Identification of Safener in Three Commercial Herbicide for Clodinafop-Propargyl by GC/MS.

Rasha M. A. El-Saman*


ABSTRACT

The purpose of this study is to figure out the chemical properties of three-different herbicide formulations (Arena7% OD, Koback24% EC, and Topik 15% WP) before and after storage at elevated temperatures of 54°C±2, and stability of formulations under study after exposure to UV rays. GC/MS was used to identify if tested formulations including safener in it is composition, and it was also used to prove mass fragmentation of tested formulations. GC/MS, analysis, demonstrates that only Topik contains safener material (Cloquintocet-mexyl), while, it was not found in both, Arena and Koback. Furthermore, four primary photolysis products were identified by GC/MS as 2-[(5-chloro-3-fluoro-2-pyridyloxy)phenoxy]propanoic acid and prop-2-ynyl-2-[(5-chloro-3-hydroxy-2-pyridyloxy)phenoxy]propanoate, Ethyl2-[(5-chloro-3-fluoro-2pyridyloxy)phenoxy]propanoate and 1-hydroxypropargyl-2-[(5-chloro-3-fluoro-2-pyridyloxy)phenoxy]propanoate were minor components. Due to paramount importance of presence of safener in herbicides, we recommend pesticide companies pay attention to adding safeners to herbicides to protect agricultural crops and reduce losses resulting from them. Also, we advise storing pesticides in typical stores (controlled by temperature and humidity) to prevent degradation of pesticides. In many cases, it produces compounds that may be more toxic than original pesticide. The aim of this paper we advise pesticides companies to add safener, and also advise farmers to use herbicides that contain the safener to protect important agricultural crops to prevent losses.

Keywords: Cloquintocet-mexyl, Elevated temperature, GC/MS, Safener, UV rays.

INTRODUCTION

Herbicides are pesticides that are applied to control or manage undesired plants. Herbicides are most typically employed in agriculture, where they are applied before or during planting to boost crop yield while lowering other vegetation. They account for nearly 60% of all pesticide sales in the United States, and can also be applied on crops in the fall to aid harvesting. Farmers in the United States spent $5.63 billion on herbicides in 1998, with an extra $1.1 billion on application costs. Herbicide use dropped to just over $5.0 billion in 1999. (Donaldson et al., 2002).

Clodinafop-propargyl is a systemic herbicide with aryloxypheoxy propionic acid groups that is used in wheat fields to control narrow-leaf weeds. Clodinafop-propargyl is absorbed via the weeds leaf one or two hours after spraying, and weed growth is inhibited after 48 hours. The effect of the herbicide can be observed after one to three weeks on weeds that are sensitive to it, Masoud Noshadi et al (2017). Clodinafop-propargyl (2-propynyl (R)-2-[4-(5-chloro-3-fluoro-2-pyridyloxy)phenoxy] propionate) is a systemic, postemergence herbicide that controls isoproturon-resistant little seed canary grass biotypes (Phalaris minor Retz.) as well as other broad-leaved wheat weeds (Triticum aestivum) (M. Airoldi, et al 1997, R. E. Blackshaw, et al 1998, U. S. Walla, 1998, C. E. Bell, 1999 and L. S. Brar, et al 1999).

This herbicide is used in conjunction with cloquintocet-mexyl as a safener, although it is hostile to auxin-type herbicides (P. Barnwell and A. H. Cobb, 1994). In sensitive grassy weeds, it prevents the formation of fatty acids required for plant growth (A. V. Toole, et al 1994).

Florasulam is N-(2, 6-difluorophenyl)-8-fluoro-5-methoxy [1, 2, 4]triazolo[1, 5-c]pyrimidine-2- sulfonamide, florasulam is a sulfonamide herbicide that is now approved for use in cereal weed control in Europe and Canada. (UNITED STATES ENVIRONMENTAL PROTECTION AGENCY WASHINGTON, DC 20465 2015).

Safeners, in particular, are a common class of herbicide chemicals, although their environmental fate is largely unknown (Sivey, J.D. 2015). Safeners are added to commercial herbicides to protect crops (such as maize and rice) from the active herbicide's fatal effects on pests (e.g., weeds). They typically make up 10-15% of the herbicide's active components (i.e., the herbicide's mass) (Sivey, J.D 2015), Woodward, E.E., et al (2018). Although safeners and other chemical additives are not the primary ingredients in commercial herbicides, their environmental outcome (i.e., transformation, degradation) could be substantial given the massive scale at which these commercial formulations are utilised. Safeners of herbicide are a broad group of chemicals, and several of them seem to work by increasing the herbicide's metabolism by the monocotyledonous crops on which it is applied. It's also chemically varied group of agrochemicals that improve weed control selectivity in cereals by shielding the crop from herbicide injury while leaving competitive weeds alone (Riechers et al, 2010). For each cereal crop application, Almost every safener is designed to work in tandem with specific post-emergence herbicides, either as a seed treatment or as a founder. (Davies and Casely, 1999, Kraehmer et al., 2014). A crop that would typically not tolerate the active ingredient can be protected by combining novel safeners with old herbicides, allowing
new chemistries to be used for weed control. (Kraehmer et al., 2014). The aromatic sulphonamides cyprosulfamide and metamifen, for example, are being utilised as herbicides in maize, acting on branched chain amino acid synthesis and tyrosine breakdown, respectively (Zheng et al., 2015).

Storage stability testing demonstrates how the quality of a product changes over time as a result of environmental factors such as temperature, humidity, and light. These investigations will show how these variables may affect product quality, safety, and performance. The main purpose of experiments was to examine how long the product’s percent active component would stay in its packaging and to collect data on how the product’s composition altered over time. New compounds may form if some substances break down at high or low temperatures and humidity, and their toxicity must be considered Rasha, M. A. El-saman (2015).

Cloquintocet-mexyl, which is combined with clodinafop-propargyl in Discover® Herbicide to protect the active component on wheat, is one of the most well-known herbicide safeners. (George W. Ware and David M. Whitacre 2004).

Photodegradation is one of the most common ways for pesticides to leave the environment. The efficacy and safety of these xenobiotics are governed by two major factors: the timing and type of degradation (Sugata Roy and Shashi B. Singh 2014).

In this paper, we studied the stability of Clodinafop-propargyl and safener (Cloquintocet-mexyl) in the three herbicide formulations during storage for 30 days at 54 ± 2°C and UV rays. Finally, identification of the tested Clodinafop-propargyl herbicides by GC/MS.

MATERIALS AND METHODS

In Table 1, Clarifying the trade name, common name, registration number and chemical structure for the tested herbicides.

Table I. Herbicides under test

<table>
<thead>
<tr>
<th>Trade name</th>
<th>Common name</th>
<th>Reg. NO.</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arena 7% OD</td>
<td>Clodinafop-propargyl 6.5%</td>
<td>2706</td>
<td></td>
</tr>
<tr>
<td>2-Florasulam 0.5%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Koback EC</td>
<td>Clodinafop-propargyl 24%</td>
<td>2517</td>
<td></td>
</tr>
<tr>
<td>Topik WP</td>
<td>Clodinafop-propargyl 15%</td>
<td>690</td>
<td></td>
</tr>
</tbody>
</table>


Storage at elevated temperature:

Three formulations were tested and stored in the oven for 30 days at 54± 2°C, according to FAO SPECIFICATIONS AND EVALUATIONS FOR AGRICULTURAL PESTICIDES (2008), samples were collected at 1, 3, 7, 14, and 30 days during the storage period to evaluate the active ingredient concentration.

**Standard preparation of Clodinafop-propargyl:**

Individual standard solutions for (0.01gm) Clodinafop-propargyl were produced in a 25 ml volumetric flask with methanol at 10mg.

**Standard preparation of Florasulam:**

Individual standard solutions for (0.01gm) Florasulam were produced in a 25 ml volumetric flask with acetonitrile at 10mg.

**Standard preparation of the safener (Cloquintocet-mexyl):**

Individual standard solutions of 10mg (0.01gm) Cloquintocet-mexyl were produced in a 25 ml volumetric flask, replete with methanol.

**Sample preparation for tested pesticides:**

For each sample, a 25 mL volumetric flask is used, accurately weigh sufficient samples formulation equivalent to 10 mg of standard, and slowly mix with methanol for (Clodinafop-propargyl) and the volume was completed with methanol; also slowly mix with Acetonitrile for (Florasulam) and the volume was completed with Acetonitrile.

**Determination of Clodinafop-propargyl by HPLC instrument:** According to DUAN Jinsheng (2013), with some modifications

Clodinafop-propargyl active ingredient was evaluated before and after storage using HPLC (Agilent Technologies 1260 Infinity II) with a UVdetector, a Quat. Pump, and a 210 nm wave length detector. The rate of flow was 1.3 ml/min and the column was C18. acetonitrile:methanol (70:30) was used as the mobile phase). The retention time (RT) of Clodinafop-propargyl was 2.153min.

**Determination of Florasulam:**

A UV-detector was employed with HPLC (Agilent Technologies 1260 Infinity II). At 210 nm, the wave length detector is used. The rate of flow was 1.3 ml/min and the column was C18. The mobile phase was 70:30 acetonitrile: methanol, and the retention time (RT) of Florasulam was 1.605 min under these conditions. This procedure was accomplished by using a Zhang Mei-feng (2010) modified method.

**Determination of Cloquintocet-mexyl.** According to (Katerina Mastovska et al 2017), with some modifications a UV-detector was employed with HPLC (Agilent Technologies 1260 Infinity II). At 210 nm, the wave length detector is used. The rate of flow was 1.3 ml/min and the column was C18. acetonitrile:methanol (70:30) was used as the mobile phase. Cloquintocet-mexyl had a retention time (RT) of 4.074 minutes under these conditions.

**GC/MS analysis revealed fingerprint characteristics for Clodinafop-propargyl formulations and its safener, Cloquintocet-mexyl.**

The Agilent 7890 B, 5977 A MSD gas chromatographic system was utilised, It was fitted with a mass spectrometric detector from Agilent, a fused silica capillary column (30 m 0.025 mm HP-5-0.25 microm -60 to 325/325 (OC) with a direct capillary interface. The following conditions were used to inject the samples: Helium was employed as the carrier gas at a rate of about 1 mL/min in a pulsed split mode with a split ratio of 10:1 and a split flow of 10 mL/min. The injection size was 1ul and the solvent delay.
was 4 minutes. The injector temperature was set at 2800°C and the oven temperature program was 500°C for 4 minutes, then a 100°C/min ramp to 2100°C for 1 minute, then a 100°C/min ramp to 2700°C for 1 minute, then a 100°C/min ramp to 3000°C and held for 2 minutes (total run time: 35 minutes). The split peaks were identified using the NIST mass spectral data base. Clofafen-propargyl and Cloquintocet-mexyl retention time (RT) were measured under these conditions are 23.444 and 24.499 min, respectively).

Effect of UV rays.

A pipette was used to apply a solution of clofafen-propargyl in acetone (10 ml, 1 mg ml⁻¹) uniformly to the inner surface of glass petriplates (20 cm in diameter) for investigations on a glass surface. At ambient temperature, the solvent was evaporated, leaving a thin film of clofafen ester behind. These plates were subjected to ultraviolet radiation for 30 days by placing them under a UV lamp at a distance of 30 cm and irradiating them for 30 days, following which they were removed with acetone (5 × 10 ml). This lamp produced a lot of irradiation at 254 nm, and the plates were exposed to UV radiation (254 nm) for 30 days. Accordingly to (Sugata Roy and Shashi B. Singh 2014).

Kinetic study:

According to the equation, the rate of degradation of the tested active component and half-life periods (T0.5) for the tested pesticides was computed. (Moye et al., 1987 and A. El Masri 2014).

\[
T0.5 = \ln 2 / K = 0.6932K \text{ and } K = \frac{1}{tX} \ln \frac{a}{bx}
\]

Were

\( K = \text{decomposition rate} \)
\( a = \text{residue at the start} \)
\( tX = \text{Time is measured in days and hours} \)
\( bx = \text{residual after x amount of time} \)

RESULTS AND DISCUSSION

1- The effect of storing Clofafen-propargyl and Florasulam at 54 ±2°C on the stability of the tested herbicide formulations. (Significant variations should be added).

The data presented in Table (2) showed that Clofafen-propargyl active ingredient of (Arena 7% OD) was 6.48% at the beginning of experiment and were degraded to (6.37, 6.33, 6.15 and 5.75%) after 3, 7, 14 and 30 days of storage at 54±2°C, respectively, and showed that Florasulam was 0.499% at the beginning of experiment and were degraded to (0.496, 0.494, 0.487 and 0.473%) after 3, 7, 14 and 30 days of storage at 54±2°C, respectively. The active ingredient of (Koback 24% EC) was 23.94% at the beginning of experiment and were degraded to (23.72, 23.4, 22.94 and 21.75%) after 3, 7, 14 and 30 days of storage at 54±2°C, respectively. The active ingredient of (Topik 15% WP) was 14.98% at the beginning of experiment and were degraded to (14.85, 14.42, 14.35 and 12.93%) after 3, 7, 14 and 30 days of storage at 54±2°C respectively as shown in Table (2). According to FAO specifications 2008 (storage at 54±2°C for 14 days) data showed that the samples conformed to these specifications.

Table 2. The effect of 54 ±2°C storage on the stability of Clofafen-propargyl formulations.

<table>
<thead>
<tr>
<th>Storage Period (days)</th>
<th>Pesticide used</th>
<th>Clofafen-propargyl</th>
<th>Clofafen-propargyl</th>
<th>Clofafen-propargyl</th>
<th>Clofafen-propargyl</th>
<th>Clofafen-propargyl</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Arena 7% OD</td>
<td>Clodinafop</td>
<td>Clodinafop</td>
<td>Clodinafop</td>
<td>Clodinafop</td>
<td>Clodinafop</td>
</tr>
<tr>
<td></td>
<td>Koback 24% EC</td>
<td>Loss</td>
<td>Loss</td>
<td>Loss</td>
<td>Loss</td>
<td>Loss</td>
</tr>
<tr>
<td></td>
<td>Topik 15% WP</td>
<td>Active ingredient</td>
<td>Active ingredient</td>
<td>Active ingredient</td>
<td>Active ingredient</td>
<td>Active ingredient</td>
</tr>
<tr>
<td></td>
<td></td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>Initial</td>
<td>6.48</td>
<td>0.31</td>
<td>0.499</td>
<td>0.2</td>
<td>23.94</td>
<td>0.25</td>
</tr>
<tr>
<td>3</td>
<td>6.37</td>
<td>2</td>
<td>0.496</td>
<td>0.8</td>
<td>23.72</td>
<td>1.17</td>
</tr>
<tr>
<td>7</td>
<td>6.33</td>
<td>2.62</td>
<td>0.494</td>
<td>1.2</td>
<td>23.4</td>
<td>2.5</td>
</tr>
<tr>
<td>14</td>
<td>6.15</td>
<td>5.38</td>
<td>0.487</td>
<td>2.6</td>
<td>22.94</td>
<td>4.42</td>
</tr>
<tr>
<td>30</td>
<td>5.75</td>
<td>11.5</td>
<td>0.473</td>
<td>2.2</td>
<td>21.75</td>
<td>9.38</td>
</tr>
<tr>
<td>bx = residual after x amount of time</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial= zero time before storage.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table (2) shows that the half-lives of clofafen-propargyl in three tested formulations were 192.55, 252.07 and 297.19 in Arena, Koback, and Topik respectively.

The results are agreement with Rasha, M. A. El-saman (2015). She found that storage stability testing demonstrates how the quality of a product changes over time as a result of environmental factors such as temperature, humidity, and light. The main purpose of experiments was to examine how long the product's percent active component would stay in its packaging and to collect data on how the product's composition altered over time. New compounds may form if some substances break down at high or low temperatures and humidity, and their toxicity must be considered.

2- The impact of storing at 54±2°C on the stability of Cloquintocet-mexyl on the tested herbicides formulations.

The data of Table (3), safener material (Cloquintocet-mexyl), showed that only found in Topik, while, Arena and Koback does not contain it. And Cloquintocet-mexyl in Topik decreases by storage condition to become 4.39 after 30 days at 54±2°C. From this data we advise pesticides companies to add safener, and also advise farmers to use herbicides that contain the safener to protect important agricultural crops to prevent losses.

The results are agreement with (Hamad R. F. et al 2021). They found that arena 7% OD in 2020 destroyed
about 20% yield of wheat in Egypt. Although it successfully the required tests, there are factors other than the specifications and quality of the Arena that led to problems in the wheat crop. From my results obtained, the effect may be due to the absence of safener.

The results are agreement with (George W. Ware and David M. Whitacre 2004). They found that herbicide which content safener with which for ex. Benoxacor, first approved in 1997, improved s-metolachlor (and metolachlor) corn tolerance. Corn tolerance to thiocarbamate herbicides is increased by dichlormid. In vulnerable species, such as wheat, fenoxprop-ethyl synergizes with the activities of fenoxprop-ethyl to minimise phytotoxicity and growth retardation. In tiny grains, mfenpyr-diethyl also protects fenoxprop-P-ethyl. When used as a seed treatment, flufloxim and oxabetrinil protect sorghum from metolachlor harm, especially when metolachlor is used in combination with a triazine herbicide. Furilazole is a herbicide safener that can be used on cereals, corn, and rice to protect against a variety of herbicides.

### Table 3. The effect of storing Cloquintocet-mexyl formulations at 54 ± 2°C on their stability.

<table>
<thead>
<tr>
<th>Pesticide used</th>
<th>Storage period (days)</th>
<th>Arena 7% OD</th>
<th>Koback 24% EC</th>
<th>Topik 15% WP</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Clodinafop-mexyl 1.625%</td>
<td>Active ingredient %</td>
<td>Loss %</td>
<td>Active ingredient %</td>
</tr>
<tr>
<td>Initial</td>
<td>UND</td>
<td>UND</td>
<td>UND</td>
<td>4.51</td>
</tr>
<tr>
<td>3</td>
<td>UND</td>
<td>UND</td>
<td>UND</td>
<td>4.49</td>
</tr>
<tr>
<td>7</td>
<td>UND</td>
<td>UND</td>
<td>UND</td>
<td>4.43</td>
</tr>
<tr>
<td>14</td>
<td>UND</td>
<td>UND</td>
<td>UND</td>
<td>4.42</td>
</tr>
<tr>
<td>30</td>
<td>UND</td>
<td>UND</td>
<td>UND</td>
<td>4.39</td>
</tr>
</tbody>
</table>

Initial= zero time before storage.

3. Identification of the presence of Clodinafop-propargyl and Cloquintocet-mexyl (Safener) in three tested formulations (Arena, Koback, and Topik) by chemical ionization GC/MS spectroscopy.

After quantitative analysis of Clodinafop-propargyl and its safener Cloquintocet-mexyl in three tested formulations by HPLC, qualitative analysis by chemical finger print was performed using GC/MS, as shown in figures (1, 2 and 3).

According to figures 3,4,5, GC/MS shows RT of Clodinafop-propargyl was 23.444 and RT of Cloquintocet-mexyl was 24.499. So proved that GC/MS shows only Topik contains a safener (Cloquintocet-mexyl).

4. The effect of UV rays.

Table (4) show that half-lives of clodinafop-propargyl in three tested formulations were 7.43, 8.01 and 6.63 respectively in Arena, Koback and Topik.

### Table 4. Effect of UV rays on the stability of the Clodinafop-propargyl formulations.

<table>
<thead>
<tr>
<th>Storage period (days)</th>
<th>Arena 7% OD</th>
<th>Florasulam</th>
<th>Koback 24% EC</th>
<th>Topik 15% WP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clodinafop-propargyl</td>
<td>Active ingredient %</td>
<td>Loss %</td>
<td>Active ingredient %</td>
<td>Loss %</td>
</tr>
<tr>
<td>Initial</td>
<td>6.47</td>
<td>0.46</td>
<td>0.498</td>
<td>0.4</td>
</tr>
<tr>
<td>3</td>
<td>3.11</td>
<td>52.15</td>
<td>0.301</td>
<td>39.8</td>
</tr>
<tr>
<td>7</td>
<td>2.75</td>
<td>57.69</td>
<td>0.255</td>
<td>49</td>
</tr>
<tr>
<td>14</td>
<td>1.15</td>
<td>82.30</td>
<td>0.177</td>
<td>64.6</td>
</tr>
<tr>
<td>30</td>
<td>0.988</td>
<td>84.8</td>
<td>0.098</td>
<td>80.4</td>
</tr>
</tbody>
</table>

Initial= zero time before storage.

These results were matched with (Sugata Roy and Shashi B. Singh 2014). During phototransformation investigations, two main metabolites, 2 and 4 (Fig. 6), were discovered. The kinetics of these two metabolites revealed that photometabolite 2 (clodinafop acid) was at its peak on the 10th day (Table 4). The greatest intensity of photometabolite 3 (i.e., hydroxylated product) was observed on the fifth day of irradiation, following which it began to decompose (Fig. 6) and Table (5). Mass spectrum analysis revealed the structure of both products. According to chemical compositions of these photometabolites, no interconversion between the two products is possible. It means that production of chemicals 2 and 4 followed two separate routes. C-O cleavage produces compound 2 and aromatic ring hydroxylation produces compound 4.

Fig. 1. GC/MS chromatogram of Clodinafop-propargyl in Arena.

Fig. 2. GC/MS chromatogram of Clodinafop-propargyl in Koback.
The herbicide clodinafop-propargyl was tested for photodegradation on a glass surface under Ultraviolet rays. MS was able to identify four photoproducts GC/MS identified the major photolysis products as 2-[(5-chloro-3-fluoro-2-pyridyloxy) phenoxy] propanoic acid and prop-2-ynyl-2-[(5-chloro-3-hydroxy-2-pyridyloxy) phenoxy] propanoate, while minor were ethyl 2-[(5-chloro-3-fluoro-2-pyridyloxy) phenoxy] propanoate and 1-hydroxypropanoyl-2-[(5-chloro-3-fluoro-2-pyridyloxy) phenoxy] propanoate, as illustrated in figure (6) and Table (5).

Table 5. products of clodinafop-propargyl formed under ultra-violet rays.

<table>
<thead>
<tr>
<th>Product</th>
<th>Molecular Weight</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clodianfop-propargyl</td>
<td>350</td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>Clodianfop acid</td>
<td>310</td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>5-Chloro-3-fluoro-2-pyridinol</td>
<td>147.5</td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>4—Hydroxy analogue</td>
<td>348</td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>Reduction product</td>
<td>339</td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>Reduction product</td>
<td>370</td>
<td><img src="image" alt="Structure" /></td>
</tr>
</tbody>
</table>

REFERENCES


Rasha M. A. El-saman


UNITED STATES ENVIRONMENTAL PROTECTION AGENCY WASHINGTON, DC 2046 2015 Q9H / GoldSky / MSTR NOTIF With Edits / 03-06-15.


العنصر المشابه للمادة المذكورة في ثلاثة مستحضرات تجارية لمبيد الحشائش الكلودينافوب بروفارجيل بواسطة جهاز الكرموترو جرافي الغازى/مطياف الكتلة من جامعة القاهرة/ كلية علوم الزراعة، 10.5% - جماعة الفحيصى - مصر

قسم بحوث تحليل المبيدات - المعالق المركزى للمبيدات - مركز البحوث الزراعية - الدقي - جماعة الصليبي - مصر

الهدف من هذا البحث هو فحص الخصائص الكيميائية للثلاثة من مبيدات الحشائش (أرث مارس 2008) 7% مركز زينز آلل للانتاج، كويك 24% مركز قابل للاستدعال، وتوبيك 15% مستحيل قابل للالتحال. قُبل بعد التخزين عند درجة حرارة مرسية 54 درجة مئوية ± 2 درجة مئوية لمدة 255 لليمين، ودراسه نتائج استخدم ما إذا كانت المستحضرات المخللة بها مادة موجهة أو لا تحتوي MCA على مادة موجهة (إيريك كي نورث) بعد المحزنات لاستخدام GC/MS و/أو GC/MS/MS تناجي أخرى للاستعمالات الحياتية إيريك كي نورث، و/أو GC/MS/MS (إيريك كي نورث) بعد المحزنات لاستخدام GC/MS/MS. تم استخدام مكير في الحشرات التحميل الحياتية كالآتي: 2-(5-كلورو-3-غلوترو-2-بيربينوكي-فيروسكيني) مكير مكير 2-(5-كلورو-3-غلوترو-2-بيربينوكي-فيروسكيني) مكير 2-(5-كلورو-3-غلوترو-2-بيربينوكي-فيروسكيني) مكير 2-(5-كلورو-3-غلوترو-2-بيربينوكي-فيروسكيني) مكير 2-(5-كلورو-3-غلوترو-2-بيربينوكي-فيروسكيني) مكير 2-(5-كلورو-3-غلوترو-2-بيربينوكي-فيروسكيني) مكير 2-(5-كلورو-3-غلوترو-2-بيربينوكي-فيروسكيني) مكير. نظرًا للأهمية الجزيئية من ناحية الثانوية والثائرة في مبيدات الحشائش، فإننا نوصي شركات المبيدات بالاهتمام بإعداد نواحي موجهة في مبيدات الحشائش، فإننا نوصي شركات المبيدات بالاهتمام بإعداد نواحي موجهة في مبيدات الحشائش، فإننا نوصي شركات المبيدات بالاهتمام بإعداد نواحي موجهة في مبيدات الحشائش، فإننا نوصي شركات المبيدات بالاهتمام بإعداد نواحي موجهة في مبيدات الحشائش، فإننا نوصي شركات المبيدات بالاهتمام بإعداد نواحي موجهة في مبيدات الحشائش، فإننا نوصي شركات المبيدات بالاهتمام بإعداد نواحي موجهة في مبيدات الحشائش، فإننا نوصي شركات المبيدات بالاهتمام بإعداد نواحي موجهة في مبيدات الحشائش، فإننا نوصي شركات المبيدات بالاهتمام بإعداد نواحي موجهة في مبيدات الحشائش، فإننا نوصي شركات المبيدات بالاهتمام بإعداد نواحي موجهة في مبيدات الحشائش، فإننا نوصي شركات المبيدات بالاهتمام بإعداد نواحي موجهة في مبيدات الحشائش، فإننا نوصي شركات المبيدات بالاهتمام بإعداد نواحي موجهة في مبيدات الحشائش، فإننا نوصي شركات المبيدات بالاهتمام بإعداد نواحي موجهة في مبيدات الحشائش، فإننا نوصي شركات المبيدات بالاهتمام بإعداد نواحي موجهة في مبيدات الحشائش، فإننا نوصي شركات المبيدات بالاهتمام بإعداد نواحي موجهة في مبيدات الحشائش، فإننا نوصي شركات المبيدات بالاهتمام بإعداد نواحي موجهة في مبيدات الحشائش، فإننا نوصي شركات المبيدات بالاهتمام لإعداد نواحي موجهة في مبيدات الحشائش.