The Effect of Pyrrolidinium Bromide Salt in The Life of The Southern Cowpea Beetle Callosobruchus Maculatus (Fab) (Coleoptera: Chrysomelidae)

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Abstract

The study aimed to evaluate the efficacy test of a chemical compound (pyrrolidinium bis - bromide salt) laboratory-prepared in the life of the southern cowpea beetle Callosobruchus maculatus, which is one of the most important pulses stored pest. The compound N1 was prepared and the structure was proved using ¹H NMR, IR technique. For treating the seeds out, three concentrations from N1, 500, 1500, 3000 ppm, were prepared. The results showed that the compound outperformed the percentage of repellent (prevention of laying eggs), with the concentration of 500 ppm registered the lowest number of eggs laid, with 96.67 eggs and an repellent rate of 53.97 %, compared to 210.00 eggs. While the results showed a significant effect when the concentration increased. This caused a 66.32 % drop in first-generation personnel from the highest rate of 95.00. The higher concentration also showed the lowest productivity compared with the rest of the concentrations, at 21.05 % compared to controlling sample 45.45%, and had no significant effect on increasing the duration of the pupal stage by 7.83 days compared to 7.50 days. Compared to 7.50 days of control, it affected the increase in the 7.50-day period of the larval stage compared to the control of 5.50 days. The 1500 ppm concentration did not affect the vitality of the seeds after being treated as they were not significantly different from control. The results also showed that not all of the compound's concentrations had a repellent effect against the southern cowpea beetle.

Keywords: Maculatus, Cowpea, Beetle.

1. Introduction

Pest that attacked stored grain caused serious damage to grains stored as a result of their feeding on these substances, causing quantity and quality decreasing due to contamination by their secretions and wastes [1]. The southern cowpea beetle is one of the most important pests affecting legumes in the world in general and Iraq in particular and is globally widespread, causing significant grain losses.[2]. It is one of the main pests in the stores, characterized by its strong seed and multi-generationality. It belongs to the Chrysomelidae family of the order of Coleoptera, which infects legumes seeds in the field and can be moved with them to the store, and prefers the seeds of cowpea to other types of seeds as they are a rich source of protein.[3]. Their seriousness lies in their lack of specialization in feeding on one specific family, but their larvae can grow and develop on about 35 types of legumes seeds, in addition to their ability to move and migrate to cause new infections in fields and stores[4] and[5]. The cowpea is one of the economic crops in the world, especially in Asia, Africa and Europe. It is a versatile crop that provides food for humans and feed for livestock, which are cash-generating goods for farmers and small entrepreneurs [6,7]. The researchers used several methods to control the southern cowpea beetle, including the use of chemical pesticides, which are one of the most common methods in the fight against insect pests because of their rapid impact and effectiveness in these insects. Pest control is largely based on the use of organic chemical pesticides, most of which are registered as neuro-pesticides affecting the nervous system [8]. Its importance lies in the fact that most of the total pesticides used are currently included in them because of their rapid impact and effectiveness in insect pests over short periods of time, their bio-stability and chemical stability and their ability to withstand environmental factors such as heat, radiation and humidity [9]. Quadruple ammonium salts are one of the most important substances used largely in cleaning materials as disinfectants for their effect as a bacterial antibiotic in addition to their use in the preparation of drugs, pesticides, dyes, etc.[10] which are polymers that are increasingly effective by increasing the length of the chain for the Al-Amin group[11]. This is why many researchers have tended to prepare and study new types of these polymers, especially those used to
disinfect surfaces from microbes, because of their ability to keep these surfaces sterile for long periods[12]. A number of organic chemical compounds were used as anti-feeding insecticides on the surface of the plant, such as carbamate and others, which are organic ring compounds[13], and whose mechanism of action remained mysterious for a long time until their effects on the nervous system in insects became apparent, and their efficiency increased in terms of toxic damage [14].

2. Materials and Methods

2.1 Insect breeding

Samples of reddish cowpea seeds infected with the southern cowpea beetle were collected. Placed in 800 ml sterile glass bottles, sealed with a well-ventilated velvet cloth, fastened to rubber belts and then placed in the incubator at a temperature of 30°C ± 2 and relative humidity 70 ± 5% left for three months to get many generations. The farm was renovated to dispose of the materials generated as a result of insect activity and breeding and to prepare new farms for use in subsequent experiments[15]. Adult insects were diagnosed at the Natural History Museum, University of Baghdad.

2.2 Laboratory preparation of bis-pyrrolidinium salt

Pyrrolidinium quadruple salts were prepared based on Menshutkin [16] and [17]. In chemistry laboratories at the college of agriculture and the college of education for pure sciences at Kirkuk university. Pyrrolidin ready-made Pyrrolidin and 1-bromo hexane were obtained from local markets taken 1 g after weighing in Baker using a delicate balance and mixed in a circular circle after adding an appropriate amount of dry toluene solvent using droper, shake the mixture by hand until the color disappears and put the container of the mixture on the device (Magnetic stirrer heater) for 48 hours, after cooling at room temperature The resulting material was purified by withdrawing toluene from it under the pressure of the vacuum evaporator (rotary evaporate was performed recrystallization) to purify the resulting material using the diethyl ether CH₂CH₂OCH₂CH₃, adding the solvent to the mixture and heating it and then filtering the mixture and then cooling the resulting material to obtain the required salt crystals[18]. The compound was prepared by adding a compound, halide al-Kyle, to the resulting material above, and followed the same steps mentioned until the compound 1.1- (hexane-1,6-diyl) bis (1-heptylpyrrolidin-1-ium) coded with N1. Based on previous research [19]. Concentrations attended 500, 1,500 and 3,000 parts per million to test her toxicity on the incomplete phases of the Southern Cowpea Beetle C. maculatus and the emergence of complete insects after treatment by taking 0.3 g of the pre-prepared compound after dissolving it in 100 ml of hexane solvent to prepare the standard stock solution with a concentration of 3000 ppm per million, which it later attended from other stacks.

2.3 The effect of pyrrolidinium bromide salt on some aspects of the life of the southern cowpea beetle

Samples of red cowpea seeds were treated with a chemical compound prepared at 20 g per replication and three replications per treatment per concentration. By submerging 20 g of seeds in 1.5 ml of the said concentrations, they were left to dry and then placed in a 300 g glass bottle, transported to 5 adult pairs, covered with a well-ventilated polished fabric and tightly closed with a rubber band, while the comparison was treated only with normal hexane.[2] Registered the number of eggs placed and the duration of the larval and pupal stages, the number of emerging adults and the calculation of the percentages of both productivity and the decline of first generation F1 members and according to the following equations [21]:

\[
\text{Percentage productivity} = \frac{\text{number of insects leaving}}{\text{number of eggs subject}} \times 100
\]

\[
\text{Percentage decline of first generation members} = \frac{\text{number of adults in comparison - number of adults in treatment}}{\text{number of adults in comparison}} \times 100
\]

2.4 Testing the gravitational and salt repellent effect on the complete stage (Adult)

This test was conducted using chemotropometer, introducing 10 complete insects per replication and three replications and then registered the number of insects moving in the tube and for a distance of 25 cm towards the two openings, and 20 minutes after the introduction of insects [15] and calculated the rate of attraction and repellent and the balance ratio according to the following equations
Percentage attraction = \( \frac{\text{number of insects that material and it's 25 cm from the centre}}{\text{Total insects}} \times 100 \)

\[ \text{Percentage repellent} = \frac{\text{number of insects that went against the substance and it's 25 cm from the centre.}}{\text{Total insects}} \times 100 \]

Balance ratio = attraction ratio - repellent rate

2.5 Salt effect on cowpea seed germination ratio L. Vigna unguiculata

To assess the effect of the chemical compound on fetal vitality, a number of healthy cowpea seeds were soaked in prepared concentrations of 1.5 ml of each concentration, after which they were placed on filtration sheets in sterile petri dishes and at 10 seeds per replication. With three replications per concentration, then sprayed with 5 ml of distilled water, the comparison treatment was treated only with distilled water, and the dishes were placed near the sunlight, the percentage of germination was estimated after 7 days [15]. Experiments were carried out using full random design (C.R.D.) The calculation averages of transactions using Duncan's multiple range test were compared with a probability level of 0.05 [22].

3. Results and Discussion

3.1 Examination and diagnosis of prepared chemical compounds

The prepared compound was diagnosed by examining it by magnetic resonance devices of proton (1HNMR) form 1 and infrared spectrum (IR) form 2, and melting point measurement.

![Figure 1. Diagnosis 1HNMR of the chemical compound prepared.](image)

3.2 Measuring the fusion score of the chemical compound prepared

The results showed that the compound had a melting point between the two degrees 228-230°.

3.3 Impact on the rate of number of eggs, the exit of the emerges insects and the percentage of productivity of the Southern Cowpea Beetle

Table 1 showed a direct impact on the number of lied eggs reached to 96.67, 143.33, 156.67 eggs at 500, 1500,3000 ppm respectively, the number of lied eggs increased by concentration increasing, which is not consistent with [23]. When the southern cowpea beetle treated with near-fatal concentrations of Thiamethoxam, which led to a significant reduction in
oviposition, surpassing Deltamethrin and fennel seed powder, it also did not agree with [24] Which found a significant decrease in the number of eggs placed by the large beetle (Bruchus rufimanus) treated at a high dose of 2 μg /microliter of match growth regulator.

Increased concentration was found to have reduced the number of basses to 32.00 at the top 3000 ppm while 44.00 and 47.00 were at 1 500ppm 500, followed by this is not consistent with [25] who used the concentration under the mortal of the Novaluron pesticide which is 0.0003 ml/L to reach high levels of inhibition of hatching eggs. The decline in the number of emerges insects has affected productivity, which in turn has declined with significant differences. It registered a high of 46.72% at 500ppm, while it fell to 29.15% at 1500ppm and had a low rate of 21.05% at 3,000ppm, and many researchers believe that the efficiency of the substances used in insect control is measured by the extent to which they have an impact on their productivity, which reduces their proportions and can therefore be used to manage that scourge and reduce its damage [15].

**Table 1.** The effect of the chemical compound on the rate of egg count and the exit of the emerges insects and the percentage of productivity of the southern cowpea beetle

| (%)productivity | Rate of number of emerging insects | Number of eggs20/ g | Concentration ppm | Compound code |
|-----------------|----------------------------------|---------------------|-----------------|---------------|
| 46.72           | 47.00                            | 96.67               | 500             |               |
| Abc             | b                                | d                   |                 |               |
| 29.15           | 44.00                            | 143.33              | 1500            | N1            |
| Bc              | b                                | dc                  |                 |               |
| 21.05           | 32.00                            | 156.67              | 3000            |               |
| C               | b                                | bc                  |                 | control       |

Averages per column that took similar letters are not significantly different at 0.05 Those who have taken separate letters differ significantly among themselves.

3.4 Effect on the percentage of egg prevention (repellent ) and the percentage of decline of first-generation F1 members

The results in Table 2 showed that the concentration of 500 ppm had the greatest impact on preventing egg laying, with the highest repellent rate of 53.97% and it was noted that the repellent rate was lower with an increased concentration of 31.75, 25.40% for each of the 1,500, 3,000 ppm, respectively, which was not consistent with its results. The rate of egg prevention developed by southern cowpea beetle (repellent ) is found to increase the concentration of inactive powders for serpentine, petait, emstone, clay and ardwas. The impact on the first generation decline was different, as it was found that increased concentration caused an increase in the decline in first-generation personnel, which reached 50.5, 53.68, 66.32% at each of the 500, 1500, 3000 ppm, and these results are consistent with [26] They noted the superiority of the imidacloprid pesticide over zeta-cypermethrin and Lufenuron in influencing the mortality rate of the trogoderma granarium beetle, which increased with increased concentration.

**Table 2.** Compound effect in percentage to prevent egg laying (repellent ) and percentage of decline of first-generation F1 members.

| Decline in individuals | Percentage repellent | Concentration ppm | Compound code |
|------------------------|----------------------|------------------|---------------|
| First generation F1    |                      |                  |               |
| 50.53 a                | 53.97 a              | 500              |               |
| 53.68 a                | 31.75 ab             | 1500             | N1            |
| 66.32 a                | 25.40 bc             | 3000             |               |

3.5 The effect of the laboratory-prepared chemical compound on the duration of the larvae and pupal phases of the southern cowpea beetle

Statistical results showed the effect of the top concentration of 3000 ppm in increasing the duration of the larvae phase of the Southern Cowpea Beetle Table 3, reaching 7.50 days compared to control of 5.50 days followed by concentrations 1500, 500 ppm for 6.33 and 6.00 days respectively and this is not consistent with [27] who noted the decrease in the duration of Hippodamia variegata's fourth larval phase when treated with imidacloprid at a near-fatal concentration. The correlation between the increased concentration of the compound and the duration of the insect's pupal phase was also 6.50, 6.66 and 7.83 days for each of the 500, 1500, and 3,000 ppm, respectively. Compared to the control registered 7.50 days, which did not notice a significant difference between it and the effect of the higher concentration of the compound, this is consistent with the results obtained [15] which noted that the average duration of the pupal phase increased by increasing the
concentration of silver nanoparticles where it reached the longest period of 9 days when concentrating 100 percent and dropped when the concentration dropped 12 percent to 6 days.

Table 3. The effect of the laboratory-prepared chemical compound on the duration of the larvae and pupal phases of the southern cowpea beetle

| Concentrations ppm | Compound code | Duration of the larvae phase (day) | The duration of the pupal phase (day) |
|--------------------|--------------|-----------------------------------|--------------------------------------|
| 500                | N1           | 6.00 cd                           | 6.50 b                               |
| 1500               |              | 6.33 bcd                          | 6.66 b                               |
| 3000               |              | 7.50 a                            | 7.83 ab                              |

5.50 d Control

3.6 Effect on the germination of red cowpea seeds V. Unguiculata

The compound had no significant impact on the rate of germination of cowpea seeds as shown in table 4, where it was found that the maximum rate at concentration was 1500 ppm with 96.66% while the concentrations registered 3000 and 500 ppm germination rate of 90.00 and 76.66%, respectively compared to control of 93.33%

Table 4. Its effect on the germination rate of red cowpea seeds V. Unguiculata.

| Germination% | Concentrations ppm | Compound code |
|--------------|--------------------|---------------|
| 76.66 ab     | 500                | N1            |
| 96.66 a      | 1500               | N1            |
| 90.00 ab     | 3000               | N1            |
| 93.33 ab     | control            | Control       |

3.7 Attraction and repellent effect test on southern cowpea beetle adults

Table 5 shows that the concentration of 3000 ppm had the highest attraction among other concentrations at 23.33%, followed by 1500 and 500 ppm at 16.66% and 6.66% after 10-20 minutes of treatment in the chemical system, while the statistical results did not show significant differences in the repellent rate of the compound. Repellent rates were 6.66, 3.33% and 16.66% for 500, 1500 and 3000 ppm. This corresponds to a study[29] when they noted that the Nephaspis oculata beetle did not avoid treatment with imidacloprid, as it did not notice a repellent effect, while the papers avoided treatment with bifenthrin, which had a repellent effect[28] also noted the repellent effect of Rosmarinus officinalis mountain wreath oil.

Table 5. Attraction and repellent effect test for chemical compound prepared on southern cowpea beetle adults

| Balance% | Repellent rate% | Attraction% | Concentrations ppm | Compound code |
|----------|----------------|-------------|--------------------|---------------|
| 0.00     | 6.66           | 6.66        | 500                | N1            |
| 13.33    | 3.33           | 16.66       | 1500               | N1            |
| 6.67     | 16.66          | 23.33       | 3000               |               |

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