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Preliminary communication

Enhancement of the metal-chelating properties of chitin and chitosan

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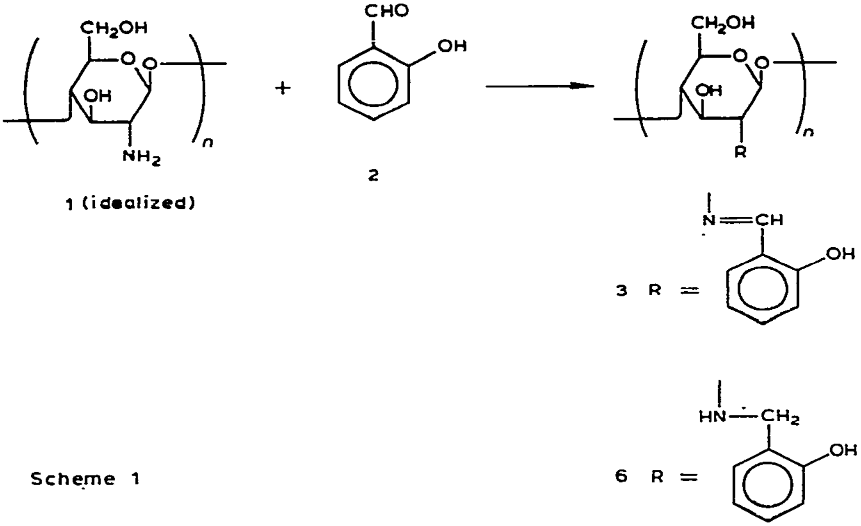
Because of their chelating properties, chitin (**4**) and chitosan (**1**), both of which are widely abundant, inexpensive polysaccharides, have found many applications in, for example, chromatography[1], the treatment of environmental pollutants[2], and catalysis[3]. Despite a number of studies of metal chelation by the native polymers[4], only a few recent attempts to improve their chelating capacity by chemical derivatization have been described[5]. As an extension of our own interest in "metal conjugation" by monosaccharides[6], including amino sugars[7], we now report on methods for substantially enhancing the metal-chelating performance of both chitin and chitosan.

Chitosan (**1**) (derived from shrimp shell, and containing 15% of NAc)* was condensed with salicylaldehyde (**2**) by following the methods of Nud'ga *et al.*[8] and Hirano *et al.*[9], to afford the Schiff-base derivative 3 (d.s. 1.0) (see Scheme 1).



Scheme 1

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*The degree of substitution (d.s.) and Cu(II) contents reported here were determined by elemental microanalysis and atomic absorption, respectively.

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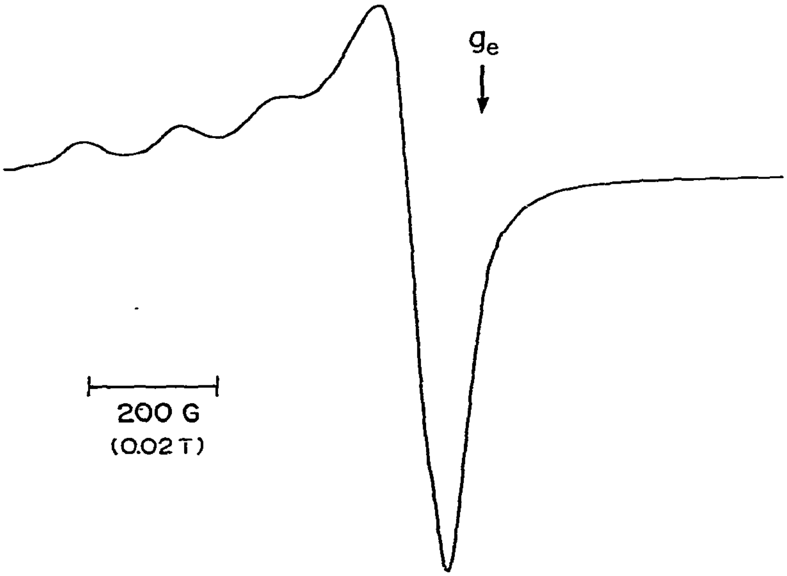

Fig. 1. E.s.r. spectrum of solid **5** under methanol, recorded with a Varian E3 spectrometer at ambient temperature.

Salicylidene-chitosan (**3**), like **1** and chitin (**4**), reacted readily with copper(II) acetate in either methanolic or aqueous solution, to produce, in analogy with the monosaccharide equivalent[7], a deep-green complex (**5**) which had incorporated 0.62 mmol of Cu(II) ions per g (20% of the theoretical value) after 12 h. Additional evidence for the polymer-bound, copper complex was obtained from the e.s.r. spectrum of solid **5** (see Fig. 1), which is characteristic of such chelates[10]; the nitrogen hyperfine-coupling is not resolved, but the spectrum indicates an axial symmetry about the copper atom. Interestingly, reduction of the azomethine function of **3** with sodium cyanoborohydride[11], simultaneous with its formation, gave the amine derivative **6**. The copper(II) complex of **6** strongly resembled that of **5** in terms of its e.s.r. spectrum and color.

The copper-chelating capacity of **6** was enhanced by a factor of ~5 [3.03 mmol of Cu(II) per g; 100% of the theoretical value] over that of **3**, and by a factor of 47 over that of **1** [0.06 mmol of Cu(II) per g; 2% of the theoretical value]. This increased capacity for chelation is presumably due, in part, to the great porosity of **6**, a fluffy, water-insoluble material which, in contrast to its solid analog **3**, swelled considerably in aqueous or alcoholic solutions. The enhanced chelation-performance of **6** is further evidenced by the fact that attempts to elute the copper ions from the complexes of **3** and **6** by using 0.1M EDTA solution at pH 8 were successful for the former, whereas ~30–40% of the copper was retained by the latter complex, which was, however, completely "de-metallated" by treatment with aqueous acid (pH 2).

We also evaluated the carboxymethyl derivative (d.s. 0.7) of chitin, prepared according to the method of Trujillo[12]; this may be a preferable complexing-agent for large-scale applications, as it is less expensive to synthesize. This derivative forms a turquoise-colored, axially symmetrical, copper(II) complex with greater efficacy [0.40 mmol of Cu(II) per g] than the native polymer **4** [0.18 mmol of Cu(II) per g], but less efficiently than salicylidene-chitosan (**3**) and compound **6**.

It should be noted that, owing to the variations in porosity and grain size (*e.g.*, chitosan flakes were employed) of the materials studied, absolute levels of metal chelation are not so informative as the relative (or enhanced) values. The derivatives reported here are also suitable for chelating a wide range of metals other than copper, which was chosen principally to demonstrate the utility of e.s.r. spectroscopy for obtaining qualitative and quantitative information on the metal complexes of glycosaminoglycans.

We believe that the concept of enhancing or modifying the metal-chelating capacity of chitin and chitosan will find widespread application in a variety of areas.

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