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DISSIPATION OF CYFLUMETOFEN IN STRAWBERRY FRUITS AND GREEN BEAN PODS UNDER GREENHOUSE CONDITIONS USING QUECHERS METHOD AND GC/(μ-ECD)

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Abstract

Strawberry and green bean are important cash crops. Both are highly infected by different pests under greenhouse conditions causing reduction in quality and yield. Mites are usually from the most common pests of beans and strawberries. Field experiment was carried out to investigate dissipation of Cyflumetofen (a novel acaricide) in strawberry fruits and green bean pods. Determination was done using quick, easy, cheap, effective, rugged, safe (QuEChERS) method and cleanup step utilizing dispersive solid-phase extraction (DSPE) followed by gas chromatography coupled with a micro electron capture detector GC/(μ-ECD). Average recoveries were within 80.75-92.15% and 80.86-82.91%, with relative standard deviations (RSDs) ranging from 2.8 to 6.6% and 3.59-4.70%. in strawberry and green bean samples, respectively at spiking levels (0.01 - 1 mg/kg). Linearity was achieved for Cyflumetofen with correlation coefficient $R^2 > 0.98$ and matrix-matched calibration also showed linearity with determination coefficients $R^2 > 0.98$. The initial deposits in strawberry fruits and green bean pods were 2.48 and 3.24 mg/kg, respectively. The half-life period (RL_{50}) in strawberry fruits and green bean pods was 1.81 and 1.16 days, respectively. According to maximum residue level (MRL) which is 0.6 mg/kg, the pre-harvest interval (PHI) was estimated to be 3 days in strawberry fruits.

Keywords: Cyflumetofen; GC/(μ-ECD); Dissipation; QuEChERS; Strawberry; Green bean.

1. Introduction

Strawberry (*Fragaria ananassa*), is an important cash crop in Egypt. It is exported fresh raw ($90.3 million) with about 3.3% of the total exported amount 6th country, and the second country from 15 exporting frozen strawberries with ($165.3 million) about 14.3% of the total exported amount during 2019.Egypt is one of the fastest-growing top exporters of frozen strawberries since 2015 (up 267.8%) [1].

Green bean (*Phaseolus vulgaris*), is widely cultivated for its high nutritive value, containing 6.2% protein, 0.2% fat, and 63% carbohydrate with a moisture content of about 90% [2]. In addition to the mature dry seed, fresh pods are often consumed as a vegetable, and the rest of the plants are used as animal fodder. Green bean is a popular raw material for the food industry to date [3]. Egyptian green beans are exported to global markets to Italy, United Kingdom, and Netherlands with 17.71%, 16.93%, and 11.40%, respectively of the Egyptian exports of green beans [4].

Various studies have reported that many insects belonging to the different orders as well as mites cause severe damage to the crops. *Tetranychus urticae* Koch (Acari: Tetranychidae), which is a serious plant pest, causes yield losses of crops worldwide annually [5].

Especially under the greenhouse conditions mites feature prominently as pests causing high injury to green bean and strawberry yield, by sucking the cell sap from leaves they may cause discoloration, deformation, or abscission [6]. Badly attacked leaves wither and dry up [7]. Furthermore, owing to their high fecundity potential and short generation time, mites easily develop resistance to acaricides [8].

Chemical pesticides are used to protect the yield. So many acaricides have been developed in the past and used. As a result, the risk to human health resulting from the widespread application of pesticides for

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many decades is well known. Consequently, considerable attention has been focused on food safety, monitoring levels of pesticide residues, and degradation rates in green beans and strawberries [9].

Cyflumetofen, 2-methoxyethyl(RS)-2-(4-tert-butyl phenyl)-2-cyano-3-oxo-3-(α,α,α-trifluoro-o-toll) propionate, is a non-systemic novel benzoyl acetonitrile acaricide active against spider mites and phytophagous mites and shows striking activity on all development stages. It is harmless to mammals and with no effect on beneficial insects and predators of mites, as it works as inhibitor of complex II in the mitochondrial electron transport chain [10].

However, according to the report of FAO/WHO 2006 meeting on Pesticide Residues, cyflumetofen is a possible carcinogen in male rats [11]. In this respect, MRLs (Maximum Residue Limits) for cyflumetofen residues have been established by the United States EPA with 0.6 mg kg^{-1} in strawberries. Meanwhile, the residue of cyflumetofen in green beans has not been established yet [12]. However, there is few data available regarding the dissipation of cyflumetofen in strawberry and green beans under greenhouse conditions. Thus, the determination of cyflumetofen residues in the green beans is urgently needed for food quality and safety.

Samples were prepared using QuEChERS method, which is quick, easy, cheap, effective, rugged and safe, first introduced by [13]. It involves pesticide dispersive solid phase extraction (dSPE), with primary secondary amine (PSA) sorbent. QuEChERS method is used in minimizing matrix effects in different samples. Achieving acceptable results for a range of pesticides with lower limit of detection (LOD) and limit of quantification (LOQ) values and analytical precision, thus it is used all over the world [14, 15, 16, 17,18].

Gas Chromatography (GC) equipped with a micro-electron capture detector (μECD) was used, as it is efficient to determine the residues of pesticides in different matrices (vegetables, water and soil).

Cyflumetofen residues in green beans and strawberries have rarely been investigated. Therefore the objective of the present work was to investigate the dissipation behavior and determine the residues of Cyflumetofen in strawberry fruits and green bean pods under greenhouse conditions at the recommended dosage for pest control. To assign the residual half-life (RL_{50}) and pre-harvest interval (PHI) based on kinetic studies of dissipation rate.

2. Materials and methods

2.1. Standards and reagents

Certified reference standard of cyflumetofen > 98% purity was obtained from Central Agricultural Pesticides Laboratory (CAPL). Acetonitrile of HPLC grade, anhydrous magnesium sulfate and sodium chloride were purchased from Merck. Bulk primary secondary amine (PSA) sorbent (Bondesil-PSA, 40 μm) was bought from Supelco. Anhydrous magnesium sulfate and sodium chloride were activated by heating at 250ºC for 4 h in the oven before use and kept in desiccators.

A stock solution of Cyflumetofen was prepared at a concentration of 0.1 mg/ml. in methanol. Calibration standard and working standard solutions of 0.01, 0.1, 0.5, 1, 1.25, 2, 5, and 10μg/ml were prepared by appropriately diluting the stock solutions with methanol. Stock solutions were stored at -20 ± 2°C, and working standard solutions were stored in the dark ≤ 4 °C when not in use. Pesticide technical formulations (Danisaraba 24% SC), was supplied by Shoura Company, Egypt. Application rate was 30ml/100L water.

2.2. Field experiment

The field experiment was carried out in the experimental farm of the Faculty of Agric. Cairo Univ. during 2020 season. The average temperature for the experimental period ranged from 27ºC to 18ºC, the relative humidity was 60%. The soil of the greenhouse was well prepared before the plantation of green bean seeds var., (Hama) and strawberry var., (Festival). The experimental area 175m^2 was divided into four plots (treatments) each of which contained 50 plants. Each treatment was replicated four times according to a complete randomized block design. The four plots were sprayed with the recommended concentration of Danisaraba 24% SC at 30ml/100L water as a single dose. A manual compressor sprayer (20 liters capacity) was used for acaricide applications. Control plot was sprayed with water only.

2.3. Sample processing:

For sampling pods were collected after 60 days of planting green beans seeds while strawberry fruits

were collected after 70 days from planting. Sampling was performed randomly by collecting 2 Kg. of green beans representative from each untreated and treated area at the following intervals: Initial (2 h) after application then 1, 2, 3, 5, 7, 10, and 14 days after spraying to study the dissipation of the pesticides. Field samples were transported in iceboxes to the laboratory and homogenized by Ultra Thorax homogenizer. The homogenate was stored at -5 °C until further steps.

2.4. Sample preparation

The samples were prepared with the modified QuEChERS method according to [13]. Ten grams of homogenized samples were weighed into a 50-mL centrifuge tube, extracted with 10 mL acetonitrile and 2 g CH_3COONa , 3 g NaCl and 4 g MgSO4 were added. The tubes were capped and immediately vortexed vigorously for 1 min followed by centrifugation at ≤ 4000 rpm for 5 min. Acetonitrile 1.0 mL was transferred into a 2.0 mL centrifuge tube for cleanup. An aliquot of 1.0 mL was transferred into the dSPE tubes containing 50 mg PSA and 150 mg MgSO4). The tubes were well capped and vortexed for 30 s., then centrifuged for 5min at ≤4000 rpm. The combined eluate was filtered through a 0.22-µm nylon syringe filter into an autosampler vial for GC injection. Fortified samples at levels (0.01, 0.1 and 1 mg.kg-1) were prepared by spiking 10g of blank strawberry fruits and green bean samples with a standard solution. The fortified samples were left for 30 min at room temperature to allow penetration of cyflumetofen into the matrix. Five replicates were analyzed for each fortification level.

2.5. Analytical instrumentation and conditions

Separations were performed on an HP6890 (Hewlett Packard, Wilmington, USA) gas chromatograph equipped with an HP 7673 auto-sampler, and a micro electron-capture detector (µ-ECD). A 30 m x 0.32 mm capillary column coated with a 0.25 µm thick film of 5% phenyl methyl polysiloxane (HP-5) from Hewlett Packard was used in combination with the following oven temperature program: Initial temperature 220 ºC for 2 min, 5 ºC / min up to 280 ºC and held for 10 min. The carrier gas (N_2) flow rate was 3 ml/min., with splitless injection of a 1µl volume. The detector and injector temperatures were 300 ºC and 280 ºC, respectively.

2.6. Method validation.

Fortifying untreated fresh strawberry fruits and green bean pods samples with cyflumetofen standards at three levels (0.01, 0.1and 1 mg. kg^{-1}) to evaluate the recovery of the method.

The accuracy was calculated as the percentage between the found and the known concentrations .The fortified samples were processed and analyzed in five replicates as previously described to evaluate the accuracy and the precision

The linearity of the method was calculated from the results directly proportional to the concentration of tested pesticide in the solvent. Linearity was assessed by the correlation coefficient (R^2) resulting from the calibration curve at levels (0.01, 0.05, 0.5, 1, 1.25, 2.5, 5 and 10 ug/ml).

The trueness, bais means of recovery was carried out in 5 replicates at 3 fortification levels (0.01, 0.1, and 1mg/kg) by spiking 10 g of blank samples with the standard solution. The obtained values indicate that the method was sensitive and able to detect and quantify the analyte at low levels, and it is suitable for the determination of tested pesticide residue in strawberries and beans. Accuracy was calculated as the percentage between the found and the known concentrations.

Trueness was calculated using the following equation:

$$\% R = (X/\mu) \times 100$$

Where

%R: recovery percentage

X: experimental concentration of cyflumetofen mg/kg

μ: calculated concentration of Cyflumetofen mg/kg

The precision was determined as relative standard deviation in repeatability conditions. Repeatability precision (%RSDr) involved repeat of recovery levels (0.01, 0.1 and 1mg/kg), five replicates for each level per day on three different days.

According to [19]. the obtained (%RSDr) value was within the acceptable range ≤20%.

%RSD = (SD / M) × 100

Where

SD: standard deviation of the replicates.

M: the mean value of the recovery.

The precision and accuracy were within accepted ranges. Matrix-matched calibration was used to compensate for the matrix effects. The matrix effects were defined as the influence of one or more co-extracted components from the sample on the measurement of tested pesticide concentration. The presence of these effects is demonstrated by comparing the response produced from the tested pesticide in a pure solvent solution with the samples which were first extracted and then spiked with the tested pesticide in the same solvent at the same concentration levels (0.01, 0.05, 0.5, 1, 1.25, 2.5, 5 and 10 mg/kg).

Matrix effects (%ME) were calculated using the equation:

ME%=[(M matrix-M solvent) / M solvent] 100%*

Where

ME: the matrix effect

M matrix: Slope of calibration curve in matrix.

M solvent: Slope of calibration curve in the pure solvent**.**

The % ME could be negative or positive and would be classified in three categories: no matrix effect (between -20% and 20%), medium matrix effect (between -50%, and -20%) or (between 20%, and 50%) and strong matrix effect (below -50% or above 50%) [20, 21].

LOD of cyflumetofen was calculated as the minimum level at which the analyte can be reliably detected and LOQ was set by determining the analyte at different detectable concentrations based on [19].

2.7. Kinetics study

The dissipation kinetics of Cyflumetofen residues in green bean and strawberry were determined by plotting residue concentration against elapsed time after application and equations of best curve fit with maximum coefficients of determination (R^2) were determined. For dissipation of cyflumetofen in strawberry and green bean, exponential relationships were found to be applicable corresponding to the general first-order kinetics [22, 23] and were calculated according to the following equation:

$Ct=C0e^{-kt}$

Where

Ct: represents the concentration of the pesticide residue at the time of *t*,

C0: represents the initial deposits after application, k: the constant rate of pesticide dissipation per day.

The Residue half-life value (RL_{50}) of the studied acaricide was determined mathematically according to [24], from the following equation

$RL_{50}: = (t_{1/2}=ln\ 2/k)$,

Where

rate of degradation K = 2.303 x slope [25, 26].

2.8. Statistical analysis

The analyses were made in five replicates for each sample. Microsoft Excel Program was used to calculate and analyze mean values and standard deviations. The other calculations were done using the above-mentioned equations**.**

3. Results and Discussion

Method Validation

Recovery was carried out on blank samples that were spiked with cyflumetofen at three levels in strawberry fruits and green bean pods samples in five replicates.

The method trueness and precision parameters in terms of average recovery and relative standard deviation were calculated and measured according to the European Union guidelines [19].

The evaluation of the calibration curve linearity of cyflumetofen was done based on injections of standard solutions prepared in pure organic methanol in a series at 0.01,0.1,0.5, 1,1.25, 2,5 and 10 mg/kg for GC/(μ-ECD). The standard calibration curve of Cyflumetofen was constructed by plotting analyte concentrations against peak areas. The correlation coefficient equals (R2 = 0.98).

For the residue analysis study, the injected sample contained large amounts of the unavoidably present co-extractives, which are responsible for the matrix effects occurring on the injector. The matrix effect was investigated by comparing the slopes of calibration curves at the same concentrations as injection in strawberry and green bean and in pure solvent.

The matrix effect for strawberry fruits differed from that of green bean pods.

ME% for strawberry= 1633-1969/1969*100= -17%

ME% for bean= 709.5-1969/1969*100= -63.9%

The results showed no matrix effect for Cyflumetofen (-17%) in strawberry fig. (1), which indicated that no interfering endogenous peak appeared and did not significantly suppress or enhance the response of the instrument. Meanwhile the matrix effect was strong (-63.9%) in green beans fig. (2).

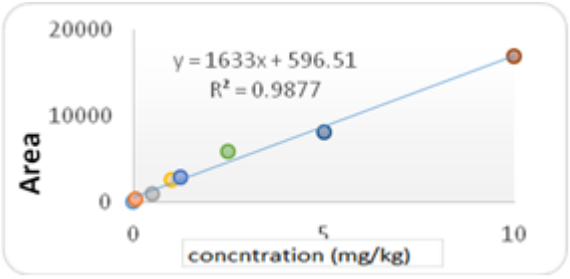

Fig (1):Matrix calibration curve of strawberry

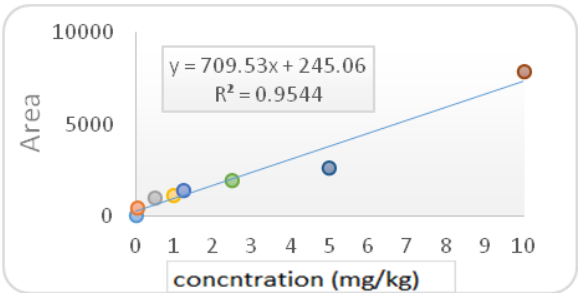

Fig. (2)Matrix calibration curve of bean

The lowest validated level of Cyflumetofen with acceptable precision and trueness. LOQ was 0.01 mg/kg for GC- (μ-ECD) analysis in strawberry and green bean. According to [27], the LOQ values are acceptable, where LOQ ≤ MRL 0.6 mg/kg for Cyflumetofen in strawberry.

The trueness, means of recovery was carried out in 5 replicates at 3 fortification levels (1, 0.1, and 0.01 mg/kg) by spiking 10 g of blank samples with the standard solution. The obtained mean recoveries ranged from 80.75 % to 92.15% with relative standard deviation (%RSD) which ranged from 2.8 to 6.6 for strawberry.

Table 1. Recovery percentages of cyflumetofen in strawberry fruits and green bean pods.

Fortification level [mg · kg–1] n = 5	Strawberry		Beans	
	%Recovery +RSD	RSD r %	%Recovery +RSD	RSD r %
0.01	80.75± 2.8	3.46	80.86±3.59	4.45
0.1	88.28± 5.45	6.17	81.57±5.82	7.14
1.0	92.15± 6.60	7.17	82.91±4.70	5.68

n - number of replicates

RSD- relative standard deviation

RSDr - relative standard deviation of reproducibility

As for green beans the percent recoveries ranged from 80.86 % to 82.91% with relative standard deviation (%RSD) between 3.59 and 5.82. According to [19], the obtained mean recoveries were within the acceptable range (70-120%).

The obtained values indicate that the method was sensitive and able to detect and quantify the analyte at low levels, and it is suitable for the determination of tested pesticide residue in strawberries and beans.

The repeatability precision (%RSDr) involved repeat of recovery levels (1, 0.1 and 0.01 mg/kg), five replicates for each level per day on three different days. The (%RSDr) value ranged from 3.46 - 7.17% and 4.45-7.14 for fruits and pods, respectively. According to [18] the obtained (%RSDr) value was within the acceptable range ≤20%.

3.7. Dissipation of Cyflumetofen in Strawberry (Fragaria ananassa) fruits

Results in Table (2) and Fig. (3), showed the dissipation of cyflumetofen in strawberry fruits.

The dissipation of cyflumetofen in strawberry fruits was studied for 14 days. The initial deposit of cyflumetofen in strawberry fruits was 2.48 mg/kg two hours after application (initial). While the sharp reduction occurred in the first 24 hours of spraying the strawberry ,with a very high loss of 45.16%. Rapid dissipation was found on the second day after spraying, in which cyflumetofen residue reached 0.43 mg/kg with 82.66% loss. The degradation continued to reach 0.11 mg/kg with 95.56% loss after 7 days after application. The residues of cyflumetofen on strawberry decreased to 0.04 mg/kg with 98.39 % loss.

The residues became undetectable on the 14th day after application.

The results are in agreement with those of [23], who reported that the highest residue content in strawberry fruits for cyflumetofen was (0.5882 mg/kg), following application at the recommended dosage and the MRL was 2 mg/kg, PHI was recommended at 7 days.

Data obtained are also consistent with [28], who reported the greatest losses of 65.07% Cyflumetofen of the initial residue (1.448 mg/kg) and with PHI value of 7.1 days. This result was confirmed by [11], who estimated the initial deposit of cyflumetofen in tomato fruits with (1.43 mg/kg).

The diverse weather conditions and different agro ecosystems in greenhouses may prolong the duration of the degradation profile of pesticide and also the growth pattern of strawberry [29].

Table (2). Cyflumetofen residues in Strawberry fruits and green bean pods after treatment

Time	Strawberry		Green Beans	
(days)	Residue* (mg/kg)	Percent Dissipation	Residue* (mg/kg)	Percent Dissipation
0-Initial	2.48±0.27	0.00	3.24±0.53	0.00
1	1.36±0.18	45.16	1.57±0.21	51.54
2	0.43±0.34	82.66	0.63±0.35	80.56
3	0.36±0.69	85.48	0.29±0.24	91.05
5	0.27±0.42	89.11	0.12±0.52	96.30
7	0.11±0.56	95.56	0.05±43	98.46
10	0.04±0.17	98.39	ND	-
14	ND	-	ND	-
MRL	0.6			
PHI	3 days			
LOQ	0.01		0.01	

ND – not detected

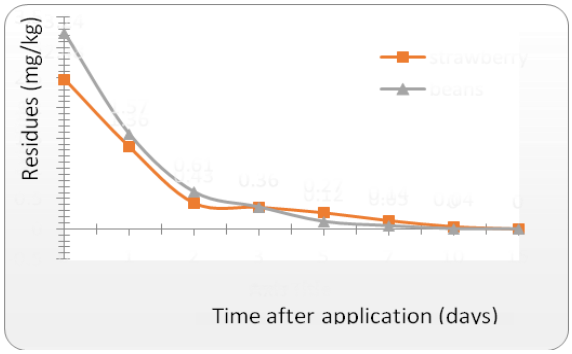

Fig. (3) Dissipation of Cyflumetofen in Strawberry fruits and Green bean pods

Based on the previous results, the calculated half-life period (RL_{50}) of cyflumetofen on strawberry fruits was 1.81 days Table (3).

Table (3). Decomposition rate (K) and half-life (RL_{50}) of cyflumetofen in strawberry fruits

Regression equation	Y=1633x + 596.51
Regression coefficient (R^2)	0.9877
K=2.303Xslope	0.49
RL_{50}(Days)	1.81

The maximum residue limit (MRL) of cyflumetofen in strawberry fruits is 0.6 mg/Kg according to [30]. The results presented herein clearly show that strawberry fruits can be consumed safely by a human after 3 days from spraying with cyflumetofen. This may be related to the solubility of cyflumetofen in water (0.0281 mg/L-1 at 20°C). [31]. Thus, owing to its low water solubility, cyflumetofen was mainly transported into the internal parts of the tomato juice and seeds [11].

3.8. Dissipation of Cyflumetofen in green bean (Phaseolus vulgaris) pods.

The dissipation pattern of cyflumetofen in green beans at different sampling intervals (0, 1, 2, 3, 5, 7, 10, and 14 days) is presented in table (2).

The highest dissipation rate of Cyflumetofen per day was found in the first day, a quick decline of Cyflumetofen concentration mainly during the first three days was observed followed by a gradual decrease until the 10th day after treatment, where it was not detected. In the same concept,[32] reported that 3 days after application green beans by Cyflumetofen are necessary to meet the European MRL requirements and zero days for the USA requirements. On the other hand, [33] found a

maximum of 0.32 mg kg-1 of Cyflumetofen residue was detected in leek samples sprayed three times at 7-day intervals until 7 days prior to harvest.

Data presented in table (2) and fig. (3) demonstrate the initial deposits as well as the residual behavior of Cyflumetofen in green bean pods. The initial deposit of Cyflumetofen in green bean pods was 3.24 mg/kg at initial time (two hours) after application. The residue of Cyflumetofen in green bean pods within the first 24 hours after application decreased to 1.57 mg/kg with 51.54% loss. The amounts of Cyflumetofen residue decreased to 0.29 mg/kg with a high percent loss (91.05%) in the third day of application. Data indicated that the dissipation of Cyflumetofen residue was rapidly within the first three days after spraying. Residues of Cyflumetofen in green bean pods then gradually decreased until 98.46% loss after 7 days of application. The residues became undetectable on the 10th after application.

Table (4). Decomposition rate (K) and half-life (RL_{50}) of cyflumetofen in green bean pods

Regression equation	y = 709.53x +245.06	
Regression coefficient (R^2)	0.9544	
K=2.303Xslope	0.60	
RL_{50}(Days)	1.16	

Based on the previous results Table (4), the calculated half-life period (RL_{50}) of Cyflumetofen in green bean pods was 1.16 days.

These results can help in calculating MRL for Cyflumetofen residues value in green beans.

The dissipation of the chemical pesticide residues in vegetables depends on a variety of factors including environmental conditions such as sunlight and temperature [35]. Also, chemical formulation, type of application, plant species, dosage [36], the intervals between application and harvest effect on the dissipation of pesticide residues in crops under greenhouse conditions [37]. In addition, the reduction of pesticides may be due to chemical or physical, biological, processes, or dilution by the growth of the crop [37, 38].

4. Conclusion

In this work, an GC/(μ-ECD) analytical method based on QuEChERS sample pretreatment procedures was used for the determination of Cyflumetofen residues in strawberry and green bean fruits. The developed method is easy and compatible for residue analyses of cyflumetofen, the mean recoveries ranged from 81–92% and 81–83% respectively, and repeatability of the method expressed as the relative standard deviation, was lower than 4%. The calculated half-life period (RL_{50}) of tested pesticides on strawberry fruits and green beans were 1,8 and 1,16 days, respectively. According to the maximum residue limit (MRL), the pre-harvest interval (PHI) of Cyflumetofen in a strawberry was 3 days after the treatment.

5. Acknowledgments

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