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A Novel Spot Test for Detection and Identification of Neonicotinoid Insecticide Imidacloprid and Possible Antidote for Imidacloprid Poisoning

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ABSTRACT

A novel chromogenic reagent and colorimetric test is reported for highly specific and sensitive detection and identification of neonicotinoid insecticide Imidacloprid (N-[1-[(6-chloropyridin-3-yl)methyl]-4,5-dihydroimidazol-2-yl]nitramide). Imidacloprid reacts with ferrous (Fe^{2+}) ions in alkaline medium to form a very intense deep pink colour. Conversely alkaline solution of Imidacloprid can be used as colorimetric reagent for detection and identification of biologically important ferrous ions. The probable use of ferrous ions as an antidote for imidacloprid poisoning cases is also discussed.

Graphical Abstract

Spot tile showing reaction product of Imidacloprid, ferrous sulphate and sodium hydroxide with each other. (A) and (D)-First imidacloprid, then NaOH and then ferrous sulphate. (B)-First Imidacloprid and then ferrous sulphate (but no sodium hydroxide), (C)-First ferrous sulphate and then NaOH (but no imidacloprid), (E)-imidacloprid and then NaOH (but no ferrous sulphate)

Keywords: Imidacloprid, Spot test for Imidacloprid, Ferrous ions, Coordination chemistry, Nitramide functional group, organic analytical reagent

INTRODUCTION

The neonicotinoid insecticide imidacloprid is used as insecticide for crops like cotton, rice, chilli, sugarcane, mango, sunflower etc. It is highly effective insecticide for crops but it has also been a cause of many suicidal and accidental poisoning cases in India, especially in cases of farmer suicides. The large number of farmer suicide cases received in Forensic Science Laboratory was concluded to be associated with imidacloprid poisoning. Very few reported methods are available for detection of this pesticide and none of them is specific to Imidacloprid. The previously reported method of p-dimethylamino benzaldehyde [**1**] is extremely unspecific as many other compounds like amines [**2**], hydrazines [**3**]; active methylene compounds [**1**] reacts with reagent.

The cobalt thiocyanate reagent [**4**] reacts with many organic nitrogen bases [**5**] and also with cocaine [**6**] and glyphosate [**7**]. Dragendorff's reagent also reacts with many tertiary amines and quaternary ammonium compounds [**8**]. Thus, a specific reagent was necessary for detection of imidacloprid. The present work represents a novel, highly sensitive and specific colorimetric reagent for instant detection and identification of insecticide imidacloprid. The work also discusses few cross-platform applications of the novel reaction.

MATERIALS AND METHODS

Reagents and chemicals: Imidacloprid commercial formulation with brand name Confidor, manufactured by Bayer, containing 17.8 % imidacloprid w/w, sodium or potassium hydroxide, and ferrous sulphate (reagent grade).

Experimental: A drop of commercial formulation of imidacloprid was taken in spot tile in depression labelled as (A). Few drops of 2N sodium hydroxide were added to it and then few crystals of ferrous sulphate were added to same depression. The deep pink colour developed instantly. To check the reproducibility of the reaction same test was repeated in depression labelled as (D). Similar results were obtained. To check the blank reaction, few drops of sodium hydroxide were added to depression labelled as (C) and then few crystals of ferrous sulphate were added. The reagent blank gave greenish mass which was due to formation of $Fe(OH)_2$. The reagent blank has completely different colour than the end product of spot test (deep pink). So blank have negligible interference in the test. To check whether, alkaline condition is necessary for the reaction the Pesticide sample was taken in depression labelled (B).

Few crystals of ferrous sulphate were added to it but sodium hydroxide was not added. The mixture didn't show any colour reaction which means alkaline condition is a vital requirement for this reaction. To check whether Imidacloprid really forms a complex with ferrous and to rule out the possibility of hydrolysis product of Imidacloprid (hypothetical) forms any coloured compound, pesticide sample was again taken in depression labelled (E) and few drops of sodium hydroxide were added to it. No coloured product was observed. All these observations clearly mean that there must be formation of a coordination complex between imidacloprid and ferrous ions only in the presence of strong alkali like sodium or potassium hydroxide.

RESULTS AND DISCUSSION

The pesticide forms a very intense deep pink colour with ferrous ions in alkaline medium probably due to formation of a charge-transfer complex, which emits in visible region (Figure 1).

The probable reaction mechanism indicates formation of charge transfer complex as shown below. The mechanism indicates formation of 2:1 complex in between pesticide and ferrous ion. The complex is formed only in alkaline medium. The stability of complex may be due to stable ring structure formed by coordination (Figure 2).

Figure 1. Spot tile showing reaction product of Imidacloprid,ferrous sulphate and sodium hydroxide with each other. (A) and (D)-First imidacloprid, then NaOH and then ferrous sulphate. (B)-First imidacloprid and then ferrous sulphate (but no sodium hydroxide), (C)-First ferrous sulphate and then NaOH (but no imidacloprid), (E)-Imidacloprid and then NaOH (but no ferrous sulphate).

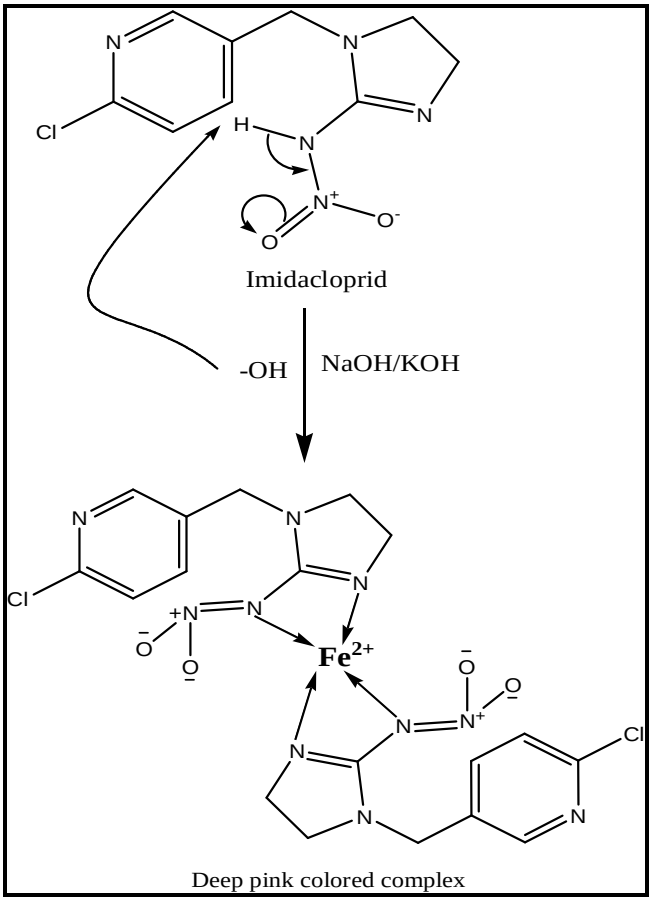

Figure 2. Probable mechanism of reaction between imidacloprid, alkali and ferrous sulphate.

Other tested pesticides including organophosphate, organochloro, and pyrethroids didn't show any colour indicating clearly the specificity of the reagent. The colour reaction is not very sensitive to reagent concentration and small changes in concentration of alkali or ferrous ions did not affect the results to any considerable extent. The reaction product is stable for many hours. We found that only ferrous ions can give this colour test. Other tested cations like Cu^{2+}, Pb^{2+}, Ni^{2+}, Sn^{2+}, Zn^{2+} and even Fe^{3+} also didn't give this colour reaction.

APPLICATION

Detection and identification of imidacloprid: The novel colour reaction can be used to detect Imidacloprid from commercial formulations and complex matrices like viscera. The reaction is highly sensitive with approximate lower detection limit of 50 μg. The reported method is very simple to follow and the reagents used are very cheap and easily available in every laboratory as basic table reagents. The current method is the only specific colorimetric method available for detection of Imidacloprid, to the best of our knowledge.

Organic analytical reagent for detection of ferrous ions: Among tested cations, as only Fe^{2+} ions show this colour reaction giving deep pink colour, the imidacloprid pesticide can also be used as "organic analytical reagent" [**9**] in coordination chemistry for detection of ferrous ions. Further, it will be interesting thing for an Inorganic chemist to develop another organic analytical reagent for ferrous ions which will have similar structure where ferrous ions bind but will not act as harmful insecticide (will not block nicotinic acetylcholine receptors). Similarly ferric ions can be reduced to ferrous ions and can be detected indirectly. The novel binding pattern of the nitramide functional group can also lead to research which can be useful in coordination chemistry. Literature review reveals that this functional group has not been given much attention in coordination chemistry yet.

Antidote for imidacloprid poisoning: As the binding of ferrous ion to imidacloprid is a novel finding and thus a solution of ferrous ions can be used as "antidote" in imidacloprid poisoning cases provided the complex formed itself is not toxic. As ferrous ions are important biologically, the effect of imidacloprid poisoning on Fe^{2+} ions metabolism should give new insights to predict its toxico-kinetics. If the complex doesn't prove to be toxic, the imidacloprid pesticide can be replaced by its ferrous complex to use as pesticide which itself is not-toxic and can break down to imidacloprid in soil which can be made acidic as complex again breaks and is converted to free Imidacloprid in acidic medium. This approach can save many lives which are being destroyed by poisoning with Imidacloprid. This will, at-least partially, may solve an important social problem of farmer suicide.

CONCLUSION

This communication not only reports a novel colorimetric reaction for highly sensitive and specific detection of insecticide Imidacloprid but it also presents and discusses its cross-platform applications in the field of coordination chemistry and Forensic medicine. The new findings are not only useful to Toxicologist but also to Inorganic chemist and medical professionals.

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