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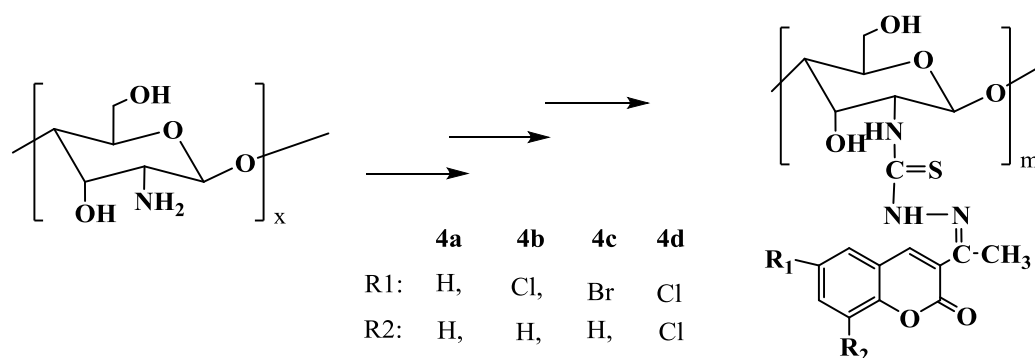
Synthesis, characterization and antifungal activity of coumarin-functionalized chitosan derivatives

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Graphical abstract



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Abstract: Four novel coumarin-functionalized chitosan derivatives **4a~4d** were synthesized via condensation reactions of thiosemicarbazide chitosan with coumarin derivatives. Their structures were confirmed by FT-IR, ^{13}C NMR, XRD and elemental analysis. Their antifungal activities against three kinds of phytopathogens, *Alternaria solani* sorauer (*A. solani*), *Fusarium oxysporum f.sp vasinfectum* (*F. oxysporum*) and *fusarium moniliforme* (*F. moniliforme*), were tested using the mycelial growth rate in vitro at 0.1, 0.5, and 1.0 mg/mL. The degree of substitution for **4a~4d** were about 40~60%. At 1 mg/ml, **4a** inhibited growth of *F. moniliforme* at 58.1%, and was higher than unmodified chitosan whose antifungal index was 9.7%. While for **4d** the inhibitory index against *F. Moniliforme* was 77.2%. The fungicidal tests showed that the synthesized chitosan derivatives have higher activity against the tested fungi compared to unmodified chitosan. Moreover, the introduction of halogen atoms into the chitosan derivatives causes an increase in antifungal activity.

Key words: chitosan derivatives; antifungal activity; thiosemicarbazone; coumarin

1. Introduction

Chitosan is prepared by the N-deacetylation of chitin, which is a naturally abundant biopolymer of N-acetyl glucosamine. In recent years, chitosan has been drawing broad attention in food science, medicine, agriculture, industry and environmental protection due to its biodegradability, biocompatibility, film-forming ability, low toxicity and antimicrobial activity [1-6]. However, the application of chitosan as a fungicide has been limited due to its lower solubility and weaker activity compared to current fungicides on the market [7-9]. Therefore, research has been focused on modification of the chitosan to obtain various derivatives showing higher solubility and activity [10-13].

The introduction of biologically active substances to chitosan can greatly improve its antimicrobial activity. For example, grafting dithiocarbamate groups [14], thiadiazole groups [15], pyrimidyl groups [16], oleoyl groups [17], thiosemicarbazone groups [18] or triazolyl groups [19] on chitosan obviously

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