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Mn^{II} catalyzed oxidation of hexane-1,6-diamine by diperiodatocuprate(III) in aqueous alkaline medium – A kinetic and mechanistic approach

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Abstract : The kinetics of Mn^{II} catalyzed oxidation of hexane-1,6-diamine (HDA) by diperiodatocuprate(III) (DPC) in aqueous alkaline medium was monitored spectrophotometrically (λ_{max} = 415 nm) at constant ionic strength of 0.1 mol dm^{-3} and 301 K. The reaction shows 1 : 4 stoichiometry between HDA and DPC. The reaction is of first order in [DPC] and [Mn^{II}] and less than unit order in [HDA] and [alkali], periodate has retarding effect on reaction rate. The ionic strength and dielectric constant of the medium has no significant effect on the rate of the reaction. The added Cu^{II} product also has no effect on the rate of reaction. The main product caprolactam was identified by FTIR, GCMS, NMR, DSC and TGA. The active forms oxidant was detected [$Cu(H_2IO_6)(H_2O)_2$]. The rate law and reaction mechanism involving three different complexes was proposed. The equilibrium constants and rate constant were calculated. The activation parameters were deliberated for catalyzed and uncatalyzed reactions at different temperatures.

Keywords : Hexane-1,6-diamine, monoperiodatocuprate(III), MnO_2, oxidation, kinetics, mechanism.

Introduction

Chemical kinetics provides hands on information about reaction mechanism and factors affecting the rate. This kinetic study is very much essential for the chemical and pharmaceutical industries. Kinetics of various chemical reactions can be studied by titrometric, stopped flow technique, flash photolysis, spectrophotometric and cyclic voltametric methods. Presently, in this paper we are reporting kinetics of Mn^{II} catalyzed oxidation of hexane-1,6-diamine by diperiodatocuprate(III) in aqueous alkaline medium by spectrophotometric method. The selected reductant HDA is the colorless water soluble compound with a strong amine odor. In earlier days it was produced by the hydrogenation of adiponitrile. HDA is moderately toxic, stable in air but combustible, due to its bifunctional structure it is used almost exclusively for the production of polyamides. Hexamethylene diisocyanate generated from hexane-1,6-diamine used as a monomer feedstock in the production of polyurethane. It also serves as a cross-linking agent in epoxy resins. HDA is a good chelating agent which is capable of binding to transition metal ions in the higher oxidation state to form chelate. The substance DPC is a flexible oxidant[1], stable in aqueous medium and has multiple equilibria between different Cu^{III} species. Cu^{III} has been investigated as a reactive intermediate in some biological reactions[2], electron transfer reactions[3] and as an analytical reagent[4]. Mn^{II} is used as an efficient catalyst in many redox reactions[5]. The literature survey reveals that the considerable amount of work has been done on the oxidation of

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Research Article

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Coumarin-Furoquinoline Conjugates as Potential Antitubercular Agents: Synthesis, Biological Evaluation and Molecular Docking Studies

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ABSTRACT

A series of novel coumarin-furoquinoline conjugates were designed, synthesized and screened for antitubercular activity against two mycobacterial strains (Mycobacterium tuberculosis H37 RV and Mycobacterium phlei). The preliminary bioassay results demonstrated that all tested compounds exhibited the activities with different degrees, and some compounds showed better effects than standard drugs used. The SAR results indicate that the compounds bearing hydroxyl group (8g), chlorine (8h, 8i, 9h, 9i, 10h, 10i) and bromine (8j, 9j, 10j) on coumarin and chlorine on furoquinoline are most effective. Further, molecular docking studies performed on all the title compounds, compound 8g and 10h resulted as potent. This is the first report assigning in vitro anti-mycobacterial and structure activity relationship with molecular docking studies on this new class of conjugates.

Keywords: Coumarin; Furoquinoline; Molecular docking; Quinoline; Anti-TB; SAR

INTRODUCTION

Tuberculosis (TB) is the first infectious disease declared by the World Health Organization (WHO) as a global health emergency [1]. According to statistics, which is considered as world's second highest killer by single infectious agent after HIV [2,3]. The drug treatment varies from six to nine months in the case of drug-sensitive disease, while in the case of drug-resistant disease the treatment could last up to two years [4]. Improper administration of the drugs can result in drug resistance, treatment failure or even death [5]. The World Health Organization (WHO) reported that globally 3.5% of naive infections already expressed resistance to the two most efficacious frontline agents used to treat the disease i.e., RIF (rifampicin) and INH (isoniazide), thereby classifying the infection as multidrug resistant tuberculosis (MDR-TB). A very common and deadly complication of Mtb infection is coinfection with human immunodeficiency virus (HIV) [6-10]. The worsening situation has prompted the World Health Organization (WHO) to declare tuberculosis a global public health crisis [11].

Coumarins are important class of oxygen heterocycles [12], which are predominantly found in higher plants and have diverse pharmacologic activity [13]. This privileged molecule, being a common moiety found in many biological active natural and therapeutic products and thus represents a very important pharmacophore [14]. In recent years, the actual trend in the field of chemistry of coumarins has been modification of the benzopyran-2-one system, which are of great interest for the theory of organic synthesis including heterocyclic chemistry and purposeful synthesis of new biologically active compounds centered on coumarin system have been reviewed [15-17]. Antitumor activity study is interesting and promising for these compounds [18-21]. Coumarins target a number of pathways in cancer pathogenesis, such as kinases inhibition, cell cycle arrest, angiogenesis inhibition, HSP90 inhibition, carbonic anhydrase inhibition, telomerase inhibition, etc. [22]. Recently, Dandriyal et al. reviewed the developments of C-4 substituted coumarin derivatives as anticancer agents [23]. The recent progress in the drug development of coumarin derivatives as potent antituberculosis agents have also been reviewed [24]. Quinoline scaffold plays an important role in anticancer drug development as their derivatives have shown excellent results through different mechanism of action such as growth inhibitors by cell cycle arrest, apoptosis, inhibition of angiogenesis, disruption of cell migration, and modulation of nuclear receptor responsiveness. The anticancer potential of several of these derivatives have been demonstrated on

3. Document for Criterion 3.3.1 - International Publication of Dr. Narshimamurthy Anegundi

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Evidence for antiangiogenic potentials of Herniarin (7-methoxycoumarin)

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ABSTRACT

Coumarins are known for their diverse biological activities. In this study, antiangiogenic potentials of Herniarin (7-methoxy derivative of coumarin-7MC) were tested using embryonic angiogenesis of zebrafish (Danio rerio) as model. Laboratory raised developing embryos (in triplicate sets of 20 embryos/set) were exposed to 0, 1, 2, 3, 4, and 5mM concentrations of 7MC from 6hpf (hours post fertilization) until completion of embryogenesis. After hatching (72hpf) development trajectory of larva was traced for a week. At 72hpf, patterning of blood vessels, detection of blood flow by the presence of red blood cells (RBC) by globin expression, cardiac anomalies/heart rates, cellular apoptosis, morphological deformities and mortality rates were recorded. IC50 (50% ISV inhibitory concentration) and LC50 (50% lethal concentration) were determined for 7MC exposed larvae. Whole mount staining for alkaline phosphatase at 72 hpf indicated that formation of major blood vessels Viz. intersegmental vessels (ISV), dorsal aorta (DA), dorsal longitudinal anastomotic vessel (DLAV), posterior cardinal vein (PCV) and common cardinal veins (CCV) was perturbed and blood flow in them was disturbed in larvae of chemical exposed embryo sin comparison with corresponding controls. Exposure of embryos to higher concentrations (> 4mM 7MC) not only interfered blood vessel patterning but resulted in a decrease in heart rates, tail distortions, increased cellular apoptosis and elevated mortality rates. These results suggest that 7MC manifests antiangiogenic effects on zebrafish embryonic angiogenesis with IC50 value of 2.64mM. This biological property of 7MC may be explored in tumour suppressor therapeutics to enhance the antiangiogenic effects drugs in synergistic combination.

Keywords: *Zebrafish, Embryo cultures, Methoxy coumarin, Angiogenesis inhibitor, Apoptosis.*

INTRODUCTION

Coumarins are phytochemicals with powerful aroma found in fruits, leafy vegetables, and herbs/ plants [1]. These compounds exhibit biological activities such as, anti-bacterial, anti-fungal, anti-inflammatory, anti-proliferative etc., therefore, derivatives of coumarins have pharmacological significance and used in the treatment of many human diseases [2-4]. Addition of a methyl group at C7 position of the aromatic nucleus of coumarin results in 7-methoxycoumarin with antibacterial (against gram-negative bacteria) and anti-microbial activity [5, 6]. 7MC extracted from plant Tagetes lucida (commonly called as Mexican marigold) exhibits cytotoxic effects on arthropods [7]. 7MC derived from a flowering plant Santolina oblongifolia (native from Spain) manifests anti-inflammatory properties [8]. One of the 7-hydroxyderivative of coumarin with a methoxy group at C6 position (Scopoletin) is used in the treatment of angiogenesis-mediated diseases, hinting that synthetic analogues of this compound may have a pro or anti angiogenic potentials [9]. Angiogenesis (a process of sprouting of blood vessels from pre-existing ones) is a

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7-Hydroxycoumarin Elicit Anti-Angiogenic Effects Through Cellular Apoptosis in Developing Embryos of Zebrafish (*Danio Rerio*)

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Abstract

Derivatives of coumarin have diverse biological activities and pharmacological significance. In this study we made an attempt to test one of the hydroxy derivative i.e. 7-hydroxycoumarin (7HC) for its anti-angiogenic potential using embryonic angiogenesis of zebrafish (*Danio rerio)* as biological model. Developing embryos of *D. rerio* were cultured in media containing one of the grade (1 mM or 2 mM or 3 mM or 4 mM or 5 mM) of concentration of 7HC from gastrula stage (~6 hrs post fertilization - hpf) until completion of embryonic development and hatching (72 hpf). Developmental trajectory of each post hatched larva was traced for two weeks. Angiogenesis and patterning of major blood vessels occurred in zebrafish embryos/ larvae between 24 - 72 hpf in controls. Exposure to 7HC resulted in an impairment in patterning of inter segmental vessels (ISVs) dorsal aorta (DA), dorsal longitudinal anastomotic vessel (DLAV), posterior cardinal vein (PCV), and common cardinal veins (CCVs) accompanied by increased site specific cellular apoptosis, declined heart rates in a dose-dependent manner. 7HC manifest anti-angiogenic effects mediated/ induced through cellular apoptosis, hence may deserve attention and consideration as tumour angiogenesis suppressors in malignancy therapeutics.

Keywords: Zebrafish, Development, Embryo cultures, Angiogenesis, 7-hydroxycoumarin

Introduction

Coumarins are phytochemicals found amply in fruits, vegetables, herbs and many plants. Derivatives of coumarin, are known to manifest variety of biological activities of medicinal value in treating human diseases and evolving therapeutics (Chen et al., 2004). For instance, many of the hydroxy derivative of coumarin, are used as an intermediate in the synthesis

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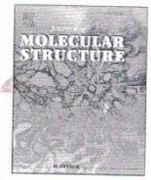

Vibrational spectra, structure, theoretical calculations of 3-Fluoro-4-Hydroxybenzaldehyde: With evidence of hydrogen bonding

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ABSTRACT

Fourier-Transform Laser Raman (3500-100 cm^{-1}) and FT-IR (4000-400 cm^{-1}) spectral measurements have been made for the solid 3-Fluoro-4-Hydroxybenzaldehyde. Geometry optimization and frequency calculations performed at two levels namely, RHF/6-31G* and B3LYP/6-31G* have yielded C_s symmetry with energies of −517.1388109 hartrees and −520.0240034 hartrees. A detailed interpretation of infrared and Raman spectra aided by the PEDs (potential energy distributions) for the computed frequencies has been reported. The PES scan yielded four distinct conformers out of which the most stable conformer is that with the orientation of C=O of aldehyde group with respect to the hydroxyl group and fluorine in the *cis* form. The Fluorine substitution is seen to affect its structure and charge distributions in its vicinity as is seen by the NBO analysis and mulliken charges distribution.

A broad IR band near 3130 cm^{-1}, due to O–H stretch shows evidence of hydrogen bonding. The aldehydic C–H vibration predicted at 2801 cm^{-1} is observed at 2750 cm^{-1}. Downshifting of the aldehydic C=O stretch vibration predicted at 1725 cm^{-1} to an intense IR band at 1670 cm^{-1}; increase in the frequency of in-plane bending vibration of O–H as a shoulder absorption band at 1290 cm^{-1} from its predicted mode 1243 cm^{-1} are all further indications of O–H···O bonding. Dimerization for the most stable conformer has been evaluated by B3LYP/6-31G* level. The dimer spectrum is seen to agree fairly well with the observed spectra. C–F stretching vibration predicted at 1235 cm^{-1} is seen to couple with ring bending vibrations and is assigned to a strong Raman band at 1259 cm^{-1}. The optimized structure and harmonic frequencies computed at B3LYP/6-31G* level are in good agreement with the experimental values.

1. Introduction

Benzaldehyde and its derivatives have been found to be extensively used in biological, chemical and medical fields [1–3]. Benzaldehyde derivatives are among the most interesting carbonyl and hydroxyl containing systems which have received attention because of their importance in structure activity relationship [4,5]. Literature survey reveals that the benzaldehyde derivatives have been subjected to various spectroscopic studies [6–9]. Halo substituted benzaldehydes [10–12] are of additional interest because of their ability to engage in hydrogen bond interactions [8,10,13]. Recent studies have shown the effect of the cylodextrin inclusion process done in benzaldehyde derivatives which in turn have found practical benefits in many areas like pharmaceuticals, textile and food industries [14]. Recently, studies done on similar systems by our group report the O–H···O bonding [15]. It was of interest to investigate whether similar hydrogen bonding occurs by replacing the Chlorine with more electronegative Fluorine. The inclusion of Fluorine is known to bring about changes in charge distributions which further leads to changes in its structure and vibrational parameters.

Hence, in the present work a combined theoretical and spectroscopic study of solid 3-Fluoro-4-Hydroxybenzaldehyde (hence forth referred as 3F4HB) has been reported. A complete assignment of the vibrational spectra of 3F4HB by Infrared and Raman spectroscopic techniques supported by electronic structure calculations carried out at *ab initio* (RHF) and hybrid (B3LYP) methods using the 6-31G* basis set has been performed using the Gaussian suite of program [16]. A conformational study to determine the most stable form has been carried out. The assignments of frequencies for the most stable conformer are computed at the B3LYP/6-31G* level which have been further supported by the PEDs. The different vibrational modes have been visualized using GaussView 3.0 [17].

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ORIGINAL ARTICLE

Kinetic Effect of Novel Osmium(VIII) for the Oxidation of Pyrazinamide by a Copper(III) Complex and Their Mechanistic Aspects

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Abstract
The oxidation of an anti-tuberculosis drug, Pyrazinamide (PYZ) by Cu(III) complex has been investigated with and without Osmium(VIII) catalyst in aqueous alkaline media at constant ionic strength using spectrophotometer. The stoichiometric ratio was found to be 1:2 in both the cases. The reaction was unit order with respect to DPC and Os(VIII), whereas less than unity with respect to PYZ. The rate increased with increase in concentration of alkali and retarding effect was observed with increase in periodate concentration in both the cases. The oxidation product was identified and characterized by spectral analysis. A plausible mechanism was proposed and physical quantities such as activation parameters and thermodynamic quantities were determined with respect to slow step. Active species for Cu(III) and Os(VIII) were $[Cu(H_2IO_6)(H_20)_2]$ and $[OsO_4(OH)_2]^{-2}$ respectively. The reaction constants involved in different steps were calculated for both the cases. The catalytic constant (K_C) for catalyzed reaction was calculated at different temperatures.

Keywords Pyrazinamide · Osmium(VIII) · Kinetics · Reaction mechanism

1 Introduction

Pyrazinamide is a potent anti-tuberculosis drug [1] which is administered in early stages of TB to shorten [2–4] the course of chemotherapy. It has unique property of killing non replicating [5] bacteria. Pyrazinamide is prescribed to patients in combination with Rifampin and Isoniazid [6]. The active form of pyrazinamide is pyarazinoic acid which acts against TB causing bacteria 'Mycobacterium tuberculosis' at little less than neutral pH. Even though the mode of action is not clearly inferred [7], but reports are available for conversion of pyrazmide into pyrazinoic acid [8] by the enzyme pyraziamidase present in cytoplasm of the bacteria, where it inhibits fatty acid synthase. This restricts the ability of bacterium to synthesize new fatty acids which are essential for growth and multiplication [9].

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The intake of pyrazinamide has also shown some of the side effects such as liver injury, arthralgia, anorexia, nausea, vomiting, dysuria, malaise, fever and sideroblastic anemia [10]. Therefore, monitoring the PYZ level in human body fluids is quite significant to find the possible lowest relative concentration that could provide nominal therapeutic dosage and toxicity [11]. It is also important to control the dosage of PYZ in biological fluids to minimize the harmful effects.

Several analytical methods have been developed, such as multivariate standardization methods [12], capillary electrophoresis [13] and chromatographic methods [14]. Its determination and *in vivo* study of metabolites were carried out by using HPLC technique [15] and electroanalytical technique [16]. From past few decades, oxidizing property of transition metals in higher oxidation state has acquired substantial attention of many researchers. The transitional metals in higher oxidation states are stabilized by using chelating ligands. Periodate complex of Cu(III) [17], Ag(III) [18] and Ni(III) [19] have been synthesized and found to have fairly good oxidizing property in alkaline media. Moreover, Cu(III) is a fine oxidant which shows better oxidizing property particularly, in alkaline media. Ramreddy et.al., [20] reported, Copper(III) as an intermediate in the copper(II) catalyzed oxidation of amino acids by peroxydisulphate. The oxidation reactions usually involve the copper(II)

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Effect of titanium dioxide and gadolinium dopants on photocatalytic behavior for acriflavine dye

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ABSTRACT

Herein, we report the experimental methodology to optimize the operational parameters of the photocatalytic degradation of acriflavine dye using TiO_2 and Gd^{3+} as dopant. A series of Gd^{3+} doped TiO_2 nanoparticles were synthesized via hydrothermal route and characterized using various techniques like FT-IR, UV, XRD, FESEM and EDS. It is observed that synthesized particles are in the range of 25–30 nm with spherical shape in nature. TiO_2 has rutile phase and the average particle size was estimated from Scherrer's equation. Energy bandgap was estimated using Tauc's plot. The photodegradation was carried out under UV light in pseudofirst order condition. To understand the kinetics, four experimental parameters were chosen as independent variables like percentage of dopant, initial concentration of dye, dosage of catalyst and pH of reaction medium. The degradation efficiency of 92% was observed for 0.5% Gd doped TiO_2 at catalyst dosage of 0.3 g/dm^3, pH 10 and dye concentration of 3×10^{-6} mol/dm^3. It is observed that, the photocatalytic activity of TiO_2 can be increased by using gadolinium as dopant only in optimum concentration. Further, this photocatalyst can be employed to degrade other organic pollutants.

1. Introduction

Water is the most essential component for the existence of life on earth. Water resources are continuously being exploited due to rapid industrialization from mid of the last century. Many organic pollutants persist in water and have been detected in the range from ng/L to mg/L,[1] but it has made adverse effect on environment. Sensitive receptors such as phytoplankton, zooplankton, including human beings and animals are facing life threatening problems[2] over the last decade due to gradual change in aquatic environment and interaction with food chain. Water resources are polluted due to organic contaminants which are discharged by manufacturing industries, pharma industries, fertilizer industries, chemical industries, textile and dyeing industries.[3] Further, the municipal waste-water, runoff from agricultural procedures and chemical spills also contribute towards contamination of water resources. Organic contaminants persist in water and enter in biological food chain which affects human health and entire ecosystem. In recent years, environmentalists and scientists have raised serious concern over growing deterioration in quality of water. Today's challenge is to get clean water which should be free from color, odor, contaminants and pollutants.

Acriflavine [AFN] is used as an antiseptic since the World War. It was synthesized by a German medical researcher, Dr. Paul Ehrlich and various researchers used it as antibacterial agent.[4] Acriflavine hydrochloride is soluble in water and generally employed to treat fungal infections of aquarium fish. It is also used in biochemistry due to its fluorescent property. Despite its medicinal importance, acriflavine is also known for its harmful effects on human beings such as skin irritation, eye irritation, breathing problems.[5] Acriflavine is also found to be toxic to aquatic plants. It also imparts fluorescent color to water which is required to be removed to meet the ideal characteristics of clean water.

In recent years, TiO_2 has emerged as a promising heterogeneous catalyst among numerous semiconductors and attracted researchers for having versatile properties like chemical stability, non-toxicity towards environment and cost effectiveness.[6] The

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Ruthenium(III) catalyzed oxidation - kinetics and mechanism of antidepressant drug bupropion hydrochloride by diperiodatocuprate (III) in aqueous alkaline medium

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Abstract

The entitled reaction was investigated and monitered spectrophotometrically (λmax = 415 nm) at constant ionic strength of 0.1 mol dm^{-3} and 301K. The reaction shows 1: 2 stoichiometry (BHC:DPC), 1st order in [DPC] and [Ru(III)] and less than unit order in [BHC], [alkali]. The periodate has retarding effect on reaction rate. The ionic strength, dielectric constant of the medium and added products has no significant effect on the rate of the reaction. The oxidation product of (bupropion hydrochloride) BHC was identified by IR, NMR and GCMS. The active forms of catalyst ruthenium and oxidant monoperiodatocuprate(III) (MPC) were detected as $[Ru(H_2O)_5(OH)]^{+2}$, $[Cu(OH)_2(H_3IO_6)]^-$ respectively. Rate law and reaction mechanism was proposed. Equilibrium constants and rate constant were calculated. The activation parameters were deliberated for catalyzed and uncatalyzed reactions.

Keywords: BHC, MPC(III), Ru(III), Oxidation, kinetics, mechanism.

Introduction: bupropion hydrochloride (BHC) belongs to aminoketone class acts as weak dopamine, known a typical antidepressant drug[1] had anti-inflammatory properties[2]. It is chemically unrelated to tricyclic, tetracyclic, selective serotonin re-uptake inhibitor. It is designated as (±)-1-(3-chlorophenyl)-2-[(1,1-dimethylethyl)amino]-1-propanone hydrochloride (molecular formula $C_{13}H_8ClNO.HCl$, molecular weight 276.2 gm mol^{-1}) as shown in the fig.1.It is white power, crystalline and highly soluble in water. It has bitter taste and produces the sensation of local anesthesia on the oral mucosa and used in treat dipressive disorder, stoping smoking and nicotine replacement therapy[3]. Diperiodatocuprate(III) DPC is act as flexible one electron oxidant [4], [5], soluble, stable in aqueous medium with an appropricate pH value, and has multiple equilibria between different Cu(II) species. Cu(II) has been investigated as a reactive intermediate in some biological reactions[6], electron transfer reactions[7] also identified as an analytical reagent[8-9]. Ruthenium was used as a catalyst in many redox reactions[10]. Ru^{III} catalysed oxidation of drug Pentoxifyline[11] and anticholinergic drug Atropine Sulfate Monohydrate[12] by diperiodatocuprate(III) was studied. However, the mechanism differs for different reactions depends on the nature of substrate, oxidant and experimental conditions[13]. The literature survey reveals that the considerable amount of work has been done on determination of bupropion hydrochloride in pharmaceutical preparations[14] but no information available on the kinetics and Ru^{III} catalyzed oxidation of BHC by DPC(III) in aqueous alkaline medium from the mechanistic view point. So there was need for understanding and elcudiate kinetic model also find thermodynamic parameters, various reactive species and oxidation products.

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Ruthenium(III) catalyzed oxidation of perazinedimaleate by diperiodatocuprate (III) in aqueous alkaline medium – A kinetic and mechanistic approach

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Abstract

The Ru^{III} catalyzed oxidation of perazinedimaleate(PDM) drug by diperiodatocuprate(III) (DPC) in aqueous alkaline medium was investigated and monitored spectrophotometrically (λmax = 415 nm) at constant ionic strength of 0.1 mol dm^{-3} and 301K. The reaction shows 1: 2 stoichiometry between PDM and DPC. The reaction is of first order in [DPC] and [Ru^{III}], less than unit order in [PDM] and negative fractional order in [alkali] and [IO_4^-]. The periodate has retarding effect on reaction rate.

The ionic strength, dielectric constant of the medium and added products has no significant effect on the rate of the reaction; intervention of free radical was observed and Ru^{III} increases the reaction rate. The oxidation product of PDM was identified by IR, NMR and GCMS. The active forms of catalyst ruthenium and oxidant monoperiodatocuprate(III) (MPC) were detected as $[Ru(H_2O)_5(OH)]^{+2}$ and $[Cu(OH)_2(H_3IO_6)]^-$ respectively. The rate law and reaction mechanism was proposed. The equilibrium constants and rate constant were calculated. The activation parameters were deliberated for catalyzed and uncatalyzed reactions.

Keywords: Kinetics, Mechanism, MPC^{III}, Oxidation, PDM, Ru^{III}.

Introduction

Chemical kinetics provides information about mechanism, selection of suitable catalyst, rate of reaction. Selecting optimum conditions for chemical reaction, one can get maximum yield. The kinetic study is essential for the chemical and pharmaceutical industries. Titrometric, stopped flow technique, flash photolysis, spectrophotometric and cyclicvoltametric methods are used to study kinetics of various chemical reactions. Perazinedimaleate is a tricyclic compound belongs to phenothiazine family having general properties similar to chlorpromazine. It is biologically active antipsychotic drug used in the treatment of psychotic conditions. It has a side chain of piperazine. Phenothiazine drug reduces the anxiety, insomnia, other symptoms related to psychological state of cancer patients[24]. It is used as an antiemetic, sedative, analgesic and inhibits tumor cell proliferation.

The perazinedimaleate is white, crystalline powder soluble in water having chemical name 10-[3-(4-mehtylpiperazine-1-yl)propyl]-phenathiazine dimaleate, empirical formula $C_{20}H_{25}N_3S$, $2C_4H_4O_4$ and molecular weight is 579.19 gm mol^{-1} as shown Fig.1. Metal chelates such as diperiodatocuprate^{III}, diperiodatoargentate^{III} and diperiodatonickelate^{IV} act as good oxidants[12,19,29] in a medium with an appropriate pH value. The substance DPC is a flexible one electron oxidant[1], soluble and stable in aqueous medium and has multiple equilibria between different Cu^{II} species. Cu^{II} has been investigated as a reactive intermediate in some biological reaction[27], electron transfer reactions.[17] Transition metal ions such as osmium, iridium and ruthenium were used as catalyst in many redox reactions[2,31,35]. Various researchers have studied the oxidation of drugs Iosartan[16], Isoniazid[11], Chloramphenicol[25], Sulfacetamide[21], Fluoroquionoline[03], Piperazine[36] etc. by diperiodatocuprate(III) and Ru^{III} catalysed oxidation of drug Pentoxifyline[32] and anticholinergic drug Atropine Sulfate Monohydrate[10] by diperiodatocuprate^{III}. However, the mechanism differs for different reactions depending upon the nature of substrate, oxidant and experimental conditions[33]. The literature survey reveals that the considerable amount of work has been done on determination of perazinedimaleate in pharmaceutical preparations[15] but no information available on the entitled reactions. So, there was need for understanding and elucidating the kinetic model.

Experimental Procedure

All chemicals and materials were of analytical grade and all solutions were freshly prepared in double distilled water throughout the work. The stock solution of PDM (Global Calcium Ltd., Hosur) was prepared by dissolving appropriate amount of the sample in double distilled water, the purity was checked by comparing it with its melting point and required concentration was obtained from stock solution. The copper (III) periodate complex was prepared[7,20,34] and standardized by the standard procedure[8]. The UV-vis spectrum with maximum absorption at 415nm verified the existence of copper(III) complex.

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Kinetic and mechanistic study of Ru(III) catalysed oxidation of anti-cholinergic drug hyoscinebutylbromide by diperiodatocuprate(III) in aqueous alkaline medium

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Hyoscine butyl bromide (HBB) is an anti-cholinergic and anti-muscarinic drug used to treat pain and discomfort caused by abdominal cramps etc. It is semi-synthetic derivative alkaloid hyoscyamine having a broad spectrum of activity. Hence the Ru(III) catalyzed the oxidation of hyoscine butyl bromide drug by diperiodatocuprate(III) (DPC) in aqueous alkaline medium was investigated and monitored spectrophotometrically (λ_{max} = 415 nm) at a constant ionic strength of 0.1 mol dm^{-3} and 301 K. The reaction shows 1:2 stoichiometry between HBB and DPC. The reaction is of the first order in [DPC] and [Ru(III)] and less than unit order in [HBB] and [alkali], periodate has a retarding effect on the reaction rate. The ionic strength, dielectric constant of the medium and added products has no significant effect on the rate of the reaction but Ru(III) increases the reaction rate. The main oxidation products of HBB were identified by spectral studies. The active forms of catalyst and oxidant were detected as Ru(III), $[Cu(H_2IO_6)(H_2O)_2]$ respectively. The rate law and reaction mechanism was proposed. The equilibrium constants and rate constants were calculated. The activation parameters were deliberated for catalyzed and uncatalyzed reactions.

Keywords: Hyoscine butyl bromide, DPC(III), Ru(III), oxidation, kinetics, mechanism.

Introduction

Chemical kinetics gives information about mechanism, selection of suitable catalyst, rate of reaction, etc., also by selecting optimum conditions for chemical reactions one can get maximum yield. Kinetic study is essential for the chemical and pharmaceutical industries. Titrometric, stopped-flow technique, flash photolysis, spectrophotometric and cyclic voltammetric methods are used to study the kinetics of various chemical reactions. Presently, in this paper, we are reporting oxidation of hyoscinebutylbromide in the absence and presence of Ru(III) catalyst by diperiodatocuprate(III) in aqueous alkaline medium by spectrophotometric method. Tropane alkaloids act as anti-cholinergic, antispasmodic and anti-muscarinic agents belong to the class of natural compounds. They are ability to decrease saliva and gastrointestinal tract secretions widely used in preoperative procedures also decrease motility of smooth muscles in the treatment of bladder spasm. They are used as stimulators in curing diseases like colic, cystitis belongs to respiratory system also antidotes in organophosphorus compounds[1].

The reductant hyoscinebutylbromide is a quaternary ammonium white, crystalline powder soluble in water which shows an anticholinergic agent[2] also antispasmodic in treating peptic ulcer, gastritis, dysmenorrhoea, discomfort caused by abdominal cramps and various disorders of the gastrointestinal tracts[3] and urinary tracts[4]. Its chemical name is [(7(*S*)-(1α,2β,4β,5α,7β)]-9-butyl-7-(3-hydroxy-1-oxo-2-phenylpropoxy)-9-methyl-3-oxa-9-azonitricyclo [3.3.1.0(2,4)] nonane bromide[4]. It melts at about 139–141°C[5]. The hyoscine butylbromide is also known as scopolamine butyl bromide, butyl scopolamine having empirical formula $C_{21}H_{30}BrNO_4$ and its molecular weight is 440.4 g mol^{-1} (360.1 g mol^{-1} without bromide atom) (Fig. 1). It showed extensive decomposition under base hydrolytic conditions also degradation by oxidant has been reported[6].

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1. Document for Criterion 3.3.1 – International Publication of Prof. X Gama

Mukt Shabd Journal **ISSN NO : 2347-3150**

Synthesis and Characterization of HgO,TiO_2, ZrO_2 and MnO_2 doped lithium Zirconate membranes

X S Gama
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Abstract: Absorption measurement plays very important role in characterize the material parameters. The growth in the uses of Li_2ZrO_3 for infrared applications has created a need for knowledge of its optical characteristics in the infrared spectral region. We report measurements of the refractive indices of Li2ZrO_3 doped with 5 wt% of HgO, TiO_2, ZrO_2 and MnO_2

Keywords: Membrane preparation, Absorption Measurements, Uv-vis spectrum

1. Introduction:
In recent years, the devices have successfully addressed the modulation requirements by using Lithium Zirconate. It is a material suitable for a variety of applications. Its optical and non linear optical properties attract designers to use it in optical waveguides. It is a suitable candidate for communication technology because of its high modulation bandwidth. A simple attempt is made to study the absorption spectra to predict the signal and wavelengths for an optical parameter of interest. Devices have therefore been fabricated with Li2ZrO3 doped with various dopants amounts of HgO, TiO2, ZrO2 and MnO2. We have measured the refractive indices of Li2ZrO3 doped with 5 wt% HgO, TiO2, ZrO2 and MnO2 [6-12].

2. Experiment:
2.1 Materials
N,N-Dimethylacetamide is obtained form Sigma-Aldrich chemie,GmbH, Germany. Manganese di-oxide, Zirconium di-oxide was purchased from S.d. fine chemicals Ltd., Mumbai, India. All the chemicals were of reagent grade and used without further purification.

2.2 Membrane preparation
Proper amount of PVA (Polyvinyl Alcohol) was dissolved in 100ml of N,N-dimethylacetamide with a constant stirring for about 24 hours at room temperature. The solution was then filtered using a fritted glass disc filter to remove un-dissolved residues particles and the solution was lest overnight to release the air bubble. 5wt% of Li2ZrO3 and MnO2 is then added to the solution and kept for constant stirring for about 24 hours at room temperature. The resulting clear solution was spread on to a glass plate in a dust free atmosphere at room temperature. After being dried for about 5 days the membrane was subsequently peeled-off and was designated as G1. Other membranes were prepared with Li2ZrO3 by the same process by using 5wt% of TiO2,HgO and ZrO2 and were designated as E1, F1 and H1

3. Experimental result:
In this section, the obtained absorption data measured at room temperatures,
Absorption Measurements:
Absorption measurement is a very important method to characterize the material parameters of photorefractive Lithium Zirconate membrane. Usually, the characteristic absorption band and absorption coefficient are used to calibrate the concentration of the corresponding absorption center. The absorption spectra of Li2ZrO3: TiO2 membrane in the wavelength range of 200–800 nm was obtained. Fig.1. shows a typical absorption spectrum of Li2ZrO3: TiO2 membrane,

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COVID-19: SYMPTOMS, PREVENTION, EFFECT, MYTHBUSTERS, IMMUUNE HEALTH AND BOOSTING MEASURES

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Abstract

Corona-viruses are belongs to a large family of viruses which may cause illness in humans. Unfortunately the virus has spread around the world, causing a pandemic and continuous to increase. In the world, the number of sick people needing care increase dramatically rapidly increases hospital capacity, leading to thousands of death. The number of new cases of corona virus reported each day is continuing to grow and is approaching dangerous levels that will test the limits of our house system. The review represents a picture of the literature in relation with the disease; In particular, I focus on public health impact, diagnosis, case management as well as key points for its control and home remedies to improve immunity.

Keywords: Symptoms, prevention, effect, Myth busters, immune health, boosting measures etc.,

Introduction

In humans, several corona-viruses are known to cause respiratory infections ranging from the common cold to more severe diseases such as Middle East Respiratory Syndrome (MERS) and Severe Acute Respiratory Syndrome (SARS). The most recently discovered corona virus causes corona virus disease COVID-19. COVID-19 is the infectious disease caused by the most recently discovered corona virus. COVID-19 is a disease caused by a new strain of corona virus. 'CO' stands for corona, 'VI' for virus, and 'D' for disease. Formerly, this disease was referred to as '2019 novel corona virus' or '2019-nCoV.

The corona virus spreads from persons to persons through respiratory droplets, either when you come directly comes in contact with the droplets from a cough, sneeze or even in the exited talking. You can also get infected when those droplets land on your surface; you touch that surface and touch your nose, mouth and eyes. The novel corona virus spreads fasters than MERS or flu. That means the each person gets it, is more likely to spread it to more and new people. The case fatality rate of COVID-19 is not as high as for SARS or MERS, but it is currently higher than the influenza.

For individuals, the most important things to do are if you are sick, you may have this corona-virus or you may not, act is to do is stay home as long as your symptoms are not serious, isolate yours self from your family or your room-mates and contact your medical provider by phone to discuss your options rather than putting others life at risk by going out. You may be have infection for up to two weeks, stay home for that longtime if you are able to. Recommended measures to prevent infection include frequent hand washing thoroughly, avoid touching your face and maintain physical distance from others. Good hygiene will protect you from infection. Physical distance of six feet between others protects you and others. If you are unknowingly infected, you may be infections even before your symptoms starts. A good role is to act as you are already infected and takes precautions to protects those around you. If you have been contacted someone who have been sick, self quarantine, keep yourself away from others for two weeks to ensure that you do not have mild infections that you can pass onto others[2].

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Synthesis and Characterization of ZrO_2,MnO_2,$CuCl_2$ and TiO_2 doped Lithium Niobate membranes

X S Gama
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Abstract: Appropriate technology plays a major role in deciding the workable layout of any network. The growth in the uses of $LiNbO_3$ for infrared applications has created a need for knowledge of its optical characteristics in the infrared spectral region for the purpose of designing phase-matched or quasiphase-matched devices. We report measurements of the refractive indices of $LiNbO_3$ membrane doped with 5 wt. % of ZrO_2, MnO_2 , $CuCl_2$ and TiO_2

Keywords: *Membrane preparation, Uv-vis spectrum*, *Absorption Measurements*

Introduction:

Lithium Niobate ($LiNbO_3$) has been used extensively in a wide variety of optical frequency-conversion devices [1-5]. Design of these devices and prediction of their behavior depend critically on precise knowledge of the spectral region of interest. Although the work on $LiNbO_3$ have been studied for many years [6-12]. Most of the data have been limited to wavelengths in the UV, visible, and near-IR spectral regions. $LiNbO_3$ is also being considered for infrared applications, so there is a need for improved knowledge of its wavelengths throughout the transmission range of this material. We have studied the absorption spectra to predict the signal and wavelengths for an optical parameter of interest. $LiNbO_3$ is subject to photorefractive changes in its optical properties, which is intolerable in many applications. Devices have therefore been fabricated with $LiNbO_3$ doped with various dopants amounts of ZrO_2, MnO_2, $CuCl_2$ and TiO_2. Only limited refractive-index data of any kind are available for this material, and the doping level of the samples. We have measured the refractive indices of $LiNbO_3$ doped with 5 wt% ZrO_2, MnO_2, $CuCl_2$ and TiO_2

2. EXPERIMENTS

2.1 Materials: N,N-Dimethylacetamide is obtained from Sigma-Aldrich chemie, GmbH, Germany. Manganese di-oxide Copper chloride, Titanium di-oxide, Zirconium di-oxide were purchased from S.d. fine chemicals Ltd., Mumbai, India. All the chemicals were of reagent grade and used without further purification.

2.2 Membrane preparation

Proper amount of PVA (Polyvinyl Alcohol) was dissolved in 100ml of N, N-dimethylacetamide with a constant stirring for about 24 hours at room temperature. The solution was then filtered using a fritted glass disc filter to remove un-dissolved residues particles and the solution was lest overnight to release the air bubble. 5wt% of $LiNbO_3$ and ZrO_2 is then added to the solution and kept for constant stirring for about 24 hours at room temperature. The resulting clear solution was spread on to a glass plate in a dust free atmosphere at room temperature. After being dried for about 5 days the membrane was subsequently peeled-off and was designated as A1. All the other membranes were further prepared with LiNbO3 by the same process by using 5wt% of MnO_2, $CuCl_2$ and TiO_2 and designated as B1, C1, D1

EXPERIMENTAL RESULT

In this section, the obtained absorption data measured at room temperatures,

Absorption Measurements: Absorption measurement is a very important method to characterize the material parameters of photorefractive Lithium Niobate membrane. Usually, the characteristic absorption band and

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Some properties of $CuCl_2$ doped Lithium Niobate membrane

Xavier S Gama
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Abstract: The growth in the uses of LiNbO3 applications has created a need for its optical characteristics; a simple attempt is made to characterize the photorefractive properties of LiNbO3 by preparing the membrane with LiNbO3 doped with 5wt% of CuCl2. The resulting membranes were characterized by Fourier transform infrared spectroscopy (FTIR), wide-angle X-ray diffraction (WXAD), thermo-gravimetric analysis (TGA) and differential scanning Calorimetry (DSC).

Keywords: Membrane preparation, FTIR,TGA,DSC and XRD

Introduction:
In recent years, the devices have successfully addressed the modulation requirements by using Lithium Niobate (LiNbO3). It is a ferroelectric material suitable for a variety of applications. Its electro-optical and non linear optical properties attract designers to use it in optical waveguides. It is a suitable candidate for communication technology because of its high intrinsic modulation bandwidth. Its Piezo-electric and photo-elastic properties had been used for various technical developments [5-9]. It is also the material of choice for the manufacture of surface acoustic wave devices.
To make measurements of light absorption at different wavelengths in and near the visible part of the spectrum an simple attempt is made to characterize the photorefractive properties of LiNbO3 by preparing the membranes with LiNbO3 doped with 5wt% of various dopants like ZrO2, MnO2, CuCl2 and TiO2.

2. EXPERIMENTS
2.1 Materials:
N,N-Dimethylacetamide is obtained from Sigma-Aldrich chemie, GmbH, Germany. Manganese di-oxide Copper chloride, Titanium di-oxide, Zirconium di-oxide were purchased from S.d. fine chemicals Ltd., Mumbai, India. All the chemicals were of reagent grade and used without further purification.

2.2 Membrane preparation
Proper amount of PVA (Polyvinyl Alcohol) was dissolved in 100ml of N, N-dimethylacetamide with a constant stirring for about 24 hours at room temperature. The solution was then filtered using a fritted glass disc filter to remove un-dissolved residues particles and the solution was lest overnight to release the air bubble. 5wt% of LiNbO3 and ZrO2 is then added to the solution and kept for constant stirring for about 24 hours at room temperature. The resulting clear solution was spread on to a glass plate in a dust free atmosphere at room temperature. After being dried for about 5 days the membrane was subsequently peeled-off and was designated as A1. All the other membranes were further prepared with LiNbO3 by the same process by using 5wt% of MnO2, CuCl2 and TiO2 and designated as B1, C1, D1

2.3 **Fourier transform infrared spectroscopy (FT-IR)**
The incorporation of different amounts of CuCl2 material and its interaction were confirmed by FTIR spectrometer and spectra were recorded in the range of and their characteristics peaks are noted down.

2.4 Wide angle X-ray diffraction
The morphology of membrane was studied at room temperature using X-ray diffractometer. The X-ray source was……the dried membranes of uniform thichness were mounted on a sample holder and scanned in the reflection mode at an angle 2 over the range at a speed of 100/min.

2.5Thermogravimetric analysis
Thermal properties of the membrane were investigated by Perkin Elmer Model STA 6000 thermo gravimetric analysisat a rate of 100/min under nitrogen atmosphere.

EXPERIMENTAL RESULT
In this section, the obtained absorption data measured at room temperatures,

5. Document for Criterion 3.3.1 – International Publication of Prof. X Gama

Pathways
(UGC Care Journal)

Synthesis and characterization of MnO_2 & Lithium Zirconate doped PVA membrane

X S Gama
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Abstract: Absorption measurement plays very important role in characterize the material parameters. The growth in the uses of Li_2ZrO_3 for infrared applications has created a need for knowledge of its optical characteristics in the infrared spectral region. An attempt is made to investigate the photorefractive properties $Li2ZrO_3$, MnO_2 doped PVA membrane is prepared and the resulting membrane is characterized by Fourier transform infrared spectroscopy (FTIR), thermo-gravimetric analysis (TGA). The lowest initial temperature (T_i) at which the onset of mass change can be detected is 400°C and final temperature (T_f) at which the decomposition completed is is at around 430°C and differential scanning Calorimetry (DSC), The peak temperature is associated with the temperature at which maximum reaction rate occurs is between 170°C to 210°C

Keywords: Membrane preparation, FTIR, TGA and DSC

1. Introduction:

Some devices have successfully addressed the modulation requirements in the recent years by using $Li2ZrO_3$,. The optical and non linear optical properties of $Li2ZrO_3$, attract designers to use it in optical waveguides. Because of its modulation bandwidth it is a regard as candidate for communication technology. A simple attempt is made to study and to predict the signal and wavelengths for an optical parameter of interest. Membrane was therefore fabricated with Li2ZrO3 doped with various 5 wt % of MnO2.

2. Experiment:

2.1 Materials

N,N-Dimethylacetamide is obtained from Sigma-Aldrich chemie,GmbH, Germany. Manganese di-oxide and Zirconium di-oxide were purchased from S.d. fine chemicals Ltd., Mumbai, India. All the chemicals were of reagent grade and used without further purification.

2.2 Membrane preparation

Proper amount of PVA (Polyvinyl Alcohol) was dissolved in 100ml of N,N-dimethylacetamide with a constant stirring for about 24 hours at room temperature. The solution was then filtered using a fritted glass disc filter to remove un- dissolved residues particles and the solution was lest overnight to release the air bubble. 5wt% of Li2ZrO3 and MnO_2 is then added to the solution and kept for constant stirring for about 24 hours at room temperature. The resulting clear solution was spread on to a glass plate in a dust free atmosphere at room temperature. After being dried for about 5 days the membrane was subsequently peeled-off and was designated as G1.

6. Document for Criterion 3.3.1 – International Publication of Prof. X Gama

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Synthesis and Characterization of Natural Oil Doped PVA Membrane

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Author's contribution

The sole author designed, analysed, interpreted and prepared the manuscript.

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Original Research Article

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ABSTRACT

In deciding the workable layout of any network an appropriate technology plays a major role and can improve accuracy and flexibility efficiently, if chosen and implemented in best possible way. The growth in the infrared applications has created a need for knowledge of its optical characteristics in the spectral region for the purpose of designing. Very little work is previously reported in natural oil doped PVA membranes. In this work, a simple attempt is made synthesize and characterize the wintergreen oil and basil oil doped PVA membranes. In investigation, basil oil and wintergreen oil doped PVA membranes were prepared and is made to characterize. The resulting membranes were characterized by Fourier transform infrared spectroscopy (FTIR), wide-angle X-ray diffraction (WXAD), thermo-gravimetric analysis (TGA) and differential scanning Calorimetry (DSC).

Keywords: Membrane preparation; FTIR; TGA; DSC and XRD.

1. INTRODUCTION

The basil oil has a watery viscosity and is pale greenish-yellow in color. Recently, there has been much research into the health benefits conferred by the essential oils found in basil [1,2,3,4]. Wintergreen once commonly referred to plants that remain green (continue photosynthesis) throughout the winter. The term evergreen is now more commonly used for this

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Year 2021-22

1. Document for Criterion 3.3.1 – International Publication of Mrs. Vinutadivya Nirmanik

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RESEARCH ARTICLE OPEN ACCESS

Comparative study on phenolic content, flavonoid content, and antioxidant activities of five species of the genus *Phaseolus*

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ABSTRACT

The current study was designed to assess five species of the genus *Phaseolus* for phenolic content, flavonoid content, and antioxidant ability. The antioxidant capacity of the sample extracts was assessed using different antioxidant models such as ferric reducing antioxidant power (FRAP), DPPH free radical scavenging, phosphomolybdenum reducing power, ferrous ion chelating activity, hydrogen peroxide radical scavenging, hydroxyl radical scavenging, deoxyribose degradation, and β-carotene bleaching assays. The results obtained discovered that the concentration of phenolics and flavonoids in the studied species ranged from 1.11 to 4.01mg TAE/g plant material and 0.11 to 1.16 mg QE/g plant material. The antioxidant activity of the extracts varied in a wide range in the different antioxidant assays depending on the genotype as well as the polarity of the solvents used to obtain the extracts. Ethanolic and aqueous extracts exhibited the maximum amount of phenolics and flavonoids among the solvents. The species studied exhibited a significant range of phenolics, flavonoids, and antioxidant capacity. Hence, the present investigation can provide a new direction by utilizing *Phaseolus* species to formulate cost-effective, eco-friendly, and value-added therapeutic products.

1. Introduction

Phaseolus (Fabaceae) is one of the most important genera encompassing herbaceous to woody annuals and perennial vines comprising about 70 species all indigenous to the Americas, mainly Meso America. The species are a rich source of carbohydrates and proteins and a significant source of vitamin B complexes such as riboflavin, thiamine, niacin, and folic acid. It also provides zinc, copper, iron, phosphorous, calcium, potassium, and magnesium additionally has a high fiber content (Rocha-Guzman and Gallegos-Infante, 2007). It is also an imperative source of polyphenols such as flavonoids, isoflavones, lignans, and tannins. These compounds offer a protective role in humans owing to their strong tendency to scavenge free radicals (Câmara et. al., 2013; Bezuhla et. al., 2018).

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The seeds of *Phaseolus* species were expended by humans worldwide as a dynamic source of proteins and fiber (Onyilagha and Islam, 2009). The consumption of seeds has previously been associated with a reduced risk of cardiovascular diseases, diabetes, and even certain types of cancer (Curran, 2012; Hayat et al., 2014). Some researchers reported that legume seeds are medicinally important due to their antioxidant, anticancer, antimicrobial, antiobesity, cardioprotective, hepatoprotective, and antiproliferative activities (Zhu et. al., 2012; Guajardo-Flores et al., 2013; Zou and Chang 2014). Several articles have appeared in the literature focused on the antioxidant potential of common beans (Amarowicz et al., 2008; Aknod et. al., 2011). Some studies evaluated the seeds of the most economically important species, *P. vulgaris*, for the presence of seed coat anthocyanin glycosides (Choung et al., 2003) and polyphenols (Espinosa-Alonso et al., 2006). The findings of Suárez-Martínez et al. (2016) reported *P. vulgaris* as a nutraceutical source for human health with favorable effects against cancer because of the antimutagenic and antiproliferative properties of their phenolic compounds, lectins, and protease inhibitors. The accessible literature revealed that *P.*

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