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Activity of Methanolic and Hydrolyzed Methanolic Extracts of *Ricinus communis* (Euphorbiaceae) and Kaempferol against *Spodoptera frugiperda* (Lepidoptera: Noctuidae)

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Abstract: *Spodoptera frugiperda* is the main pest of maize. One of the alternatives proposed for its control is the implementation of products of botanical origin, such as those derived from *Ricinus communis*. In this work, the insecticidal and insectistatic activities of methanolic and hydrolyzed methanolic extracts of the aerial parts of *R. communis* and kaempferol against *S. frugiperda* are evaluated. The methanolic extract presented a larval mortality rate of 55% and an accumulated mortality rate of 65% starting at 4000 ppm, with LC_{50} values of 3503 (larvae) and 2851 (accumulated); meanwhile, from a concentration of 1000 ppm, a decrease in pupa weight at 24 h of 20.5 mg was observed when compared to the control. The hydrolyzed methanolic extract presented a larval mortality and accumulated mortality rate of 60% from a concentration of 1000 ppm, and a decrease in pupa weight at 24 h of 35.31 mg was observed, when compared to the control. For the compound kaempferol 3-β-D-glucopyranoside, a larval mortality rate of 65% and an accumulated mortality rate of 80% were observed from 800 ppm, with LC_{50} values of 525.2 (larvae) and 335.6 ppm (accumulated); meanwhile, at 300 ppm, a decrease in pupa weight of 25.59 mg after 24 h was observed when compared to the control.

Keywords: FAW; insecticidal; insectistatic; castor

1. Introduction

Corn (*Zea mays* L. (Poaceae)) is one of the most important crops worldwide due to its high nutritional value, its use as a raw material to produce processed products (e.g., flour, starch, oil, and syrup), and its use as food for cattle [1,2]. The global production of this grain is over one billion metric tons per year, and maize for dry grain is grown on 197 M Ha around the world [3]. For these reasons, a decrease in crop production can mean a problem for food security worldwide, with diseases and pests being the main agents responsible for this impact [4,5]. Among the pests that affect this crop, such as birds, rodents, and arthropods, insects stand out, of which the genus *Spodoptera* includes several species that can seriously affect the crop (e.g., *Spodoptera exigua*, *Spodoptera littoralis*, and *S. frugiperda*) due to the fact that their infestations can cause total losses for the plantations [6,7]. *S. frugiperda* is an insect of the order Lepidoptera and a member of the Noctuidae family, which is native

to America [8]; however, its presence has also been reported in Africa, Asia, Europe [9], and, recently, in Oceania [10]. Therefore, it is considered one of the most important pests of this crop [7,11,12]. Synthetic chemical insecticides are the most-used method to control the damage caused by this pest, which mainly belong to the groups of organophosphates, carbamates, and pyrethroids. Due to the indiscriminate use of these products, this insect has been able to develop resistance [13,14]. In addition, these chemicals can have negative effects on human health, causing diseases such as cancer or poisoning that can cause death [15], and contribute to the contamination of soil and surface and underground water bodies [16–19]. Among the alternatives proposed to reduce the use of synthetic insecticides, the application of products made from botanical extracts is an effective option for the control of *S. frugiperda* [20]. Some of the extracts that present insecticidal and insectistatic activities against this pest include those obtained from *Nicotiana tabacum* L. (Solanaceae), *Cymbopogon citratus* DC. (Poaceae), *Azadirachta indica* A. Juss. (Meliaceae), *Lippia javanica* Burm f. (Verbenaceae), and *Ricinus communis* L. (Euphorbiaceae) [21,22]. *R. communis* is a plant which is native to Africa and distributed worldwide, from which various compounds have been isolated, including fatty acids, coumarins, alkaloids, terpenoids, and flavonoids [23,24]. Notably, ricin from the group of alkaloids and the compounds kaempferol-3-O-beta-D-rutinoside and kaempferol-3-O-beta-D-xylopyranose from the group of flavonoids have been shown to possess insecticidal and insectistatic potential in a large number of insects, as in the case of *S. frugiperda* [25–27]. The insecticide activity of pesticides is mostly due to the inhibition of the acetylcholinesterase enzyme, causing an interruption in the transmission of nerve impulses which leads to muscle convulsions, paralysis, and poisoning by an acetylcholine excess [28,29]. Natural compounds such as alkaloids, terpenoids, coumarins, phenolics, and flavonoids have displayed inhibitory activity of the acetylcholinesterase enzyme [30–32]. Quercetin, a flavonoid found in *R. communis*, has demonstrated acetylcholinesterase inhibition through in vitro assays [33]. These secondary metabolites, such as kaempferol-3-O-beta-D-rutinoside and kaempferol-3-O-beta-D-xylopyranose, can be obtained in their aglycone forms through extraction techniques that involve acid hydrolysis processes [25,34]. Therefore, the aim of this project is to evaluate the insecticidal and insectistatic capacities of methanolic and hydrolyzed methanolic extracts of the aerial parts of *R. communis* and kaempferol against *S. frugiperda* larvae.

2. Materials and Methods

2.1. Collection of Plant Material and Preparation of Extracts

The aerial parts of *R. communis* were collected in the municipality of Querétaro, Querétaro (coordinates: latitude, 20°35′41.3″ N; longitude, 100°24′49.1″ W), after being identified and authenticated by PhD. Stephen D. Koch with registration (CHAPA-001) and deposited in the Hortorio Herbarium of the College of Postgraduates in Agricultural Sciences. Subsequently, the collected plant material was transferred to the Laboratory of Natural Insecticide Compounds of the Faculty of Chemistry of the Autonomous University of Querétaro (FQ-UAQ) and dehydrated for 3 weeks in environmental conditions under shade. Subsequently, it was pulverized in an IKA-WERKE M20 mill (Staufen, Germany). The dry and ground plant material was subjected to reflux extraction using J.T. Baker (Phillipsburg, NJ, USA) technical-grade methanol in a 1:5 ratio (plant material: solvent) at a constant temperature of 65 °C for 8 h. Finally, the solvent was removed under vacuum using an IKA (Staufen, Germany) RV10 rotary evaporator at 40 °C until dry.

2.2. Hydrolyzation of the Methanolic Extract of Ricinus communis

After obtaining the methanolic extract of *R. communis*, it was subjected to acid hydrolysis. Initially, 35 mL of methanol (J.T. Baker®, reagent grade) was added for every 10 g of the extract to dissolve it and it was transferred to a round-bottom flask. The hydrolysis process was conducted using the steam stripping technique for 3 h at 95 °C, employing 285 mL of 0.25 M sulfuric acid (J.T. Baker, reagent grade). Subsequently, the reaction was neutralized with 350 mL of 10% sodium bicarbonate solution. Finally, the hydrolyzed compounds were

extracted with 100 mL of ethyl acetate (J.T. Baker, reagent grade). In order to remove the solvent, the mixture was evaporated to dryness using an IKA RV10 digital drive rotary evaporator.

2.3. Reproduction of Spodoptera frugiperda

The larvae of *S. frugiperda* were collected in corn fields in the Amazcala community belonging to the municipality of El Marqués (coordinates: latitude, 16°47′44″ N; longitude, 99°49′14″ W) in the state of Querétaro. Larvae were individually confined in #0 PRIMO brand plastic containers (Ecatepec, Mexico) and were fed with the diet previously described by Ramos-López et al. [22] (Table 1). Once the pupal phase was reached, they were transferred in groups of 30 individuals to 1 L plastic containers. The moths that emerged from these pupae were placed inside white paper bags with dimensions of 8 cm × 5 cm × 15 cm, from which the putties of eggs deposited on the walls of the bag were collected. The ovipositions were moved to 0.5 L plastic containers, along with artificial diet, such that they would later hatch and grow until reaching the second larval instar. Rearing conditions were controlled using a bioclimatic chamber maintaining a temperature of 27 ± 2 °C, 70 ± 5% relative humidity, and a 14:10 (light/dark) photoperiod.

Table 1. Composition of 1 kg of artificial diet for *S. frugiperda* [20].

Substance	Amount
Ground corn	120 g
Ground bean	60 g
Yeast	20 g
Neomycin	0.6 g
Multivitamin	2.5 g
Ascorbic acid	1.7 g
Methyl 4-hydroxybenzoate	1.7 g
Bacteriological agar	10 g
Formaldehyde 10%	2.5 mL
Water	800 mL
Ethanol 96%	17 mL

2.4. Evaluation of the Biological Activity of the Methanolic and Hydrolyzed Methanolic Extracts of Ricinus communis on Spodoptera frugiperda

To determine the concentrations used in the test, a preliminary test was carried out, in which five logarithmic concentrations and a control were tested to determine the maximum and minimum concentrations where a biological response existed (0, 0.5, 5.0, 50, 500, and 5000 ppm). From the above, to carry out the biological activity test, five different concentrations and a control were chosen. These were chosen after completing the logarithmic bioassay. The selection criteria were the minimum and maximum biological response and then three concentrations were selected between them, and they were: 5000, 4000, 2000, 1000, 500, and 0 ppm, according to our previous studies [35,36], adding each concentration during the preparation of the artificial diet for *S. frugiperda*. To carry out the test, 20 #0 polyethylene PRIMO brand cups (Ecatepec, Mexico) were used, in which a piece of the food with an approximate volume of 1 cm^3 containing the corresponding concentration of each extract of *R. communis* was placed. The vessels were contained within a bioclimatic chamber with a temperature of 27 ± 2 °C, relative humidity of 70 ± 5%, and a light/dark photoperiod of 14 and 10 h. A completely randomized experimental design was used, comprising 4 replicates with 5 experimental units (EUs) each, placing each second instar larvae in a #0 polyethylene PRIMO brand cup (Ecatepec, Mexico) with a 1 cm^3 diet cube, all under the same conditions as those of the breeding stock. This bioassay was reviewed

every 24 h until the larvae reached the sixth instar. At this point the dependent variables (larval mortality, pupal mortality, cumulative mortality, and mean lethal concentration LC_{50}) were evaluated.

2.5. Biological Activity of Kaempferol on Spodoptera frugiperda

To determine the insecticidal and insectistatic activity of kaempferol, concentrations of 1000, 800, 500, 300, and 100 ppm of kaempferol 3-β-D-glucopyranoside were evaluated. This compound was of analytical grade and obtained from Sigma Aldrich (St. Louis, MO, USA), following the same methodology described in the bioassay of methanolic extracts. A completely randomized experimental design was used, comprising 4 replicates with 5 experimental units (EUs) each, placing each second instar larvae in a PRIMO brand #0 polyethylene cup (Ecatepec, Mexico) with a 1 cm^3 diet cube, under the same conditions as those of the breeding stock. This bioassay was reviewed every 24 h until the larvae reached the sixth instar; at this point, the dependent variables (larval mortality, pupal mortality, cumulative mortality, and mean lethal concentration—LC_{50}) were evaluated.

2.6. Identification and Quantification of Kaempferol in the Methanolic and Hydrolyzed Methanolic Extracts of Aerial Parts of R. communis

The identification and quantification of kaempferol in the hydrolyzed methanolic and methanolic extracts of *R. communis* were carried out through high-resolution liquid chromatography (HPLC) using Waters Alliance model equipment (Milford, MA, USA), composed of a model e2695 quaternary pump and a model 2998 diode array detector (DAD). Data acquisition and processing were carried out using Empower 3 software. In addition, a C18 column (5 µm, 150 × 4.5 mm) was used. Acetic acid at a concentration of 12.5 mM and acetonitrile (CH_3CN) were used as the mobile phase, using the gradient described in Table 2.

Table 2. Elution gradient for kaempferol analysis.

Time (mins)	Acetic Acid 12.5 mM	Acetonitrile
0	95%	5%
2	95%	5%
5	85%	15%
20	50%	50%
25	95%	5%
35	95%	5%

The flow of the mobile phase was 1.0 mL min^{-1}, the wavelength used for detection was 363 nm, and an injection volume of 10 µL and an analysis time of 35 min were used. The retention time for the kaempferol standard was 20.3 min. Analyses for kaempferol quantification were performed in triplicate.

2.7. Statistical Analysis

A one-way analysis of variance (ANOVA) was performed with the data obtained from the bioassays. Subsequently, the Tukey test was performed with a confidence level of 95% and the LC_{50} was determined through a probit analysis. All analyses were conducted using Systat 9 software.

3. Results

3.1. Performance of Methanolic and Hydrolyzed Methanolic Extract of Ricinus communis

The yield obtained when carrying out the methanolic extraction of the aerial parts of *R. communis* was 7.45%, while that when carrying out hydrolyzation of the methanolic extract of this plant was 23.23%.

3.2. Insecticidal Activity of the Methanolic Extract of Ricinus communis on Spodoptera frugiperda

Figure 1 shows that the methanolic extract presented larvicidal activity of 55% from 4000 ppm.

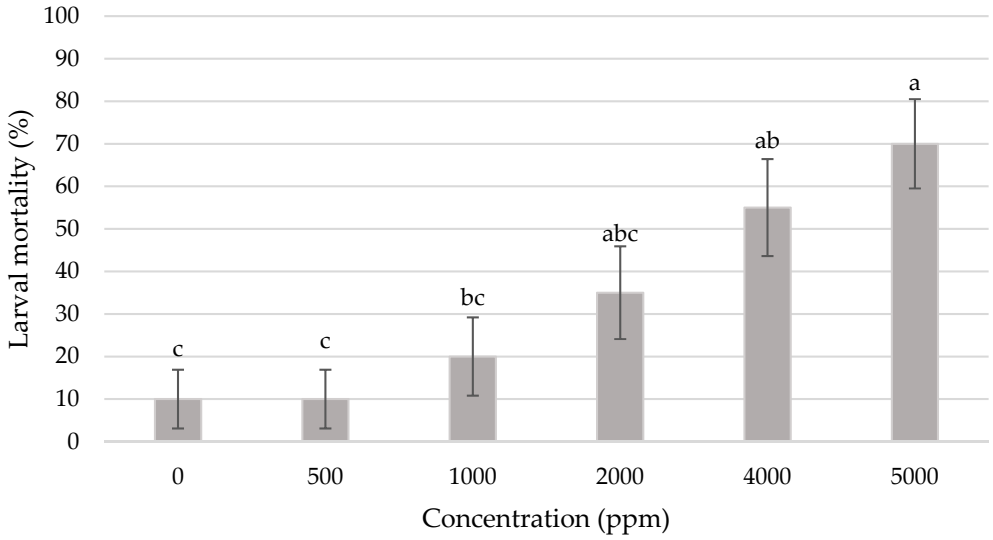

Figure 1. Larval mortality of the methanolic extract of *R. communis*. Data are the average of 20 measurements ± standard error. Different letters imply a significant difference according to the Tukey test with $p = 0.05$.

On the other hand, when evaluating pupal mortality, no biological activity was found to be significantly different from the control under any of the treatments, as detailed in Figure 2.

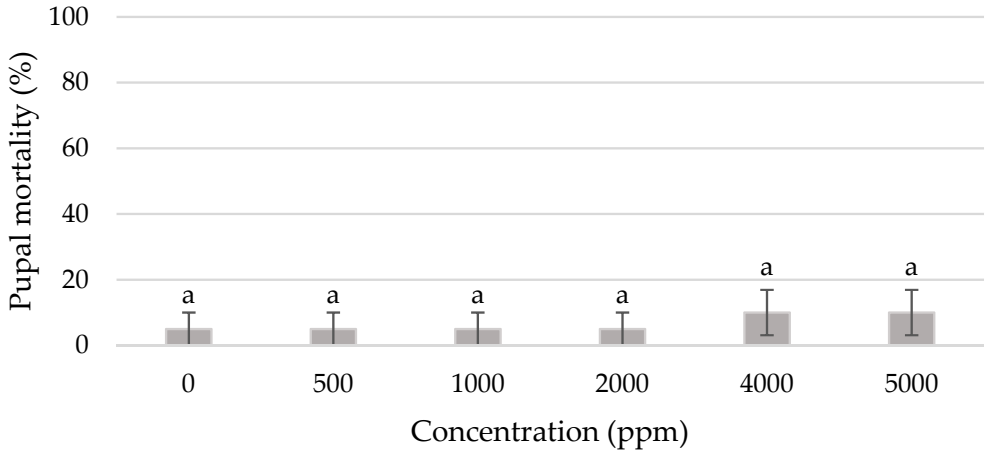

Figure 2. Pupal mortality of the methanolic extract of *R. communis*. Data are the average of 20 measurements ± standard error. Different letters imply a significant difference according to the Tukey test with $p = 0.05$.

When determining the accumulated mortality it was observed that, from 4000 ppm, there was a significant difference with respect to the control, as detailed in Figure 3. The average lethal concentration of larval mortality was 3503 ppm and that for accumulated mortality was 2851 ppm.

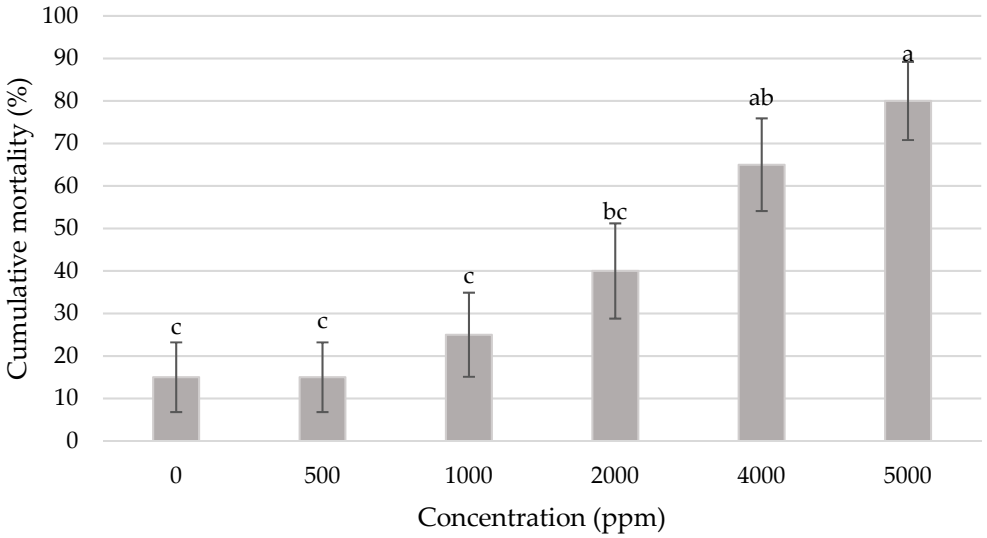

Figure 3. Cumulative mortality of the methanolic extract of *R. communis*. Data are the average of 20 measurements ± standard error. Different letters imply a significant difference according to the Tukey test with $p = 0.05$.

3.3. Insectistatic Activity of the Methanolic Extract of Ricinus communis on Spodoptera frugiperda

An increase in larval duration was observed with an increase in the concentration of extract in the treatments, with a significant difference with respect to the control starting at 1000 ppm. Likewise, pupal duration increased as the treatment concentration increased.

In contrast, a decrease in the weight of the pupae was observed as the concentration of the extract increased, presenting a significant difference starting at 1000 ppm, as detailed in Table 3.

Table 3. Insectistatic activity of the methanolic extract of *Ricinus communis*.

Treatment (ppm)	Larval Duration (d)	Pupal Duration (d)	Pupal Weight 24 h (mg)
5000	31 ± 1.6 a	15 ± 0.6 a	166 ± 15.6 a
4000	24 ± 0.5 b	13 ± 0.4 bc	191 ± 4.4 ab
2000	23 ± 0.2 bc	12 ± 0.2 bc	211 ± 4.02 b
1000	22 ± 0.4 cd	12 ± 0.2 cd	233.7 ± 4.0 c
500	20 ± 0.3 de	11 ± 0.2 de	239.8 ± 4.3 cd
0	20 ± 0.3 e	10 ± 0.3 e	254.2 ± 3.7 d

Data are the average of 20 measurements ± standard error. Means with different letters imply a significant difference according to the Tukey test with $p = 0.05$.

3.4. Insecticidal Activity of the Hydrolyzed Methanolic Extract of Ricinus communis on Spodoptera frugiperda

The hydrolyzed methanolic extract presented insecticidal activity of 60% from 1000 ppm. Meanwhile, when evaluating pupal mortality, no effect was found on the pupae as, in all cases, the surviving larvae emerged and developed into their adult stage. Therefore, when determining the accumulated mortality, it was equal to the larval mortality; therefore, the accumulated mortality presented insecticidal activity starting at 1000 ppm. In this sense, both larval and accumulated LC_{50} values were 1057 ppm, as shown in Figure 4.

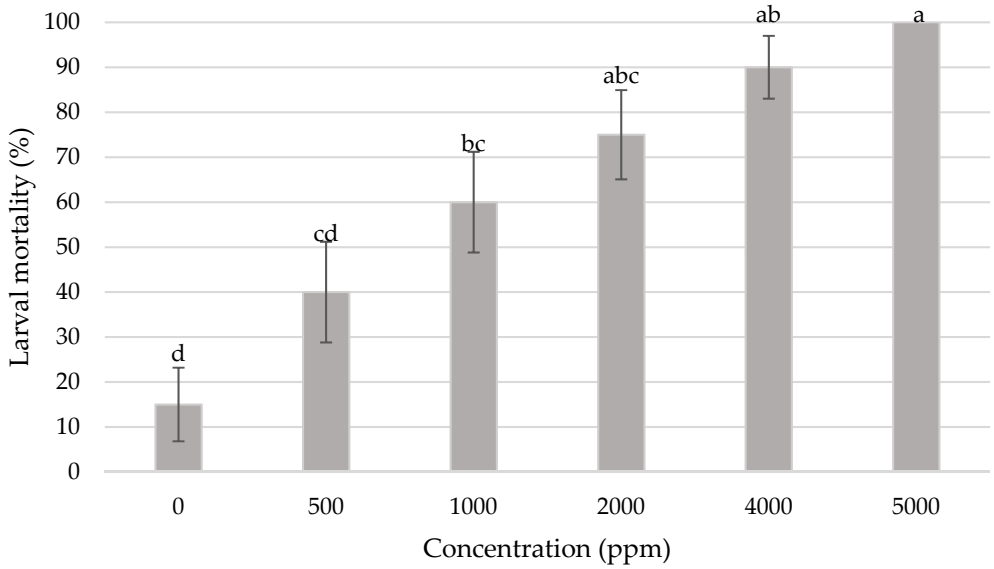

Figure 4. Larval mortality of the hydrolyzed methanolic extract of *R. communis*. Data are the average of 20 measurements ± standard error. Different letters imply a significant difference according to the Tukey test with p= 0.05.

3.5. Insectistatic Activity of the Hydrolyzed Methanolic Extract of Ricinus communis on Spodoptera frugiperda

The hydrolyzed methanolic extract showed an increase in larval duration starting at 4000 ppm, reaching up to 29 days; meanwhile, at a concentration of 500 ppm, the larval duration was only 18 days, below that observed for the control (which reached 22.5 days). Continuing from the above, when evaluating the pupal duration, a decrease in the duration of the pupae was observed at all concentrations, where 2000 ppm was the value at which the pupae showed the shortest duration of 9.8 days—a time shorter than that reported for the control (11.5 days). Likewise, when evaluating the weight of the pupae at 24 h, we aimed determine the concentration of the extract at which a decrease in the weight of the pupae occurred. This value in the control was 232.94 mg while, at 1000 ppm, the pupae presented a significant difference compared to the control with a weight at 24 h of 197.63 mg, as detailed in Table 4.

Table 4. Insectistatic activity of the hydrolyzed methanolic extract of *Ricinus communis*.

Treatment (ppm)	Larval Duration (d)	Pupal Duration (d)	Pupal Weight 24 h (mg)
4000	29 ± 0.000 a	10.5 ± 0.5 a	178.50 ± 5.50 b
2000	22.8 ± 0.970 ab	9.8 ± 0.583 b	185.6 ± 10.3 b
1000	19.5 ± 0.598 bc	10.125 ± 0.295 b	197.63 ± 8.00 b
500	18 ± 0.461 c	9.917 ± 0.229 b	206.67 ± 4.16 ab
0	22.529 ± 0.974 b	11.529 ± 0.311 a	232.94 ± 8.45 a

Data are the average of 20 measurements ± standard error. Means with different letters imply a significant difference according to the Tukey test with p = 0.05.

3.6. Identification and Quantification of Kaempferol in the Methanolic and Hydrolyzed Methanolic Extracts of Aerial Parts of R. communis

The retention time obtained when analyzing the kaempferol standard was 20.3 min, giving a maximum absorption at 363 nm. When running the methanolic extract of *R. communis*, the presence of kaempferol was detected; however, due to the chromatographic method used, it could not be quantified, as seen in Figure 5.

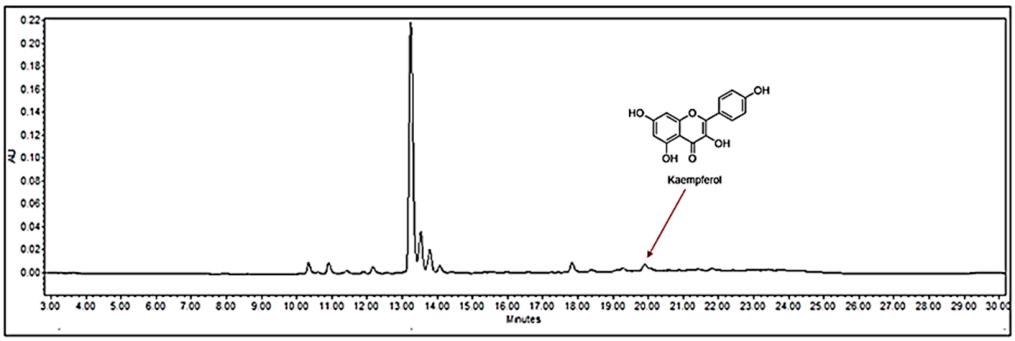

Figure 5. Chromatogram of the methanolic extract of *R. communis*.

After acid hydrolysis of the methanolic extract, a greater presence of kaempferol was observed, as shown in Figure 6, which was quantified and obtained at a concentration of 1.65 ± 0.22 µg mg^{-1}. Furthermore, quercetin was found in a greater proportion; however, its quantification was not the objective of study in the present work.

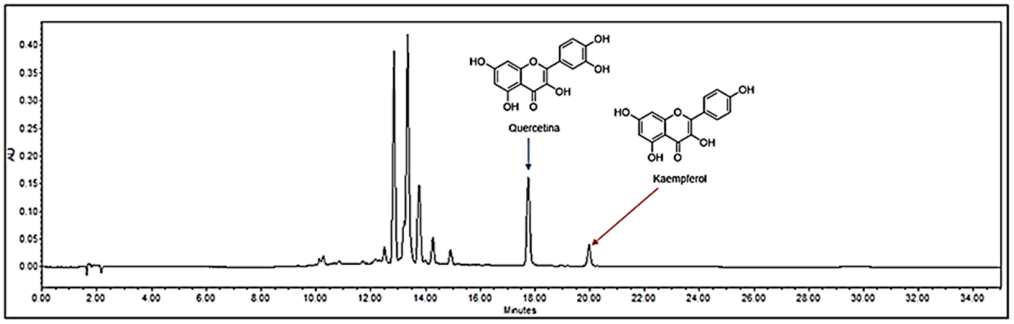

Figure 6. Chromatogram of the hydrolyzed methanolic extract of *R. communis*.

3.7. Insecticidal Activity of Kaempferol on Spodoptera frugiperda

Kaempferol presented a larval mortality rate of 65% under the 800 ppm treatment, while that in the control was 15%, as shown in Figure 7.

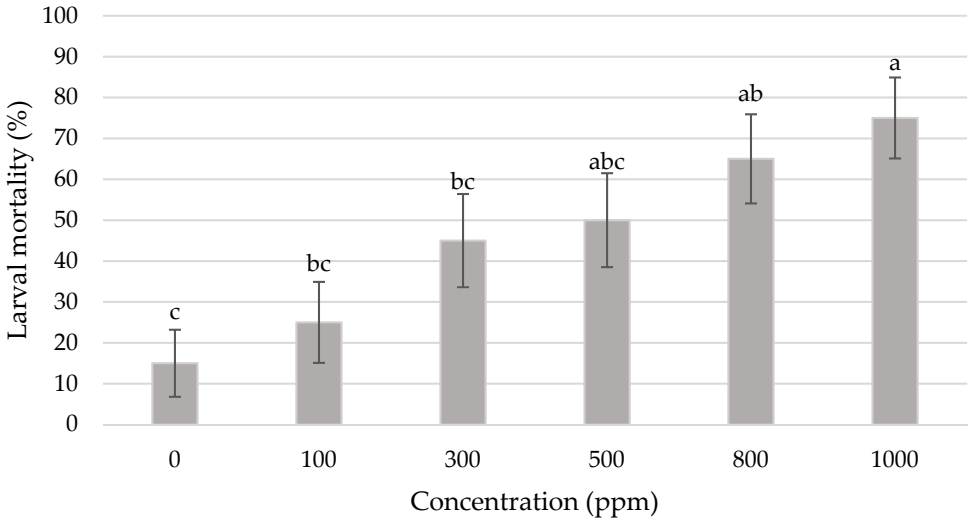

Figure 7. Larval mortality of kaempferol. Data are the average of 20 measurements ± standard error. Different letters imply a significant difference according to the Tukey test with p= 0.05.

Under this scheme, when evaluating pupal mortality, no significant difference was found for any of the treatments when compared to the control, as detailed in Figure 8.

Consequently, when determining the accumulated mortality, it was observed that, from 800 ppm, there was a significant difference with respect to the control (going from 80% to 20%), as shown in Figure 9.

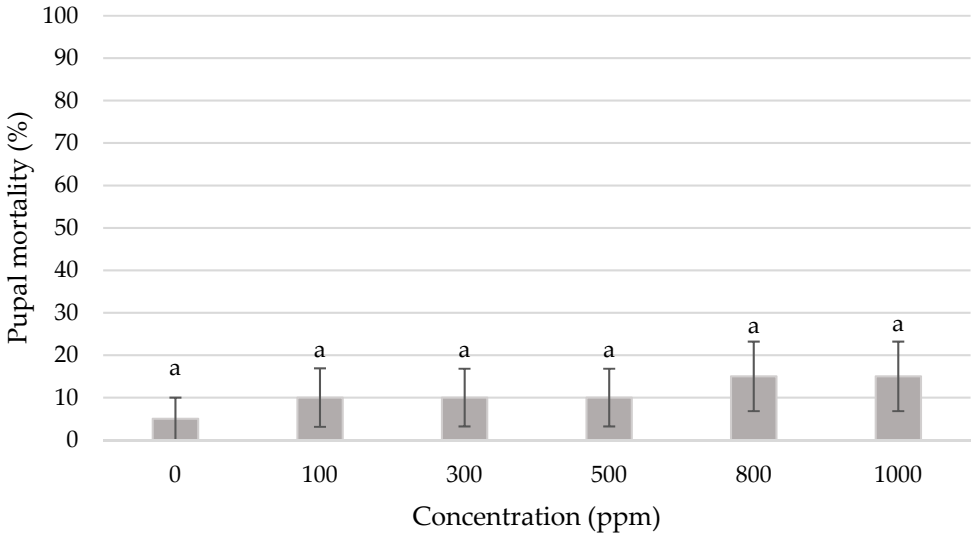

Figure 8. Pupal mortality of kaempferol. Data are the average of 20 measurements ± standard error. Different letters imply a significant difference according to the Tukey test with $p = 0.05$.

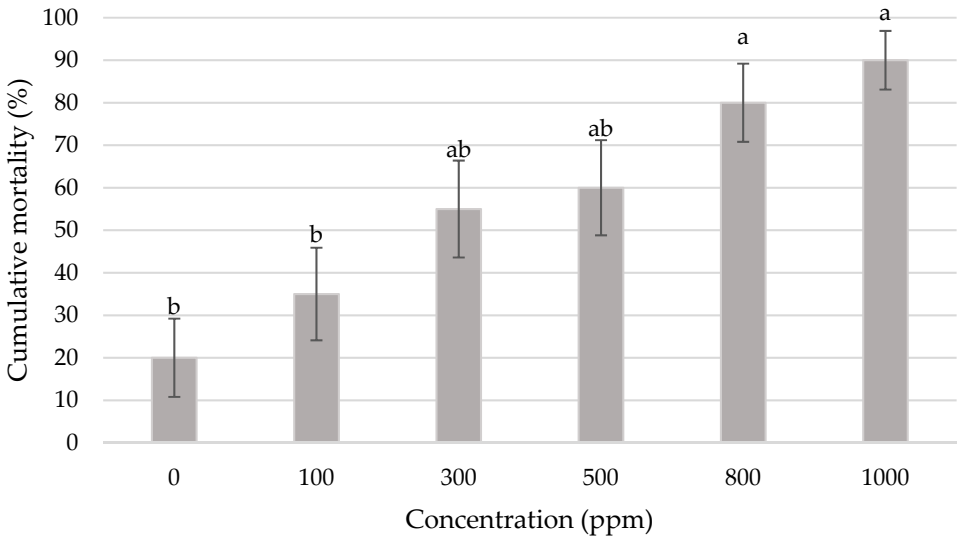

Figure 9. Cumulative mortality of Kaempferol. Data are the average of 20 measurements ± standard error. Different letters imply a significant difference according to the Tukey test with $p = 0.05$.

3.8. Insectistatic Activity of Kaempferol on Spodoptera frugiperda

Both larval duration and pupal duration increased as the concentration of kaempferol increased, being notably different from the control starting at 300 ppm for both parameters. The pupal weight decreased in comparison to the control as the concentration increased, presenting a relative difference starting at 300 ppm, as detailed in Table 5.

Table 5. Insectistatic activity of kaempferol.

Treatment (ppm)	Larval Duration (d)	Pupal Duration (d)	Pupal Weight 24 h (mg)
1000	33 ± 1.4 a	17 ± 0.5 a	127.4 ± 10.7 d
800	29 ± 0.95 b	16 ± 0.8 a	167.14 ± 7.1 c
500	25 ± 0.4 c	14 ± 0.3 b	191.1 ± 4 bc
300	22 ± 0.4 d	13 ± 0.3 b	205 ± 5 b
100	21 ± 0.4 de	11 ± 0.4 c	210.2 ± 4.4 ab
0	20 ± 0.4 e	11 ± 0.3 c	230.6 ± 6.4 a

Data are the average of 20 measurements ± standard error. Means with different letters imply a significant difference according to the Tukey test with $p = 0.05$.

4. Discussion

4.1. Evaluation of Extract Yields

In previous studies, the methanolic extract of *R. communis* leaves has presented different yields: Ramos-López et al. [22] obtained 9.82%, while Carolina et al. [37] observed a performance of 10.64%; in the same sense, García et al. [38] achieved a performance of 18.45%. In the present work the yield obtained from the methanolic extraction of the aerial parts was 7.45%, which is similar to that reported by Ramos-López et al. [22] and Carolina et al. [37]. On the other hand, the performance obtained by García et al. [38] was slightly more than double; according to Yang et al. [39], this variation may be due to factors such as plant variety, collection location, and environmental factors.

4.2. Evaluation of the Insecticidal Activity of the Methanolic and Hydrolyzed Methanolic Extracts of Ricinus communis against Spodoptera frugiperda

Ramos-López et al. [22] observed that the methanolic extract of *R. communis* leaves presented a biological activity that was significantly different from the control starting at 1600 ppm, with a larval mortality rate of 21%, which increased as the treatment concentration increased, reaching up to 100% with a concentration of 24,000 ppm. Likewise, pupal mortality presented a significant difference with respect to the control starting at 1600 ppm, with a value of 16.5%, which increased with the concentration of the treatment. Compared to the results obtained in the present work, where methanolic extracts of *R. communis* were also used, a higher mortality was observed at a lower concentration of the extract.

Almeida et al. [40] evaluated ethanolic extracts of the leaves of *Euphorbia pulcherrima* Willd. ex Klotzsch (Euphorbiaceae) both in the vegetative and reproductive stages on *S. frugiperda* at concentrations of 5000 and 10,000 ppm, and they reported a larval mortality rate of 26% when using the extracts of the leaves in their reproductive stage; although a different alcohol and a plant from the same family but different genus were used for the extraction, minimal mortality was observed at very high concentrations, compared to those in this work.

Santos et al. [41] evaluated the biological activity of methanolic extracts of fresh and dried leaves of seven different accessions of *Jatropha curcas* L. (Euphorbiaceae) against *S. frugiperda*, finding maximum larval mortality rates of 60% and 56.67%, respectively, in one accession in particular. These results, when compared with the 1000 ppm treatment in this work, indicate that larval mortality was doubled.

Delvas et al. [42] studied the phenolic compounds present in *Picea glauca* Moench Voss (Pinaceae), as they observed that there were susceptible individuals and others resistant to *Choristoneura fumiferana* (Lepidoptera: Tortricidae). They observed that, in aqueous acetone extracts (70%), two compounds in particular varied, with those for susceptible individuals being picein and pungenin, while those for resistant individuals were their aglycone forms (i.e., piceol and pungenol). Furthermore, they supplied these aglycones in artificial diets and found that the combination of 5400 ppm of pungenol and 6740 ppm of piceol caused the highest larval mortality (66%).

According to Dowd et al. [43], natural plant compounds present greater biological activity against insects when they are in aglycone form with respect to their glycoside form. Pentzold et al. [44] explained that the conversion of glycosides to aglycones occurs in nature. In particular, the secondary metabolites accumulated in plants are typically found as glycosides and the beta-glucosidase enzymes—which are spatially separated—are capable of enzymatically hydrolyzing these metabolites to aglycones when they are preyed upon by insects, resulting in mostly toxic compounds. Therefore, the greater insecticidal activity of the hydrolyzed methanolic extract of *R. communis* obtained in this work is related to the fact that secondary metabolites were found in aglycone form (including kaempferol).

As specified by Godlewska et al. [45], the application of botanical extracts could be beneficial for sustainable production due to several advantages, such as low toxicity to the environment and human health, better quality of crops, as well as a reduction in the use of synthetic pesticides.

4.3. Evaluation of the Insecticidal Activity of Kaempferol against Spodoptera frugiperda

Su et al. [46] reported that, through incorporating different flavonoids in the diet of *S. litura* larvae, an insecticidal effect was observed, where 100 ppm and higher of kaempferol showed a significant difference compared to the control, with a larval mortality rate of 17% compared to 2.5% with the control. Similarly, at 1000 ppm, a larval mortality rate of 35% was observed. Kaempferol, quercetin (42.5%), and rutin (47.5%) were the flavonoids that presented greater insecticidal activity, which was lower than that presented in this work (where the highest insecticidal activity obtained was 75% at 1000 ppm). It must be remembered that, despite being of the same genus, the species are different, which could explain the greater activity observed in this study. In the same sense, Herrera-Mayorga et al. [47] evaluated the insecticidal activity of some flavonoids (e.g., quercetin), as well as some phenolic acids (e.g., chlorogenic acid), against *S. frugiperda* larvae, and they found that quercetin had a mean lethal concentration (LC_{50}) of 157 ppm, lower than that presented in this study (525 ppm). Likewise, Herrera-Mayorga et al. [47] evaluated a 1:1 mixture of quercetin with chlorogenic acid, which presented an LC_{50} of 729 ppm—higher than that obtained in this research.

4.4. Evaluation of the Insectistatic Activity of the Methanolic and Hydrolyzed Methanolic Extracts of Ricinus communis against Spodoptera frugiperda

Almeida et al. [40] observed an extension of the larval duration of up to 5.8 days in *S. frugiperda* when treated with 5000 ppm of ethanolic extracts of *E. pulcherrima* leaves in the reproductive stage. Meanwhile, the pupae also presented a reduction in weight, presenting weights of 182 mg in pupae treated with 5000 ppm of extract from leaves of the plant in the reproductive stage, while the pupae treated with 5000 ppm of leaf extract from plant in the vegetative stage showed weights of 205 mg and 201 mg for males and females, respectively.

Ramos-López et al. [22] noted that larvae treated with the foliar methanolic extract of *R. communis* exhibited significant prolongation of the duration of the larval stage starting at 560 ppm (e.g., 2 days), which increased as the treatment concentration increased, extending their larval life by up to 12 days under the 16,000 ppm treatment. Meanwhile, extension of the pupal duration occurred from 8000 ppm, causing an increase of 1 d. The weight of the pupae decreased considerably when the larvae were treated with 16,000 ppm of extract, decreasing by 35 mg compared to the control.

In contrast, Delvas et al. [42] also evaluated the larval duration and weight of *C. fumiferana* pupae when treated with the two aglycones pungenol and piceol. Incorporating these in a combination of 6740 ppm and 5400 ppm of piceol and pungenol, respectively, caused an extension of larval life of 6 d compared to the control; furthermore, the pupae decreased in weight by up to 27% compared to the control.

In the present work, it was noted that treatment with the hydrolyzed methanolic extract of *R. communis* yielded greater insectistatic activity. According to Onyilagha et al. [48], the biological activity of flavonoids depends strictly on the substituents of the compound,

varying considerably if the molecule has O-glycoside or hydroxyl substituents. However, at low concentrations, the hydrolyzed extract showed different behavior, decreasing larval and pupal duration considerably and maintaining pupal weight similar to those of the control, indicating that the hydrolyzed methanolic extract acted in a phagostimulating manner. Other natural compounds have been shown to possess this type of behavior, as in the case of tannins, due to tolerance exhibited by the aphid *Schlechtendalia chinensis* (Hemiptera: Aphididae) when infesting *Rhus chinensis* Mill. (Anacardiaceae) [49]. Castillo and Rossini [50] have reported that monoterpene compounds, such as iridoids, caused phagostimulation in larvae of *Ceratomia catalpae* (Lepidoptera: Sphingidae) when feeding on plants that produce this type of metabolite in nature. Sun et al. [51] have described that some insects can tolerate and adapt to the consumption of some secondary metabolites, as in the case of *Helicoverpa assulta* (Lepidoptera: Noctuidae), which found a diet containing nicotine or capsaicin—belonging to the alkaloid family—to be appetizing.

4.5. Identification and Quantification of Kaempferol in the Methanolic and Hydrolyzed Methanolic Extracts of Aerial Parts of R. communis

Kostikova and Veklich [52] studied the phenolic compounds found in aqueous ethanolic extracts (40%) of leaves and inflorescences of *Sorbaria pallasii* Pojark. (Rosaceae) and their hydrolysates through HPLC. They observed that kaempferol was not detected in the ethanol extracts, being only present in the extract that was hydrolyzed with 2 N HCl for 2 h at a concentration of 1.90 mg g^{-1}; furthermore, quercetin was found in a higher proportion than kaempferol (4.28:1).

A similar result was observed by de Santiago et al. [53] when analyzing the phenolic compounds extracted through successive extraction (50% methanol, 70% acetone, and distilled water) from cladodes of *Opuntia ficus-indica* (L.) Mill. (Cactaceae) through HPLC after the extracts were subjected to different hydrolysis conditions. In particular, they only observed the presence of kaempferol in the hydrolyzed extract. Furthermore, they determined that the best hydrolysis conditions were when it was carried out with 1.5 M HCl for 2 h at 90 °C, under which they obtained a concentration of 0.36 mg g^{-1}. When subjected to less acidic conditions (as in the case of HCl 0.6 M), the carbohydrates are not completely released from the glycosidic compounds; meanwhile, when carried out under more acidic conditions and for a longer time, the aglycones that are produced during the process are degraded. They also noted that quercetin was present in a higher proportion with respect to kaempferol under all hydrolysis conditions.

Therefore, it is possible to improve the accumulation of kaempferol from the hydrolyzed extract by reducing the acidity of the medium and the hydrolysis time, as detailed in the present study. Furthermore, it is very likely that other compounds that passed into their aglycone form also contributed to the biological activity of this hydrolysate—such as quercetin, which is found in an even greater proportion.

4.6. Evaluation of the Insectistatic Activity of Kaempferol against Spodoptera frugiperda

Henagamage et al. [54] reported that ethyl acetate extracts of *Tagetes erecta* L. (Asteraceae) and *Datura metel* L. (Solanaceae) induced anti-feeding activity against *S. frugiperda* at 0.2, 0.4, and 0.6 µg μL^{-1} in the quantification of phytochemicals. It was observed that, among the most abundant compounds in the extract of *T. erecta,* phenols and flavonoids ranked highest (at 107 mg g^{-1} and 128 mg g^{-1}, respectively); meanwhile, in the extract of *D. metel,* 89.4 mg g^{-1} of phenols was found, while 83.7 mg g^{-1} of flavonoids was found.

The results of our study suggest that the methanolic and hydrolyzed methanolic extracts of aerial parts of *R. communis*, as well as kaempferol, have insecticidal and insectistatic activities against *S. frugiperda* larvae.

In a previous work of our team, it was demonstrated that the biological activity of the methanolic extract of *R. communis* aerial parts resulted from ricinine [22] and now also kaempferol since it is a secondary metabolite present in this plant extract. In addition to

this, the mechanism of action of kaempferol involved in the biological activity of any insect has not been described so far.

5. Conclusions

In the present study, methanolic and hydrolyzed methanolic extracts of the aerial parts of *R. communis* exhibited insecticidal activity at concentrations of 4000 and 1000 ppm, respectively.

While the insectistatic activity against *S. frugiperda* larvae occurred from 1000 ppm for the methanolic extract, the hydrolyzed methanolic extract achieved a significant prolongation of larval duration at 4000 ppm and a reduction in weight of pupae at 1000 ppm.

This suggests that the hydrolyzed methanolic extract elicits a stronger response against *S. frugiperda*. The increase in the biological activity of the methanolic extract of *R. communis* aerial parts against *S. frugiperda* was attributed to secondary metabolites present in aglycone form, resulting from the hydrolysis of glucoside forms. One such metabolite was kaempferol, which also exhibited insecticidal and insectistatic activities against the fall armyworm at concentrations of 800 and 300 ppm, respectively.

According to this, the methanolic and hydrolyzed methanolic extracts of the aerial parts of *R. communis* can be used as an alternative to chemical synthetic insecticides for the control of *S. frugiperda*, due to their high effectiveness under laboratory conditions; however, in subsequent studies, their effectiveness under field conditions and ecotoxicological effects should be assessed; furthermore, the best hydrolysis conditions could be evaluated in order to obtain a higher load of secondary aglycone compounds in the extracts.

The identification of the action mechanism of the biological compounds in the methanolic extract of aerial parts of *R. communis* and the development of a standardized extract that could be used by agricultural producers are the next challenges of our team.

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