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TOXICITY OF SULFOXIMINE ON SOME APHIDS

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Abstract

Sulfoximine is a neurotoxin which categorized under neonicotionids.It proved its highly and fastly lethal effects against some aphids such as *Macrosiphum euphorbiae, Macrosiphum rosae, , Myzus persicae,Myzus ascalionicus , Rhopalosiphum maidis, Chaetosiphon fragaefoli, Aphis gossypii and Hyalopterus pruni*.Laboratory evaluations showed that sulfoximine LC50's ranged between 22.62 ppm to 49.13 ppm against *M. euphorbiae* and *A. gossypii* ,respectively.In the same trend , field evaluations showed that the highest general effect was against *M. euphorbiae* (96.43%)and the lowest was against *A. gossypii* (92.14%). Sulfoximine evaluation results were discussed depending on the mode of action and its totally safety to mammals.

Key Words: Sulfoximine, *Macrosiphum euphorbiae , Macrosiphum rosae, ,Myzus persicae,Myzus ascalionicus , Rhopalosiphum maidis , Chaetosiphon fragaefoli, Aphis gossypii and Hyalopterus pruni*

INTRODUCTION

Neonicotinoid insecticides were used rapidly worldwide for controlling insects because of their high potency, low mammalian toxicity, broad insecticidal spectra, and good systemic properties. Neonicotinoids interacting with nicotinic acetylcholine receptors (nAChR), have a higher affinity for the insect receptor than for the mammalian (Nishimura *et al.*1994, Mori *et al.*2002), and are relatively safe toward mammals and aquatic life. The development of resistance to insecticide in insect populations is a well recognized phenomenon and there are well documented cases of resistance for the major classes of insecticides.

Although the neonicotinoids have proved relatively resilient to the development of resistance. Therefore, new insecticides that lack cross-resistance to currently available insecticides are imminently required. In recent years, *N*-substituted (pyridyl) alkyl sulfoximine derivatives (Wakita *et a*l. 2000, Bai *et a*l. 1991), were described by Dow AgroSciences (Loso *et al.*2007, Loso *et al.* 2008, Zhu *et al.* 2008), beside synthesized sulfoximines (Yu *et al.* 2008). It has been reported that these compounds lack of cross-resistance on insect pests that have developed resistance to one ore more classes of insecticides including imidacloprid and other neonicotinoids.Sulfoximines have been used as chiral auxiliaries (Adrien *et al.* 2007), building blocks of pseudopeptides (Bolm *et al.*2003), and chiral ligands.(McGrath and Bolm,2007).

This study was directed to control certain important aphids which capable to transport many serious viruses which could destroy production of vegetables and field crops,even aphid infested weeds such as *Hyalopterus pruni* which infested *Phragmites australis* ,was used in this study because of its importance in virus transporting.

The present study aimed to evaluate the aphicidal activity of sulfoximine against some aphid species at its recommended concentration (10 ml/100 Liters of Water) firstly under laboratory conditions and then under field conditions beside computing LC50's,LC90's and slopes of sulfoximine against tested aphids, with valuable discussion about the difference in the mode of actions of sulfoximine compounds on mammals and insects.

MATERIALS AND METHODS

1-Tested pesticide

Trade Name : Sulfoxaflor ,Sulfoximine.

IUPAC : N-[[methyl(oxo){1-[6-(trifluoromethyl)-3-pyridyl]ethyl}-λ^4-sulfany-lidene] cyanamide.

Molecular Formula: $C_{10}H_{10}F_3N_3OS$

A.I.(Conc.) : 240g/L. (SC) from Dow AgroSciences .

2-Tested aphids

Macrosiphum euphorbiae,Macrosiphum rosae, Myzus persicae,Myzus ascalionicus, Rhopalosiphum maidis , Chaetosiphon fragaefoli, Aphis gossypii and Hyalopterus pruni. Table(1).

Table 1. Tested aphids and their infested plants

Aphids		Plants	
English Name	Latin Name	English Name	Latin Name
Potato Aphid	*Macrosiphum euphorbiae*(Thomas)	Potato	*Solanum tuberosum* L.
Rose Aphid	*Macrosiphum rosae* (L.)	Rose	*Rosa damasscena* L.
Green Peach Aphid	*Myzus persicae* (Sulzer)	Potato	*Solanum tuberosum* L.
Straw Colored Aphid	*Myzus ascalonicus* Doncaster	Strawberry	*Fragaria ananassa* Duchesne
Corn leaf Aphid	*Rhopalosiphum maidis* (Fitch)	Corn	*Zea mays* L.
Straw Creamy White Aphid	*Chaetosiphon fragaefoli* (Cockerell)	Strawberry	*Fragaria ananassa* Duchesne
Cotton Aphid	*Aphis gossypii* (Glover)	Cotton	*Gossypium hirsutum*
Mealy Plum Aphid	*Hyalopterus pruni* (Geoffroy)	Common reed	*Phragmites australis* (Cav.) Trin.

3-Laboratory evaluation of sulfoximine

Leaves from field collections containing adult aphids of each species were obtained. Thirty aphids were dipped in sulfoximine suspensions at the recommended concentration (10 ml/100 Liters of Water) and mortality percentages recorded after 1 hour of treatment.Then ,120 aphids were exposed to four concentrations of sulfoximine .All aphid species were tested with three replicate leaves per concentration .Three leaves with 30aphids treated with water and used as a control. Once treated leaves had dried, treated aphids were transferred to untreated leaves within small plastic containers in a constant environment room maintained under 25±1°C., 50% RH, and 16:8 (L:D) photoperiod.Mortality was assessed after 16 hrs. and corrected using Abbott's formula(1925).LC50's, LC90's and slope values were calculated using Probit analysis (Finny 1971).

4-Field evaluation of sulfoximine

Infested plants ,which mentioned in Table (1),with every species of tested aphids were sprayed with (10 ml/100 Liters of Water) of sulfoximine under field conditions.Every experiment was replicated trible ,every replicate had 10 infested plants .Untreated plants infested of each species of aphids were sprayed with water only . For each sampled plant, a thorough whole-plant survey was conducted in the field to count the aphids numbers of each replicate before spraying immediately and after 1,3 ,7 ,10 and 14 days post-treatments(Wu and Liu 1992). Mortality percentages of aphids species were determined using Abott's formula (1925). Reduction percentages were estimated according Henderson and Tilton(1955) and in order to avoid the problem to divide by 0, empty sampling units were replaced by the insignificant small value 10-5 (Gartenbau,2000).

RESULTS AND DISCUSSION

1.Aphicidal Activity Under Laboratory Conditions

Sulfoximine had improved its highly efficacy even under laboratory or field conditions against mostly severe aphids .Laboratory bioassay of sulfoximine showed that it had generally fastly lethal effect on all tested aphids species after 1 hour of treatments ,Table (2).Mortality percentages were 100% in case of *M. euphorbiae,M. rosae, M. persicae, M. ascalionicus, C. fragaefoli and H. pruni*, respectively. Therefore,mortality percentages were 96.67% and 93.33% in case of *R.maidis* and *A.gossypii*,respectively.Fast mortality at the recommended rate (10 ml/100 Liters of Water) contribute directly to decrease movement of treated aphids on the plant leaves as occurred in the present study.On the contrary,many insecticides stimulate the aphid's nervous system, causing it to move from plant to plant very rapidly. This results in the infection of more plants than that which occur in those visited by a non-intoxicated aphid, which settles down and feeds on one plant before moving to another one. This occurs before the insecticide has a lethal impact on the aphid. (Summers *at al.*2005).

Table 2 . Effect of sulfoximine (10 ml/100 L Water) on tested aphids under laboratory conditions.

Aphids		Plant	% Mortality After (1 Hour)
Macrosiphum	*euphorbiae*	Potato	100
	rosae	Rose	100
Myzus	*persicae*	Potato	100
	ascalonicus	Straw	100
Rhopalosiphum	*maidis*	Corn	96.67
Chaetosiphon	*fragaefoli*	Straw	100
Aphis	*gossypii*	Cotton	93.33
Hyalopterus	*pruni*	Weeds	100

LC50's ,LC90's and their corresponding slopes were tabulated in Table(3). Comparing the relative toxicities of sulfoximine against mentioned aphids,it showed that the most affected aphid species was *M. euphorbiae* and the least affected aphid was

A.gossypii. Descending order of Sulfoximine LC50's was (49.13,47.38,40.78, 37.81, 34.75,33.80,25.77 and 22.62) ppm,of *A. gossypii* , *C. fragaefoli* , *M. persicae* , *H. pruni* , *M. ascalionicus, M. rosae, R. maidis* and *M. euphorbiae,* respectively. Therefore, Ascending order of Sulfoximine LC90's were (99.48,109.24,159.45, 174.67,175.41,202.35,207.33 and 375.09)ppm of *M. euphorbiae, H. pruni, M. rosae, R. maidis* , *M. persicae, C. fragaefoli, M. ascalionicus and A. gossypii* ,respectively.

Slopes values were estimated and the most highly was recorded by *H. pruni* (2.78) and the lowest value was recorded by *A. gossypii* (1.45).Considering the LC90/LC50 ratio,Table (3) , sulfoximine which possessed the highest slope of toxicity line against *H. pruni* recorded the lowest ratio(2.89),whereas sulfoximine against *A. gossypii*,had the lowest slope,recorded the highest ratio (7.63).

Table 3 . Toxicity of sulfoximine against adult females of tested aphids species under laboratory conditions.

Aphids		Plant	LC50 95% Fiducial Limits	LC90 95% Fiducial Limits	Slope	Toxicity Index	LC90/ LC50
Macrosiphum	*euphorbiae*	Potato	22.62 37.32-13.71	99.48 164.14-60.29	1.99	100	4.40
	rosae	Rose	33.80 46.98-24.32	159.45 221.64-114.71	1.90	66.92	4.72
Myzus	*persicae*	Potato	40.78 49.34-33.70	175.41 212.25-144.97	2.02	55.47	4.30
	ascalionicus	Straw	34.75 55.95-21.58	207.33 333.80-128.78	1.65	65.09	5.97
Rhopalosiphum	*maidis*	Corn	25.77 37.11-17.89	174.67 251.52-121.29	1.54	87.78	6.78
Chaetosiphon	*fragaefoli*	Straw	47.38 89.55-26.07	202.35 382.44-107.06	2.03	47.42	4.27
Aphis	*gossypii*	Cotton	49.13 58.96-40.94	375.09 450.11-312.58	1.45	46.04	7.63
Hyalopterus	*pruni*	Weeds	37.81 46.51-30.74	109.24 134.37-88.81	2.78	59.83	2.89

2-Aphicidal Activity Under Field Conditions

2.1.Initial Kill Evaluation : Field evaluation of sulfoximine showed in Table (4).Initial kill (I.K)% values after 1 and 3 days, were 98.86, 96.72, 96.80, 96.67, 98.25, 96.78, 95.95 and 97.17 % for *M. euphorbiae, M. rosae, ,M. persicae ,M. ascalionicus ,R. maidis ,C. fragaefoli ,A. gossypii and H. pruni*, respectively.That means that sulfoximine had the most highly intial kill effect on *R. maidis* while the lowest effect was in the case of *A. gossypii* .

Reduction percentages after 7 days of spraying with sulfoximine recorded 100% against all tested aphids on all experimental plants.After 10 days of spraying ,the reduction percentages decreased to (96.00,92.00,93.00,94.00,95.00,90.00,91.00 and 91.00)%, respectively, and more decrease occurred after 14 days of spraying (89.00, 85.00, 78.00, 82.00, 82.00 ,81.00,74.00 and 83.00)%, respectively, for *M. euphorbiae, M. rosae, ,M. persicae ,M. ascalionicus ,R. maidis ,C. fragaefoli ,A. gossypii and H. pruni*, respectively.That means that sulfoximine caused highly reduction percentage after 14 days of spraying on *M. euphorbiae* while the least percentage caused on *A. gossypii* .

2-2-Residual Effect Evaluation : Residual effect of sulfoximine was measured against all tested aphids,Table(4).It was ranged between 95% of *M. euphorbiae* and 88.33% reduction for *A. gossypii* .General reduction percentages also were estimated depending on both initial kill and reduction after spraying percentages.They recorded 96.43,94.53,93.57,94.34,95.29,93.56,92.14 and 94.25 %, respectively, for *M. euphorbiae, M. rosae, ,M. persicae ,M. ascalionicus ,R. maidis ,C. fragaefoli ,A. gossypii and H. pruni*, respectively,which mean that sulfoximine had the most highly general reduction percentage against *M. euphorbiae* while the least percentage caused against *A. gossypii* .

The aforementioned encouraged the best role of sulfoximine to control aphids as serious pests caused direct injury as virus transmitters.

The mode of action of sulfoximine targeted the neuromuscular junction where the neurotransmitter in insects is glutamate while it is Ach in the case of mammals which means that this compound is so safe to untargeted alive organisms. This hint resembles to that of nicotine which target the same area. In order to explain more of sulfoximine mode of action , Ni and Parpura (2009) mentioned that vesicular glutamate transporters (VGLUTs) are responsible for vesicular glutamate storage and exocytotic glutamate release in neurons and astrocytes. They selectively and efficiently overexpressed individual VGLUT proteins (VGLUT1, 2, or 3) in solitary astrocytes and studied their effects on mechanical stimulation-induced Ca(2+)-dependent glutamate release. Neither VGLUT1 nor VGLUT2 overexpression changed the amount of glutamate release, whereas overexpression of VGLUT3 significantly enhanced Ca(2+)-dependent glutamate release from astrocytes. None of the VGLUT overexpression affected mechanically induced intracellular Ca(2+) increase. Inhibition of glutamine synthetase activity by L-methionine sulfoximine in astrocytes, which leads to increased cytosolic glutamate concentration, greatly increased their mechanically induced Ca(2+)-dependent glutamate release, without affecting intracellular Ca(2+) dynamics. Taken together, these data indicate that both VGLUT3 and the cytosolic concentration of glutamate are key limiting factors in regulating the Ca(2+)-dependent release of glutamate from astrocytes.

Although some reviews refused to categorize sulfoximines under neonicotinoids,but this point is not right because sulfoximines are so close to neonicotinoids at two axis , structure and mode of action beside more effects were caused by sulfoximines.

Sulfoximine and its derivatives work as very specific inhibitors of glutamine synthetase (E.C.6.3.1.2)-an enzyme catalyzing formation of glutamine from glutamate and ammonium ion,which is the one of the most important enzymes in nitrogen metabolism. Due to glutamine synthetase activity, inorganic nitrogen is incorporated in the cell metabolism and is further used in biosynthesis of several highly important metabolites.(Berlicki,2008).The direct result is the totally stop of the synthesis of glutamate and stop in transporting of nerve signals.

If a widely look taken over the nervous system of mammals and especially humans ,it can be shown that most nAch receptors located in the brain and in the same time glutamate located in neurons junctions.This location support glutamate to protect the unadenylate enzymes (with Mn++ or Mg++)and the adenylated form (Mn++)against inhibition by methionine sulfoximine with highly selectively role.Therefore Methionine sulfoximine as an inhibitor of glutamine synthetase in human and rats have potential medical applications.Such as the role of methionine sulfoximine which act as effective anti-tuberculosis agents with high selectivity towards the pathogenic bacteria. Moreover, it was also shown that glutamine synthetase inhibitors could be successfully applied in cancer therapy. (Berlicki,2008).In the same trend, Hajieva *et al.*(2009) reported that aromatic imines may be interesting lead structures for a potential antioxidant therapy of Parkinson's disease and other disorders accompanied by glutathione deregulation.Beside that,Savarino *et al.*(2009) added to class I HDACIs the glutathione-synthesis inhibitor buthionine sulfoximine (BSO), in an attempt to create an intracellular environment that would facilitate HIV-1 activation. The basis for this strategy was that HIV-1 replication decreases the intracellular levels of reduced glutathione, creating a prooxidant environment which in turn stimulates HIV-1 transcription. They found that BSO increased the ability of class I HDACIs to activate HIV-1. This interaction allowed the use of both types of drugs at concentrations that were non-toxic for uninfected cells, whereas the infected cell cultures succumbed more readily to the drug combination.

In conclusion ,sulfoximine and its derivatives make a suitable base of new pesticides can be used against the wide range of pests with absolutely no worry about side effects to non target organisms and mammals.

Table 4 . Effect of sulfoximine (10 ml/100 L Water) on the reduction percentages of some aphids infesting different plants under field conditions

Aphids		Plant	%Reduction After (days)		% Initial Kill (% I.K)	%Reduction After (days)			% Residual Effect	% General Reduction
Genus	Species		1	3		7	10	14		
Macrosiphum	*euphorbiae*	Potato	95.71	100.00	98.86	100.00	96.00	89.00	95.00	96.43
	rosae	Rose	93.44	100.00	96.72	100.00	92.00	85.00	92.33	94.53
Myzus	*persicae*	Potato	93.59	100.00	96.80	100.00	93.00	78.00	90.33	93.57
	ascalionicus	Straw	93.33	100.00	96.67	100.00	94.00	82.00	92.00	94.34
Rhopalosiphum	*maidis*	Corn	96.49	100.00	98.25	100.00	95.00	82.00	92.33	95.29
Chaetosiphon	*fragaefoli*	Straw	93.55	100.00	96.78	100.00	90.00	81.00	90.33	93.56
Aphis	*gossypii*	Cotton	91.89	100.00	95.95	100.00	91.00	74.00	88.33	92.14
Hyalopterus	*pruni*	Weeds	94.34	100.00	97.17	100.00	91.00	83.00	91.33	94.25

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