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The quality of fluazifop-P-butyl formulations currently applied in Egypt

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ABSTRACT: Four commercial fluazifop-P-butyl emulsifiable concentrate (EC) formulations 12.5% were collected from the Egyptian market (manufactured by four different companies) named as (source I, II, III, and IV) to investigate the stability of fluazifop-P-butyl after storage at 54 ±2 ºC and in sunlight for 70 days, also identification of some degradation products after storage in sunlight using GC-MS. The obtained results showed that, fluazifop-P-butyl was stable after storage at 54 ±2 ºC for 14 days, but with the increase in the period of storage there was an increase in the rate of degradation for all sources. Fluazifop-P-butyl was less stable after storage in sunlight than storage at 54 ±2 ºC and there was no difference in the rate of degradation for all fluazifop-P-butyl formulations except fluazifop-P-butyl from source I. Analysis of samples after storage in sunlight using GC-MS identified five degradation products: fluazifop acid, 2-(4-hydroxyphenoxy)-5-trifluoro-methyl pyridine, 2-(4-hydroxyphenoxy) propionic acid, 2-hydroxy-5-trifluoromethylpyridine and 3-(trifluoromethyl) pyridine.

Keywords: Fluazifop-P-butyl, Fluazifop acid, Degradation, Degradation products, GC-MS.

1.INTRODUCTION

Fluazifop-P-butyl is one of the most important chemical groups for weeds control is called aryloxyphenoxypropionate acid herbicides **(Délye 2005)**, has been permitted for use in Egypt since decades. There are currently 15 products registered in Egypt that contain fluazifop-P-butyl as the active ingredient and the average quantities used in the previous three years about 14 tons of active ingredient **(APC 2020)**. The fluazifop-P-butyl formulations registered in Egypt has been recommended to control annual and perennial grasses in many crops such as potatoes, onions, peanuts, tomatoes, citrus and stone fruits **(APC 2020)**. Fluazifop-P-butyl doesn't affect ground water pollution; also it has low toxicity to birds and mammals **(Tu et al., 2001)**. Fluazifop-P-butyl is highly toxic to fish that penetrate fish tissues and LC_{50} >10 mg/l **(EXTOXNET 1996),** also it has significant impact on non-target organisms **(Abdel-Mallek et al., 1996)** and **(Gorlach-Lira et al., 1997)**. In environment the degradation of fluazifop-P-butyl is very rapid to form fluazifop acid **(Negre et al., 1988)** followed by another transformation to 2-hydroxy-5-trifluoromethylpyridine **(Mills and Simmons, 1998)**. High percentage of fluazifop-P-butyl about 97% can break down undergo hydrolysis to fluazifop acid within 24 h in soils **(Bewick 1986)**. In water fluazifop-P-butyl degradation was very rapid and the half-lives of enantiomers were in range 0.34 to 2.52 days, also fluazifop-P-butyl enantiomers can be broken down faster by alkaline conditions than acidic conditions **(Qi et al., 2016)**. Fluazifop-P-butyl can break down undergo hydrolysis to fluazifop acid in soils and water, that the increasing in temperatures can increase the hydrolysis percentage **(Balinova and Lalova 1992)**.

The aim target of this work is to investigate and study the stability of four commercial fluazifop-P-butyl emulsifiable concentrate formulations 12.5% collected from the Egyptian market (manufactured by four different companies) after storage at different intervals of temperature (54 ±2 ºC) and sunlight. The Identification of some degradation products after storage in sunlight using GC-MS was also studied. The chemical structure of fluazifop-P-butyl is shown in Fig. 1.

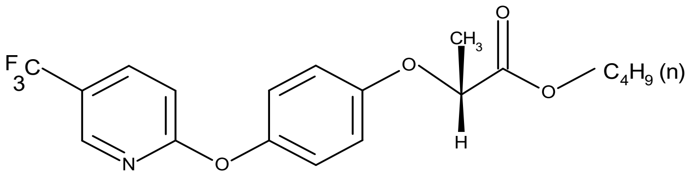


Fig. 1. Chemical structure of fluazifop-p-butyl

2.MATERIALS AND METHODS

2.1.Chemicals

Analytical standard of fluazifop-P-butyl (butyl (*R*)-2-[4-(5-trifluoromethyl-2-pyridyloxy) phenoxy] propionate; CAS RN [79241-46-6] with 95% purity), was obtained from Sigma Aldrich. The commercial formulations of fluazifop-P-butyl 12.5% EC (w/v) were obtained from four different sources in Egypt (Manufactured by four different companies). Methanol HPLC Grade (Merck) was used.

2.2.Accelerated storage procedures (CIPAC MT 46, 1995)

Emulsifiable concentrate formulations of fluazifop-P-butyl (12.5%) were placed in bottles (about 50 ml). These bottles were divided into two groups and subjected to different treatments as follows: The first group was exposed to storage at 54 ±2 °C for 70 days, while the second group was exposed to sunlight for 70 days. Samples from the two tested groups were taken at different periods of 0, 14, 28, 42, 56, and 70 days.

2.3.Standard Preparation

Weight 10 mg of fluazifop-P-butyl analytical standard into a 25 ml volumetric flask then dissolve it and complete to the final volume with methanol.

2.4.Sample Preparation

Accurately weight sufficient sample of fluazifop-P-butyl formulation 12.5% to equivalent 10 mg of fluazifop-P-butyl standard into a 25 ml volumetric flask mix slowly with methanol and complete the volume with methanol.

2.5.Measurements

2.5.1. HPLC Determination

This procedure according to **CIPAC 467/TC/M/-(1995).** The HPLC analyses were carried out with Agilent Technologies 1260 infinity II auto sampling system, consisting of quaternary pump, column and UV detector. The chromatographic separation was performed with Agilent Zorbax Eclipse plus C_{18} (4.6 mm ID x 250 mm x 5 µm) chromatographic column. The mobile phase was acetonitrile – methanol (70:30), at a flow rate of 1 ml/min. Fluazifop-P-butyl was detected by UV detector at wavelength of 210 nm. The injection volume was 5 µl. Under these conditions the typical retention time of fluazifop-P-butyl was 3.12 min.

2.5.2.Gas chromatography-mass spectrometry analysis (GC-MS)

The GC-MS analysis was performed with an Agilent 7890B gas chromatograph equipped with 5977 A MSD Aglient mass spectrometric detector, with a direct capillary interface and fused silica capillary column HP-5MS (30 m x 0.25 mm x 0.25 µm film thickness). Helium was used as carrier gas at approximately 1.0 ml/min pulsed split mode. The injection volume was 1 µl. The GC temperature program was held at 50 °C for 0.5 min, then ramp 10 °C /min to 190 °C for 1 min. followed by ramp 10 °C /min to 300 and held for 2 min °C (total run time 29.5 min). The injector temperature was set at 280 °C. The mass spectra were identified using Wiley mass spectral data base Library.

2.5.3. Kinetic study

According to (**FAO 2000)** the content of fluazifop-P-butyl after storage should not be lower than 95% relative to the content of fluazifop-P-butyl before storage. Shelf life of fluazifop-P-butyl was calculated according to (**Moye et al., 1987)** and **(Anderson and Scott 1991)**.

t_{95} for fluazifop-P-butyl = 0.0513/K

$K = (1/t_x) \ln (a/b_x)$

Where, t_{95} = the time required to reach 95% of the initial fluazifop-P-butyl concentration.

K = rate of degradation

0.0513 = Ln (0.95)

a = initial concentration

t_x = time in days

b_x = concentration at x time

3.RESULTS AND DISCUSSION

3.1.Effect of storage on stability of fluazifop-P-butyl 12.5% EC content.

Table 1 and Fig. 2 demonstrated the effect of storage at 54 ±2 °C for 70 days on stability of four commercial fluazifop-P-butyl formulations and indicated that, fluazifop-P-butyl has not been changed by storage at 54 ±2 °C for 14 days for all sources under investigation, but with the increase in the period of storage, it is observed that there was an increase in the rate of degradation for all sources and the loss percentages increased to reach 18.99, 12.11 12.41 and 10.75%, also shelf-lives were 17.05, 27.82, 27.10 and 31.56 days for source I, II, III and IV, respectively. Fluazifop-P-butyl was less stable after storage in sunlight than storage at 54 ±2 °C for 70 days and the data in Table 2 and Fig. 3 showed the stability of four commercial fluazifop-P-butyl formulations after storage in sunlight for 70 days and the results indicated that the loss percentages after 70 days were found to be 23.80, 15.80, 12.97 and 10.83%, and also the shelf-lives were 13.29, 19.73, 25.85 and 28.50 days for source I, II, III and IV, respectively. The previously mentioned results clearly showed that the rate of degradation of the four fluazifop-P-butyl formulations under investigation was influenced by long period storage at 54 ±2 °C as well as exposure to sunlight. There is no difference in the rate of degradation for all fluazifop-P-butyl formulations except fluazifop-P-butyl from source I, as it was observed that the rate of degradation was faster and its stability was less than other sources of fluazifop-P-butyl and this is the result of being affected by many factors such as manufacturing process, sources of starting materials, adjuvants,

Table (1): Effect of storage on stability of fluazifop-P-butyl 12.5% EC collected from four different manufactured sources at 54 ±2 °C

Storage Periods (Days)	Source I		Source II		Source III		Source IV	
	fluazifop-P-butyl content (w/v)	Loss %	fluazifop-P-butyl content (w/v)	Loss %	fluazifop-P-butyl content (w/v)	Loss %	fluazifop-P-butyl content (w/v)	Loss %
0	12.48*	0	12.47	0	12.49	0	12.46	0
14	12.47	0.08	12.33	1.12	12.27	1.76	12.41	0.40
28	11.04	11.54	11.52	7.62	11.66	6.65	12.14	2.57
42	10.67	14.50	11.25	9.78	11.31	9.45	11.81	5.22
56	10.51	15.79	11.10	10.99	11.21	10.25	11.53	7.46
70	10.11	18.99	10.96	12.11	10.94	12.41	11.12	10.75
t_{95} (days)	**17.05		27.82		27.10		31.56	

* Samples before and after storage stability test analyzed together to reduce the analytical error.

** The time required to reach 95% of the initial fluazifop-P-butyl concentration.

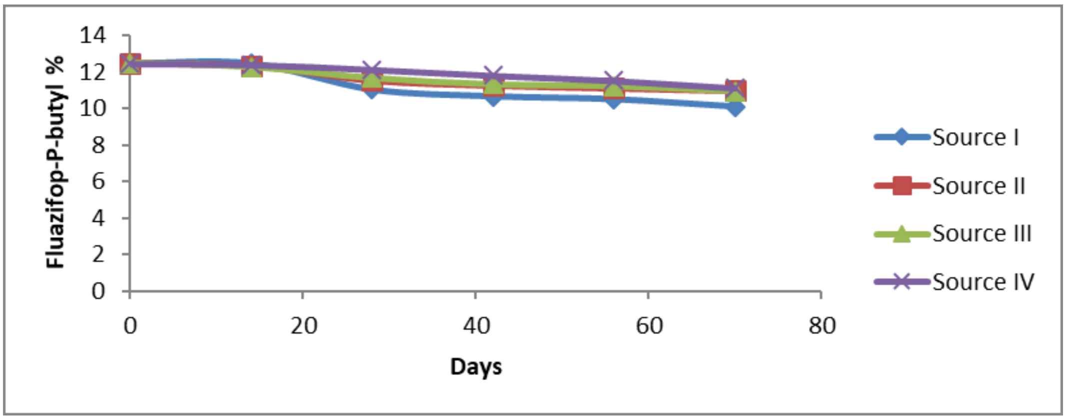


Fig. (2). Effect of storage on stability of fluazifop-P-butyl 12.5% EC collected from four different manufactured sources at 54 ±2 °C.

Table (2): Effect of storage on stability of fluazifop-P-butyl 12.5% EC collected from four different manufactured sources in sunlight.

Storage Periods (Days)	Source I		Source II		Source III		Source IV	
	fluazifop-P-butyl content (w/v)	Loss %	fluazifop-P-butyl content (w/v)	Loss %	fluazifop-P-butyl content (w/v)	Loss %	fluazifop-P-butyl content (w/v)	Loss %
0	12.48*	0	12.47	0	12.49	0	12.46	0
14	11.48	8.01	11.66	6.50	12.04	3.60	12.37	0.72
28	10.88	12.82	11.28	9.54	11.43	8.49	11.93	4.25
42	10.09	19.15	10.99	11.87	11.26	9.85	11.61	6.82
56	9.91	20.59	10.80	13.39	10.93	12.49	11.35	8.91
70	9.51	23.80	10.50	15.80	10.87	12.97	11.11	10.83
t_{95} (days)	**13.29		19.73		25.85		28.50	

* Samples before and after storage stability test analyzed together to reduce the analytical error.

** The time required to reach 95% of the initial fluazifop-P-butyl concentration.

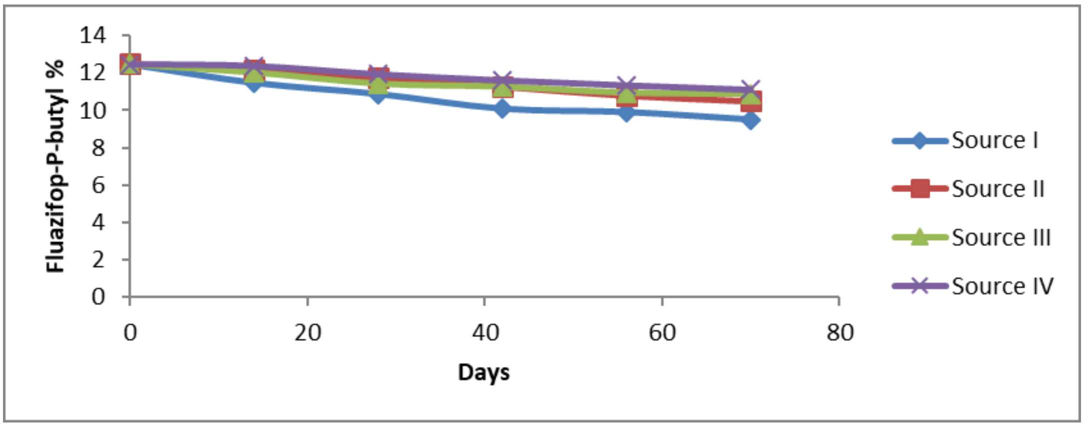


Fig. (3). Effect of storage on stability of fluazifop-P-butyl 12.5% EC collected from four different manufactured sources in sunlight.

exposure to air, light and elevated temperature, and also hydrolysis can cause a break-down in the fluazifop-P-butyl content quickly. Great interest to note that the degradation rate of fluazifop-P-butyl after storage in sunlight was more than the storage at 54 ±2 °C.

Our findings are in harmony with **(JMPR 2016)** reported that the content of fluazifop-P-butyl decreased to 89% after 64 days by sunlight photolysis, also the obtained results compatible with several investigators **(Bewick, 1986, Negre et al., 1988, Balinova and Lalova 1992** and **Qi et al., 2016)**.

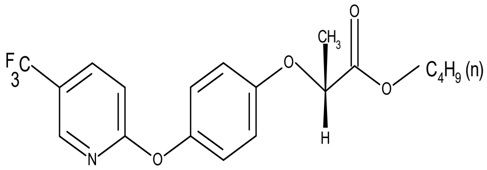
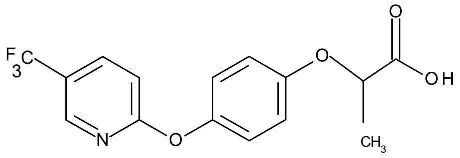
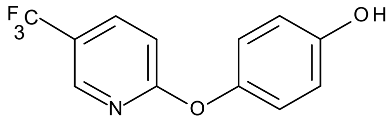
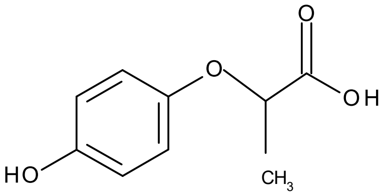
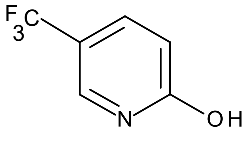
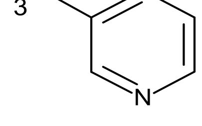
3.2. Identification of the degradation products of fluazifop-P-butyl by GC-MS

The samples of fluazifop-P-butyl were analyzed after storage in sunlight for 70 days using GC-MS to identify the degradation products, and found that the characteristic ions at m/z 383, 327, 253 [M^{+}-2], 182, 163 and 148 [M^{+}+1], were molecular ions of fluazifop-P-butyl, fluazifop acid, 2-(4-hydroxyphenoxy)-5-trifluoro-methyl pyridine, 2-(4-hydroxyphenoxy) propionicacid, 2-hydroxy-5-trifluoromethylpyridine and 3-(trifluoromethyl)pyridine, respectively, however Table 3 indicated that, identification of the degradation products of fluazifop-P-butyl by GC-MS.

By examine the chemical structure of fluazifop-P-butyl, it is observed that fluazifop-P-butyl has two ether bonds and one ester bond that this bonds easy to break by several ways such as hydrolysis and photolysis. Fluazifop-P-butyl can be easily degraded to fluazifop acid m/z 327 by hydrolysis and photolysis and that by cleavage the ester bond then followed by another degradation to form 2-hydroxy-5-trifluoromethyl pyridine m/z 163 **((Negre et al., 1988; Balinova and Lalova 1992 and Mills and Simmons, 1998).** Fluazifop acid m/z 327 may be degraded by many ways to form many degradation products, it can be degraded to form 2-(4-hydroxyphenoxy)propionic acid m/z 182 by cleavage ether bond, Furthermore fluazifop acid can be degraded to form 3-(trifluoromethyl)pyridine m/z 148 $[M^+ +1]$ by cleavage the first ether bond, and also the second ether bond can be broke to form 2-(4-hydroxyphenoxy)-5-trifluoro-methyl pyridine m/z 253 $[M^+ -2]$ followed by another transformation to give 2-hydroxy-5-trifluoromethyl pyridine m/z 163 **(wang et al., 2017).**

Fluazifop-P-butyl can be degraded by cleavage the first ether bond to form 3-(trifluoromethyl) pyridine m/z 148$[M^+ +1]$, also it can be degraded to form 2-(4-hydroxyphenoxy)-5-trifluoro-methyl pyridine m/z 253 $[M^+ -2]$ by cleavage the second ether bond and losing the butyl propionate part in the structure of fluazifop-P-butyl then it can be degraded to form 2-hydroxy-5-trifluoromethyl pyridine m/z 163 **(Li et al., 2019)**.

Table (3): Identification of the degradation products of fluazifop-P-butyl by GC-MS after exposure to sunlight for 70 days

Structure	RT(min)	Characteristic ions (m/z)
	28.53	$[M]^+$ =383,327,282,254,146 fluazifop-P-butyl
	19.28	$[M]^+$ =327,282,254,146 fluazifop acid
	14.23	$[M]^+$=253$[M^+ -2]$, 236$[M^+ -2]$, 162,146,78 2-(4-hydroxyphenoxy)-5-trifluoro-methyl pyridine
	19.86	$[M]^+$ =182,165,138,91$[M^+ -2]$,77 2-(4-hydroxyphenoxy)propionic acid
	11.70	$[M]^+$ =163,146,78 2-hydroxy-5-trifluoromethylpyridine
	12.99	$[M]^+$ =148$[M^+ +1]$, 127,78 3-(trifluoromethyl)pyridine

All the previous reactions can be explained in the Fig. 4 where shows the possible degradation pathways of fluazifop-P-butyl.

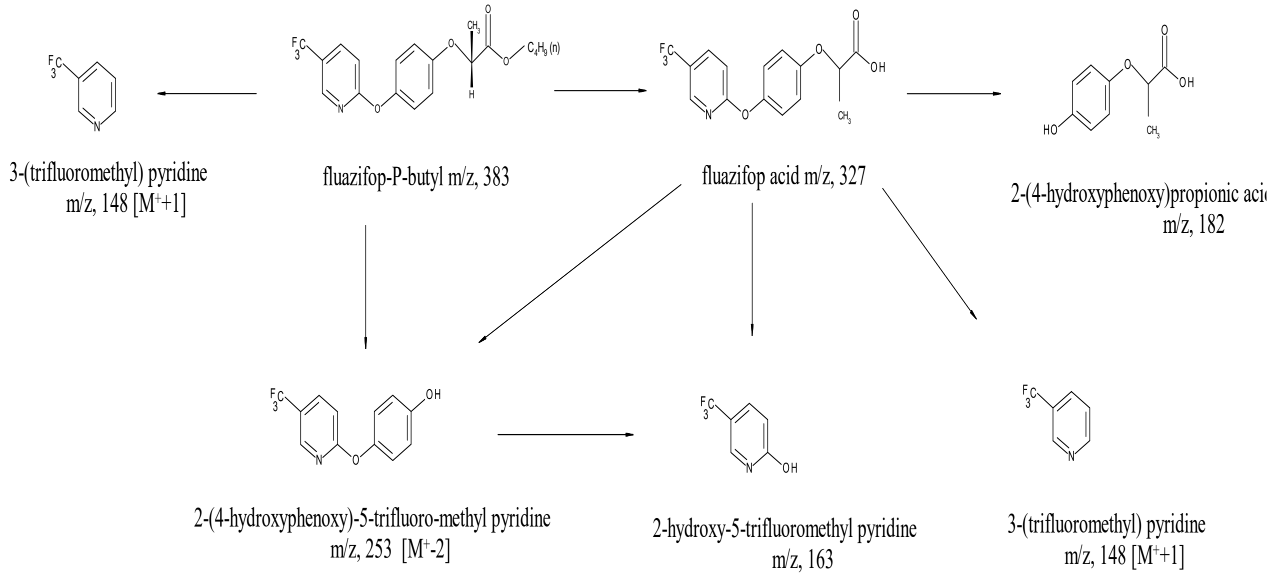


Fig (4). The possible degradation pathways of fluazifop-P-butyl after exposure to sunlight for 70 days

CONCLUSIONS

Fluazifop-P-butyl was affected by accelerated storage especially storage in sunlight. There are many factors affected on the quality of fluazifop-P-butyl such as the manufacturing process, sources of technical materials, using different types of adjuvants and long period of storage in bad conditions. Fluazifop-P-butyl can be degraded to many degradation products by hydrolysis and photolysis.

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مدى جودة بعض مستحضرات فلوازيفوب – بى – بيوتيل المتداولة فى مصر

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المعمل المركزى للمبيدات - مركز البحوث الزراعية - الدقى - جيزه - مصر

الملخص العربى:

أربعة مستحضرات تجارية قابلة للاستحلاب من مبيد الحشائش فلوازيفوب – بى –بيوتيل ١٢,٥% من اربعة مصادر مختلفة وذلك لفحص ثبات فلوازيفوب – بى –بيوتيل بعد التخزين عند ٥٤ ± ٢ مْ والتخزين فى الشمس لمدة ٧٠ يوم وايضا التعرف على بعض نواتج التكسير بعد التخزين فى الشمس باستخدام جهاز GC/MS. النتائج المتحصل عليها تشير الى ان فلوازيفوب – بى –بيوتيل كان ثابتاً بعد التخزين عند ٥٤ ± ٢ مْ لمدة ١٤ يوم ولكن مع طول فترة التخزين كان هناك زيادة فى معدل انهيار فلوازيفوب – بى –بيوتيل, علاوة على ذلك فإن فلوازيفوب – بى –بيوتيل كان أقل ثباتاً بعد التخزين فى الشمس من التخزين فى درجة حرارة ٥٤ ± ٢ مْ , ولا يوجد اى اختلاف فى معدل انهيار مستحضرات فلوازيفوب – بى –بيوتيل الا المستحضر من المصدر الاول. تم التعرف على خمسة نواتج تكسير باستخدام جهاز GC/MS بعد التخزين فى الشمس وهم:

أ. fluazifop acid

ب. 2-(4-hydroxyphenoxy)-5-trifluoro-methyl pyridine

ج. 2-(4-hydroxyphenoxy) propionic acid

د. 2-hydroxy-5-trifluoromethylpyridine

هـ. 3-(trifluoromethyl)pyridine