Carbohydrate Polymers 252 (2021) 117181

Contents lists available at ScienceDirect

Carbohydrate Polymers

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

Interaction-induced structural transformation of lysozyme and kappa-carrageenan in binary complexes

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ARTICLE INFO

Keywords:
κ-Carrageenan
Lysozyme
Protein-polysaccharide complexes
Conformation
FTIR-spectroscopy
Computer simulations

ABSTRACT

The interactions between κ-carrageenan and hen egg-white lysozyme have been studied. In dilute solutions, the insoluble complexes with constant κ-carrageenan/lysozyme ratio of 0.3, or 12 disaccharide units per mole of protein are formed. FTIR-spectroscopy revealed that κ-carrageenan retains its unordered conformation and induces the rise of β-structure in lysozyme. In the complexes formed in concentrated mixtures, κ-carrageenan adopts helical conformation and lysozyme retains its native-like structure. These complexes contain 21 disaccharide units per mole of protein. Molecular modeling showed that flexible coil and rigid double helix of κ-carrageenan have different binding patterns to lysozyme surface. The latter has a strong preference to positively charged spots in lysozyme α-domain while the former also interacts to protein β-domain and stabilizes short-living β-structures. The obtained results confirm the preference of unordered κ-carrageenan to β-structure rich protein regions, which can be further used in the development of carrageenan-based protection of amyloid-like aggregation of proteins.

1. Introduction

A large group of degenerative diseases, known as amyloidosis, is caused by protein misfolding and deposition in tissues in the form of amyloid fibrils. In the human body, many different peptides and proteins were shown to form pathological amyloid aggregates, and fibrillation is often considered as a generic property of a polypeptide chain (Uversky & Fink, 2006). While the structure of the amyloidogenic proteins in the native state is different, the aggregation process is always driven by the assembly of the β-sheet structural elements. One of the possible mechanisms of fibrillation involves partial unfolding of the protein with formation of a β-sheet rich structure, which undergoes further aggregation (Cao, Jiang, & Han, 2017). Thus, compounds that can bind to β-structural fragments of proteins may be useful both for preventing the fibril formation and disruption of existing amyloid aggregates (Wang et al., 2013). Different proteins are extensively used to study the process of amyloid fibril formation. One of such proteins is hen egg white lysozyme (hereinafter lysozyme), which is well characterized in both functional and structural aspects. It is a small 14 kDa enzyme with pI ~10.5 whose three-dimensional structure was firstly resolved in 1965 (Blake et al., 1965). The spatial structure of lysozyme is organized in two domains, the first one consists of four α-helices and the second one contains three strands of antiparallel β-sheets. One of the natural lysozyme functions is the oligosaccharide hydrolysis. The active site of the enzyme is situated in the cleft between two domains. The oligosaccharide ligand bound to this center interacts with protein β-sheets (Dreele, 2005). Moreover, there are some known examples of fibril disaggregation and inhibition of fibrillation of different proteins, including lysozyme, under the influence of oligo- and polysaccharides (Dai et al., 2015; Sakuragi, Shimada, Sakurai, & Shinkai, 2006; Olasehinde, Mabinya, Olaniranc, & Okoha, 2019; Zhou et al., 2020), while in some cases polysaccharides promoted fibril formation (Bravo et al., 2008; Valle-Delgado et al., 2010). These results drive the interest in unraveling the structural aspects of complexation between lysozyme and carbohydrates.

There are many other insufficiently studied aspects of protein-polysaccharide interactions. Protein-polysaccharide complexes are ubiquitous in living organisms and provide the basis for numerous bio-

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https://doi.org/10.1016/j.carbpol.2020.117181
Received 9 July 2020; Received in revised form 16 September 2020; Accepted 28 September 2020
Available online 5 October 2020