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Synthesis and characterization of Schiff bases from chitosan and salicylaldehyde derivatives

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Abstract

The introduction of salicylaldehyde and derivatives at the C-2 nitrogen position of chitosan with low degree of acetylation has been investigated. Chitosan was reacted with salicylaldehyde and its 5-bromo, 5-chloro, 5-nitro, 5-methyl and 5-methoxy derivatives. The resulting biopolymeric Schiff bases were characterized by elemental analysis (C, H, N), IR spectroscopy, ^{1}H NMR spectroscopy and conductimetric titration. The ^{1}H NMR spectroscopy was used for the determination of degree of acetylation of chitosan. The degree of acetylation was determined from the ratio between the integrated area of the proton signal corresponding to the acetamido group (H-Ac) and that of the proton (H-2) of the GlucN unit. A procedure for the determination of the degree of substitution based on ^{1}H NMR data is proposed. The substitution degree was calculated from the ratio between the integrated area of the proton signal of the imine group and of the proton (H-2) of the GlucN unit. Substitution degrees varying from 4.6 to 68.5% depending on the *R* group have been measured. No significant change on the acetylation degree during the reaction was observed.

Keywords: Chitosan; Schiff bases; Degree of substitution

1. Introduction

Chitosan is the *N*-deacetylated derivative of chitin, although this *N*-deacetylation is almost never complete (Matteus, 1997). Chitin is the most important natural polysaccharide after cellulose, and is found in crustacean shells or in fungi cell walls. The term chitosan is usually used when the polymers become soluble in a dilute acid solution. The solubility is also controlled by the distribution of the acetyl groups remaining along the chain (Matteus, 1997). This biopolymer has applications ranging from cosmetics, artificial skin, photography, food and nutrition, ophthalmology and wastewater treatment (Narang,1990; Ravi-Kumar, 2000).

The chitosan is insoluble in water, but it dissolves in aqueous solutions of organic acids as acetic, formic, citric, besides inorganic acids, as diluted hydrochloric acid resulting in viscous solutions. (Rinaudo; Pavlov, & Desbriéres, 1999). It is well known that some of the structural characteristics such as degree of acetylation (DA) and molecular weight controlled the solubility the in chitosan.

The determination of the DA of chitosan has been largely discussed in the literature. The main techniques suggested for this determination are conductimetric titration, infrared spectroscopy, ^{1}H NMR, HPLC, thermal analysis, and others (Jiang, Chen, & Zhong, 2003; Raymond, Morin & Marchessault, 1993).

The presence of amminic groups in the polymeric chain leads to the possibility of a several chemical modifications, including the preparation of Schiff bases by reaction with aldehydes and ketones (Moore & Roberts, 1981; Muzzarelli, Jeunieux, & Gooday, 1985).

The reaction of chitosan with aromatic aldehydes in acetic acid to produce the corresponding Schiff bases has

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been described by Tirkistani, 1998. This author prepared, characterized and investigated the thermal properties of the derivatives.

Schiff base compounds containing an imine group (–RC=N–), are usually formed by the condensation of a primary amine with an active carbonyl. Its attractiveness as analytical reagents raises from the fact that they enable simple and inexpensive determinations of various organic and inorganic substances (Cimerman, Galic, & Bosner, 1997).

The insertion of functional groups in the chitosan matrix may improve its capacity of interaction with metallic ions by complexation. In this sense the modification of chitosan with aldehydes to produce Schiff bases may result in a potentially complexing material for metallic species with potential analytical and environmental applications (Hall & Yalpani, 1980; Rodrigues, Laranjeira, de-Favere, & Sadler, 1998).

According to Kurita, Mori, Nishiyama, and Harata (2002) the introduction of carbonyl groups in a chitosan results in Schiff bases whose degree of substitution is dependent on the stoichiometric amount of aldehyde used in the reaction. The degree of substitution (DS) of the Schiff bases was calculated from ratio C/N of elemental analysis.

The present work describes the preparation of biopolymeric Schiff bases by the reaction of low molecular weight chitosan with salicylaldehyde and five derivatives: 5-bromo, 5-cloro, 5-nitro, 5-methyl, 5-methoxy. The characterization of products has been performed by elemental analysis, ^{1}H NMR and infrared spectroscopy.

2. Experimental

2.1. Materials

Chitosan with low molecular weight was supplied by Aldrich (cat. number 44,865-9) and purified according to Matteus (1997) and Signini and Campana-Filho (2001).

Salicylaldehyde and its 5-bromo, 5-chloro, 5-nitro, 5-methyl, 5-methoxy derivatives and deuterium oxide (Aldrich) were used without additional purification.

2.2. Methods

The ^{1}H NMR spectra were measured in a Brucker AMX 400 spectrometer. For these measurements, a suspension of 10 mg of samples with 1 mL of 1% HCl/D_2O (v/v) solution and was prepared and stirred for 15 h. All the measurements were performed at 343 K, using pulse accumulating of 16 scans and the LB parameter of 0.30 Hz. The spectral width and data points were 8000 Hz and 32 K points, respectively. 3-(trimethylsilyl)-1-propanesulfonic acid-d4 (TSPA from Aldrich) was used as an external standard.

The elemental analyses were performed in a FISONS-EA1108 analyzer.

For the IR spectra the samples (1.5 mg), which were dried overnight at 60 °C under reduced pressure, were mechanically mixed with 100 mg of KBr, previously dried. A KBr disc was prepared from the mixed power and dried for 15 h at 110 °C under reduced pressure. The IR spectra were recorded in an MB102 FT-IR spectrophotometer (Bomen-Michelson) using a disk of 100 mg KBr as a reference.

The molecular weight distribution and subsequent characteristics were obtained in an AVS-350 viscometer coupled to an automatic dilution device Schott Gerate ViscoDoser AVS 20. The molecular weight of the chitosan was estimated based on the parameters described by Mark–Houwink equation $[\eta]=K_m M^a$ where $K_m=0.076$ and $a=0.76$ (Rinaudo, Milas, & Dung, 1993). The average viscometric molecular weight $M_V=69{,}000$ was estimated from the intrinsic viscosity determined in a 0.3 mol L^{-1} acetic acid–0.2 mol L^{-1} sodium acetate buffer solution at 25±0.01 °C as the mean of five replicates.

2.3. Chitosan sample purification

The chitosan samples (CA) were purified by dissolution in 0.5 mol L^{-1} CH_3COOH during 15 h. The resulting solution was filtered through 5 and 0.8 μm cellulose nitrate membranes (Sartorius) successively and then neutralized with 15 mol L^{-1} NH_4OH up to pH 8. The precipitate was washed with water several times followed by methanol. The resulting gel was then dried at room temperature for 18 h (Matteus, 1997; Signini & Campana-Filho, 2001).

2.4. Synthesis of biopolymeric Schiff bases

Previously purified chitosan was dissolved in 0.1 mol L^{-1} acetic acid and stirred at room temperature for 6 h. Then salicylaldehyde derivatives dissolved in methanol (2:1, v/v) were added to the resulting viscous solution. This mixture was stirred for 16 h. The formation of a deep yellow gel reveals the formation of the Schiff base on chitosan matrix. The resulting gel was concentrated in a rotatory evaporator under vacuum and washed with ethanol several times, filtered and dried at room temperature in a vacuum oven at 60 °C for 15 h.

The Schiff bases were prepared from salicylaldehyde (SB-1); and its 5-bromo (SB-2), 5-cloro (SB-3), 5-nitro (SB-4), 5-methyl (SB-5) and 5-methoxy (SB-6) derivatives.

3. Results and discussion

In the Schiff base preparation, chitosan acts as the primary amine reacting with aromatic aldehyde to produce the corresponding biopolymeric derivative. The