

# Design, Synthesis, Characterization and Biological Evaluation of Cu(II), Pd(II) Complexes with Novel Schiff Base Ligand Derived from 3-Amino Coumarin

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## ABSTRACT

Coumarins(-oxo-2H-chromene) belong to the family of lactones containing benzopyrone skeletal framework that are isolated from plant as well as total synthesis in the laboratory. Furthermore, the pharmacological and biochemical properties as well as therapeutic applications of coumarins depend up on the pattern of substitution. In view of this coumarins have attracted intense interest in recent years because of their pharmacological properties, Hence coumarins have been reported to possess, among others, anticonvulsants, anti-inflammatory, antioxidants, analgesic, anticoagulants, anti-tumor, antiviral activities. The novel Schiff base ligand (FYMAC) synthesized by the condensation of furfuraldehyde and 3-aminocoumarin. The nature bonding and geometry of the transition metal complexes as well as ligand have been deduced from elemental analysis, mass, NMR, IR, ESR & thermal analysis. The complexes are found to have ML<sub>4</sub> based on elemental, conductance and spectral studies octahedral (Cu), square planar (Pd) geometry was assigned for these complexes. The ligand as tetradentate and co-ordinate through N-atom of azo methine group, O-atom of keto group of 3-aminocoumarin.

**Keywords:** Schiff base; 3-aminocoumarin; Metal complexes.

## INTRODUCTION

Around the world much work was already reported in the literature in the field of Schiff base metal complexes and their biological activity. But we found fewer reports in the field of novel Schiff bases derived from 3-aminocoumarin and their metal complexes. Coumarin & 3-aminocoumarin are biologically active moieties. Hence we synthesized Schiff bases of coumarins and utilized them as ligands for the synthesis of metal complexes. Furthermore we compared the biological activity of Schiff base ligands with that of their corresponding metal complexes. Around the world, much research has been occurring in the field of synthesis of metal complexes.

Amino coumarins which contain an amino group bonded to the benzene nucleus are widely investigated, where as those containing amino group in  $\alpha$ -pyrone ring have received great attention in recent years. From the group of amino coumarins, 3-amino coumarin and its derivatives are not well studied. The 3-aminocoumarin moiety can be recognized in the molecular structure of several natural antibiotics, such as novobiocin, chlorobiocin, coumermycin, etc. These antibiotics and their derivatives are in the research focus [1]. First synthesis of 3-amino coumarin was reported by Linch in 1912. He tried two possible ways of preparing 3-amino coumarin. One of the method, based on Perkin reaction involved condensation of salicylaldehyde with glycine [2]. The maximum yield of 3-acetyl amino coumarin in this method was only 25-30%. Hence, the method was considered to be unsatisfactory. An alternate method

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involved the condensation of 3-acetyl coumarin with hydroxyl amine hydrochloride. The oxime of this compound when treated with phosphorus trichloride and phosphorous pentachloride underwent Beckmann rearrangement to give 3-acetylamino coumarin in about 75% yield. The subsequent acid catalyzed hydrolysis of 3-acetylamino coumarin gave 3-aminocoumarin in 65% yield.

The Schiff base ligands are one of the most widely used ligands due to the ease of formation and remarkable versatility. They have played an important role in the development of coordination chemistry as they readily form stable complexes with most of the transition metals. The research field dealing with Schiff base metal complexes is very broad due to their potential interest for a number of interdisciplinary areas that include bioinorganic chemistry and catalysis [3-8].

In the area of bioinorganic chemistry the interest in the Schiff base complexes lies in that they provide synthetic models for the metal-containing sites in metalloproteins and enzymes. Also, chiral Schiff base complexes have been found to be efficient catalysts for some organic reactions. Schiff base complexes have also been used as models for the activation of small molecules. Many of them are centered on the catalytic activity of Schiff base complexes in a large number of homogeneous and heterogeneous reactions.

## MATERIALS AND METHODS

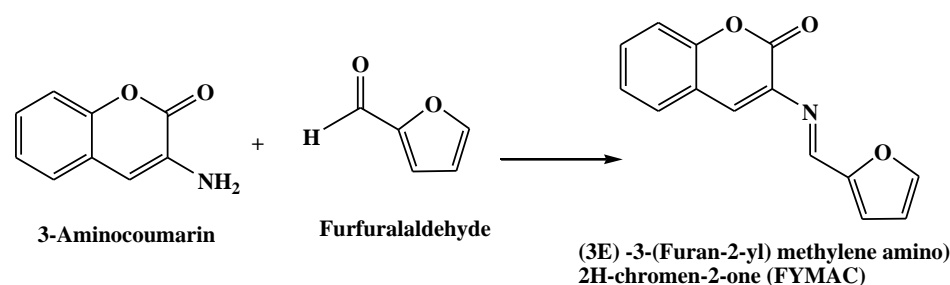
### Reagents and materials:

Salicylaldehyde, glycine, sodiumacetate, methanol, acetic acid and furfuraldehyde and Cu(II),Pd(II)metal salts.

### Synthesis of Schiff base ligand (3E) -3-(furan-2-yl) methylene amino)2H-chromen-2-one (FYMAC)

Amino coumarin (0.0375 mol) is dissolved in methanol (10mL), to this furfuraldehyde (0.0375 mol) dissolved in methanol (10mL) was added drop wise with constant stirring. Then the reaction mixture was refluxed for about 4 hrs on a hot plate stirrer. A dark brown color solid separated out. It was re-crystallized from hot methanol. The product was found to be TLC pure in 3:7 ethyl acetate and n-hexane mixture.

The ligand FYMAC was synthesized by treating 3-amino coumarin with furfuraldehyde in 1:1 ratio. The synthesis of FYMAC



### Synthesis of Schiff base Cu(II) and Pd(II) Complexes

A general preparation method was used for the synthesis of all the above complexes of new Schiff base ligand i.e. the ligand and corresponding metal salts 1:1 ratio was taken by using methanol solvent refluxed until solid separates out to get solid 4-6 hrs time was taken and recrystallized by the use of different solvents.

## CHARACTERIZATION

### Characterization Schiff base ligands:

The ligands was characterized by elemental, Mass, ald

#### a) *Elemental analysis:*

The percentage of carbon, hydrogen, nitrogen and oxygen of all these ligands were experimentally determined by using CHN analyzer. The physical and analytical data

#### b) *Mass spectral analysis:*

The mass spectra of ligand FYMAC showed the molecular ion peaks at  $m/z$  239(24%) respectively. This data is in good agreement with the respective molecular formulae of FYMAC .

#### c) *Infrared spectral analysis:*

A strong intensity band is appeared in the IR spectra of Schiff base ligands in the range of 1603-1618  $\text{cm}^{-1}$  which is attributed to  $\nu_{\text{C}=\text{N}}$  [9]. This provides a strong evidence for the condensation of carbonyl compound with the  $-\text{NH}_2$  group of 3-amino coumarin. The ligands show a signal around 1705-1721  $\text{cm}^{-1}$  corresponding to  $\nu_{\text{C}=\text{O}}$  of coumarin moiety [10]. The IR spectra of the HPEAC and DPEAC ligands which contains phenolic-OH shown a broad band in the range of 3427-3432  $\text{cm}^{-1}$  corresponding to  $\nu_{\text{OH}}$  vibrations and a high intensity band in the region 1290-1300  $\text{cm}^{-1}$  was assigned to phenolic  $\text{m}(\text{C}-\text{O})$  vibration [11]. For the ligand CBAC the medium intensity band at 1090  $\text{cm}^{-1}$  is assigned to  $\text{m}(\text{C}-\text{Cl})$  of the benzene ring. Aromatic ring stretching frequencies are observed for all the ligands in the range of 1360-1497  $\text{cm}^{-1}$  and wagging frequencies are observed in the range of 3007-3081  $\text{cm}^{-1}$  [12-13].

#### d) *$^1\text{H}$ NMR spectral analysis:*

In the  $^1\text{H}$  NMR spectra of Schiff base ligands, the integral intensities of each signal are found to agree with the number of different types of protons present. In the spectra of ligand FYMAC a singlet signal was appeared for  $\text{CH}=\text{N}$  protons in the range of 9.15-8.35 ppm [14]. This supports the formation of a Schiff base by the condensation of carbonyl compound with 3-aminocoumarin which is also supported by the disappearance of peak around 9.98 ppm coehydric protons and 4.33 ppm corresponding to amine protons in 3-amino coumarin .

#### e) *$^{13}\text{C}$ NMR spectral analysis:*

$^{13}\text{C}$  NMR spectra of all the ligands contain a signal in the range of 163.8-164.8 ppm indicating the presence of carbon which is doubly bonded to nitrogen [8,15]. The spectra of all ligands contain signals in the range of 131.5-133.7 & 140.6-146.5 ppm indicating the presence of lactonyl carbon and ketonic carbon of lactonyl ring was appeared in the range of 158.6-162.8 ppm.

## Characterization of Cu(II),Pd(II) complexes

### a) **Physical and analytical data:**

Six new hexa-coordinated Schiff base Cu(II) (Pd)compounds have been prepared by treating metal salts with six ligands separately. The percentages of carbon, hydrogen and nitrogen were determined experimentally using CHN analyzer. The percentage of copper in these Schiff base Cu(II),(Pd) compounds was determined by literature method. The analytical data is good agreement with the proposed molecular formulae.

### b) **Mass spectral analysis:**

The Schiff base Cu(II) compounds contains molecular ion peaks at  $m/z$  ( $M^+$ ) 610. The Schiff base Pd(II) complexes contains molecular ion peaks at  $m/z$  ( $M^+$ ) 654 these value are in good agreement with the respective weights of the Schiff base Cu(II), Pd(II) complexes calculated on the basis proposed molecular formulae.

**c) Thermal analysis:**

The thermogravimetric analysis data of the Cu(II),Pd(II) complexes is obtained using less than 10 mg of the compound. The TG-DTG and DSC curves of both complexes of FYMAC is given in **fig**. The thermograms of all the Cu(II),Pd(II) complexes show two important clear stages of decomposition, the first corresponding to decomposition of the complex with the loss of organic moiety and second due to formation of metal oxide.

The thermograms of all Cu(II),(Pd(II) complexes have not shown any initial weight loss in the temperature range of 70-125 °C, also the DSC curve of these complexes have not shown any endothermic peak in the above temperature range further giving evidence for the absence of lattice water molecules. In addition, the thermograms of all the Cu(II),(Pd(II) complexes have not exhibited any weight loss in the temperature range of 150-200°C further, the DSC curve of the complexes have not shown any endothermic peak in the above temperature range further giving evidence for the absence of coordinated water molecules. All these complexes showed first decomposition curve at around 300 °C corresponding to loss of organic moiety. This is further evidenced by the DSC curve, which show exothermic peak around this temperature range. The final products of decomposition in all the complexes above 500 °C correspond to metal oxide [16].

**d) Infrared spectral analysis:**

The IR spectra of Schiff base Cu(II),Pd(II) complexes was studied by comparing with the IR spectra of free ligands to know the binding modes of metal and ligand. In the IR spectra of the Schiff base ligands, a high intensity  $\nu_{C=N}$  band was observed in the range of 1603-1618  $\text{cm}^{-1}$ . This band is shifted towards lower side about 1570-1592  $\text{cm}^{-1}$  in Schiff base complexes. This downward shift shows the coordination of azomethine Nitrogen to the central metal ion. This fact is further supported by the appearance of a medium intensity band in the region of 480–525  $\text{cm}^{-1}$  assignable to  $\nu_{Cu-N}$  vibration.

In the spectra of ligands the  $\nu_{C=O}$  band of coumarin is observed at 1721-1705  $\text{cm}^{-1}$ . This was shifted to downwards and observed at 1691-1712  $\text{cm}^{-1}$ . This clearly indicates the coordination of lactonyl oxygen to Cu (II) ion.

**e) Magnetic properties:**

The magnetic moment values of Cu(II) complexes at room temperature lie in the range of 1.90-1.98 B.M [17] corresponding to one unpaired electron. The magnetic moment data of the Cu(II) complexes confirming octahedral geometry around the metal ion.

The magnetic susceptibility measurements have been carried out for Schiff base Pd(II) complexes and these compounds were found to be diamagnetic and hence Pd(II) ion is in low spin configuration. The diamagnetic nature of complexes was further confirmed by the sharp well defined signals in the  $^1\text{H}$  NMR spectra.

**f) Conductance measurements:**

The molar conductance values for the Schiff base Cu(II) complexes ( $10^{-3}\text{M}$ ) are determined in dichloromethane. These values are found to be low (13.1-19.3  $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ ) indicating non-electrolytic nature of the complex and also indicating that ligand is placed in coordination sphere.

The molar conductance values for the Schiff base Pd(II) compounds ( $10^{-3}\text{M}$ ) were determined in dimethyl formamide. These values were found between 54.5-62.5  $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$  indicating 1:2 electrolytic nature of complex. The electrolytic nature of these compounds is due to the presence of two chloride ions outside the coordination sphere.

**g) Electronic spectral analysis:**

The electronic spectra of the Cu(II),Pd(II) complexes were recorded in DMF. The Cu(II) complex showed an intensive band at about 732-685 nm and a broad band around 474-406 nm are due to d-d transitions, which are assigned to  $^2A_{1g} \leftarrow ^2B_{1g}$  transition and  $^2E_g \leftarrow ^2T_{2g}$  suggesting tetragonal geometry (distorted octahedral geometry). The observed magnetic moment values for Cu(II) complexes are in the range of 1.81-1.79 BM, which is slightly higher than the spin only value of 1.73 BM expected for one unpaired electron, which offers possibility of an octahedral geometry [18-19].

The Pd(II) complexes shown a broad d-d transition band in the region of 486-461 nm assignable to  ${}^1B_{1g} \leftarrow {}^1A_{1g}$  transition confirming the square planar geometry. Further a relatively strong charge transfer band has been observed in the spectra of all the Pd(II) complexes in the range of 320-293 nm. From the electronic spectral data and the diamagnetic behavior of the complexes the square planar geometry has been proposed to all the Pd(II) complexes.

#### **h) ESR Analysis:**

The ESR spectra of Cu(II) complexes in solid state at room temperature and liquid nitrogen temperature have been recorded and the bonding parameters are calculated using approximations of Kneubuhl. The spectra of all the Cu(II) complexes contain two clear peaks at room temperature. One of the two peaks is an intense absorption peak at high field and other a less intense peak at low field. The  $g_{||}$ ,  $g_{\perp}$ ,  $g_{avg}$ , and  $G$  is calculated for the two peaks as described in literature[.20]

The  $g_{||}$  and  $g_{\perp}$  values calculated are useful in distinguishing the coordination environment around the Cu(II) ion. As an example the tetragonal distortions in octahedral geometry can occur either by compression or by elongation. In the case of  $g_{\perp} > g_{||}$  distortions occur by compression and in the case of  $g_{||} > g_{\perp}$  by elongation[21-22]. In the all complexes  $g_{||} > g_{\perp}$  indicate elongated tetragonal distortion in the octahedral geometry.

According to Kivelson and Neiman [23] the  $g_{||}$  is a moderately sensitive function for indicating covalency of metal ligand bonds in the complexes. The  $g_{2.3} > g_{||}$  normally indicates ionic environment round the metal ion while  $g_{2.3} < g_{||}$  indicates covalent environment. It can be noticed from the table that the  $g_{||}$  values for all the five complexes are less than 2.3 indicating covalent nature. The trend  $g_{||} > g_{\perp} > 2.0023$  observed for all the complexes indicate that the unpaired electron is most likely in the  $d_{x^2-y^2}$  orbital of Cu(II) ion [24]

The  $g$  values obtained by Kneubuhl's approximations [25] are subjected to inaccuracy to the extent that they ignore the effect of the hyperfine coupling constants. In conformity with this the  $g$  values of the complexes are fairly consistent. The  $g_{||}$  values are from 2.196-2.225 while  $g_{\perp}$  values are from 2.036-2.085.

As observed by Procter et al,  $G$  value indicates whether the metal ion is in crystallographically equivalent environment or not. They observed that complexes with  $G$  values  $>4$  have their Cu(II) ion in crystallographically equivalent environment while the complexes with  $G$  value  $<4$  has the Cu(II) ion in the non-equivalent crystallographic sites. The  $G$  value of FYMAC complexes calculated from the given expression has been found to be  $>4$ . On the basis of the above two investigations it can be said that, in these complexes, crystallographic equivalent environment exists.

#### **i) ${}^1H$ NMR spectral analysis:**

The  ${}^1H$  NMR spectra of free ligands and Schiff base Pd(II) complexes were recorded to confirm the binding nature of Schiff base ligands to Pd(II) ion. The integral intensities of each signal in the  ${}^1H$  NMR spectra of the ligands and the corresponding Schiff base Pd(II) complexes were found to agree with the number of different types of protons present. In all the ligands signals CH=N protons were appeared in the range of 9.15-8.35 ppm [26]. However, in the spectra of Schiff base Pd(II) complexes, these signals are observed in the regions of 9.72-9.14 ppm confirming the coordination of nitrogen atom of this group to Pd(II) ion [27]

In the spectra of Schiff base Pd (II) complex of HPEAC, DPEAC ligands, signal at 9.96-9.65 ppm was appeared corresponding to OH proton. This peak was completely disappeared in the corresponding Pd (II) complex, showing that the deprotonation of OH group and eventually, the coordination of phenolic oxygen to central metal ion.

The peak position of  $CH_3$  protons remains the same in complexes as well as in ligands and appeared at 3.10 ppm. There is no appreciable change in the peak positions corresponding to olefinic and aromatic protons.

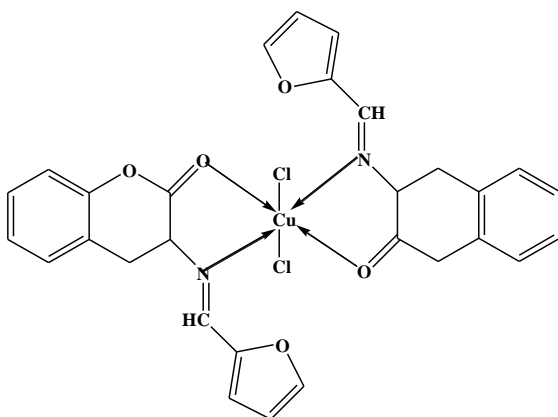
#### **j) ${}^{13}C$ NMR spectral analysis:**

${}^{13}C$  NMR signals for the Schiff base Pd(II) complexes are assigned by the comparison with the spectra of corresponding Schiff base ligands and the chemical shifts in  ${}^{13}C$  NMR spectra revealed a consistent pattern[28]. The spectra of  ${}^{13}C$  NMR signals for the Schiff base Pd(II) complexes are assigned by the comparison with the spectra of corresponding Schiff base ligands and the chemical shifts in  ${}^{13}C$  NMR spectra revealed a consistent pattern. The spectra of all the ligands contain signals in the range of 163.8-164.8 ppm due to the presence of carbon which is doubly bonded to nitrogen. However, in the spectra of Schiff base Pd(II) complexes, a down field shift in peak position is

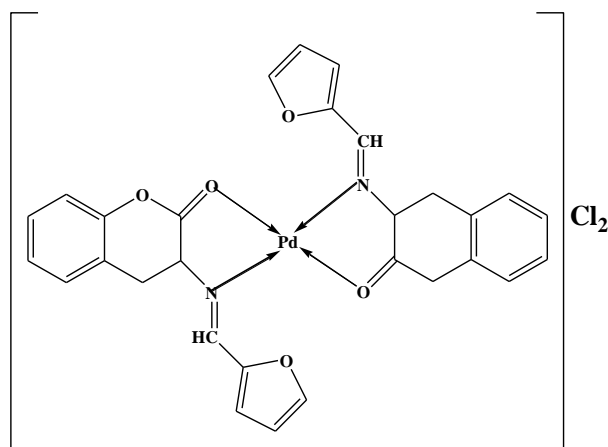
observed in the range of 172.6-178.1 ppm . This fact confirms that all the ligands coordinate through the nitrogen atoms.

The spectra of all ligands contain two peaks in the range of 131.5-133.7 ppm and 140.6-146.5 corresponding to the lactonyl carbon, in the case corresponding complexes these peaks were shifted to slightly downfield.

Appreciable changes in peak positions were not observed with respect to aryl carbons and carbons adjacent to oxygen



4.5 [Cu(FYMAC)<sub>2</sub>Cl<sub>2</sub>]



6.5 [Pd(FYMAC)<sub>2</sub>Cl<sub>2</sub>]

## ANTIMICROBIAL ACTIVITY

*Preliminary antibacterial screening of new Schiff base ligands against four different bacteria:*

**Zones of inhibitions of ligands against four different bacteria.**

|      | Ligands      | Conc.<br>( $\mu\text{g/ml}$ ) | Zone of inhibition (mm) |              |              |              |
|------|--------------|-------------------------------|-------------------------|--------------|--------------|--------------|
|      |              |                               | MTCC-<br>619            | MTCC -<br>96 | MTCC-<br>722 | MTCC-<br>109 |
| STD. | Streptomycin | 40 units                      | 15                      | 13           | 20           | 20           |
| 5.   | FYMAC        | 1000                          | 15                      | 14           | 15           | 12           |

The investigated compounds were categorized into four classes according to their anti bacterial activity (zone of inhibition) and the number of bacteria. Class-I: Active on all four strains, Class-II: Active on three strains, Class-III: Active on two strains and Class-IV: Active for one strain. From the preliminary screening of ligands, about two compounds viz. OCYMB and FYMAC were found to be active against the four different bacteria and are designated as class-I. The compounds HPEAC and DPEAC were active against three strains of bacteria and designated as class-II. Only one compound CBAC was active against two strains of bacteria and designated as class-III. However no single compound was found in class-IV acting on one strain. FYMAC is found to have good activity based on the extent of zone of inhibition.

*Preliminary antibacterial screening of Cu(II) complexes against four different bacteria:*

*Zones of inhibitions of Cu(II) complexes against four different bacteria.*

| Cu (II) complexes<br>(1000 µg/ml)          | Zone of inhibition (mm) |          |          |          |
|--|-------------------------|----------|----------|----------|
|  | MTCC-619                | MTCC -96 | MTCC-722 | MTCC-109 |
| [Cu (FYMAC) <sub>2</sub> Cl <sub>2</sub> ] | 18                      | 18       | 19       | 16       |

From the preliminary screening, the Cu(II) complexes were found to be active against four different strains of bacteria

*Preliminary antibacterial screening of Pd(II) complexes against four different bacteria:*

*Zones of inhibitions of Pd (II) complexes against four different bacteria.*

| Pd(II) complexes<br>(1000 µg/ml)          | Zone of inhibition (mm) |          |          |          |
|---|-------------------------|----------|----------|----------|
|   | MTCC-619                | MTCC -96 | MTCC-722 | MTCC-109 |
| [Pd(FYMAC) <sub>2</sub> Cl <sub>2</sub> ] | 18                      | 18       | 19       | 17       |

From the preliminary screening, the Pd (II) complexes were found to be active against four different strains of bacteria

*Antibacterial activity of the active Schiff bases at different dilutions against four different bacteria:*

From the preliminary screening of the five ligands, only two ligands were found to be very active against all four strains of bacteria. These two compounds were further tested at different dilutions. The different concentrations of the active compounds at different levels were used to find out the minimum inhibitory concentration (MIC) by agar diffusion method.

**Zones of inhibitions of FYMAC against four different bacteria at different dilutions.**

| S. No | Conc.<br>(µg/ml) | Zone of inhibition (mm) |          |          |          |
|-------|------------------|-------------------------|----------|----------|----------|
|       |                  | MTCC-619                | MTCC -96 | MTCC-722 | MTCC-109 |
| 1.    | 1000             | 30                      | 31       | 28       | 29       |
| 2.    | 200              | 29                      | 27       | 26       | 26       |
| 3.    | 100              | 24                      | 23       | 25       | 24       |
| 4.    | 20               | 19                      | 20       | 22       | 21       |
| 5.    | 15               | 14                      | 19       | 20       | 18       |
| 6.    | 09               | -                       | 16       | 17       | 15       |
| 7.    | 06               | -                       | -        | 15       | 13       |
| 8.    | 02               | -                       | -        | 14       | -        |
| 9.    | 02               | -                       | -        | 11       | -        |

The MIC of OCYMB against MTCC-619, MTCC-96 and MTCC-109 was observed at 5µg/ml and against MTCC-722 was observed at 1µg/ml. The MIC of FYMAC against MTCC-619 at 15µg/ml, MTCC-96 at 10µg/ml, MTCC-109 at 5µg/ml and MTCC-722 at 1µg/ml were observed respectively.

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