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SYNTHESIS OF WATER-SOLUBLE DERIVATIVES OF THE PROTEINS OF HIDE GLUE

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New methods have been developed for obtaining β-chloroethylated, hydroxyethylated, and cyanoethylated proteins from hide glue, and their physicochemical constants and relative and specific viscosities have been determined.

After chemical modification, partially hydrolyzed protein (hide glue) — a protein waste of the leather industry [1] — may find new use, as, for example, a modifier of viscose silk. When hide glue is added to a viscose solution, the dyeability of the silk with acid dyes is improved and its heat resistance is raised.

In order to obtain modified proteins soluble in water [2, 3], animal proteins are treated with ethylene chlorohydrin in the presence of acids or alkalis at room temperature. We carried out the synthesis of β-chloroethylated protein by dissolving hide glue in the presence of the catalyst H_2SO_4. The influence of the concentration of the catalyst on the yields of β-chloroethylated and hydroxyethylated proteins was investigated (Table 1).

The highest yield (237 g) of β-chloroethylated protein was observed at a catalyst concentration of 4%.

The β-chloroethylated protein had mp 130—133°C, dissolved well in water, and was insoluble in nonpolar solvents. The maximum nitrogen content in the β-chloroethylated protein was observed at concentrations of the catalyst (H_2SO_4) of 1—4%. Raising the catalyst concentration to 8% led to a decrease in the amount of nitrogen in the reaction products, which was connected with degradation of the protein.

Hydroxyethylated protein was also synthesized from hide glue, with the use of caustic soda as catalyst. The highest yield of hydroxyethylated protein (252 g) was observed when the reaction was performed at a 2.7% concentration of catalyst for 3 h. The hydroxyethylated protein had mp 116—118°C and was soluble in water, giving colorless clear solutions. At a catalyst concentration greater than 3% the nitrogen content of the hydroxyethylated protein fell, which was connected with the degradation of the product itself.

The cyanoethylated protein was synthesized by dissolving the hide glue in acrylonitrile [5] in the presence of a 2% solution of caustic soda. The results of a study of the influence of the catalyst concentration on the yield of cyanoethylated protein (15 g of hide glue, 100 ml of acrylonitrile) are given in Table 2.

The highest yield (25.50 g) of cyanoethylated protein with the maximum nitrogen content (20.84%) was observed when the reaction was carried out in 5% caustic soda. The cyanoethylated protein dissolved in water, swelled strongly in dimethylformamide, and did not dissolve in nonpolar solvents, mp 180—183°C. An increase in the amount of catalyst to 10% led to a fall in the yield of nitrogen in the product. The structures of the products were shown by IR spectral analysis.

The relative viscosities of solutions of the initial, the hydroxy-, the β-chloro-, and the cyanoethylated proteins were measured in an Ostwald viscometer (⌀ = 0.75mm) at 25±0.01°C. A definite amount of protein was dissolved in ethylene chlorohydrin, which had an outflow time of 53 s.

Relative and specific viscosities were calculated by a known procedure [6].

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TABLE 1. Influence of the Concentration of Catalyst on the Yields of β-Chloroethylated and Hydroxyethylated Proteins

Experiment No.	Catalyst concentration, %		Yield, g	Elementary composition, %	
	H_2SO_4	NaOH		nitrogen	chlorine
1	1.0		209	14.55	0.68
2	2.0		215	12.75	11.75
3	4.0		237	12.40	14.64
4	8.0		192	10.94	18.51
5		1.0	215	13.50	-
6		1.27	226	13.50	-
7		2.7	252	11.02	-
8		4.0	244	9.45	-
9		5.0	171	3.72	-

TABLE 2. Influence of the Catalyst Concentration on the Yield of Cyanoethylated Protein

Experiment No.	Amount of alkali, %	Yield of product, g	Nitrogen content, g
1	1.0	16.5	16.34
2	2.0	18.72	17.00
3	5.0	25.50	20.84
4	10.0	10.48	9.76

TABLE 3. Viscosities of Solutions of Various Protein Derivatives

Compound	Outflow time of the solution, s	Viscosity, dl/g	
		relative	specific
Hide glue derivative			
β-chloroethylated	70	1.32	0.32
hydroxyethylated	59	1.11	0.11
cyanoethylated	74	1.39	0.39
Hide glue, purified	95	1.79	0.79

As can be seen from Table 3, the relative and specific viscosities of the protein derivatives were lower than those of the initial protein (hide glue). This shows that on the treatment of hide glue with acid and alkaline catalysts partial degradation takes place.

Thus, we have developed new methods for obtaining β-chloroethylated, hydroxyethylated,and cyanoethylated proteins from hide glue and have determined their physicochemical constants and their relative and specific viscosities.

EXPERIMENTAL

Synthesis of the β-Chloroethylated Protein. To a stirred solution of hide glue (200 g) in 1 liter of ethylene chlorohydrin was added, dropwise, 25 ml of conc. H_2SO_4, which corresponded to 4% of sulfuric acid in the reaction mixture. Stirring of the mixture at room temperature was continued for 4 h. Then it was neutralized with aqueous ammonia (25%) and precipitated with dioxane (2 liters). The dry residue was washed with dioxane and dried at 80—85°C under vacuum. Yield 237 g.

Synthesis of the Hydroxyethylated Protein. To a solution of hide glue (200 g) in 1 liter of ethylene chlorohydrin kept at a temperature of 20—25°C was added 162 ml of 20% caustic soda solution, which corresponded to 2.7% of caustic soda in the reaction mixture The reaction mixture was kept with constant stirring for 3 h and was then neutralized with HCl (3%), and the product was precipitated with acetone. Yield 252 g.

Synthesis of the Cyanoethylated Protein. To 15 g of hide glue that had been treated for 15 min with 50 ml of a 16% solution of caustic soda, which corresponds to 5% of caustic soda in the reaction mixture was added 100 ml of acrylonitrile. The reaction was carried out with constant stirring at 50°C for 4 h. The resulting viscous mass was precipitated with acetone. The yield of product after drying at 90—100°C under vacuum was 25.5 g.

IR spectra were taken on IK-10 and Specord HIR (Carl Zeiss, Jena) instruments.

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