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King crab gills as a new source of chitin/chitosan and protein hydrolysates

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Abstract

This is the first report on the physicochemical properties of chitin obtained from gills of the king crab *Paralithodes camtschaticus*. In the present study, we investigated the chemical composition of red king crab gills and considered methods of its complex processing to obtain chitin and enzymatic protein hydrolysates. The gills contained approximately 21% chitin in terms of dry matter. For the first time, the gills of the king crab were investigated as a source of chitin and chitosan.

Chitin was isolated from crab gills using chemical and enzymatic methods. The physicochemical properties of chitin and chitosan from the gills were investigated. By performing infrared spectroscopy and X-ray phase analyses, the chitin present in the gills was established to be α-chitin. The physical and chemical properties (degree of deacetylation, molecular weight and crystal structure) of gill chitin and chitosan were absolutely similar to those of crab shell.

Crab gills can be used as an additional source of chitin in the integrated processing of king crabs. The yield of chitin from the gills is up to 45% of the yield of chitin from the crab carapace.

Introduction

Since its discovery >200 years ago, chitin has attracted the attention of scientists due to its unique physicochemical and biological properties. Scientific interest in chitin and its derivative, chitosan, is increasing, as evidenced by numerous scientific publications covering various fields of scientific and industrial activities, from the development of new natural sources of chitin to the application of chitin substances in medicine, biotechnology, agriculture, cosmetics, microbiology, and nanotechnology [1].

The reserves of this natural polysaccharide are estimated at approximately 10^{12}–10^{14} tons [2]. Unlike its analog cellulose, chitin is present in nature in a dispersed form and is a part of the exoskeletons of crustaceans and insects and the cell walls of fungi and diatoms. Therefore, the main factor for the industrial use of chitin is the availability of raw materials. At present, nearly all chitin is extracted from crustacean processing waste, such as the shells of crabs and shrimp.

Expansion of the resource supply for chitin/chitosan production remains an important issue. Different methods to recover chitin from insects, mushrooms, and mollusks have been reported. However, traditional subjects of large-scale marine fisheries, such as crustaceans, receive the most attention, and the industrial processing of these organisms generates large volumes of unused chitin-containing waste.

The traditional source for extracting chitin/chitosan is shell-containing waste from various crustaceans, such as crabs [3], [4], crayfish [5], [6], shrimp [7], [8], and krill [9], [10].

Both chemical [11] and enzymatic technologies for extracting protein from shells are used [12], [13].

The red king crab (*Paralithodes camtschaticus*) and its acclimatized form living in the Barents Sea are the best-studied objects [14]. Comprehensive research conducted by PINRO included studies of the possibility of recovering chitin, chitosan, D(+)-glucosamine [15] and protein enzymatic hydrolysates from shell containing waste of crab, as well as extracting enzyme preparations from its hepatopancreas [16]. Other crab viscera remain unused or, at best, are processed into fish meal. The carapace and limb shells are not the only sources of chitin in crabs. It is also contained in internal organs, such as gills.

One of the interesting yet neglected sources by the processing industry of raw material is king crab gills, the yield of which ranges from 3.5 to 4.0% after dissecting the crab. As long ago as in the first half of the 20th century, studies of the chemical composition of king crab gills showed that they contain not only proteins but also a significant amount of chitin, ranging from 6 to 10% of the weight of dry gills [17]. However, to date, articles devoted to obtaining and studying the properties of chitin from crab gills have not been published in the literature. Later publications suggest that this value varies within quite a wide range; for example, according to A.G. Slizkin and S.G. Safronov [18], chitin constitutes 15 to 70% of dry gill weight, although the upper limit seems rather overestimated. No other data on the chitin content in crab gills have been reported in the scientific literature. As gills are the internal organs of the crab, we would expect the properties of chitin isolated from gills to be different from those of chitin isolated from the outer shell.

Chitin occurs in various living organisms and is synthesized in various polymorphic modifications with different supramolecular structures. Notably, α-, β-, and γ-modifications of chitin have been identified [2], [19], [20], [21], [22]. Comparative studies were mainly performed on α-chitin isolated from shells of crustaceans and insects and on β-chitin obtained from squid gladii. Very few studies have analyzed differences in the polymorphic states of chitin in different organs of the same organism. One study [23] attempted to compare the chitin structure in different parts of bee bodies. Using thermogravimetry and IR methods, the chitin in different body parts was shown to be α-chitin with a generally similar structure. Only the lower thermal stability of bee head chitin was noted. Importantly, the study compared cuticle chitin in different body parts, which apparently explains its similarity. The polymorphic form of α-chitin as a component of crustacean shells has been studied in sufficient detail. No data are available on polymorphic forms of chitin in other crab organs in the scientific literature. Therefore, studies of the physicochemical properties of chitin from different internal organs, particularly crab gills, are of interest.

Chitin in gills was discovered many years ago, but this paper is the first to investigate its properties and evaluate the possibility of producing chitin and chitosan along with polysaccharides traditionally derived from the carapace. In the present study, we investigated the chemical composition of the gills of red king crab acclimatized in the Barents Sea and discussed the methods for its integrated processing to obtain chitin and enzymatic protein hydrolysates. For the first time, the structure of gill chitin was studied, and the scientific problem of whether the chitin that constitutes the different organs of the same crustacean differs or has the same structure was resolved.

Thus, the research aimed to achieve the following objectives:

– practical task — to obtain chitin from gills and to estimate its yield and quality.

- theoretical task — to establish possible differences in the structure of chitin in different organs of living organisms.

The bibliographic search did not reveal any publications mentioning the properties of gill chitin or any reports on the possibility of isolating chitin as an end product of crab entrails processing. Therefore, the present publication is the first to provide characterization and describe the extraction of chitin from crab gills.

Section snippets

Materials

Gills and carapace (carapace) of king crab harvested wet during the course of industrial processing of live crabs at Antey Sever LLC (Murmansk) in January 2021 and frozen at −20°C were used as research objects.

As an enzyme preparation, a complex enzyme preparation obtained from the hepatopancreas of the king crab using the method described in a previous study [24] consisting of the isolation of a fraction of proteins with high proteolytic activity on micro- and ultrafiltration membranes. This…

Chemical composition of king crab gills

Chitin is present in almost all tissues of crabs. At present, the external covers—carapace shell, legs and claws of the king crab—are used in the industrial production of chitin.

We compared the chitin content in the carapace, including the protein film adjacent directly to the carapace and the gills. The mass fraction of chitin in terms of dry matter was 16.5% in the shell, 6.3% in the film, and 20.8% in the gills. As the shells used to obtain chitin are usually processed without preliminary …

Conclusions

The physical and chemical properties of chitin and chitosan obtained from the gills of the red king crab *P. camtschaticus* were studied.

For the first time, a method for the integrated processing of king crab gills is proposed, and it provides a chitin yield ranging from 2.6 to 3.2%, i.e., approximately half of the chitin yield from crab carapace. The yield of enzymatic protein hydrolysate was 9.5%.

The experimental data showed that the physicochemical properties of the obtained chitin and…

CRediT authorship contribution statement

V. Yu. Novikov: Conceptualization, Methodology, Investigation, FTIR, Discussion of results, Writing and Editing.

K. S. Rysakova: Investigation, Data curation, Discussion of results, Writing and Editing.

N. V. Shumskaya: Investigation, HPLC.

A. M. Mukhortova: Investigation, Chemical composition.

K. A. Kesarev: Investigation, XRD.…

Declaration of competing interest

Vitaly Novikov reports financial support was provided by Nikolai M Knipovich Polar Research Institute of Marine Fisheries and Oceanography Murmansk, Russian Federation. Vitaly Novikov reports a relationship with Nikolai M Knipovich Polar Research Institute of Marine Fisheries and Oceanography Murmansk, Russian Federation that includes: employment.…

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