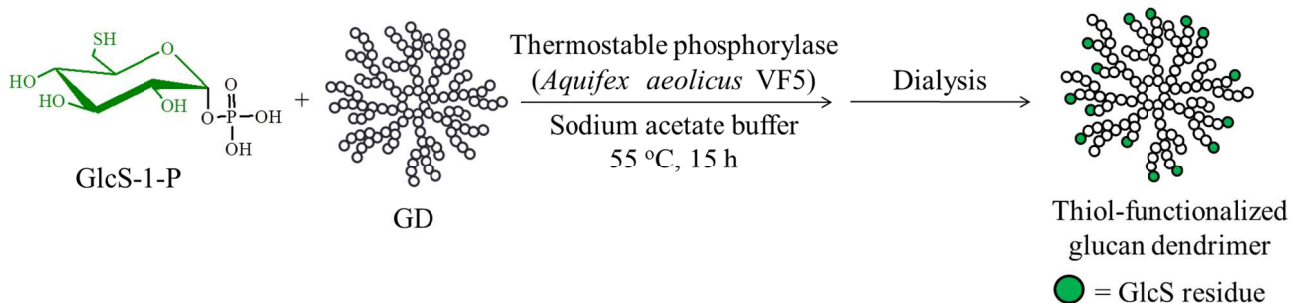


Precision Synthesis of Thiol-functionalized Polysaccharides by Phosphorylase-catalyzed Enzymatic Reaction

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Abstract

Polysaccharides with reactive groups, such as carboxy, amino, and thiol groups, are expected as new functional materials. Especially, because a thiol group shows specific reactivity, thiol-functionalized polysaccharides have a potential to be applied as practical materials. On the other hand, because phosphorylase shows weak specificity for the recognition of substrates, it recognizes several analogue substrates of native one, i.e., α -D-glucose 1-phosphate (Glc-1-P), as glycosyl donors in glycosylations to give non-natural polysaccharides. For example, we have found that thermostable phosphorylase recognizes α -D-glucuronic acid 1-phosphate (GlcA-1-P) and α -D-glucosamine 1-phosphate (GlcN-1-P) as glycosyl donors in enzymatic glycosylations [1,2]. By means of these reactions, furthermore, amphoteric polysaccharides were synthesized using glucan dendrimer (GD), a highly branched glucan, as a glycosyl acceptor [3,4]. In this study, we investigated the phosphorylase-catalyzed enzymatic glycosylation using 6-deoxy-6-sulfanyl- α -D-glucose 1-phosphate (GlcS-1-P) as a new glycosyl donor and GD as a glycosyl acceptor to give a thiol-functionalized polysaccharide. The reaction was carried out in 2 : 1 donor / acceptor feed ratio in the presence of thermostable phosphorylase in acetate buffer (pH 6.2) at 55 °C for 15 h. The crude product was isolated by dialysis and its structure was determined by ^1H NMR spectrum.



Scheme 1. Enzymatic synthesis of thiol-functionalized polysaccharide by thermostable phosphorylase-catalyzed glycosylation using GlcS-1-P as a glycosyl donor.

References

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