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Synthesis of Chitin/Chitosan Stereoisomers by Phosphorylase-catalyzed Enzymatic Polymerization

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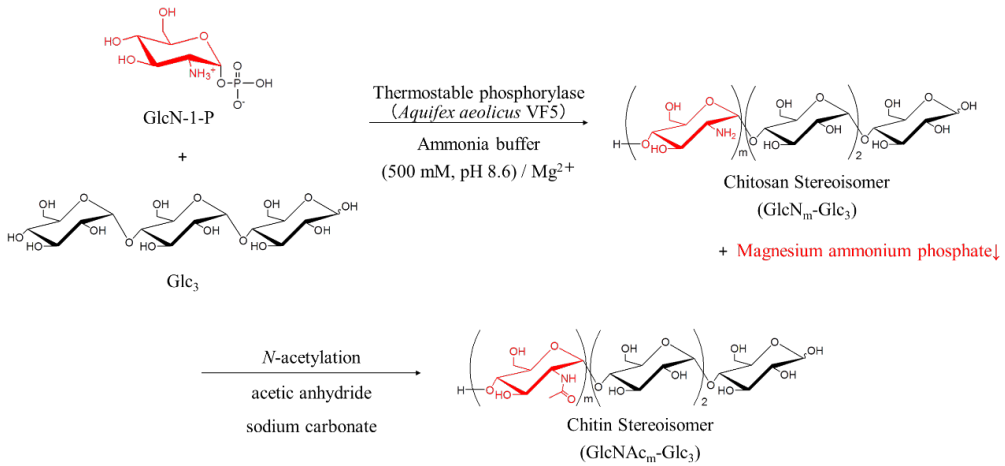
Abstract

Phosphorylase catalyzes enzymatic polymerization of α-D-glucose 1-phosphate (Glc-1-P) as a monomer using a maltooligosaccharide primer according to the manner of successive glucosylations to produce α-(1→4)-glucan with liberating inorganic phosphate [1]. Because of loose specificity for the recognition of substrates, we previously reported that α-D-glucosamine 1-phosphate (GlcN-1-P) could be used as a glycosyl donor in potato phosphorylase-catalyzed enzymatic glucosaminylation to give oligosaccharides having a glucosamine (GlcN) residue at a nonreducing end [2]. Because it is known that thermostable phosphorylase differs in recognition ability of substrates from potato phosphorylase, in this study, we performed the thermostable phosphorylase-catalyzed enzymatic polymerization of GlcN-1-P as a monomer using a maltotriose primer under the conditions with removal of inorganic phosphate from the reaction media to give α-(1→4)-linked glucosamine polymer, that is, chitosan stereoisomer (Scheme 1) [3]. To produce chitin stereoisomer, furthermore, we also carried out *N*-acetylation of the obtained chitosan stereoisomer by using acetic anhydride and sodium carbonate. The ^{1}H NMR spectra of the products supported the structures of the chitin/chitosan stereoisomers.



Scheme 1. Enzymatic Synthesis of Chitin/Chitosan Stereoisomers by Thermostable Phosphorylase-catalyzed Polymerization

References

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3) J. Kadokawa, R. Shimohigoshi, K. Yamashita, K. Yamamoto, *Org. Biomol. Chem.*, **13**, 4336 (2015).