Process Biochemistry 51 (2016) 989–998

Contents lists available at ScienceDirect

Process Biochemistry

journal homepage: www.elsevier.com/locate/procbio

Review

"Algae's sulfated polysaccharides modifications: Potential use of microbial enzymes"

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ARTICLE INFO

Article history:
Received 10 December 2015
Received in revised form 29 March 2016
Accepted 20 April 2016
Available online 21 April 2016

Keywords:
Biological activity
Hydrolases
Lyases
Marine algae
Microorganisms
Sulfatases
Sulfotransferases

ABSTRACT

Marine algae are valuable sources of structurally diverse bioactive compounds, among them, the group of sulfated polysaccharides (SPs). As an example of SPs, it could be cited the fucoidans in brown algae, carrageenans in red algae and ulvans in green algae. Since the past decades, SPs have been extracted from algae and evaluated in respect to their beneficial biological activities such as anti-inflammatory, antioxidative, antimicrobial, anticoagulant, antithrombotic, immunological and anticancer. This review deals with the presentation of natively bioactive SPs structural features in addition to already employed approaches of SPs structure modifications, such as chemical and physical methods. Moreover, this article presents the advantages and the importance of using enzymatic methods during SPs modification, and particularly, the use of microorganisms as enzymes sources. Enzymes such as hydrolases/glycosidases (e.g. fucoidanase, fucosidase, agarase and carrageenase), lyases, sulfotransferases and sulfatases could be used for this purpose. It has been shown that more studies are necessary to obtain/identify opportunities to create novel, or to intensify, SPs biological properties. Considering the advantages in the use of microbial enzymes in biotransformation processes, studies related to the modification of SPs by microorganisms should be stimulated.

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http://dx.doi.org/10.1016/j.procbio.2016.04.020

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1. Introduction

Sulfated polysaccharides (SPs) are one group of the most interesting and attractive components of marine algae cell walls. They are a class of compounds with hemi-ester sulfate groups on a polysaccharide backbone [1]. Based on the algae classification, red, green or brown, polysaccharides may vary accordingly to the more abundant monosaccharide (carbohydrate structure), molecular weight, degree of sulfate esterification, the linking position of glycosidic bonds, sulpho groups and other substituents [2]. Fucoidans, sulfated fucans and laminarans are commonly reported in brown algae, while carrageenans and sulfated galactans in red algae, ulvans and sulfated heteropolysaccharides in green [3].

Despite the focus of SPs in food industry applications, in recent years, attention has shifted to the exploitation of potential biological activities and pharmacological properties [4]. Therefore, studies that aim to evaluate the importance of polysaccharide structures over bioactivity are crucial. Anticoagulation, antiviral, anti-tumor, anti-inflammatory and antioxidant are some biological activities already studied. However, relatively few studies have interpreted the biological activity of SPs (e.g. fucoidans, sulfated fucans and sulfated galactans) in terms of molecular structure [5].

Structural elucidation of algal polysaccharides is needed to correlate their physico-chemical or biological properties. Furthermore, the analysis of distinct structural features may lead to the improvement of beneficial properties by specific modifications (chemical, physical or enzymatic). Prior to structural modifications, structural analysis is required in addition to a whole set of modern analytical procedures, sometimes together with specific additional methods, as those for purification steps, for example [6].

Considering that biological activities depend on the molecular structure, we have to take a careful look of the poly and oligosaccharide structure and strategies have to be developed to produce pure oligosaccharides [7].

Recent insights into the structures of some algal polysaccharides may help to explain their activity mode, which depend on the use of enzymes degrading polysaccharides [8]. Nevertheless, only a few studies regarding the isolation and characterization of enzymes used in sulfated polysaccharides modification have been performed.

Since microorganisms are potential producers of enzymes with biotechnological interest, the screening and identification of them also remains a challenge.

This review aims to give an up-to-date view of the general structural properties of SPs from marine algae and to present a discussion of the employed methods for polysaccharides modifications, focusing on specific microbial enzymes, which are expected to simplify structural and structure/function studies.

2. Marine algae

The world's surface is covered by oceans in more than 70%. In this sense, the wide diversity of marine organisms could be a rich source of natural products. Among those organisms, marine algae present diverse bioactive compounds with various biological activities [9].

The term "algae" refers to a complex association of photosynthetic organisms with different origin and evolutionary history. In a practical manner, algae could be separate into two groups: 1) multicellular marine organisms (macrophytes, seaweeds) and 2) unicellular or colonial microalgae that inhabit not only oceans, but fresh water lakes, rivers, ponds and soil [6].

Seaweeds are macroalgae that can be represented by red (Rodophyta), brown (Phaeophyceae) and green (Chlorophyta) algae [6].

During the last decades, seaweeds have been studied because of their composition, which correspond to their edible characteristics and other commercial purposes, such as their pharmaceutical properties [4]. The bioactive compounds of marine algae include polyphenols, polysaccharides [10], proteins, lipids, vitamins and minerals [11]. The total concentration of components, in dry weight, will depend on the algae type and growth conditions: polysaccharides can range from 4 to 76%, protein content in green and red algae vary from 10 to 30% in comparison to 5–15% of brown algae, lipids can account for 1–5% of cell composition (major classes: phospholipids and glycolipids). Other important chemical groups are phenolic and mineral compounds, that vary qualitatively and quantitatively [11].

Marine algae have attracted a special interest because of their richness in sulfated polysaccharide [9].

3. Sulfated polysaccharide from marine algae

Sulfated polysaccharides, SPs, are complex macromolecules with broad spectrum of activity as a function of a chemical structure rich in polyanions, which allows its connection to a large number of proteins in solution (cell matrix or blood plasma) [12]. These structures have a wide distribution in nature, being found in microorganisms, seaweeds, vertebrates and invertebrates [13]. In fact, a great amount of SPs seaweed with biological properties was so far investigated, showing complex and heterogeneous structures [14].

The major constituent (sugar) in red algae is galactose, being designated as galactans [14]. Carrageenans and agar (galactans) are the main SPs produced by red seaweeds (Rhodophyta) [11].

In green algae (Chlorophyta), the major polysaccharides are, in turn, polydisperse heteropolysaccharides where glucuronoxylorhamnans, glucuronoxylorhamnogalactans or xyloarabinogalactans are the three main groups, whereas alginate is mainly found in brown seaweeds (Phaeophyceae) [11]. Studies of alginates indicate that their constitution is based on the existence of two different uronic acid residues in blocks of homopolymeric sequences of either D-mannuronic acid residues (M-blocks) and/or L-guluronic acid residues (G-blocks), separated by long sequences of heteropolymeric material (MG-blocks) [15]. Furthermore, fucans include, among others, compounds such as fucoidin, fucoidan, sargassan, which are SPs that can also be found in brown seaweeds,