Original Article

Determination of Residues of Chlorpyrifos and Its Oxygen Analog in Dates

Sameeh A. MANSOUR*

Plant Protection Research Division, Ministry of Agriculture, Iraq

(Received April 23, 1985)

Residues of chlorpyrifos (*O,O*-diethyl-*O*-3,5,6-trichloro-2-pyridyl phosphorothioate) and its oxygen analog (*O,O*-diethyl-*O*-3,5,6-trichloro-2-pyridyl phosphate) were determined in dates following the application of Dursban® on palm trees by a gas chromatographic method. Residues of chlorpyrifos decreased sharply within 2 weeks after application, but detectable amounts remained up to 8 weeks. The oxygen analog of chlorpyrifos seemed to be more persistent than chlorpyrifos itself. To keep fruits clean from excessive contamination by chlorpyrifos, the shortest waiting period of 8 weeks between insecticide application and fruit harvest is recommended.

INTRODUCTION

Chlorpyrifos (Dursban®, *O,O*-diethyl-*O*-3,5,6-trichloro-2-pyridyl phosphorothioate) is a promising insecticide which is active against a wide spectrum of insect pests.¹⁾

Among promising insecticides, chlorpyrifos has been evaluated for the control of some insect pests of dates in palm orchards in Iraq (e.g. *Ommatissus binotatus* FIEB. and *Batrachedra amydraula* MEYR.). A valid recommendation with any pesticide should take in consideration the residue data in edible plants at least, which might be associated with the use of such a pesticide under the local environmental conditions. So, the aim of the present investigation is to determine the residues of chlorpyrifos and its oxygen analog (*O,O*-diethyl-*O*-3,5,6-trichloro-2-pyridyl phosphate) in dates following the application of Dursban on palm trees.

MATERIALS AND METHODS

1. Special Reagents

Chlorpyrifos and its oxygen analog, analyti-

cal reference standards, were obtained from Dow Chemical Co., Midland, U.S.A. Silica gel 60, 70/230 mesh (ASTM, Merck) was reactivated before use by heating overnight at 110°C in an electric oven. Solvents used were of reagent grades and redistilled in glass.

2. Field Application and Sampling

Trials were carried out in a palm orchard at Abu-Ghraib, Baghdad, Iraq. Palm trees were sprayed with a commercial formulation of Dursban (40.8% EC) at a rate of 245 g a.i./donum (or 980 g a.i./ha) with high pressure ground sprayers on June 12, 1979 (shortly after fruiting and infestation). Samples from both treated and control plots were taken 1, 15, 29, 43, 57, 71 and 85 days after application and stored at -12°C until analyzed.

3. Extraction and Cleanup

Prior to extraction, stones were removed from dates and 50 g subsamples (ca. 8-25 fruits/50 g, depending on the date of sampling) were taken for analyses. Extraction and cleanup of chlorpyrifos and its oxygen analog were accomplished according to the method described previously²⁾ after a slight modification in the cleanup stage. In the original

* Present address: National Research Centre, Dokki, Cairo, Egypt.

Table 1 Elution pattern of chlorpyrifos and its oxygen analog on a silica gel column chromatography eluted with 120 ml and 100 ml of benzene and acetone, respectively.

Benzene fractions ^{a)}	Recovered (C)		Acetone fractions ^{a)}	Recovered (COA)	
	μg	%		μg	%
f ₁	5.4	10.8	f ₁	4.8	9.6
f ₂	40.8	80.0	f ₂	32.2	64.4
f ₃	1.4	2.8	f ₃	11.5	23.0
f ₄	1.2	2.4	f ₄	0.0	0.0
f ₅	1.0	2.0	f ₅	0.0	0.0
f ₆	0.0	0.0			
Total	49.0	98.0	Total	48.5	97.0
Added	50.0		Added	50.0	

^{a)} Each fraction represents 20 ml aliquots collected subsequently from the column and analyzed by GC for chlorpyrifos (C) and its oxygen analog (COA).

method, benzene-sample extract is cleaned-up on a silica gel column using 90 ml of benzene. The first 20 ml of eluate is discarded and the next 70 ml is collected for chlorpyrifos analysis. Thereafter, the column is eluted with 60 ml of acetone to separate the oxygen analog.

In the present study, the column (2.5×50 cm) was firstly eluted with 100 ml of benzene and collected all for chlorpyrifos analysis. Then, the column was eluted with acetone as described in the original method. The elution pattern of chlorpyrifos and its oxygen analog on the silica gel column is represented by Table 1.

4. Gas Chromatographic (GC) Analyses

GC analyses were performed on a Perkin-Elmer Model 3920 instrument equipped with a thermionic detector (TID-Rb Br) and a 6 ft×1/4 in o.d. glass column packed with 5% OV-17 on 80/100 mesh Gas Chrom Q. Gas flow rates were 30, 100 and 40 ml/min for nitrogen, air and hydrogen, respectively. The temperature was 220°C at column, injector and detector. Under these conditions, the retention times (*R_t*) for chlorpyrifos and its oxygen analog were 4 min 54 sec and 4 min 18 sec, respectively. Peak heights obtained from the injection of extracts of unknown samples were compared with appropriate standards to calculate the residues.

5. Thin-layer Chromatographic (TLC) Analyses

TLC was performed on 20×20 cm glass plates coated with a 0.3 mm-thick layer of silica gel DGF (Riedel-De-Haën AG, Hannover). Different concentrations of pure materials were prepared (in benzene), spotted on the silica gel plates and developed in benzene+ethyl acetate (9+1; v/v). Spots were examined under a UV lamp (254 nm). Under these conditions, *R_f* values were 0.97 and 0.36 for chlorpyrifos and its oxygen analog, respectively. The detection limits for these compounds were 0.5 μg and 0.2 μg , respectively. Benzene and/or acetone extracts remained after GC analyses were concentrated more (*ca.* 5 ml), and 50 μl portions were spotted on the silica gel layers. Spots appearing after development were compared with those of corresponding authentic standards for identification.

RESULTS AND DISCUSSION

Although several gas chromatographic methods have been published for chlorpyrifos analysis,³⁻⁵⁾ few methods were published for the analysis of chlorpyrifos and its oxygen analog.²⁾ In the latter method,²⁾ detection of the analyzed compounds is achieved by a flame photometric detector. In the present study, a thermionic detector was used. Both types of detectors are quite sensitive to phosphorus. Determination limit for chlorpyrifos and its oxygen analog, in the present study, was

Table 2 Per cent recovery of chlorpyrifos and its oxygen analog from dates at various levels of fortification.

Compounds	Fortification, ppm						Av.
	0.01	0.05	0.1	0.5	1.0	2.0	
Chlorpyrifos	90.2	94.3	95.0	102.3	88.2	89.0	93.1%
Oxygen analog	78.5	85.3	83.1	91.7	88.0	76.8	83.9%

N.B. Each recovery value represents an average of 2 analyses.

Table 3 Residues of chlorpyrifos and its oxygen analog in dates at different time intervals following spraying of Dursban on palm trees.

Date of sampling	Days after application	Residues, ^{a)} ppm	
		Chlorpyrifos	Oxygen analog
13/6/79	1	1.28	ND
27/6	15	0.20	0.50
11/7	29	0.05	0.32
25/7	43	0.03	0.30
8/8	57	0.01	0.21
22/8	71	ND	0.15
5/9	85	ND	0.10

^{a)} Each value represents an average of 3 analyses.

ND: Not detected.

found to be 0.01 ppm and 0.05 ppm, respectively. Total recovery of the analytical method was satisfactory as shown in Table 2. On the other hand, TLC confirmed GC results concerning the presence of chlorpyrifos in benzene extracts of treated date samples as well as the oxygen analog in the acetone extracts.

Residues of chlorpyrifos and its oxygen analog in dates, at different time intervals after the application of Dursban, are presented in Table 3. Concentrations of chlorpyrifos decreased sharply within 2 weeks after the application. Thereafter, it remained at a low level up to 8 weeks after the application. Concentration of the oxygen analog reached 0.5 ppm 15 days after the application, then decreased slowly all through the season. This behavior may indicate that the oxygen analog was more persistent than the parent compound. Moreover, by comparing the residues of both compounds (Table 3), one could conclude that other degradation products may be as-

sociated with the application of Dursban on palm trees. Studies of metabolism of chlorpyrifos in plants, previously investigated,⁶⁾ support the above-mentioned conclusion. Furthermore, it has been also reported⁶⁾ that chlorpyrifos is not absorbed into plants, but it accumulates on their surfaces where it decomposes by ultraviolet light. This may interpret the rapid dissipation of chlorpyrifos from dates, as shown in the present study.

To determine the safety of chlorpyrifos application on palm trees, the data presented in Table 3 indicate that a waiting period of 8 weeks after application should elapse before the fruit is harvested to get its chlorpyrifos concentration of 0.01 ppm or less. After 8 weeks dates can be harvested nearly free from chlorpyrifos. Dates in Iraq are usually harvested during the first middle of August. This may lead to suggest the safety of chlorpyrifos residues in dates.

Unfortunately, no recommendations concerning the maximum permissible residue limit for chlorpyrifos in dates are yet available. There are recommendations for other crops such as cauliflower, red cabbage and potatoes in which 0.01 ppm of chlorpyrifos is considered a maximum permissible residue limit by FAO/WHO⁷⁾. Even if we apply the FAO/WHO recommendation to dates, this will support the safety of chlorpyrifos residues in dates, provided that the dates should be harvested not before 8 weeks after the insecticide is applied on palm trees.

It has to be noted that FAO/WHO recommendations excluded the oxygen analog of chlorpyrifos from terminal residues to be determined for regulatory purposes. This may be based on that residue and metabolism studies on other crops showed low persistency of the

compound as compared with the mother one. Results of the present study may denote a special case on the dates. So if residues of the oxygen analog is also taken into the account, the situation would be completely different.

ACKNOWLEDGEMENTS

The author thanks Mrs. Intsar M. Nassif, Laboratory of Pesticides, Plant Protection Research Division, Abu-Ghraib, Baghdad for her assistance in the field experiments. Also, thanks to Dow Chemical Co. for supporting the analytical reference standards used in this study.

REFERENCES

- 1) E. E. Kenaga, W. K. Whitney, J. L. Hardy & A. E. Doty: *J. Econ. Entomol.* **58**, 1043 (1965)
- 2) M. C. Bowman & M. J. Beroza: *J. Agric. Food Chem.* **15**, 651 (1967)
- 3) J. R. Rice & H. J. Dishburger: *J. Agric. Food Chem.* **16**, 867 (1968)
- 4) L. M. Hunt, B. N. Gilbert & J. C. Schlinke: *J. Agric. Food Chem.* **17**, 1166 (1969)
- 5) M. E. Dusch, W. E. Westlake & F. A. Gunther:

J. Agric. Food Chem. **18**, 178 (1970)

- 6) G. N. Smith, B. S. Watson & F. S. Fischer: *J. Agric. Food Chem.* **15**, 870 (1967)
- 7) Anonymous: "Pesticide Residues in Food—1977," FAO Plant Production and Protection Paper, 10 Rev., 1978

要 約

ナツメヤシ果実中のクロルピリホスとそのオキシ体の残留分析

Sameeh A. Mansour

クロルピリホスをナツメヤシに散布後、本薬剤とそのオキシ体の果実中での残留量を熱イオン検出器を装着したガスクロマトグラフにより経時的に定量した。クロルピリホスの残留量は2週間後には急速に減少しているが、8週間後までなお低濃度で検出される。一方、オキシ体は残留性が高く、12週間後でも検出される。したがってナツメヤシの収穫は、オキシ体の残留を問題としない場合でも、クロルピリホス散布後少なくとも8週間経過してから行なわれるべきであると考ええる。