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Abstract:

Corn weevil, *Sitophilus zeamais* Motschulsky, is a primary pest of stored grain causing significant quantitative and qualitative loss worldwide; its control mainly depends on synthetic insecticides such as organophosphates and pyrethroids. Several organic compounds derived from plant such as ketones represent "green" alternatives to conventional pesticides. The aim of this study was to develop a bioactive silo bag with natural formulation consisting of plant-based ketones (binary mixture of thymoquinone and pulegone 1:1 mass ratio) in its inner layer (LDPE) to compare the efficiency of the process and relationship with the physicochemical properties of the molecules. Thus, we evaluated their optical, chemical, mechanical and biological properties. No differences in the morphology between the active and control silo bags were found. The repellent and insecticidal activities of the bioactive silo bag were tested against *S. zeamais*, primary pest of storage crops, showing a repellent index (RI) around 70% and 100% mortality, respectively. Therefore, a formulation with organic compounds (pulegone and thymoquinone) incorporated in the hermetic structure of the storage system could be used as an eco-friendly tool for sustainable pest management.

Keywords: Silo bag, multilayer co-extrusion process, terpene ketones, corn weevil.

Resumen:

El gorgojo del maíz, *Sitophilus zeamais* Motschulsky, es una plaga primaria de granos almacenados que causa pérdidas significativas cuantitativas y cualitativas en todo el mundo; su control depende principalmente de insecticidas sintéticos como organofosforados y piretroides. Varios compuestos orgánicos derivados de plantas como las cetonas representan una alternativa "verde" a los pesticidas convencionales. El objetivo del presente estudio fue desarrollar un silo bolsa bioactivo incorporando en la capa interna (PEBD) una formulación que consiste en cetonas de origen vegetal (mezcla binaria de timoquinona y pulegona en una relación de masa 1:1) para comparar la eficiencia del proceso y la relación con las propiedades fisicoquímicas de las moléculas. Así, evaluamos sus propiedades ópticas, químicas, mecánicas y biológicas. No se encontraron diferencias en la morfología entre el silo bolsa activo y control. Las actividad repelente e insecticida del silo bolsa bioactivo se probaron contra S. *zeamais*, plaga principal de los granos almacenados, mostrando un índice repelente (IR) de alrededor del 70 % y 100 % de mortalidad, respectivamente. Por lo tanto, la formulación con compuestos orgánicos (pulegona y timoquinona) incorporados a la estructura hermética de almacenamiento podría utilizarse como una herramienta ecológica para el manejo sostenible de plagas.

Palabras clave: Silo bolsa, tecnología de coextrusión, cetonas terpénicas, picudo del maíz.

INTRODUCTION

Corn weevil, *S. zeamais,* is a primary pest of stored grain causing significant quantitative and qualitative losses (Acheampong *et al*., 2019); its control mainly depends on synthetic insecticides such as organophosphates and pyrethroids (Carpaneto *et al*., 2016; Vélez *et al*., 2017). Recently, there has been a growing interest in organic products as in organic agriculture, where sustainable pest management comprises biological control agents with microorganisms, and green chemicals (Hasan *et al*., 2021; Souto *et al*., 2021). However, few works describe the developedment of active packaging for protection crops during storage (Goñi *et al*., 2017; Herrera *et al*., 2017; Herrera *et al*., 2021). For this reason, developments of new sustainable technologies for pest management, which include "green" organic compounds, are required. Plant-based terpenes are easily biodegradable, they have shown no described resistance and are environmentally friendly (EPA, 2022). Hence, the European Union (EU) approved the use of their derivatives for controlling pest (Commission implementing regulation (EU) 485/2013, 2018). Terpenes showed insecticidal, repellent and fungicidal effects toward pests of stored products (Herrera *et al*., 2015; Pizzolitto *et al*., 2015; Herrera *et al*., 2017). Particularly, thymoquinone and pulegone are α β-unsaturated ketones reported as the most toxic terpenes against insects of stored grains (Chan, 2008; Pérez-Garrido *et al*., 2010; Yildirim *et al*., 2013; Herrera *et al*., 2015). These ketones are extracted from several plants such as *Nigella sativa* and *Mentha sp,* respectively, by hydrodistillation (Demo *et al.*, 2005). In addition, these compounds are moderately toxic in mammals (EPA, 2022), used as antioxidant food (Nair, 2001; Woo *et al.*, 2012). In a previous study, formulation with these ketones showed synergistic effect with a lethal concentration (LC_{50}) value of 7.12 µL/L air, lower than that found in individual compounds (Herrera *et al.*, 2015; Pizzolitto *et al.*, 2015; Herrera *et al.*, 2017). These ketones act by inhibiting the Acetylcholinesterase (AChE) enzyme (Herrera *et al.*, 2015). Ketones have high volatility and reactivity to external factors. To protect and retain them, previous work showed the incorporation of natural compounds into the polymeric matrix as low-density polyethylene LDPE and LDPE/ sepiolite nanocomposite films by supercritical CO. impregnation (Goñi *et al.*, 2017; Herrera *et al.*, 2017). However, to develop active packaging at an industrial level, the technique of impregnation with supercritical CO. is not frequently used. The multilayer co-extrusion is a low-cost conventional process industrially relevant in developing bags as in the silo bag system made with a mixture of polyethylene (IpesaSilo 2021). In the field, the multilayer silo bag is used for protecting stored cereal grains, and acts as a hermetic system holding around 200 tons, 60 m long and 2.7 in widths. During storage of grains in silo bag, an atmosphere poor in O.and rich in CO_2 prevents the development or infestation of pests, including insects and fungi (Freitas *et al.*, 2016; Silva *et al.*, 2018). However, the system could be damaged by improper management, creating an environment unable to control pest (Subramanyam *et al.*, 2012). Due to this, in silo bags phosphine fumigation is used (Ridley *et al.*, 2011; Carpaneto *et al.*, 2016). The aim of this study was to develop a three-layer bioactive silo bag with the addition of insecticidal formulation ketones (binary mixture of thymoquinone and pulegone 1:1 mass ratio) in its inner layer (LDPE). Thus, we evaluated the optical, chemical and mechanical properties of the bioactive silo bag. The repellent and insecticidal activity of the bioactive silo bag was also tested against *S. zeamais*, a primary pest of storage crops (Almeida *et al.*, 2014).

MATERIALS AND METHODS

Materials

Natural insecticides, *R*-(+)-pulegone and thymoquinone were purchased from Sigma-Aldrich (Steinheim, Germany). Methanol (grade HPLC) was provided from Sintorgan (Argentina). Braskem Idesa (México) supplied pellets of LDPE and HDPE for the manufacture of silo bags. Stabilizing additives (UV and light blocking) such as titanium dioxide (TiO_2) and carbon black were purchased from Ampacet (México).

Insects

Weevils of *S. zeamais* Motschulsky (Coleoptera: *Curculionidae*) were collected from INTA Manfredi, Córdoba, Argentina. Adult insects were reared on maize grains, without exposure to pesticides, in unsealed containers at 28 °C under a 12:12 h light-dark cycle (FAO 1974) and 70% humidity. Adult weevils of *S. zeamais* were used, both sexes and with different age in all experiments.

Development of bioactive silo bag

A prototype three-layer silo bag of pilot size was manufactured by co-extrusion process. It was mixing pellets of LDPE (internal and middle layers) and HDPE (external layer) and UV stabilizers (middle and external layer) (Beutelspacher, México CDMX, México), at Centro de Investigación en Alimentación y Desarrollo, A.C. campus Hermosillo, México, following conditions similar to those described in a previous study (Herrera *et al.*, 2021). Temperature range was 100-150 °C for LDPE and 130-160 °C for HDPE. An insecticide formulation consisting of terpene ketones (binary mixture of thymoquinone and pulegone, 1:1 mass ratio) was incorporated in the inner layer (LDPE) of the silo bag at an 8% w/w. The control silo bag was made without the insecticide formulation. It was used a micrometer apparatus to measure the thickness in the silo bags (E.J. CADY & CO, USA).

Optical, mechanical and chemical characterization of active silo bag

Five samples of silo bags (bioactive and control) were characterized following the methodology described by Herrera *et al.* (2021). Briefly, optical characterization was performed through Confocal Laser Microscopy (OLYMPUS LEXT OLS4000), and light transmission (UV-VIS) was analyzed with spectrophotometer (Varian Cary 50, Mulgrave, Victoria, Australia) at 400-500 nm. Were performed Mechanical studies by tensile testing following ASTM standards (D 882-02). Finally, chemical characterization was carried out by Fourier Transform Infrared (FTIR) spectrophotometer (Thermo Scientific, Nicolet IS50 FTIR, USA) using a wavenumber range of 600-4000 cm^{-1} with 32 scans.

Bioinsecticide quantification from the silo bag

The quantification of bioinsecticide compounds was performed in methanol extracts following the methodology described by Herrera *et al.* (2021). Five samples of 5 × 5 cm were placed in amber vials (40 mL) with 10 mL of methanol. The vials were then placed in the sonicator (TESLAB, TB04TDCD, Argentina) at 40 °C for 5 h. Gas chromatograph analysis in a Clarus 600 GC-MS Perkin-Elmer (GCMS) was used to identified and quantified the terpene ketones. Bioinsecticide components were separated in a DB-5 (30 m, 0.25 mm ID, 0.25 µm film thickness) capillary column. Helium was used as the carrier gas (flow rate 1 mL/min), and compounds were identified by comparing their retention times and mass spectra with published data (Adams, 2007) and available libraries (NIST, 2014). Mainly compounds were confirmed by co-injection of pure standards (Sigma, USA). Finally, the efficiency of the co-extrusion process was determined according to equation 1.

$$\mathrm{E}\ (\%) = \frac{mquant}{mload}\ X\ 100 \tag{1}$$

Where *mquant* is the mass of bioinsecticide compounds incorporated into the silo bag and *mload* is the total amount of the formulation loaded before the process.

Repellent effect of bioactive silo bag

The behavioral response of weevil adults to bioactive silo bag was evaluated in a choice olfactometer assay described by Brito *et al.* (2021), with some modifications. A sample of bioactive silo bag (25 cm^2) was placed in one of the flasks (250 mL) with corn grains (2.3 ± 0.28 g) while in the other flask only grains were placed. The size of sample was defined through quantified concentration and bibliographic data (Herrera *et al.*, 2015; Herrera *et al.*, 2017). Then, twenty insects deprived of food for 48 h were placed in olfactometer for two hours in a chamber at 28 °C and 70% humidity. The sample of the silo bag without insecticides was used as a control treatment. Five replicates for each treatment in different times were done. For each treatment, a response index (RI) was calculated through equation 2.

$$RI = [(T - C)/Tot]\ X\ 100 \tag{2}$$

Where T is the number of insects responding to the treatment, C is the number of insects responding to the control, and Tot is the total number of insects. Negative values of RI indicate repellence to the treatment, while positive values indicate attraction (Phillips *et al.*, 1993).

Insecticidal effect of bioactive silo bag against S. zeamais

Silo bags (bioactive and control) at laboratory scale (192 cm^2) were manufactured. Thus, 100 g of maize grains and 15 insect adults of *S. zeamais* were placed into silo bags without differentiating sex or age. Then, the bags were sealed with heat sealer. Finally, the silo bags were incubated in chamber at controlled temperature and humidity (25 °C and 70%, respectively). The experiment were performed in triplicate. After 15 days, was observed by each silo bag the mortality percentage (%) of insects in order to evaluate the immediate toxicity.

Data analysis

The Shapiro-Wilk test was used to test Normality of the data. The mean of RI of each treatment was determined using a paired-comparison analysis. The insecticidal effect of the bioactive and control silo bag was carried out by a one-way analysis. Subsequently, all differences between treatments were classified by a test-T ($p \leq 0.05$) using INFOSTAT/Professional software (Di Rienzo *et al.*, 2015).

RESULTS AND DISCUSSION

Characterization of bioactive silo bag

The measurement of silo bags manufactured at pilot scale was around 6 m long and 0.17 m wide. Figure 1 shows images taken from Confocal Laser Microscopy. No differences were observed between the active and control silo bags in the morphology of the external and inner layers.

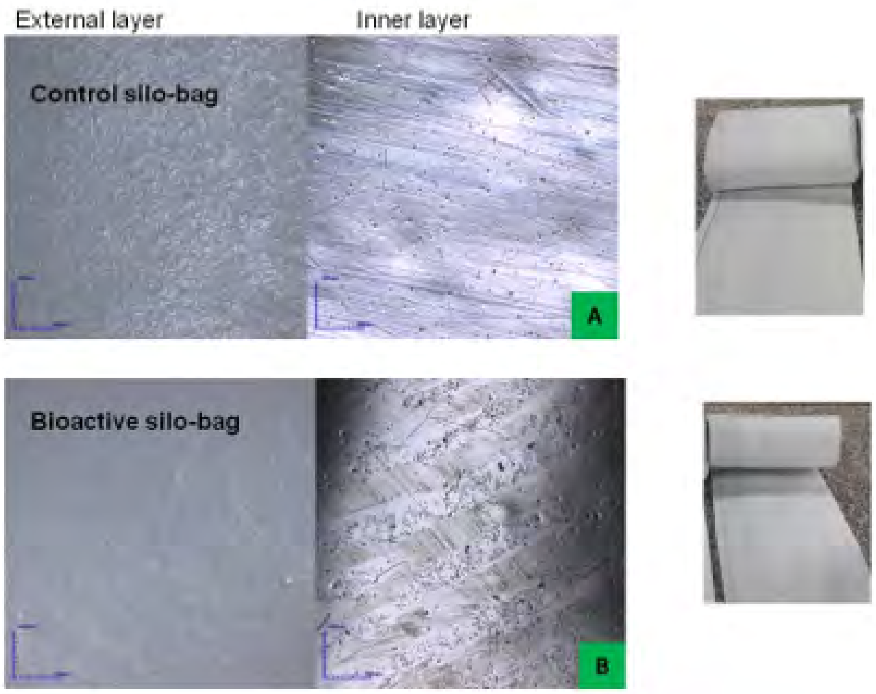


FIG. 1.
Laser Confocal (108X) images from the Control (A) and Bioactive silo bag (B).

According to Table 1, no significant differences were found in the light transmission and mechanical characterization of the silo bags extruded, except in the effort to break as shown by the bioactive silo bag, which could result from the greater thickness of the active silo bag.

TABLE 1.
Light transmission and mechanical characterization of silo bags extruded.

Film	Thickness (µm)	T * (%)	Penetration (g-µm)	Deformation (%)	Effort to break (MPa)
Control silo bag	208 ± 10^{a}	0^{a}	12.8 ± 2^{a}	445 ± 61^{a}	154 ± 13^{a}
Bioactive silo bag	235 ± 30^{a}	0^{a}	12.2 ± 1.9^{a}	389 ± 55^{a}	115 ± 13^{b}

*Light transmission at 400- 500 nm. Values are average ± standard deviation in five replicates, different letters show significant differences ($p \leq 0.05$).

A recent study reported by our research group (Herrera *et al.*, 2021) described similar values for the optical and mechanical properties of the silo bag with the incorporation of essential oil from *Mentha piperita* at around 7% w/w in the inner layer, without altering its polymeric morphology.

Figure 2 shows the presence of the ketone insecticides in the silo bag confirmed by FTIR. Therefore, common polyethylene (PE) absorption band can be seen at 1450 cm^{-1}, attributed to the C-H_2 functional group (Goñi *et al.*, 2017). Additionally, two characteristic bands are attributed to the C =O and C-H functional groups of ketones at 1657 and 1377 cm^{-1}, respectively (Fuertes Ruitón and Munguía Chipana, 2001; Goñi *et al.*, 2017).

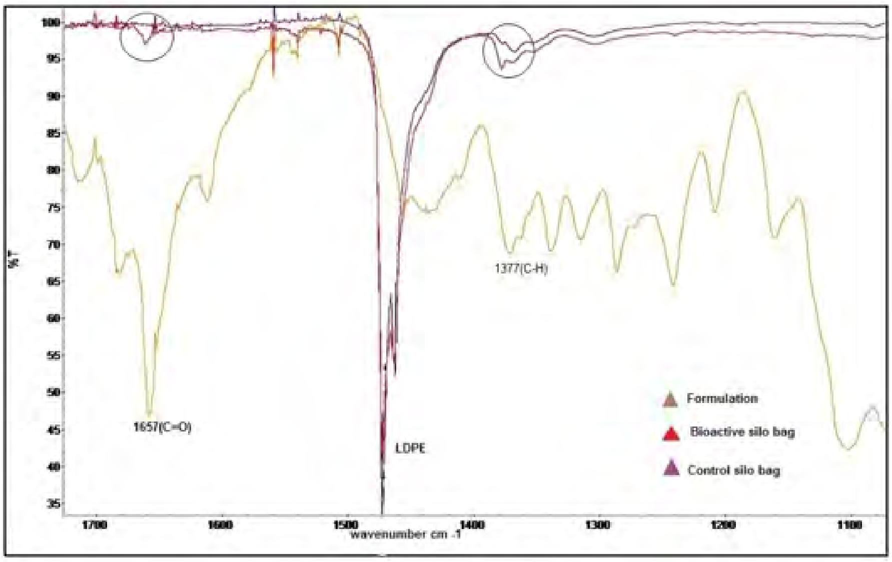
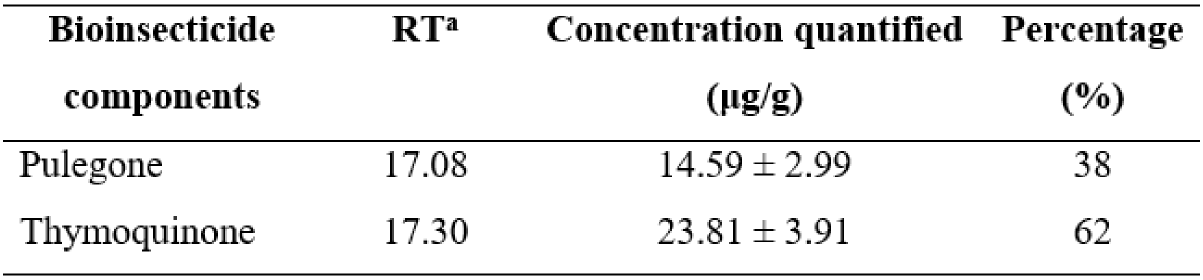


FIG. 2.
Fourier Transform Infrared (FTIR) spectra of bioactive silo bag (▲), Control silo bag (▲) and Formulation (▲).

Table 2 shows pulegone and thymoquinone terpenes quantified through silo bag with a mixture of 8% w/w in 1:1 mass ratio before the co-extrusion process. The chromatographic study revealed that thymoquinone was better incorporated in the inner layer (LEDP) of the silo bag than pulegone during the extrusion process. As the extrusion technique used high temperatures (100-180 °C) to melt polymer pellets, this difference could be attributed to the fact that the boiling point value of thymoquinone is higher than that of the pulegone (232 and 224 °C), respectively (Sigma-Aldrich, 2021; Herrera *et al.*, 2015). In addition, the efficiency extrusion process to incorporate ketone insecticides was 51.2%, while other reports revealed values near 30% for terpenes with a lower boiling point such as menthol, menthone and limonene into polyethylene three-layer films using the same operational conditions of co-extrusion technique (Herrera *et al.*, 2021). In contrast, for eugenol with a higher boiling point, an efficiency near to 60% by coextruded antimicrobial films was reported (Higuera-Barraza *et al.*, 2015). Results indicate that the addition of compounds with the extrusion technology into the polymeric matrix mostly depends on physicochemical properties, including the volatility or boiling point of the agent, due to high processing temperatures.

TABLE 2.
Concentrations of pulegone and thymoquinone from bioactive silo bag.



Bioinsecticide components	RT[a]	Concentration quantified (µg/g)	Percentage (%)
Pulegone	17.08	14.59 ± 2.99	38
Thymoquinone	17.30	23.81 ± 3.91	62

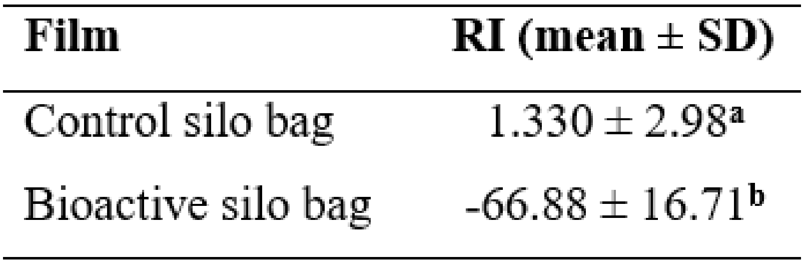
a Retention time on ELITE-5 column. Values are means ± standard deviation of three replicates.

Repellent and insecticidal activities of bioactive silo bag against S. zeamais

The bioactive films showed repellent response after 2 h exposure (Table 3).Previous studies found repellent values by pure individual compounds thymoquinone and pulegone, 77.8 ± 8.5 and 47.0 ± 12.2 at 4 µL/L air, respectively (Pizzolitto *et al.*, 2015). Thus, the behavioral responses of insects to the ketone formulation in the polymeric matrix still show repellent action. Taking into account the quantified concentration of the ketone formulation in the films, the estimated concentration in repellent assay was of 75 µL/L air; however, after 2 h exposure, not all formulation was released from the silo bag. In a previous study we reported the diffusion of menthol and menthone from the inner layer of the silo bag at different temperatures; hence, between 25 and 30 °C, the major release occurred on the seventh day (Herrera *et al.*, 2021).

TABLE 3.

Behavioral response of *S. zeamais* to silo bags, after 2 h exposure in a two-choice olfactometer.



Film	RI (mean ± SD)
Control silo bag	1.330 ± 2.98^{a}
Bioactive silo bag	-66.88 ± 16.71^{b}

Values of IR with different letters show significant differences through test-T ($p<0.05$, n=5). (+) values of RI indicate attraction. (−) values of RI indicate repellence.

Finally, the bioactive silo bag showed 100% of mortality toward S. zeamais, while the control silo bag (without formulation added) exhibited 0% of mortality. Previous studies showed the strong insecticidal activity of pulegone and thymoquinone against pest of stored products (Pizzolitto *et al.*, 2015; Herrera *et al.*, 2017) associated with neurotoxic effect through inhibition of AChE enzyme (Herrera *et al.*, 2015). In addition, α-β-unsaturated ketones were described as potent inhibitors of the enzymes Glutathione-S-transferases involved in the metabolism of xenobiotics (Yu and Abo-Elghar, 2000; Abdelgaleil *et al.*, 2009). On the other hand, further study should analyze the effect of active silo bags on grain quality for longer times. Various studies showed that the hermetic system preserved the quality of grains during 120 days of storage (Silva *et al.*, 2018). However, in the field, the commercial silo bags could be affected, not allowing their internal atmosphere to produce a lethal environment toward insects or fungi (Subramanyam *et al.*, 2012). Thus, the bioactive silo bag containing organic compounds in its inner layer could be an alternative to conventional pesticides for pest control (Zhang *et al.*, 2015; Vélez *et al.*, 2017), therefore, the bioactive silo bag should be registered as a bio-input.

CONCLUSION

The formulation of ketones in the hermetic structure of storage could be applied as a potential mechanism to control *S. zeamais*, which, in turn, could be extended to other pests that affect stored grains. Hence, biopesticides are a green alternative for organic agricultural with high selectivity, low impact on human health, and the environment.

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