Available online at www.sciencedirect.com
SCIENCE DIRECT®
Bioorganic & Medicinal Chemistry Letters 15 (2005) 4600–4603
Bioorganic & Medicinal Chemistry Letters

The synthesis and antioxidant activity of the Schiff bases of chitosan and carboxymethyl chitosan

Zhanyong Guo,[a,b] Ronge Xing,[a,b] Song Liu,[a,b] Huahua Yu,[a,b] Pibo Wang,[a,b] Cuiping Li[a,b] and Pengcheng Li[a,*]

[a]*Institute of Oceanology, The Chinese Academy of Sciences, Qingdao 266071, China*
[b]*Graduate School of the Chinese Academy of Sciences, Beijing 100039, China*

Received 4 April 2005; revised 24 June 2005; accepted 27 June 2005
Available online 24 August 2005

Abstract—Five kinds of Schiff bases of chitosan and carboxymethyl chitosan (CMCTS) have been prepared according to a previous method and the antioxidant activity was studied using an established system, such as superoxide and hydroxyl radical scavenging. Obvious differences between the Schiff bases of chitosan and CMCTS were observed, which might be related to contents of the active hydroxyl and amino groups in the molecular chains.

1. Introduction

As one of the most abundant natural resources, chitosan has been attracting people's attention for its unique physiochemical characteristics and bioactivities.[1–4] With the development of the study on the sciences of chitosan, chitosan and its derivatives are being increasingly used in more and more fields, especially in biomedicine. It has been found that chitosan has antioxidant activity, and that, many chitosan derivatives were synthesized and their antioxidant activity was assessed accordingly.[5–8] In this paper, five Schiff bases of chitosan and CMCTS were prepared, according to Qu's method[9] and their antioxidant activity was measured.

2. Chemical

Chitosan was purchased from Qingdao Baicheng Biochemical Corp. (China). The degree of deacetylation was 97% and the viscosity average-molecular weight was 2.0×10^5. CMCTS was prepared according to a previous method,[10] and the synthesis of 2-hydroxy-5-chlorobenzaldehyde and 2-hydroxy-5-nitrobenzaldehyde was carried out according to Liu[11] and Zhang.[12] The Schiff bases of chitosan and CMCTS were synthesized as follows (Scheme 1). Three grams of chitosan (or CMCTS) was dispersed into 95% EtOH (100 ml), and various aldehydes were added with stirring. The mixture was refluxed for 8 h and then filter. Unreacted aldehydes and other inorganic products were Soxhlet-extracted with EtOH and ether for 2 days. The Schiff bases were obtained by drying under vacuum for 24 h. The elemental analysis results and the IR spectrum data of the derivatives are shown in Table 1 and Figure 1. There were strong peaks at about 1630–1660 cm^{-1} assigned to the characteristic absorbance of C=N, which showed the Schiff bases that were obtained.

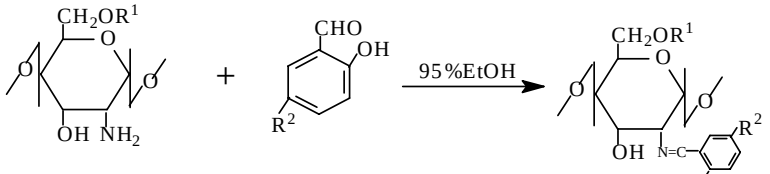
3. The antioxidant activity of the derivatives of chitosan

3.1. Scavenging ability of hydroxyl radical

According to the reference,[13] the reaction mixture, total volume 4.5 ml, containing the Schiff bases samples, was incubated with EDTA-Fe^{2+} (220 μM), safranine O (0.23 μM), and H_2O_2 (60 μM) in potassium phosphate buffer (150 mM, pH 7.4) for 30 min at 37 °C. The absorbance of the mixture was measured at 520 nm. Hydroxyl radical bleached the safranine O, so decreased absorbance of the reaction mixture indicated decreased hydroxyl radical scavenging ability.

Keywords: Schiff bases; Chitosan; Carboxymethyl chitosan; Antioxidant activity.
* Corresponding author. Tel.: +86 532 82898707; fax: +86 532 8296895?; e-mail addresses: guozhanyong@ms.qdio.ac.cn; pcli@ms.qdio.ac.cn

0960-894X/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.bmcl.2005.06.095



(a) R^1=H, R^2=NO_2
(b) R^1=CH_2COOH, R^2=NO_2
(c) R^1=H, R^2=Cl
(d) R^1=CH_2COOH, R^2=Cl
(e) R^1=CH_2COOH, R^2=H

Scheme 1. Synthetic pathway of the Schiff bases of chitosan and CMCTS.

Table 1. The elemental analysis results and the IR spectrum data of the Schiff bases of chitosan and CMCTS

Compound	Elemental analysis (%)			IR (KBr) (cm^{-1})
	C	N	H	
(a)	48.08	8.93	4.75	3441.31, 2876.05, 1640.47(C=N), 1530.75, 1069.18, 750.07
(b)	47.66	7.30	4.82	3444.76, 2923.16, 1660.13(C=N), 1542.44, 1508.40, 1437.25, 753.34
(c)	51.48	5.15	4.89	3446.26, 2892.36, 1631.90(C=N), 1577.81, 1482.93, 1072.81, 819.98
(d)	48.49	4.59	5.36	3445.45, 2878.52, 1642.09(C=N), 1557.97, 1408.82, 1138.40, 758.46
(e)	52.22	5.00	5.53	3438.89, 2891.21, 1632.57(C=N), 1573.69, 1503.96, 1457.45, 1067.92, 758.46

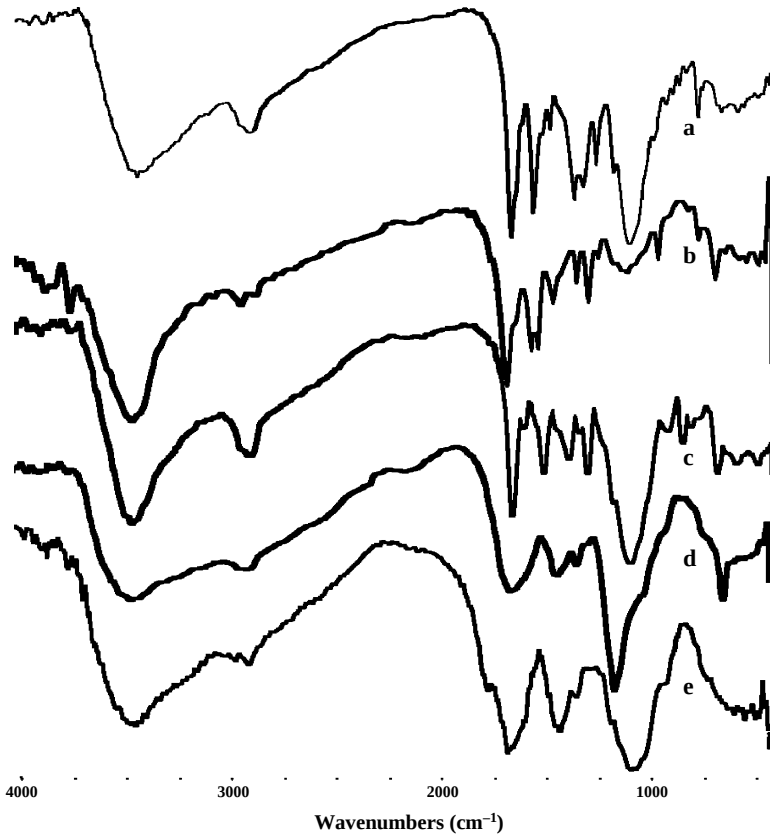


Figure 1. The IR spectra of the Schiff bases of chitosan and CMCTS.

$$\text{Scavenging effect } (\%) = [(A_{\text{sample 520 nm}} - A_{\text{blank 520 nm}})/(A_{\text{control 520 nm}} - A_{\text{blank 520 nm}})] \times 100,$$

where $A_{\text{blank 520nm}}$ is the absorbance of the blank (distilled water, instead of the Schiff bases) and $A_{\text{control 520 nm}}$ is the absorbance of the control (distilled water, instead of H_2O_2).