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Conventional and microwave-assisted synthesis of coumarin-3-yl-2-oxoethyl carbamodithioates and their DNA cleavage studies

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In situ one pot synthesis of coumarin based dithiocarbamates have been studied under conventional and microwave methods. Syntheses of coumarin based dithiocarbamates have been optimized using NaOH, K_3PO_4 as a base in conventional method whereas K_3PO_4 has given good yields in less time. The syntheses of dithiocarbamates have been carried out under microwave conditions using K_3PO_4 as base. The generality of microwave method has been demonstrated by synthesizing a variety of substituents in excellent yields, having short reaction time with good purity compared to those under classical conditions. All the products have been characterized by their IR, GC-MS, ^{1}H and ^{13}C NMR spectral data. Except **2h**, **2k**, **2l**, all these compounds have complete DNA cleavage activity.

Keywords: Microwave, coumarins, dithiocarbamates, one-pot, *in situ*, DNA cleavage

The last few decades have witnessed a substantial growth in the chemistry utilizing the dithiocarbamate unit as a cornerstone in terms of the design and synthesis of new compounds. Sequentially linking several different components in one reaction vessel has been studied intensively as a rapid way to increase molecular building while avoiding time, costly materials, unfriendly isolation and purification of intermediates. Dithiocarbamate derivatives are important intermediates in the synthesis a variety of heterocyclic compounds. Dithiocarbamates (DTC) are applied in several areas such as agricultural products, fungicides[1], pesticides and repellents[2,3], industry, as additives for vulcanization of rubber[4], organic synthesis as precursors[5], chelating agents[6,7], lubricants[8] as well in the medical fields[9-11]. In medicinal chemistry, dithiocarbamates are also used in the treatment of cancer[12,13].

Chromen-2-ones are an important class of heterocycles which are omnipresent in natural products and synthetic origin as well. Chromen-2-one also called as coumarin known to exhibit a broad spectrum of biological activities such as anticancer[14], anti-inflammatory[15], antioxidant[16], antimicrobial[17] and anticoagulant[18] activities. Among the coumarins family, 4-bromomethyl coumarins have gained popularity as a reactant.

In view of the biological significance of coumarin and dithiocarbamate moieties, we planned to take-up the synthesis of coumarin-3-yl-2-oxoethyl carbamodithioates as a molecular scaffold. In this context, literature review at this stage revealed that a method is available on the synthesis of coumarin-3-yl-2-oxoethyl carbamodithioates[19]. However, it is surprising to note that there are no reports available on microwave synthesis. With this background, herein report the microwave method for the synthesis of compounds **2a-2n** in 3-5min.

Results and Discussion

The 3-bromoacetyl coumarins[20] **1a,b** were synthesized according to the previously mentioned method. The synthesis of the target compounds was carried out as outlined in Scheme I. It was observed that microwave approach proved to be extremely fast providing method which given excellent yields (90-98%) as compared to conventional methods (70-91%). The results are summarized in Table I. The most noticeable advancement was the speed with which the reaction proceeded. The reaction was