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Design and synthesis of novel *N, N′*-substituted benzamide derivatives as potential insecticidal agents against the white mango scale insect, *Aulacaspis tubercularis* (Hemiptera: Diaspididae)

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A B S T R A C T

The white mango scale insect *Aulacaspis tubercularis* (Newstead) (Hemiptera: Diaspididae), which causes defoliation, drying out of young twigs, dieback, poor flowering, and decreased fruit output, causes serious damage to mango trees in Egypt. Attacks on mango fruits result in pink imperfections that lower their value as a commercial and export item. The current report aims to support the development of integrated management plans to combat *A. tuberculosis* and to identify more effective, eco-friendly insecticides. The bug may cause a considerable decrease in mango production and jeopardize the sustainability of mango plantation production if no management measures are taken. Currently, the application of a small number of insecticides—the majority of which have poor performance and are disruptive is the primary method used to manage *A. tubercularis*. In order to suppress this insect, we created novel pesticides called insect growth regulators (N, N′-substituted benzamide derivatives). By using both traditional and elemental spectroscopic investigations (IR, ^{1}HNMR, and ^{13}CNMR), these synthesized compounds which are linked to the most well-known insect growth regulator insecticides had their structures validated. The findings showed that *A. tubercularis* nymphs were more responsive to the evaluated treatments than adult females. After one day of application, all tested treatments resulted in a sizable proportion of mortality; the percentage of mortality increased with time for both *A. tubercularis* nymphs and adult females. Furthermore, the treatment with compound **3b** was more effective than other synthesized compounds, with a LC_{50} of 0.318 ppm against nymphs and a LC_{50} of 0.993 ppm against adult females of *A. tubercularis*. While the treatment with compound **5** was the least toxic for controlling this pest, many assessments are essential to studying the efficacy of these treatments on advantageous insects.

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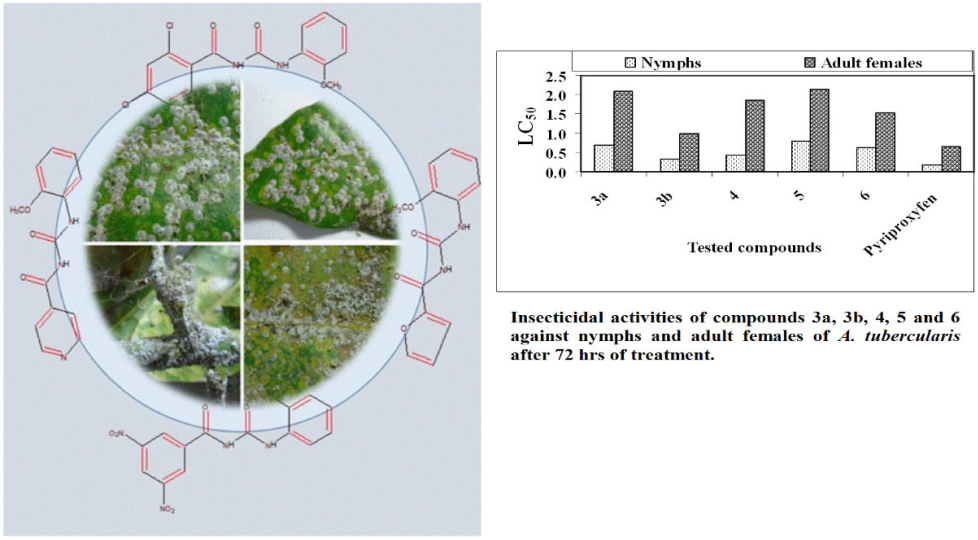


Insecticidal activities of compounds 3a, 3b, 4, 5 and 6 against nymphs and adult females of *A. tubercularis* after 72 hrs of treatment.

Graphic Abstract

1. Introduction

The white mango scale insect, *Aulacaspis tubercularis* (Newstead) (Hemiptera: Diaspididae), is one of the most devastating pests of the mango trees in Egypt.[1] The population estimates of white mango scale were formerly recorded on mangoes in a few parts of the world.[2] This pest injures mango by feeding on the plant sap through leaves, twigs, and mainly fruits, causing defoliation, drying up of young twigs, dieback, poor blossoming, and decreased fruit bearing. Fruits may mature with insufficient juice, and total death of the plant can become evident if infestation occurs at the nursery stage.[3] Attacks of the pest on mango fruits cause the development of conspicuous pink blemishes around its feeding sites, and as a result, the export potential of the fruits and their commercial value are greatly affected.[4,5] In mango orchards, the insect can result in a greater reduction of the mango yield and threaten the sustainability of mango production if no management measures are taken. Heterocyclic chemistry is currently one of the most dynamically developing branches of science. New compounds of this class are still wanted, due to wide application of these compounds, both in medicine as well as in industry.[6-10]

Insect Growth Regulators (IGRs), also called third-generation insecticides, are pesticides that disrupt the normal activity of the endocrine or hormone system of insects, affecting the development, reproduction, or metamorphosis of the target insect.[11,12] Several features of insect growth regulators (IGRs) make them attractive as alternatives to broad-spectrum insecticides.[13,14] Because they are more selective, they are less harmful to the environment and more compatible with pest management systems that include biological controls for example Pyriproxyfen, Figure 1.[15,16]

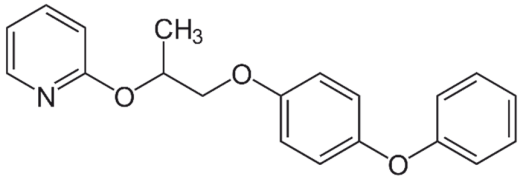


Fig. 1. Chemical Structure of Insect Growth Regulators Pyriproxyfen

These activities have been presumed to be due to depriving metals by thiourea.[17,18]. Accordingly, this work was aiming to (1) designing & characterizing of different compounds of poly functional novel benzamide. (2) Investigating their insecticidal effectiveness toward *A. tubercularis*. Our data is measured the first phase in insecticide discovery which it might be appreciated for insecticidal activity companies to enhance novel insecticides.

2. Material and Methods

All prepared target compounds were estimated melting point by the Fisher–John mechanical technique. Instrumentation and Chemicals. For this study, chemicals and solvents were purchased from Sigma-Aldrich. The IR spectra of the prepared compounds were analyzed using the KBr method, and ^{1}H NMR and ^{13}C NMR spectra were recorded on the spectrometer model Bruker ADVANCE 400 MHz. Pyriproxyfen reference insecticide was bought from Sigma-Aldrich. The insecticidal

activity of the target synthesized compounds and Pyriproxyfen was tested against nymphs and adult female of *A. tubercularis* under laboratory and field conditions.

2.1. The insecticide bio-activity

The original batches of *A. tubercularis* insects were collected from five different locations of Mango orchards (Goleck variety) at Esna district, Luxor governorate in first week of November, 2022. *A. tubercularis* nymphs and adult females' stages were used to determine toxicity under laboratory conditions of this study.

2.2. Bioassay Screening

Under the laboratory conditions at Agricultural Research Station, plant protection department in El-Mattana, Esna district, Luxor Governorate, the toxicological effectiveness of the all target synthetic components were evaluated via the mango leaf dipping techniques under the laboratory environments.[19-28] Concentrations of each compounds derivatives & 0.11% tween-80 used like surfactant. Only 50 *A. tubercularis* nymphs and 50 adults females were dipping for ten second in each concentration of prepared components (repeat 3 times). Insects which tested were stand to dray at 25 ^{0}C for about half hour in which the control (were dunked in H_2O and tween-80 only) of insects are also utilized. Applications are carried out at 5% relative humidity & at room temperature. After the employed pest had withered, they were transferred to glass jars containing distilled H_2O. With a novel binocular microscope the died & alive individuals were inspected, estimated and registered after one day, two days and three days after exposure. *A. tubercularis* that unable to move were considered dead. *A. tubercularis* individuals that unable to move were considered dead. The corrected mortality percentages were estimated according to Abbott formula.[29] The corrected mortality percentage of each compound was statistically computed according to Finney.[30]

$$\text{Corrected mortality percentage} = \left(1-\frac{\text{No. in T after treatment}}{\text{No. in C after treatment}}\right)\times 100$$

where: *T* = Mortality percentage in treatment.
C = Mortality percentage in control.

The average total efficacy percentage (General Mortality %) is the average of mortality percentages for the treatment through three times after application.[31]

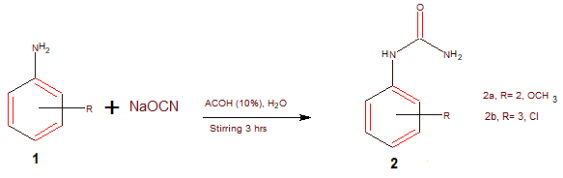
$$GM = \frac{A}{B+C}\times 100$$

GM= The average general mortality (%)
A= Sum of the overall corrected mortality of every application period (%).
B= Number of days after application.
C= Initial death date

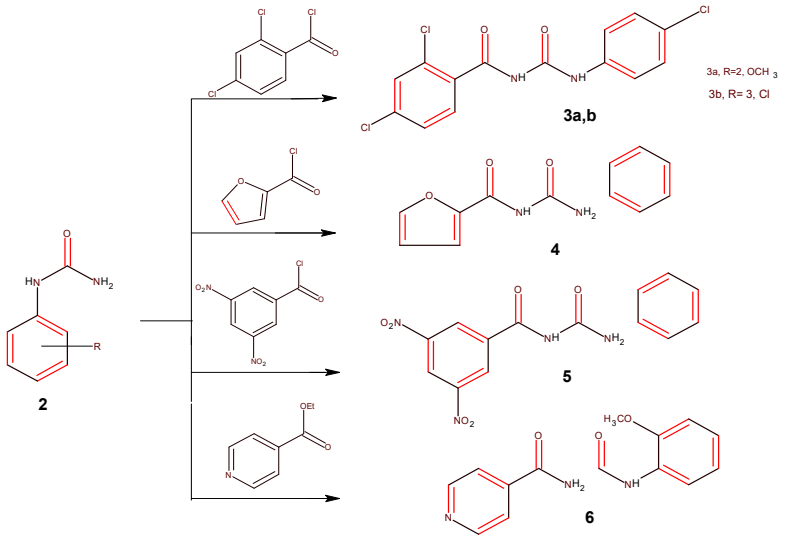
3. Result and Discussion

3.1. Synthesis

N-substituted phenylureas **3a, 3b, 4, 5** and **6** were synthesized by reaction of substituted anilines with sodium cyanate solution in presence of acetic acid. Under the same previous condition, compounds **2a,b**[32] were allowed to react with 2,4-dichlorobenzoyl chloride, fuoryl chloride, ethylpyridine-4-carboxylate or 3,5-dinitrobenzoyl chloride to afford 2,4-dichloro-*N*-[(2-methoxyphenyl)carbamoyl]benzamide **3a**, *N*-[(2-methoxyphenyl)carbamoyl]furan-2-carboxamide **4,** N-[(2-methoxy phenyl)carbamoyl]-3,5-dinitrobenzamide **5,** *N*-[(2-methoxyphenyl)carba mo yl]pyridine-4-carboxamide **6,** and *N*-[(3-chlorophenyl)carbamoyl]-2,4-dichlorobenzamide **3b ,** respectively. The structures of these compounds were elucidated by elemental and spectral analyses. The IR (ν, cm^{-1}) spectra of compounds **3a, 3b, 4, 5** and **6** showed absorption bands corresponding to NH_2 group while exhibit new absorption bands at 3223 cm^{-1} corresponding to NH, 1671-1620 corresponding to C=O groups. ^{1}HNMR (DMSO*d6*, δ, ppm) spectra revealed NH groups (exch) at 11.0 beside the 7H aromatic for (**3a, 3b** and **5**), 8H aromatic for (**6**).



Scheme 1: Synthesis of compounds **2a-b**



Scheme 2. Synthesis of compounds **3a-b, 4, 5** and **6**

3.2 Efficacy of the target synthesized compounds **3a, 3b, 4, 5, 6** and reference insecticide pyriproxyfen against different stages of *A. tubercularis* on mango leaves

3.2.1 On *A. tubercularis* nymphs

Effectiveness of the target synthesized compounds **3a, 3b, 4, 5, 6** and pyriproxyfen insecticides against *A. tubercularis* nymphs on mango leaves under laboratory conditions was executed as shown in (Table 1 and Figures 2- 4). The laboratory studies detected that the target synthesized compounds **3a, 3b, 4, 5, 6** and pyriproxyfen insecticide were toxic to *A. tubercularis nymphs* (Table 1). However, there were no initial kills (% of mortality was 0) among the tested treatments, but, their activities revealed a good impact against *A. tubercularis* nymphs Table 1, Figure 2.

The data mentioned that the percentages of mortality in *A. tubercularis* nymphs varied significantly between five synthesized compounds and reference insecticide pyriproxyfen at three days after application. The average mortality percentage was registered by 74.83 ± 0.70% after first day of application. Also, there were highly significant variances were observed among the five synthesized compounds and pyriproxyfen insecticide on the mortality percentage, the LSD value was 0.76** Table 1. Over the second day after application, the mortality percentages increased at all studied compounds. The average mortality percentage was listed by 77.72 ± 0.72% after the second day of treatment. LSD value between studied treatments was 1.12** (**Table 1**). Similarly after third day after the application, the mortality percentage increased than the previous periods in all tested treatments with an average (79.83 ± 0.88%). As well, there were obvious variances in the percentages of mortality between the assessed treatments (LSD value was 1.56**, **Table 1**).

From the general observations, it was found that the effectiveness of tested treatments on *A. tubercularis* nymphs were obvious from the first day after application, and continued gradually up to the third day, i.e., the longer the period after application, the greater the deaths **Table 1** and **Figs. 2-3**. It evident that the differences in percentages of deaths of *A. tubercularis* nymphs in the studied treatments, which may be due to the differences in the synthesis of chemistry of these the treatments and the different days after treatment, shown in **Figs. 2-3**.

Table 1. Nymphs mortality percentage of *A. tubercularis* under the target synthesized compounds 3a, 3b 4, 5, 6 and pyriproxyfen as references insecticide on mango leaves under laboratory conditions.

Compounds	Initial death	Mortality % ± S.E.			L.S.D. (Within days) at 0.05	Residual Efficacy (Accumulative mortality %)	Total Efficacy (General Mortality %)
		1st Day	2nd Day	3rd Day			
3a	0.0	74.93 ± 0.48	78.13 ± 0.71	80.07 ± 0.64	2.36 **	77.71 ± 0.81	58.28 ± 1.30
3b	0.0	76.13 ± 0.13	79.60 ± 1.01	81.87 ± 0.93	2.43 **	79.20 ± 0.92	59.40 ± 1.44
4	0.0	73.07 ± 0.58	76.33 ± 0.79	78.67 ± 0.35	1.72 **	76.02 ± 0.87	57.02 ± 1.41
5	0.0	71.73 ± 0.35	74.53 ± 0.53	75.60 ± 0.40	0.48 **	73.96 ± 0.62	55.47 ± 1.00
6	0.0	72.67 ± 0.35	75.07 ± 0.27	76.53 ± 0.13	1.03 **	74.76 ± 0.58	56.07 ± 0.98
Pyriproxyfen	0.0	80.47 ± 0.18	82.67 ± 0.67	86.27 ± 0.13	1.28 **	83.13 ± 0.87	62.35 ± 1.46
Average Mortality % /Day	0.0	74.83 ± 0.70	77.72 ± 0.72	79.83 ± 0.88	---------	77.46 ± 0.52	29.05 ± 0.55
L.S.D. (Within day) at 0.05	0.0	0.76 **	1.12**	1.56**	0.67**	0.48**	-------
L.S.D. (Within days × treatments) at 0.05				1.17**			

S.E = Standard error; * Significant at P ≤ 0.05; ** Highly significant at P ≤ 0.01; L.S.D. = Least significant difference.

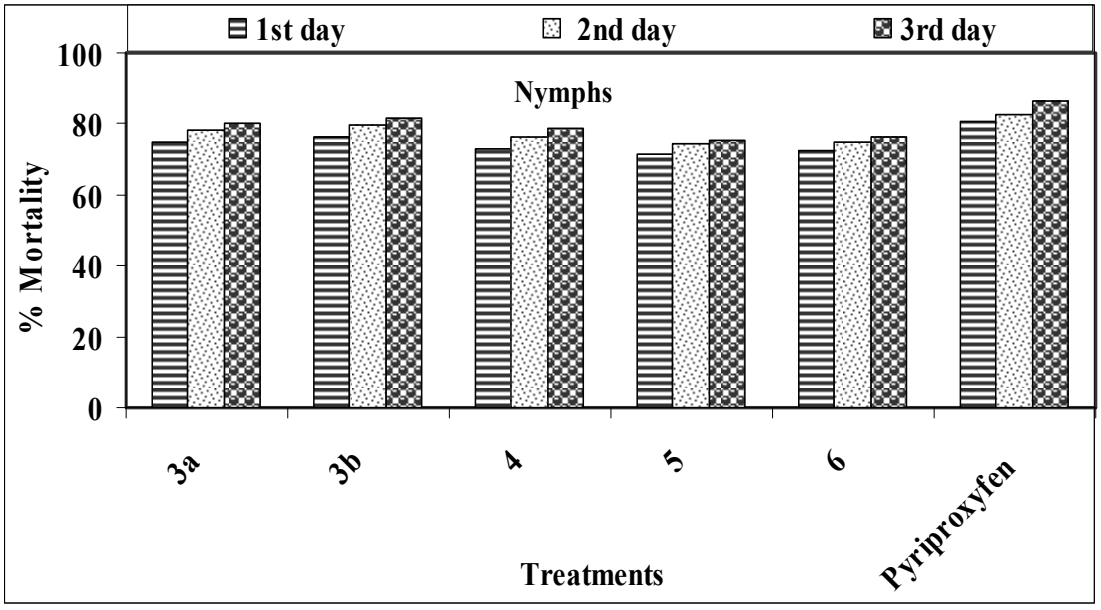


Fig. 2. Effectiveness of the target synthesized compounds and pyriproxyfen insecticide against *A. tubercularis* nymphs on mango leaves under laboratory conditions

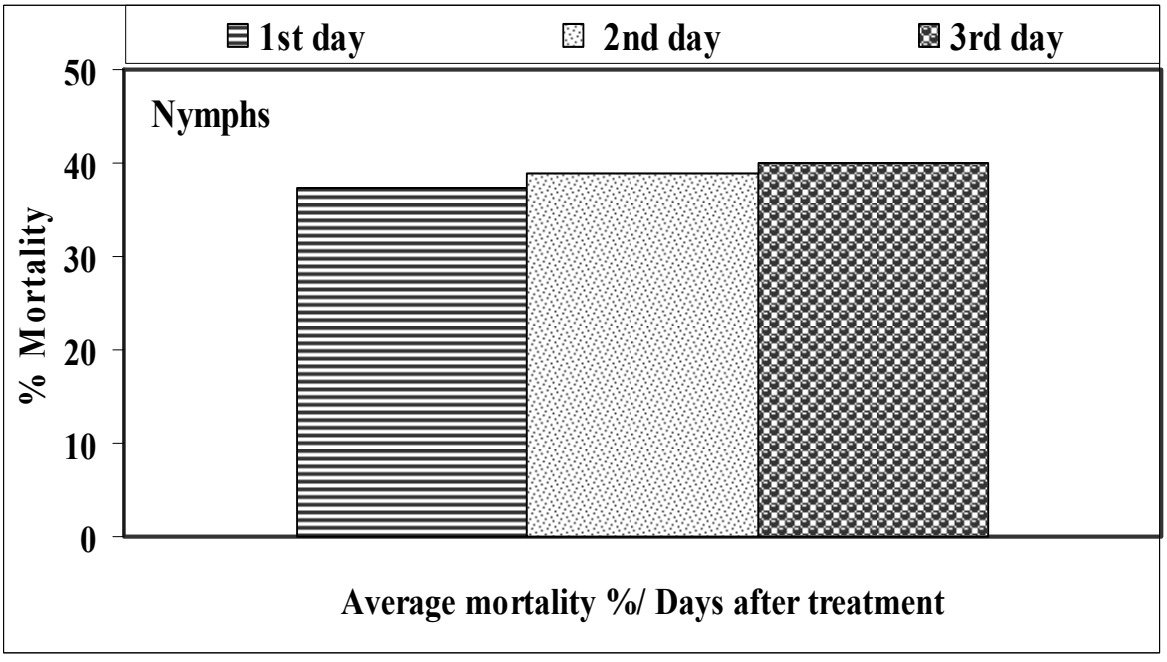


Fig. 3. Duration effects of the target synthesized compounds and pyriproxyfen insecticide against *A. tubercularis* nymphs on mango leaves under laboratory conditions

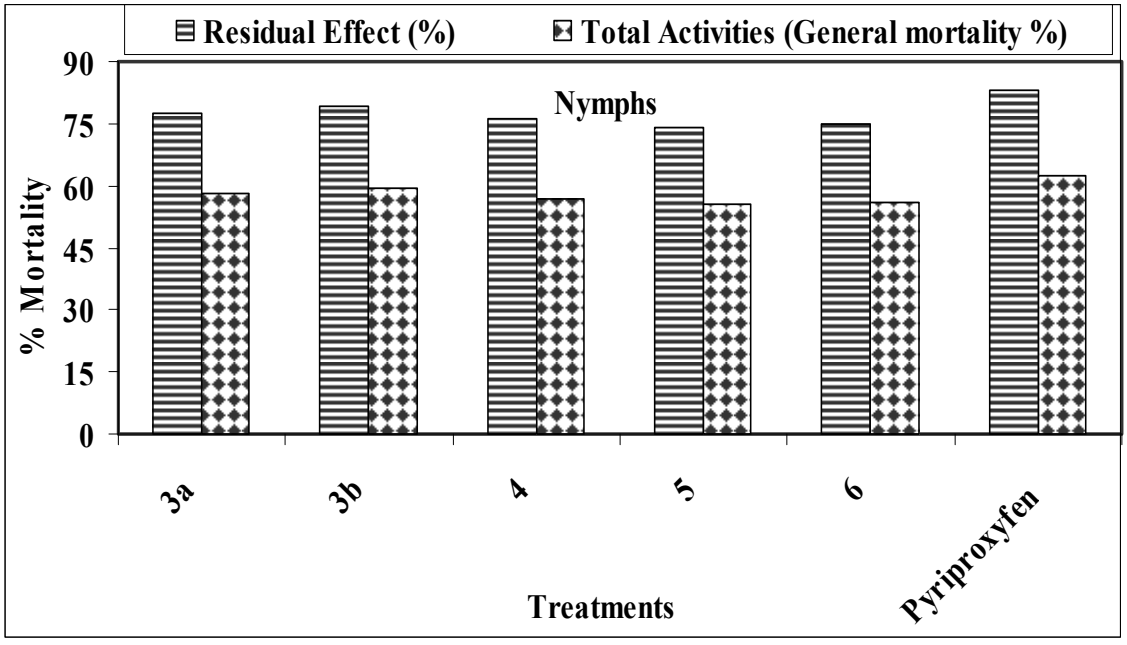


Fig. 4. Residual and total efficacy of influences of the target synthesized compounds and pyriproxyfen insecticide against *A. tubercularis* nymphs on mango leaves under laboratory conditions.

The treatment with compound **3b** appeared higher efficacy in the residual impact of death by 79.20 ± 0.92% as compared to the tested other tested treatments. However, the treatment with compound **5** was offered less efficacy in the percentage of accumulative mortality by 73.96 ± 0.62%. Furthermore, the average of the total general mortality raised in the compound **3b** by (59.40 ± 1.44%) as compared to the studied compounds. On contrarily, the least effectiveness was found in compound 5 by (55.47 ± 1.00%), show in Table 1 and Figure 4.

Moreover, the combined interaction between the studied treatments and times after application (in days) had a highly important differences on the nymphs mortality percentage (LSD value was 1.17**) was represented Table 1.

3.2.2- On *A. tubercularis* adult females:

The percentages of mortality of *A. tubercularis* adult females within three days under the target synthesized compounds **3a, 3b, 4, 5, 6** and pyriproxyfen insecticide were assessed on mango leaves under laboratory conditions Table 2 and Figures 5-7. Efficacy of the target synthesized compounds **3a, 3b, 4, 5, 6** and pyriproxyfen insecticide were toxic against *A. tubercularis* adult females within the laboratory **Table 2**.

The data showed that the percentages of death were zero in their initial efficiency between the studied treatments. Afterthat, the percentages of mortality in *A. tubercularis* adult females varied significantly between the five synthesized compounds and reference insecticide pyriproxyfen during the three days after application. The average death percentage was exhibited by 72.09 ± 0.55% after first day of treatment. In addition, the statistical analysis of data demonstrated that there were significant differences among tested treatments in their efficiency one day post treatment, the LSD value was 1.40 ** **Table 2**.

Tested treatments gave moderate control against *A. tubercularis* adult females at the second days after application. Also, the death percentages increased gradually at all tested compounds; the average mortality percentage was 74.33 ± 0.64%. LSD value between tested treatments was 1.30** **Table 2**. Likewise after third day after the application, the mortality

percentage raised compared to the previous days in all assessed treatments with an average (75.76 ± 0.83%). Moreover, the statistical analysis of the data revealed significant variances in the percentages of mortality among studied treatments (L.S.D. value was 1.11**, **Table 2**).

Clearly, the effectiveness of assessed treatments on *A. tubercularis* adult females were significant from the first day after application, and continued gradually up to the third day, i.e. the longer the period after application, the greater the deaths Table 2 and Figures 5-6. It could be mentioned that the mortality percentages varied based on the treatments used and chemistry structure of these treatments and the time after exposure, shown in Figures 5-7. The statistical analysis gave significant variances in the percentages of mortality between duration after application (three days), were recorded at all tested treatments, shown in **Table 2**.

For explanation, the treatment with compound **3b** appeared higher efficacy in the residual effect of death for adult females by 75.51 ± 0.63% than the assessed other compounds. While, the treatment with compound **5** exhibited less efficacy in the residual impact of death by 71.42 ± 0.44%. As well, the average of the total general mortality of adult females increased in the compound **3b** by (56.63 ± 1.03%) as compared to the tested other compounds. Contrarily, the least efficacy was found in compound **5** by (53.57 ± 0.67%), as seen in (**Table 2** and **Figs. 5-7**). In addition, the combined interaction among the assessed treatments and times after application (in days) had a very important variances on the adult females mortality percentage LSD value was 1.43**, **Table 2**.

Table 2. Adult females' mortality percentage of *A. tubercularis* under the target synthesized compounds **3a, 3b 4, 5, 6** and pyriproxyfen as references insecticide on mango leaves under laboratory conditions.

Compounds	Initial death	Mortality % ± S.E.			L.S.D. (Within days) at 0.05	Residual Efficacy (Accumulative mortality %)	Total Efficacy (General Mortality %)
		1st Day	2nd Day	3rd Day			
3a	0.0	71.87 ± 0.27	74.40 ± 0.46	75.33 ± 0.74	2.34 *	73.87 ± 0.58	55.40 ± 0.90
3b	0.0	73.47 ± 0.13	75.47 ± 0.35	77.60 ± 0.61	1.91 **	75.51 ± 0.63	56.63 ± 1.03
4	0.0	70.80 ± 0.61	72.93 ± 0.71	73.47 ± 0.27	1.96 *	72.40 ± 0.49	54.30 ± 0.71
5	0.0	70.00 ± 0.40	71.60 ± 0.40	72.67 ± 0.48	2.02 *	71.42 ± 0.44	53.57 ± 0.67
6	0.0	70.27 ± 0.48	72.27 ± 0.27	73.20 ± 0.46	1.98 *	71.91 ± 0.48	53.93 ± 0.75
Pyriproxyfen	0.0	76.13 ± 0.81	79.33 ± 0.35	82.27 ± 0.27	2.50 **	79.24 ± 0.92	59.43 ± 1.53
Average Mortality % /Day	0.0	72.09 ± 0.55	74.33 ± 0.64	75.76 ± 0.83	---------	74.06 ± 0.44	55.54 ± 0.46
L.S.D. (Within day) at 0.05	0.0	1.40 **	1.30 **	1.11 **	0.82 **	0.58 **	-------
L.S.D. (Within days × treatments) at 0.05	1.43**						

S.E = Standard error; * Significant at P ≤ 0.05; ** Highly significant at P ≤ 0.01; L.S.D. = Least significant difference.

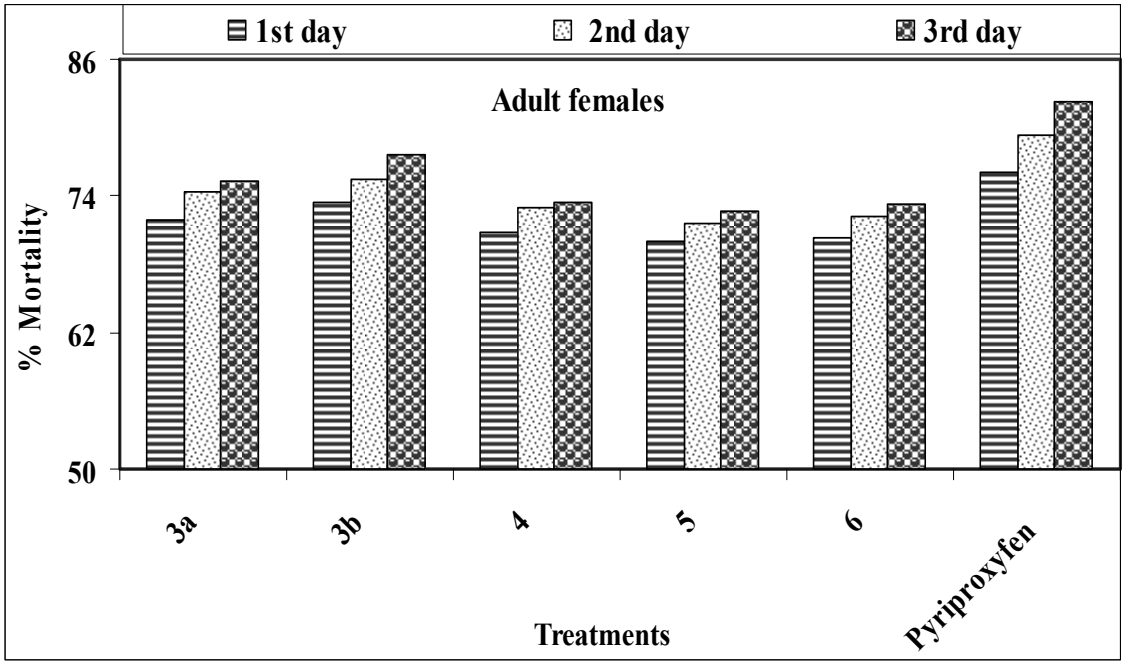


Fig. 5. Effectiveness of the target synthesized compounds and pyriproxyfen insecticide against *A. tubercularis* adult females on mango leaves under laboratory conditions.

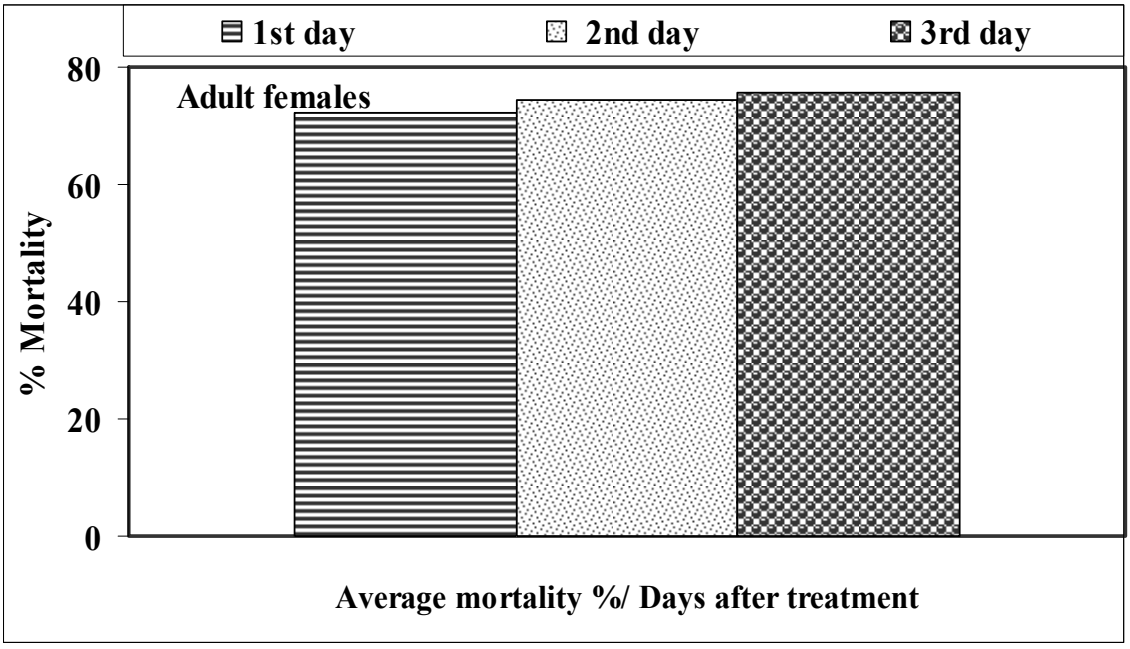


Fig. 6. Duration effects of the target synthesized compounds and pyriproxyfen insecticide against *A. tubercularis* adult females on mango leaves under laboratory conditions.

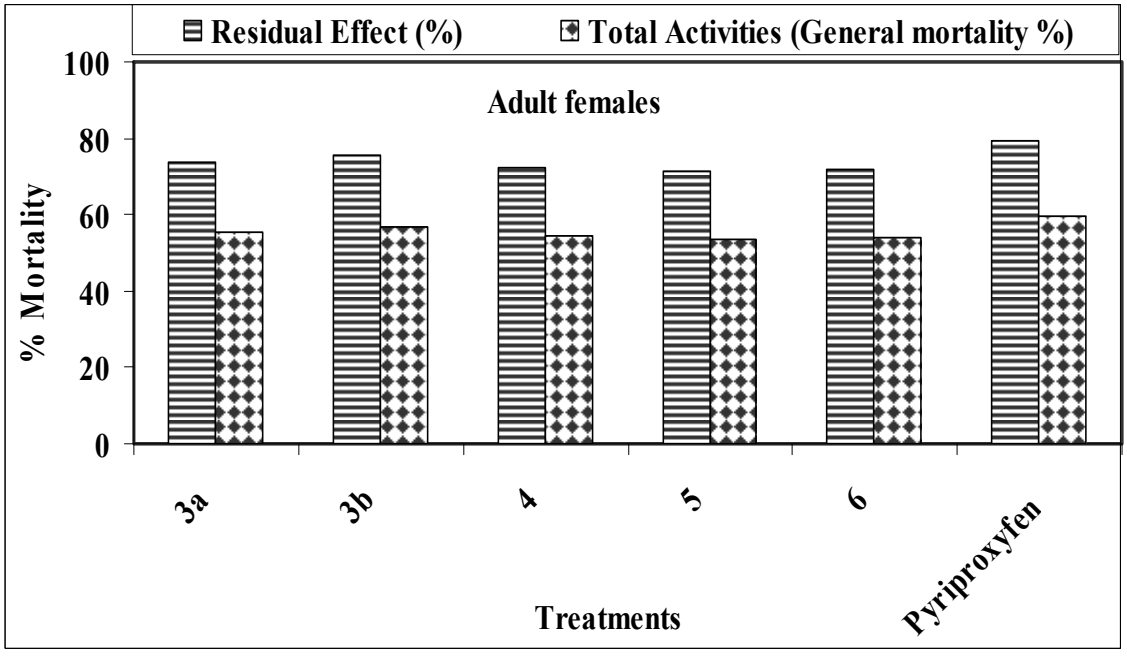


Fig. 7. Residual and total efficacy of influences of the target synthesized compounds and pyriproxyfen insecticide against *A. tubercularis* adult females on mango leaves under laboratory conditions**.**

Clearly those *A. tubercularis* nymphs were more susceptible to all tested treatments than adult females. All tested treatments caused a significant percentage of mortality after one day of application as the percentage of mortality increased gradually with time for both *A. tubercularis* nymphs and adult females. In addition, the treatment with compound **5** was the lowest toxic in controlling the nymphs and adult female stages of *A. tubercularis* on mango leaves. However, the treatment with compound **3b** was the highest efficacy against this pest. The results exhibited that there were very variances between tested treatments and time after exposure. Also, the assessed treatments had no adverse influence on the mango leaves.

Table 3: Insecticidal effectiveness of components **3a, 3b, 4, 5**, **6** and Pyriproxyfen as references insecticide against nymphs & adults female of *A. tubercularis* insects after 72 hrs of treatment.

	Nymphs				Adult females			
Comp.	LC_{50} (ppm)	Slope	Toxic ratio[a]	$\chi 2$	LC_{50} (ppm)	slope	Toxic ratio	$\chi 2$
3a	0.690	0.514 ± 0.267	24.20	0.049	2.092	0.581 ± 0.265	31.00	0.183
3b	0.318	0.492 ± 0.277	52.51	0.036	0.993	0.590 ± 0.278	65.25	0.335
4	0.426	0.487 ± 0.274	39.20	0.110	1.858	0.571 ± 0.265	34.87	0.344
5	0.808	0.534 ± 0.273	20.66	0.036	2.132	0.588 ± 0.272	30.39	0.169
6	0.626	0.487 ± 0.274	26.67	0.042	1.540	0.605 ± 0.268	42.07	0.123
Pyriproxyfen	0.167	0.402± 0.278	100	0.075	0.648	0.497 ± 0.274	100	0.105

Notes: [a]Toxicity ratio is calculated as Pyriproxyfen's LC_{50} value for baseline toxicity / the compounds' LC_{50} value χ 100.

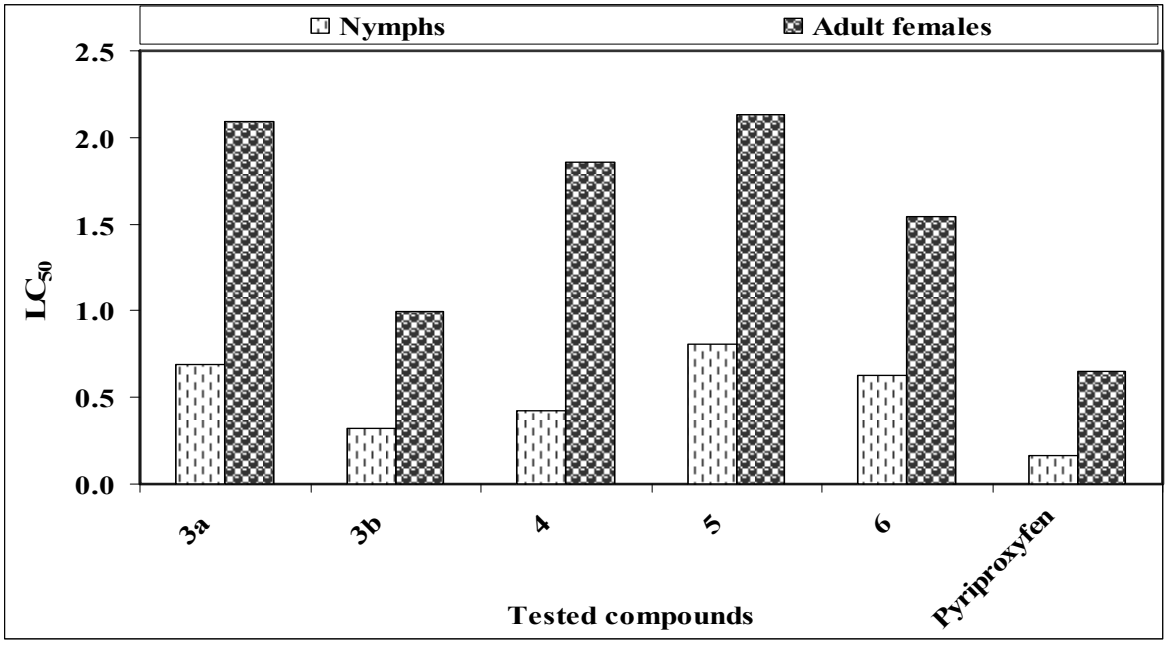


Fig. 8. Insecticidal activities of compounds **3a, 3b, 4, 5** and **6** against nymphs and adult females of *A. tubercularis* after 72 hrs of treatment

3.3. Insecticidal bio-efficacy screening

Toxicity test for the nymphs of *A. tubercularis* as shown in **Table 3** and **Fig. 8** that compounds **3a, 3b, 4, 5** and **6,** respectively shows the LC_{50} values of 0.690, 0.318, 0.426, 0.808, and 0.626, respectively. However, LC_{50} of Pyriproxyfen was 0.167 ppm. The toxicity index being 24.20, 52.51, 39.20, 20.66 and 26.67% for **3a, 3b, 4, 5** and **6,** respectively. Toxicity test for the adult female of *A. tubercularis* as shown in Table 3 and Figure 8 that compounds **3a, 3b, 4, 5** and **6**, respectively shows the LC_{50} values of 2.092, 0.993, 1.858, 2.132 and 1.540 ppm, respectively. However, LC_{50} of Pyriproxyfen was 0.648 ppm. The toxicity index being 31.00, 65.25, 34.87, 30.39 and 42.07% for **3a, 3b, 4, 5** and **6**, respectively.

4. Structure-action relationship (SAR)

According to the toxicity value in **Table 3** and **Fig. 8** by using a computerized regression analysis program, the median lethal concentration (LC_{50}) and slope values of the target compounds were computed and reported as parts per million (ppm). The insecticidal activity of the synthesized compounds (**3a, 3b, 4, 5** and **6**) were compared with Pyriproxyfen against nymphs of *A. tubercularis* which represented by red lines and adult female which represented by black lines after 72 h of treatment Figure 9. The structure-action relationship was established. The benzamide compound **3b** is more active against nymphs and adult females of pest than the other benzamide synthesized derivatives. The high in activity of compound **3b** may be due to the presence of 2,4-dichloro phenyl and ortho methyl moiety in their structure. The presence of chloro phenyl and methoxy moieties in this compound which is considered as an electron-withdrawing groups increase the activity than the other urea and/or benzamid synthesized derivatives compared to the commercial Pyriproxyfen. On the other hand, the compound **4** gave good activity may be due to the presence of the methoxy phenyl and furoyl moiety in its structure.

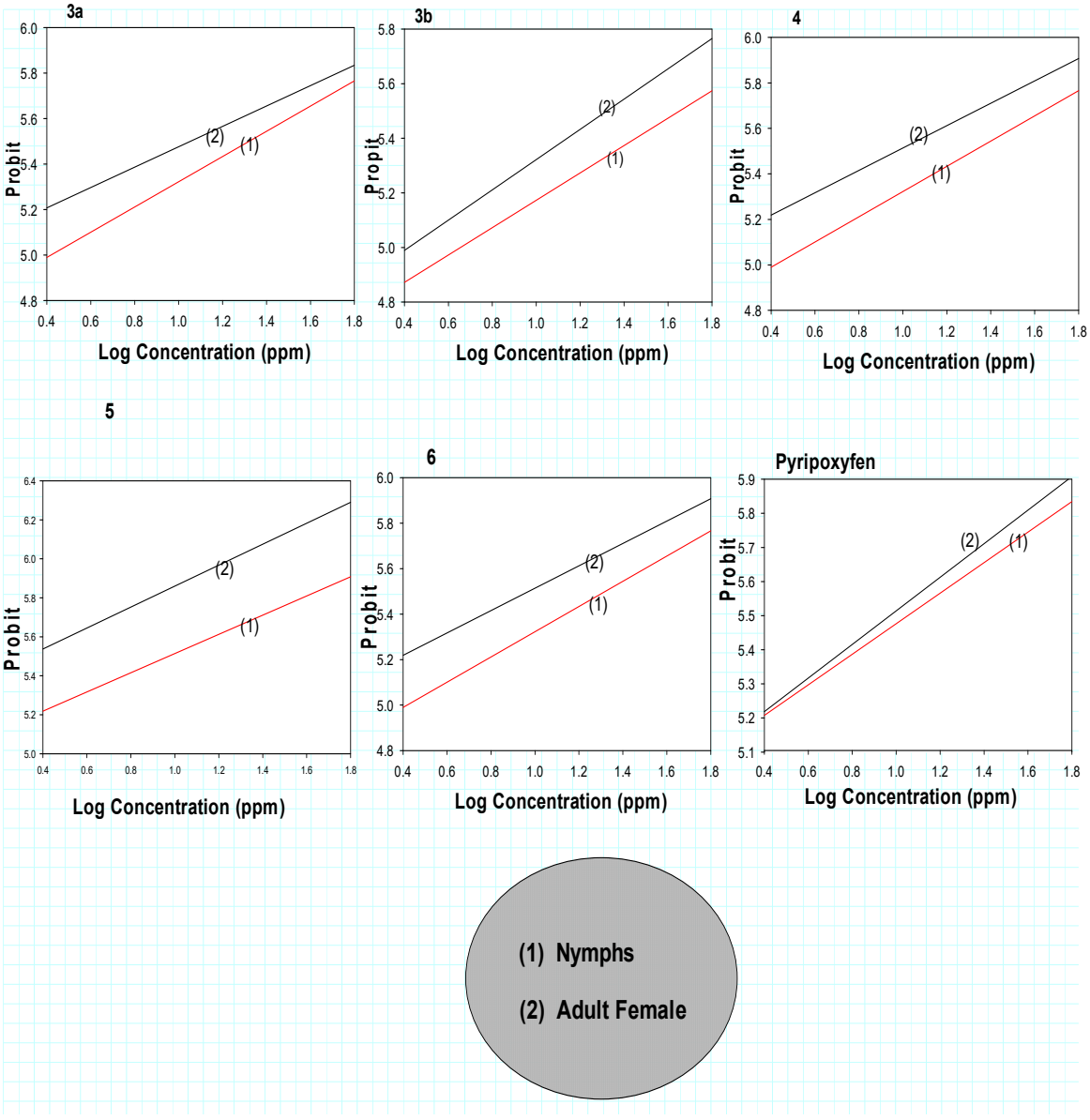


Fig. 9. insecticidal activities of compounds **3a, 3b, 4, 5** and **6** against nymphs and adult female of *A. tubercularis* after 72 hrs of treatment

5. Experimental

All melting points are uncorrected and were determined by Kofeler melting point apparatus. IR (cm^{-1}) spectra were recorded (KBr disc) on a Shimadzu DR-8001 spectrophotometer. ^{1}HNMR (DMSO-d_6) spectra were recorded at 200 MHz and at 400 MHz on a Varian Gemini NMR spectrometer and also at 400 MHz , the chemical shift is expressed in δ value (ppm) using TMS as an internal reference. Elemental analyses were carried out on a Perkin-Elmer 240°C Micro analyzer. The mass spectra were performed on Micro mass 7070 E spectrometer using Direct Inlet and Shimadzu Qp-2010 Plus mass spectrometer using Electronic Ionization mode operating.

General procedure for synthesis of compounds 3a,b-6

Synthesis of phenyl urea derivatives 2

Amino derivatives (10 mmole) dissolved in 100 ml dil. AcOH (10%) was added to 50 ml water solution of sodium cyanate (0.1mol) and stirred for 6 hours. The precipitated product was flirted off and crystallized from 1, 4-dioxane. A mixture of 1-(4-methoxyphenyl)urea (14mmole) and Acid chloride (2 mmole) was refluxed under dry conditions for 5

hours, cooled and treated several times with petroleum ether (80-100). The formed ppt was filtered off and crystallized from ethanol.

2,4-dichloro-*N*-[(2-methoxyphenyl)carbamoyl]benzamide 3a

White solid (70% yield), mp. 125-127 ˚C; IR (ν, cm^{-1}): 3448 (OH), 3323 (NH), 2926.3 (CH_{alph}), 1662 (C=O). ^{1}HNMR (DMSO-d_6), (δ ppm): 9.79 (s, 1H, NH_{exch}), 7.87-6.96 (m, 7H, H_{arom}+NH_{exch}), 3.86 (s, 3H, CH_3). Mass spectrum showed molecular ion peaks at m/z= 339 (M^+ 22.8%), 295.72 (57.7%), 293.75 (84.7%), 233.04 (17.04%), 194.18 (26.0%), 190.02 (80.4%), 151.16 (100%), 146.34 (9.2%), 144.4(15.9%), 86.87(6.8%). ^{13}CNMR (DMSO-d_6), (δ ppm): 164.1(**C**=O), 151.03 (**C**=O), 150.3 (**C**-OMe), 149.6 (O-**C**H_3), 148.6 (**C**-Cl, o-position), 148.1 (**C**-Cl, p-position), 148.0 (**C**-NH), 139.9 (**C**-CO), other aromatic **C**-H carbons at 136.2 , 134.27, 131.2, 129.9, 129.8, 128.9, 128.0. Anal. for $C_{15}H_{12}Cl_2N_2O_3$ (339.17) calcd/found: C: 53.12/53.21, H: 3.57/3.25 and N: 8.36/8.50%.

***N*-[(3-chlorophenyl)carbamoyl]-2,4-dichlorobenzamide 3b**

White solid (66% yield), mp. 119-120˚C. IR (ν, cm^{-1}): 3476.1(O-H), 3270.3 (N-H), 3047.6 (CH_{arom}), 1707 (C=O); ^{1}HNMR (DMSO-d_6), (δ, ppm): 12.28 (s, 1H, NH_{exch}), 12.11 (s, 1H, NH_{exch}), 7.94-7.34 (m, 7H, H_{arom}). Mass spectrum showed molecular ion peaks at m/z= 343 (M^+ 0.61%), 233.03 (12.45%), 190.02 (2.37%), 148.05 (13.02%), 100.99 (7.97%), 89.08 (12.79%). ^{13}CNMR (DMSO-d_6), (δ ppm): 181.12(**C**=O), 180.6 (**C**=O), 151.3 (**C**- Cl, p-position), 150.6 (**C**-Cl, o-position), 148.1 (**C**-Cl, o-position), 144.0 (**C**-NH), 141.3 (**C**-CO), other aromatic **C**-H carbons at 139.9, 138.9, 137.8, 136.09, 132.9, 128.9, 128.1. Anal. For $C_{14}H_9Cl_3N_2O_2$ (343.6) calcd/found: C: 48.94/48.99, H: 2.64/2.56 and N: 8.15/8.25%.

***N*-[(2-methoxyphenyl)carbamoyl]furan-2-carboxamide 4**

White solid (73% yeild), mp. 213 ˚C; IR (ν, cm^{-1}): 3408 (OH), 3223.3 (NH), 2926.3 (CH_{alph}), 1671 (C=O); ^{1}HNMR (DMSO-d_6), (δ ppm): 11.0 (s, 1H, NH_{exch}), 10.93(s, 1H, NH_{exch}), 8.02-6.76 (m, 7H, H_{arom}), 3.86 (s, 3H, CH_3). Mass spectrum showed molecular ion peaks at m/z= 260 (M^+ 7.9%), 230.12 (9.45%), 154.12 (6.36%), 100.01 (7.12%), 78.11 (11.17%). ^{13}CNMR (DMSO-d_6),(δ ppm): 158.91(**C**=O), 151.03 (**C**=O), 145.2 (**C**-OMe), 139.9 (O-**C**H_3), 138.3(**C**-NH), 135.23 (**C**-CO), other aromatic **C**-H carbons at 132.2, 129.5, 128.7, 127.2, 122.8, 121.6. Anal. for $C_{13}H_{12}N_2O_4$ (260.21): calcd/found: C:60.12/60.21, H: 4.67/4.45 and N:10.76/10.56%.

***N*-[(2-methoxyphenyl)carbamoyl]-3,5-dinitrobenzamide 5**

Brown solid (41% yield) mp. 180˚C; IR (ν, cm^{-1}): 3430.1 (OH), 3282.7(NH), 3010 (CH_{arom}), 1633.21 (C=O). ^{1}HNMR (DMSO-d_6), (δ ppm): 11.04 (S, 1H, NH_{exch}), 10.79 (S, 1H, NH_{exch}), 7.83-7.5(m, 7H, CH_{arom}), 3.4 (S, 3H, CH_3). Mass spectrum showed molecular ion peaks at m/z= 360 (M^+ 12.56%), 254.15 (7.36%), 196.18 (5.36%), 108.13 (13.78%), 78.11 (7.17%). ^{13}CNMR (DMSO-d_6), (δ ppm): 180.2(**C**=O), 177.03 (**C**=O), 172.23 (**C**-OMe), 167.9 (C-O**C**H_3), 155.5 (**C**-NO_2), 143.8 (**C**-NH), 139.3 (**C**-CO), other aromatic **C**-H carbons at 134.2, 129.5, 128.8, 1282, 127.8, 112.6. Anal. For 122.9 (C-CH3); Anal. Calcd. For $C_{15}H_{12}N_4O_7$ (360.27): calcd/found: C: 54.01/54.11, H: 3.36/3.42 and N:15.55/15.50%.

***N*-[(2-methoxyphenyl)carbamoyl]pyridine-4-carboxamide 6**

White solid crystals mp.205 ˚C ; IR (ν, cm^{-1}): 3468 (NH), 3350 (NH), 1658 (C=O), 1620 (C=O). ^{1}HNMR (DMSO-d_6), (δ ppm): 14.09 (s, 1H, NH_{exch}), 7.87-6.46 (m, 8H, H_{arom} + NH_{exch}). Mass spectrum showed molecular ion peaks at m/z= 271 (M^+ 9.30%), 241.24 (11.23%), 212.36 (14.23%), 195.18 (3.12%), 151.16 (4.12 %), 122.12 (1.02 %), 108.02 (13.17%), 87.11 (2.96%).^{13}CNMR (DMSO-d_6), (δ ppm): 167.1 (**C**=O), 165.03 (**C**=O), 150.0 (**C**-OMe), 145.6 (O-**C**H_3), 140.5 (**C**-NH), 139.9 (**C**-CO), other aromatic **C**-H carbons at 135.2, 130.2, 128.9, 129.8, 128.9, 128.0. Anal. calcd for $C_{14}H_{13}N_3O_3$ (271.27): C, 61.99, H:4.83/4.66 N:15.49/15.59%.

6. Conclusion

A new series of benzoyl urea analogue were chemically synthesized and their chemical structure was established based on spectral and elemental data. The activity of new five target compounds was tested against nymphs and adult females of *A. tubercularis* after 72 hrs of treatment and they showed good toxicological activities. It has been found that the compound **3b** has an activity close to that of the standard reference insecticide Pyriproxyfen against nymphs, who's LC50 was found to be 0.318 ppm, whereas the LC50 for Pyriproxyfen was 0.167 ppm. Furthermore, the treatment with compound **3b** against adult females of *A. tubercularis* was more effective, with a LC50 of 0.993 ppm , while the LC50 of Pyriproxyfen was 0.648 ppm.

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