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Carrageenan

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AMF alkali-modified flour
ARC alternatively refined carrageenan
ERF enzyme-resistant fractions

GC	gas chromatography
GPC	gel permeation chromatography
GRAS	generally recognized as safe
HPAEC	high-performance anion-exchange chromatography
HPLC	high-performance liquid chromatography
IR	infrared
MALLS	multi-angle laser-light scattering
MMB	methylmorpholine-borane
NMR	nuclear magnetic resonance
PES	processed *Eucheuma* seaweed
PNG	Philippines natural grade
SEC	size exclusion chromatography
SRC	semi-refined carrageenan

1 Introduction

Carrageenan is the generic name for a family of gel-forming, viscosifying polysaccharides that are obtained commercially by extraction of certain species of red seaweeds (*Rhodophyceae*). The main species responsible for most of today's carrageenan production belong to the following genera:

- *Gigartina* (Argentina/Chile, France, Morocco),
- *Chondrus* (France, North Atlantic),
- *Iridaea* (Chile), and
- *Eucheuma* (Philippines/Indonesia).

Carrageenans are composed of a linear galactose backbone with a varying degree of sulfatation (between 15% and 40%). Different carrageenan types differ in composition and conformation, resulting in a wide range of rheological and functional properties. Carrageenans are used in a variety of commercial applications as gelling, thickening, and stabilizing agents, especially in food products such as frozen desserts, chocolate milk, cottage cheese, whipped cream, instant products, yogurt, jellies, pet foods, and sauces. Aside from these functions, carrageenans are used in pharmaceutical formulations, cosmetics, and industrial applications such as mining.

2 Historical Outline

For several hundred years, carrageenan has been used as a thickening and stabilizing agent in food in Europe and the Far East. In Europe the use of carrageenan started more than 600 years ago in Ireland. In the village of Carraghen on the south Irish coast, flans were made by cooking the so-called Irish moss (red seaweed species *Chondrus crispus*) in milk. The name carrageenin, the old name for carrageenan, was first used in 1862 for the extract from *C. crispus* and was dedicated to this village (Tseng, 1945). Schmidt described the extraction procedure in 1844.

Since the 19th century, Irish moss also has been used for industrial beer clarification and textile sizing. The commercial production began in the 1930s in the U.S. During that time, the trading shifted from dried seaweed meal to refined carrageenan (Therkelsen, 1993). After the Second World War, a general increase in the standard of living forced an increase in carrageenan production.

Fractionation of crude carrageenan extracts started in the early 1950s (Smith et al., 1955), resulting in the characterization of the different carrageenan types. A Greek prefix was introduced to identify the different carrageenans. In the same period, the molecular structure of carrageenans was determined (O'Neill 1955a,b). The structure of 3,6-anhydro-D-galactose in κ-carrageenan, as well as the type of linkages between galactose and anhydrogalactose rings, was determined.

Today, the industrial manufacture of carrageenan is no longer limited to extraction from Irish moss, and numerous red seaweed species are used. Traditionally, these seaweeds have been harvested from naturally occurring populations. Seaweed farming to increase the production started almost 200 years ago in Japan. Scientific information about the seaweed life cycles allowed artificial seeding in the 1950s. Today, nearly a dozen seaweed taxa are cultivated commercially, lowering the pressure on naturally occurring populations.

During the past few years, the total carrageenan market has shown a growth rate of 3% per year, reaching estimated worldwide sales of 310 million US$ in 2000. At the end of the 20th century, a few large corporations that account for over 80% of the supply dominate the carrageenan market, including:

- FMC Corporation (USA),
- CP Kelco (USA),
- Degussa (Germany),
- Danisco (Denmark),
- Ceamsa (Spain), and
- Quest International (The Netherlands).

3 Chemical Structure

3.1 General Description

Carrageenan is a high molecular mass material with a high degree of polydispersity. The molecular mass distribution varies from sample to sample, depending upon the sample history, e.g., age of the harvested seaweed, season of harvesting, way of extracting, and duration of heat treatment. Commercial (food-grade) carrageenans have a weight average molecular mass (M_w) ranging from 400–600 kDa with a minimum of 100 kDa. This minimum is set in response to reports of cecal and colonic ulceration induced by highly degraded carrageenan. In 1976 the U.S. Food and Drug Administration defined food-grade carrageenan as having a water viscosity of no less than 5 mPa·s (5 cP) at 1.5% concentration and 75°C, which corresponds to the above-mentioned 100 kDa.

Besides the traditionally extracted carrageenan, called refined carrageenan in trade, a new type of carrageenan product is promoted by a group of Philippine producers (Seaweed Industry Association of the Philippines). This product is marketed under the name Philippines natural grade (PNG). Other synonyms for this type of carrageenan product are processed *Eucheuma* seaweed (PES is the regulatory name), semi-refined carrageenan (SRC), alternatively refined carrageenan (ARC), and alkali-modified flour (AMF). These *Eucheuma* seaweeds (*E. cottonii* and *E. spinosum*) are harvested around Indonesia and the Philippines and treated with a more cost-effective process that avoids extraction of carrageenan in dilute solutions (see Section 9.3). The above-mentioned carrageenan differs from the traditionally refined carrageenan in that it contains 8% to 15% acid-insoluble matter compared with 2% in extracted carrageenan. The acid-insoluble matter consists mainly of cellulose, which is normally present in algae cell walls. Also, the heavy metal content of processed *Eucheuma* seaweed is higher than that of traditionally refined carrageenan (Imeson, 2000). The water-soluble component in PES is κ-carrageenan and is almost indistinguishable from the refined carrageenan. The molecular mass of κ-carrageenan present in PES can be slightly higher than that of refined carrageenan (Hoffmann et al., 1996).

3.2 Molecular Structure

Carrageenan is not a single biopolymer but a mixture of water-soluble, linear, sulfated galactans. They are composed of alternating 3-linked β-D-galactopyranose (G-units) and 4-linked α-D-galactopyranose (D-units) or 4-linked 3,6-anhydrogalactose (DA-units), forming the "ideal" disaccharide-repeating unit of carrageenans (see Figure 1). The sulfated galactans are classified according to the presence of the 3,6-anhydrogalactose on the 4-linked residue and the position and number of sulfate groups. For commercial carrageenan, the sulfate content falls within the range of 22% to 38% (w/w). Besides galactose and sulfate, other carbohydrate residues (e.g., xylose, glucose, and uronic acids) and substituents (e.g., methyl ethers and pyruvate groups) are present in carrageenans. Since natural carrageenan is a mixture of nonhomologous polysaccharides, the term disaccharide-repeating unit refers to the idealized structure. To describe more complex structures, a letter-code-based nomenclature for red algae galactans has been developed (Knutsen et al., 1994).

The most common types of carrageenan are traditionally identified by a Greek prefix. The three commercially most important carrageenans are called ι-, κ-, and λ-carrageenan. The corresponding IUPAC (International Union of Pure and Applied Chemistry) names and letter codes are carrageenose 2,4′-sulfate (G4S-DA2S), carrageenose 4′-sulfate (G4S-DA), and carrageenan 2,6,2′-trisulfate (G2S-D2S,6S). ι- and κ-carrageenan are gel-forming carrageenans, whereas λ-carrageenan is a thickener/viscosity builder.

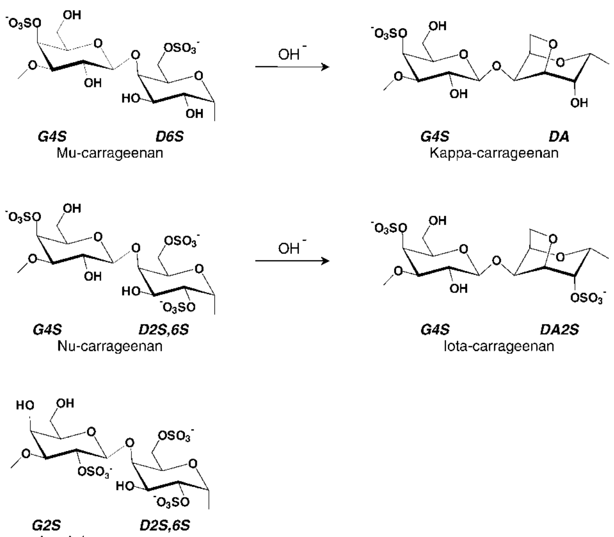

Fig. 1 Schematic representation of the different idealized repeating units of carrageenans. The letter codes refer to the alternative nomenclature (Knutsen et al., 1994).

The difference in rheological behavior between ι- and κ-carrageenan on the one hand and λ-carrageenan on the other results from the fact that the DA-units of the gelling ones have the $^{1}C_{4}$-conformation that results from the 3,6-anhydro bridges and λ-carrageenan does not. The natural precursors of ι- and κ-carrageenan are called ν- and μ-carrageenan (letter code G4S-D2S,6S and G4S-D6S, respectively) and are also non-gelling carrageenans with the D-units in the $^{4}C_{1}$-conformation as a consequence of the absence of the 3,6-anhydro bridge.

The 3,6-anhydro bridges are formed by the elimination of the sulfate from the C-6 sulfate ester of the precursors and the concomitant formation of the 3,6-anhydro bridge. *In vivo*, ι- and κ-carrageenan are formed enzymatically from their precursors, by a sulfohydrolase (see also Section 7). In industrial processing, the cyclization reaction is carried out with OH^- as a catalyst. The $^{1}C_{4}$-conformation of the 3,6-anhydro-D-galactopyranosyl units in ι- and κ-carrageenan allows for a helical tertiary structure, which is essential for the gel-forming properties. Occurrence of disaccharide units without the 3,6-anhydro ring and, as a consequence, with a $^{4}C_{1}$-conformation causes "kinks" in the regular chain and prevents the formation of helical strands, thus, preventing the gelation of the carrageenan.

4 Occurrence

All of the seaweeds that produce carrageenan as their main cell-wall material belong to the class of the red algae, or Rhodophyceae (Figure 2). Different seaweed species produce different types of carrageenans. The

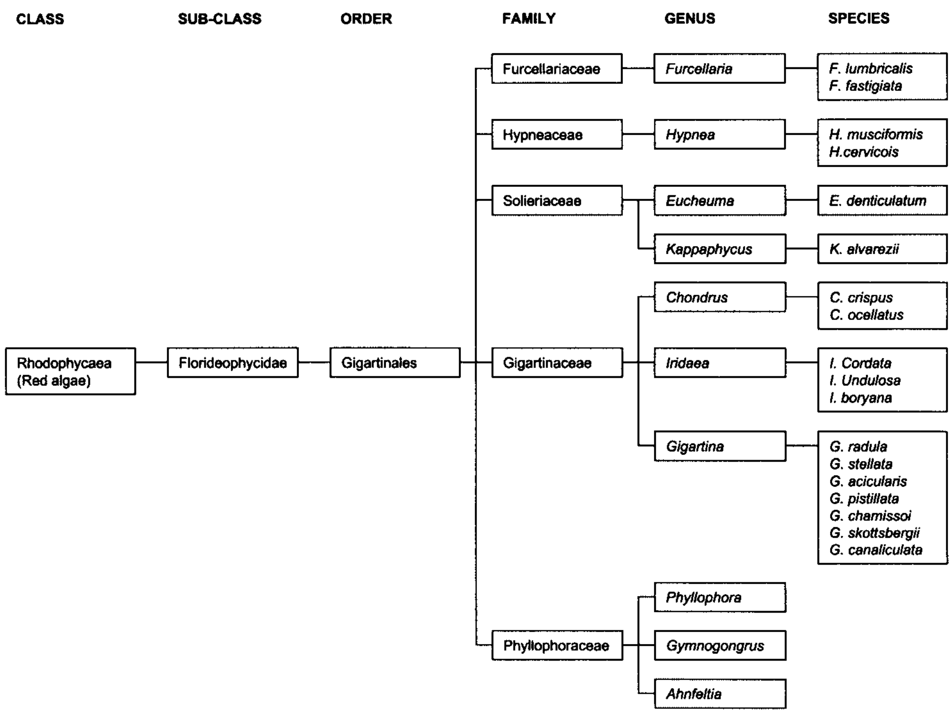

Fig. 2 Taxonomical tree of carrageenan-bearing seaweeds.