Comprehensive in vitro analyses of phosphorylated glucan chains originating from varoius starch granule surfaces

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Starch is the most important energy and carbon store, enabling plants to survive periods when photosynthesis is impaired. To survive these periods, proper starch degradation is crucial; this begins with the formation of phosphoesters on glucosyl units within the amylopectin molecules on the starch granule surface, carried out by two starch-associated dikinasases (α-glucan water dikinasase (GWD) and phosphoglucan water dikinasase (PWD)). The phosphoesterification is currently the only naturally occurring covalent modification of starch and is closely linked to significant changes in the properties of the granule surface. GWD phosphorylates exclusively the OH-group at the C6 position, whilst PWD phosphorylates only the OH-group at the C3 position [1]. Moreover, it has been demonstrated that the action of the dikinases lead to the formation of mono-, di- and tri-phosphorylated α-glucans; nevertheless, the position within the glucan chain at which the phosphate group is incorporated remains uncertain [2].

Using ^{33}P labelling and MALDI-TOF-MS and MS/MS analyses, it has been demonstrated that the phosphate groups within the α-glucans are not always esterified at the same position relative to the reducing ends. However, GWD penetrates the surface of the starch granule and phosphorylates the glucosyl units near branching points, thereby converting the highly ordered glucan chains into a less ordered state and making them accessible to the downstream hydrolases [3]. In contrast, PWD phosphorylation shows a shift towards a greater distance from the reducing end or branching position, averaging approximately three glucosyl units further away. Neither the origin of the two enzymes (GWD and PWD) nor the associated sequence differences, nor the different types of starch, influence these positions.

Industry has a keen interest in starch, as phosphorylated starches are a promising biomaterial for various biomedical applications. A detailed understanding of the mechanisms of starch phosphorylation on the granule surface and their targeted modification could therefore represent a significant step forward in optimising protein and drug delivery, as well as the properties of orthopaedic implants, to name just a few possible applications and areas.

Keywords:
Phosphorylation, starch granule surface

References:

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[2] Mahdi Hejazi, Joerg Fettke, Oskar Paris, Martin Steup. Plant Physiology 150(2): 962-976. 2009. The two plastidial starch-related dikinases sequentially phosphorylate glucosyl residues at the surface of both the A- and B-type allomorphs of crystallized maltodextrins but the mode of action differs.

[3] Julia Compart, Ardha Apriyanto , Joerg Fettke. Carbohydrate Polymers 321:121321. 2023. Glucan, water dikinase (GWD) penetrates the starch granule surface and introduces C6 phosphate in the vicinity of branching points.