

WATER-SOLUBLE N-(n-FATTY ACYL)CHITOSANS

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Water-soluble chitins have been prepared by N-deacetylation of chitin [1] and N-acetylation of chitosan [2], but little is known about water-soluble N-n-long-chain fatty acyl derivatives of chitosan [3]. The present paper reports the effects of the degree of substitution (d.s.) and chemical structure for N-acyl group on the solubility of N-(n-fatty acyl)chitosans not only in water but also in 2 % aq. NaOH and 2 % acetic acid solutions.

Materials and Methods

Crab shell chitosan (0.16 g, d.s. <0.01 for NAc, MW ca. 15×10^4) was dissolved in 2 % aq. acetic acid (20 mL)-methanol (40 mL), and a n-fatty acid anhydride (0.1 to 3.1 mol/GlcN) was added with mechanical stirring [4] to give rise to a product in liquid, hydrogel or swelling state. The reaction mixture was adjusted at pH 8-10 with 15 % aq. sodium hydroxide. After retaining at room temperature overnight, the mixture was dialyzed against running water to give rise to a product. The product was adjusted at pH 4-5 with 2 % aq. hydrochloride, and free fatty acids were extracted with chloroform several times to give rise to an aq. solution. To the solution were added three volumes of ethanol, the precipitates produced were collected by filtration, washed with ethanol, and dried to give rise to the corresponding white precipitates (75-85 % yields). The d.s. for N-acyl was calculated on the basis of the elemental analyses, and the structures were confirmed by FTIR spectral analysis: ν_{\max} (KBr) 2960-2900 (CH), 1654-1648 and 1558-1553 (C=O and NH for N-acyl) cm^{-1} .

Results and Discussion

The partially N-n-fatty acyl derivatives obtained above are classified into three groups on the basis of their solubility (Fig. 1). Group A, which was soluble in water, 2 % aq. acetic acid and 2 % aq. NaOH, is the derivatives at d.s. 0.42-0.82 (d.s. 0.40 width) for N-acetyl, d.s. 0.45-0.76 (d.s. 0.31 width) for N-propionyl, d.s. 0.52-0.71 (d.s. 0.19 width) for N-butyryl, d.s. 0.54-0.64 (d.s. 0.10 width) for N-pentanoyl, and d.s. ca. 0.58 (a narrow width) for N-hexanoyl. Group B, which was soluble in 2 % aq. acetic acid but insoluble in water and 2% aq. NaOH solutions, is the derivatives at d.s. < 0.42 for N-acetyl, d.s. < 0.45 for N-propionyl, d.s. < 0.52 for N-butyryl, d.s. < 0.54 for N-pentanoyl, d.s. < 0.58 for N-hexanoyl, d.s. < 0.42 for N-octanoyl, d.s. < 0.24 for N-decanoyl, d.s. < 0.15 for N-lauroyl, and d.s. < 0.05 for N-myristoyl. Group C, which was insoluble in the above three solutions, is the derivatives at d.s. > 0.82 for N-acetyl, d.s. > 0.76 for N-propionyl, d.s. > 0.71 for N-butyryl, d.s. > 0.64 for N-pentanoyl, d.s. > 0.58 for N-hexanoyl, d.s. > 0.42 for N-octanoyl, d.s. > 0.24 for N-decanoyl, d.s. > 0.15 for N-lauroyl, d.s. > 0.05 for N-myristoyl, and d.s. > ca. 0.01 for N-palmitoyl and N-stearoyl.

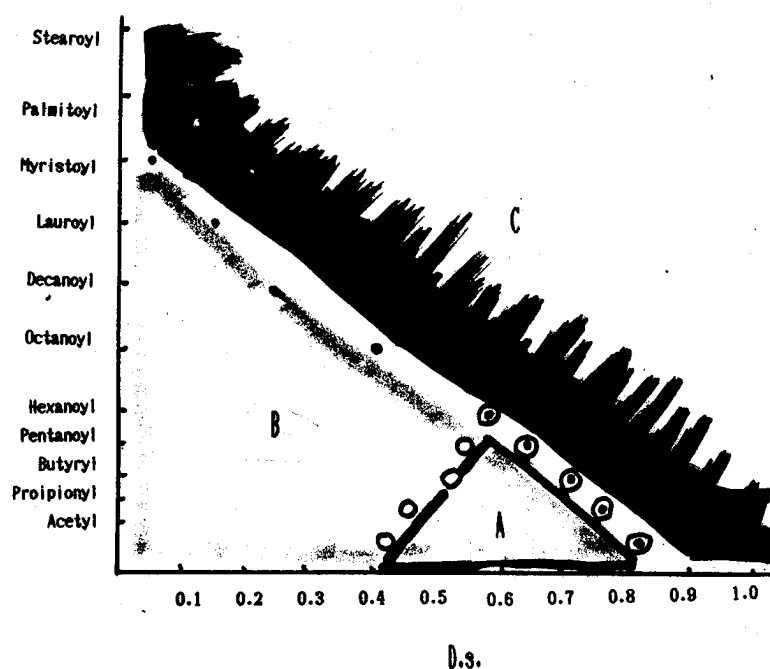


Fig. 1. The solubility of *N*-(*n*-fatty acyl)chitosans in water, 2 % aq. NaOH and 2 % aq. acetic acid solutions.

A hydrogel was produced by treatments with each of acetic, propionic, butyric and pentanoic anhydrides at >1.9 mol per GlcN, with hexanoic anhydride at >1.3 mol per GlcN, and with octanoic anhydride at >1.1 mol per GlcN. Some precipitates were produced by treatments with each of decanoic, lauric, myristic, palmitic and stearic anhydrides at $> \text{ca. } 0.5$ mol per GlcN.

The derivatives in group A, which had been isolated by addition of ethanol, were insoluble any more in water. For resolubilization in water, the derivative was redissolved in 2% aq. acetic acid, neutralized with alkali, and dialyzed against water to give rise to the original aq. solution. *N*-*n*-Fatty acyl groups exist heterogeneously over the partially *N*-acylated chitosan chain [5]. In the aq. solutions, the hydrophobic *N*-*n*-fatty acyl groups exist in an inner part of the clusters, and the hydrophilic amino groups exist in an outer part. The solubility depends on the proportion and distribution of both the groups over the chain.

References

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