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COMPARATIVE STUDY OF SYNTHESIZED SCHIFF BASES

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ABSTRACT

The reaction of primary aromatic amines (4- Morpholinoaniline) with O-Vanillin is found to be catalyzed by lemon juice or Grapes juice or pomegranate juice as natural acid under solvent-free conditions or traditional method to give the corresponding Schiff bases . Compared with Conventional methods, this eco-friendly reaction has many advantages like economical, environmental, mild reaction conditions and simple work-up with high product yields. The synthesized imines were identified by its physical properties, melting point, characterized by IR, NMR and mass spectrometry.

INTRODUCTION

Green chemistry is the branch of chemistry that involves tools techniques and technologies. Green chemistry have been formulated the basic principles such as waste or by – products, minimum incorporation of the reagents into the final product, prevention or minimization of hazardous products, products obtained should be biodegradable, energy requirement for the synthesis should be minimum. The latest challenges to chemists to development of non-hazardous synthetic methods for organic synthesis. The developing concern for the environment demands, the development of a simple and efficient method, using eco-friendly approach as well as economical process is in great demand in organic and in coordination chemistry. The most of the solvents are either toxic or flammable and considerably to the cost of an overall synthesis, so in recent years solvent –free conditions organic reactions having popularity [1-2]. The solvent –free reactions usually more efficient work, shorter reaction time, in expensive, non toxic, safer, more improved selectivities and simplifies separation and purification of products than the traditional method.[3-5] .It is going to now become an essential tool in the synthetic chemistry [6]. The biocatalytical transformations using edible plants, plant root, plant tubers and plant leave extract can be applied in many organic reactions [7-10]. Due to the beneficial properties, concern for the environmental demands, fruit juices are

powerful and selective natural acid catalyst for the condensation reaction [11-14]. So fruit juices are used in the synthesis of Schiff base, it is condensation product of carbonyl compound and primary amine. In present my work fruit juices like lemon, Grape and pomegranate juices are used as a solvent free catalyst for the synthesis of Schiff base from O-Vanillin and 4-Morpholinoaniline .The formation of carbon–nitrogen double bond plays important role in organic synthesis. Schiff bases, known as Imines are compounds containing azomethine group -(HC=N)- and represented by the general formula $R_3R_2C=NR_1$. They are the condensed products of aldehydes or ketones and were first reported by Hugo Schiff in 1864[15] .This can be achieved by the reaction of aldehydes and amines in acidic medium which leads to synthesis of Schiff bases (imines). Schiff bases have attracted considerable attention of organic chemists due to their significant biological activities like anticancer [16],antibacterial[17] ,antitumor [18], Antimicrobial [19],DNA binding affinity and anti oxidative activity [20],anti cataract[21], anti fungicidal[22], and bactericidal[23] .Schiff bases are playing an important role in living organisms, such as decarboxylation and C-C band cleavage[24]. Schiff bases having the coordination ability of the metals within the polymer based macromolecules permits these materials to act as sensors [25].

2. MATERIALS: O-Vanillin, 4-morpholino aniline purchased from Sigma –Aldrich. Lemon, Grapes, Pomegranate and Methanol.

3. PREPARATION OF NATURAL CATALYST:

1. Liquid Lemon juice preparation:

Lemon is originating in the north –west region of India. In India it is also cultivated in the home gardens. While lime fruits was peeled off with knife and fruit slices were pressed into fruit juice to get semisolid mass. It was then filtered with muslin cloth to get liquid juice. Lemon juice is sour in taste. The juice contains 1% citric acid and 0.5% ascorbic acid along with some organic acids, moisture, carbohydrates, protein, fat, minerals and fibbers. It is a powerful and selective natural acid catalyst for condensation reaction [1, 26-28].

2. Liquid pomegranate juice preparation:

Pomegranate fruits were peeled off with knife and seeds were pressed into fruit juice to get semisolid mass. It was then filtered with muslin cloth to get liquid juice. It contain 85% water 10% total sugars and 1.5% pectin , organic acid such as ascorbic acid ,citric acid and malic acid .It was used as catalyst in the preparation of Schiff base.

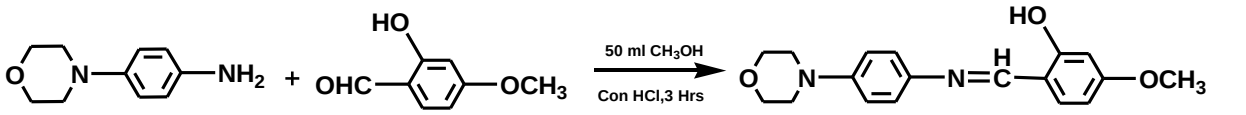
3. Liquid Grape juice preparation:

Grapes were washed with water and pressed into fruit juice to get semisolid mass. It was then filtered with muslin cloth to get liquid juice. It contains many organic acids including amino acids, but tartaric and malic acid account for over 90% of the total acids present. It was used as catalyst in the preparation of Schiff base

4. Preparation of Ligand: (2-(4-morpholinophenylimino) methyl) -5 –methoxy phenol):

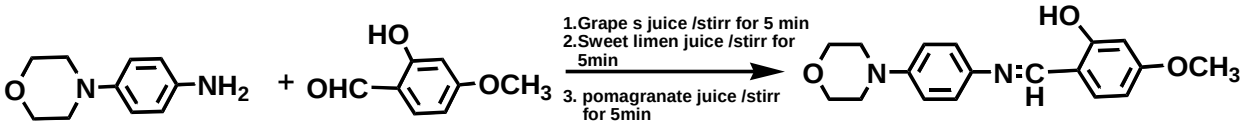
4.1 Conventional methods: In traditional method Schiff base prepared, Equimolar (0.01mole) concentrations of 4-Morpholinoaniline and O- Vanillin were dissolved individually in 50 ml of methanol and the both the solutions are transferred in to 250 ml round bottom flask. The mixture was refluxed on a water bath with constant starring for about 3 hours. Yellow precipitate was formed on cooling in crushed ice for 2-3 hours. It was filtered, washed with methanol. It was recrystalization with ether and dried. The yield, colour, melting point was posted in Table -1 and equation is represented in Fig: A

4.2. Green method: The equimolar (0.01mole) amount of 4-Morpholinoaniline with O -Vanillin was taken in different beakers.



4-morpholinobenzenamine 2-hydroxy-4-methoxybenzaldehyde 2-((4-morpholinophenylimino)methyl)-5-methoxyphenol

Fig:A



4-morpholinobenzenamine 2-hydroxy-4-methoxybenzaldehyde 2-((4-morpholinophenylimino)methyl)-5-methoxyphenol

Fig:B

Table-1: physical properties of Schiff base ligand

S.no	Name of catalyst	Colour	Solubility	Melting point	Percentage of yield
1	Lemon juice	Yellow	Soluble in methanol And insoluble in water	158-161	96
2	Grapes juice	Yellow		159-160	97
3	Pomegranate juice	Yellow		158-160	94
4	Hydrochloric acid	Yellow		158-160	92

Table 2: Important IR spectral bands (Cm^{-1}) of Schiff base (OVMA) ligand obtain from Conventional and green method

Method		*v*(O-H) phenolic	*v* -C=N
Conventional Method		3402	1612
Green method	Pomegranate juice	3387	1612
	Grape juice	3919	1620
	Lemon juice	3834	1612

Table: 3 Conventional and Green method synthesized Schiff base m/z values.

Method of Schiff base preparation	m/z values
Conventional method	312, 313
Green method	312,313

Table 4: Important ^{1} H NMR spectral data of Schiff base (OVMA) ligand obtain from Conventional and green method

Method		H-C=N	Ar-H	-OCH_3	-OH	protons in morph aniline
Conventional Method		8.64	6.8-7.2	3.89	4.17	3.2-3.9
Green method	Pomegranate juice	8.65	6.8-7.2	3.89	4.17	3.2-3.9
	Grape juice	8.65	6.8-7.2	3.89	4.17	3.2-3.9
	Lemon juice	8.65	6.8-7.2	3.89	4.17	3.2-3.9

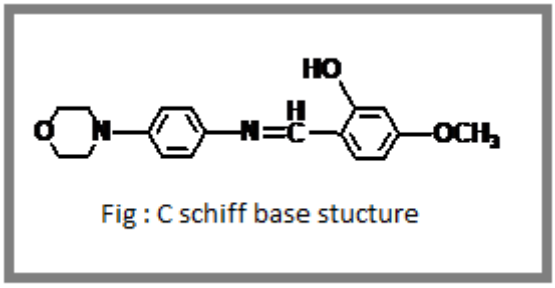


Fig : C schiff base stucture

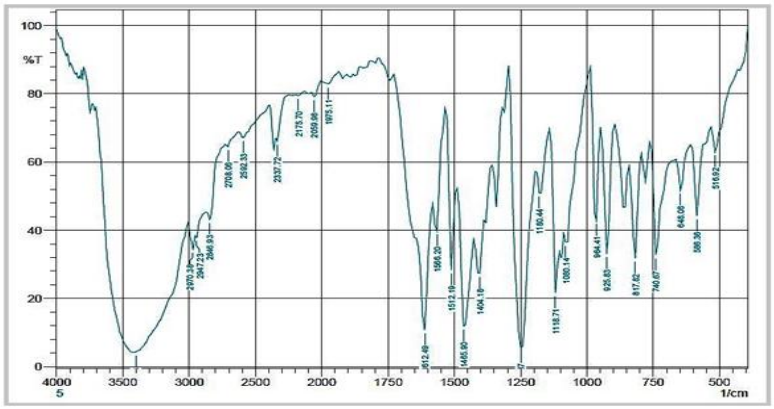


Fig: 1 FTIR Specta of schiff base ligand synthasized form Conventional method

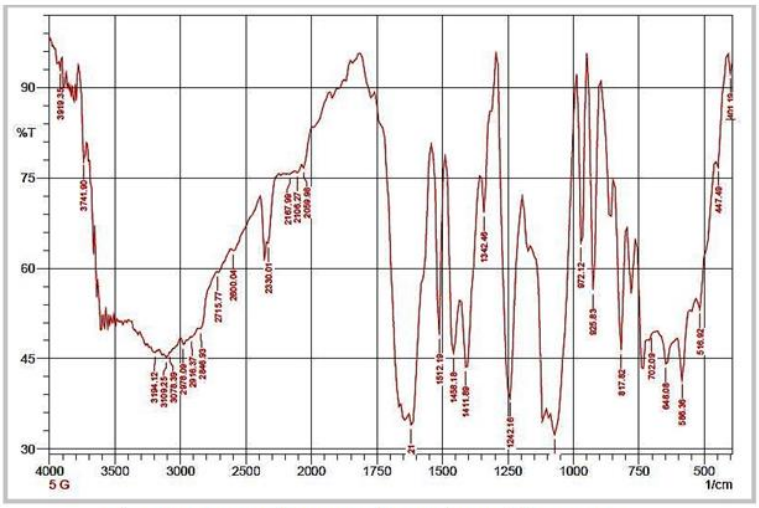


Fig:2 FTIR spectra of schiff base synthaized by using grape juice as a catalyst

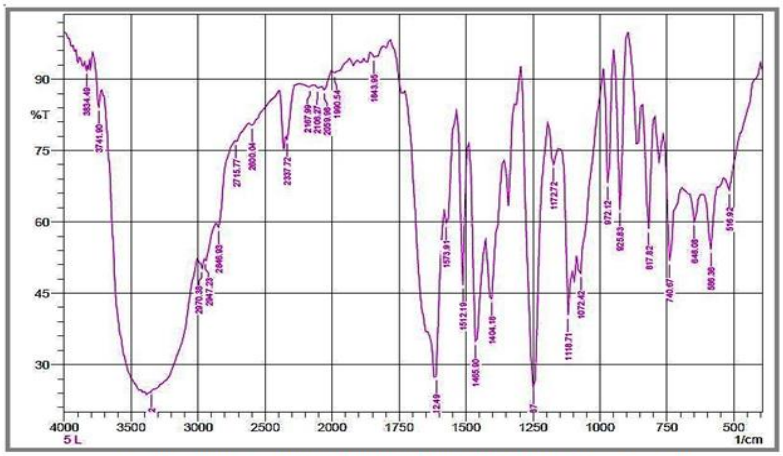


Fig: 3 FTIR spectra of schiff base ligand synthesized by using lemon juice as a catalyst

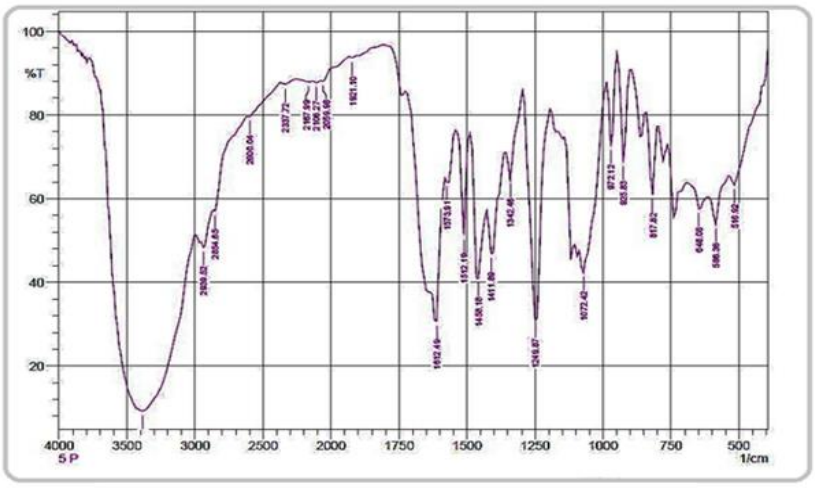


Fig : 4 FTIR spectra of schiff base synthesized by using pomegranate juice as a catalyst

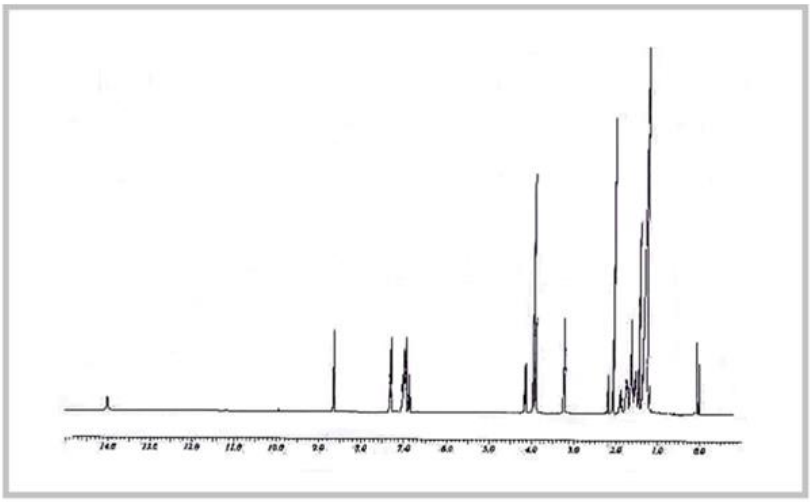


Fig: 5 NMR Spectra of Schiff base synthesized byusing conventional method

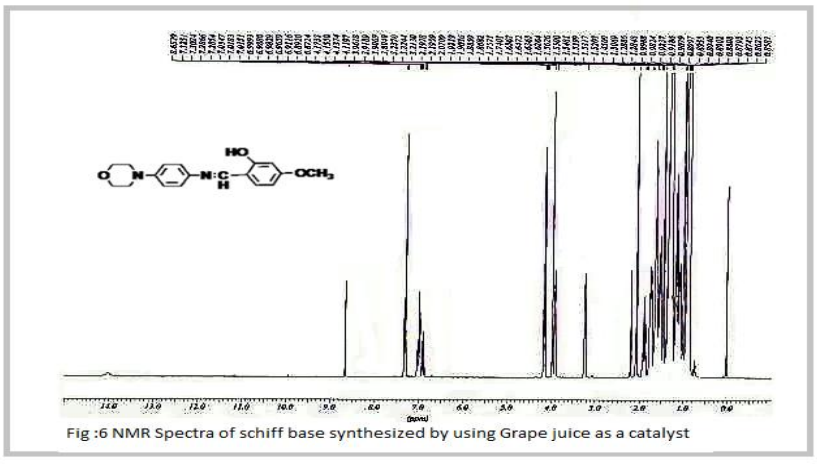


Fig :6 NMR Spectra of schiff base synthesized by using Grape juice as a catalyst

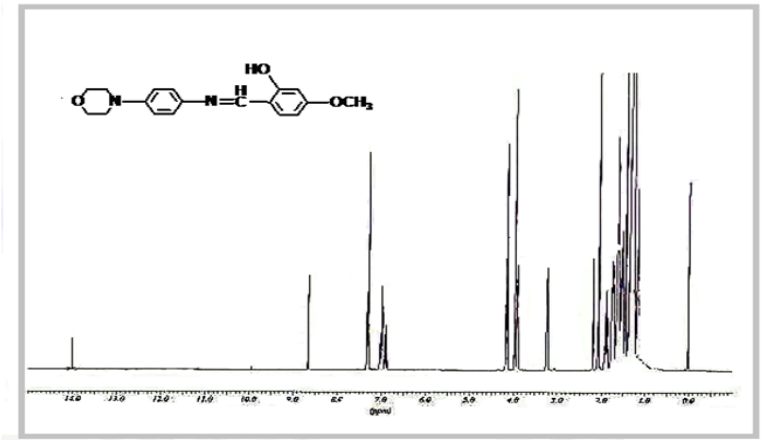


FIG : 7 NMR spectra of schiff base synthesized by using lemon juice as a catalyst

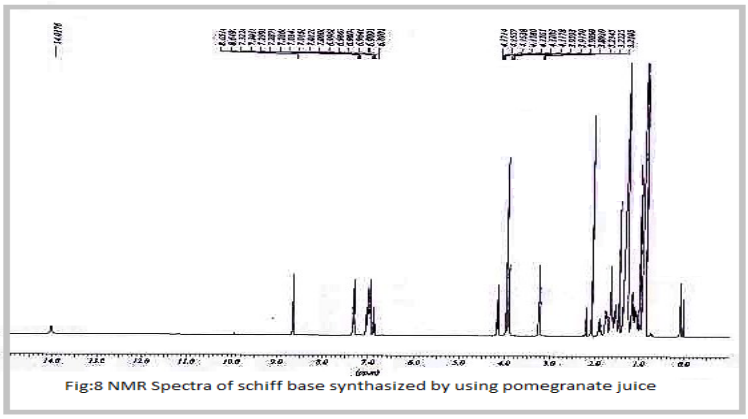


Fig:8 NMR Spectra of schiff base synthasized by using pomegranate juice

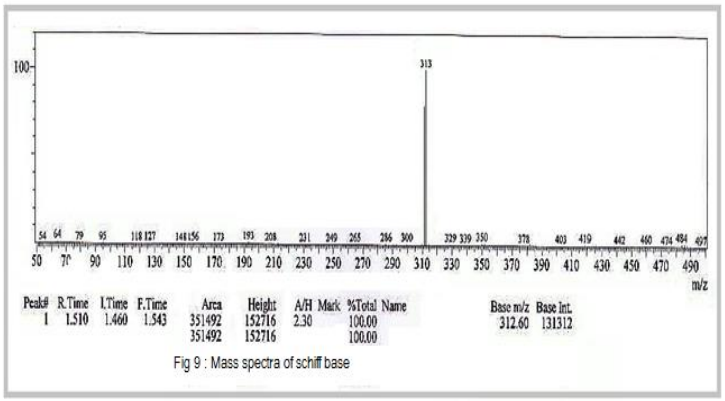


Fig 9 : Mass spectra of schiff base

To those reaction mixtures natural acid catalyst (Lemon juice) were added and then starring for 5-10 minutes at room temperature. The yellow solid crude product was appearing. The product was washed with distilled water and purified by recrystallization with ether. Further, same procedure is repeated with grape juice and pomegranate juice. In this method more yield of Schiff base is produced than the Conventional method. Physical properties of Schiff bases are posted in the Table-1 and the equation is represented in the Fig: B

5. RESULTS AND DISCUSSION:

The compounds are stable at room temperature and non hygroscopic. They decompose at high temperature and soluble in methanol and insoluble in water. The melting point of the ligand and metal complex recoded open capillaries on capillary melting point apparatus. The IR

spectra were recorded In KBr medium and FTIR Affinity –I techniques on a shimadzu spectrometer in wave number region 4000-400 Cm^{-1} in Annamacharya pharmacy college, Rajampet, Kadapa. The NMR spectra of the ligand and metal complex were recorded on AV-400 M-HZ NMR spectrometer in IICT, Hyderabad in DMSO-D6 and $CDCl_3$ solvents at room temperature. The Mass spectra of the ligand and metal complex were recorded at Hyderabad central university, Hyderabad**.** The traditional and green method synthesized Schiff base having nearly same melting point .The product is yellow in colour. Compare the traditional method green method was gives the more percentage of yields. The order of percentage of yield showed the following trend. Grape juice > Lemon juice > Pomegranate juice > Conventional method

5.1 IR spectra of Schiff base:

The comparative analysis of the IR spectra of the Schiff base synthesized from tradition method and Green method, the stretching vibration of azomethine group (–C=N-) is appears at 1612cm^{-1} for traditionally synthesized Schiff base and naturally acid catalyzed (lemon juice and pomegranate juice) synthesized Schiff base but in Grape juice catalyzed Schiff base Schiff base the stretching vibration of azomethine group (–C=N-) is obtain at 1620cm^{-1} . The FTIR spectra of traditionally and green synthesized Schiff base are represented in the Fig: 1,2,3,4. The Conventional and green method synthesized Schiff base FTIR values are represented in the Table: 2

5.2 Mass spectra of Schiff base:

Mass spectra are the most perfect method for confirming the molecular mass of the compound and its elemental composition. The mass spectra are a plot showing the m/z values of various ions against their corresponding relative abundance. In this technique, molecules are ionized and broken up many fragments when molecules are bombarded with a beam of energetic electrons. Mass spectra of Schiff base show a molecular ion peak at 313 with 100% relative abundance. So it is base peak of spectra which corresponds to the one additional molecular weight of the synthesized Schiff base because calculated molecular weight of the compound is 312 gm/ mole. Same value is formed with green method and conventionally synthesized Schiff base. The formation of Schiff base is also conformed to molecular spectroscopy. The mass spectra of Schiff base are represented in the Fig: 9. Conventional and Green synthesized Schiff base ligand m/z values are reported in the table -3

5.3 NMR spectra of Schiff base:

Fig 5,6,7,8 was shows the NMR spectra of Schiff base (OVMA) ligand synthesized from green method and Conventional method. Conventional and green method synthesized Schiff base ligand NMR values are represented in the table -4

6. CONCLUSION:

In this article, we are reporting a new eco-friendly route with good yield for the synthesis of Schiff bases by using sweet Lemon Juice , Grapes juice and pomegranate juice .The products can be purified by recrystallization using appropriate solvents. Compared to Conventional methods, this new method is cleaner, safer and more eco-friendly, prevention or minimization of hazardous products, prevention of by products, minimum incorporation of the reagents in to final product, involving mild reaction conditions such as time, temperature, simple workup. Compare to the Conventional method this Green method was maintaining good yield of product. Based on the above results the structure of Schiff base was represented in the Fig : C

7. Acknowledgement:

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