PC 11 - In-Gel Carboxyethylation of Chitosan by β-Halopropionic Acids

A.V. Pestov[(1)],Y.A. Skorik[(2)],Y.G. Yatluk[(1)]

[(1)]I. Ya. Postovsky Institute of Organic Synthesis, Urals Division of the Russian Academy of Sciences, 20 Kovalevskoy St., 620219 Ekaterinburg, Russia - [(2)]Department of Chemistry, University of Pittsburgh, 219 Parkman Avenue, Pittsburgh, PA 15260, USA

Carboxyethyl-chitosan (CEC), a novel water-soluble chitosan derivative, has been prepared via reaction of low-molecular weight chitosan with β-halopropionic acids in aqueous solution. In later works, metal complex formation and potential applications as antioxidant and antimutagenic agents have been studied. In this paper, we present a simple and efficient method for carboxyethylation of chitosan using β-halopropionic acids "in-gel-synthesis", that was possible to add acrylic acid.

Reactions were performed using gels of chitosan in concentrated solutions of chloro-, bromo- or iodopropionic acids with subsequent addition of a base heated to 60°C for 24 h. Using 1H NMR spectral data, it was concluded that alkylation of chitosan by β-halopropionic acids under the reaction conditions gives N,O-CEC. It was also observed that the reaction is accompanied by the by-processes of hydrolysis and dehydrohalogenation of the β-halopropionic acids, yielding β-hydroxypropionic acid, bis(2-carboxyethyl) ether, and acrylic acid.

The degree of carboxyethyl substitution (DS) of N,O-CEC and the reaction rates varied significantly depending on the reaction conditions and nature of the base used. The results testify that even in the absence of base, high degrees of alkylation are obtained (DS=0.26–0.36). At addition of the base, the degree of alkylation increases (DS=0.83–1.02); in true solutions, such high values of DS can be attained in only five days. At carboxyethylation of chitosan with the alkaline β-bromopropionates, the DS increases in the order: Cs, Rb, K, Na, Li. Among the organic bases applied (tetrabutylammonium hydroxide, triethylamine, trimethylamine, pyridine, 4-N,N-dimethylaminopyridine, 2,6-lutidine and 1,5-diazabicyclo[4.3.0]non-5-ene), the highest DS was obtained using a moderately strong base triethylamine.

Thus, the suggested method of chitosan carboxyethylation in the gel state using halopropionic acids appears to be the most convenient, requiring the shortest reaction time and ensuring the highest DSs. The in-gel method can also be applied for synthesis of well-known carboxymethyl-chitosan via reaction with haloacetic acids.