

Contact toxicological compatibility of N- (phenyl) -2 hydroxy salicylimide and N- (p-chlorophenyle) -2 hydroxy salicylimide against pulse beetle, *Callosobruchus chinensis* L. (Coleoptera : Bruchidae) on chickpea

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Abstract

The present manuscript covers the insecticidal bioefficacy of some new synthesized amides of salicylic acid viz; N-(phenyl)-2 hydroxy salicylimide, N-(p-tolyl) -2-hydroxy salicylimide, N-(p-chlorophenyl)-2 hydroxysalicylimide, N-(P-methoxy Phenyl)-2 hydroxy salicylimide and N-(p-chlorophenyle) -2 hydroxy salicylimide on seeds of chickpea, *Cicer arietinum* L. var. K- 805 were treated with different concentration (0.06%, 0.12%, 0.25%, 0.50% and 1.00%) levels against the attack of chickpea bruchid *Callosobruchus chinensis* Linn. (Coleoptera : Bruchidae). These compounds are found effective in controlling the insect infestation in chickpea under storage condition. In the present paper we describe the insecticidal activity of these amides against early emerged adults of *C. chinensis* L. of both male and female, respectively. Successful adoption of new synthesized amides of salicylic acid in the protection of food commodities promises an eco-friendly option compatible with international bio-safety regulations. The newly synthesized amides such as $C_{13}H_{11}NO_2 > C_{13}H_{10}NO_2Cl > C_{13}H_{10}NO_2Br > C_{14}H_{13}NO_2 > C_{14}H_{13}NO_3$ insecticidal compound exhibited lethal concentration LC_{50} values in following respective descending as 0.34 > 2.01 > 2.12 > 2.97 3.53, respectively. It was found that the compounds show moderate efficacy against the insect.

Keywords: insecticidal bioefficacy, *Callosobruchus chinensis*, amides of salicylic acid

1. Introduction

The world's total production of chickpeas hovers around 8.5 million metric tons annually and is grown over 10 million hectares of land approximately. Our country is the largest producer of this pulse contributing to around 70% of the world's total production. Chickpea, *Cicer arietinum* (Leguminosae) is fifth most important legume crop in the world it ranks third among the 8.5 million metric tons world's pulse crops after dry bean and dry pea. *Cicer arietinum* is grown in India over 10 million hectares of land approximately [1]. The Desi type chickpea contribute to around 80% and the Kabuli type around 20% of the total production. As per FAO (Food and Agriculture Organisation (FAO) report the pulse production is about 12 million metric tons in 2011 of total world production [2].

Chickpea is a major and cheap source of protein compare to animal protein. Pulses contain 20-30% of protein and some essential amino acids, enrich the soil through Symbiotic nitrogen fixing from atmosphere. The pulse protein is three times higher than that found in cereals [3]. Among the insect pests attacking stored products, pulse beetle, *C. chinensis* is a serious one [4, 5]. Chickpea has been reported to cause serious damage to pulses in India and many countries of the world [6].

As it is evident that *Callosobruchus* spp. cause heavy losses every year and affect the economy of the country, suitable control measures should be taken against them. The pulse seeds suffer a great damage during storage due to insect

attack. Many entomologist reported that pulse beetle, *C. chinensis* a destructive pest of chickpea under storage conditions [7, 8, 9, 10, 11].

In recent year literature survey revealed that Amines in general have been known to be biologically active [12] and the effect of presence of various constituents in the amines increases insecticidal activity, has been investigated [13, 14]. Insects are found in almost all types of environment. The compounds containing amide moiety has also attracted attention due to their important role as insecticides and pesticides to save our Indian crops [15]. In view of the, important behavior of amines and amino acid, the present communication deals with the synthesis, characterization and insecticidal activity of some new amide of salicylic acid against early emerged adults of *C. chinensis* Linn [16].

2. Materials and Methods

Experiments were conducted to test the toxic effect of four amides of salicylic acid in the Bio-pesticide and herbal extract laboratory, Department of Zoology, Entomology, D.B.S. College, Kanpur Affiliated to C.S.J.M University, Kanpur, India.

2.1 Preparation of new organic compounds

In the present investigation four amides of salicylic acid were prepared. The amide was generally prepared by using following method:

Aromatic amine + salicylic acid (in water bath reflux) --- Amides

Equimolar quantities of aromatic amine and salicylic acid are taken in a hard glass tube and heated over oil bath for 6-7 hours. After completion of reaction, product poured in cold water, lumps are formed, then crushed and wash with cold water. Finally, re-crystallized with ethanol-water (V/V) solution. Brownish needle shaped crystal are formed. Which are identified as N-(phenyl)-2-hydroxy salicylimide, N-(p-tolyl)-2-hydroxy salicylimide, N-(p-chlorophenyl)-2-hydroxy salicylimide, N-(p-methoxy phenyl)-2-hydroxy salicylimide and N-(p-bromophenyl)-2-hydroxy salicylimide, respectively. All the compounds were crystalline solid and quite stable at room temperature with good yield (70-75%).

2.2 Rearing of the test insect

Adults of *Callosobruchus chinensis* were drawn from laboratory mass cultures reared in glass jars at temperature $25 \pm 1^\circ\text{C}$ without controlling conditions. Mass culture of *C. chinensis* was maintained using the procedure described by Strong *et al.* (1968). Adults emerged from this culture were used for the bioassay within 48 hrs to 72 hrs of emergence and fed on chickpea (channa).

2.3 Apparatus used for experiment

Small plastic jars (capacity 50 ml) were used for the experiment; there was one set of two jars joined by clear plastic pipe of 1 cm diameter at an angle of 180 degree for each replication. One jar of each set was provided with 10 g of grains given the name 'T' while the other jar was kept empty and given the name 'C'. In jar 'T', the grains treated with extracts were placed, while the jar B remained empty. The jars used for experiment were disinfected with alcohol.

2.4 Experimental Protocol

For testing the contact toxic effect, the chickpea (channa) seeds were used as food. Ten (five male and five female), 24 hours starved early emerged adults treated with different concentrations (0.06%, 0.12%, 0.25%, 0.50% and 1.00%) of four amides of salicylic acid with top spray for two minutes. The treated adults were kept in jar (23cm x 10cm) on moist filter paper. The untreated adults were introduced with emulsified water only. There are three treatment were introduced and each treatment was replicates thrice were maintained. Number of early emerged adults beetle were died were counted where as moribund adults were counted as dead. Observations on the mortality of the early emerged adults beetle were recorded after 24 hours from their release. The early emerged adults beetle, which showed movement, were considered alive, while those, which were in dying state with no visible movement, were taken as moribund. The moribund adults beetle were also included with the dead for calculating the percentage of mortality under each treatment

3. Results

The newly prepared compounds were crystallized after vacuum distillation. The compounds have sharp melting point. The further characterization of these entire compounds was done by elemental analysis, I.R and NMR spectral data

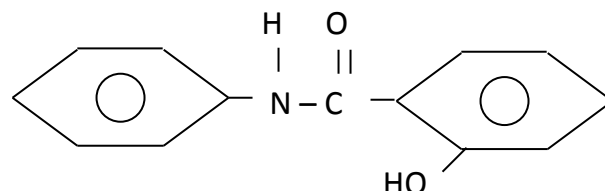
followed by insecticidal activity. as N (phenyl)-2-hydroxy Salicylimide, N-(p-chlorophenyl)-2-hydroxy salicylimide, N-(p-tolyl)-2-hydroxy Salicylimide and N-(p-methoxy phenyl)-2-hydroxy Salicylimide, N-(p-bromophenyl)-2-hydroxy salicylimide, respectively.

The structure of the synthesized compounds are given below:

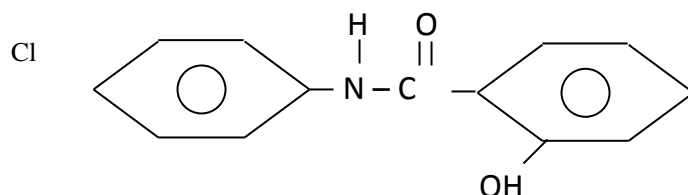
3.1 Structural Formula

The structure of the synthesized compounds are given below:

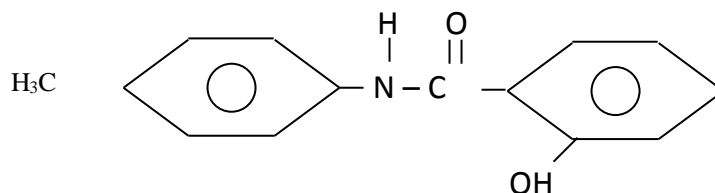
(1) $\text{C}_{13}\text{H}_{11}\text{NO}_2$ [N-(phenyl)-2-hydroxy Salicylimide]



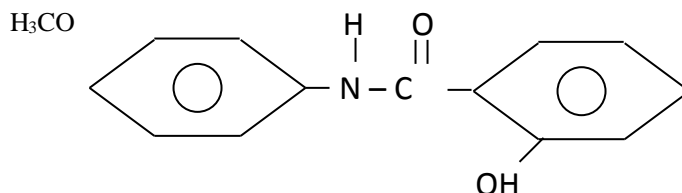
(2) $\text{C}_{13}\text{H}_{10}\text{NO}_2\text{Cl}$ [N-(p-chlorophenyl)-2-hydroxy salicylimide]



(3) $\text{C}_{14}\text{H}_{13}\text{NO}_2$ [N-(p-tolyl)-2-hydroxy salicylimide]



(4) $\text{C}_{14}\text{H}_{13}\text{NO}_3$ [N-(p-methoxy phenyl)-2-hydroxy Salicylimide]



(5) $\text{C}_{13}\text{H}_{10}\text{NO}_2\text{Br}$ [N-(p-bromophenyl)-2-hydroxy salicylimide]

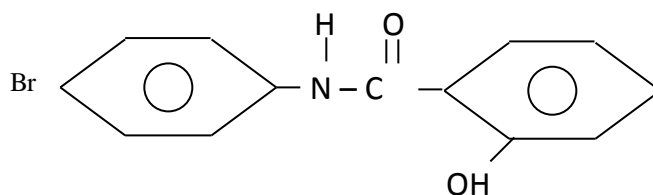
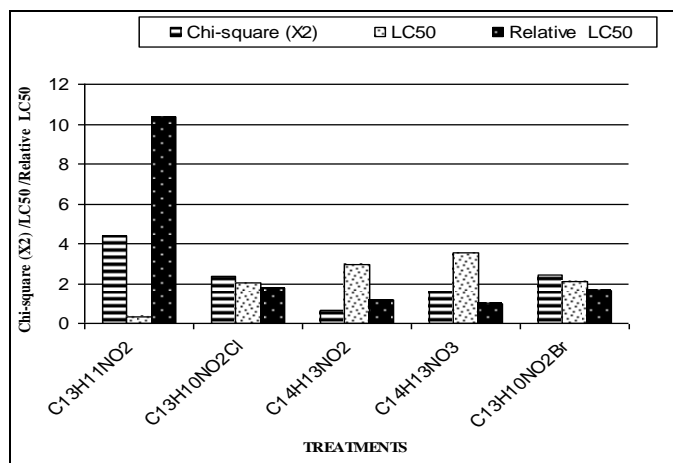
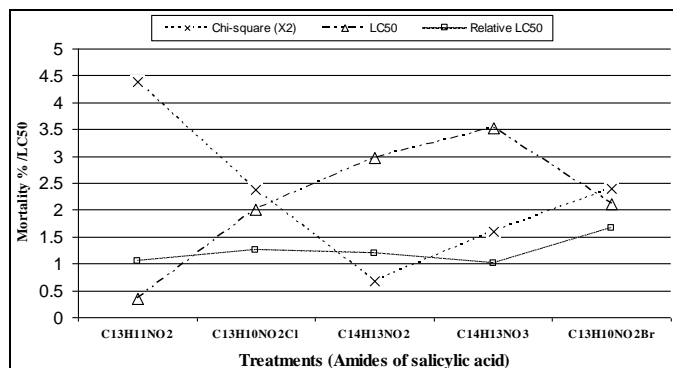


Table 1: Contact Toxicity of early emerged adults of *C. hinensis* due to amides of salicylic acid at 24 hrs.

Compounds	Het.*	Chi-square (X ²)	Slope (Y)	LC ₅₀	Fiducial limits	New prepared amides (IUPAC Name of amides)
N (phenyl) -2 hydroxy Salicylimide	3	4.39	Y=1.97 ± 0.16	0.34	M ₁ =0.29 M ₂ = 0.39	C ₁₃ H ₁₁ NO ₂
N- (p- chlorophenyle) -2 hydroxysalicylimide	3	2.38	Y=1.32±0.20	2.01	M ₁ =1.33 M ₂ = 3.99	C ₁₃ H ₁₀ NO ₂ Cl
N- (p-tolyl) -2-hydroxy Salicylimide	3	0.68	Y=1.01±0.17	2.97	M ₁ =1.61 M ₂ = 9.55	C ₁₄ H ₁₃ NO ₂
N- (P-methoxy Phenyl-2 hydroxySalicylimide	3	1.60	Y=1.09±0.19	3.53	M ₁ =1.33 M ₂ = 3.99	C ₁₄ H ₁₃ NO ₃
N-(p- bromophenyle) -2 hydroxysalicylimide	3	2.40	Y=1.36±0.22	2.12	M ₁ =1.37 M ₂ = 4.03	C ₁₃ H ₁₀ NO ₂ Br

In case of X² was found non- significant heterogeneous at P=0.05, Y=Probit Mortality, X=Log Concentration X 10². D.F.=Degree of Freedom, LC₅₀= Conc. Calculated at given 50% mortality

**Fig 1:** Contact toxicity of early emerged adults of *C. chinensis* due to amides of salicylic acid at 24hrs.**Fig 2:** Mean mortality % four amides of salicylic acid against *C. chinensis*

3.2 Insecticidal contact toxicity

The data of result depicted from the Table -1 and Figure-1 and 2 that above mentioned newly synthesized amides can be used as an alternative to synthetic insecticides to control early emerged adults of *C. hinensis* infesting on chickpea under storage condition. The N (phenyl) -2 hydroxy Salicylimide showed the highest mean mortality to early emerged adults of *C. hinensis*. Similarly N-(p- bromophenyle) -2 hydroxysalicylimide showed potential mortality against early emerged adults of *C. hinensis*. The remaining two newly synthesized amides such as N- (p- bromophenyle) -2

hydroxysalicylimide, N- (p-tolyl) -2-hydroxy Salicylimide showed less mortality than the other whereas N- (P-methoxy Phenyl-2 hydroxy Salicylimide was proved the least effective in controlling the early emerged adults of *C. hinensis* and taken as unit. The newly synthesized amides :- C₁₃H₁₁NO₂ (0.34), C₁₃H₁₀NO₂Cl (2.01), C₁₃H₁₀NO₂Br (2.12), C₁₄H₁₃NO₂ (2.97) and C₁₄H₁₃NO₃ (3.53) have the potential to be used as an ideal approach for the insect control programmes.

4. Discussion

In the support of above findings the works of various workers on use of certain new amides of salicylic acid against their target insect pest and reported considerable contact insecticidal effect. [17, 18]. Synthesis of some new amides and their and there promising insecticidal biopotency was reported against their test insect [19, 20]. Similarly, synthesis, characterization and evaluation of biological application of certain organic compounds were reported significant results [21, 22, 23]. The synthesis, characterization and study of biological activity of some transition metal ion complexes with [n - (o - methoxy benzaldehyde) - 2 -amino phenol] (NOMBAP) was also gave the considerable mortality to the test organism [24, 25]. In the support of above findings the works of various entomologist and biochemist gave their views that these organic chemicals might be use for the control of insect infestation on crop and under storage condition. The amides of salicylic acid can be used as alternative approach to *C. chinensis* control on chickpea.

5. Conclusion

Conclusively, the present investigation revealed that there appears prospects in selected amides of salicylic acid might encourage the search for novel, natural organic insecticides offering an alternative to hazardous toxic synthetic insecticides. The amides of salicylic acid like N- (phenyl) -2 hydroxy Salicylimide and N-(p- chlorophenyle) -2 hydroxy salicylimide have the potential to be used as an ideal approach for the management of pulse beetle, *Callosobruchus chinensis* under storage conditions.

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