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COMPLEXES OF RESISTANT STARCH WITH NUTRIENTS

Abstract

Starch is a very important component of nutritional ecosystem. In virtualy all human populations, starch is the major component of the diet. The aim of this experiment was to explain the possibility of forming complexes between physically modified starches and nutrients, i.e. tyrosine, folic acid, cholic acid and cholesterol in pH corresponding to the intestine environment. The studies were carried out on physically modiefied starches: retrograded tapioca, maize and wheat; termamyl-digested potato and wheat; autoclaved and spray-dried potato and wheat. The obtained results prove that only cholesterol can form the complexes with processed starches. The investigated substances are characterized by different hydrophilic-hydrophobic properties. Formation of the complex only between cholesterol and processed starches suggests that the initial organisation of the complex within a starch granule is specifically changed during the physical modification of starch. Considering our results, we can propose the following model of these changes. V-amylose helix, sugar-lipid complex and free amylose chain form the specific complex with the hydrophobic tunnel domains. This complex we regard as a resistant starch component of starch granule. The hydrophobic character of this complex is the cause of its resistance to the action of enzymes. It means that only hydrophobic substances can interact with this complex. In conclusion, our investigations enable us to suggest an initial hypothesis for the biological role of resistant starch in the intestinal tract. In the intestinal tract, resistant starch could first of all play the role of a thickening agent. Therefore, resistant starch is the complexing agent of nutrients to a lesser degree.

Introduction

Starch is a very important component of nutritional ecosystem. In virtually all human populations, starch is the major component of the diet [1]. Because uncooked starch is poorly digested in the human alimentary tract, the main function of the various methods of cooking starch materials is so convert starch granules into a form that can be attacked readily by the amylolytic enzymes of the digestive system. In nutritional terms it is common practice to describe two groups of polysaccharides; the latter group being major components "dietary fibre" and, in general representing polysaccha-

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rides that are resistant to digestion in upper alimentary system of non-ruminants. At present modified starch containing fraction of resistant starch is classified to the second group. This problem concerns two very interesting questions. What is the biological role of resistant starch? To what degree resistant starch is similar to dietary fibre?

It is worth noting that the native components of starch can form the complexes with lipids, proteins, non-protein nitrogen substances and metals [2].

The aim of this experiment was to explain the possibility of forming complexes between physically modified starches and the nutrients, i.e. tyrosine, folic acid, cholic acid and cholesterol in pH corresponding to the intestine.

Materials and methods

The studies were carried out on physically modiefied starches: retrograded tapioca, maize and wheat; Termamyl – digested potato and wheat; autoclaved and spray – dried potato and wheat. Analysis of resistant starch was carried out using the method by Champ [3]

The solutions of the investigated substances and the incubations with nutrients were made as follows:

A. Cholesterol, samples of the processed starches (100mg) were incubated with emulsion consisted of phosphate buffer, pH 6.8, cholesterol (9%), phosphatidyl choline (40%) and cholic acid (51%) at 37°C for 1h. The content of cholesterol was determined by the BIOCHEMTEST cholesterol colorimetric kit (POCH – Gliwice – Poland).
B. Tyrosine, (50 mg) was dissolved in 50ml of phosphate buffer, pH 7.6, at 50°C. The working solutions were prepared as follows: 3.00, 1.50 and 0.25 ml of the starting solution were diluted to 10 ml with phosphate buffer.
C. Cholic acid (6 mg) was dissolved in 1 ml of methanol and diluted to 10 ml with of phosphate buffer.
D. Folic acid (6 mg) was dissolved in 10 ml of phosphate buffer.

The working solutions of the cholic acid and folic acid were prepared as follows: 0.7, 0.5 and 0.3 ml of the starting solutions were diluted to 10 ml with phosphate buffer. The samples of the processed starches (50 mg) were incubated with the working solutions (10ml) of investigated nutrients at 37°C for 2 h and then centrifuged at 3500 x g for 10 min. The supernatants (tyrosine – 275 nm, folic acid – 280 nm, cholic acid – 222 nm) and absorption spectra were measured by using Beckman's spectrophotometer DU 7500.

Results and discussion

It seems logical and necessary before starting of the presentation and discussion of the results to present the chemical nature of starch complexes with lipids, protein and metals and also the hydrophobic – hydrophilic properties of the investigated nutrients.

It is know that only starch granules from cereal grains, including maize and wheat, contain significant amounts of internal lipid [4], potato starch, in common with starch granules from other tubers and from legume seeds does not contain this type of internal lipid. From point of view the forming of the complexes between starch and lipids was the proving that the significance of the monoacyl character of starch internal lipids lies in the fact that these can form helical inclusion complexes with amylose, whereas di-or tri-acyl lipids do not form such complexes [5].

Starch also forms complexes with proteins. Average values for protein content of commercial starches have been quoted as maize (0.35%), wheat (0.40%) and potato (0.06%).

Careful washing can reduce protein values of cereal starches. In precise Lowy's et al. [6] investigations of wheat starch, the true protein content (by amino acid analysis) of well-washed, pure A starch was found to 0.1%, dry weight basis. Approximately 10% of the starch protein appeared to be associated with the granule surface, in that it could be removed with strong salt solutions of sodium dodecylsulphate (SDS) failed to remove any more protein. However, extraction with hot solutions of SDS, in which the starch was gelatinized, liberated the remaining protein.

The phosphorus belongs to the minor components of starch. The phosphorus content of potato starch (0.06 – 0.10 % as P, dry weight), unlike the lipid phosphorus of cereal starch is due to direct esterification of glucose residues in amylopectin and accounts for about 1 phosphate group per 300 glucose nuits [7].

On the basis of these data and from theoretical point of view, we can conclude that the different components of starch can from clathrates and inclusion and adsorption complexes. Stabitity of these complexes depends on the stereochemistry of the components, the kind of bonds and the type of the interactions. The main role in the forming of these complexes is played by the hydrogen bonds, and to a lesser degree ionic bonds and hydrophobic-hydrophilic interactions. As the results of the adsorption of the all investigated nutrients by the processed starches were very similar, the processed wheat starches were selected to exemplity. The results presented in Fig. 1–6 prove that only cholesterol can form the complex with processed starch. The investigated substances are characterized by different hydrophilic-hydrophobic properties. The chemical structure of these substances shows the they can be ranked according to the hydrophilic-hydrophobic properties as follows: folic acid-tyrosine-cholic acid-cholesterol. Formation of the complex only between cholesterol and processed starches suggests that the initial organisation of the complexes within a starch granule was specifically changed during the physical modification of starch. Considering our results, we can propose the following model of these changes, witch is a transformation of the Blanshard's model, Fig. 7, [8]. V-amylose helix, sugar – lipid complex and free amylose chain form the specific complex with the hydrophobic tunnel domains. This complex we regard as a resistant starch component of starch granule. The hydrophobic character of this complex is the cause of its resistance for the action of enzymes. It means that only low molecular hydrophobic substances can interact with this complex. In the face of this fact it is interesting to ask, why the investigated hydrophobic-hydrophilic molecules do not form the complexes with other components present in a starch molecule? The reason of the phenomenon could be the inverse nature of the hydrophobic-hydrophilic residues in the molecule. The assumption has been made that only part of the hybrid amylose/amylopectin helix can be hydrated. It means that only this area is available for the functional molecules. In this context only hydrophilic part of molecule can form hydrogen bonds with the external hydroxyl glucose groups of the amylose/amylopectin helix. However, these interactions are blocked by the hydrophobic groups because these groups show the tendency to scape from a water medium.

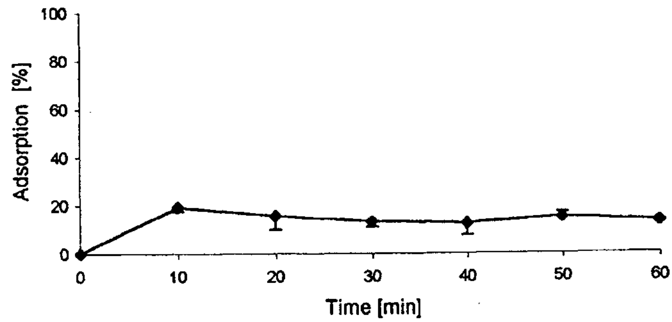

Fig. 1. Adsorption of cholesterol by termamyl-digested wheat starch.

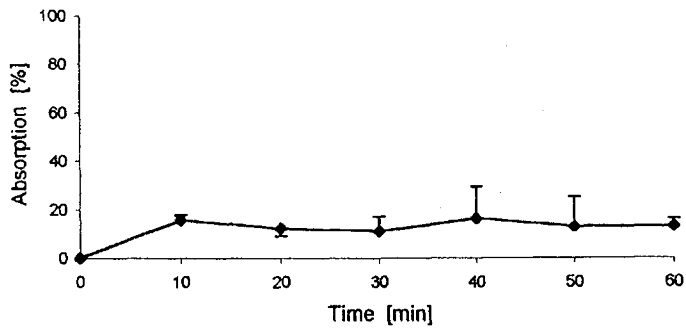

Fig. 2. Adsorption of cholesterol by autoclaved and spray-dried wheat starch.

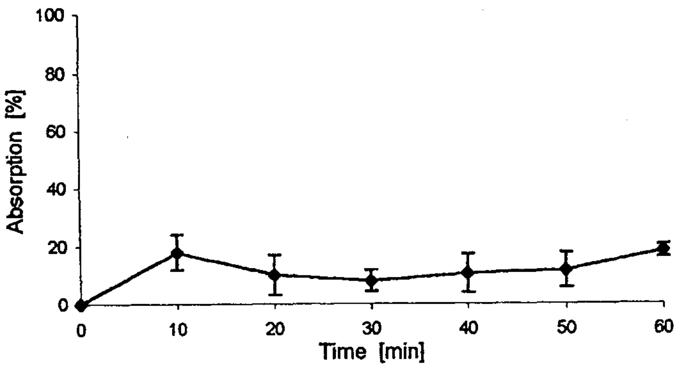

Fig. 3. Adsorption of cholesterol by retrograded wheat starch.

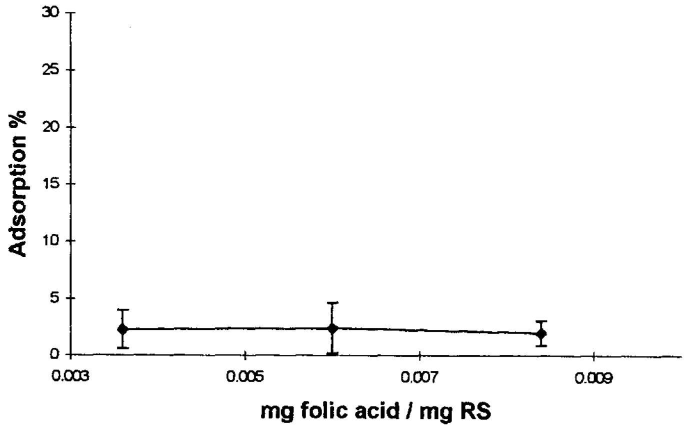

Fig. 4. Adsorption of folic acid by termamyl-digested wheat starch.

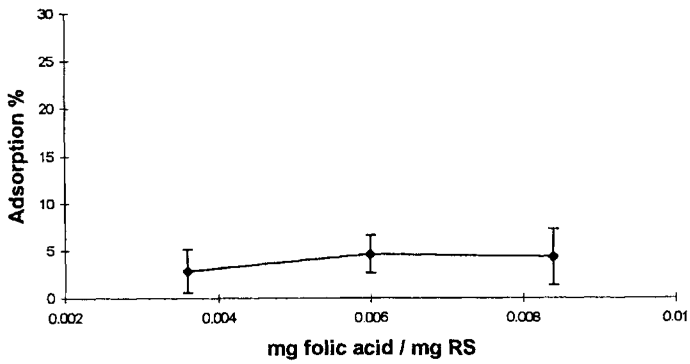

Fig. 5. Adsorption of folic acid by autoclaved and spray-dried wheat starch.

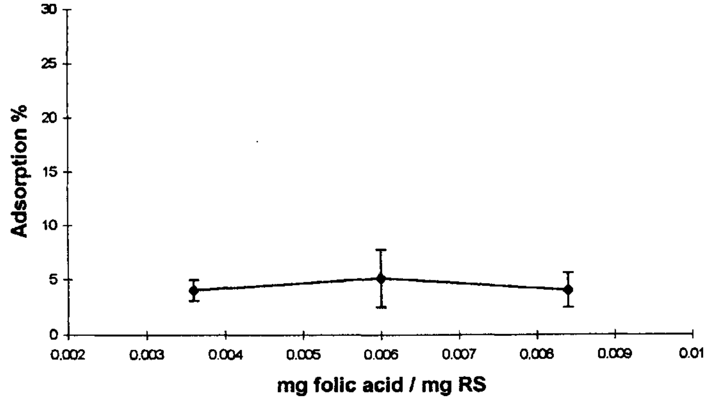

Fig. 6. Adsorption of folic acid by retrograded wheat starch.

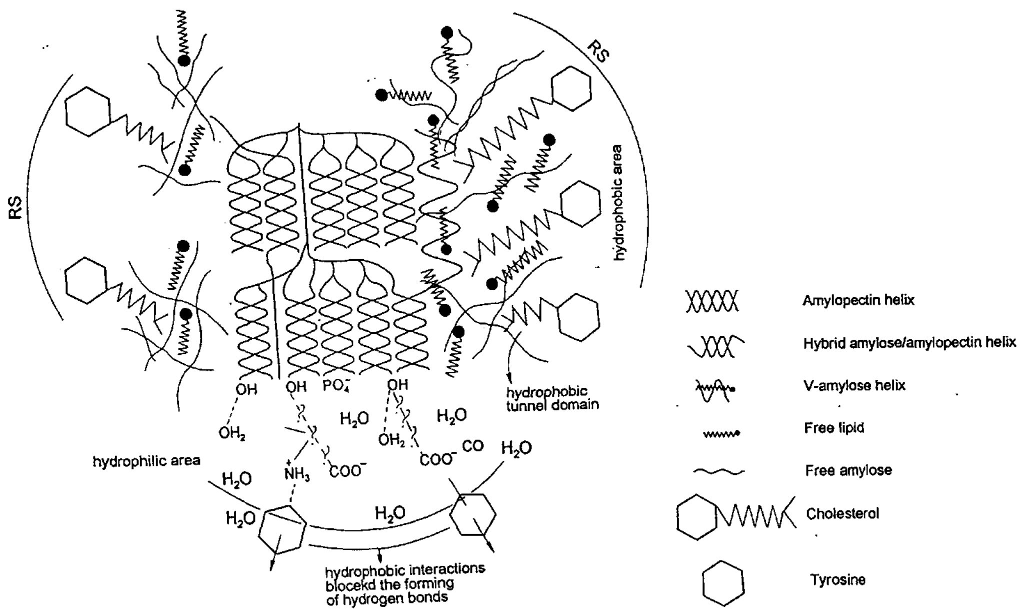

Fig. 7. Model of processed starch showing the possible positivning and interactions of various compounents.

In conclusion our investigations enable us to suggest an initial hypothesis for the biological role of resistant starch in the intestinal tract. In our opinion, resistant starch could play in the intestinal tract first of all the role of a thickening agent. Therefore, resistant starch is a lesser degree the complexing agent of nutrients.

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KOMPLEKSY SKROBI ODPORNEJ ZE SKŁADNIKAMI POKARMOWYMI

Streszczenie

Skrobia jest ważnym składnikiem ekosystemu żywieniowego. W rzeczywistości jest ona dla całej ludzkiej populacji głównym składnikiem diety. Celem pracy było wyjaśnienie możliwości tworzenia kompleksów pomiędzy modyfikowanymi skrobiami i składnikami żywności, tj.: tyrozyna, kwas foliowy i cholowy oraz cholesterol w warunkach pH odpowiadających środowisku jelita. Badania przeprowadzono używając fizycznie modyfikowane-retrogradowane, autoklawowane oraz enzymatycznie-po działaniu termamylu skrobie: tapiokową, kukurydzianą, ziemniaczaną i pszenną. Uzyskane wyniki dowiodły, że tylko cholesterol tworzy kompleksy z modyfikowanymi skrobiami.

Uzyskane wyniki sugerują, że podczas modyfikacji skrobi zachodzą przemiany konformacyjne jej składników i tworzą się nowe układy kompleksowe. Helikalna V-amyloza, kompleksy lipidowo-amylozowe i amyloza łańcuchowa tworzą specyficzny kompleks z hydrofobowymi tunelowymi domenami. Ten kompleks uważamy za składnik skrobi odporny na amylolizę. Hydrofobowy charakter tego kompleksu powoduje jego odporność na działanie enzymów. Wydaje się, że tylko hydrofobowe związki mogą wchodzić z tym kompleksem w interakcje. Uzyskane wyniki pozwoliły nam na wysunięcie hipotezy, że rola biologiczna skrobi odpornej na amylolizę w przewodzie pokarmowym polega głównie na pełnieniu funkcji zagęstnika treści pokarmowej, a w mniejszym stopniu jako czynnik kompleksujący.