



RESEARCH ARTICLE

NOVEL SYNTHESIS OF AMINE RICH CHITIN AND CHITOSAN FROM D-GLUCOSE

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ABSTRACT

The present study reports the first time and novel synthetic methodology for halogenation & C-N bond formation reactions in the backbone of D-Glucose. The key steps include chlorination and amination of glucose. The synthesized products are designated as Glucose chloride & Synthesized Chitosan respectively. Synthesized Chitosan resembles with the unit structure of Chitosan i.e. Oligomeric Chitosan and it is water soluble. FTIR spectrum of D-Glucose the characteristic broad peak at 3350cm^{-1} for stretching of hydroxyl ($-\text{OH}-$) group has disappeared in halogenation reaction showing the substitution of chloride & having characteristic sharp peak at 3150cm^{-1} for stretching of Amine ($-\text{NH}_2-$) group indicating replacement of chloride group with amine. The synthesis was completely characterized by FT-IR, C H N S analysis, ^1H NMR, ^{13}C NMR, DEPT 135 NMR, XRD and GC-MS.

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INTRODUCTION

Carbohydrates are multifunctional biomolecule. These are very difficult to alter their backbone by chemical synthesis. Development of new synthetic methodology for altered functional group molecules is an important subject of recent research in carbohydrate chemistry. Carbohydrate chemistry is primarily concerned with the synthesis, structure, and function of carbohydrate structures. Due to the general structure of carbohydrates, their synthesis is often preoccupied with the selective formation of glycosidic linkages and the selective reaction of hydroxyl groups. As a result, this chemistry relies heavily on the use of protecting groups. Natural saccharides are generally built of simple carbohydrates called monosaccharides with general formula $(\text{CH}_2\text{O})_n$ where n is three or more. A typical monosaccharide has the structure $\text{H}-(\text{CHOH})_x(\text{C}=\text{O})-(\text{CHOH})_y-\text{H}$, that is, an aldehyde or ketone with many hydroxyl groups added, usually one on each carbon atom that is not part of the aldehyde or ketone functional group. Examples of monosaccharides are glucose, fructose, and glyceraldehyde. The open-chain form of a monosaccharide often coexists with a closed ring form where the aldehyde/ketone carbonyl group carbon ($\text{C}=\text{O}$) and hydroxyl group ($-\text{OH}$) react forming a hemiacetal with a new C-O-C bridge. Monosaccharides can be linked together into what are called polysaccharides (or oligosaccharides) in a large variety of ways. Many carbohydrates contain one or more modified monosaccharide units that have had one or more groups replaced or removed. For example, chitin is composed of repeating units of N-acetylglucosamine, a nitrogen-containing form of glucose. (Matthews *et al.*, 1999)

Chitosan is polymer composed of randomly distributed \square (1 \square 4) linked D-glucosamine (deacetylated unit) and N-acetyl-D-glucosamine (acetylated unit) and can be obtained by the partial deacetylation of chitin, from crustacean shells, the second most abundant natural polymer after cellulose (Illum, 1998., Nunthanid *et al.*, 2001). Chitin is insoluble in aqueous media while chitosan is soluble in acidic conditions due to the free protonable amino groups present in the D-glucosamine units. Due to their natural origin, both chitin and chitosan cannot be defined as a unique chemical structure but as a family of polymers which present a high variability in their chemical and physical properties. This variability is related not only to the origin of the samples but also to their method of preparation. Chitosan has been widely used in vastly diverse fields, ranging from waste management to food processing, medicine and biotechnology (Savant *et al.*, 1995). It becomes an interesting material in various applications due to its biodegradability and biocompatibility (Borchard *et al.*, 2001), and low toxicity (Karlsen *et al.*, 1991). The success of chitin and chitosan in each of these specific applications is directly related to deep research into their physicochemical properties. In recent years, several researchers covering different aspects of the synthesis and applications of chitin and chitosan have been published. However, these researchers have addressed the possibility of synthesizing amine enriched water soluble chitosan like material using non marine source i.e. D-Glucose.

MATERIALS AND METHODS

Chemicals

Glucose ($\text{C}_6\text{H}_{12}\text{O}_6$), Carbon Tetra Chloride (CCl_4), Triphenylphosphine (PPh_3), Pentane, Dry Benzene,

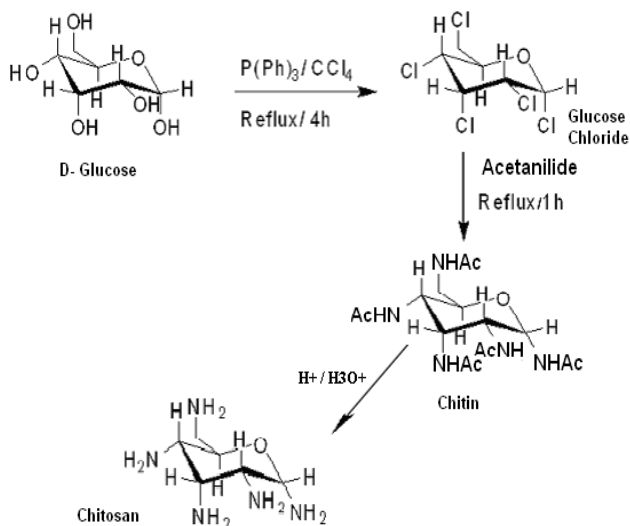
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Acetanilide and Hydrochloric acid (all make: - Merck, Germany) were used.

Method

In a well dried, 500ml round bottom flask glucose (0.1mole, 18 g), triphenylphosphine (0.11 mole, 29 g) and 200 ml of anhydrous carbon tetrachloride were added. The flask was fitted with a condenser (drying tube) and refluxed (steam bath) for 4 hours. The flask was then cooled at room temperature and 200 ml of pentane was added to precipitate the bulk of the triphenylphosphine oxide. The mixture was filtered and the filtrate was fractionally distilled and the product was Glucose chloride. (Lee *et al.*, 1967 and Friederang *et al.*, 1968). Glucose chloride (1gm), Acetanilide (1gm) and 100 ml ethanol was taken in a round bottomed flask. The mixture was refluxed on steam bath for one hour; the resultant solution was cooled and dried in oven at 140°C for two hours. The product obtained was amine rich Chitin.

Amine rich Chitin was acid hydrolyzed and Amine rich Chitosan was obtained. The chemical reaction is



CHARACTERIZATION

The material was characterized by the following:-

(1) FTIR Study

The functional group identification of product was done by FTIR analysis within the scanning range 4000–500cm⁻¹.

(2) C H N S Study

The Elemental analysis of the products was done by C,H,N,S analyzer.

(3)GC-MS Study

The retention time and molecular weight determined was done by GC-MS.

(4) XRD Study

The diffraction pattern of the synthesized product was done by using XRD.

(5) NMR Study

Proton, Carbon & DEPT 135 determination of the product was done by NMR.

RESULTS AND DISCUSSION

FTIR Study

Figure 1 shows the FTIR spectrum of glucose having characteristic broad peak at 3350cm⁻¹ for stretching of hydroxyl (-OH-) group. Figure 2 shows the FTIR spectrum of glucose chloride the characteristic broad peak at 3350cm⁻¹ for stretching of hydroxyl (-OH-) group of Figure1 has disappeared showing the substitution of hydroxyl (-OH-) group by chloride. Figure 3 shows the FTIR spectrum of Synthesized Chitosan having characteristic sharp peak at 3150cm⁻¹ for stretching of Amine (-NH₂-) group indicating replacement of chloride group with amine in the synthesis.

C H N S Study

C H N S study showed in table No. 1 the elemental composition of the reactant and products. The result clearly illustrates increased amine content in chitosan for its proposed application.

NMR Study

Figure 2 shows the 1H NMR spectrum of the Synthesized Chitosan gives the following peaks:-1H NMR data (CDCl₃) δ (ppm) 2.25 (s, 3, -CH₂-), 5.01 (m, 4, -CH-), 7.14 -8.20 (m, -NH₂-). These peaks appear to correspond with the Synthesized Chitosan. Figure 3 shows the 13C NMR spectrum of the Synthesized Chitosan gives the following peaks:-13 C NMR data (CDCl₃) δ (ppm) 40 (s, 3, -C-), 60 (s, 4, -C-), 126-137 (m,-C- - NH₂-). These peaks appear to correspond with the Synthesized Chitosan. Figure 4 shows the DEPT 135 NMR spectrum of the Synthesized Chitosan gives the following peaks:- DEPT 135 NMR data (CDCl₃) δ (ppm) 40 (s, 6 -C- -- CH₂--), 127-133 (m, -C- NH₂-). These peaks appear to correspond with the Synthesized Chitosan.

XRD Study

Figure 5 shows the X-ray diffraction pattern of the synthesized chitosan. Where characteristic peak is seen at position of 15.22°. This peak is representative of chitosan like skeleton. Taking into account the broadening of each peak in XRD, mean crystallite size has been calculated using Scherer's equation, that is, $D = 0.9 \lambda / (B \cos \theta)$, where D is the average crystallite size in Å. B is the peak broadening of the diffraction line measured at half of its maximum intensity in "radian," λ is the wavelength of X-rays, and θ is the Bragg's diffraction angle. The mean crystallite size is found to be 150 um.

GC-MS Study

The retention time and molecular weight of the chitosan was determined by GC-MS. Figure 6 showed that the retention time of the chitosan is 18.01 min. Figure 7 showed that the molecular weight of the chitosan is 479.95 which correspond to the Synthesized Chitosan. The molecular weights 428.90 to 412.83 and 340.76 to 324.67 significantly showed that there is

decrease of molecular weight by 16 a.m.u. due to the removal fragment of $-NH_2$ group.

Conclusion

The original research work presented here in the manuscript. Synthesized Chitosan appears to have nitrogen content of 40%. It will be applied in various industrial applications & will be reported in forthcoming articles.

Figures & Table:-

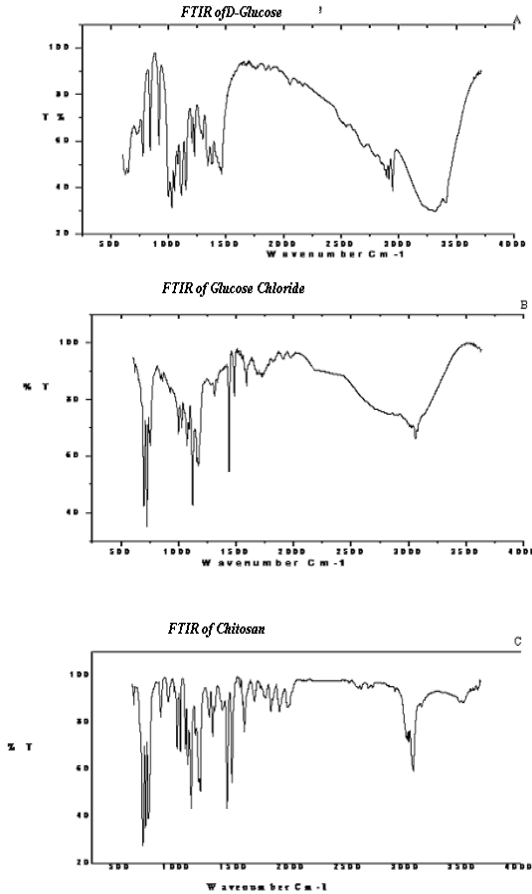


Fig. 1:- FTIR Spectrum of (A) D- Glucose (B) Glucose Chloride (C) Synthesized Chitosan

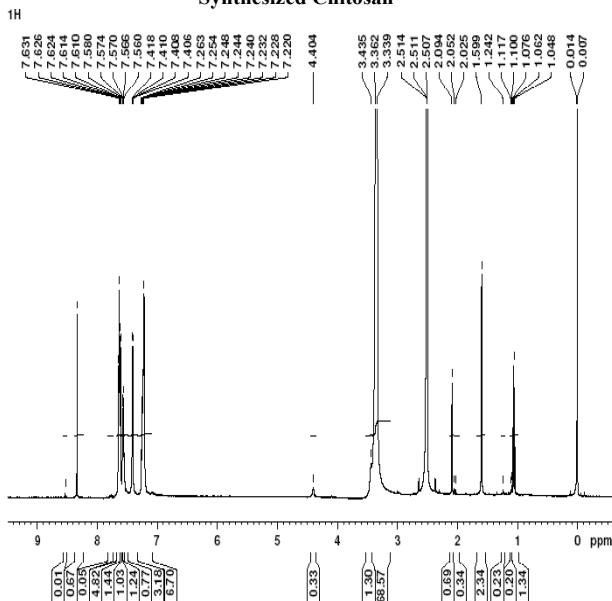


Fig. 2. 1H NMR of Synthesized Chitosan

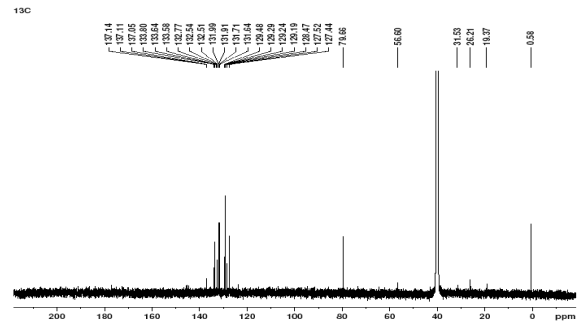


Fig. 3. 13C NMR of Synthesized Chitosan

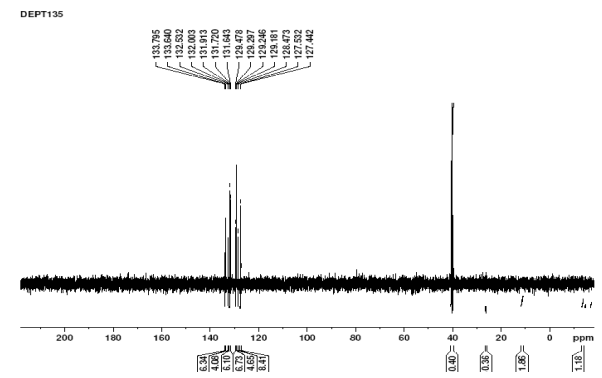


Fig. 4. DEPT 135 NMR of Synthesized Chitosan

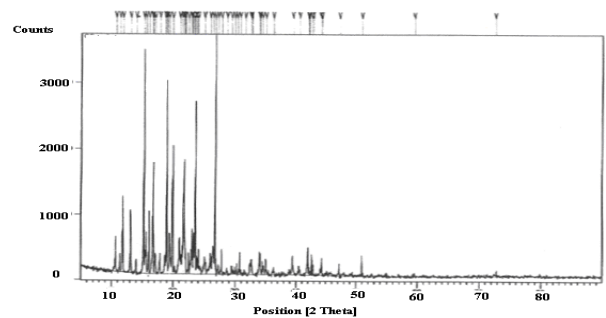


Fig. 5. XRD of Synthesized Chitosan

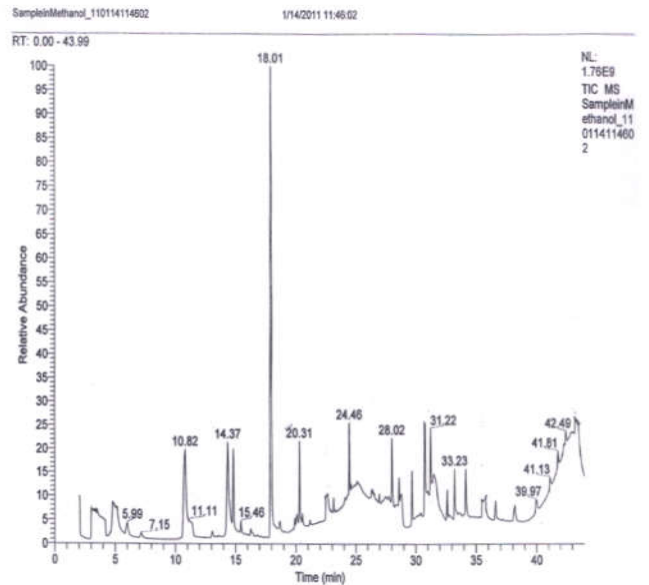


Fig. 6. Gas Chromatogram of Synthesized Chitosan

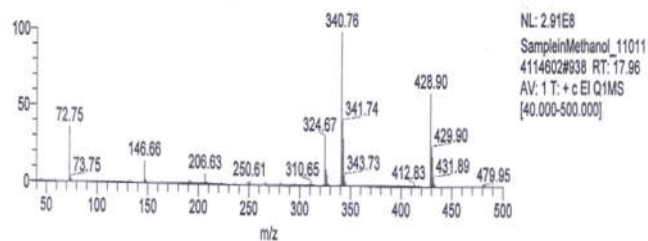


Fig. 7:- Mass Spectrum of Synthesized Chitosan

Table 1. CHN analysis of reactant & synthesized product

| Sr. No. | Compound | C % | H% | N% |
|---------|------------------|-------|------|-------|
| 1 | Glucose | 39.94 | 7.01 | 0.14 |
| 2 | Glucose Chloride | 80.70 | 5.91 | 0.17 |
| 3 | Chitin | 57.35 | 7.92 | 31.57 |
| 4 | Chitosan | 41.14 | 9.71 | 40.01 |

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