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MODIFICATION-INDUCED CHANGES IN POTATO STARCH SUSCEPTIBILITY TO AMYLOLYTIC ENZYME ACTION

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Potato starch was esterified with phosphoric acid (V), saturated with iron cations (III) and heated with glycine. The mono-starch phosphate made was additionally saturated with iron cations (III) or heated with glycine. The susceptibility of the preparations to the action of α-amylase and gluco-amylase was determined. The modifications of potato starch induced a lowering of the starch susceptibility to the action of amylolytic enzymes. The most resistant to amylase action was the preparation obtained by heating mono-starch phosphate (V) with glycine.

INTRODUCTION

Starch is a monosaccharide composed of glucose residues that occur in all living plant organisms in the form of granules, also called grains. Due to the complicated structure of the molecule and granule, starch possesses characteristic physical and chemical properties which are naturally differentiated depending on the plant species it was extracted from. These properties can be changed by various physical and chemical agents applied to the starch. Products of such modifications find broad application in almost all spheres of economy, this being the reason for the constantly rising demand for starch in its technically pure form extracted from various plant materials.

One of the more important raw materials for starch production is the potato. Potato starch is characterised by specific properties, constituting almost pure hydrocarbon, with small amounts of ester-bound phosphoric acid (V) residues and ionically-bound cations. It contains only trace amounts of proteins and lipids, in which it differs from corn starch, where these substances are integral, relatively large constituents of granules [Sitowy & Ramadan, 2001].

One of characteristic properties of potato starch is its almost total resistance to amylolytic enzyme action when in the form of granules; and almost complete hydrolysis by the same enzymes after earlier agglutination. The current nutritional trends in the highly industrialized countries tend to restrict high-energy components in human food, and to increase components which are not absorbed in the small intestine, collectively called fibre. This includes also ”resistant starch” which does not undergo depolymerisation by amylolytic enzymes.

Resistant starch is the sum of starch and its decomposition products which are not absorbed in the small intestine of a healthy human. Beside of resistant starch occurring naturally in the form of granules (*e.g.* potato or banana starch), it can arise due to physical agents, as a result of retrograding or chemical modification.

The aim of the present work was to determine the effect of potato starch modification with selected chemical and physical agents on its susceptibility to enzymatic hydrolysis.

MATERIALS AND METHODS

Commercial potato starch was used in the investigation. It was subjected to modifications by esterification with phosphoric acid (V) by the method of Richter *et al.* [1968], saturation with ferric cations (III) according to Leszczyński [1985] and heating with glycine at 160°C. The obtained mono-starch phosphate was saturated with iron (III) or heated with glycine at 160°C. The preparations made and unmodified starch were subjected to microwave radiation. The modified and unmodified samples of potato starch were subjected to the activity of amylolytic enzymes.

Glues made of the starches investigated were incubated separately with α-amylase (Fungamyl from Novo Nordisk) at a temperature of 60°C, pH 5.6, and glucoamylase (AMG 300 from Novo Nordisk) at 60°C and pH 4.0. After 30 to 120 min the amount of sugars produced was determined by the method of Golachowski and Leszczyński [1980]. A part of starch that hydrolysed within the first 30 min was classified as rapidly digestible starch (RDS), and the remaining not digested starch – as resistant starch (RS). The degree of hydrolysis of modified starches was compared with the results obtained with unmodified starch, using variance analysis at a confidence level of $p<0.05$ and Statistica 6.0 PL program [Stanisz, 2001].

RESULTS AND DISCUSSION

Based on the results obtained, it can be stated that the applied modifications of potato starch induced changes in

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its susceptibility to the action of the amylolytic enzymes used. These changes depended on the type of modifying agents.

Figure 1 shows the degree of hydrolysis of the starch preparations, modified for 30 to 120 min, induced by α-amylase. Natural potato starch subjected to microwave radiation showed an increased rate of hydrolysis which occurred because of an increased amount of starch digested by α-amylase in 30 min (RDS) at the expense of the slowly digested starch (SDS). The majority of the products of chemical modification of potato starch were characterized by a lower susceptibility to α-amylase than the natural starch. Of the preparations made, the least susceptible to the enzyme was the product of heating mono-starch phosphate (V) with glycine. Also mono-starch phosphate and mono-starch phosphate saturated with iron (III) were significantly less susceptible to α-amylase than natural starch. Similarly, to a lesser degree than natural starch, products of heating starch with glycine and starch saturated with iron (III), *e.g.* ferric starch, were susceptible to α-amylase. When subjected to microwave radiation, the two samples showed increased hydrolysis, mostly slow starch (SDS).

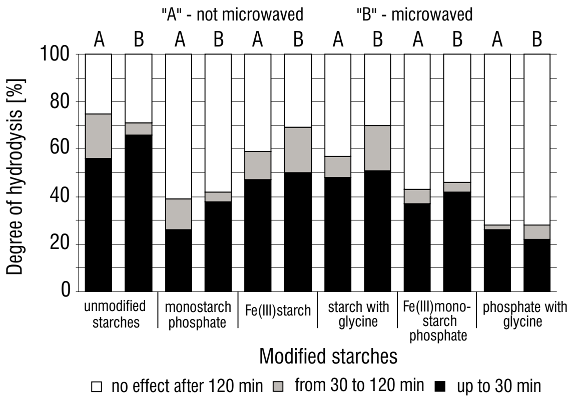

FIGURE 1. Action of α-amylase on modified potato starch.

The lowering of glucoamylase effect due to starch modification was markedly smaller than that of α-amylase (Figure 2). The most resistant to glucoamylase was the product of heating mono-starch phosphate (V) with glycine. Saturating starch with iron (III) and heating it with glycine affected its glucoamylase susceptibility to a relatively small degree.

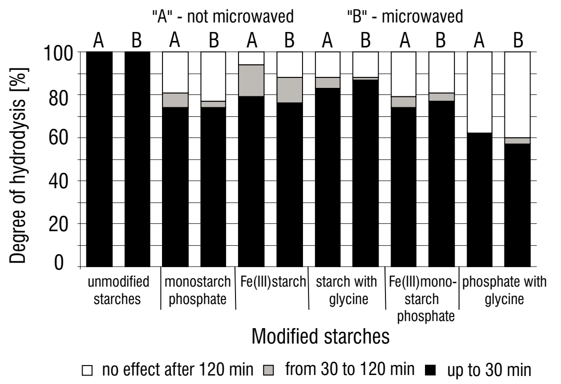

FIGURE 2. Saccharification degree of modified potato starch by glucoamylase.

Figure 3 shows the effect of potato starch modification on its non-hydrolysed amount when subjected to α-amylase for 120 min, compared with unmodified starch. After hydrolysis of modified starch the amount of starch not digested by α-amylase was substantially larger than after hydrolysis of unmodified starch. The most of such starch, nearly 3 times more than in the case of natural starch, remained after hydrolysis of mono-starch phosphate heated with glycine. After hydrolysis of mono-starch phosphate and phosphate saturation with iron (III), there remained over two times more resistant starch than in the case of natural starch hydrolysis. When subjected to microwave radiation, most of the samples showed lowered amounts of starch resistant to α-amylase. An increase in resistant starch resulting from microwave radiation occurred only in the case of natural starch.

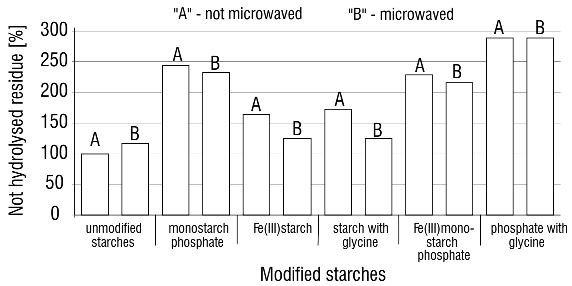

FIGURE 3. The influence of potato starch modification on the content of not-hydrolysed by α-amylase residue (in % of unmodified starch).

Figure 4 shows the effect of potato starch modification on the amount of undigested starch, resistant to glucoamylase. The natural potato starch hydrolyses fully under the action of glucoamylase. After hydrolysis of the modified starches studied, there remained more or less of undigested starch, resistant to glucoamylase. Of all the preparations studied the largest amount of such resistant starch remained after hydrolysis with glucoamylase of the product of heating mono-starch phosphate (V) with glycine. Considerable amounts of resistant starch remained after saccharification of mono-starch phosphate and mono-starch phosphate saturated with iron cations. Irradiation with microwaves of mono-starch phosphate and starch saturated with iron, and of mono-starch phosphate heated with glycine caused an increase in the amount of starch resistant to glucoamylase action.

Some of the results obtained correlate with data reported by other authors. In the study by Sitowy and Ramadana [2001], mono-starch phosphates were also characterised by lowered susceptibility to α-amylase, the

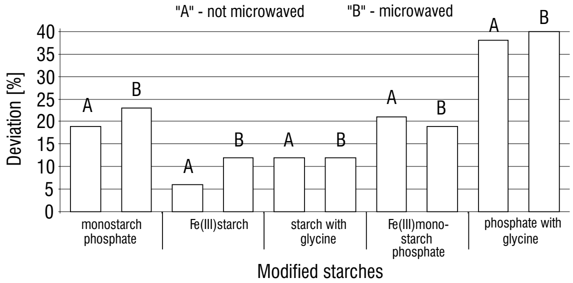

FIGURE 4. A decrease in saccharification degree of starch as a result of some methods of modification (deviation in % unmodified starch).

resistance increasing with the degree of substitution. In those studies, the susceptibility of starch phosphates to glucoamylase was, however, not determined. In our earlier investigations [Leszczyński, 2001], it was found that saturation of potato starch with iron induces a lowering of its susceptibility to α-amylase and glucoamylase. Presumably, both esterification of starch with phosphoric acid and its saturation with iron makes the approach of enzymes to starch chains more difficult. This may be due to the presence of additional phosphate esters in the starch, and to cross-linking of neighbour chains by 3-valence ferric ions. Kroh and Schumacher [1996] reported that the products of starch depolymerisation heated with glycine showed decreased susceptibility to amylolytic enzymes. Heating of starch with amino acids causes, as found by Kramhöller *et al.* [1993], the formation of Maillard's reaction products. Presumably, these products impose restriction on hydrolysis of starch chains conducted by amylolytic enzymes.

In the investigations done, mono-starch phosphate, starch saturated with iron cations and starch heated with glycine after irradiation with microwaves were characterised with lowered susceptibility to glucoamylase action; and the unmodified starch – to α-amylase action. The products subjected to microwaves experience warming, even to high temperature. It seems likely that the warming was one of the reasons for the lowered susceptibility to amylolytic enzymes. The authors mentioned above [Kroh & Schumacher, 1996] found that heating of macromolecular products of starch polymerisation induces a lowering of their susceptibility to amylolytic enzymes, presumably as a result of changes in the structure of starch chains.

In the present work it was assumed that the products of the potato starch modification done, whose susceptibility to amylolytic enzymes was less than 50% that of unmodified starch, were classified as resistant starch. Such a product proved to be mono-starch phosphate heated with glycine (37% hydrolysis by α-amylase and *ca.* 60% by glucoamylase, compared with unmodified starch). Similar properties showed mono-starch phosphate (52% hydrolysis by α-amylase and ca. 80% by glucoamylase).

CONCLUSIONS

Esterification of potato starch with phosphoric acid, its saturation with ferric cations and heating with glycine induced a lowering of its susceptibility to α-amylase and glucoamylase action. Mono-starch phosphate saturation with ferric cations and mono-starch phosphate heated with glycine were characterised by a lower susceptibility to amylolytic enzymes than unmodified starch. Microwave irradiation of potato starch induced a decrease in its susceptibility to α-amylase. Microwave radiation caused a decrease in hydrolysis of mono-starch phosphate and starch saturation with iron. Mono-starch phosphate heated with glycine exhibited features of resistant starch.

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