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Development of Analytical Method for the Detection of Nemacur Residues in Cucumber Fruits

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Abstract

Application of Nemacur (Fenamiphos) for pest control may contaminate soil, water and plant with harmful residues and pose threats to human life. This study developed an easy method for the determination of Nemacur residues in cucumber fruits collected from the central markets and from the farm. The method is based on extracting the active ingredients of Nemacur from the commercial formulation and used as a standard material to calibrate the HPLC to determine Nemacur residues in cucumber fruits collected from the central market. Results showed that more than 70% of the active ingredient was extracted from the commercial formulations. Standardization of HPLC with extracted materials showed strong positive association between concentration and peak area relationship. Bioassay investigation showed high mortality of tested organism (fish). Statistical analysis of mortality % between the commercial formulation and those of the extracted ingredient showed no significant differences. These results demonstrated the effectiveness of extracted Nemacur to calibrate HPLC and in bioassay test. Nemacur residues in Cucumber fruits collected from the market were below the detection limit of HPLC, recovery % of Nemacur from control group of cucumber was above 80%. It can be concluded that the method is easily developed and validated by bioassay and chemo-assay.

Keywords

Nemacur, Fenamiphos, Analytical Method, HPLC

1. Introduction

Application of pesticides in Gaza strip Palestine is progressively increased due to

the intensive agricultural activity. The use of pesticides has been associated with pesticide residues in fruits and vegetables [1] [2] [3]. Furthermore, contamination of food with pesticide residues has created many health problems such as cancer cases [4] [5], biochemical changes among farmers [6], obstructive polumery disease among green house farmers [7], poisoning cases among farmers [8] and suicidal attempts among general population [9]. So far, application of pesticides has damaged the eco-system elsewhere [10], destroyed fish population [11] [12] [13], had toxicity to cyanobacterial mats [14] [15] [16] [17]. Nemacur was chosen because it is widely used in Gaza for insects and weed control and their application is associated with health damage to farmers [18]. Chemo-assay of pesticides residues using GC and HPLC is well known and widely used techniques for pesticide determination in fruits and vegetables. These techniques some times are not able to detect low concentrations of pesticides. Furthermore, few studies used bioassay techniques for pesticide residues analysis, which included test plant assay [19] [20] enzymatic assay such as using choline esterase as a biomarker for organophosphorus insecticides [21]. The limitations of the above mentioned methods are that they used ultra-pure technical materials of pesticides to prepare the standard solutions for the laboratory scale for determining residues in environmental samples. Currently, there are many difficulties in Gaza Strip, Palestine to purchase technical materials at high purity (99.5%) for pesticide residue analysis in vegetable, fruits and water systems due to the current political situation. In addition, determination of pesticide residues in the absence of pure materials was poorly investigated or remained untested. Our objective in this study was to use the commercial formulation for extracting the active ingredient and to further purify it through crystallization and to use the pure crystals to calibrate the HPLC machine for determining Nemacur residues in cucumber fruits collected from the market and field.

2. Materials and Methods

2.1. Study Area

Gaza strip is a semi-arid zone with large agricultural activity in green house technology. Gaza Strip is an important part of State of Palestine. It consists of five Governorates, the northern area, Gaza, the middle (Deir al-blah), Khan Yunis and Rafah Governorates. It is one of the most densely populated areas in the world (2638 people/km^2), has limited and declining resources and has already started to experience deterioration of environmental quality. Two thirds of the Gaza Strip (total 365 km^2) is an agricultural area [22]. The global and local coordination (GPS) were specified as shown in **Table 1**.

Application of Nemacur tends to increase due to the intensive agricultural application. In **Table 2** we demonstrate the use of pesticides by their functions.

Nemacur is an organophosphorus compound with a molecular weight 303.4, its solubility in water is about 0.4 g/L. It is a solid material at room temperature with a milting point 49˚C. It has a pKa value of 10.5, and has a Henry's Law

constant at 20˚C equal 9.1×10^{-5} Pa m^3/mol, Tomlin [23]. Molecular structure is shown in Figure 1.

2.2. Analytical Method

Commercial formulation (emulsifiable concentrate) containing 40% of active ingredient of was purchased from a certified pesticide shop in Gaza Strip, Palestine. So far, Nemacur, is originally from Dow Agro Sciences Co., USA.

Following the procedure described previously [24], a 10 mL of commercial Nemacur were suspended in 90 mL of water to form 100 ml, and shacked very

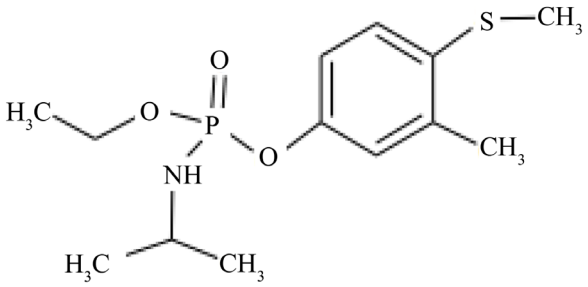

Figure 1. Molecular structure of Nemacur.

Table 1. Global and palestinian coordinates.

Sample	UTM WGS 84—Coordinates		Palestine grid Coordinates	
	East	North	East	North
Sandy soil	34˚20'41"E	31˚24'17"N	87682.00 E	90620.00 N
Clay soil	34˚20'25"E	31˚24'22"N	87274.00 E	90774.00 N

Application of Nemacur tends to increase due to the intensive agricultural application. In Table 2, we demonstrate the use of pesticides by their functions.

Table 2. Quantities of pesticides (liter) used in Gaza Strip in the past years.

Year	H	I	F	F & H	Total (L)	N
2005	20,440	56,714	74,336	980	453,170	NA
2006	24,940	55,270	55,650	855	248,315	NA
2007	18,800	35,580	34,270	3500	185,950	NA
2008	18,200	49,650	42,200	60,828	364,478	NA
2009	39,432	139,337	123,694	10,771	711,802	18,120
2010	18,780	144,682	99,630	61,327	486,819	13,836
2011	27,054	220,169	136,477	7429	484,164	30,440
2012	25,609	232,488	137,911	5209	544,427	19,968
2013	24,251	180,664	104,705	8577	443,887	23,015
2014	NA	NA	NA	NA	NA	27,618
2015	NA	NA	NA	NA	NA	39,355

H = Herbicides, I = insecticides, F = fungicides, F & H = fumigants and hormones, N = Nemacur. All amounts are in liters Adopted from Ministry of Agriculture [25].

well to form an emulsion. 10 ml of the emulsion was transferred to the extraction tube containing 10 ml dichloromethane. Then the mixture was vortexed at high speed for 3 min. The mixture was left for 1 hour until an organic layer was formed. The organic layer was removed in a 50 ml flask. Then the extraction procedure was repeated three times in total to insure complete extraction of pure ingredient of Nemacur. The total volume of extract, 28 ml organic layer, was dried using anhydrous sodium sulfate. Then dichloromethane was evaporated under stream of nitrogen gas, and the residue was recrystallized using methanol. The white solid was collected by filtration. The purity of Nemacur was tested using HPLC and bioassay. And Methanol of HPLC grade, purity 99.9% was purchased from Sigma Aldrich Co., Germany, was purchased from Gaza.

2.3. HPLC-Measurement

HPLC (Agilent 1620) analyses were performed on isocratic system [26]. Nemacur concentrations in the supernatant were determined by Diode Array Detector (DAD) equipped with manual-injection system. The column was Reverse-phase. Packing ODS-BP5 μm (C18), and a 150 mm × 4.6 mm (i.d.). Injection volume is 50 μl and wave length of detection was 250 nm, Mobile phase is water: methanol 20:80. The flow rate was maintained at 2 ml·min. other conditions were as used for the silica gel column. External calibration was used for quantification of Nemacur.

2.4. Standard Curve of Nemacur

As described previously [27] [28] [29] [30], concentration-peak area relationships were established in the range on 0.0 - 1 mg/L. The absorption was measured by HPLC at wavelength 250 nm and retention time 2.004 min.

2.5. Nemacur Recovery Test from Cucumber

A one kg cucumber of cucumber was mixed and homogenized with 2 mg pure Nemacur (collected from the extracted materials mentioned above). Then, three sets of 10 g homogenate were collected severalty and used from Nemacur extraction from fruit following the previous method [31] [32]. The extracts were then analyzed by our method as shown below.

2.6. Control Group

A one kg cucumber of cucumber from the same market was mixed homogenized using a blinder. Then, three sets of 10 g homogenate were collected severalty and extracted for possible Nemacur residues following the procedure described above. The extracts were then analyzed by our method as shown below.

2.7. Nemacur Bio-Activity Test

The bioactivity of Nemacur was tested against fish larvae, have 5 ± 0.5 g body weight each according to previous report [33] [34]. The tested concentrations were in the range of 0.0, 0.004, 0.04, 0.4, 0.8, 1.6 mg/L. Mortality of fish was de-

termined according to previous reports [35].

2.8. Cucumber Planting

Sandy and clay soil samples were collected of an agricultural area have at least five years history free from Nemacur application. The selected soil samples were dried for 48 h, and then passed through a 2-mm sieve, as described in study by [35] [36] [37] [38]. Two sets of 16 pots each set, were filled with sandy and clay soil. The volume of each pot is 10 L. Cucumber seedlings were planted in the sandy and clay soil in 32 pots, then transferred to the greenhouse to protect the seedlings from the weather conditions. Nemacur was applied at 0.0, 0.5F, 1F, and 2F, where F is the field rate which equal 2 L/1000 m^2. The field concentration was calculated for each pot according to surface area for the pot [39] [40] [41] [42]. The concentrations are as follows, 0.0, 6.59, 13.17, 26.35 mg/kg soil respectively. Four replicates were used for each concentration in both soil types. The pots were irrigated with 8.5 L of water during the growth season (3 months). Cucumber plant had a normal growth under a normal condition at specified greenhouse.

2.9. Fruits Collection

Cucumber fruit were harvested from the plants whenever it reached 10 cm long, or 2 cm in diameter. The fruits of each treatment were mixed together to form a complex sample. Then a one kg sample was taken, cut, grounded and homogenized. Then 10 g was extracted with mixture of organic solvent [43] [44] [45] and analyzed by HPLC. Furthermore, cucumber fruits were also collected from the central market in deir al-balah. Six samples of cucumber fruits were collected randomly from the market. The samples were transferred to the laboratory and prepared as described above for analysis on HPLC and bio-assay as mentioned above.

2.10. Statistical Analysis

Average and standard deviation of Nemacur concentrations were calculated for each sample. T-test was used to detect significant differences among treatment at p-value = 0.05.

3. Results and Discussion

3.1. Extracted Nemacur

It appeared that more than 80% of Nemacur was extracted from the commercial formulation indicating the efficacy of extraction. So far the extracted material was pure and has a while color similar to those described by Tomlin [23]. These materials were collected in glass tube and used as ultra-pure to calibrate the HPLC and for bio-assay test.

3.2. UV Spectrum of Extract Nemacur

The UV spectrum of extract Nemacur is shown in **Figure 2**. The presented data

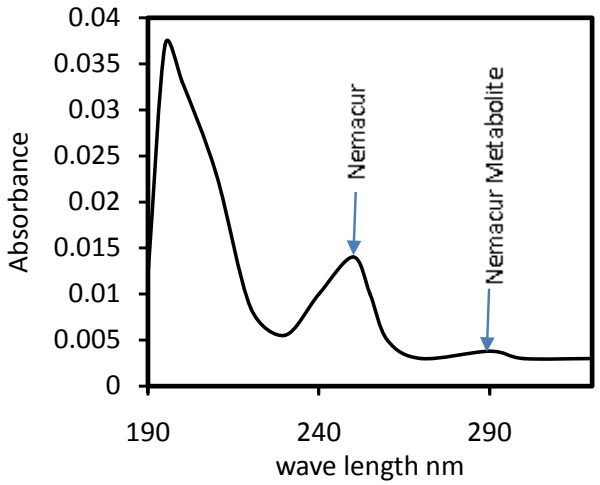

Figure 2. Absorbance spectrum of Nemacur as shown by UV-spectroscopy. A sharp peak is obvious at 250 nm with a reduced peak at 280 nm.

clearly showed the absorbance spectrum of Nemacur extracted from the commercial formation. It is obvious that a strong peak appeared at wave length 250 nm with a reduced peak at 280 nm. This indicates strong absorption spectra at the uv-range. Our results agree with AOAC method (1995) which revealed that fenamiphos and its sulfoxide and sulfone metabolites can be detected by UV-detection. Furthermore, this method of validation is similar to that obtained by Ref [46] [47] [48] for other cases. Furthermore, the HPLC chromatogram (**Figure 3**) shows a sharp peak at low convention, indication of the sensitivity of the method. According to these observations, Nemacur concentrations in cucumber were determined at 250 nm.

3.3. HPLC-Chromatogram of Nemacur

An HPLC chromatogram of Nemacur is shown in **Figure 3**. It is obvious that a sharp peak with considerable peak area were obtained at 2.043 min. This indicates the accuracy of the used method for determination.

So far, the appeared peak at 250 nm after 2 min of retention time, indicates the validation n of our method. Regardless, to nearly short retention time, Nemacur was detected normally without any interference with the solvent. Nevertheless, it is possible to increase the retention time to be after 4 min by increasing water % from 20 to 40 in the mobile phase. However, no interfering peaks (metabolites or other pollutants) appeared with Nemacur so that the analytical procedure went smoothly.

In addition, the relationship between peak area and gradient concentrations of Nemacur showed a linear relationship (**Figure 4**). This indicates strong positive association between concentration and peak area. Regression analysis showed a correlation coefficient (R^2) of 0.9951. This linearity indicates the validity and the suitability of the used method and allows direct measurements of Nemacur in

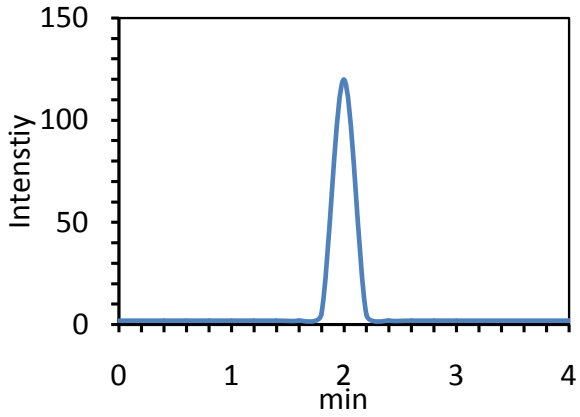

Figure 3. HPLC-Chromatogram of Nemacur after two min. of retention time in methanol water 80:20 ration and one ml/min.

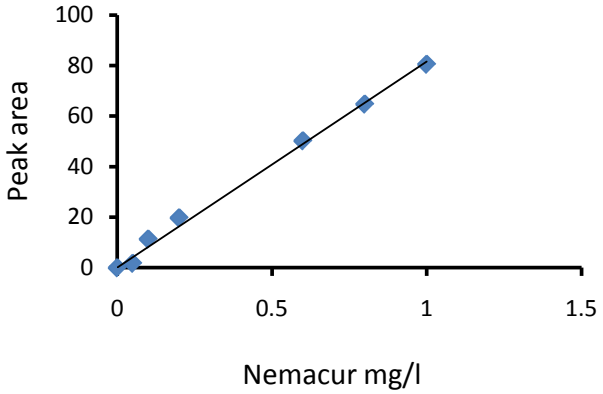

Figure 4. Relationship between peak area and standard concentration of Nemacur.

the supernatants by HPLC. Similar results were obtained for other cases [49] [50].

3.4. Bioassay Technique (Mortality Test)

The idea stands behind this test is to insure the biological activity of Nemacur at various concentration. Furthermore, fish was used as a test organism due to high sensitivity. There has been a progressive increase between fish mortality and gradient concentration of Nemacur. 100% fish mortality was observed at 1 mg/L (Data not shown). The effect can be visualized in **Figure 5**. It is obvious that mortality of fish is high in all tested concentrations. This mortality of fish is due to inhibition of acetylcholinesterase by Nemacur. Toxicity of organophosphorus insecticides to fish has previously been reported [51] [52] [53] [54].

3.5. Nemacur Residues in Cucumber

Nemacur residues in cucumber collected from the central market and from two different fields are shown in **Table 3**.

Figure 5. Visual rating of fish mortality as exposed to low concentrations of Nemacur extracted from commercial formulation.

Table 3. Concentration of Nemacur (mg/kg) in cucumber fruits.

Cucumber Harvesting date	Nemacur mg/kg		
	Market sample	Field sample	
		Clay soil	Sandy soil
1st harvest (30 day)	BD	a0.24 ± 0.17	a0.74 ± 0.13
2nd harvest 45 day	BD	b1.93 ± 0.46	b1.60 ± 0.61

Where BD is below detection limit, values have the same letter in a column do not significantly different at p = 0.05.

It can be seen that market samples have Nemacur concentration below detection limit of the HPLC whereas cucumber fruits of the experiment have nearly high concentrations. So far the concentrations of 1st harvest are lower than the 2nd harvest in both soils. The explanation of these results is that the market samples were not sprayed with Nemacur during the growth season or the values are below the detection limit. Moreover, the lower values of the 1st harvest fruits can be explained by the fact that accumulation on Nemacur in cucumber fruits is a function on plant age, younger plant contains lower concentration than older plant due to high exposure time, as Nemacur tend to accumulate in the root zone and be absorbed by plant root in due time. This explanation agrees previous reports [55] [56] [57] [58] which found similar results with other cases. Furthermore, cucumber fruits in the sandy soil have higher concentration than clay soil in the 1st harvest and the opposite is right in the 2nd harvest. These results are explained by the fact that clay has adsorption capacity than sand, accordingly low fraction of Nemacur is available for plant absorption consequently low fraction of Nemacur was accumulated in the 1st harvest. After 45 days, 2nd harvest, clay reached to the maximum adsorption capacity, then Nemacur tends to accumulate in soil solution and be absorbed by plant. In this case high concentration was accumulated in plant fruits. These results agree with previous

reports [59]-[65] which revealed the adsorption capacity of clays in due time.

4. Conclusion

The present study developed an easy applicable method. The results demonstrated high extracted amount on Nemacur and its purification procedure. The biological activity of extracted Nemacur was similar to the commercial formulation, indicating the efficacy of extraction procedure. Testing the method enabled determination of Nemacur in different cucumber samples. Considerable concentration of Nemacur was found in all extracted tested samples. The result revealed lower concentrations of Nemacur in cucumber collected in the 1st harvest than the 2nd harvest. Nemacur residues do not appear in random samples taken from the market. It is recommended to use this method for determining pesticide residues in fruits and vegetables to save the cost and to reduce time of waiting to purchase ultra-pure active ingredient of pesticides.

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