



Novel Synthesis of Coordination Bipolymer Precursors of Sulfated Macromolecules as Alternative Promising in Biomedicine, pharmaceuticals and Engineering Industry by Oxidation of Sustainable and Biodegradable Sulfated Iota-Carrageenan by Alkaline Permanganate

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Abstract

Keto-acid derivatives of sulfated iota -carrageenan (ICAR) was quantitatively prepared by the oxidation of iota- carrageenan as sulfated macromolecules by potassium permanganate in alkaline medium at pH's > 12. The diketo-derivative was characterized by formation of 2,4-dinitrophenyl hydrazone and dioxime derivatives when reacting with 2,4-dinitrophenyl hydrazine and hydroxyl amine, respectively. This oxidation product can be used as a dietary fiber and a functional fiber when added to food. In addition, it found that the product has a high affinity for chelation with most of divalent and polyvalent metal ions forming stable coordination biopolymer complexes. The product is characterized by its non-toxicity, low cost and high performance.

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Introduction

Carrageenans (CAR) are water-soluble sulfated polysaccharides of linear block copolymer structure builds up of alternating 3-linked- β -D-galactopyranose and 4-linked- α -D-galactopyranose units [1-4]. They have wide applications in biomedicine, pharmaceuticals, food and other industrial technology owing to their outstanding advantages such as sustainability, biodegradability, compatibility and low cost.

They used as gelling agents in most of food industry formulations for thickening and filling, anti-agulant of blood, tooth paste, textile industry as stiffening bind materials, printing, thickening latex emulsion paints, ceramic glazing and as antibiotics ice in fishing boats [1,4].

Permanganate ion is a strong oxidant, which has been used for oxidation of most organic [5-10] and inorganic [11-13] substrates. Again, Hassan and coworkers were studied the kinetics of oxidation of some macromolecules containing secondary alcoholic groups either natural [14-16] or synthetic [17] polymers by alkaline permanganate at pH's > 12. They reported that oxidation of secondary alcoholic groups was led to formation of the corresponding keto-derivatives in alginates [18] pectates [19] and carboxymethyl cellulose [20], methyl cellulose [21], chondroitin-4-sulfate [22] and kappa-carrageenan [23] as biopolymer precursors. However, a little attention has been focused to the oxidation of macromolecules in particularly sulfated polysaccharides that containing both primary and secondary alcohols by this oxidant [24]. This fact may be attributed to the complexity of the reaction kinetics which may not allow a mechanistic conclusion.

Therefore, the present work of permanganate oxidation of iota carrageenan as natural polymers containing both primary and secondary alcoholic groups is of great significant to gain further information on the nature of the products as well as the interaction of this macromolecule in aqueous alkaline solutions with a special sight on the influence of the nature of the functional groups on the mechanistics and kinetics in this redox system. In addition, this work aims to synthesize ketoacid derivatives as biopolymer precursors. These biopolymers could be used to encapsulate, protect and deliver bioactive or functional components such as minerals, peptides, proteins, enzymes, drugs, lipids or dietary fibers. The mono- or diketoacid derivatives formed as final oxidation products would useful as precursors for synthesis of new biopolymers as selective biochelating agents for polyvalent cations forming ionotropic gels. These gels would be useful as conductors, selective cation sieves, semi-permeable membranes, biocatalysts and cation exchange resins.

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Experimental

Materials

All materials used were of analytical grade. Doubly distilled water was used in all preparations.

Iota-Carrageenan (I-CAR) employed in the present study (Fluka) was used without further purification. This procedure was performed by the addition of carrageenan's powder reagent to bidistilled water whilst rapidly stirring the solution to avoid the formation of lumps which swell with difficult. A stock solution of permanganate was prepared, stored and standardized as described elsewhere [20]. All other reagents were prepared by dissolving the requisite amounts of the sample in doubly distilled water.

Synthesis of Keto-Acid Derivatives of Sulfated Carrageenans. A Typical Example is Diketo-Acid Iota-Carrageenan (DKA-ICAR)

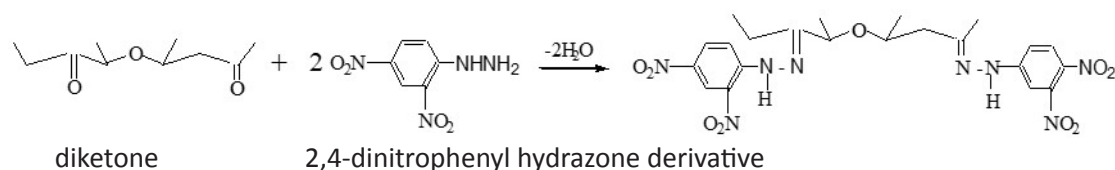
Iota-carrageenan (I-CAR) powder (5 g) was dissolved in 350 cm³ of deionized water whose pH was previously adjusted to pH \geq 12 using sodium hydroxide. This process was performed by stepwise addition of the powder to the solution while stirring rapidly and continuously the solution to avoid the formation of aggregates [23]. A 150 cm³ solution containing 5.17 g of potassium permanganate and 5.43 g of sodium fluoride was then added stepwise over 2 hours to the carrageenan solution. The reaction mixture was stirred for 48 h at room temperature, the formed MnF₄ was filtered off, and the solution was concentrated to one-fifth of the original solution using a rotary evaporator. A portion of this concentrated solution was acidified using dilute acetic acid to a pH of ca. 5-6. The resultant solution dried under vacuum, and then subjected to elemental analysis and IR spectroscopy.

Condensation Tests

The diketone were also identified by 2,4-dinitrophenyl hydrazine and hydroxyl amine, condensation tests, as follows:

With 2,4-Dinitrophenyl Hydrazine

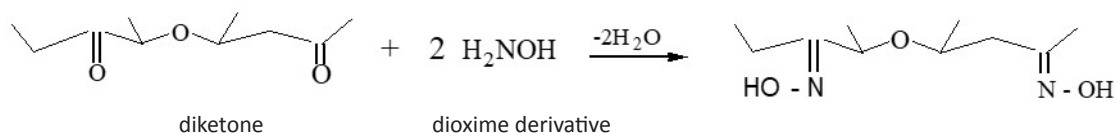
A solution of diketone was heated with a solution of 2,4-dinitrophenyl hydrazine on water-bath and gave yellow precipitate of the hydrazone derivative of ICAR



ANAL: 2,4-dinitrophenyl hydrazone derivative of iota-carrageenan C₂₄H₂₀O₂₂N₈S₂ (836): Calcd. (found): C, 34.45 (34.56); H, 2.39 (2.43); N, 13.39 (13.42). IR: 3415 (OH of COOH group); 3320 (NH of hydrazone); 1660 (C=N of hydrazone) and 1262 cm⁻¹ (C—O—C of ICAR).

With Hydroxyl Amine

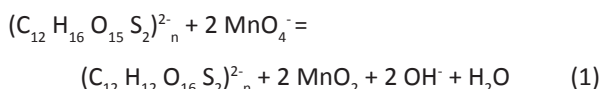
The diketone solution gave white precipitate when heated with hydroxyl amine on water-bath. The precipitate was dioxime derivative of iota-carrageenan



ANAL: Dioxime derivative of iota-carrageenan $C_{12}H_{14}O_{16}N_2S_2$ (506): Calcd. (found): C, 28.46 (28.23); H, 2.77 (2.73); N, 5.53 (5.62). IR: 3325-3355 (OH of COOH and oxime); 1670 (C=N); 1685 (C=O of COOH) and 1240 cm^{-1} (C—O—C of iota-CAR).

Results and Discussion

The stoichiometry of oxidation of iota-carrageenan by potassium permanganate conform the following equation,

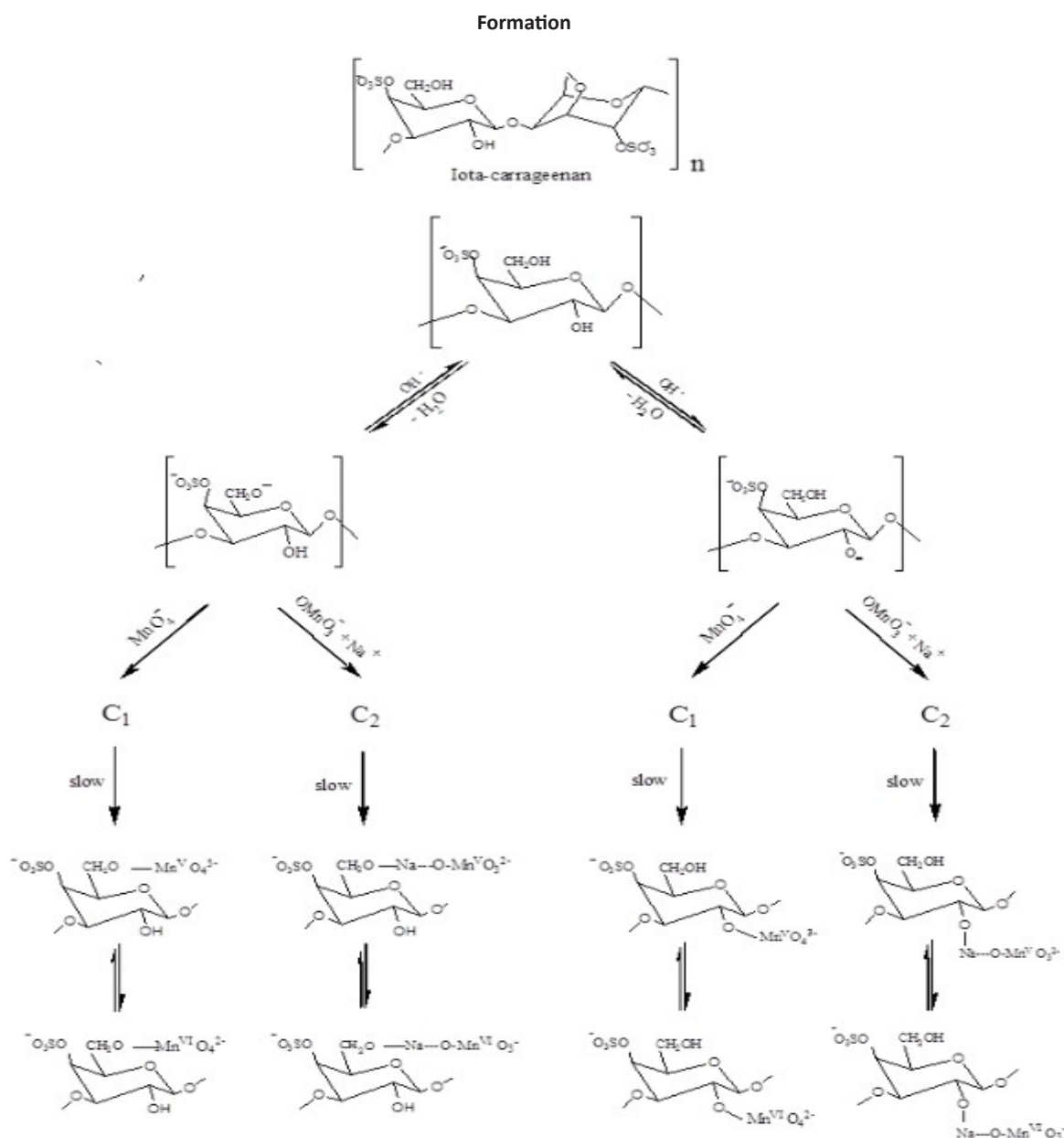


where $(C_{12}H_{16}O_{15}S_2)_n^{2-}$ and $(C_{12}H_{12}O_{16}S_2)_n^{2-}$ are the corresponding iota - carrageenan and keto-acid oxidation derivatives, respectively.

This diketo-acid derivative was reacted with 2,4-dinitrophenyl

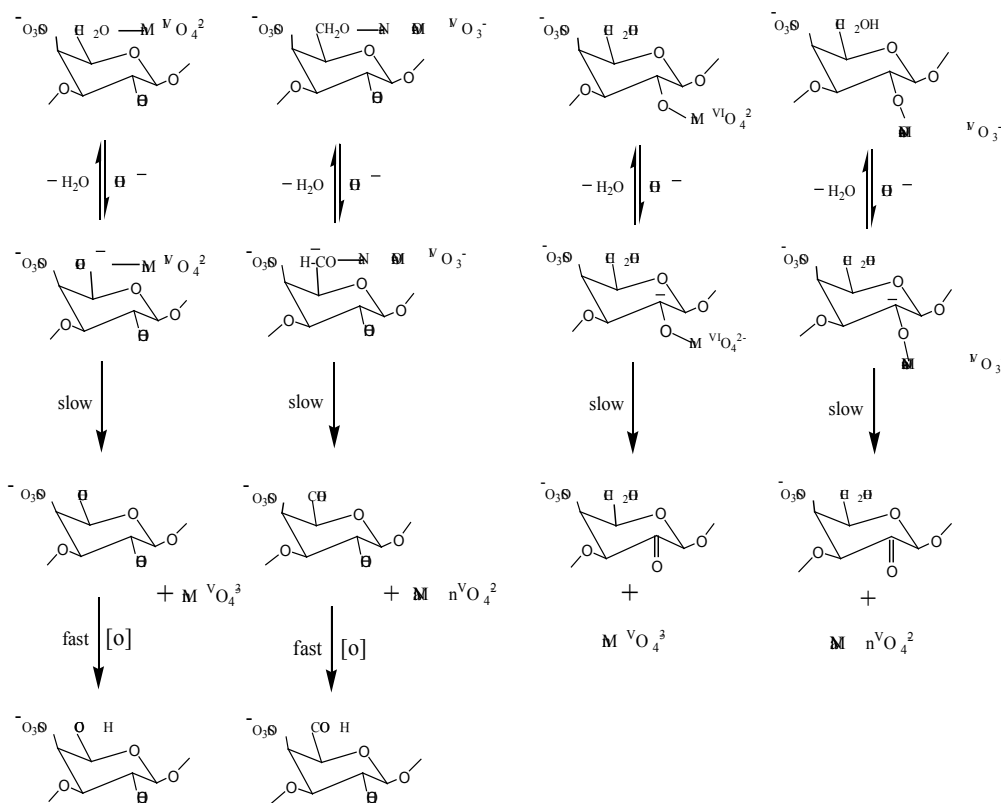
hydrazine and hydroxylamine to afford the corresponding bis-2,4-dinitrophenyl hydrazone and dioxime derivatives which gave satisfactory elemental analysis and spectroscopic data. The yield was 96.2%.

The oxidation of ICAR by alkaline permanganate was found to occur stepwise through formation of detectable intermediate complex $[ICAR-Mn^{VI}O_4^{2-}]$ and/or $[ICAR-Mn^{V}O_4^{3-}]$ involving manganate(VI) and/or hypomanganate(V) transient species [25,26]. As these intermediates build up, a slow decay takes place to give the products. A tentative reaction mechanism for the oxidation process is illustrated in Schemes I and II



Scheme I

Decomposition



Scheme II

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