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Structural Analysis of Chitosan Polymers and Modifying Enzymes by Enzymatic Mass Spectrometric Fingerprinting

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PURPOSE OF THE ABSTRACT

Chitosans are a diverse class of functional biopolymers that have interesting physicochemical properties and exhibit a variety of biological activities. The partially N-acetylated beta-(1,4)-linked poly-D-glucosamines differ in their degree of polymerization (DP), as well as in their fraction and pattern of acetylation (FA and PA). Chitosans are obtained from renewable biological resources and find numerous applications in different fields, including e.g. agriculture, environmental technology, food industry, and biomedical applications. The diverse structures and activities of chitosans demand analytical tools to characterize the oligo- as well as polysaccharides in order to understand their structure-function relationships.

Chitosan modifying enzymes can be valuable tools to produce defined chitosans in an environmentally-friendly manner. These include hydrolyzing enzymes, such as chitinases and chitosanases that can be used to produce oligomers from polymers. Additionally, chitin deacetylases (CDAs) can be used to remove acetyl groups from oligomers and polymers.

We developed a hydrophilic interaction liquid chromatography (HILIC) electrospray ionization (ESI) mass spectrometry (MS) based method to quantitatively determine the DP, FA and PA of complex mixtures of partially acetylated chitosan oligosaccharides (paCOS) [1]. The combination of quantitative HILIC-ESI-MS and Python-based MS data analysis tools allows for high-throughput analyses of enzymatic hydrolysates. In this way, it facilitates the rapid and detailed characterization of subsite specificities of chitin and chitosan hydrolyzing enzymes [2,3].

We additionally investigated the use of well-characterized chitosanalytic enzymes for structural fingerprinting of chitosan polymers. The combination of a hydrolase with very specific cleavage pattern [4], HILIC-ESI-MS, in silico simulation techniques, and multivariate modeling approaches enabled us to not only investigate the FA [5] of chitosan polymers, but also their PA. This in turn allowed us to compare how different chitin deacetylases can be used to change the PA of polymeric chitosans from a random towards a more regular pattern of acetylation with block-wise or alternating characteristics.

In future, the knowledge gained by these new analytical tools will allow for the production of tailor-made polymers with well-defined FA and PA by enzymatic means.

FIGURES

FIGURE 1

FIGURE 2

KEYWORDS

chitosan | enzymatic fingerprinting | glycoside hydrolase | chitin deacetylase

BIBLIOGRAPHY

- [1] S. Cord-Landwehr, P. Ihmor, A. Niehues, et al., *Anal. Chem.* 2017, 89, 2893-2900.
- [2] T. Weikert, A. Niehues, S. Cord-Landwehr, et al., *Nat. Commun.* 2017, 8, 1698.
- [3] E. K. Regel, T. Weikert, A. Niehues, et al., *Biotechnol. Bioeng.* 2018, 115, 863-873.
- [4] M. Kohlhoff, A. Niehues, J. Wattjes, et al., *Carbohydr. Polym.* 2017, 174.
- [5] A. Niehues, J. Wattjes, J. Bénéteau, et al., *Anal. Chem.* 2017, 89, 12602-12608.