A C T A A L I M E N T A R I A P O L O N I C A

Vol. XI (XXXV), No. 1 1985

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STRUCTURE OF MACRO-MOLECULAR DEXTRINS

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Key words: high molecular dextrins degradation of potato starch, amylolytic enzymes.

The aim of this work was to study macro-molecular dextrins obtained in the process of acid degradation of potato starch, performed by two methods. The first concerned lintnerization of starch, i.e. action of acid on starch in water suspension at room temperature for 7 days. The second covered dextrinization of starch by its torrefaction with the supplement of a small amount of acid at 125°C.

Influence of acids on starch and the resulting chemical reactions have been attracting the attention of many research workers for a long time [3, 4, 12]. Better knowledge of the mechanism of catalytic splitting of glucoside bonds in starch was gained during studies on the kinetics of starch hydrolysis [1, 9].

Most frequently, however, the studies concern processes of far-advanced hydrolysis of starch, which result in products having the character of low-molecular compounds, e.g. low-molecular dextrins, poly- or monosaccharides. Similar interest has been aroused by the process of starch degradation in a "dry" form, i.e. by dextrinization of starch at high temperature [11]. Known are here chemical reactions occurring during the reversion processes as well as the formation of various types of poly-condensation reactions [10, 13].

Hydrolysis of starch conducted in milder conditions than in the production of syrups or low-molecular dextrins, is a less known problem. Acid, when acting on starch grains in the process of starch lintnerization or dextrinization, damages their structure, especially in amorphic layers of the grain, and therefore, in changes the distribution of molecules and their linkings [2, 7, 8].

Treatment of such changed residues of starch hydrolysis, with a glycoside bond-splitting enzyme, would allow to characterize the direction of reactions which take place between the molecules of starch components.

The purpose of the present work was to examine the possibilities and trends of structural changes occurring in starch, as affected by acids.

EXPERIMENTAL

Acid modification of potato starch was conducted by two separate methods:

— in a "wet" form — by 7-day acting of 2n HCl or HNO_3 on starch in suspension, at 20°C (acc. to Lintner)

— in a "dry" form — by torrefaction of dry starch under "mild conditions", i.e. at a temperature lower than in case of industrial dextrinization of starch, and namely at 125°C, with a small addition of acid (expressed as 0.5 g of anhydrous HCl or HNO_3 for 1000 g of starch).

In macro-molecular products of starch dextrinization, deprived of water-soluble, low-molecular products of hydrolysis viscosity, reducibility and mean molecular weight (ferricyanide method [5]), number of final groups and degree of branching of molecules (method of oxidation of dextrins with periodate [6]), were determined.

The obtained dextrins were subjected to enzymatic hydrolysis with participation of β-amylase preparation. After determination of reducing sugars level in hydrolysates, the latter were concentrated under vacuum and then the limit dextrins were precipitated with 95% ethyl alcohol [4]. The thus obtained limit dextrins were exhaustively saccharified with a glucoamylase preparation. The results of analyses and conditions of the enzymatic reactions are given in the Tables to follow.

DISCUSSION OF RESULTS

It results from the physico-chemical analysis of macro-molecular products of starch dextrinization that even at room temperature strong acids reveal a strong effect catalysing the hydrolytic degradation of starch. This is evidenced by the low values of viscosity of pastes made from these products and also by low values (in comparison with natural starch) of mean molecular weights.

When analysing the results listed in Table 1, it may be stated that dextrinization of starch in more destructive conditions (at elevated temperature) causes a higher degree of starch degradation and it leads to products with lower molecular weights. Simultaneous studies on the degree of branching of molecules and on the number of glucose residues in particular sections of polysaccharides molecules demonstrate that products of acid degradation of starch, obtained under various conditions, have a different intramolecular structure. It was found that molecules of

Table 1. Physico-chemical properties of macro-molecular dextrins

Macro-molecular dextrin obtained as a result of:	Viscosity of 1% pastes mPa · s	Reducibility, % glucose	Mean molecular weight	Number of final groups	Number of branchings	Number of straight segments in molecule	Mean molecular weight of segment	Number of glucose residues in one segment
Lintnerization of starch with hydrochloric acid	1.86	0.31	58 113	19	18	37	1570	10
Lintnerization of starch with nitric acid	1.89	0.28	64 339	22	21	43	1497	9
Dextrinization of starch with hydrochloric acid	1.25	0.37	48 689	13	12	25	1948	12
Dextrinization of starch with nitric acid	1.30	0.35	51 471	15	14	29	1774	11

polysaccharides obtained from "dry" dextrinization of starch at increased temperature, have a less branched structure but longer chains (Table 1). Such results lead on to believe that during the dextrinization of starch, processes going in the direction of a degradation of starch molecules as well as those oriented at reactions of transglucosidation and polycondensation, take place.

These assumptions were confirmed by two-stage, enzymatic studies of dextrins, and namely, limiting hydrolysis of dextrins with the use of β-amylase preparation and then, complete saccharification of the limit dextrins obtained as a result of β-amylolysis with the use of glucoamylase preparation.

The saccharification values of macro-molecular dextrins, with the use of β-amylase preparation, distinctly shows that acid-and-heat modified starches are more resistant to the hydrolytic effect of the enzyme (limiting saccharification 22.1 and 25.2%) than lintnerized starches (40.2 and 45%) (Table 2).

Table 2. Results of limiting saccharification of macro-molecular dextrins with barley β-amylase preparation. Conditions of reaction: concentration of substrate 6%; pH of reaction = 4.5; temp. of hydrolysis = 50 °C, amount of enzymatic preparation = 0.25%/DM

Macro-molecular dextrin obtained as a result of:	Level of reducing sugars in % of maltose/ /DM hydrolysate
Lintnerization of starch with hydrochloric acid	40.2
Lintnerization of starch with nitric acid	45.0
Dextrinization of starch with hydrochloric acid	22.1
Dextrinization of starch with nitric acid	25.2
Natural potato starch	59.7

For better interpretation of the results, natural potato starch saccharified in 60% by β-amylase, was also subjected to hydrolysis. There are two reasons for such big differences in saccharification of starch before and after its modification. The first is that during acid treatment, the part of starch components with a linear and with a branched structure was hydrolysed to smaller segments which were removed by rinsing starch with water during the process of obtaining macro-molecular dextrins.

The second reason, explaining the low saccharification of dextrins are structural changes occurring in starch molecules, during the acid modification of starch. These changes concern probably the newly-formed bonds between the molecules of polysaccharides or inside a given molecule.

Such linkages are an obstacle for the selective action of β-amylase, which splits only α-1,4 glucoside bonds.

The above conclusions are also confirmed by studies of limit dextrins, resulting after the saccharification of macro-molecular dextrins. It was shown that limit dextrins with larger molecules were formed from dextrins which were less saccharified and therefore more resistant to β-amylase action (Table 3).

Table 3. Physico-chemical properties of limit dextrins obtained as a result of β-amylolysis of macro-molecular dextrins.

Limit dextrin obtained as a result of β-amylolysis of macro-molecular dextrins, produced during:	Viscosity of 1% pastes mPs · s	Reducibility % glucose	Mean molecular weight
Lintnerization of starch with hydrochloric acid	1.06	0.52	34 752
Lintnerization of starch with nitric acid	1.12	0.51	35 323
Dextrinization of starch with hydrochloric acid	1.18	0.48	37 531
Dextrinization of starch with nitric acid	1.20	0.47	38 329

Successive enzymatic studies of dextrins, consisting in exhausting saccharification of limit dextrins with glucoamylase, confirmed the possibility of various-type reactions, including also polycondensation reaction during the process of dextrin formation. Glucoamylase, splitting α-1,4 and α-1,6 glucoside bonds in starch, hydrolysed limit dextrins only partially (Table 4).

Table 4. Results of saccharification of limiting dextrins with glucoamylase NOVO 200 Conditions of reaction: concentration of substrate 6%; pH of reaction = 4.5; temp. of hydrolysis = 60 °C, amount of enzym. preparation = 0.25% DM.

Limit dextrin obtained as a result of β-amylolysis of macro-molecular dextrins produced during:	Level of reducing sugars (% glucose DM hydrolysate) during enzymatic hydrolysis of dextrins in the time of:			
	24 h	48 h	72 h	78 h
Lintnerization of starch with hydrochloric acid	59.8	63.3	66.6	66.7
Lintnerization of starch with nitric acid	58.5	60.5	65.3	65.2
Dextrinization of starch with hydrochloric acid	44.1	52.5	56.4	56.5
Dextrinization of starch with nitric acid	43.4	46.7	50.6	50.6

CONCLUSIONS

1. Potato starch subjected to acid-heat modification is more resistant to the action of β-amylase than lintnerized starch, and the latter is more resistant than natural starch.

2. Limit dextrins obtained as a result of the β-amylolysis of macromolecular dextrins resulting from the acid and acid-heat modification of starch, become saccharified by glucoamylase only in 50-60%, and not in total.

3. During the acid and acid-heat modification of starch, changes in the properties and intramolecular structure of starch take place, suggesting the formation of new bonds, differing from α-1,4 and α-1,6 glucoside bonds, appearing between polysaccharides molecules or inside the molecules.

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Streszczenie

W pracy podjęto badania dekstryn wielkocząsteczkowych otrzymanych w procesie kwasowego rozpadu skrobi ziemniaczanej, prowadzonego dwiema metodami. Pierwsza dotyczyła lintneryzacji skrobi, czyli działania kwasu na skrobię w postaci zawiesiny wodnej, w temperaturze pokojowej w ciągu 7 dób. Druga metoda polegała

na dekstrynizacji skrobi przez jej prażenie z dodatkiem niewielkiej ilości kwasu w temp. 125°C. Badane dekstryny wielkocząsteczkowe otrzymywane były w stanie czystym, tj. po usunięciu ostatecznych i rozpuszczalnych w wodzie niskocząsteczkowych produktów hydrolizy skrobi.

Przeprowadzona analiza fizykochemiczna wymienionych dekstryn, dotycząca wyznaczenia średniej masy cząsteczkowej, liczby grup końcowych w cząsteczce, stopnia rozgałęzienia i stopnia polimeryzacji odcinków prostych w cząsteczce pozwoliła stwierdzić, że podczas procesu dekstrynizacji skrobi zachodzą obok reakcji o charakterze hydrolitycznym — reakcje transglukozydacji. Przypuszczenia takie potwierdziły przeprowadzone w dalszej części pracy badania enzymatyczne dekstryn, a mianowicie β-amyloliza tych dekstryn, a następnie hydroliza uzyskanych dekstryn granicznych z udziałem glukoamylazy. Badania te pomogły określić możliwość i kierunki reakcji kondensacji wewnątrz- lub międzycząsteczkowej dekstryn.

Dekstryny wielkocząsteczkowe otrzymano w wyniku łagodnej hydrolizy skrobi, tj. przez lintneryzację oraz częściową dekstrynizację skrobi. Badania fizykochemiczne i enzymatyczne tych dekstryn pomogły określić możliwość zachodzenia reakcji kondensacji wewnątrz- lub międzycząsteczkowej dekstryn.