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SYNTHESIS AND INSECTICIDAL ACTIVITY OF SOME NOVEL THIOXAZAPHOSPHOLANES AGAINST *HELICOVERPA ARMIGERA* (HUBNER)

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ABSTRACT

In search for new efficient ecofriendly pesticides in place of conventional chemicals like endosulfan and carbaryl, four novel thioxazaphospholanes were synthesized, characterized and their bioefficacy was tested on *Helicoverpa armigera* (Hubner) at reduced doses with a view to overcome the development of resistance to pesticides, maintain biodiversity of natural enemies and increase biodegradability of pesticides in atmosphere which can save ecosystem. The new chemicals were found to be almost at par with the standard check endosulfan. This study also highlights the importance of bulky substitutents and electrophilic phosphorus moiety in the pesticides for enhanced insecticidal activity.

Key words: Thioxazaphospholanes, Cyclic thiophosphates, *Helicoverpa*, Insecticidal Activity.

The tomato fruit borer or gram pod borer, *Helicoverpa armigera* (Hubner) is one of the most serious polyphagous insect pest infesting many crops like gram, tomato, chilly reducing the quality as well as quantity of the harvested crops (Kakar *et al.*, 1980; Tewari and Krishnamoorthy, 1984; Lal and Lal, 1996; Selvanarayanan, 2000). Initially the pest damages foliage, flower buds and flowers; later on, it bores into the fruits causing drastic reduction in yields (Rath and Nath, 1997). For the management of *H. armigera* farmers rely mostly on the chemical pesticides because of the quick knockdown effect. The dependence on conventional chemical pesticides like endosulfan, carbaryl, quinalphos and others for managing the pest has resulted in several problems like reduction of biodiversity of natural enemies, outbreak of secondary pests, development of resistance to pesticides, pesticides induce resurgence, contamination of food (Mitra *et al.*, 1997) and breakdown of food web in ecosystems (Krishnamoorthy, 1999). These drawbacks have emphasized the need to identify alternate ecofriendly chemicals to manage the pest. In the present investigation the bioefficacy of some novel thioxazaphospholanes at reduced doses against *H. armigera* was tested. Four novel thioxazaphospholanes (cyclic thiophosphates) incorporating a pyridine nucleus, were synthesized by the reported synthetic strategy of Kabra *et al.* (2007).

In the synthesis N-substituted 2-amino pyridinium salts through a one pot synthetic route gets connected to novel thioxazaphospholane moiety via phosphorylation by phsphorustrichloride followed by further substitution and oxidation by a binucleophile that is aminoalcohol and sulfur respectively. In literature cyclic thiophosphates have been reported to possess insecticidal activity (Venugopal, 2001). On this ground these novel compounds were subjected to bioassay against *Helicoverpa armigera* (Hubner) using leaf dipping method.

MATERIALS AND METHOD

The second instar larvae of *H. armigera* were collected from chickpea fields of Agriculture Research Station Durgapura, Jaipur. The larvae along with fresh gram leaves were singly placed in porous plastic containers (10 g capacity). The containers were regularly cleaned up and fresh food (gram leaves) was introduced to avoid any infection. As the larvae turned into pupal stage, they were collected (date wise) in Petri dishes and placed into BOD incubator maintained at a temperature of 20 ± 2°C.

The pupae were then placed into the glass pots with seedlings of gram; 20 pupae were introduced in each glass pot. In these pots 10 per cent sucrose solution, fortified with vitamin 'E' soaked cotton wool, was hung in a glass tube, which served as food for the emerging adults. The entire pot was covered with a muslin cloth. The adults emerged out from the pupae after 4-8 days.

The females laid shining, yellow, spherical eggs on the leaves of the plant. The eggs hatched out into 1st instar larvae. The larvae were allowed to feed on the plant

for 6-7 days by which time they transformed into 2nd instar stage. This stage of the pest was used for bioassay of newly synthesized organophosphorous compounds. The 2nd instar larvae were again individually trapped into the plastic container on fresh gram leaves.

Three concentrations (100 ppm, 140 ppm and 180 ppm) of the four test compounds were made. For this purpose, 5 mg of the compound was dissolved in 1-2 ml of acetone and the solution was made up to 50 ml by adding distilled water. Thus, a solution of 100 ppm concentration was obtained. Further 7 mg and 9 mg compounds were dissolved in 1-2 ml acetone and again made up to 50 ml by adding distilled water thus solutions of 140 ppm and 180 ppm respectively were obtained.

2nd instar larvae were selected for the study. For this, 2-3 gm of gram shoots were soaked in the solutions made earlier and was dried under electric fan. These shoots were then introduced in the plastic container having larvae.

Nine such containers were prepared for each compound and there were three replicates for each treatment at different concentrations. A parallel set of three replicates of the standard check endosulfan, at 1710 ppm and the untreated control was also run.

All the insects were placed into BOD incubator maintained at a temperature of 20 ± 2°C. The mortality of the test insect was checked daily for 10 days and expressed as a percentage.The percentage figures were then converted to the angular values, which were subjected to statistical analysis using completely randomized design (CRD) technique.

RESULTS AND DISCUSSION

The per cent mortality of the test insect *H. armigera* after treatment has been shown in the Table 1. After first day of the treatment no significant difference was observed among the tested compounds and the standard check. After second day of the introduction of the insect to the treated leaves, highest mortality of 46.67 per cent was observed in the treatment T_3 (2-(N-(2-benzyloxy-2-oxoethyl)pyridin –2'-ylidenamido)-3-methyl-(1,3,2)-oxazaphospholane-2-sulfides) at 180 ppm which was significantly more than all the other tested compounds including T_{13}, standard check endosulfan 1710 ppm. In all the other treatments the mortality ranged between 6.67 to 26.66 per cent. No mortality was observed in untreated control.

On the third day the mortality of test insect increased up to 60 per cent in the treatment (T_3) at 180 ppm which was at par with standard check endosulfan, 1710 ppm (T_{13}) in which 53.33 per cent insect mortality was observed. Both these treatments were significantly superior to all the other treatments. No mortality was observed in untreated control.

On the fourth day of the observation no change in the trend was observed. On the fifth day of the treatment highest mortality of 66.67 per cent was obtained in the treatment (T_3) 180 ppm which was at par with T_{13} standard check endosulfan, 1710 ppm which registered 60 per cent insect mortality. However, the lower dose of the compound (2-N-(2-benzyloxy-2-oxoethyl)pyridin –2'-ylidenamido)-3-methyl-(1,3,2)-oxazaphospholane-2-sulfides) that is T_2 at 140 ppm was at par with the standard check endosulfan with 53.33 per cent insect mortality.

On the sixth day the compound T_3 at 180 ppm registered 73.33 per cent mortality which was at par with T_{13} endosulfan (60 per cent mortality) and T_7, 2-(N-benzylpyridin-2'-ylidenamido)-3-ethyl-(1,3,2)-oxazaphospholane-2-sulfides at 100 ppm.

On the seventh day all the three doses (100 ppm, 140 ppm and 180 ppm) of the compound (2-(N-(2-benzyloxy-2-oxoethyl)pyridin-2'-ylidenamido)-3-methyl-(1,3,2)-oxazaphospholane-2-sulfides) i.e. T_1, T_2 and T_3 were at par with each other registering 60 – 86.67 per cent insect mortality which was found to be at par with T_{13} standard check endosulfan at 1710 ppm and highest dose of 180 ppm of the compound 2-(N-(N-(2-ethoxy-2-oxoethyl)pyridin –2'-ylidenamido)- 3-methyl-(1,3,2)-oxazaphospholane-2-sulfides T_6.

On the eighth day the compound (2-(N-(2-benzyloxy-2-oxoethyl)pyridin –2'-ylidenamido)-3-methyl-(1,32)-oxazaphospholane-2-sulfides) at 180 ppm (T_3) continued to register highest mortality (93.33 per cent) which was at par with its lower doses of 140 ppm (T_2), standard check endosulfan T_{13} and highest dose 180 ppm in (T_6) No mortality was registered in the untreated control.

On ninth day of the treatment the compound 2-(N-(2-benzyloxy-2-oxoethyl)pyridin-2'-ylidenamido)-3-methyl-(1,3,2)-oxazaphospholane-2-sulfides at 180 ppm (T_3) and the standard check endosulfan at 1710 ppm (T_{13}) registered 100 per cent cumulative mortality of the insect *H. armigera*. Both these treatment were at par with the lower doses i.e. 140 ppm and 100 ppm of the above cited synthesized compound with 93.33 and 86.87 per cent insect mortality respectively.

The final observation on the mortality of the *H. armigera* was taken on tenth day of the treatment on which 180 ppm dose of 2-(N-(2-ethoxy-2-oxoethyl) pyridine-2'-ylidenamido)-3-methyl-(1,3,2)-oxazaphospholane-2-sulfides (T_6) with 93.33 per cent mortality was also found to be at par with all the three doses of the compound 2-(N-(2-benzyloxy-2-oxoethyl)pyridin-2'-ylidenamido)- 3-(methyl-(1,3,2)-

Table 1. Cumulative mortality (%) of *H. armigera* after treatment (Leaf-dip method)

S. No.	Chemical name of the compound	Doses	Days 1	2	3	4	5	6	7	8	9	10
T_1	2-(N-2-benzyloxy-2-oxoethyl)pyridin-	100ppm	6.67	26.67	26.67	40.00	46.67	53.33	60.00	73.33	86.67	93.33
	2'ylidenamido)-3-methyl-[1,3,2]-		(14.96)	(31.09)	(31.09)	(39.23)	(43.09)	(46.91)	(50.77)	(58.91)	(68.58)	(75.04)
T_2	oxazaphospholane-2-sulfides	140 ppm	13.33	26.67	40.00	40.00	53.33	53.33	66.67	80.00	3.33	93.33
			(21.42)	(31.09)	(39.23)	(39.23)	(46.91)	(46.91)	(54.74)	(63.43)	(75.04)	(75.04)
T_3		180 ppm	20.00	46.67	60.00	60.00	66.67	73.33	86.67	93.33	100	100
			(26.57)	(43.09)	(50.77)	(50.77)	(54.74)	(58.91)	(68.58)	(75.04)	(90)	(90)
T_4	2-(N-2-ethoxy-2-oxoethyl)pyridin-2'-	100 ppm	13.33	26.67	26.67	33.33	40.00	46.67	53.33	66.67	80.00	86.67
	ylidenamido)-3-methyl-[1,3,2]-		(21.42)	(31.09)	(31.09)	(35.26)	(39.23)	(43.09)	(46.91)	(54.74)	(63.43)	(68.58)
T_5	oxazaphospholane-2-sulfides	140 ppm	13.33	20.00	26.67	33.33	33.33	46.67	60.00	66.67	80.00	80.00
			(21.42)	(26.57)	(31.09)	(35.26)	(35.26)	(43.09)	(50.77)	(54.74)	(63.43)	(63.43)
T_6		180 ppm	13.33	20.00	40.00	46.67	46.67	46.67	66.67	80.00	86.67	93.33
			(21.42)	(26.57)	(39.23)	(43.09)	(43.09)	(43.09)	(54.74)	(63.43)	(68.58)	(75.04)
T_7	2-(N-benzylpyridin-2'-ylidenamdio)-	100 ppm	6.67	13.33	26.67	33.33	33.33	60.00	60.00	60.00	80.00	80.00
	3-ethyl-[1,3,2]-oxazaphosphlone-2-		(14.96)	(21.42)	(31.09)	(35.26)	(35.26)	(50.77)	(50.77)	(50.77)	(63.43)	(63.43)
T_8	sulfides	140 ppm	6.67	6.67	13.33	26.67	26.67	33.33	40.00	53.33	66.67	66.67
			(14.96)	(14.96)	(21.42)	(31.09)	(31.09)	(35.26)	(39.23)	(46.91)	(54.74)	(54.74)
T_9		180 ppm	6.67	20.00	33.33	40.00	40.00	53.33	60.00	66.67	73.33	73.33
			(14.96)	(26.57)	(35.28)	(39.23)	(39.23)	(46.91)	(50.77)	(54.74)	(58.91)	(58.91)
T_{10}	2-(N-benzylpyridin-2'-ylidenamdio)-	100 ppm	6.67	13.33	20.00	26.67	40.00	40.00	46.67	66.67	66.67	66.67
	3-methyl-[1,3,2]-oxazaphosphlone-2-		(14.96)	(21.42)	(26.57)	(31.09)	(39.23)	(39.23)	(43.09)	(54.74)	(54.74)	(54.74)
T_{11}	sulfides	140 ppm	0	6.67	20.00	26.67	33.33	40.00	46.67	53.33	60.00	60.00
			(0.00)	(14.96)	(26.57)	(31.09)	(35.26)	(39.23)	(43.09)	(46.91)	(50.77)	(50.77)
T_{12}		180 ppm	13.33	13.33	26.67	33.33	33.33	40.00	53.33	60.00	66.67	66.66
			(21.42)	(21.42)	(31.09)	(35.26)	(35.26)	(39.23)	(46.91)	(50.77)	(54.74)	(54.74)
T_{13}	Endosulfan (standard check)	1710 ppm	20.00	20.00	53.33	53.33	60.00	60.00	73.33	86.67	100	100
			(26.57)	(26.57)	(46.91)	(46.91)	(50.77)	(50.77)	(58.91)	(68.58)	(90)	(90)
T_{14}	Untreated Control (water)	-	0	0	0	0	0	0	0	0	0	0
			(0.00)	(0.00)	(0.00)	(0.00)	(0.00)	(0.00)	(0.00)	(0.00)	(0.00)	(0.00)
		C.D. at 5%	N.S.	19.63	12.22	12.30	10.94	11.52	15.17	14.94	21.34	19.17

Figures in parenthesis are angular transformed values.

oxazaphospholane-2-sulfides (T_1, T_2 and T_3) and standard check endosulfan (T_{13}).

Schrader (1947) first of all proposed the basic structure of organophosphates, which was responsible for insecticidal activity of a chemical. This work was strengthened by the work of Fukoto (1957) who concluded that together with the basic structure given by Schrader if bulky substituents are present in the chemical together with electron withdrawing substituents attached to phosphorus atom, latter becomes more electrophilic and due to steric effect of bulky groups the normal activity of the enzyme acetyl cholinesterase was retarded that enhanced insecticidal activity. These two factors were clearly visible in our study also. Where treatment T_3 2-(N-(2-benzyloxy-2-oxoethyl) pyridin-2'-ylidenamido)-3-methyl-(1,3,2)-oxazaphospholane-2-sulfides with bulky benzyl ester group ($CH_2COOCH_2C_6H_5$) and electron withdrawing substituents was the most active during bioassay, which was at par with the standard check. Next potent compound observed was 2-(N-(2-ethoxy-2-oxoethyl)pyridine-2'-ylidenamido)-3-methyl-(1,3,2)-oxazaphospholane-2-sulfides T_6 which also incorporates an electron withdrawing ester substituent but this is less bulky than 2-(N-(2-benzyloxy-2-oxoethyl)pyridin –2'-ylidenamido)- 3-methyl-(1,3,2)-oxazaphospholane-2-sulfides T_3.

2-(N-benzylpyridin-2'-ylidenamdio)-3-ethyl-(1,3,2)-oxazaphosphlone-2-sulfides and 2-(N-benzylpyridin-2'-ylidenamdio)-3-methyl-(1,3,2)-oxazaphosphlone-2-sulfides with less bulky as well as electron releasing (CH_3, CH_2-C_6H_5) substituents were least effective.

The result confirms our observations reported earlier (Kabra *et al.*, 2009) that the basic factors responsible for high insecticidal activities are steric effect due to bulky substituents as well as electrophilic tendency of phosphorus due to eletron withdrawing substituents.

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