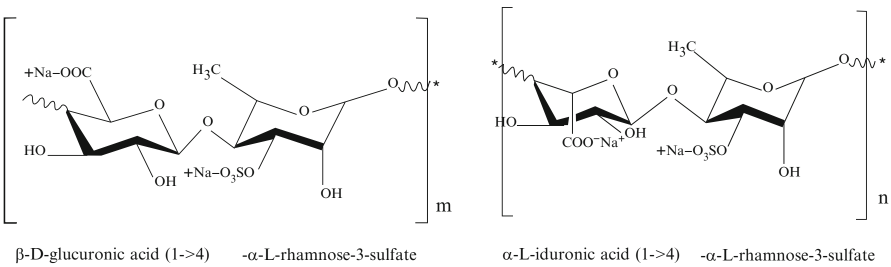


**Fig. 9.7** Structure of ulvan.

anti-coagulant, anti-hyperlipidemic, immunostimulating and anti-proliferative towards cancer cells.

### 9.3.4 Bioactive Natural Products

Nature is continuously a broad arsenal of structurally diverse and pharmacologically active compounds that are used as highly effective drugs or lead structures for the development of novel synthetically derived drugs to combat a multitude of diseases. Natural products have been the most successful source of potential drug leads. It has estimated that over 50 % of the current drugs in use are either harvested from natural sources or from synthetic compounds based on natural products. Approximately 60 % of all drugs now in clinical trials are either natural products or their derivatives. The oceans, covering more than 70 % of the earth's surface, represent an enormous resource for the discovery of novel chemotherapeutics. The biodiversity in marine environment is remarkably high and their unique organisms also are exclusively living in sea. Marine algae represent a relatively untapped resource for discovering novel natural products. In order to survive in the highly competitive environments, marine algae have developed unique defense strategies that result in a tremendous diversity of compounds from different metabolic pathways.

The emergence of drug resistant pathogens and new diseases necessitated finding out novel drugs. The discovery of this chemical diversity to support finding of novel drugs is important. Marine algae offered a wide variety of novel natural products with different biological activities. They live in an unique environment, where they compete for space and nutrients and have the great adaptation strategy for living in different physico-chemical conditions. So, they have evolved with a wonderful defence strategy, and produce novel secondary metabolites (natural products). Generally, the production of bioactive substances differ in the same species of seaweed which depends on factors like environmental conditions, seasons, geographic locations, the stage of life cycle, and part of the seaweed. The synthesis of secondary metabolites mostly for chemical defence against the biotic pressure by predators, consumers, epibionts and the abiotic pressure from the surrounding environment (e.g. desiccation, nutrient availability, UV) can influence their synthesis.

The role of these secondary metabolites in marine algae is defense against herbivores, fouling organisms and pathogens. They also play a role in reproduction, protection from UV radiation and as allelopathic agents. Eventhough, the secondary metabolites are varied genetically and environmentally, transplant experiments showed that environmental conditions are able to alter the concentrations of secondary metabolites, but the types of compounds are genetically fixed. The production of secondary metabolites in seaweeds is different in their life history and maximum concentration of defense chemicals were found in new Halimeda species. Even though, marine algae offered huge number of chemicals which still remained largely unexploited. The bioactive compounds isolated from marine algae include proteins, peptides, terpenoids, phlorotanins, fucoidans, sterols and glycolipids, and the crude extracts or the compounds from algae exhibits a wide range of pharmacological properties which include anticancer, antibacterial, antifungal, antiviral, anti-inflammatory, antcoagulant, anti-oxidant, hypoglycaemic, hypolipidemic, anti-melanogenic, anti-bone loss, hepatoprotective and neuroprotective activities. Marine algae are a potential renewable resource in the marine environment. They are an excellent source of bioactive compounds, carotenoids, dietary fibre, protein, essential fatty acids, vitamins and minerals.

### *9.3.5 Nutraceuticals*

Seaweeds are also commonly known as sea vegetables. Seaweeds are extensively used as food by coastal peoples, particularly in East Asia such as China and Vietnam, but also in some parts of Europe including Scotland. An archaeological investigation in Chile recoded that seaweeds have been used by humans for about 14,000 years. The use of seaweeds as food for their richness in protein, vitamin, trace minerals, and dietary fibre content has gained importance in many countries for exploitation of this natural renewable resource. Some food products directly made from seaweeds have a long tradition, and it was consumed during the fourth century in Japan and the sixth century in China (Tseng, 1987; Mc Hugh, 2003). The Japanese has the world's largest seaweed consumption per capita, with 10–15 % of their diet consisting of algae, and is also associated with a significantly lower rate of cancer, thyroid diseases, heart disease and dementia than western cultures. Marine algae are still considered an underexploited plant resource despite being used in diets and traditional remedies for centuries. They are also referred as treasure house of novel healthy food ingredients and biologically active compounds, due to their phenomenal biodiversity. In addition, they are a rich source of dietary fibre (DF), with a content ranging from 33 to 50 g/100 g dry weight placing them as an important candidate in the development of new functional foods.

The studies on nutritional potential of marine algae showed that they contain great nutritional potential and it can, therefore, be used as alternative dietary sources. The nutritional composition can vary with season, environment, and geographical regions. Moisture content of fresh seaweed is high and can account up to 94 % of the algal biomass. That of ash content is up to 55 % dry weight, macrominerals (Na, K, Ca, Mg) and trace elements (Fe, Zn, Mn, Cu, etc.), and it is much higher in algae than in terrestrial plants. The minerals are attributed to various ions associated with charged polysaccharides. The bioavailability of minerals depends on the type of linkage between the polysaccharide and the mineral, and also on polysaccharide digestibility. The halogenated compounds such as chloride are naturally produced by red and brown seaweeds. Generally the protein content is high and it also depends on the type of seaweeds used. The green seaweeds' protein content ranges from 8 to 26 %, in brown seaweeds it ranges from 5 to 26 % and in red seaweeds from 7 to 47 % algal dry weight.

Most of the seaweed contain all essential amino acids and they are also rich source of the aspartic and glutamic acid. Amino acid score of a seaweed protein ranges from 60 to 100 and this is higher than that of the proteins in cereal and vegetables. The protein content in marine algae is comparable to those found in high-protein vegetables such as soybeans. In the cultured seaweed *Saccharina latissima* the protein content was higher than the wild seaweeds. The fat content is generally lower than 2 % of dry weight and there are also some exceptions. But, this fat is high-quality oil, comprising mainly essential and polyunsaturated fatty acids (including omega-3 and omega-6). Marine algae are an excellent source of dietary fibre with a high ratio of soluble to total dietary fibre fraction. The dietary fibre in seaweeds is mainly formed from nondigestible polysaccharides which are resistant to human digestive enzymes. Majority of dietary fibre from edible seaweeds comprises soluble anionic polysaccharides that are scarcely degraded or not fermented at all by the human colonic microbiota.

### *9.3.6 Cosmeceuticals*

The seaweed extracts are often found on the ingredients of cosmetic packages, particularly in face, hand and body creams or lotions. This usually refers to the use of phycocolloids alginate or carrageenan in the product. It is useful in various ways, including relief of rheumatic pain or the removal of cellulite. The marine algal compounds such as phlorotannins, sulphated polysaccharides and tyrosinase inhibitors are useful in cosmeceutical applications. The bioactive substances isolated from marine algae have diverse functional roles as a secondary metabolite, and these properties can be utilised in the development of cosmeceuticals. The fucoxanthin isolated from *Laminaria japonica* has reported to suppress tyrosinase activity in UVB-irradiated guinea pig and melanogenesis in UVB-irradiated mice. Fucoxanthin treated orally, significantly suppressed skin mRNA expression related to melanogenesis, suggesting that fucoxanthin negatively regulated melanogenesis factor at transcriptional level. Brown algal secondary metabolites phloroglucinol exhibits tyrosinase inhibitory activity because of their ability to chelate copper in this enzyme. The brown algae polyphenols, phlorotannins act as potential cancer chemopreventive agents against photocarcinogenesis and other adverse effects of UVB exposure. The majority of the phlorotannins and sulphated polysaccharides reported were from the members of the species *Ecklonia* and *Eisenia*.

### *9.3.7 Bioenergy*

The ever rising need of energy is linked with rapid increases in industrialization and population. The depletion of fossil fuel has led to a search for alternate bioenergy sources. At present, throughout the world, energy crisis and environmental issues are the most important concern. Approximately 81 % of the energy supply is from fossil fuels, followed by 16 % renewable energy and 2.8 % nuclear energy. The utilization of fossil fuel as energy has disadvantages and affect the environment (Demirbas, 2010). Another issue is their uneven distribution in the world where 63 % of the global petroleum fuel resources are located in the Middle East with equity, environmental, economic and geopolitical implications. So, the biomass-based energy can serve as an alternative energy source to meet the present and future demand, including transportation fuel, although presently only about 0.6 % of transportation fuel is supplied as biofuels. Major sources of fossil fuels are petroleum, natural gas, coal, hydro and nuclear. Energy from the biological sources is one of the great alternatives to overcome the negative environmental effects like greenhouse gas emissions and substitute of fossil fuel. In addition, biodiesel is non-toxic and biodegradable with low pollutant. Generally, crops such as soya bean, jatropha, castor, coconut, animal fats and fish oils have been used to produce biodiesel but the price and supply of those sources are unstable. Marine algae are identified as one promising source of biofuels and they would be harvested and turned into a carbon neutral fuel source. So, the use of algae can be a suitable alternative as a potential source of the future renewable bioenergy.

In the past several years, as global petroleum supplies have diminished and serious environmental problems have arisen from greenhouse gas emissions, renewable energy sources have received much interest as a solution to the large reliance on fossil fuels and nuclear power. The renewable green energy includes wind, solar, tidal, biomass, and geothermal energies. In these sources, algae, in particular, are now considered one of the most important sources of biomass, because they can provide a significant contribution to liquid fuels. Marine algae are the source for the production of biofuels such as biodiesel, ethanol, and hydrogen gas (Table 9.2). The use of marine biosources as an alternative feed stock for bioethanol and biogas production could also reduce environmental problems in the sea because some sea pollutants could be utilized as bio-ethanol biomass. The algae contain carbon, hydrogen, oxygen, nitrogen and phosphorus. Typical ratios of these elements are reported as 106:263:110:16:1. They contain both carbohydrates and lipids. Carbohydrates can be converted to bioethanol through fermentation. Algal lipids can be converted to biodiesel through transesterification. The algae as biofuel feedstock provide economically and environmentally beneficial effects such as: they do not compete with food and water resources; they grow significantly faster than land crops used for biodiesel and they can treat wastewaters; they are carbon-neutral and can capture carbon dioxide; their low-temperature fuel properties and energy density of algae fuel make it suitable as jet fuel; they ensure a continuous supply; they can also provide valuable by-products like protein-rich feed for farm animals, organic fertilizer, and feedstock for producing biogas.

The application of microalgae as a source of fuel is not new, but it is now being taken seriously because of the increasing price of petroleum fuel, more significantly, the emerging concern about global warming that is associated with burning fossil fuels. Nowadays, the potential value of microalgal biodiesel is widely recognized. Bio-refinery of microalgae can be used to reduce the cost of making microalgal

**Table 9.2** Biochemical composition of some marine algal biofuel feedstock (% w/w)

| Algae | Carbohydrate | Protein | Lipid |
|---|---|---|---|
| Macroalgae | | | |
| *Caulerpa lentillifera* | 44–46 | 11–12 | 1–2 |
| *Ulva lactuca* | 70 | 7.06 | 1.64 |
| *Eucheuma cottonii* | 35–36 | 10–12 | 1–2 |
| *Gracilaria cervicornis* | 63 | 19.7 | 0.427 |
| *Hypnea japonica* | 57.4 | 19 | 1.42 |
| *Sargassum vulgare* | 61 | 13.6 | 0.491 |
| *Laminaria hyperborea* | 50–52 | 8.9 | <1 |
| *Ascophyllum nodosum* | 45–55 | 4.8–9.8 | 1–5 |
| Microalgae | | | |
| *Botryococcus brauni* | 2 | 40 | 33 |
| *Prymnesium parvum* | 25–33 | 28–45 | 22–38 |
| *Isochrysis* sp. | 15–5 | 29.5 | 23.4 |
| *Chlorella vulgaris* | 12–17 | 51–58 | 14–22 |
| *Porphyridium cruentum* | 40–57 | 28–39 | 9–14 |

biodiesel and microalgal-based carbon sequestration technologies cover the cost of carbon capture and sequestration. Generally biodiesel is similar to petroleum-derived diesel in its major characteristics such as cetane number, energy content, viscosity and phase changes and can be blended in any proportion with fossil. It is estimated that the use of biodiesel can decrease approximately by 90 % air toxicity and by 95 % cancers resulting from fossil diesel use. The marine microalgae appear to be one of the important sources to capture solar energy as they are sunlight-driven cell factories that convert carbon dioxide to potential biofuel. Some species contain much higher percentage of oil than conventional oil crops. They can multiply their biomass in few days, whereas higher plants take many months or years. Moreover, their chemical composition can be manipulated by altering the growth environment of the algal species.

The industrial $CO_2$ emission can be used as a source of carbon for algal growth. They can be cultivated in seawater or brackish water, raceway ponds on non-arable land and do not compete for resources with conventional agriculture. Their biomass can be harvested during all seasons. The seaweeds lack lignin but contain high amount of carbohydrates which makes them potentially suitable feedstock for the production of bioethanol. The seaweed phycocolloids can be converted into bioethanol, but direct use of these phycocolloids for bioethanol production will not be economically feasible. The industrial wastes of seaweeds derived from remaining pulp after extraction of the high value polysaccharides, still contain high amount of carbohydrates which may be used as a source of raw material for ethanol production. As the pulp contains high amount of carbohydrates and other organic materials, these can be converted into bioethanol through saccharification and fermentation. Bioethanol production from the seaweeds should be integrated with the higher value components. *Saccharomyces cerevisiae* and *Zymomonas mobilis* are the two most important microorganisms used for bioethanol production, but they have a very narrow substrate range. The *Pichia angophorae* is a more appropriate organism for ethanol production from seaweed. It can utilise both substrates such as mannitol as well as laminaran, simultaneously.

The principle selection of crops for bioenergy production is high growth rate, lower cost and biomass properties (moisture, ash, alkali and sugar contents). The green alga *U. lactuca* has been evaluated as a potential feedstock for energy production in USA since 1978 because of its high growth rate and high sugar contents. *U. lactuca* has been used to produce butanol (4 g $L^{-1}$) in the fermentation broth. Marine algae utilization as a substrate for biogas production is not well practised probably due to the availability of other important economic avenues. The seaweeds can be converted to biofuels by various processes including thermal treatment and fermentation, but the direct route to obtain energy from macroalgae is via its anaerobic digestion (AD) to biogas (~60 % methane). The biochemical conversion pathway is an anaerobic digestion of biomass by methanogenic bacteria, producing a mixture of gases which consist approximately two-thirds $CH_4$, one-third $CO_2$, water vapours and some impurities. Hydrogen is a future energy carrier and the rise in fossil fuel prices and their environmental destruction has drawn attention to renewable energy including hydrogen produced from renewable sources. Hydrogen is a clean and renewable energy source that does not produce $CO_2$ as a by-product, when used in fuel cells for electricity generation. It is evidenced from the recent research that the red algae *Gelidium amansii* and the brown algae *Laminaria japonica* are both potential biomass sources for biohydrogen production through anaerobic fermentation.

### *9.3.8 Pigments*

There are different classes of pigments in marine algae generally occurring in bound and non-bound forms in the cells. Chlorophylls are greenish pigments which contain a porphyrin ring around which are electrons free to migrate. Because the electrons transfer freely, the porphyrin ring has the potential to gain or lose electrons easily, and thus the potential to provide energized electrons to other molecules. This is the fundamental process by which chlorophyll captures the energy of sunlight. On the other hand, carotenoids are usually red, orange, or yellow pigments, do not dissolve in water and must be attached to membranes within the cell. Carotenoids cannot transfer sunlight energy directly to the photosynthetic pathway, but pass their absorbed energy from one chlorophyll molecule to another. For this reason, they are called accessory pigments. The carotenoids are natural pigments derived from five-carbon isoprene units that are polymerized enzymatically to form regular highly conjugated 40-carbon structures (with up to 15 conjugated double bonds). Carotenoids are essential constituents of the photosynthetic organisms, and they are as accessory pigments for light-harvesting processes during photosynthesis, as structural stabilizers for protein assembly in photosystems, and as inhibitors of both photo and free radical oxidation provoked by excess light exposure. In human nutritions some carotenoids offer provitamin A activity and they directly provide photoprotection against UV light photooxidation in the skin. The ketocarotenoid astaxanthin play a key role in the prevention of several human pathological processes, such as skin UV-mediated photooxidation, inflammation, prostate and mammary carcinogenesis, ulcers due to *Helicobacter pylori* infection and age-related diseases. The results of several investigations have confirmed that these compounds can play important roles in prevention (and even treatment) of human diseases and health conditions, e.g., cancer, cardiovascular problems, atherosclerosis, rheumatoid arthritis, muscular dystrophy, cataracts and some neurological disorders. Carotenoids are effective antioxidants, they can quench singlet oxygen ($^1O_2$), suppress lipidperoxidation and prevent oxidative damage. The consumption of carotenoid-rich vegetables and fruits could protect humans against cardiovascular disease, certain cancers and other degenerative diseases as evidenced from several investigations (Hu et al., 2008). The average concentration of carotenoids in most of the algae is only 0.1–2 %, but *Dunaliella* when grown under the right conditions of high salinity and light intensity will produce up to 14 % beta-carotene.

### *9.3.9 Biofertilizer*

Marine algae are used as manure in farming practice by coastal people. As the wet seaweeds are heavy in most part they are used only in farms near to the coastal areas. In some part of the world, seaweeds are mixed with sands and applied in the farms. In Brittany, France, farmers regularly collect algae from over a few hundred kilometres and use in inlands up to a kilometre. Marine algal species *Ascophyllum*, *Ecklonia* and *Fucus* are commonly utilized as fertilizer. They contain comparable amount of nitrogen and potassium like animal manure and organic fertilizers, but the phosphorus content is low. The carbohydrates content in the brown seaweeds are high. So, they are potent candidates in improving the soil quality in various ways like increasing the aeration, retention of moisture etc. "Afrikelp" is commercially available dried seaweed (*E. maxima*) collected from Africa and Namibia.

In the controlling of top soil loss, the brown seaweed *Ascophyllum* is used. They form strong gels when added with calcium, because of the alginate content. Application of seaweed fertilizers showed many favourable results such as increasing health and yield. They also increase the biochemical potential of plants. The seaweed extract contains micro-nutrients, auxins, cytokinins, betaines and other growth promoting constituents. These hormones play an important role in enhancement of cell size and cell division, and together they complement each other as cytokinins are effective in shoot generation and auxins in root development and micro-nutrients improve soil health.

The application of seaweed extracts to the soil, stimulated the plant growth (Blunden, 1971). The yield and quality of the fruits of *Zizyphus mauritiana* increased upon the application of *Sargassum wightii* extracts (Rama Rao, 1991). Seaweed liquid fertilizers improve the moisture holding capacity and also make favourable condition for growth of soil microorganisms. It enhances the soil health by increasing the micronutrients and microbial diversity. The seaweed *Ascophyllum nodosum* extract (0.2 %) sprayed in carrot plants showed significant defence against fungi diseases caused by *Alternaria radicina* and *Botrytis cinerea*. Extract of this seaweed enhances disease resistance in carrot, likely through induction of defence related enzymes, genes or proteins (Jayaraj et al., 2008). The application of seaweed extract as and/or seed treatment exhibited encouraging results on enhancement of vegetative growth and yield of several crops. The efficiency of SLF on seed germination varied between red, brown and green algae, may be because of the variability in the chemical nature between these species. The maximum germination was induced in root and shoot growth in Ragi by liquid fertilizers of *Ulva lactuca, Sargassum wightii* and *Gelidella acerosa*. The extract of *Enteromorpha intestinalis* enhanced the seed germination, root, shoot length and chlorophyll content of *Sesamum indicum*.

The extract of *Gracilaria edulis* (1 %) applied in the soil maximizes the germination, growth and development of *Zea mays* and *Phaseolus mungo. Hydroclathrtus* extracts showed considerable increase in the growth parameters of *Sorghum*. The foliar spray of *Gracilaria verucosa* and *Chaetomorpha linum* exhibited good results on vegetative growth of black gram, brinjal and tomato. The SLF of *Sargassum wightii* increases the height and number of branches in *Arachis hypogaea* when comparing to the chemical treatments. *Sargassum johnstonii* extract enhances the vegetative growth of *Lycopersicon esculentum*. The application of seaweed fertilizers with traditional fertilizers also yielded positive results on plant growth enhancement. The seaweed extracts not only enhance the plant vegetative growth but it also stimulates the early flowering and fruiting in crops. The biochemical properties of the plants also increased in the SLF treated plants. The pigment concentrations, protein, total soluble sugar, reducing sugar, starch, phenols, lycope, free aminoacids and vitamin C content were increased in several plants treated with seaweed liquid extracts. Seaweed fertilizers increase the fertility of soil by supplying various trace elements, by improving water holding capacity, by changing the soil structure. But, the chemical fertilizers have adverse effects such as increasing the acidic properties of the soil.

### *9.3.10 Bioplastics*

The plastics are organic polymers and most of the plastics are derived from petrochemicals. The major challenge with plastics is their degradability and will take many centuries. It is one of the pollution causing agents in the earth. Hence, it is necessary to finding the new types of plastics with easily degradable and environmental friendly nature. The organic renewable biomass can be utilized for the production of plastics and these eco-friendly plastics are called as bioplastics. The advantages of the bioplastics are numerable and most important property is their quick degradability. Bioplastics utilization will help to reduce the massive emission of $CO_2$ from the fossil fuel and also preserve the fossil resource. Recently, the interest of feedstock for bioplastic is marine algae as an alternative raw material. The important factors include their rapid growing capabilities up to 20 % per day, easy cultivation and vast diversity. Development of raw material from marine algae can ensure a sustainable raw material for producing plastics. The moisture barrier content of plastic film derived from red algae agar displayed is better than cassava starch-based plastics and their mechanical properties were also similar to some low-density polyethylene plastics. The algae based bioplastic production is in infancy stage and rapid research is needed to commercialize and expand their utilizations.

## 9.4 Conclusion

The greatest diversity of marine algae provides the diverse amount of industrially important chemicals. Marine algal phycocolloids such as agar, alginates and carrageenan are important industrial products with several applications such as nutraceutical, pharmaceutical and biotechnological industries. In the process of novel drug development from the nature for treating various diseases, marine algal compounds are a significant source. Marine algae based functional food contains various essential nutrients and provide health benefits for human. Algal liquid fertilizers are having significant improvements in the plant growth, yield and soil fertility. Application of marine algae as the raw feedstock in biofuel and bioplastic productions has an immense opportunity to overcome the environmental pollution and produce enough bioenergy. Even though, several industrially important chemicals are obtained from the marine algae it is necessary to bring advancement in the production and its applications.

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