

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

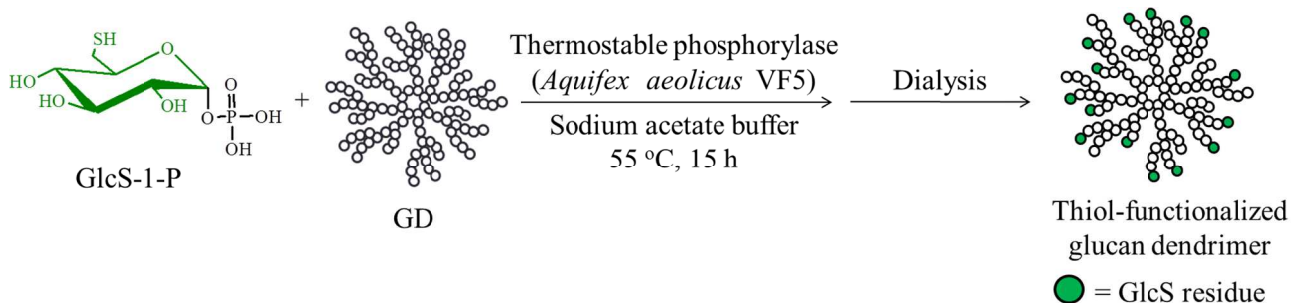
著者	JODOI Taiji, YAMAMOTO Kazuya, KADOKAWA Jun-ichi
journal or publication title	The Research Reports of the Faculty of Engineering, Kagoshima University
volume	59
page range	28-28
year	2017-12
URL	http://hdl.handle.net/10232/00029952

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

Taiji Jodoi, Kazuya Yamamoto, Jun-ichi Kadokawa

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

- 1) M. Nawaji, H. Izawa, Y. Kaneko, J. Kadokawa, *Carbohydr. Res.*, **2008**, 343, 2692.
- 2) Y. Umegatani, H. Izawa, M. Nawaji, K. Yamamoto, A. Kubo, M. Yanase, T. Takaha, J. Kadokawa, *Carbohydr. Res.*, **2012**, 350, 81.
- 3) Y. Takemoto, H. Izawa, Y. Umegatani, K. Yamamoto, A. Kubo, M. Yanase, T. Takaha, J. Kadokawa, *Carbohydr. Res.*, **2013**, 366, 38.
- 4) Y. Takata, R. Shimohigoshi, K. Yamamoto, J. Kadokawa, *Macromol. Biosci.*, **2014**, 14, 1437.

Department of Chemistry, Biotechnology, and Chemical Engineering, Graduate School of Science and Engineering, Kagoshima University, Kagoshima 890-0065, Japan