

Highly substituted hydroxyethylstarch

II. Preparation and characterization of fractions from acid-hydrolyzed hydroxyethyl derivative of native starch

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Procedures for hydroxyethylation of native potato starch, acid hydrolysis of the obtained product, and fractionation by partial precipitation of aqueous solutions of the degraded hydroxyethylstarch with polar organic solvents were elaborated. The individual fractions were characterized by relative molecular mass and degree of substitution.

Разработаны методики гидроксиэтилирования природного картофельного крахмала, кислого гидролиза полученного продукта и фракционирования парциальным осаждением водных растворов деградированного гидроксиэтилкрахмала полярными органическими растворителями. У отдельных фракций гидроксиэтилкрахмала была определена относительная молекулярная масса и степень замещения.

In the previous paper [1] we have described the preparation and characterization of low-molecular fractions of hydroxyethylstarch obtained by hydroxyethylation of acid-hydrolyzed potato starch. In the present work similar fractions were prepared but in the reversed way. In the first step, the native potato starch was hydroxyethylated with oxirane in a polar solvent (2-propanol) in alkaline medium. In further steps acid hydrolysis, neutralization, and fractionation of aqueous solutions by precipitation with polar organic solvents were performed. The advantage of this procedure over that described in [1] is higher utilization of oxirane (up to 90 %) and that alkali-labile compounds are not formed since hydroxyethylation of the native starch takes place predominantly [2] on the hydroxyl group at C-2 and the reducing groups, formed on subsequent acid hydrolysis, are stabilized against endiol rearrangement.

Higher utilization of oxirane in hydroxyethylation of native starch than in that of acid-hydrolyzed starch can be explained by the fact that, during acid hydrolysis, the more reactive amorphous regions of starch grains are degraded first while the remaining crystalline regions react with oxirane slower.

Hydroxyethylation at low temperature (45 °C) results in suspension of substituted native starch that retains the granular form (pasting does not occur) and therefore, acid hydrolysis can be effected without isolation of the intermediate and removal of the solvent. Hydrolysis of hydroxyethylstarch after addition of hydrochloric acid in suspension of a polar organic solvent (e.g. 2-propanol) is rather rapid and the desired decrease in relative molecular mass is achieved within 2—3 h at 70 °C.

At present, on account of safety, hydroxyethylation with oxirane in industrial application is effected at higher temperatures (100 °C and higher) by adding oxirane into the reaction vessel portionwise. The reaction rate at elevated temperatures is so high that oxirane reacts almost immediately and thus, its concentration is much lower than in the case of simple addition of the whole amount at the beginning of the reaction. The advantage of this procedure, besides safety, is shorter reaction time. However, when this procedure is applied to native starch the resulting product loses its granular form due to pasting and treating of the gelatinous hydroxyethylstarch in further step, acid hydrolysis, is rather difficult. To obtain a product similar as in [1] by acid hydrolysis of hydroxyethylstarch prepared at higher temperature, it is necessary to remove the polar organic solvent (oligo(ethylene glycols) formed by side reaction are present in the filtrate) and add the acid only into the homogeneous dispersion in water.

Fractional precipitation of aqueous solutions of partially hydrolyzed hydroxyethylstarches was effected by methanol, 2-propanol, and acetone. It was shown that the most advantageous way, *i.e.* using methanol at the beginning and then, after obtaining the first fractions, precipitating the evaporated solutions with acetone, gave a sufficiently wide range of fractions (Table 1). Precipitation with 2-propanol was less effective, the aqueous solution of hydroxyethylstarch turned turbid only after addition of a large amount of 2-propanol, then suddenly a large fraction

Table 1

Characterization of fractions obtained by precipitation with methanol and acetone

Fraction	$\eta/(\text{mm}^2 \text{s}^{-1})$	$(M_n)_r$	M.S.	Colour with iodine
II	5.241	113.570	0.59	Violet
III	5.256	90.430	0.64	Red
IV	4.566	71.740	1.03	Brown

Table 2

Fractional precipitation with 2-propanol

ΔV (2-propanol)/cm ³	95	5	30
m (fraction)/g	0	4.2	3.5

precipitated and further addition of the precipitant resulted in one more fraction only. Precipitation of aqueous solution of hydroxyethylstarch with 2-propanol is exemplified by the results in Table 2. The results of precipitation of aqueous solutions of hydroxyethylstarch with methanol and acetone, respectively, were compared in the previous paper [1] where the effect of degree of substitution and relative molecular mass on fractionation was discussed (at the achieved degree of substitution, inoculation of the starch macromolecule with poly(ethylene glycol) chains was excluded [2]).

Experimental

Instruments and methods

Relative molecular mass (M_n), was determined by membrane osmometric measurement on a Knauer apparatus (West Berlin). The intrinsic viscosity (η) of 6% aqueous solutions was measured using a U-3 Ubbelohde viscometer at 20 °C. Hydroxyethyl groups were determined by the method of Morgan as modified by Lortz [3] and calculated as molecular degree of substitution (M.S.).

Hydroxyethylation and acid hydrolysis

Procedure A

Into a reaction vessel provided with a stirrer and a reflux a suspension of native potato starch (100 g, dry material 83%, 0.501 mol) in 2-propanol (100 cm³) was placed and at boiling and stirring aqueous solution of sodium hydroxide (10 cm³, 40 mass %) was added dropwise. Boiling and stirring were continued for 1 h ensuring homogeneous distribution of alkali in the starch grains. The obtained suspension of alkalistarch in 2-propanol was then transferred into a pressurized vessel, oxirane (22 g, 0.5 mol) was added and shaken for 24 h at 40–45 °C. At almost 90% utilization of oxirane the degree of substitution was 0.9. After the reaction was finished, the cooled suspension was transferred into the reaction vessel, neutralized with diluted hydrochloric acid, and heated to 70 °C. Then concentrated

hydrochloric acid (2 cm³) was added and hydrolysis, proceeding for 21/2 h at 70 °C, was terminated by addition of 1 M-CH₃COONa (50 cm³). 2-Propanol was removed by filtration of the suspension.

Procedure B

Suspension of alkalistarch in 2-propanol was prepared according to the procedure A. Hydroxyethylation was performed in an autoclave after heating the suspension to 100 °C by addition of oxirane in small portions always after the decrease of pressure to the initial value. When hydroxyethylation was over, 2-propanol was filtered off and to the pasty hydroxyethylstarch, water (350 cm³) was added. After swelling and neutralization the gel was heated to 50 °C, concentrated hydrochloric acid (15 cm³) was added and the temperature (50 °C) was maintained for 3 h. Acid hydrolysis was terminated by addition of 1 M-CH₃COONa (400 cm³).

Fractionation

To the aqueous solution prepared by the procedure B (or to hydroxyethylstarch obtained by the procedure A in water (750 cm³)) methanol (400 cm³) was added slowly with stirring and centrifuged. Drying of the centrifugate afforded 22.4 g of substance (fraction I). To the supernatant increased amount of methanol (500 cm³) was added and centrifugation gave 21.5 g of substance (fraction II). The supernatant was evaporated *in vacuo* to 200 cm³ and acetone (150 cm³) was added dropwise with stirring. After centrifugation and drying, 19.6 g of substance was obtained (fraction III). The supernatant was precipitated with acetone (300 cm³), centrifuged and dried to give 24.0 g of substance (fraction IV). Evaporation of the supernatant *in vacuo* resulted in 35.0 g of oily compound containing also inorganic salts (fraction V); this fraction was not characterized further.

Results

Both procedures for the preparation of hydroxyethylstarch and its fractionation led to fractions of similar properties. The product prepared by the procedure B was fractionated according to the method described in Experimental and the fractions obtained are characterized in Table 1. The fraction I was insoluble in water and was characterized only with the degree of substitution (M.S. 0.33).

Fractional precipitation with 2-propanol afforded only few fractions as seen from the precipitation pattern (100 cm³, 10 mass % aqueous solution of hydroxyethylstarch) in Table 2. After obtaining two fractions, addition of further 2-propanol brought about gel formation.

References

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