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10TH

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AUGUST 10-13, 1997

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Kinetics Study of Glucose Acetylation in Starch Polymers by Quantitative ^{13}C NMR Spectroscopy

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Introduction

Naturally abundant glucose polymers are chemically modified and developed as alternative sources of materials in polymer industries. In the course of a program devoted to the chemical derivatization of starch macromolecules, the acylation kinetics and the rate of modification on each of the monomer positions was investigated. It was found that products having similar acetyl percentages but obtained by different chemical modifications processes had different substitution patterns for intermediate modification (1). In order to determine the relative acetylation rates on positions -2, -3, and -6 of the glucopyranose monomer subunit the acetylation kinetics for each of these positions was analysed.

NMR Study

NMR is the method of choice for investigating the substitution distribution in chemically modified polysaccharides. With a large spectral width, ^{13}C NMR gives a broad spectrum of well differentiated resonances for closely related chemical structures. It is thereby possible to assign and quantify well separated peaks. In order to perform ^{13}C resonance quantification, it is necessary to suppress NOE effects and leave enough time for the magnetization to return to equilibrium with the help of a relaxation agent. Under these conditions, a satisfactory degree of accuracy in the measurement of the area of each peak can be obtained (2).

Quantitative determination of polymaltoside esters

Starch macromolecules are polymaltosides constituted of poly- $\alpha(1\rightarrow4)$ -glucopyranosyl- subunits on which one primary (-OH -6) and two secondary (-OH -2, -OH -3) hydroxyl groups can be esterified (figure 1)

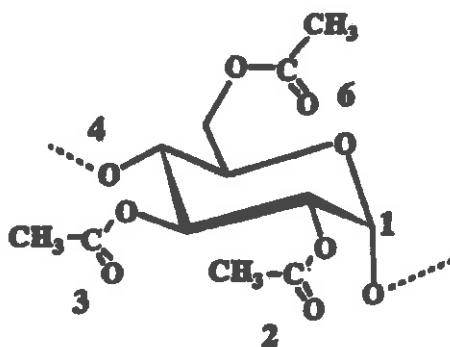


figure 1

The carbonyl ester carbon atoms are separated on the ^{13}C NMR spectra and assigned through long distance ^1H - ^{13}C coupling with each corresponding glucopyranose ring proton. δ 169.3 (C3), 170.2 (C6), 170.6 (C2) ppm for the triacetate and δ 172.8, 173.8 and 174.0 ppm for the amylose tripropionate in deuteriochloroform.

Methods

A chromium salt ($\text{Cr}(\text{Acac})_3$) is added as a relaxation agent to bring the repetition time to ca. 5 s. The spectra were recorded at 75.4 MHz on a AC 300 Bruker spectrometer with a minimum of 1000 scans. A quantitative ^{13}C nmr spectrum (3) is decomposed into a sum of lorentzian peaks with a non-linear adjustment technique. The parameters (width, height and resonance frequencies), obtained after a first analysis of the different peaks, are optimized through a Levenberg-Marquardt (4) type procedure. The areas of the 2, 3, and 6 peaks, the sum of which is proportional to the total substitution degree as determined by titrimetry, can be obtained by the values of these parameters. Partial substitution degrees can thus be determined.

Kinetics study

Acetylation kinetics were investigated on each -2, -3 and -6 position in the course of two different chemical processes. In the first one (method A), native starch was physically destructured by solubilisation in water, lyophilisation followed by dissolution in pyridine and reaction with two -OH equivalents of acetic anhydride for 2, 3, 4 and 5 hours (5). In the second experimental conditions (method B), starch was submitted to acetylation following the procedure of Mehlretter et al. (6). An aliquote was sampled after 1, 2, 3, 4, or 5 hours. The remaining OH groups on each sample were acylated as propionates with propionic anhydride in pyridine for 24 h (7) providing deuteriochloroform soluble triacylated bi-esters. IR spectra were recorded to confirm the absence of OH groups.

Results

The results of the kinetics are shown in figure 2

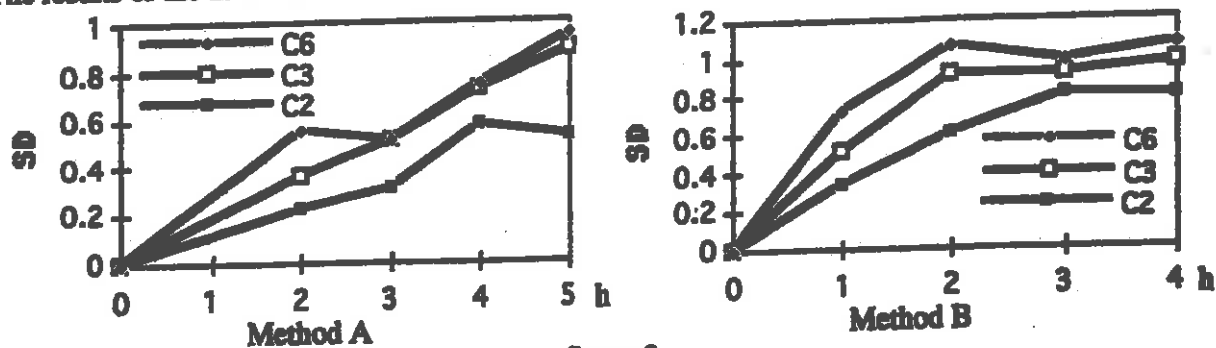


figure 2

Results show that in method A the reactivity of the secondary position -3 is surprisingly close to the primary one in position -6 and even if the primary -OH reacts faster in method B, the difference in reactivity between position -6 and position -3 is the same as that observed between position -3 and position -2.

Conclusion

In this paper ^{13}C NMR spectra of acetylated starch samples were recorded and quantitative ^{13}C NMR allowed the measurement of the relative rates of acetylation on each -OH position during the course of two different chemical processes.

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