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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COMPOSITION OF YELLOW DEXTRINS

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Key words: dextrin, molecular weight, dextrin fraction, oligosaccharides, paper chromatography.

Dextrins obtained from potato starch both under industrial and laboratory conditions are always a mixture of carbohydrates with a differentiated size of molecules. Structure of yellow dextrins considerably differs from that of amylose and amylopectin. Dextrins were separated into fractions and their quantities, mean molecular weights, degree of branchings and content of mono- and oligosaccharides, were determined.

Dextrins obtained from potato starch under industrial and laboratory conditions are always a mixture of carbohydrates with a differentiated size of molecules [6, 10]. Apart from big molecules of dextrin, there are small quantities of mono- and oligosaccharides [1, 12]. The structure of yellow dextrins, especially of fractions with higher molecular weight differs considerably from that of amylose and amylopectin [8, 9, 11]. Molecules of dextrins composed of glucose residues are more branched than the initial starch and possess in addition to α-1.4 and 1.6 bonds, other bonds, mainly of β-type. These bonds are formed during roasting of starch, as a result of reversion and transglucosidation processes [7, 8, 12].

An examination of molecular weights and degrees of branching of these dextrins and of other physico-chemical properties gives, mean results [11]. The numeric values of these results are strongly affected by mono- and oligosaccharides present in dextrins in small quantities.

The purpose of the present work was to determine the size molecules which appear in yellow dextrins. The dextrins were, therefore separated into five fractions in which the following determinations were made: percentage share of fractions, mean molecular weight and number of end groups from which the degree of branching was calculated.

MATERIALS AND METHODS

Yellow dextrins with mean viscosity, produced with an addition of nitric acid as catalyser and dextrins with low viscosity produced with the addition of hydrochloric acid, were used for the experiment. Roasting of samples was conducted at 180°C for 240 min. Analyses of physico-chemical properties of the dextrins [6] carried out acc. to Polish Standard, are presented in Table 1. Separation of the samples was performed in a

Table 1. Properties of yellow dextrins

	Type of acid used	pH	Acidity versus methyl orange °N	Reductivity %	Solubility %	Specific rotation $( )_D^{20}$	Viscosity mPa · sec	Brightness %
1	HCL	2.9	1.3	2.2	99.2	164.5	85.0	59.5
2	HNO_3	3.0	1.1	1.8	99.0	178.0	138.0	71.0

Temperature of roasting 180 °C
Time of roasting 240 min

cellulose-packed column using various concentrations of ethyl alcohol for elution. The fractionation of the obtained dextrins was conducted in the following way: to a column with a wood cellulose bed, 10 cm^3 of a 20% solution of dextrin was introduced and then ethyl alcohol at a varying concentration of 95 to 0% was added, eluating successively the individual dextrin fractions. With the decrease of alcohol concentration, fractions with higher molecular weight were eluted. The flow rate of eluate from the column was regulated so as to make it amount to 1 cm^3/min. Mean concentration of alcohol in eluate of the particular fractions was 92, 82, 62, 38 and 14%. In order to obtain appropriate quantities of substrates (fractions) eluation of each dextrin sample was repeated many times. The obtained eluates of fractions were concentrated and analysed, determining the percentage content of a given fraction, its mean molecular weight and number of end groups (Table 2). The mean molecular weight of fraction was determined by chemical methods, performing a reaction with potassium ferricyanide and dinitrosalicylic acid [3, 4, 5]. Determination of end groups was made by an oxidation of samples with sodium meta periodate at +2°C [2]. Besides, determinations of mono- and oligosaccharides were made by the chromatographic method in dextrins and fractions with the lowest molecular weight.

Chromatographic determinations of these carbohydrates were made on Whatman paper No. 1. Solutions of the dextrins were prepared in a mixture of water, n-propanol and ethyl acetate in ratio 3:6:1. The sample of dextrin was dissolved in water and then n-propanol and ethyl acetate

Table 2. Composition and characteristic of dextrins fractions

Number of fraction	Concentration of alcohol discharged from the column %	Level of fraction in dextrin %	Mean molecular weight	Number of end groups	Number of segments in molecule	Number of glucose residues in one segment
Dextrin with low viscosity 1						
1	95	7.5	980	2	3	2
2	82	4.2	1 650	3	5	2
3	62	16.7	3 660	4	7	3
4	38	31.9	8 850	6	11	4
5	14	36.5	14 630	14	27	3
Dextrin with mean viscosity 2						
1	95	8.3	1 400	2	3	3
2	82	3.5	1 760	2	3	3
3	62	10.8	4 160	3	5	5
4	38	34.0	6 450	5	9	4
5	14	38.5	16 600	9	17	5

were added in a required ratio. In such a mixture, mono- and oligosaccharides with molecules containing maximally 7-8 glucose residues remained in the solution. Dextrins with larger molecules were precipitated in the form of sediment. The applied method allowed to remove dextrins with larger molecules which were an obstacle in this analysis since they made it difficult to properly develop the chromatogram.

DISCUSSION OF RESULTS

Analysis of the particular fractions of dextrins revealed that yellow dextrins possessed the smallest quantity of fractions with low molecular weight from 980 to 1760, the amount of these fractions not exceeding 11%. The largest fraction was composed by dextrins with molecular weight 14 630 and 16 600 and their quantities constituted 36.5 and 38.5%. Dextrins with a molecular weight above 16 600 constituted a small percent (max. 5%) (Table 2).

The highest determined molecular weight of about 16 000 was stated for the fifth fraction of dextrin with mean viscosity. Besides, yellow dextrins have small quantities of fractions with molecular weight higher than 16 600 which have not been eluated from the separating column.

Comparison of the examined dextrins shows that in general, molecular weights of the particular fractions of dextrins with mean viscosity are

higher than those of dextrin fractions with lower viscosity (Figs. 1, 2). The results of determinations by oxidation with sodium periodate demonstrated that yellow dextrins are composed of widely branched molecules, considerably more branched than the initial starch. On average, in fractions with low molecular weight, the quantity of glucose residues contained in the straight segment of the branched chain is 2-3; in larger molecules, these quantities amount to 4-5 residues.

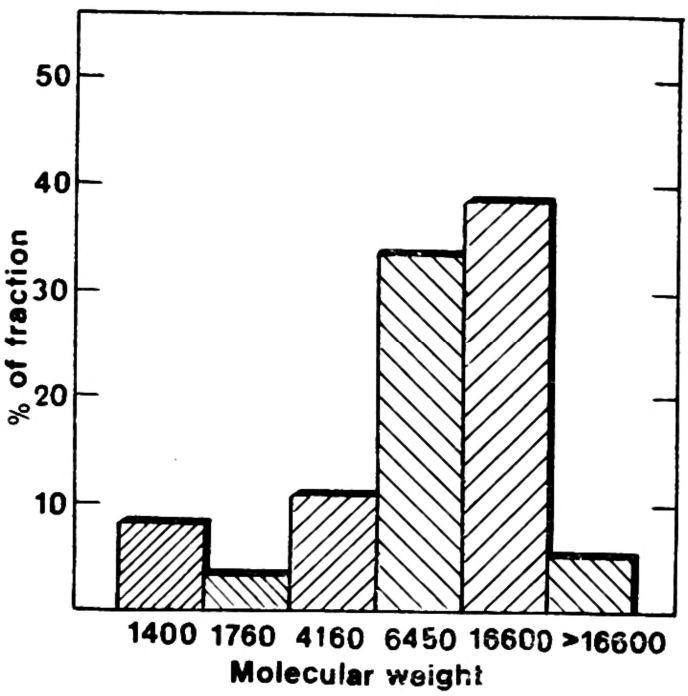

Fig. 1. Percent composition of dextrin fractionated depending on molecular weight; dextrin with low viscosity

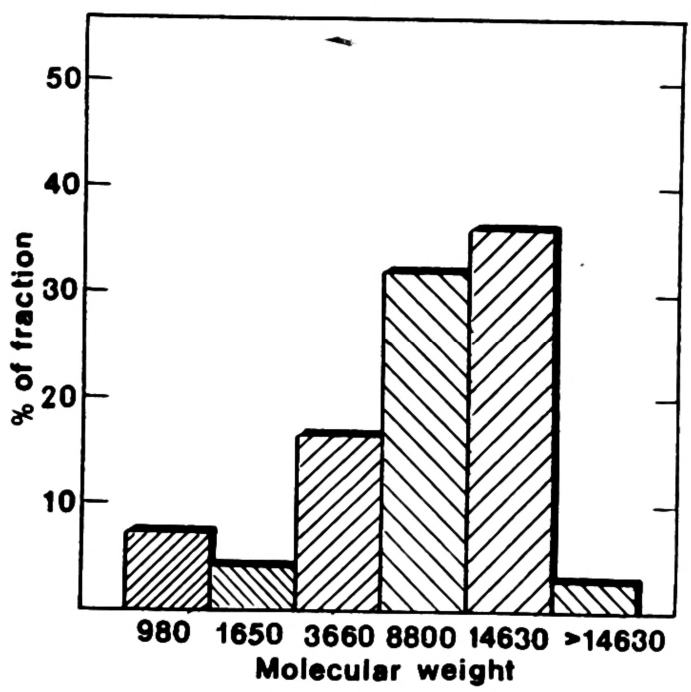

Fig. 2. Percent composition of dextrin fractionated depending on molecular weight; dextrin with mean viscosity

A comparison of fractions of dextrins with large molecules and approximate molecular weights 14 630 and 16 600 (Table 2) allows to state that dextrins produced with an addition of HCl at lower pH had more branched molecules — 27 segments in one molecule. Dextrins obtained in milder conditions (with an addition of HNO_3 and at pH = 3) contained smaller quantities of branches, i.e. about 17 segments in a molecule.

Fractions of dextrins with the lowest molecular weight constituted a small percentage in dextrins (7.5% and 8.3%). Besides mono- and oligosaccharides, these fractions included also products of starch degradation, or rather of glucose.

A chromatographic analysis of the fractions showed that besides glucose, maltose and a number of maltose-type sugars, they also comprise iso-sugars with bond 1-6, most probably of the β-type. Quantitative chromatographic determinations of glucose and other simple sugars in dextrins, made by comparison with the standards, revealed that the glucose level is 0.1-0.2% while that of sugars and degradation products

amounts to a total of 2.5-3.0%. Among the degradation products, hydroxymethyl-furfural and furfural as well as unidentified carbohydrates with a molecular weight lower than that of glucose were found in dextrins.

Chromatograms of the examined samples, developed with the use of resorcin reagent revealed the presence of ketoze-type compounds in the dextrin degradation products.

CONCLUSIONS

1. Yellow dextrins possess the greatest share of fractions with a mean molecular weight comprised within the limits of 6450 to 16 600.

2. More degradated yellow dextrins produced with the use of HCl as a catalyst with low viscosity, have more branched molecules than dextrins with mean viscosity.

3. Mean molecular weights of the particular fractions of less degradated dextrin with mean viscosity are in general higher than dextrins with low viscosity. This shows that dextrins with less branched molecules are more easily eluated with alcohol from the bed.

4. Dextrins contain small quantities of mono- and oligosaccharides. Besides maltose-type sugars, they have also iso-sugars which were formed during roasting of dextrins as a result of reversion processes.

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S t r e s z c z e n i e

Dekstryny otrzymane ze skrobi ziemniaczanej, zarówno w warunkach przemysłowych, jak i laboratoryjnych są zawsze mieszaniną węglowodanów o zróżnicowanej wielkości cząstek. Struktura dekstryn żółtych, zwłaszcza frakcji o większej masie cząsteczkowej znacznie się różni od struktury amylozy i amylopektyny. Cząsteczki dekstryn zbudowane są z reszt glukozowych, ale są bardziej rozgałęzione i mają dodatkowo inne wiązania, obok występujących w naturalnej skrobi. Aby stwierdzić jakiej wielkości cząstki występują w dekstrynach żółtych podzielono je na pięć frakcji. Rozdział prowadzono w taki sposób, że dekstrynę osadzoną w kolumnie na złożu celulozowym, wypłukiwano alkoholem etylowym o zmniejszającym się stężeniu od 95-14%. W otrzymanych frakcjach oznaczano średnią masę cząsteczkową, stopień rozgałęzień i procentowy udział frakcji.

W pierwszej frakcji wymywanej alkoholem o najwyższym stężeniu średnia masa cząsteczkowa była niska od 980-1400, w następnych wzrastała do 16 000. Stopień rozgałęzień w dekstrynach, jak również we frakcjach był dużo większy niż w skrobi wyjściowej, a proste odcinki łańcuchów w cząsteczce zawierały przeważnie od 3-5 reszt glukozowych. Badane dekstryny otrzymane w wyniku prażenia skrobi, mają ilościowo najwięcej frakcji o masie cząsteczkowej od 5000-10 000. Frakcja o najmniejszej masie cząsteczkowej, obok dekstryn zawierała w niewielkiej ilości cukry proste, jak glukoza, maltoza, maltotrioza, izocukry i wyższe oraz produkty rozkładu glukozy.