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Carrageenan: Nutraceutical and Functional Food as Future Food

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Abstract. Functional foods and nutraceuticals provide an opportunity to improve the human health, reduce health care costs and support economic development in rural communities. Global demand for macroalgal such as carrageenan is growing, and algae are increasingly being consumed for functional benefits beyond the traditional considerations of nutrition and health. Carrageenans are sulphated linear polysaccharides of D-galactose and 3,6-anhydro-D-galactose extracted from certain red seaweeds of the Rhodophyceae class. They have been extensively used of carrageenan in the functional food industry as thickening, gelling and protein-suspending agents. Among marine resources, marine algae are valuable sources of structurally diverse bioactive compounds. The cell walls of marine algae are rich in sulfated polysaccharides (SPs) such as carrageenans in red algae. Therefore, marine algae derived SPs have great potential for further development as products in nutraceutical, pharmaceutical and cosmeceutical. The beneficial biological activities of low molecular of carrageenan such as anticoagulant, antiviral, antioxidative, anticancer and immunomodulating activities. This paper presents an overview of potential health of benefits of κ -carrageenan derived from marine algae.

Keywords: Carrageenan, Nutraceuticals, Functional Food, Future food.

1. Introduction

Recently, there is an interest in nutraceutical and functional food that increase significantly. This is supported by recent invention to recognize the properties and potential application of nutraceutical substances, and added by balance in consumer demand and interest. Nutracritical is a combination of nutrition and pharmaceutical. This term means “any element which is categorically included as food or part of food that supply medical and health benefits, including the precaution and medication of disease”. The definition of functional foods are “foods or dietary components that may provide a health benefit beyond basic nutrition”[1]. Carrageenan is a carbohydrate (polysaccharide) that naturally get from edible red seaweeds. The term Carrageenan is obtained from the *Chondrus crispus* species of seaweed known as Carrageen Moss or Irish Moss in England, and Carraigin in Ireland. Carraigin was used in Ireland as a gelatin and as a coughs and colds medicine since 400 AD. This seaweed is mostly found along the coasts of North America and Europe. High molecular weight fraction (HMWF) of carrageenan is used in many mercantile applications or functional foods as gelling, stabilising agent, and thickening, as in meat, sauces, and other products. A side from this application, low molecular weight fraction (LMWF) of carrageenans are applied in nutracritical such as drug, cosmetic, pharmaceutical formula, and other industry. The molecular weight of carrageenan for nutraceutical application < 20 kDa[2].



The type of carrageenan is divided by iota (ι -), kappa (κ -) and lambda (λ)-carrageenan. The most widely used is the κ -carrageenan. This carrageenan is composed of D-galactose units linked with $\beta(1,3)$ -D-galactose-4-sulfate and $\alpha(1-4)$ -3,6-anhydro-D-galactose alternately [3]. The chemical structure of κ -carrageenan is shown in Fig. 1.

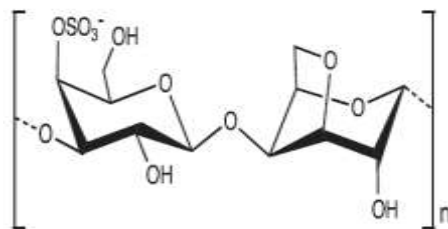


Figure 1. Chemical Structure of κ -Carrageenan

2. Chemical and Physical Properties of Carrageenan

The chemical properties of carrageenan consist of a mean relative molecular mass above 100 kDa and sulfated polygalactan with 15–40% of ester-sulfate content. It is formed by alternate units of D-galactose and 3,6-anhydro-galactose (3,6-AG) joined by α -1,3 and β -1,4-glycosidic linkage. Carrageenan is grouped by several types such as λ , κ , ι , ϵ , μ , all including 22 to 35% sulphate groups. This group was classified by their solubility in potassium chloride. The main reasons which influence the properties of carrageenan type are the number and the position of ester sulfate groups [4].

The physical properties of carrageenans in many applications depends largely on their rheological properties. Carrageenans are linear and water-soluble polymers. This polymer is typically form highly viscous aqueous solutions. Viscosity relies on concentration, temperature, the presence of other solutes, and the type of carrageenan and its molecular weight [5]. Viscosity increases with the concentration and decreases with the temperature. The high temperature and low pH may quickly loss their function [2, 6].

The use of a natural biopolymer such as carrageenan is usually specified by their molar mass, molar mass distribution, size, shape and viscoelastic properties. Moreover, it also depend on the temperature and solvent composition as many biopolymers dilute in solution [3]. The characteristic and properties of this polymer in solution is the key to know the properties of their products [7, 8].

Carrageenans have great physical function characteristic such as thickening, gelling and stabilizing agent, hence it is commonly used in many industry. It has been used to increase the texture quality of cottage cheese, to maintain the viscosity of pudding and dairy products, and as binders and stabilizers in the production of patties, sausages, hamburgers and meat-processing. The food industry contributes to 70–80% of the total world production, in region about 45,000 metric tonnes per year, which is consist of dairy product for about 45% and meat or meat derivatives for about 30%. It is calculated that the total market of carrageenan industries are on US \$300 million/year [9].

Carrageenans are utilized in many non-food products, among them are pharmaceutical, cosmetics, printing and textile formulations [10]. Carrageenans help stabilizing in production of toothpaste, it can also take up liquid body if mixed in wound dressings and contact with human carotene hence giving soft skin and silky hair in body lotion and shampoo, for each of them. They can be used for tablet of excipients because of the great compatibility, high robustness and persistent viscoelasticity of the tablet during compression. Such characteristic indicates that carrageenans are compatible excipients for sustained-release formulations [11].

3. Classifying Nutraceutical Factors Based on Chemical Nature

Sorting based on their chemical properties is another method to classify. This method permits nutraceuticals to be classified by their molecular or elemental categories. Firstly, this model contains some large categories, which then supply a basis for sub categories, and so on. One way to category of nutraceuticals simply is as follows: Isoprenoid derivatives, Phenolic substances,

Fatty acids and structural lipids, Carbohydrates and derivatives, Amino acid-based substances, Microbes and Minerals.

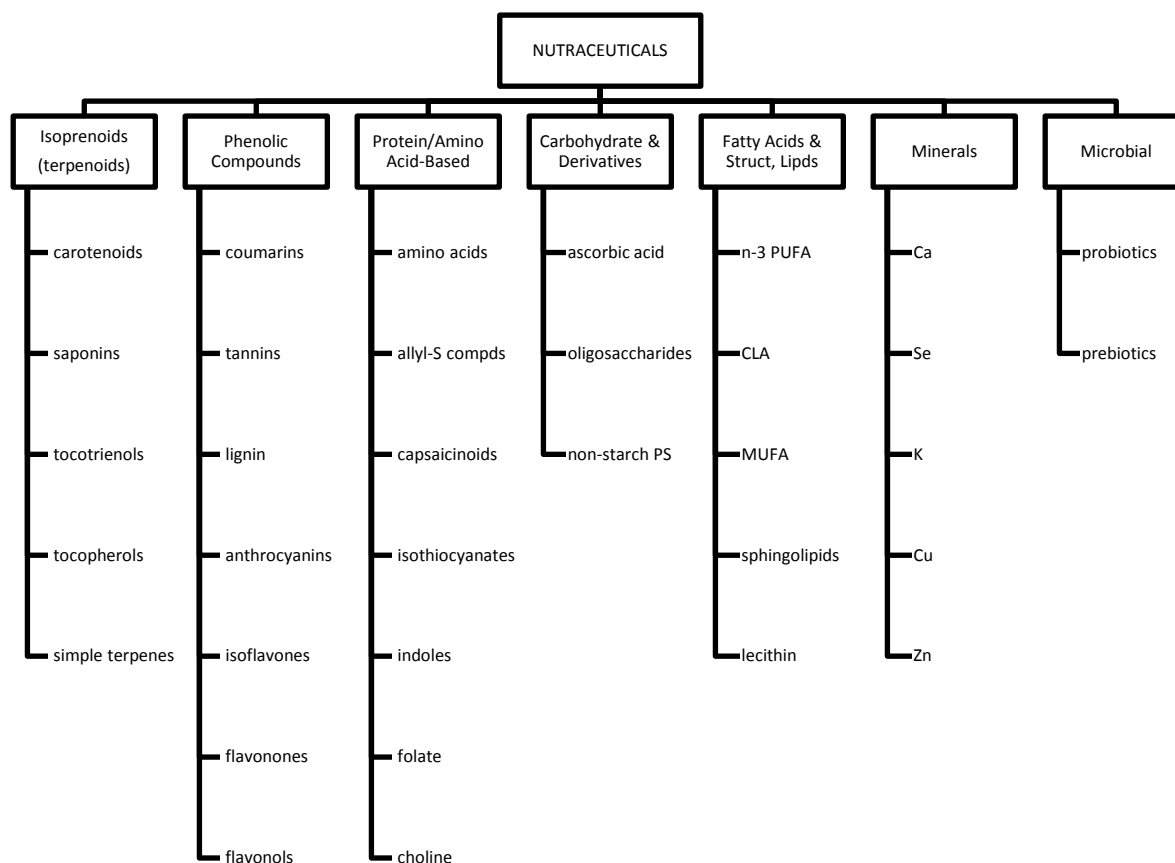


Figure 2. Organizational scheme for nutraceuticals

In functional food industry, high molecular weight fraction (HMWF) of carrageenan are mostly used because of their great physical properties, such as thickening, gelling and stabilizing abilities [12]. Carrageenans have many functions however, their further utilization in nonfood applications has been limited by their superior gelling and viscosity properties. Changing high molecular weight fraction (HMWF) of carrageenan into low molecular weight fraction (LMWF) of carrageenan or oligo-carrageenan will increase the bioavailability and expand the potential applications of carrageenan in nutraceutical, pharmaceutical and biomedical fields [13, 14]. It was reported that LMWF of carrageenan had a significant role in biological activity such as anticoagulant [15 – 18], inhibit tumor growth [19 - 21], antiviral [15 -16], antioxidant [18, 22], and other biological activities. Carrageenan has a high electronegative charge density from their sulfated esters which allow it to interact electrostatically with specific proteins, triggering in consequence its biological effects. LMWF of carrageenan shows stronger antioxidant activity than HMWF of carrageenan, because it can interact with cells more efficiently and effectively [23 - 24]. The biological activity of LMWF of carrageenan depends on the size of the molecule, the degree of sulfation, and branching of glycosides [5, 25]. Several different techniques have been used to depolymerize carrageenan, such as thermal depolymerization [26], acid hydrolysis [7, 16, 2, 27], and enzymatic hydrolysis [13,14, 16, 23, 26,27]. Other techniques were by microwave [28], sonication [29 – 31], irradiation [18, 32], and oxidation

utilizing H₂O₂ [22, 33]. This study aims to compare the chemical and physical properties of HMWF of carrageenan and LMWF of carrageenan for the function of nutraceuticals and functional food industry.

4. Material and Methods

4.1. Raw material

The raw material used in this work was κ -carrageenan derived from seaweed *Kappaphycus alvarezii*. High molecular weight (HMWF) of κ -carrageenan was used as material and produced by CV. Karagen Indonesia. The low molecular weight of κ -carrageenan was produced by combination of ozonation and ultrasonication. Mix the κ -carrageenan with purified water to make 1 % (w/v) solution. All chemical reagents were of analytical grade and directly used without further purification.

4.2. Reduction of LMWF of carrageenan

This experiment was executed in a reactor of glass completed with an ozone bubble diffuser and ultrasonic equipment. Two hundred milliliters of sample was brought to specified temperatures ($29 \pm 1^\circ\text{C}$) and put into ultrasound device, Krisbow type KLS 303365, with frequency of 42 kHz. The device was equipped with thermostatic water bath. To minimize error due to uneven power transfer and temperature fluctuation during the ultrasonic process, the sample was placed right above the ultrasound source. Ozone gas with a concentration of 80 ± 2 ppm was made by an ozone generator (Dipo Technology Indonesia). In this research, ozone is then generated with passing the air among two electrodes with a high potential difference (approximately 30 kV). Ozone was then sparked into a solution with a continual flow rate of $3 \text{ L} \cdot \text{min}^{-1}$. The experiments were then conducted at pH of 7. The pH of the κ -carrageenan solution was set with hydrochloric acid or sodium hydroxide solution and measured with a pH meter (Hanna Instruments HI 98107). The experiment was conducted at different times, i.e. 0 (control), 5, 10, 15, and 20 minutes. κ -carrageenan produced by this process was taken up, washed with purified water, and filtered with Buchner funnel. The residue was dried at 60°C for a day in a set air oven for further analysis.

4.3. Physical analysis

4.3.1. Viscosity analysis

The viscosity of carrageenan in aqueous 0.1 M NaCl solution was measured using a Brookfield viscometer of RDVE model (Brookfield Engineering Laboratories, Stoughton, MA). The solution was put in the sample container placed in water bath to equilibrate the temperature to $65 \pm 0.1^\circ\text{C}$. Viscosity was measured using spindle number 2 and the speed of the spindle was set at 60 rpm. Viscosity value was read in units of centipoise (cP).

4.3.2. Molecular Weight Determination

The number-average molecular weight of κ -carrageenan was determined by Mark-Houwink equation relating intrinsic viscosity to the molecular weight [5] as follows:

$$[\eta] = k_{\text{MH}} \cdot M^\alpha \quad \dots\dots\dots (1)$$

where $[\eta]$ is intrinsic viscosity, k_{MH} and α are constants, and M is the number-average molecular weight. The values of k_{MH} and α for the κ -carrageenan solution in water at 25°C are 0.00778 and 0.90, respectively [6, 7]. The intrinsic viscosity is obtained using Huggins equation:

$$\eta_{\text{sp}}/C = [\eta] + k_{\text{H}} [\eta]^2 C \quad \dots\dots\dots (2)$$

where η_{sp} , C , and k_H are specific viscosity, concentration of the solution, and Huggins constant of which value is 0.3 [34].

4.4. Chemical analysis

4.4.1. FTIR analysis

Ozone-oxidized of κ -carrageenan samples and FT-IR spectra of native were measured with an FT-IR Prestige-21, Shimadzu, in wavenumber range of 4000–400 cm^{-1} . Pellets were arranged with mixing the sample with KBr with a ratio of 1:100 (sample : KBr).

5. Results and Discussion

5.1. Physical analysis of κ -carrageenan

5.1.1. Viscosity analysis

The effect of ozone and ultrasound treatment on the viscosity of κ -carrageenan solution is shown in Table 1. The viscosity of HMWF of carrageenan is 45.13 ± 0.12 cP. After depolymerized process, the viscosity of carrageenan decrease. Ozone and ultrasound treatment process gives significant effect on the reduction of κ -carrageenan viscosity. In 25 minutes of treatment, the viscosity decreases from 45.13 ± 0.12 cP to 11.17 ± 0.23 cP at pH 3. The reduction of viscosity of κ -carrageenan is closely related to the effectiveness of depolymerization process. The compare of the viscosity of HMWF of carrageenan and LMWF of κ -carrageenan is shown in Table 1.

Table 1. Viscosity of HMWF of κ -carrageenan and LMWF of κ -carrageenan

Viscosity κ -carrageenan (Cps)	
HMWF	LMWF
45.13 ± 0.12	11.17 ± 0.23

5.1.2. Molecular weight analysis

The compare of the molecular weight of HMWF of carrageenan and LMWF of κ -carrageenan is shown in Figure 3. The molecular weight of HMWF of carrageenan is 545 kDa and the molecular weight of LMWF of carrageenan is 19 kDa.

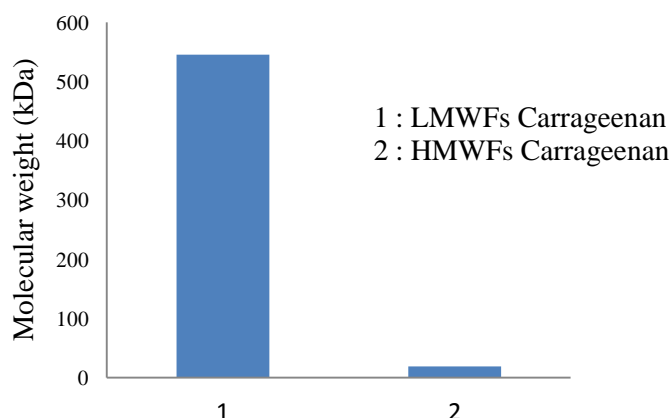


Figure 3. The molecular weight of HMWF of carrageenan and LMWF of carrageenan

5.2. FT-IR spectroscopy analysis

The FT-IR spectra can provide useful information of polymeric hydrogen bond network. Many types of carrageenan structure is classified by the number and position of sulfate groups, the existence of 3,6-anhydro-D-galactose, and form of the pyranosidic ring [35]. Their great rheological properties is caused by their chemical composition and configuration which support their applications such as gelling, thickening and stabilizing agents, in the food, pharmaceutical, and cosmetic industries. The FT-IR spectra for HMWF of carrageenan and LMWF of κ -carrageenan are presented in Figure 4.

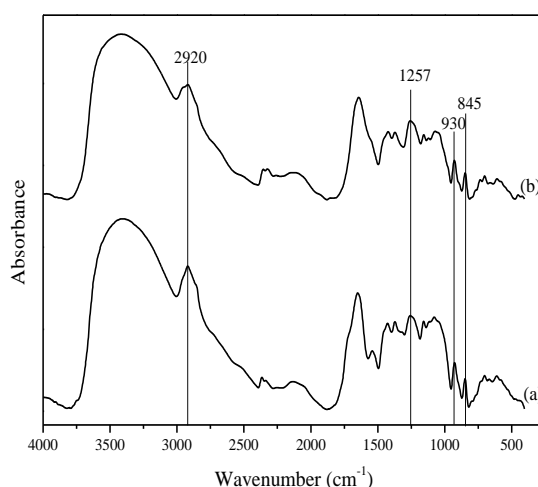


Figure 4. FT-IR spectra of κ -carrageenan (a) HMWF of carrageenan (b) LMWF of κ -carrageenan

The existence of sulfate groups in the FT-IR spectra of κ -carrageenan can be identified in the region of 1230-1270 cm^{-1} . A clear band at 840-850 cm^{-1} indicates C₄ position (in the galactose ring). The band at 928-933 cm^{-1} is associated with a coupling of the C–O stretching vibrations of 3,6-anhydro bridges [3, 24]. This research shows that absorption peaks appearing at 1257 and 845 cm^{-1} contribute to S=O of sulfate esters and C–O–S of axial secondary sulfate on C–4 of galactose, each. Meanwhile, the band at 930 cm^{-1} is characteristic of C–O of 3,6-anhydro-D-galactose. These characteristic absorption peaks found in the FT-IR spectra are indicative of the structural integrity of κ -carrageenan in the depolymerization process. This research shows the existence of sulfate group in the LMWF of κ -carrageenan.

6. Conclusion

Carrageenan have the function for nutraceutical and functional food. High molecular weight fraction of carrageenans are used in functional foods and low molecular weight fraction of carrageenans are used in nutraceutical applications. HMWF of κ -carrageenan have high molecular weight and high viscosity. The viscosity of HMWF of κ -carrageenan is 45.13 ± 0.12 cP and the viscosity of LMWF of carrageenan is 11.17 ± 0.23 cP. The molecular weight of HMWF of carrageenan is 545 kDa and the molecular weight of LMWF of carrageenan is 19 kDa. This research shows the existence of sulfate group in the LMWF of κ -carrageenan. The FT-IR spectra shows that there are no significant differences in the functional groups of HMWF of κ -carrageenan and LMWF of κ -carrageenan.

7. Acknowledgments

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