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Radiation degradation studies of carrageenans

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ABSTRACT

The radiation degradation yield (G_d) of kappa, iota and lambda carrageenans was compared in solid and in 1% aqueous solution in air at ambient temperature. G_ds obtained in solid and aqueous form did not vary with the different types of carrageenan.

The chemical structural changes of carrageenans were accompanied by appearance of UV absorbance peak at 260 nm and a characteristic FT-IR band at 1728 cm^{-1}. Changes in the FT-IR finger print regions were observed at high doses of the aqueous solution.

Radiation-induced desulfation increased the acidity of the carrageenans. The number of reducing end groups increased with dose with greater susceptibility in κ-carrageenan.

1. Introduction

Carrageenan belongs to the family of polysaccharides, extracted from many species of red algae, the Rhodophyceae. They are mixtures of water-soluble, linear, sulfated galactans. The main types of carrageenan are kappa (κ-), iota (ι-) and lambda (λ-). These different types are classified according to the number and position of sulfate groups. Kappa carrageenan is composed of alternating α(1,3)-D-galactose-4-sulfated and β(1-4)-3,6-anhydro-D-galactose. Iota carrageenan on the other hand is composed of alternating α(1,3)-D-galactose-4-sulfated and β(1-4)-3,6-anhydro-D-galactose-2-sulfate. Lambda carrageenan differs from kappa and iota carrageenan by having a disulfated-D-galactose residue and no 4-sulfate ester group but has varying amounts of 2-sulfate ester groups (Fig. 1).

Degradation of polysaccharides has recently drawn considerable interest due to their enormous applications especially in the field of medicine. The oligomers formed have found concrete uses in the acceleration of wound healing process, reduction of cholesterol level in blood, some anti-cancer and tumor activity. Oligomers from carrageenan have also been quite useful in the medical field. Oligo-kappa carrageenans induce secretion of laminarinase from Rubus cells and protoplast (Patier et al., 1995). Degraded λ-carrageenan is reported to have tumor inhibiting activities (Zhou, Sun, Xin, Zhang, & Xu, 2004; Zhou et al., 2005). Oligomers from carrageenans suggest promising antiherpetic, anti-HIV (human immunodeficiency virus) activities and as anti-infectants (Carlucci et al., 1997; Cáceres, Carlucci, Damonte, Matsuhiro, & Zúñiga, 2000; Katsuraya et al., 1994; Yamada, Ogamo, Saito, Uchiyama, & Nakagawa, 2000; Yamada et al., 1997).

Degradation of polysaccharides can easily be carried out either by chemical or enzymatic hydrolysis. Recently, degradation by radiation processing of polysaccharides has gained much attention due to its technological effectiveness in producing low molecular weight oligomers. Oligomers prepared from radiation degradation have found concrete application not only in the biomedical field but also in agriculture, as plant growth promoter (Hien et al., 2000; Kume, Nagasawa, & Yoshii, 2002). In recent years, development of new products from radiation processed/modified carrageenan has been a subject of research. Products such as PVP-carrageenan hydrogel, radiation dose indicator, and radiation processed carrageenan oligomers as plant growth promoter have been developed from carrageenan (De la Rosa, Abad, Relleve, & Aranilla, 2002). Carboxymethyl carrageenan has been synthesized and tested as metal adsorbent (Aranilla, 2008). The key to the successful development of materials from radiation processed carrageenan is the knowledge of the radiolytic products formed after degradation. Some related researches on this topic have already been published (Abad, Okabe, Koizumi, & Shibayama, 2006; Abad et al., 2004, 2008; Relleve et al., 2005). This paper would focus on the chemical and structural characterization of irradiated carrageenans (κ-, ι-, and λ-carrageenan) in solid and aqueous form.

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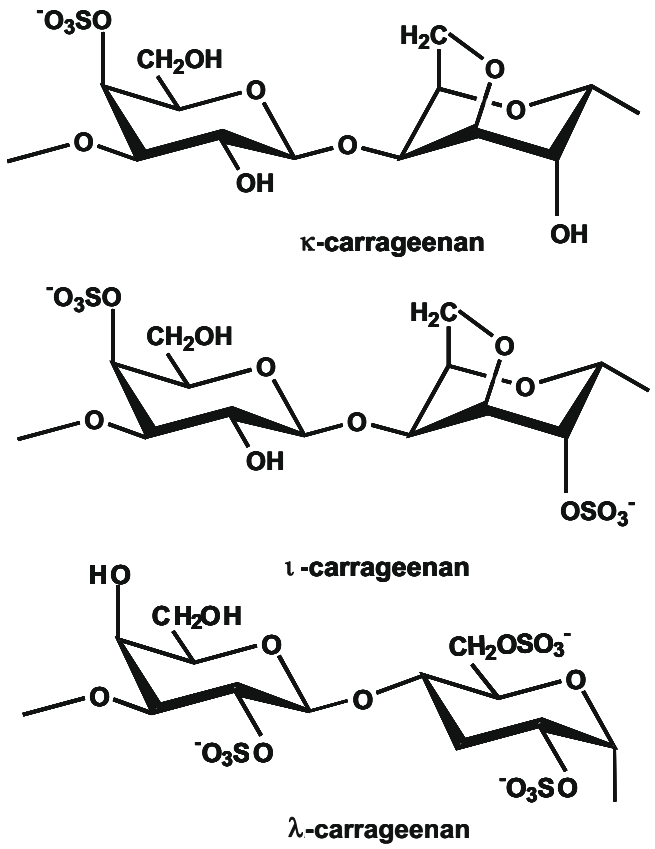

Fig. 1. Idealized structure of κ-, ι-, and λ-carrageenan.

2. Materials and methods

2.1. Materials

Refined κ-, ι-, and λ-carrageenan were obtained from Shemberg Corporation, Philippines. The carrageenans were dissolved in distilled water and precipitated with isopropyl alcohol. The precipitated carrageenans were dissolved in a buffer solution containing 0.1 M NaCl and 0.005 M ethylenediaminetetraacetic acid (EDTA). The samples were dialyzed (Mol. wt. cut-off = 12,000–14,000) against a NaH_2PO_4/Na_2HPO_4 buffer solution for 72 h. The dialyzed solutions were reprecipitated with isopropyl alcohol and freeze dried.

2.2. Irradiation of kappa carrageenan

Irradiation of the purified kappa carrageenan was carried out using the Co-60 facility of the Takasaki Radiation Chemistry Research Establishment at different conditions (powder and 1% aqueous solution in air and at ambient temperature). Samples were irradiated at a dose rate of 10 kGy/h (for 10–200 kGy) and 1 kGy/hr (for 0.5–6 kGy).

2.3. Molecular weight measurement

GPC analyses were performed on a Tosoh chromatograph equipped with DP-8020 pump, CO-8020 column oven, RI-8020 refractive index detector and four TSK gel PWXL columns in series (G6000 PWXL, G4000 PWXL, G3000 PWXL, and G2500 PWXL. Elution was carried out using 0.1 M $NaNO_3$ (to suppress electrostatic effects) as the mobile phase at a flow rate of 0.5 ml/min. The temperatures of the column and detector were both maintained at 40 °C. A calibration curve was constructed using polyethylene oxide as standards. All molecular masses reported in this work are based on PEO standards and are not absolute.

2.4. Spectral analyses

FT-IR spectra of samples in KBr pellets (1 mg/100 mg KBr) were measured using an FT-IR Nicolet Magna 550 at ambient temperature in the region of 4000–400 cm^{-1}.

UV–visible spectroscopy of carrageenan solutions was performed using a Shimadzu spectrophotometer UV-265 FW at ambient temperature and at 0.025% (w/v) concentration.

2.5. Chemical analyses

The reducing group of the carrageenans was determined using the Nelson–Somogyi method of analysis with galactose as the standard (Hodge & Hofreiter, 1962).

The total acidity of the carrageenans was determined by acid–base titration method. Carrageenan solutions were titrated against standardized NaOH using a phenolphthalein indicator to determine end point. The acidity was reported as % H_2SO_4 in carrageenan.

3. Results and discussion

3.1. Radiation degradation yield of carrageenans

Radiation degradation yield (*Gd*) is defined as radiation chemical yield which represents the number of radiolysis events caused by the absorption of 100 eV of radiation. G_d (mol/J) expresses the degradation susceptibility of the polymer during radiation and can be calculated according to the equation based on the theory of radiation degradation:

$$G_d = \frac{1}{D}\left(\frac{1}{Mn} - \frac{1}{Mn_0}\right) \quad (1)$$

where Mn is the number-average molecular weight at absorption dose; Mn_0 is the initial number-average molecular weight; D is the absorbed dose in kGy. GPC profiles of the different carrageenans show the typical curves of increasing retention time with increasing radiation dose due to degradation as demonstrated in Fig. 2A–C (ι-carrageenan only). Fig. 3-A1 and B1 shows the degradation of the different carrageenans with radiation dose in powder and aqueous form. Both show a steep decrease in weight average molecular weight (Mw) with dose for all types of carrageenan. Decrease in Mw starts to plateau at a dose of 50 kGy for the solid carrageenans while the plateau starts at a small dose of 2 kGy for 1% aqueous solution. This is expected in solutions due to the indirect effect of water radiolysis products (OH radical) on the polysaccharide. Previous paper also reported this same trend (Relleve et al., 2005). The reciprocals of Mw are shown in Fig. 3A2 and B2. The slope of each curve gives the G_d. As seen from the graph, very slight differences in G_d were observed for the different types of carrageenans both in solid and aqueous solution. The computed G_d of the carrageenans at different conditions is shown in Table 1. The G_ds in powder form were as follows: 2.5, 2.7, and 2.3×10^{-7} mol/J for κ-, ι-, and λ-, respectively. These values are slightly higher than what was previously reported (G_d = 1–1.3 × 10^{-7} mol/J) (Relleve et al., 2005) probably because the carrageenans used in this study were purified.

In aqueous solution, the concentration of the polymer has to be considered in the computation of the G_d since Eq. (1) is based on 1 kg polymer. Hence, the G_d in aqueous solution is as follows:

$$G_d = \frac{c}{D}\left(\frac{1}{Mn} - \frac{1}{Mn_0}\right) \quad (2)$$