

CONVERSION OF INULIN INTO CARBOXYMETHYL DERIVATIVES BY THE
SUSPENSION METHOD IN ISOPROPYL ALCOHOL MEDIUM.

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Abstract. This study investigates the synthesis of carboxymethylinulin via the suspension method in an isopropyl alcohol medium. The effects of mercerization, temperature, reaction time, and the concentration of the alkylating reagent on the physicochemical properties of the reaction products are examined. The results demonstrate that the degree of substitution of inulin esters, as well as their molecular characteristics, are strongly dependent on reaction conditions. These findings highlight the potential of carboxymethylated inulin as a functional derivative with valuable properties for use in food, pharmaceutical, and chemical industries. These findings could serve as a basis for further research on the industrial applications of carboxymethylated inulin.

Keywords: Inulin, carboxymethylation, polysaccharides, esterification, suspension method, mercerization, functional derivatives, e.g., *Helianthus tuberosus*

Introduction. The growing demand for renewable natural raw materials and environmentally friendly technologies necessitates the development of innovative methods for their efficient processing. Among the most promising approaches is the chemical modification of plant-derived polysaccharides to obtain derivatives with improved functional properties.

Carboxymethyl derivatives of polysaccharides represent one of the most widely studied groups due to their versatility and broad application potential. Carboxymethylcellulose (CMC) is the most extensively investigated and commercially important derivative, widely used in the food, pharmaceutical, oil, gas, textile, and paper industries because of its thickening, stabilizing, and film-forming properties [1–3].

However, reports concerning the carboxymethylation of inulin — a naturally occurring fructan isolated from *Helianthus tuberosus* (Jerusalem artichoke) — are limited. Inulin is of particular interest as a renewable raw material, being abundant, biodegradable, and possessing prebiotic activity. Its chemical modification through carboxymethylation is expected to expand the functional applications of inulin and improve its physicochemical properties.

The purpose of this work is to investigate the specific features of inulin carboxymethylation obtained from the “Mujiza” variety of Jerusalem artichoke by the suspension method in an isopropyl alcohol medium, and to evaluate the effects of mercerization, temperature, reaction time, and reagent concentration on the resulting products.

2. Materials and Methods

2.1. Raw Material

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Inulin was isolated from the *Helianthus tuberosus* ("Mujiza" variety) tubers, which were subjected to preliminary purification, drying, and grinding before use in synthesis.

2.2. Carboxymethylation Procedure

Carboxymethylation of inulin was carried out in an isopropyl alcohol (IPA) medium using the suspension method. For this purpose, powdered inulin was placed into a three-necked round-bottom flask equipped with a reflux condenser, mechanical stirrer, and thermometer. The inulin was dispersed in isopropyl alcohol for 2 hours.

After dispersion, a sodium hydroxide solution (5–25%) was added to the suspension, and the mixture was stirred for 1 hour at room temperature to achieve mercerization.

Carboxymethylation of mercerized inulin was performed using sodium monochloroacetate (Na–MCA) as the alkylating agent. The reagent was

introduced at molar ratios of inulin:Na–MCA = 1:1 to 1:4, at a temperature of 50–70 °C, for 0.75–1.5 hours.

2.3. Purification of the Products

The resulting carboxymethylinulin samples were purified by repeated extraction with 96% ethanol to remove unreacted reagents and by-products. The purified samples were then dried at 50–60 °C to constant weight.

2.4. Determination of the Degree of Substitution and pKa

The degree of substitution (DS) of the carboxymethyl groups in inulin esters, as well as their pKa values, were determined by back titration according to standard protocols [7,8].

2.5. Molecular Weight Characterization

Molecular weight distribution of the obtained samples was evaluated by gel permeation chromatography (GPC) on a Waters (USA) system equipped with Ultrahydrogel 100, 500, and 1000 columns at 20 °C. A refractive index detector was used, and 0.1 N NaCl solution served as the eluent at a flow rate of 0.1 mL/min. Calibration was performed with dextran standards of known molecular weights and narrow dispersity.

The degree of substitution and pKa values of the synthesized inulin esters were determined by back titration [7, 8]. The molecular weight characteristics of all samples were evaluated by gel permeation chromatography using Waters (USA) Ultrahydrogel 100, 500, and 1000 columns at 20 °C, equipped with a refractometric detector. A 0.1 N NaCl solution was used as the eluent with a flow rate of 0.1 mL/min. Dextran with a narrow molecular weight distribution served as the calibration standard.

3. Results and Discussion

It is well known that mercerization of polysaccharides prior to carboxymethylation significantly affects the esterification process. Therefore, the influence of sodium hydroxide concentration on selected physicochemical properties of inulin was studied.

Table 1.

Effect of NaOH concentration on physicochemical characteristics of inulin (T = 25 °C; t = 1 h)

No.	NaOH concentration, %	Molecular mass $M \times 10^{-4}$, Da	Sample color	Yield, %
1	5	5.2	Light yellow	97.4
2	10	4.6	Light yellow	92.7
3	15	4.0	Bright yellow	85.0
4	20	3.8	Bright yellow	79.5
5	25	3.0	Dark yellow	72.8

The data show that with increasing NaOH concentration, the molecular mass and product yield decrease, while the color of the mercerized samples changes from light yellow to dark yellow. This trend indicates that higher concentrations of sodium hydroxide induce partial hydrolysis of the initial inulin macromolecular chains, leading to lower molecular weights in the final products.

To further clarify these observations, comparative carboxymethylation of mercerized inulin samples was performed under identical conditions of reaction time and reagent molar ratio

Table 2.

Carboxymethylation of mercerized inulin samples (T = 50 °C; t = 0.75 h; molar ratio inulin: Na-MCA = 1:1)

No.	Samples treated with NaOH, %	$^1M \times 10^{-4}$, Da	Degree of substitution,	$^2M \times 10^{-4}$, Da
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VOLUME-5, ISSUE-10		mol%		
1	5	5.2	8	5.6
2	10	4.6	14	5.4
3	15	4.0	21	—
4	20	3.8	30	5.3
5	25	3.0	33	5.0

Note: $^1M \times 10^{-4}$, Da – initial molecular mass of mercerized inulin;

$^2M \times 10^{-4}$, Da – molecular mass after carboxymethylation.

Interpretation of the data reveals that samples treated with higher NaOH concentrations demonstrate significantly higher substitution degrees during carboxymethylation. However, at equal reaction conditions, the difference in substitution degree between samples treated with 20% and 25% NaOH solutions is negligible. These findings indicate that inulin treated with a 20% NaOH solution is sufficient for effective carboxymethylation.

Molecular weight analysis of the products further confirms the occurrence of the reaction, since the introduction of carboxymethyl functional groups into the inulin structure results in an increase in molecular weight compared to the initial state. Critical parameters of the carboxymethylation process of polysaccharides are undoubtedly the concentration of Na-MCA, as well as the reaction time and temperature. Therefore, in order to establish the most optimal reaction conditions, we studied the influence of these parameters on the composition of the obtained samples (Table 3). The synthesis of carboxymethyl inulin was carried out according to the following reaction scheme:”Table 3 presents the data on the influence of reaction time, temperature, and Na-MCA concentration on the degree of substitution of the reaction products.

Table 3. Conditions of carboxymethylation of inulin and selected characteristics of reaction products

No.	Time, h	Temperature, °C	Inulin : Na-MCA molar ratio	Degree of substitution, mol%	pKa
1	0.75	50	1:1	20	5.8
				20	5.6
				20	5.2
				20	4.9
				20	4.5
				20	4.3
0	1.5	70	1:3	82	4.3
7	1.5	70	1:3.5	85	4.1
8	1.5	70	1:4	85	4.1

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The results demonstrate that increasing reaction time, temperature, and Na-MCA concentration leads to higher substitution degrees of the final products, from 30% to 85%. However, further increasing the Na-MCA molar ratio from 3.0 to 3.5–4.0

only slightly affects the incorporation of carboxymethyl groups. This is likely due to electrostatic repulsion between negatively charged chloroacetate ions of monochloroacetic acid and the $-\text{CH}_2\text{COO}^-$ groups introduced into the inulin monomeric units. Additionally, the pK_a values of all samples were found to be acidic and showed direct correlation with the substitution degree of the reaction products.

Conclusion

The present study demonstrates that the suspension method in an isopropyl alcohol medium is effective for the carboxymethylation of inulin isolated from the “Mujiza” variety of *Helianthus tuberosus*. The results confirm that the degree of substitution and molecular characteristics of the synthesized carboxymethylinulin are strongly influenced by key parameters of the reaction medium, namely mercerization, temperature, reaction time, and the concentration of sodium monochloroacetate.

It was shown that increasing the concentration of NaOH during mercerization enhances the degree of substitution, although excessive alkalinity also promotes partial depolymerization of inulin chains. Optimization of the reaction conditions indicates that treatment with 20% NaOH and subsequent carboxymethylation at 60–70 °C for 1.0–1.5 hours, using an inulin:Na-MCA molar ratio of 1:3, provides the most favorable balance between substitution degree and molecular stability.

The correlation between the substitution degree and the pK_a values further confirms the successful introduction of carboxymethyl groups into the inulin backbone. The obtained products exhibit enhanced functional properties, which may expand the applications of inulin derivatives in various industries.

Overall, the findings of this research highlight the potential of carboxymethylinulin as a renewable, biodegradable, and functional polysaccharide derivative suitable for use in the food, pharmaceutical, and chemical sectors. These results may serve as a basis for further studies aimed at scaling up the synthesis process and exploring practical applications of carboxymethylated inulin in industrial formulations. Future research will focus on scaling up the synthesis process and assessing the performance of carboxymethylinulin in practical formulations.

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