Applications of Vanillin Schiff Base ligands and their complexes: A Review

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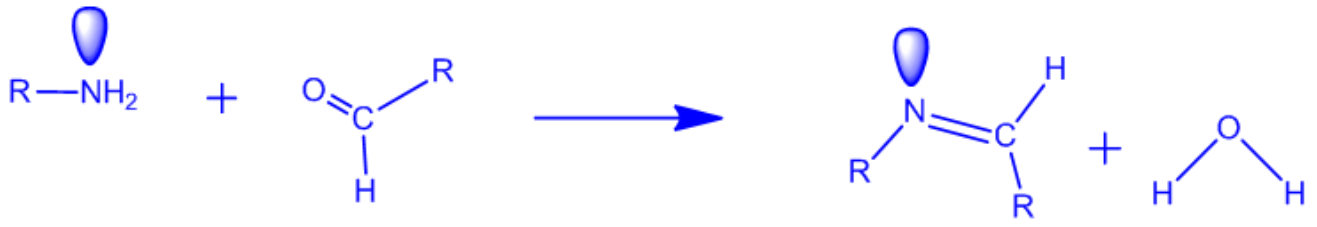
Abstract**—** *Vanillin which is a naturally occurring food component found in plants is used for the manufacture of Schiff base chelates. The chelates and complexes find applications as anti mutagen, anticlastogen, DNA PK inhibitor, anticarcinogen, inhibitor of non-homogenous DNA end-joining (NHEJ) etc. They form complexes with a wide variety of metals including rare earths. They are incorporated in polymer matrix for various applications. This paper reviews the vanillin Schiff base chelates their complexes and their applications.*

Keywords**— *Vanillin, Schiff base, Chelates, complexes.***

I. INTRODUCTION

Schiff bases are a novel class of organic compounds synthesized by the condensation of primary amine and carbonyl compound[1], with structure R-N=CHR, containing azomethine (-CH=N-) group, where **R** is aliphatic or aromatic group.The Schiff bases of aliphatic aldehydes are relatively unstable and undergo polymerization [2-4],but that of aromatic aldehydes are stable[5-8]. These Schiff bases can act as a ligand due to the lone pair of electrons on Nitrogen atom of the azomethine group.



(Monodentate Schiff base)

R= Alkyl or Aryl group.

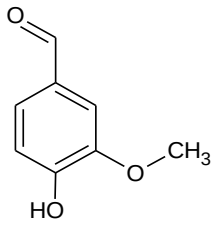
Usually they are mono-dentate, but most of them act as bi-dentate due to the presence of another donor group in the molecule. These ligands are capable of forming very stable coordination compounds with wide applications [9-11]. They are the basic unit of certain dyes, catalysts, improves the ageing resistance of natural rubber, can show toxicities against insects, and even possess antitumor activity.

The condensation of amines with aldehydes and ketones are used in the preparation of new compounds, identification, detection and estimation of aldehydes or ketones, purification of carbonyl or amino groups and protection of these groups during complex or sensitive reactions. In organic synthesis, these reactions are useful for making carbon-nitrogen bonds, some of the compounds are even used as liquid crystals. The Schiff bases may be mono, bi or even polydentate (rare) depending on the nature of amines and carbonyl compounds used.

Vanillin (3-methoxy-4-hydroxy benzaldehyde) **1**, is a naturally occurring food component found in the vanilla plant. Vanillin is a food component having anti mutagen, anticlastogen, DNA PK inhibitor, anticarcinogen, inhibitor of non-homogenous DNA end-joining (NHEJ) etc.

II. VANILLIN SCHIFF BASE WITH ANTIBACTERIAL AND ANTIFUNGAL PROPERTIES

Schiff base of Vanillin with amino acids such as lysine, α-amino butyric acid, tryptophan and n-pheny alananine **2, 3, 4** and **5** have been reported[12-18].



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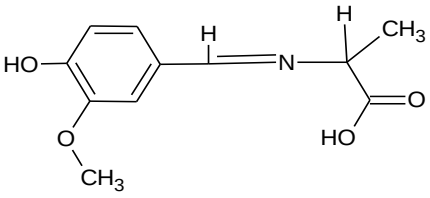

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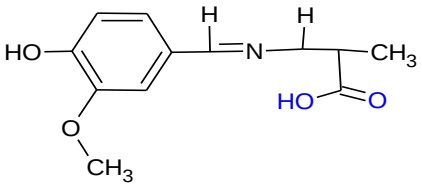

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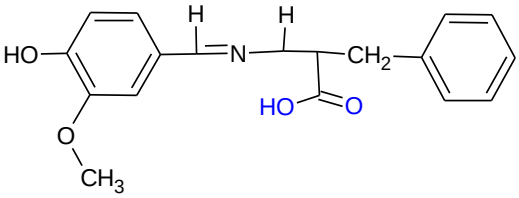

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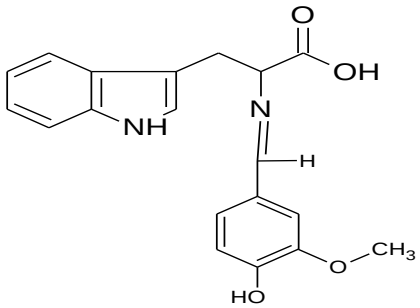

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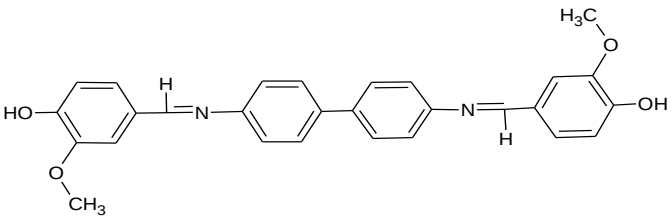
The compound **2** acts as a tridentate ligand. The complexes of Co^{+2}, Ni^{+2}, Cu^{+2} and Zn^{+2} with Schiff base **2** are reported. The compound 2 is reported to have antibacterial and antifungal properties. Compound **3** and its complexes with Co^{+2}, Ni^{+2} and Cu^{+2} are reported to have antibacterial property. The Schiff base 4 and its complexes with lanthanides such as Nd, Pr, Yb, Sm, Eu, Dy have been reported to have antitumor properties. The Schiff base prepared with tryptophan and vanillin[19] is studied for their interaction with herring. The complexes of vanillin with benzidine and anisidine (**6** and **7**) with heavier metals such as Ta forms complexes with 7 to form 3,4 [bis(vanillin)benzidine] complex is reported.



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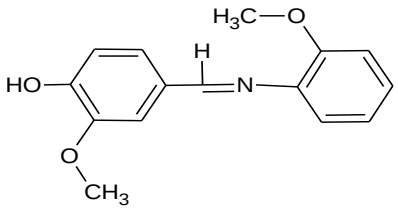

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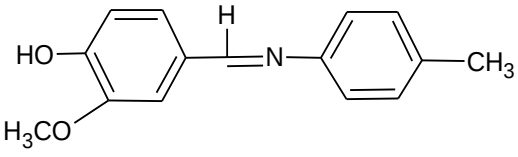
Complex with Y^{+2} and La^{+3} and Schiff base 6 is reported. Vanillin[20] Schiff base with p-toluidine **8** and its complexes with rare earth nitrate metals such as La, Ce, Pr, Nd, Sm, and Eu is reported. The Schiff base **8** is used for the preparation of complexes with inner transition metals La- Lu except Pm. Their vibration spectra have been reported.



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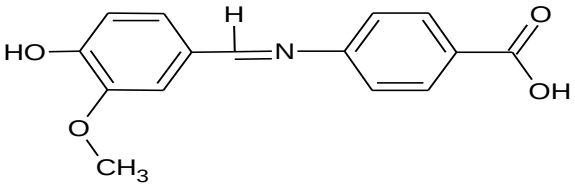

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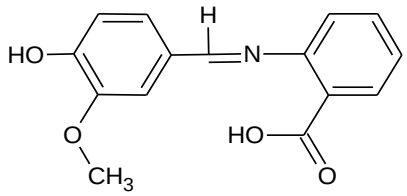
Vanillin Schiff base with anthranilic acid 9 is reported to form complexes with Ru^{+3} and is studied for the physico-chemical and biological properties. The Schiff base **9** is reported to have antifungal and antiviral property. The ortho isomer of anthranillic acid is used for preparing the Schiff base with vanillin 10. Their complex with dioxouranium (VI) complex[21] is reported. The Schiff base **10** also forms complexes with Iridium (III) complexes and is reported to have antifungal anti viral property. Iridium[22] complexes with Schiff base derivatives of vanillin with o and p amino benzoic acid **9** and **10** has been reported to have antifungal and antiviral properties.



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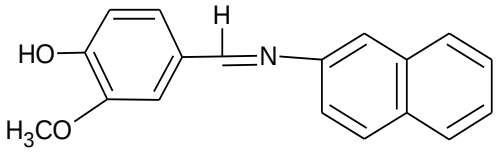

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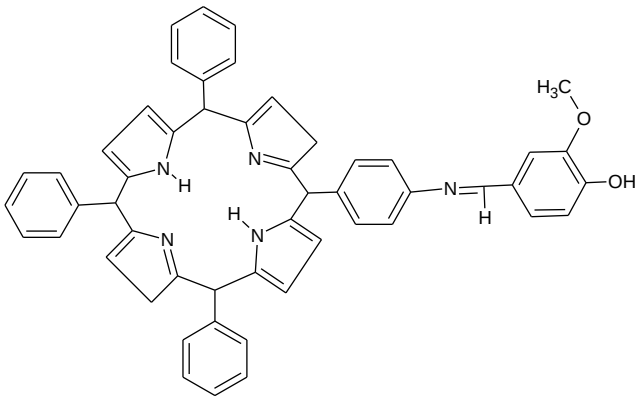
Schiffs base of vanillin and 2-naphthyl amine **11** is reported to form complexes with rare earth metals such as La, Pr, Nd, Sm, Eu, Tb, Dy, Er, Yb and Lu.



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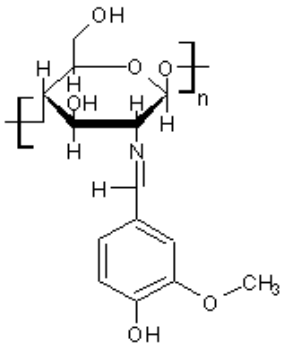
Ethyl vanillin is used for the purification of porphyrin[23] which is reported to form Schiff base **12** used in the purification of porphyrins.

III. VANILLIN SCHIFF BASE IN WATER PURIFICATION

Polymers are prepared incorporating vanillin in the polymer chain used for the isolation of metal ions. Chitosan membranes[24] are modified with the help of vanillin which is reported to form Schiff base **13**, its thermodynamic property for the adsorption of Cu(II) from solution is reported.



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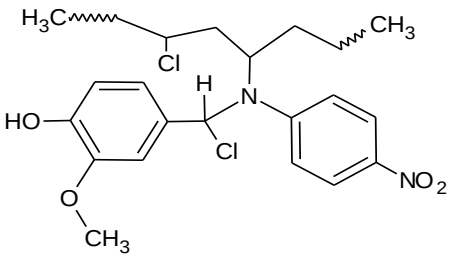

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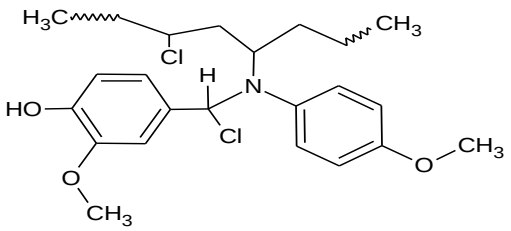

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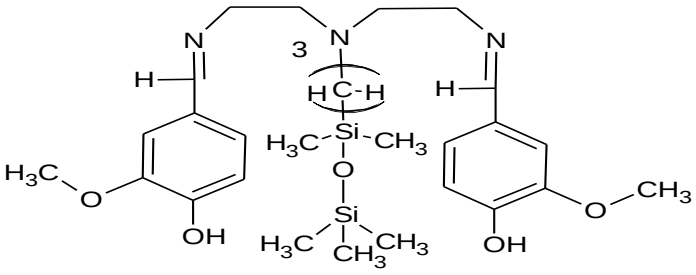
Vanillin Schiff bases are used for preparing polymers such as chitosan[24-26], PVC and silica gel. The Schiffs of vanillin with chitosan **13** is studied for the adsorption of Cu^{+2} from water. The Schiff base of vanillin incorporated to the PVC matrix **14** and **15** is reported to act as a co stabilizer for PVC. The vanillin Schiff base with p-nitro benzene and p-nitro aniline is reported to be used as stabilizers for PVC **14** and **15**. The Schiff base of vanillin and ethylene diamine is immobilized on silica gel **14** and **15** as a derivative. This is used for the solid phase extraction and determination of chromium (III).



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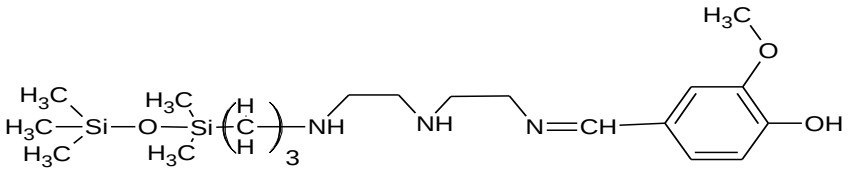

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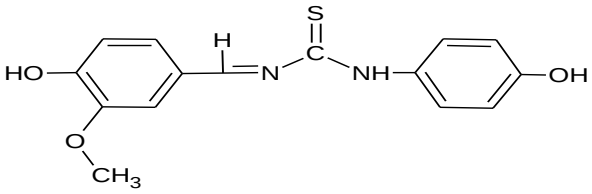
The silica gel-immobilized – vanillin derivative 16 and 17 are reported as solid phase extract ants for the determination of Chromium (III) in environmental samples.



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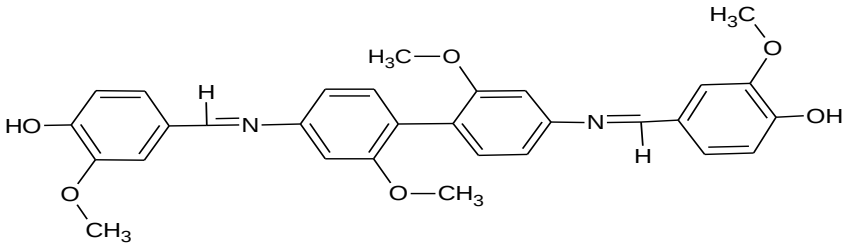
The poly (azo methane esters) having phenyl thio urea units have been synthesized characterized and reported[27].



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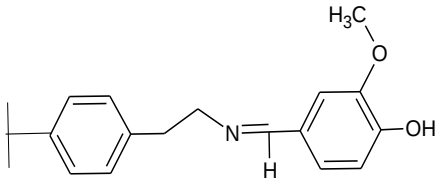
Polyphenols derived from o-anisidine and vanillin **19** is reported and the solubility[28], thermal stability and electrical properties have been reported. Vanillin Schiff base is anchored on polystyrene **20** and is reported for its ion exchange property[29].



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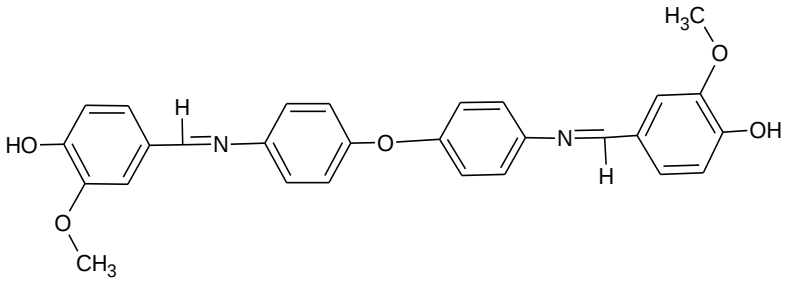

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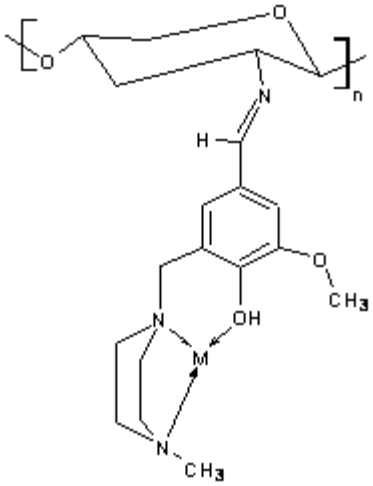
Vanillin Schiff base with polyphenol[30] from bis (4-amino phenyl) ether is reported for its electrical conductivity, solubility and optical band gap. Chitosan is reported to react with vanillin[31] aldehyde by Schiff base reaction in water. A polymer product- VCG is prepared[32]. The graft percentage is studied with reaction time, temperature and monomer concentration. A cross linked chitosan[33-35] vanillin Schiff base is reported with formaldehyde under microwave radiation. The structure was reported using IR and XRD. The product is reported to have selective adsorption for Cu^{+2}.

New chitosan biopolymer derivative (CTSL) **22** is reported by anchoring a new vanillin- based complexing agent or ligand 4-hydroxy-3-methoxy-5-[(4-methylpiperazin-1yl) methyl] benzaldehyde (L) with chitosan (CTS) by means of condensation.



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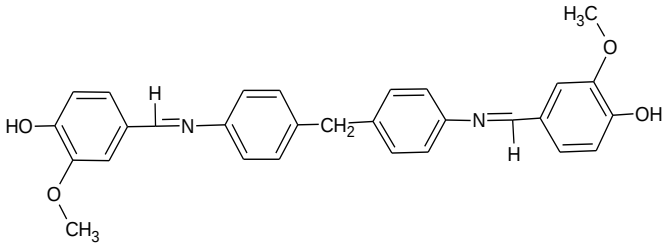

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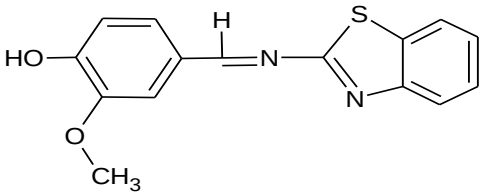
Polystyrene anchored Schiff base is reported to remove Fe^{+3} from water. Liquid crystalline epoxy (LCE) with azo methane[36] cured with diamine is reported **23**.

IV. VANILLIN SCHIFF BASE WITH HETROCYCLIC COMPOUNDS

Vanillin Schiff base with hetrocyclic compounds such as 2-aminobenzo thiazole[37] **24**, 4-amino-1,3 dimethyl-2,6 pyrimidine-dione[38] **29**, thiazolyl **25**, 2-aminopyridine[39] **26**, trimethoprim[40]**27**, coumarinyl[41] **28** , etc, have been reported.



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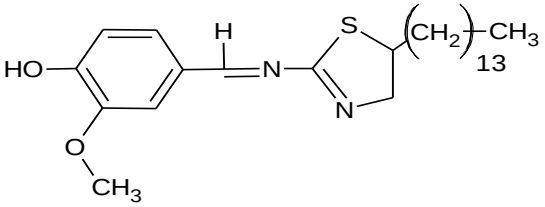

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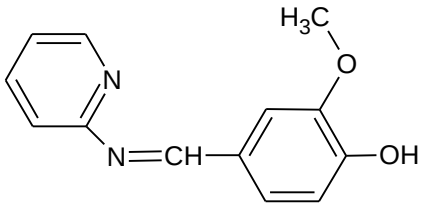

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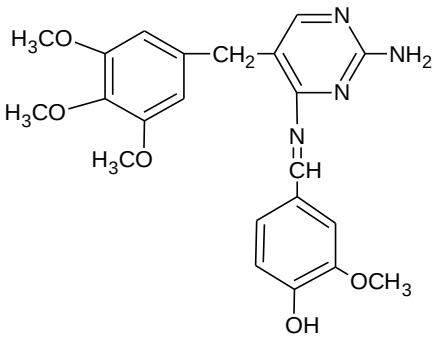

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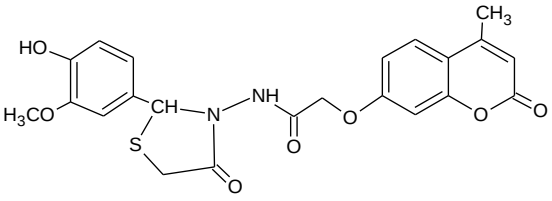

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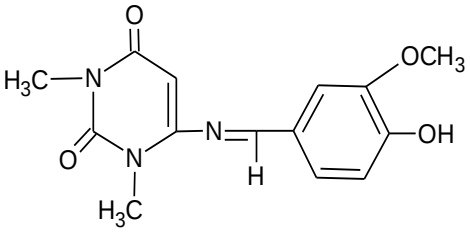


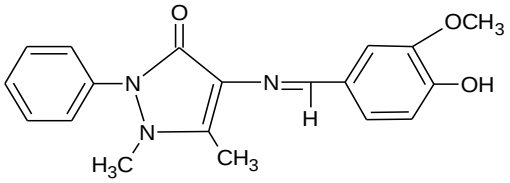
29

24 and **25** have been reported to have influence on pig cartilage. The Schiff base of vanillin and 2-aminopyridine and its metal complexes with Co^{+2}, Ni^{+2}, Cu^{+2}, Th^{+4} and U^{+6} have been reported. This Schiff base acts as a monodentate ligand bonding through nitrogen of pyridine group. The Schiff base of vanillin and coumarinyl **28** is reported to have antibacterial property.

The Schiff bases of 4-aminoantipyrine[42] **30** and sulphanilamide[45] **31** have been reported for their corrosion prevention properties. The Schiff base **30** is also reported for their acoustical properties[43] in different solvents.

V. VANILLIN SCHIFF BASES USED IN THERAPY

Schiff base **30** and **31** are reported for the corrosion prevention on mild steel under 2M HCl.



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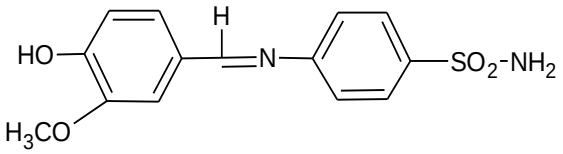

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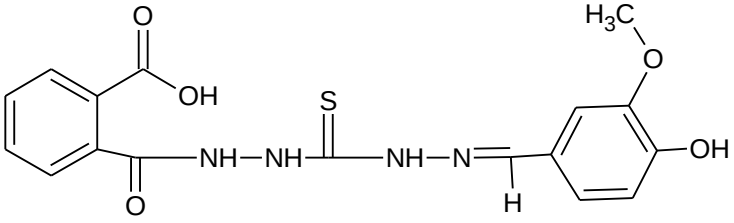

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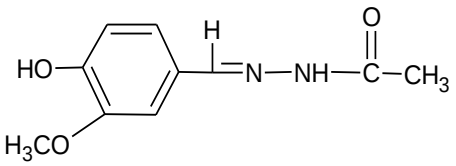
Schiff base compound of vanillin and phthaloyl thio carbohydrazide[44] is reported **32** to have corrosion prevention on mild steel in acid solution.

The Schiff base with vanillin and several hydrazides[46-55] such as acetohydrazide **33**, thio semi carbazone **34**, hydrazide containing coumarin moiety **35**, benzohydrazide **36**, phthaloyl carbohydrazide, acetic acid hydrazide, etc **37-42** have been reported.



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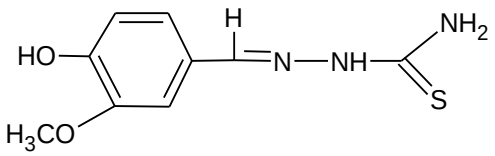

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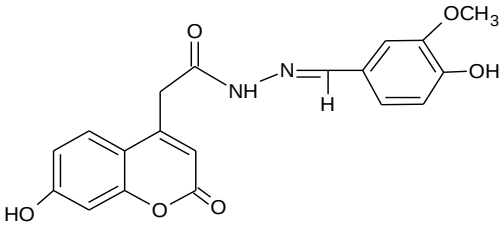

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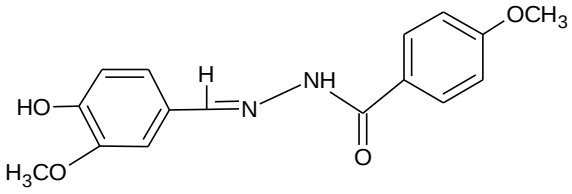

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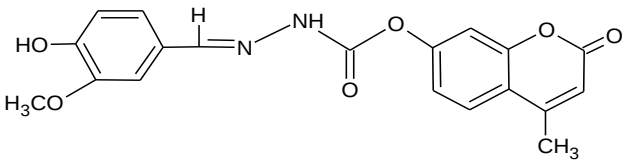

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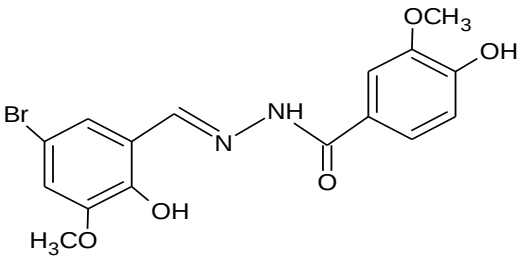

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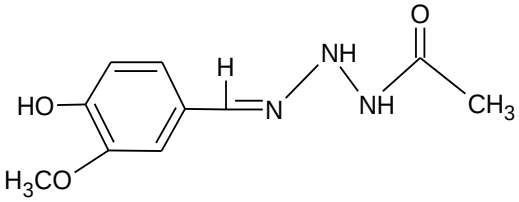

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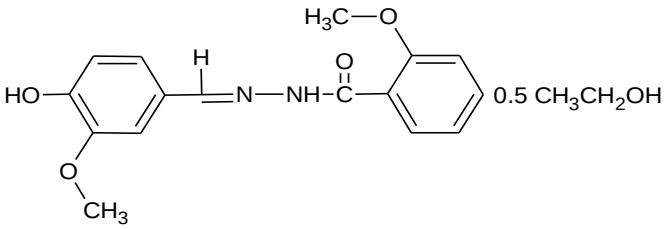

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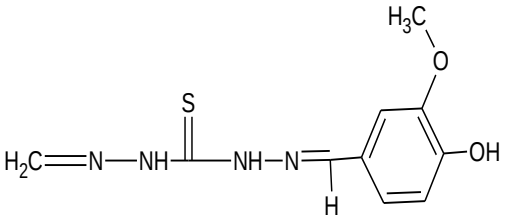

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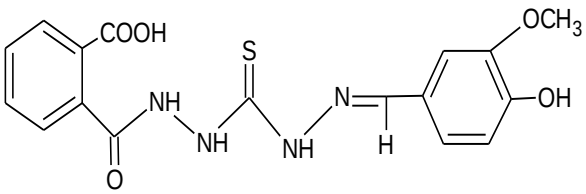

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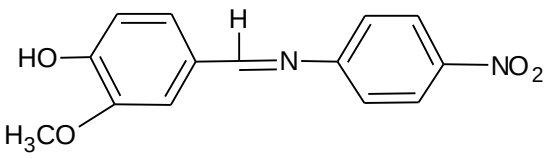
Schiff base of vanillin with photosensitivity **43** to **47** have been reported[56-58].



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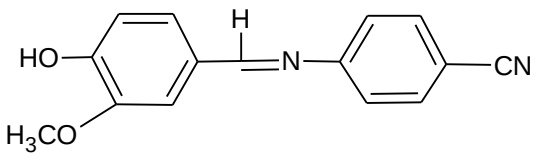

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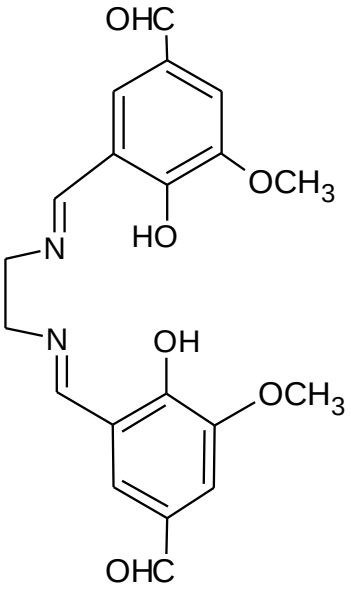

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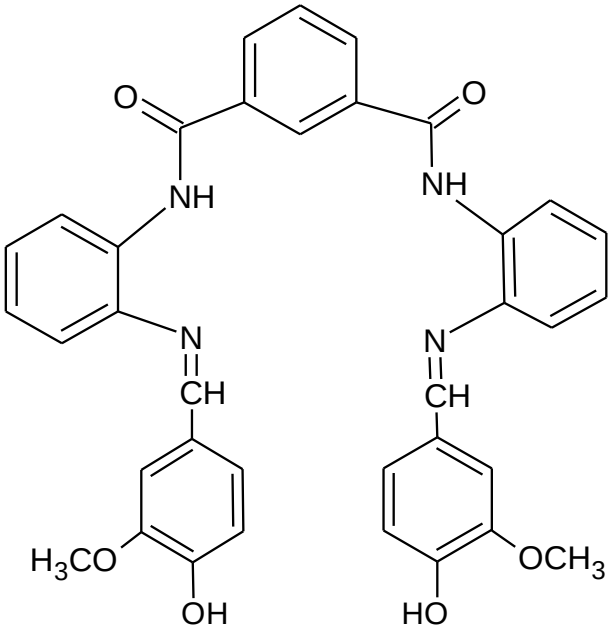

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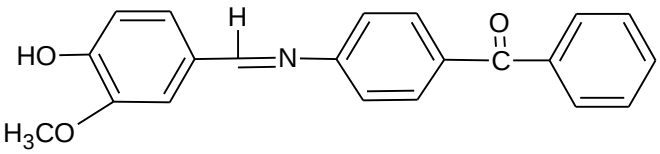
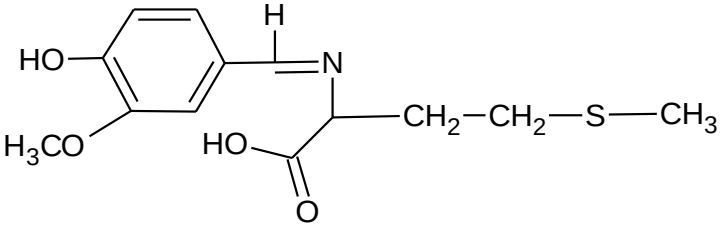


47

Vanillin Schiff bases used in therapy[59-62] have been reported. One of the important compounds is vanillin cross-linked chitosan microspheres for the controlled release of resveratrol.



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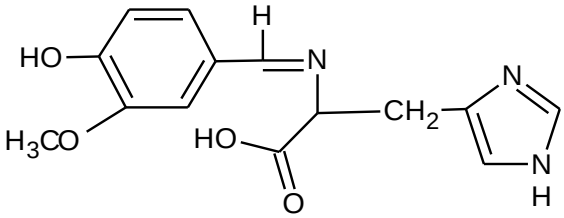


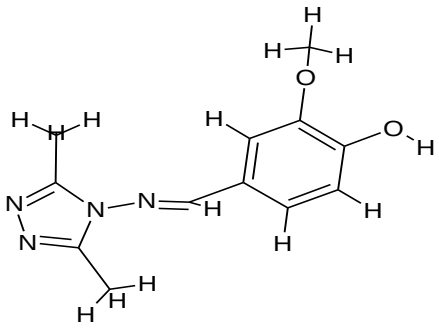
49

The rumen protected essential aminoacids **48, 49** have been reported is used in medicine and is patented. The interaction of tryptophan, vanillin Schiff base have been reported and is studied for its interaction with herring.

VI. VANILLIN SCHIFF BASES AS CATALYST

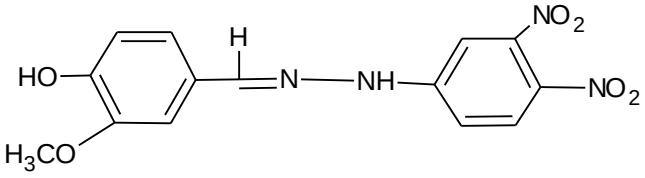
Vanillin Schiff bases are also reported to act as catalysts[63-64]. The 2-hydroxy-3-methoxy benzaliminopropyl immobilized on aerosol as catalysts on ozone decomposition is reported.

The catalytic activity of 4-hydroxy-3-methoxy benzaldehyde Schiff bases and complexes has been reported **50**.



50

Ion selective electrode[65] based on vanillin-diethylene triamine- Nickel (II) metallic complex as a neutral carrier have been reported to be very efficient to ion identification. **51-55** have been reported for their complex with Cr (III) ions[66]. Schiff base of Calix [4] resorcinorene **56** is reported[67].



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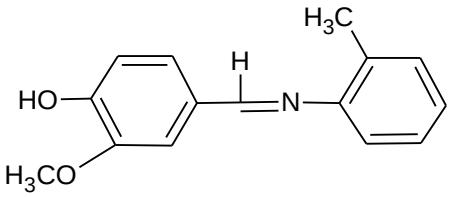

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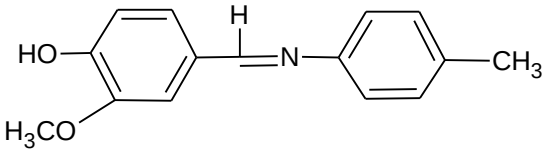

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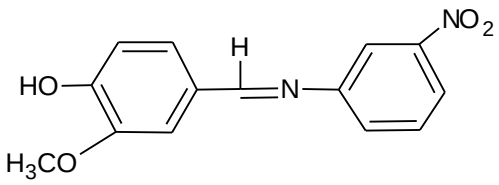

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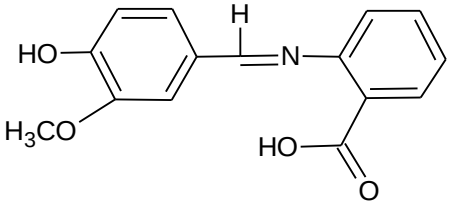

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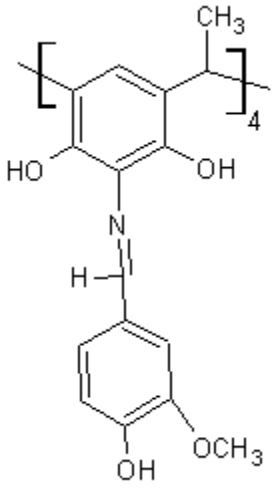
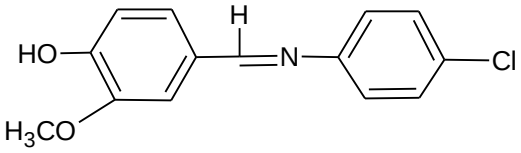


56

The Schiff base from vanillin and aromatic amines **57-62** has been reported[68].



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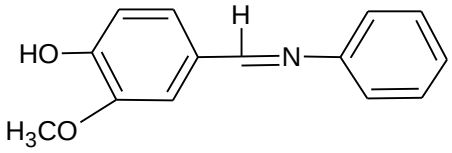

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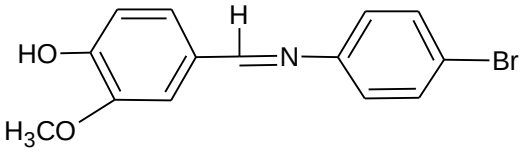

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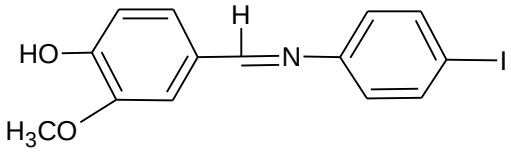

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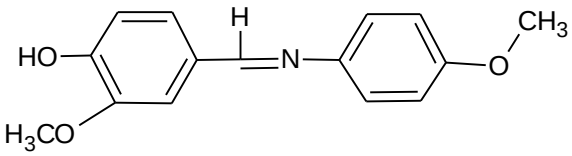

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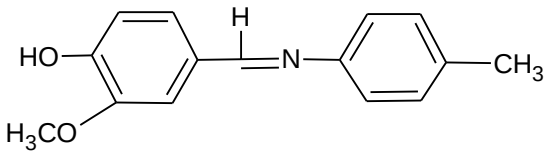
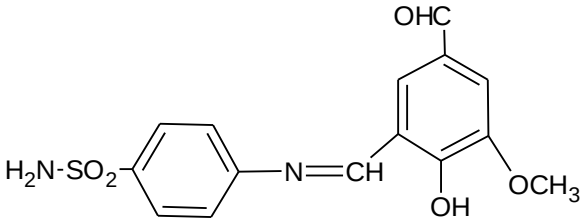


62

The synthesis and characterization of some new complexes of Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) with mixed ligands donor ligands **63** have been reported[69].



63

VII. CONCLUDING REMARKS

Schiff bases of vanillin have been explored for various applications in microbial activity, antifungal, antibacterial, anti corrosive properties. The research in this area is incipient and of much clinical interest. Schiff base compounds have shown promising leads for the design of more efficient Schiff bases. The avenues are open in the areas of water purification and drug release in medicine.

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