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DEGRADATION OF CARBOXYMETHYLSTARCH UNDER THE ACTION OF γ-RADIATION

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It has been shown that the main process in the radiolysis of carboxymethylstarch (CMS) is the degradation of the polysaccharide accompanied by a contraction of the MWD. Conditions have been developed for obtaining sodium-CMS with given molecular-weight and hydrodynamic parameters.

The main aim of this work was to obtain products with different molecular-weight and hydrodynamic parameters for their subsequent medicobiological investigations as polymeric carriers for drugs.

Sodium carboxymethylstarch (CMS) was obtained by the mechanochemical method [1]. The change in the supermolecular structure of the CMS in the dispersion process permits it to be irradiated in solution under dynamic conditions at a controlled pH, i.e., permits the degradation of the polymer to be carried out uniformly throughout its bulk and the depth of oxidative transformations to be lowered.

The radiolysis of aqueous solutions of CMS was accompanied by falls in the molecular weight of the polysaccharide and in the viscosity of the solutions (Table 1), i.e., the process of degradation was predominating. A comparison of these parameters with the analogous parameters for the hydroxyethylstarch (HES) used in clinical practice, which includes acid hydrolysis as a stage in production [2], permitted the conclusions that the viscosities and molecular weights of the CMS and the HES of equal degrees of substitution were close (Table 2), while the molecular weight of clinical dextran with the same characteristic

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TABLE 1. Change in the Main Parameters of a 6% Solution of CMS during Radiolysis

Degree of substitution	Radiation dose, Mrad	pH	η_{rel}	$[\eta]$, dl/g	$\overline{M}_W \cdot 10^3$	s	RS, mole/g	D (λ 265 nm), arb. units
0.4	2	6,8	5,05	0,315	429,2	1,0	0.037	0,130
	4	6,7	2,80	0,195	144,1	3,1	0,061	0,405
	6	6,5	2,07	0,144	87,9	5,1	0,125	0,530
	8	6,4	1,83	0,125	59,6	7,5	0,212	0,615
0.6	2	7,3	2,90	0,244	250,0	1,8	0,038	0,090
	3	7,3	2,70	0,180	125,0	3,6	0,042	0,235
	4	7,0	2,39	0,150	89,6	5,0	0,062	0,310
	6	6,7	1,83	0,128	65,5	6,8	0,100	0,430

TABLE 2. Comparison of the Viscosities and Molecular Weights of CMS, HES, and Dextran

CMS (D.S. = 0.6)		HES (D.S. = 0.6)		Dextran	
$[\eta]$	$\overline{M}_W \cdot 10^3$	$[\eta]$	$\overline{M}_W \cdot 10^3$	$[\eta]$	$\overline{M}_W \cdot 10^3$
0,244	250,0	0,241	271,0	0,252	65,6
0,180	125,0	0,173	124,0	0,214	50,0
0,150	80,0	0,151	71,8	0,182	31,4
0,128	55,5	0,130	54,8	0,133	18,4

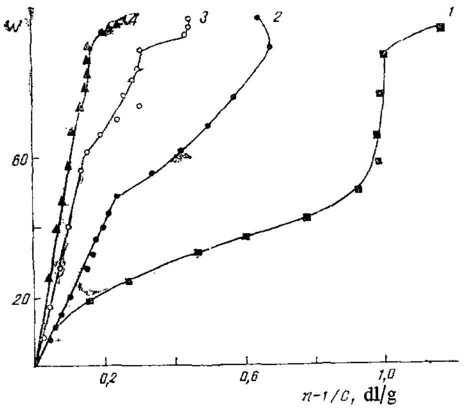

Fig. 1

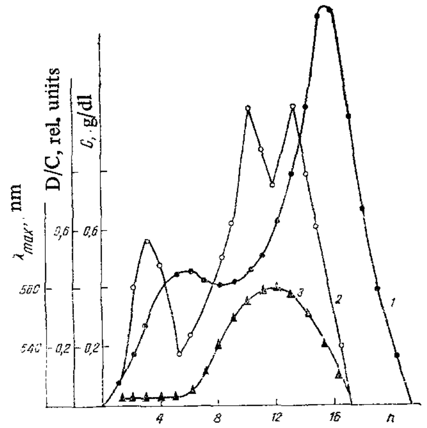

Fig. 2

Fig. 1. Integral curves of the viscosity distribution of irradiated CMS with a degree of substitution of 0.6 (W — cumulative weight fraction). Radiation dose: 1) 0; 2) 1.0; 3) 2.5; 4) 4.0 Mrad.

Fig. 2. Gel chromatogram of CMS with a degree of substitution of 0.6. Radiation dose 2.5 Mrad: 1) elution curve; 2) optical density at the maximum of the absorption of the iodine complexes of the fractions; 3) maximum wavelength of the absorption of the iodine complexes of the fractions.

viscosity $[\eta]$ was five times lower, which is a consequence of the branched structure of starches and of the introduction of substituents.

The CMS was subjected to fractionation by the GPC method and the fractions were characterized with respect to $[\eta]$ and $\overline{M}_W$, which enabled us to establish the Mark–Kuhn–Houwink relationship for the radiolyzed CMS. At a degree of substitution of 0.6

$$[\eta] = 5.65 \cdot 10^{-4} \overline{M}_W 0{,}49.$$

This equation may also be used with adequate accuracy (~5%) for radiolyzed CMS with a degree of substitution of 0.4.

When the CMS was irradiated, its molecular-weight distribution underwent transformation with a contraction, as we have established previously for native starch [3] and for dextran [4].

Figure 1 shows the integral viscosity distribution of the CMS (D.S. = 0.6) irradiated with doses of 0–4.0 Mrad, from which it can be seen that it was mainly the high-molecular-weight fractions that underwent breakdown. This is particularly important, since they promote the aggregation of erythrocytes, damage the clotting system of the blood, and cause other undesirable reactions [5]. Even at a dose of 2.5 Mrad the amount of high-molecular-weight amylopectin fractions ($[\eta] = 0.440$, $\overline{M}_W = 800 \cdot 10^3$) did not exceed 10% (Fig. 2), and at a dose of 4 Mrad they were practically absent. This permits the exclusion of a fractionation stage in the technological production process and thereby increases the practical yield of product.

As can be seen from Table 1, with a rise in the degree of substitution of the CMS the intensity of the UV absorption and the reducing capacity (RS) of the irradiated samples, due both to the terminal reducing groups and to α-hydrocarbonyl groups formed in oxidative reactions, decreased, although the number of ruptures of glycosidic bonds (S) in the initial macromolecule increased. At the same time, the pH of the irradiated solutions did not fall below 6.0 even at dose of 12 Mrad. Apparently, the $R{-}CH_2COONa{-}R{-}COOH$ buffer system formed on irradiation, where R is the residue of the starch macromolecule, modifies the action of all the possible factors changing the pH and, moreover, the total number of hydroxy groups capable of oxidation falls with a rise in the degree of substitution of the CMS.

Thus, a variation in the degree of substitution of the CMS and in the radiation dose enables us to obtain starch products with given physicochemical and biological indices.

Medicobiological investigations of them have shown that they are sterile, nontoxic, and fully compatible with the animal organism.

EXPERIMENTAL

Sodium CMS was dissolved in a 0.9% solution of sodium chloride and the solution was poured into glass tubes, and subjected to γ-radiation with doses of from 2 to 12 Mrad. The power of the ^{60}Co γ-source was 300 r/sec.

From the nature of its substituents, sodium CMS is a polyelectrolyte and, since the acetate ion is the conjugate base of a weak acid, after the achievement of equilibrium the solution will be basic. The initial pH of 6% solution was 8.5, and $(\eta - 1)/c$ was 1.5 dl/g.

The weight-average molecular weights ($\overline{M}_W$) were determined by the light-scattering method on a FPS-3 instrument at a wavelength λ of 546 nm. The refractive index increment determined on a differential diffractometer for the given wavelength had a value $(\partial n/\partial c) = 0.144$. The solvent used was 0.9% sodium chloride.

The relative and intrinsic viscosities were measured on an Ubbelohde viscometer at 20 and 25°C, respectively, and the concentrations of the solutions on a previously calibrated ITR-2 interferometer.

Preparative fractionation was carried out by the GPC method, as described previously [1], on Sephadex G-200. The fractions were characterized by their iodine-binding capacity, according to [6].

SUMMARY

It has been shown that the main process in the radiolysis of aqueous solutions of CMS is degradation, accompanied by a contraction of the MWD.

Conditions have been worked out for obtaining CMS with given molecular-weight and hydrodynamic parameters.

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CARBOHYDRATES OF *Alium*.

VII. CHARACTERISTICS OF THE POLYSACCHARIDES OF THE SKIN OF *Alium cepa*

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The polysaccharides in the skin of the garden onion have been investigated. Their qualitative and quantitative compositions have been determined. The physicochemical characteristics of the pectin substances are given and the water-soluble polysaccharide is characterized.

Continuing investigations of the carbohydrates of plants of the family of Alliaceae [1], we have studied the carbohydrate composition of three samples of the skin of the garden onion *Allium cepa* (Samarkandskii krasnyi variety) obtained in the "serp i molot" ["Sickle and Hammer"] Preserving Combine (Samarkand). The first specimen was obtained after supplementary factory treatment with water at 95-97°C, and the second and third differed in their times of harvesting. From a single sample, after treatment with chloroform to eliminate extractive substances, the ethanol-soluble fraction (ES), the water-soluble polysaccharides (WSPSs) the pectin substances (PSs), and the hemicelluloses (HMCs) A and B were extracted successively with 96 and 80% ethanol. The results of the investigations are given in Table 1.

As can be seen from Table 1, the amounts of polysaccharides in this skin of the food onion were different, pectin substances predominating. The ethanol-solution fractions of samples I-III contained fructose, glucose, sucrose, and raffinose, which were identified by PC (system 1).

The WSPs-III formed a cream-colored powder readily soluble in water and insoluble in organic solvents. The molecular weight of the WSPs-III determined by gel chromatography on a column of Sephadex G-75 was 5700.

In the product of complete acid hydrolysis, fructose (main spot) and glucose (weak spot) were detected with the aid of PC (system 1). The IR spectrum was similar to the spectra of glucofructans of the mixed type [1].

Samples of the pectin substances and of the hemicelluloses A and B were subjected to complete acid hydrolysis. The hydrolysates were analyzed by PC (system 2) and GLC in the form of the corresponding aldononitrile acetates and polyol acetates [2].

The IR spectra of the pectin substances contained the absorption bands also characteristic for other pectins [3, 4].

Vibrations in the 1150 cm^{-1} region are probably connected with the maximum degree of esterification [3] and triplets of pyranose rings (815, 870, 910 cm^{-1}) show the presence of 1,4-bonds and the predominance of α-glycosidic bonds between the galacturonic acid and monosaccharide residues.

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*Deceased.

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