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The synthesis of macrocyclic ligand, diquinolinenono[1,3,7,9]tetraazacyclododecine-7, 15 (14H, 16H)-dibenzene(L), is described. The metal complexes of the type [MLX₂], where (M = Co(II) (1), Cu(II) (2) and X = (Cl), have been synthesized by the reaction of ligand(L) with the corresponding metal salts, and characterized by elemental analysis, FT-IR, ¹H-NMR and electronic spectra. The binding property of the complexes with CT-DNA was studied by absorption spectra, viscosity measurements, as well as thermal denaturation studies. The absorption spectral results indicate that the complexes (1) and (2) are binds with base pairs of DNA. The intrinsic binding constant $K_b$ had the value $3.8 \times 10^9$ M⁻¹ for (1) and $3.3 \times 10^9$ M⁻¹ for (2), respectively, in 5 mM Tris-HCl/50 mM NaCl buffer at pH 7.2. The viscosity measurement results show the viscosity of sonicated rod-like DNA fragments increased when the complex were added to the solution of calf thymus-DNA. The synthesized ligand and its metal complexes have been screened for antibacterial and antifungal activities.

**Keywords:** Quinoline, macrocyclic complexes, DNA binding, viscosity measurements, antimicrobial activity

1. Introduction

The high selectivity and strong coordination ability of macrocyclic ligands towards transition metal ions have attracted attention of chemists all over the world due to the wide range of applications in areas like catalysis (1-3) electron carriers in redox reactions (4), dioxygen carriers (5, 6), ionospheres in a number of biochemical processes (7-9), separation and extraction of valuable and precious metals from waste materials (10), as anti-tumor drugs (11), as model compounds that mimic naturally occurring metalloproteins (12), and metalloenzymes used as photosensitizers in photodynamic therapy (PDT) (13). Thus, the transition metal complexes of mixed donor macrocyclic ligands constitute a potentially important class of molecules for molecular electronics and catalytic reductions (14).

Macrocyclic complexes were best prepared with the aid of metal ions as template to direct the steric course of the condensation reaction, which ultimately results in ring closure (15). Various macrocyclic ligands have been synthesized and their complexes have been reported (16, 17). A variety of macrocyclic complexes derived from o-phenylenediamine including dinuclear macrocyclic complexes have been reported (18, 19).

The interaction of transition metal complexes with DNA has been extensively studied in the past few years. Among the first row transition metal ions, such as cobalt, nickel, manganese and copper offer the choice of biocompatibility in biological systems and have been recognized as having important biological effects (20). The study of DNA binding properties and anti-tumor activity of these metal complexes have been well documented in the literature (21, 22). Barton and co-workers (23, 24) have studied the interaction of enantiomers of Ru(phen)_3 with various DNA; the results lead them to the conclusion that there were two modes of interaction, intercalative and electrostatic binding. Kharatishvili et al. (25) also reported the effect on DNA binding in the presence of a planar intercalating ligand such as quinoline for both mononuclear and
Nucleosides, Nucleotides and Nucleic Acids

Synthesis and DNA Binding Studies of Novel Heterocyclic Substituted Quinoline Schiff Bases: A Potent Antimicrobial Agent

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SYNTHESIS AND DNA BINDING STUDIES OF NOVEL HETEROCYCLIC SUBSTITUTED QUINOLINE SCHIFF BASES: A POTENT ANTIMICROBIAL AGENT

Devappa. S. Lamani,¹ Kallam. R. Venugopala Reddy,¹ H. S. Bhojya Naik,¹ A. Savyasachi,¹ and H. Raja. Naik²

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The present article deals with the synthesis of 2-chloroquinoline-3-carbaldehyde [(2-hydroxy-1-naphthyl) methylene] hydrazone (CQCMH) (2a-c) and 2-chloroquinoline-3-carbaldehyde [4-(dimethylamino) benzylidene] hydrazone (CQCDBH) (3a-c) from quinoline derivatives under suitable experimental conditions. The synthesized compounds were characterized by elemental analysis, FTIR, ¹HNMR, and mass spectral data. The selected compounds were studied for interaction with calf thymus-DNA (CT-DNA) by electronic spectra, viscosity measurements as well as thermal denaturation studies. On binding to DNA, the absorption spectrum underwent bathochromic and hypochromic shifts. The binding constant (Kb) had value of 2.3×10⁶ M⁻¹ for (2a) and 2.5×10⁶ M⁻¹ for (3a). The viscosity measurements indicated that the viscosity of sonicated rod like DNA fragments increased. The synthesized derivatives have been screened for antibacterial and antifungal activities.

Keywords Quinoline; Schiff bases; DNA binding; viscosity measurement; antimicrobial anticancer agents

INTRODUCTION

Schiff-bases are currently being extensively studied for biological and anticancer activities.¹¹-⁵¹ The pharmacological properties of quinoline and their derivatives attracted worldwide attention in the last few decades.
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Pyrimido[4,5-b]quinoline-2-thiolol: microwave-induced one-pot synthesis, DNA binding and cleavage studies

H.R. Prakash Naik*; H.S. Bhojya Naik*; T.R. Ravikumar Naik*; H. Raja Naik*; D. S. Lamani*; T. Aravinda*

* Department of PG Studies and Research in Industrial Chemistry, School of Chemical Sciences, Kuvempu University, Shankaraghatta, Karnataka, India
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Pyrimido[4,5-b]quinoline-2-thiol/ol: microwave-induced one-pot synthesis, DNA binding and cleavage studies


*Department of PG Studies and Research in Industrial Chemistry, School of Chemical Sciences, Kuvempu University, Shankaraghatta, Karnataka, India; †Department of PG Studies and Research in Biotechnology, School of Biological Sciences, Kuvempu University, Shankaraghatta, Karnataka, India

(Received 23 April 2008; final version received 3 August 2008)

This article describes the synthesis of pyrimido[4,5-b]quinoline-2-thiol/ol (3a/3b) by microwave irradiation technique. The dynamic interaction of compounds with deoxyribonucleic acid (DNA) was investigated by absorption spectra, viscosity measurements, and thermal denaturation studies. Intrinsic binding constants ($K_b$) had values $3.1 \times 10^4$ for 3a and $2.3 \times 10^3$ for 3b. The proposed DNA binding mode supports the large enhancement in the relative viscosity of calf thymus (CT-DNA) on binding to compounds. Results suggest that 3a/3b can bind to CT-DNA by intercalation via the aromatic ring into the base pairs of DNA. Moreover, efficient DNA damage was observed on oxidative cleavage in the presence of 3a/3b.

Keywords: pyrimidoquinolines; microwave irradiation; CT-DNA binding; oxidative cleavage; viscosity-thermal

1. Introduction

Dihydropyrimidinones (DHPMs) constitute a very important class of organic compounds due to their attractive pharmacological properties, including antiviral, antitumor, and antibacterial activities. The dihydropyrimidinone core is also found in many natural products that explain the important efforts devoted to the synthesis of these heterocycles (1). Quinoline alkaloids, such as quinine, chloroquine, mefloquine, and amodiaquine, are used as efficient drugs for the treatment of malaria (2–6). Several derivatives of quinoline have been reported to be associated with interesting pharmacological properties like antibacterial, antifungal and antimalarial agents (7–14). A literature survey shows that there is evidence that antitumor activity is due to the intercalation of drug between the base pairs of DNA and interferences with the normal functioning of enzyme topoisomerase II which is involved in the breaking and releasing of DNA strands (15).
Nanostructured TiO₂ Catalyzed Microwave Assisted Synthesis of Fused Quinolines–DNA Binding, Molecular Docking and Antioxidant Activity

H.R. Prakash Naik,a H.S. Bhojya Naik,a T.R. Ravikumar Naik,a P.J. Bindu,a H. Raja Naik,b T. Aravinda and D.S. Lamanf

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Abstract: The use of nanostructured TiO₂ as mixed phase photocatalyst in the synthesis of 2H-pyrano[2,3-b]quinoline-2-carboxylic acid (2a/2b) is described. The binding modes of 2a/2b with ds DNA fragments d(CGCGAATTCCGCG) were predicted by molecular docking studies. The lowest energy was found in the compound 2b with a binding energy of -7.44 Kcal/mol and inhibition constant of 5.39 × 10⁻⁶. The interaction study with CT DNA was carried out by absorption spectra, (Kₛ constant obtained for 2a is 3.5 × 10⁶ and for 2b it is 2.9 × 10⁶), viscosity and thermal denaturation methods. The in vitro antioxidant activities were evaluated. Finally, the results showed that the intercalated 2a/2b compounds are strong antioxidants and they protect oxidative DNA damage from harmful free radicals.

INTRODUCTION

Iron oxide, cadmium sulfide and zinc sulfide have been used as photocatalysts in past research. Recently, the semiconductor titanium dioxide (TiO₂) is extensively used as photocatalyst due to the strong oxidizing power of its holes, high photostability and redox selectivity [1]. To produce chemical energy and catalytic activity, it is important to prevent the electron from recombining with the valence band hole [1]. On the other hand, the significant examples of organic transformations employed for synthetic purposes are oxidation and reduction reactions, isomerization reactions, C–H bond activations, C–C and C–N bond forming reactions [2-6].

A literature survey showed that there is evidence to infer that antitumor activity is due to the intercalation between the base pairs of DNA and interferences with the normal functioning of enzyme topoisomerase II, which is involved in the breaking and releasing of DNA strands [7]. The antitumor drugs that intercalate DNA are of growing interest in the field of anticancer derivatives. Particularly, they are characterized by planar chromophores, which are often constituted by three or four condensed rings, which can intercalate into base pairs. Results of these various binding studies have been useful in designing new and promising anticancer agents for clinical use [8]. DNA binding studies of pyrimido-thienoquinolines have been recently reported [9, 10].

In order to demonstrate the potential antioxidant activity of heterocyclic compounds, the interactions of nitrogen, sulfur and oxygen containing molecules with DNA are of major biochemical and biological importance [11]. It has been suggested that quinolines can chelate Fe(II) or Fe(III) and prevent free radical production in Fenton reaction [12] and quinolines themselves can also intercalate DNA duplex and react with free radicals in order to protect DNA from oxidative damage [13, 14].

In continuation of our work [15], on synthesis of fused quinolines derivatives, herein we describe the synthesis of 2H-pyrano[2,3-b]quinoline-2-carboxylic acids by using nanostructured TiO₂ catalyst. And also, the in vitro antioxidant activity, docking and interaction studies with ds-DNA are presented.

MATERIALS AND METHODS

Chemicals

All reagents and solvents used were of AR grade and commercially purchased. Tris-HCl buffer, ferric chloride, l,l-diphenyl-2-picryl-hydrazyl (DPPH), nicotinamide adenine dinucleotide (NADH), butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), and trichloracetic acid (TCA) were purchased from Sigma (Sigma-Aldrich, E. Merck, Himedia, Qualigens, Mumbai, India), calf thymus DNA (CT-DNA) and pUC 19 DNA were purchased from Bangalore Gene, Bangalore, India and solution was prepared using deionised double distilled water. Melting points were determined in an open capillary tube and are uncorrected. IR spectra were recorded in KBr pellets on Perkin-Elmer 157 IR spectrophotometer. ¹H NMR spectra were recorded in DMSO-d₆ on EM-390(300MHz) NMR spectrometer. Mass spectra were recorded on MASPEC low resolution instrument operating at 70 eV and UV-Visible spectra were recorded using SHIMADZU, UV-1650 PC model. JELO JSM-35 JE instrument was used for SEM photograph.

Preparation of Semiconductor Titanium Dioxide Nanoparticles in Colloidal Solutions

Titanium dioxide nanoparticles used in the experiments was synthesized according to the reported procedure [16] in...
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A facile one pot synthesis of 4-methylthieno[2,3-b]quinolin-3(2H)-one and 4-methylseleno[2,3-b]quinolin-3(2H)-one's by microwave irradiation under solvent free condition

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ABSTRACT

A simple and efficient procedure has been developed for the synthesis of quinolines containing thiotetronic ring and selenotetronic ring system. The methodology is based on cyclization reaction of 2-chloro, 2seleno-4-methyl quinoline with thiglycolic acid and chloroacetic acid by microwave irradiation in presence of anhydrous potassium carbonate catalyst under solvent free condition. The new compounds were characterized by elemental analysis, IR, ¹H NMR and mass spectral data.

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INTRODUCTION

In recent years several synthetic methods gaining prominence for accessing sulfur and selenium containing compounds, especially five and six membered heterocycles fused to quinoline ring in linear fashion are found in natural products as well as in the synthetic compounds of biological importance¹⁴-⁴⁶. In addition, the basic thiolactone ring(Figure 1) system is integral part of a number of naturally occurring thiotetic acids which exhibit a wide range of biological activities, such as antibacterial¹⁷-²⁴, antiallergenic²⁵, antifungal²⁶, hypcholesteremic, hypolemic²⁷ and antiviral²⁸ activities.

Further, it is well known that number of heterocyclic compounds containing S and Se exhibit a wide variety of biological activities²⁹-³¹. Even though sulfur and selenium are considered to be isosteric as defined by Langmuir³² and Erlenmeyer³³, the reports about selenium-containing heterocyclics are few³⁴-³⁶. However, the medicinal application of isosterism has been reviewed by Klayman and Gunther³⁷. The antioxidant and anticancer activity of selenium containing compounds have been reported³⁸-³⁹ recently. Selenium plays an important role in decreasing oxidative stress in HIV-effected cells and possibly suppressing the rate of HIV replication⁴⁰-⁴². Recent research proposes that HIV may be capable of incorporating host selenium into viral seleno proteins that have glutathione-peroxide activity. Though the significance of these findings require further clarification, they suggest that both human immune system
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