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THE EFFECTS OF 2-HYDROXY CHALCONE AND ITS DERIVATIVE ON THE LARVAE AND ADULTS OF *TRIBOLIUM CONFUSUM*

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ABSTRACT:
2-Hydroxy Chalcone and its derivatives (compounds 1and 2) were used in a toxicity test on the larvae and adults of confused flour beetle Tribolium confusum (Du Val). Mortality tests were done by applying different concentrations (0.01, 0.02 and 0.04 ppm) on 2-Hydroxy Chalcone and its derivatives which were exposed by topical application with 5 µL of each compound and the data were recorded after 24 h of treatments. The mortality % of [7-Hydroxy-9-(pyridine-4-yl)-6H-benzo[C]chromen-6-one] in (compound 2) were 26.6, 50 and 76.67% and 16.67, 36.67 and 63.3% and 13.3, 23.3 and 36.6 % to 3rd, 5th instar larvae and adults, respectively. While in [3-thinyl-1-(2-hydroxynaphthyl) -1-propene] (compound 1), the mortality % were 23.3, 40 and 66.6% and 13.3, 30 and 56.6% and 6.6, 16.6 and 26.6 % to 3rd, 5th instar larvae and adults, respectively. The results indicated that (comp.2) was the most toxic one and (comp.1) was the least toxic to confused flour beetle when applied singly. The calculated LC50 values to (compound 2) were 0.019, 0.028 and 0.074 ppm to 3rd, 5th instar larvae and adults, respectively. While to (compound 1), the LC50 values were 0.025, 0.034 and 0.106 ppm to 3rd, 5th instar larvae and adults, respectively. The order of toxicity of the chemical compounds was 2 > 1. These chemical compounds can be used to control confused flour beetle.

KEYWORDS: Tribolium Confusum, Toxicity, Chalcones and its Derivatives.

1. INTRODUCTION

Tribolium confusum (Du Val) is considered as a suitable insect species for bioassays since it exhibits moderate tolerance to most insecticides (Champ and Campbell-Brown 1970). In this investigation, 2 chemical compounds (1 and 2) were used to evaluate their action on the confused flour beetle, *Tribolium confusum* (Du Val).
Confused flour beetle *Tribolum confusum* is one of the worldwide insect pests of mills, food warehouses, retail stores, and urban homes (Park, 2002 and Esmaili, *et.al*. 2013). The pest can cause damage to stored-products by feeding and hence severely reducing the quality of crops due to product excrement and larval feces. This pest makes serious damage on flour and crush cereal particularly at larval and adults stages. Also, the pest causes damage to the seeds containing high humidity (usually above 12%) converting flour color to gray and creates bad smell see table2. The continuous exposure of the grain and flour to this pest encourages mold growth (Weston, and Rattlingourd 2000 and Park, 2002).
Recently, chlorinated hydrocarbons were replaced in confused flour beetle control program by pesticides of other chemical groups, especially by certain organophosphorous (O-P) insecticides (Pedigo, 1989). The O-P compounds selected are safer to humans and environment where it can effectively replace the chlorinated hydrocarbon (Smith, 1970 and Zettler & Arthur, 2000).
Chalcones are one of the most popular compounds in plants, such as vegetables, fruits, tea, and have various pharmacological activities; as anti-inflammatory, antifungal, antimalarial, cytotoxic, anti-tumor, and anti-oxidant (Zhuang, 2017). In addition, it is a basic moiety of many heterocyclic systems containing O, S and N. N with heterocyclic derivatives synthesized from chalcones which exhibited anti-inflammatory, antioxidant, anti-tubercular and anti-bacterial activities. Naphthylchalcone and 2-hydroxy chalcones derivatives were proved to have activity and toxicity against mycobacterium tuberculosis at low concentrations with low cytotoxicity against human cells (Macaev, *et. Al*. 2014). Simplicity of their synthesis at low cost is an advantage of chalcones as potential anti-tuberculosis. An attempt has been made to synthesize chalcone (comp.1) by the reaction of 2-acetyl thiophene with 2- hydroxy naphthylaldehyde. In addition, one of the chalcones derivatives was prepared as follow [pyridine-2-yl-6H-benzo[c] chromen-6-one] (comp. 2). The synthesized compounds have been characterized by physical properties, IR, 1HNMR data.

2. MATERIALS AND METHODS

1. Insect rearing
The confused flour beetle adults were obtained from a laboratory colony of Department of Biology, Faculty of Science/ Zakho University. The pest was reared in 1000 ml glass container. The insects were fed on flour containing 5% powdered dry yeast (Park, and Frank, 1948; Park, 1962; and Zyromska-Rudzka, 1966). The glass containers were maintained in the dark incubator (LAB TECH. Korea) at 30 ± 1 °C, 70 ± 5% RH conditions. The 3rd and 5th instars larvae of *T. confusum* were used in the present experiments, whereas the adults age were 1 week after emergence.

2. Chemistry
Melting points were determined in an open capillary tube and were uncorrected. IR spectra were recorded on a Bruker -Alpha with Platinum-ART spectrometer (Germany). 1H- NMR spectra were recorded on a Bruker BioSpin Gmbh 100.65-MHz instrument in DMSO as solvent and TMS as an internal standard.

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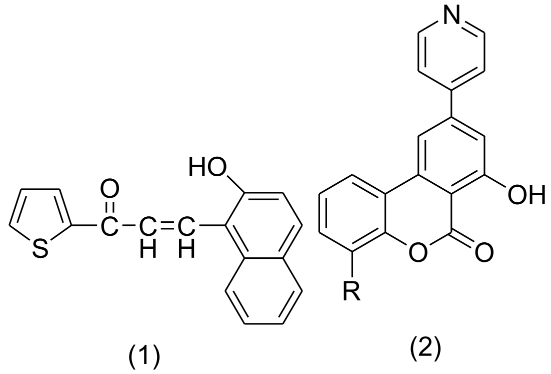

Fig 1. General procedure for synthesis of [6H-benzo[c]chromen-6-one.] compound 2. (Galdino, 2011).

In the current study, 2 chalcones were synthesized by Claisen-Schmidt condensation (a modied Aldol condensation reaction) with minor modifications. The classical method for synthesis of chalcones involves reaction of equimolar amounts of 2-acetyl thiophene with 2-hydroxy naphthaldehydes at room temperature in presence of sodium hydroxide or potassium hydroxide as base catalyst to give the compounds 1.

General procedure for synthesis of [6H-benzo[c]chromen-6-one.] comp.2 (Mazimba, 2015)**.**

2-Hydroxy-Pyridin-4-yl-chalcone (2 mmol), potassium carbonate powder (20 mol %) and ethyl-acetoacetate (2 mol) were taken in ethanol and stirred at 60 ^{0}C for 30 min. Then, the reaction mixture was cooled and poured into cold water. The precipitated solid was collected by filtration and recrystallized in ethanol to give [7-Hydroxy-9-(pyridin-2-yl)-6H-benzo[c]chromen-6-one] (Comp. 2).

Table 1. Physical properties and IR-spectra of compounds 1 and 2.

n	Nomenclature	Chemica l formula	Color	M. P.	Solubility	IR- cm^{-1}					
						C=O	C=C	-OH	C-O	=C-H	Aromatic
1	3-thinyl-1-(2-hydroxynaphthyl) -1-propene	$C_{17}H_{12}SO_2$	Brown	96-98	Ethanol	1630	1586	3180	1160	2882	1458-741
2	7-Hydroxy-9-(pyridine-4-yl)-6H-benzo[C] chromen-6-one	$C_{18}H_{11}NO_3$	White solid	160-162	Ethanol	1649	----	3362	1236, 1151 C-O-C	----	1451-985

Table 2. 1HNMR-spectra of compounds 1 and 2.

n	Cα-H	Cβ-H	Aromatic-H	-OH	Pyridinyl-H	Cromen-one-H
1	1H,7.87,d	1H,8.12,d	9H,7.20-7.61,m	1H,12.05,s	-----	-----
2	-----	-----	4H,7.60-7.81,m	1H,8.8,s	4H,8.40-8.73,m	2H,7.10-7.20,dd

3. Bioassay

Three different concentrations 0.01, 0.02 and 0.04 ppm were used for 3rd, 5th instars larvae and adults of confused flour beetle. Compounds 1 and 2 were diluted with ethanol; 10 larvae and 10 adults were exposed by topical application (the solution was injected over the insect's thorax by 50 capacity microliter syringe) (Galdino, 2011) with 5 µL of different compounds concentrations and covered by a Petri dish to prevent the escaping of the insects. The treatments were replicated 3 times and each replicate consisted of 10 3rd, 5th instar larvae and 10 adults, the control group received 5 µL of 50% ethanol. The bioassay containers were maintained in a glass door incubator at 30 ± 1 ºC and 70% ±5 relative humidity throughout the experimental. The mortality % for larvae and adults was recorded after 24 h. The mortality was corrected according to Abbott's (1925).

4. Determination of lethal concentration (LC50)

Deadly dose values were determined for 50% of the tested insects and Upper and lower confidence limits using a system called MS-DOS according to Probit. Exe, probit. Statistical analysis of the results of toxicological tests were calculated according to Finney (1971). So as to get low doses of the pesticide to kill 50% of the experiment insects.

5. Statistical analysis

All statistical analyses were performed with the Graph Pad Prism program (Version 6.01) (GraphPad Software, Finland) by a Newmanns- Keuls of one-way analysis of variance (ANOVA) and the data were expressed as means ± standard error of mean (SEM). In all tables the letters (a, b and c) are representing significant differences in the means at the 0.05, respectively.

3. RESULTS AND DISCUSSION

1. Larvicidal activity of compounds1 and 2.

Table (3) shows the results of exposing the 3rd instar larvae of *T. confusum* to compounds concentrations of 0.01, 0.02 and 0.04 ppm. Larval mortality was significantly different ($P<0.05$) among the 3 doses and control which were 26.6 ±3.33, 50.0 ± 0.08 and 76.67 ±3.33 % with compound 2, and 23.3 ±3.33, 40.0 ±0.14 and 66.6 ±3.33% with compound1, respectively. These results indicated that a concentration dependent mortality for both compounds were obvious. Also, Table (3) shows that the LC_{50} of compound 2 (0. 019 ppm) was more toxic than that of compound 1 (0.025 ppm) on the 3rd instar larvae of confused flour beetle. The present study revealed that compound 2 possesses a high level of potency as larvicide against *T. confusum.* Such a phenomenon was noticed in the 70% mortality of 3rd instar larvae of compound 2 treatment with 0.04 ppm, while the mortality % reached 63.3% with 5th instar larvae indicating a higher instar resistant with increasing larvae age.

Martin, *et. Al.* (2000) showed that the 1st instar larvae of the *Helicoverpa Armigera* were very sensitive to the chemical pesticide and then the sensitivity decreased significantly in subsequent successive larval stages, where sensitivity decreased with advancement of larval instar.

Table 3. Mortality %, concentration value of LC_{50} for different concentrations of compounds 1 and 2 on the 3rd instar larvae of *T. confusum*.

Concentrations Ppm	Control	Compound 2		Compound 1	
		% Mortality	LC_{50}	% Mortality	LC_{50}
0.01	3.33[a]± 2.1	26.6[b] ±3.33	0.019	23.3[b] ±3.33	0.025
0.02		50.0[b] ± 0.08		40.0[c] ±0.14	
0.04		76.67[b] ±3.33		66.6[b] ±3.33	

Table (4) shows the results of exposing 5th instar larvae of *T. confusum* to 0.01, 0.02 and 0.04 ppm of compounds 1 and 2. Significant differences were noticed ($P<0.05$) among the 3 doses and control where the larval mortality was 16.67 ±3.33, 36.67 ±3.33 and 63.3 ±3.33% with compound 2 and 13.3 ±3.33, 30.0 ±1.32 and 56.6 ±3.31% with compound 1, respectively. These results indicated that a concentration dependent mortality for both compounds were obvious. Also, Table (4) shows that the LC_{50} of (compound 2) (0.028 ppm) was more toxic than that of (compound 1) (0.034 ppm) on the 5th instar larvae of confused flour beetle.

Table 4. Mortality %, concentration value of LC_{50} for different concentrations of compounds1 and 2 on 5th instar larvae of *T. confusum*.

Concentrations ppm	Control	Compound 2		Compound 1	
		% Mortality	LC_{50}	% Mortality	LC_{50}
0.01	0[a]	16.67[b] ±3.33	0.028	13.3[b] ±3.33	0.034
0.02		36.67[c] ±3.33		30.0[b] ±1.32	
0.04		63.3[b] ±3.33		56.6[b] ±3.31	

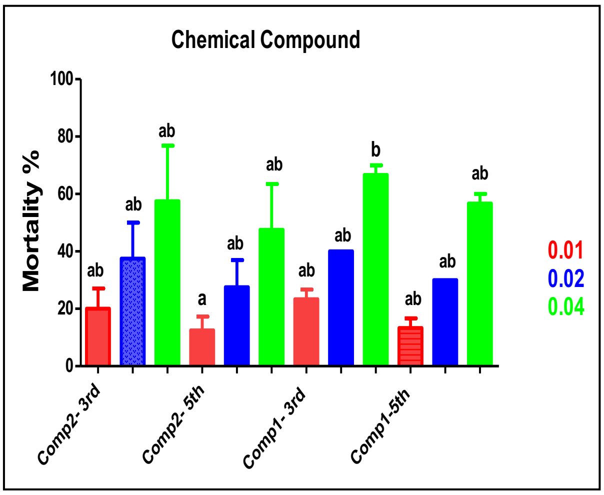

Figure 2. Effects of different concentrations of compounds 1 and 2 on the larval mortality of *T. confusum*

The present study showed that compounds 1 and 2 may induce insecticidal and larvicidal effects against *T. confusum* (Figure 1). The LC_{50} for both larval instars mortality was higher than the control group although the effect of compound 2 was more than the effect of compound 1. It is expected that smaller amounts of both compounds were sufficient to induce mortality in the larval stage.

2- Adulticidal activity of the compounds 1 and 2

The percentage of mortality on *T. confusum* adults with 0.01, 0.02 and 0.04 ppm of compounds 1 and 2 revealed significantly elevation ($P<0.05$) on all 3 doses when compared with the control group which were of 13.3 ±3.33, 23.3 ±3.33 and 36.6 ±3.33 % with compound 2 and 6.66 ±3.33, 16.6 ±3.33 and 26.6 ±3.33% with compound 1, respectively (see Table 5).

Table 5 also shows that the LC_{50} of (compound 2) (0.074 ppm) was more toxic than that of (compound 1) (0.106 ppm) on the of confused flour beetle.

Table 5. Mortality %, concentrations value of LC_{50} for different concentrations of compounds1 and 2 on *T. confusum* adults.

Concentrations Ppm	Control	Compound 2		Compound 1	
		% Mortality	LC_{50}	% Mortality	LC_{50}
0.01	0[a]	13.3[b] ±3.33	0.074	6.66[c] ±3.33	0.106
0.02		23.3[b] ±3.33		16.6[b] ±3.33	
0.04		36.6[b] ±3.33		26.6[c] ±3.33	

Cassida (1970) and Sun & Johnson (1972) revealed that the basic mechanism of chemical action is to inhibit various oxidation enzymes. This confirms our conclusion about insect susceptibility to pesticides, which is mainly due to the different levels of metabolizing enzymes in the insecticide; this conclusion is consistent with the findings of Cassida, 1966 and Franklin, 1972 as the rate of inhibition depends on the chemical concentration.

The compounds containing hydroxy and methoxy substituents showed antioxidant activity. Chalcones showed a good insect antifeedant activity against the 4th instar larvae *Achoea Janata* L. with castor leaf disc bio-assay method (Thirunarayanan, 2014).

4. CONCLUSION

In conclusion, the results of the present study revealed that 7-Hydroxy-9-(pyridine-4-yl)-6H-benzo[C] chromen-6-one (compound 2) showed significantly larvicidal and adulticidal against *T. confusum* than the 3-thinyl-1-(2-hydroxynaphthyl) - 1-propene (compound 1) effects.

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