Concurrent Session 4: Resistant Starch

Digestibility of starches: effects of polymer conformation and food structure
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Background – Resistant starch is that fraction of dietary starch that escapes digestion in the human small intestine with consequent fermentation in the colon. There are three potential mechanisms by which unmodified starches may avoid hydrolysis by salivary and/or pancreatic alpha amylases. One is the presence of intact granules e.g. in uncooked grains, a second is through encapsulation of starches e.g. intact plant tissues that do not disintegrate during digestion, and the third is through adoption of double helical conformations by segments of starch molecules. The first two mechanisms are based on the presence of structural barriers that limit the access of amylase to the starch component. The third mechanism is based on the inability of a starch double helix to fit into the active site of human alpha amylases. This latter mechanism offers the greatest scope for optimization via food processing, and is the only relevant route for common starchy foods such as breads, many breakfast cereals, and extruded products.

Results – Techniques for characterizing the molecular conformation of starch polymers (NMR, FTIR) and the way in which these are organized at the supramolecular level (XRD, SAXS) have been developed and applied to native and processed high amylose maize starches before and after digestion with alpha amylase. 13C CPMAS (solid state) NMR is used to quantify the double helical content of ‘dry’ starches (1) and to calibrate FTIR spectra, previously shown to be sensitive to starch crystallinity (2). Levels of double helices in native starches are reduced significantly or completely after laboratory processing under a range of ‘cooking’ and ‘drying’ conditions. Similarly, structural features of starch granules detected by XRD and SAXS and interpreted in terms of a side chain liquid crystalline assembly of polymers (3) are reduced or eliminated by laboratory processing. These results may suggest that processed high amylose maize starches would not exhibit resistance to alpha amylase digestion. However, in vitro simulated digestion under conditions that mimic in vivo digestion (4) resulted in significant yields of ‘resistant’ starch. Structural analysis of this fraction showed the presence of double helices (NMR) arranged into different crystalline polymorphs depending on the processing conditions applied (XRD) with an apparent repeating motif different to both native granules and processed material (SAXS). These characteristics are similar to the structure of enzyme-resistant amylose from retrograded (high double helix content) starches (5). In addition, differential scanning calorimetry (DSC) showed that processed starch materials of low double helix content have characteristic endotherms for amylose double helix melting at 130-160°C in excess water.

Conclusions – Taken together, the data obtained suggest that rehydration of processed high amylose maize starch leads to adoption of significant double helix formation, and that this fraction subsequently forms the basis for resistance to enzyme digestion. The inference is that double helix formation triggered by hydration is faster than extensive enzymic depolymerisation of starch, as this would slow down or prevent double helix formation. We propose that the physical structure of foods containing processed high amylose maize starch is likely to be a determinant of resistant starch levels in vivo by influencing the relative rates of rehydration, retrogradation and enzyme attack during the digestive process.

References