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Effect of gamma irradiation on the structure of fucoidan

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HIGHLIGHTS

- Fucoidan was degraded by gamma-irradiation.
- Structural changes after irradiation were characterized by GPC, UV, and FTIR.
- The polydispersity decreased by radiation degradation.
- Sulfate content was not changed by gamma irradiation.

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ABSTRACT

The change of molecular structure of fucoidan by gamma irradiation was analyzed by spectral and chemical methods. Fucoidan samples with different molecular weights of 85, 30, 15, and 7 kDa were prepared by radiation degradation of 217 kDa fucoidan. In the molecular weight analysis, the polydispersity decreased by gamma radiation because of further degradation of higher weight molecules. Ultraviolet absorption and Fourier-transform infrared spectroscopy analyses were carried out to define the changes of the functional groups in fucoidan by gamma irradiation. Carboxyl groups and carbon double bonds increased by gamma irradiation; however, sulfate content remained unchanged. The granular fissures were observed from scanning electron microscopy in gamma-irradiated fucoidan.

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1. Introduction

Fucoidan is a homo- and heteropolysaccharide containing substantial numbers of fucose and sulfate groups. Galactose, mannose, xylose, and rhamnose moieties have also been found in various fucoidans. This molecule is extracted mainly from brown algae. Fucoidan has a variety of biological activities, including anticoagulant, antibacterial, antivirulent, anti-inflammatory, and antioxidant activities (Li et al., 2008).

The biological activities of fucoidan depend on several structural parameters, such as sugar type and fucose linkage, the content of the sulfate group, and the molecular weight of the polysaccharides. Several reports have indicated that low molecular weight fucoidan shows higher antioxidative and anticoagulation activities (Wang et al., 2010a, 2010b). In addition, low molecular weight fucoidan promotes revascularization of hindlimb ischemia in rats (Luyt et al., 2003), boosts osteoblast proliferation for bone regeneration (Igondjo Tchen Changotades et al., 2008), and enhances human endothelial cell formation (Lake et al., 2006).

Low molecular weight fucoidan can be prepared by acidic, enzymatic, and radical methods. In the acidic method, higher temperature or acidity leads to lower molecular weight products, but the content of sulfate group necessary for many of the bioactivities also decreases (Pomin et al., 2005). Fucoidanase isolated from bacteria and the digestive glands of marine invertebrates has also been studied (Holtkamp et al., 2009). However, because of low enzyme activity and the different molecular structures of fucoidan from different sources, the commercial utilization of these enzymes remains infeasible.

The radical method utilizes hydrogen peroxide to generate hydroxyl, superoxide, and hydroperoxyl radicals (Hou et al., 2012). These radicals degrade polysaccharides by attacking and breaking glycosidic linkages. But, the radical method using hydrogen peroxide has some problems including a long processing period, additional neutralization and purification steps, and difficulties adjusting the molecular weight. Recently, several studies on the radical degradation of polysaccharides by gamma irradiation

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have been published (Byun et al., 2008; Choi et al., 2009, 2010 and 2011).

Gamma irradiation has been used as a sanitary decontamination treatment for food and medical devices. The free radicals generated by gamma irradiation can be used to degrade polysaccharides. In some case, degradation by gamma irradiation enhances antioxidant activities of polysaccharides (Choi et al., 2011; Choi and Kim, 2013). Choi and Kim (2013) reported that the low molecular weight fucoidan degraded by gamma irradiation has increased antioxidant activities. But, the molecular structure of low molecular fucoidan degraded by gamma irradiation has not been reported. The molecular structure will be the key to define the reason for the enhanced biological activities of low molecular weight fucoidan.

Therefore, the present study was conducted to characterize the molecular structure of low molecular weight fucoidan prepared by gamma irradiation using spectroscopic and chemical analytical methods.

2. Materials and methods

2.1. Preparation of low molecular fucoidan by gamma irradiation

Fucoidan, with molecular weight of 217 kDa and originating from *Fucus vesiculosus*, was purchased from Sigma Chemical Co. (St. Louis, MO, USA). Low molecular weight fucoidan was prepared by gamma irradiation following the method of Choi and Kim (2013). The average molecular weight of prepared fucoidan samples was 85, 30, 15, and 7 kDa. The applied doses were 8 kGy, 10.5 kGy, 30 kGy, and 100 kGy. The fucoidan was dissolved in water and gamma-irradiated in a ^{60}cobalt gamma-irradiator (IR-221, Nordion International Ltd., Ontario, Canada) with a strength of 11.1 pBq at 22 ± 2 °C at a dose rate of 10 kGy/h.

2.2. Molecular weight distribution

The molecular weight distribution of the fucoidan samples was measured by gel permeation chromatography using the following system (Choi et al., 2011): A separation module (Waters 2690, Waters Co., Milford, MA, USA), refractive index detector (Waters 2410, Waters Co.), Empower software (System Software, Emp7ower option GPC, Waters Co.), and PL aquagel-OH -60, -40, and -30 columns (300×7.5 mm^2, 8 μm, Polymer Laboratories Ltd., Shropshire, UK) were used in the analysis. The mobile phase was 0.1 M sodium nitrate at a flow rate of 1 mL/min, and analyses were performed at 40 °C. Injection volume was 200 μL, and calibration was carried out using pullulan as the standard (Showa Denko K. K., Tokyo, Japan). Polydispersity was determined by the ratio of weight average molecular weight to number average molecular weight.

2.3. Ultraviolet (UV) absorption

The UV spectra of fucoidan samples were measured at 25 °C using a spectrophotometer (UV-1601PC, Shimadzu, Tokyo, Japan). The UV spectra were recorded at 200–400 nm. The polysaccharide concentration of aqueous solution used for the spectroscopy was 0.02% (w/v).

2.4. Fourier-transform infrared (FT-IR) spectroscopy

FT-IR spectra were acquired using a Bruker Spectrometer VERTEX 70 (Billerica, MA, USA) at a wavelength of 455–3996 cm^{-1}. Samples were prepared as a thin film of fucoidan mixed with KBr at a polymer/KBr (w/w) ratio of 1:100. The spectra obtained were the result of 24 scans at a spectrophotometer resolution of 8 cm^{-1}.

2.5. Determination of sulfate contents

The sulfate content in fucoidan was determined following the method of Farndale et al. (1986). The sample solution (10 mg/mL fucoidan, 0.1 mL) was added to 0.2 mL of 1,9-dimethyl-methylene blue (DMMB) reagent (16 mg DMMB, 3.04 g glycine, and 2.37 g sodium chloride per 1 L). The absorbance of the reaction mixture was measured after thorough mixing at 525 nm.

2.6. Scanning electron microscopy (SEM)

The microstructural changes in the fucoidan samples were observed by scanning electron microscopy (JEOL, Tokyo, Japan) using the method of Rayas-Duarte and Rupnow (1993). Samples were fixed on a cylindrical microscope stub covered with a carbon strip and coated with a thin layer of gold, followed by observation. A 100× magnification was used.

3. Results and discussion

3.1. Molecular weight distribution

The original molecular weight of fucoidan was about 217 kDa. Low molecular weight fucoidan samples with average molecular weights of 85, 30, 15, and 7 kDa were prepared by gamma irradiation. Choi and Kim (2013) reported that the average molecular weight of fucoidan decreased following gamma irradiation depending on the absorbed dose. The molecular weight distribution of each fucoidan sample was measured by GPC analysis. Fig. 1 shows the polydispersity of fucoidan samples with different molecular weights. The polydispersity of high molecular weight fucoidan (217 kDa) was 2.22. However, the polydispersity decreased to 1.46 in fucoidan with a molecular weight of 85 kDa and further decreased to 1.2 in fucoidan with a molecular weight of 30 kDa. Polydispersity tended to decrease further in 7 kDa fucoidan, but the difference was not significant ($p > 0.05$). A similar result has been observed in low molecular weight laminarin samples prepared by gamma irradiation (Choi et al., 2011). Polysaccharides with a higher molecular weight are more severely degraded by gamma irradiation than those with a lower molecular weight (Choi et al., 2008, 2011). Therefore, polydispersity decreased during gamma irradiation. In addition, the extent of degradation of polysaccharides is also dependent on molecular weight. The extent of decrease in molecular weight is more

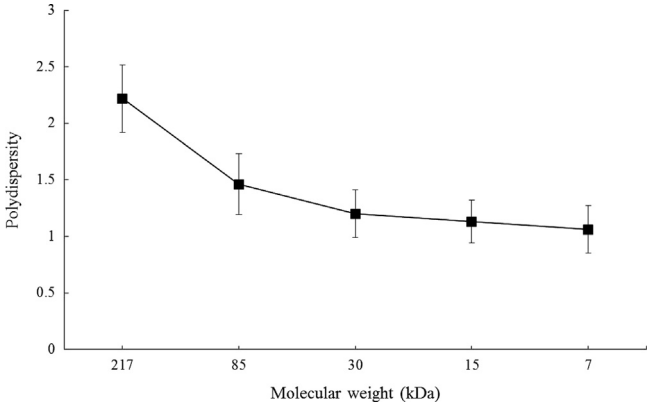

Fig. 1. The polydispersity of different molecular weight fucoidan samples prepared by gamma irradiation.

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