Arabinoxylans of wheat starch and their influence on the shaping of hydrolysates properties

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In contrast to potato and corn starch, the chemical composition of wheat starch is characterized by the presence of non-starch polysaccharides. These primarily include pentosans—β-1,4 xylose polymers with β-1,3 arabinose branches. During the process of isolation wheat starch from flour, some pentosans (arabinoxylans) may adsorb onto the surface of starch granules. During their enzymatic hydrolysis, this can negatively affect the yield and quality of the glucose hydrolysates obtained. This can be observed through a reduction in their degree of saccharification and filtration rate. Scientific literature reports indicate that the presence of pentosans can negatively impact the filtration rate of hydrolysates produced from wheat starch. The water-soluble WEAX pentosan fraction is mainly responsible for the filtration properties of the hydrolysates. WEAX has a higher water absorption capacity than the water-insoluble WUAX fraction. Consequently, its aqueous solutions exhibit higher viscosity and a tendency to form gelatinous sediments, even at low concentrations, clogging filter pores during the purification of glucose hydrolysates. Additionally, this fraction is more reactive and can form complexes with the soluble starch and protein fractions, making these compounds unavailable to amylolytic enzymes, which negatively affects starch gelatinization and lowers the quality of enzymatic starch hydrolysis products.

Therefore, the objective of this study was to determine the influence of arabinoxylans present on the surface of starch granules on the physicochemical properties of starch and enzymatic hydrolysates, depending on the hardness of the wheat grain and its growing season. The scope of the study included investigating to what extent the presence of arabinoxylans adsorbed onto the surface of starch granules during their isolation from flour, obtained from wheat grain with varying hardness and growing periods, determines the physicochemical properties of natural starch. Additionally, an attempt was made to explain the interaction strength of arabinoxylans on the surface of wheat starch granules with other non-carbohydrate components present on the surface of starch granules, such as lipids and proteins, and their impact on starch properties. A significant aspect of this study was to investigate the effect of arabinoxylans on the thermodynamics of starch gelatinization and the transformations of the amylose-lipid AML complex in natural starch, starch devoid of arabinoxylans by chemical methods, and starch containing arabinoxylans with modified quantity and structure, depending on the duration of the modification process using endoxylanase-type enzymes at temperatures below the gelatinization temperature, both in the absence and presence of α-amylase. The study also examined the effect of the structure (degree of branching and substitution profile of xylose molecules with arabinose: unsubstituted, mono-, and disubstituted), molecular weight, and concentration of non-starch polysaccharides in wheat starch, depending on its hardness and growing season, on the physicochemical properties of enzymatic glucose hydrolysates, particularly their filtration ability, compressibility of post-filtration sediments, degree of saccharification, and color. An important element of the study was to determine whether ferulic acid, responsible for arabinoxylan cross-linking, is responsible for the gel-forming ability of arabinoxylans adsorbed onto the surface of wheat starch granules.

From a technological perspective, in terms of hydrolysate filtration ability, it was demonstrated that a higher proportion of soluble WEAX in the overall AX fraction positively influences the improvement of this parameter. A clear direct proportional relationship between the compressibility of post-filtration sediment and the hardness of wheat grain from which the starch was isolated was demonstrated. With increasing wheat hardness, sediment compressibility increased (r=0.95). This relationship was observed when only glucoamylase was used during saccharification. There is a clear correlation between the hydrolysate filtration rate and the nature of the sediments (compressibility). For these parameters, the relationship was inversely proportional, with r=-0.95, indicating that with increased sediment compressibility, hydrolysate filtration ability improved, shortening the filtration time.

Depending on the hardness of the wheat grain, the degradation of arabinoxylans during starch hydrolysis occurs differently, which is reflected in the compressibility of post-filtration sediments and, consequently, in the filtration abilities of glucose hydrolysates. It was further demonstrated that removing the non-starch polysaccharide AX fraction from wheat starch significantly affects changes in its physicochemical properties. There was also a strong correlation between these property changes and wheat grain hardness.

In general, it was concluded that starches isolated from hard wheat varieties gelatinize more difficultly compared to those from soft wheat varieties, as indicated by higher gelatinization temperatures. It was noted that the AX fraction on the surface of starch granules significantly affects changes in their gelatinization thermodynamics. Contrary to literature data, it was shown that starches previously devoid of AX reach gelatinization maxima at higher temperatures than natural starches. However, considering the onset temperature of the gelatinization process, gelatinization begins at a lower temperature compared to natural starches. A significant difference was also observed in the amount of the AML complex, its polymorphic form, and its ability to rebuild in AX-depleted starches compared to natural ones. Along with the removal of AX fractions, a significant portion of the AML complex was simultaneously removed, which exhibited an unusually high tendency to rebuild during cooling compared to native starches.

The degree of wheat hardness affects the strength of protein interactions with arabinoxylan fractions (AX) on the surface of starch granules. Soft wheat varieties are characterized by stronger interactions than hard varieties. The strength of arabinoxylan-protein interactions depends on the degree of branching of non-starch polysaccharides. The more disubstituted xylose residues with arabinose in the polysaccharide chain, the stronger the interaction. For AX preparations isolated from soft wheat starch, the M/D ratios were higher compared to hard varieties, indicating that xylose molecules in these preparations are more disubstituted.

The arabinose to xylose (A/X) ratio in preparations isolated from starch, for both soluble (WEAX) and insoluble (WUAX) fractions, reaches high values (about 0.8-1), higher than for AX preparations isolated from wheat flour. It is higher for water-insoluble arabinoxylan fractions and depends on the wheat grain's growing season. Starches from winter wheat varieties have higher values of this ratio compared to starches from spring wheat varieties. This trend holds for both WEAX and WUAX fractions. It was shown that the xylose substitution by arabinose (M/D mono- to disubstituted) ratio reaches higher values in winter wheat starches and for water-insoluble arabinoxylan fractions (WUAX). Higher values of this ratio can also be observed for arabinoxylans isolated from harder wheat grains.

The degree of starch crystallinity clearly changes when non-starch polysaccharides, specifically arabinoxylans, are removed from the starch. Natural starches exhibit lower crystallinity values. Based on the obtained results, it was found that the growing season of the wheat from which starch is isolated affects the protein interactions with arabinoxylans on the surface of starch granules. Stronger interactions occur in starch from spring wheat varieties. Furthermore, the degree of AX branching (particularly water-soluble fractions) influences the strength of their interaction with proteins. It can be concluded that the higher the degree of AX branching, the stronger the interactions with proteins on the starch surface.

It was also found that the wheat growing season may influence the strength of AX interactions with lipids on the starch surface. In winter wheat varieties, this interaction is stronger. It was demonstrated that the non-starch polysaccharide fraction has a stronger affinity for interacting with proteins than with lipids on the starch surface.

The study revealed that the absence of non-starch polysaccharide fractions on the surface of wheat starch significantly improves the physical parameters of its enzymatic hydrolysis products, particularly their filtration ability and transparency, compared to those obtained from natural starches (subjected to both glucoamylase and xylanase action).

It was also shown that arabinoxylans play a significant role in shaping the properties of post-filtration sediments, particularly their compressibility. Their absence results in less "gelatinous" sediments, making them more compressible, which is reflected in improved hydrolysate filtration capabilities.

In AX-depleted starches, with increasing hardness, hydrolysate filtration time lengthens, whereas, for natural starches, this trend is reversed.

Another important finding is that the removal of AXs significantly changes the polymorphic form of starch, making it more crystalline. However, despite this, it undergoes hydrolysis equally well under the same conditions, i.e., starch slurry concentration, pH, temperature, time, and enzymatic preparations. The AML complex in AX-depleted starches in the presence of α-amylase does not tend to change from amorphous to crystalline, as is the case with natural starches. Post-filtration dry residues obtained from AX-depleted starch hydrolyzed with glucoamylase are characterized by a predominance of amorphous areas, whereas natural starches exhibit more crystalline regions.

Moreover, removing AXs from the surface of wheat starch positively affects its gelatinization thermodynamics. Using thermal analysis, it was shown that such starches are more susceptible to α-amylase action during liquefaction. Thermal analysis also revealed that the AML complex in AX-depleted starches in the presence of α-amylase is amorphous, while in native starches under the same conditions, it tends to remain in a more crystalline form, less susceptible to breakdown under hydrolysis conditions.

In summary, it can be unequivocally stated that the presence of non-starch polysaccharides on the surface of wheat starch significantly deteriorates the quality of glucose hydrolysates. By removing these compounds, particularly their soluble fraction by enzymatic methods, the quality of the resulting hydrolysates improves, particularly regarding their filtration capacity.