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Full Length Research Paper

Synthesis and insecticidal activities of some selected hydroxytriazenes

Ombaka, O* and Gichumbi, J.M

Department of Basic Sciences, Chuka University College, Box 109, Chuka, Kenya.

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Eight hydroxytriazenes were synthesized and then subjected to spot tests. The composition of these hydroxytriazenes was analyzed using elemental analysis and their physical characteristics like melting point, crystal shape and colour were studied into details. The synthesized compounds were screened for their insecticidal activities against one day old male *Drosophila melanogaster Meig* (vinegar flies or fruit flies). Out of all the eight compounds screened, 3-hydroxy-3-m-tolyl-1-m-nitrophenyltriazene, 3-hydroxy-3-m-tolyl-1-p-methoxyphenyltriazene, 3-hydroxy-3-n-propyl-1-o-chlorophenyltriazene were the most active having LC_{50} values of 2.898, 3.898 and 1.812 ppm respectively. The least active compound is 3-hydroxy-3-m-tolyl-1-phenyltriazene having the value of 16.850 ppm. Heptachlor, a commercial product, had LC_{50} value of 1.570 ppm.

Key words: Insecticidal activity, Hydroxytriazenes, *Drosophila melanogaster* Meig.

INTRODUCTION

Nearly all insecticides have the potential to significantly alter ecosystems, many are toxic to humans and others are concentrated in the food chain. Heptachlor, an organochlorine compound, is used as an insecticide, exterminator and as termicide. This insecticide is highly toxic to humans and can be absorbed through the skin, lungs and gastrointestinal tract. Furthermore, it is a stable compound that persists in the environment for decades (Goswami et al., 2005). Development of safer insecticides with unique modes of action is necessary to combat widespread insecticide resistance (Cordova et al., 2006; Lahm et al., 2009; Lahm et al., 2007). Triazene, which have some similarity in its structure to hydroxytriazene, have been used as herbicides (Goswami et al., 2005; Kumar et al., 2003), fungicides (Naulakha et al., 2009), insecticides (Ombaka et al., 1998; Ombaka et al., 2001; Lijie et al., 2011; Olga et al., 2011) and pesticides (Singh et al., 2009; Chauhan et al., 2010). Thus hydroxytriazene is a candidate for use as an insecticide.

The objective of this investigation was therefore, to investigate the activity of hydroxytriazene against *Drosophila melanogaster* Meig. The analysis was done alongside a commercially established insecticide, heptachlor.

*Corresponding author. E-mail:ombaka2020@yahoo.com.

METHODOLOGY

Synthesis of hydroxytriazenes

There are three methods for the synthesis of hydroxytriazenes reported in the literature. The first method involves reduction of nitrosobenzene or substituted phenylhydrazenes to give hydroxytriazene (Khanam et al., 2010; Kumar et al., 2009; Kalpana et al., 2008; Manu et al., 2008). In the second method, an alkyl or arylhydroxylamine is coupled with diazonium salt at 0-5°C in 1:1 molar proportion to give the corresponding hydroxytriazenes (Chauhan et al., 2010; Ombaka et al., 2001; Singh et al., 2008). The third method involves oxidation of diazoaminobenzene with peroxybenzoic acid under mild conditions (Kalpana et al., 2008; Naulakha et al., 2009; Singh et al., 2009).

The second method has advantages over other two methods because of better yield and ease of preparation (Chauhan et al., 2010). Eight hydroxytriazenes samples were prepared by coupling an alkyl or arylhydroxylamine with diazonium salt at 0-5°C in 1:1 molar proportion, in 1% sodium acetate buffer medium to maintain pH between 5 to 6. The compounds were recrystalized either from aqueous alcoholic (1:4 v/v) or acetone to yield pure crystals. These

Table 2. LC_{50} Values and relative toxicity.

Reagent No.	Name of the reagent	LC_{50} values of the reagent in ppm	Relative toxicity
i	3-Hydroxy-3-m-tolyl-1-phenyltriazene	16.850	10.732
ii	3-Hydroxy-3-m-tolyl-1-o-chlorophenyltriazene	10.070	6.414
iii	3-Hydroxy-3-m-tolyl-1-p-chlorophenyltriazene	9.124	5.811
iv	3-Hydroxy-3-m-tolyl-1-m-nitrophenyltriazene	2.898	1.845
v	3-Hydroxy-3-m-tolyl-1-p-methoxyphenyltriazene	3.898	2.483
vi	3-Hydroxy-3-phenyl-1-p-chlorophenyltriazene	12.567	8.004
vii	3-Hydroxy-3-n-propyl-1-o-chlorophenyltriazene	1.812	1.154
viii	3-Hydroxy-3-m-tolyl-1-o- arboxyxyphenyltriazene	9.232	5.880
ix	Heptachlor	1.570	1.0

Third column: shows lethal concentration of hydroxytriazenes and heptachlor that kills half of the population under the same experimental condition. Fourth column: shows the number of times heptachlor is more toxic than hydroxytriazenes under the same experimental conditions.

synthesized compounds were subjected to four spot tests, which are; α-naphthylamine test, picric acid test, N, N-dimethylamine test and sulphuric acid test. The compounds were characterized by melting point apparatus (Model Kruess M 500), elemental analyzer Perkins Elmers model 2400 CHN/O Analyzer. The theoretical results were calculated based on the structural formula of the compound which was expected as the method used has been verified by other researchers including Ombaka et al. (1998), Ombaka et al. (2001), Chauhan et al. (2010), Goswami et al. (2005) to name just a few. The composition of these compounds was verified by their elemental analysis.

Details of culture

The method reported by Kumar et al. (2009) and Gupta (1998) was used to prepare the culture medium. 75 g of maize flour, 65 g of Jaggery, A and 10 g of gar-agar, 11 g of yeast were thoroughly mixed in 750 ml of distilled water and the mixture heated while stirring until it boiled. Thereafter, 1 ml propionic acid was added quickly as stirring continued. The contents were then transferred to six 250 ml conical flasks were labelledA_1 to A_6. The flask and content were allowed to cool for 24 h. In each flask, about 20 insects of *D. melanogaster Meig* were transferred into them and the flask covered immediately by muslin cloth. The newly emerged one day old male flies were used for investigation.

Toxicity

Micro bioassay was done using one day old male *D. melanogaster Meig* by residue film method.

A stock solution of 1000 ppm of each hydroxytriazenes was prepared in ethanol and acetone. Solutions of lower concentrations were prepared by proper dilution of stock solution with the solvent Residue film of one ml of the solution of each hydroxytriazene was prepared on Petri dish (10 cm diameter) by spreading 0.5 ml of the solution on each of the two parts of the Petri dish. The solution in both parts of the Petri dish was swirled gently in order to coat the entire surface. After complete drying of the solvent, about 0.5 g of the prepared diet was placed in the Petri dish. Thereafter, one day old male *D. melanogaster Meig* were released in each pair of the Petri dish and exposed for 24 h at 27± 1°C (Kumar et al., 2009; Lijie et al., 2011; Neelam et al., 2009; Ombaka et al., 1998). Three replicates were done in each treatment. The insects were anaesthetized by keeping them in deep freeze for about 3 min in order to make them inactive for about one minute before exposure to the hydrotriezene To record the natural mortality, a control in three replicates was also run alongside side in a similar manner to the above but instead of using the hydrotriezene, the meal and ethanol or acetone was used. The mortality was taken after 24 h of exposure moribund insects were also counted as dead. The control experiment was used to establish that it was not the prepared meal or the acetone or ethanol that was responsible for the death of the insects.

For the estimation of LC_{50} values, a method of probit analysis has been applied which involves changing of observed percent mortality to corrected percent mortality. For the sake of brevity all the table and data of regression equation have not been incorporated. The concentration range used for the test compound ranged between 0.25 to 48 ppm, depending on the response of individual concentration.

RESULTS AND DISCUSSION

Physical characteristic and elemental analysis

Table 1 consists of the results of the physical characteristics and elemental analysis. The hydroxytriazenes prepared were either light yellow coloured shining needles, pale yellow coloured shining needles, light yellow coloured powder and olive green coloured silky needles. The melting point of these compounds ranged from 70 to 178°C. Ethanol or acetone was used to crystallize these compounds. The results of C, H, N indicates that the theoretical values and experimental values are identical.

LC_{50} Values and relative toxicity of hydroxytriazenes

Table 2 show LC_{50} values and relative toxicity of hydroxytriazenes against one day old male *D. melanogaster* Meig.

The results show that out of the eight compound

Table 1. Physical characteristic and elemental analysis of hydroxytriazenes.

Reagent No.	Synthesized Hydroxytriazene	Physical characteristics			Elemental analysis						Molecular formula
		Colour and shape of crystals	Crystallized from	M.P	%C		%H		%N		
					Th	Exp	Th	Exp	Th	Exp	
i	3-Hydroxy-3-m-tolyl-1-phenyltriazene	Light yellow shining needles	ethanol	124	68.68	69.91	5.76	5.57	18.50	18.23	$C_{13}H_{13}N_3O$
ii	3-Hydroxy-3-m-tolyl-1-o-chlorophenyltriazene	light yellow shining needles	acetone	70	59.64	59.34	4.62	4.39	16.06	16.77	$C_{13}H_{12}N_3OCl$
iii	3-Hydroxy-3-m-tolyl-1-p-chlorophenyltriazene	Pale yellow shining needles	acetone	148	59.64	58.27	4.62	5.19	16.06	16.56	$C_{13}H_{12}N_3OCl$
iv	3-Hydroxy-3-m-tolyl-1-m-nitrophenyltriazene	Light yellow powder	acetone	152	57.32	56.62	4.44	4.62	20.58	19.71	$C_{13}H_{12}N_4O_3$
v	3-Hydroxy-3-m-tolyl-1-p-methoxyphenyltriazene	light yellow shining needles	ethanol	112	65.33	64.56	5.88	5.77	16.34	16.87	$C_{14}H_{15}N_3O_2$
vi	3-Hydroxy-3-phenyl-1-p-chlorophenyltriazene	Olive green silky needles	acetone	140	58.16	57.93	4.07	3.94	16.97	16.62	$C_{12}H_{10}N_3OCl$
vii	3-Hydroxy-3-n-propyl-1-o-chlorophenyltriazene	Light yellow shining needles	ethanol	80	50.56	50.24	5.66	5.37	19.67	20.28	$C_9H_{12}N_3OCl$
viii	3-Hydroxy-3-m-tolyl-1-o-carboxyxyphenyltriazene	Light yellow shining needles	ethanol	178	61.96	61.44	4.83	4.69	15.49	14.66	$C_{14}H_{13}N_3O_3$

'Th': values obtained on theoretical data; 'Exp' : values obtained based on experimental data.

screened, compound number (iv),(v) and(vi) separately showed a considerably low values of LC_{50} .Their LC_{50} values were 2.898, 3.898, 1.812 ppm respectively. Whereas compound number (i) is the least active having a value of 16.850 ppm. Other compounds have LC_{50} values in the range of 12.567 to 9.124 ppm. The results of compounds number (iv), (v) and (vii) indicate that they have fairly good toxicity against *D. melanogaster Meig* and their toxicity are comparable with those of heptachlor, a commercial product. However, in case of other compounds results are not promising.

On the basis of the structures of hydroxytriazenes, it is found that methyl group at meta position at ring (Ar_2) and alkyl group increases activities against *D. melanogaster* Meig. The activity of hydroxytriazenes also increases when chloro group is at "p" position of the ring (Ar_1). However, the activity of hydroxytriazenes decreases when chloro group is at "O" position at ring (Ar_1). The chloro group at the *para* position was shown to increase the LC50 values.

Conclusion

Compound number (iv), (v), (vii) exhibit insecticidal properties against *D. melanogaster Meig* which are comparable with that of Heptachlor, a commercial product. Hence, these three compounds have insecticidal properties which can be commercially exploited. The insecticidal activities of hydroxytriazenes depends on which group is at *meta, ortho, para* at ring (Ar_2) or (Ar_1).The insecticidal activities increases when alkyl group is replaced(Ar_2). In general insecticidal activities against *D. melanogaster Meig* depend on its structure.

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