GLC Determination of Ekalux® Residues in Various Crops

by

R. MAES and R. H. DROST

Laboratory of Toxicology and Biotransformation
State University of Utrecht, The Netherlands

and

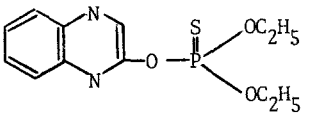
H. SAUER

Agrochemical Research Division
SANDOZ A.G., Basel, Switzerland

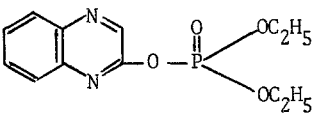
INTRODUCTION

Ekalux®25 is the emulsifiable concentrate of an organophosphorus insecticide, containing the active ingredient 0,0-diethyl-0-[quinoxalinyl-(2)] thionophosphate with the proposed ISO common name quinalphos (I). It acts as contact and stomach insecticide with good penetration properties and controlls insect pests which attack fruit and field crops, especially groundnuts, vegetables and rice.

Due to the present knowledge of its metabolism in plants the only important residues concerning health hazards are the active ingredient itself and its P = O metabolite, quinalphos oxygen analog (II).



(I)



(II)

In the past few years a gaschromatographic procedure has been developed for the residue determination of the insecticide without however, determining the metabolite II. This method involved a time-consuming extraction and clean up procedure. (DRAGER, G. 1969)

Independently, we developed a quicker and more sensitive method for determining the active ingredient as well as its metabolite. The described procedure was successfully applied to fruit and vegetables.

EXPERIMENTAL PROCEDURE

Materials

The growing of the plant material, its treatment and harvest was done according to good agricultural practice. Samples were taken from plants treated with aqueous spray emulsions containing 0,2% of Ekalux 25.

Bulletin of Environmental Contamination & Toxicology,
Vol. 11, No. 2 © 1974 by Springer-Verlag New York Inc.

The samples were grown and collected at the SANDOZ Research Station Klushof BL, Switzerland. The samples were packed in coolboxes with dry CO_2 and shipped to the laboratory, where they were kept at-20°C until extraction and analysis.

Extraction

From the prepared subsample, 20 g was blended with 60 ml of ethylacetate and 10 g of anhydrous sodium sulphate for 3 minutes.

The slurry was vacuum filtered through Whatman no. 1 paper.
The filter cake was reextracted three times with 30 ml of ethylacetate, each extraction being followed by vacuum filtering.

The combined extracts were evaporated in a Büchi rotatory evaporator on a waterbath ($t < 30^{o}C$).

The remainder was dissolved in 2,0 ml of ethylacetate.

Clean-up

The dissolved extract (2 ml) was injected completely into a Sweep co-destillation apparatus (Kontes Glass Co., Vineland) according to Storherr & Watts (1965), Storherr et al. (1967).

The apparatus was most operational at an oven temperature of 172°C and a nitrogen flow of 600 ml $min.^{-1}$. The Florisil (Pennsylvania Glass Sand Corp., Pittsburgh, Pa) used to fill the condenser tube of the sweep co-destiller was activated by heating overnight to drive off water before deactivating with 2,5% (v/w) water.

Following the sample injection, subsequently each 2 ml of petroleum-ether (25^{o} - 70°C) were injected every three minutes during 45 minutes. The combined distillates were collected in calibrated test tubes (Kontess Glass Co., No. K-57005, 10 E) and evaporated to dryness using a nitrogen jet. The concentrating tubes were kept in a water bath at room temperature during the whole clean-up procedure.

The final remainder was dissolved in 1,0 ml of ethylacetate before injecting into the gas chromatograph.

Determination

The amount of residue in the extract was determined by injecting a 2,0 µl aliquot of the cleaned up sample into a gas chromatograph with a series 701 N Hamilton syringe.

A Varian Aerograph gaschromatograph model 1740-1, equipped with a cesium bromide thermionic detector was employed. Glass columns, 1,8 mm x 2 mm I.D. were packed with 80/100 Gas Chrom. Q (Applied Science Labs, State College, Pa) coated with 3% OV-25 + OV-210 (0,7/0,4).

The columns were conditioned at 250°C for 25 hours with a nitrogen flow of 25 ml/min.

Optimum detector response was reached by using a hydrogen flow of 18 ml $min.^{-1}$ and an air flow of 170 ml $min.^{-1}$.

With a column and detector temperature of 205°C and 210°C respectively and a carrier gas flow of 25 ml of nitrogen $min.^{-1}$, the retention time of quinalphos was 3,28 min., that of its P = O metabolite (II) 4,05 min. (Fig. 1).

RESULTS AND DISCUSSION

The recovery of quinalphos from control samples which had been fortified with various concentrations of the chemical, ranged from 80 to 85% and from 85 to 90% at the 0,1 ppm and 1 ppm level respectively. For the P = O metabolite, we recovered from 70 to 80% and from 80 to 85% at the 0,1 ppm and the 1 ppm level respectively.
Typical chromatograms are shown in figure 1. Line b represents the glc recorder response of a calibration solution of 10 ng. μl^{-1} of quinalphos and its P = O metabolite, line c that of an assayed rice sample containing 0,85 ppm of quinalphos, and line a shows the gas chromatogram of a rice control sample.

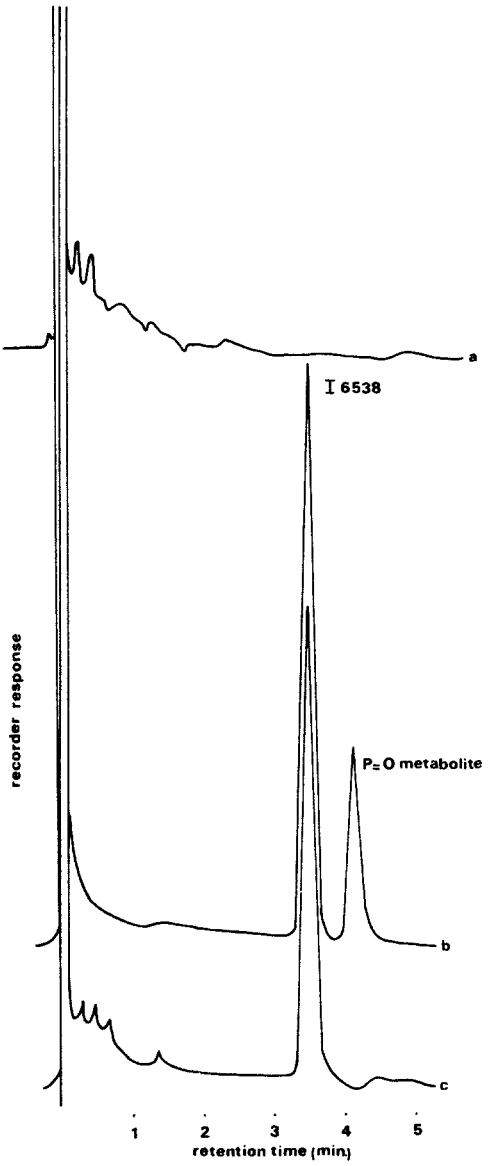


Figure 1: Typical gaschromatogram of Ekalux residues in rice plants
a. Control (2 µl)
b. Standard quinalphos + P = O metabolite (2 µl)
c. Extract of rice plants, treated with 0,2% of Ekalux 25 (sample taken a few hours after spraying) (2 µl)

Gas chromatograms of numerous control samples of untreated plant material did not show any significant peaks interfering with those of the Ekalux residues.
Therefore the application of sweep co-destillation for clean-up of Ekalux residues has proved to be very efficient. The method requires relatively little working time and is suitable for semi automatisation.

The limit of sensitivity injecting a 2,0 µl aliquot representing 20 g of plant material in 1,0 ml of final solution was 0,002 ppm for quinalphos as well as for the P = O metabolite.

TABLE 1

Residues of quinalphos (ppm) in vegetables treated with 0,2% of Ekalux 25

	Days after treatment					
	0	3	5	7	10	20
Salad	1,84	0,50	0,33	0,26	0,02	0,008
Mangold	0,80	0,16	0,15	0,12	0,03	0,006
Savoy Cabbage	0,71	0,40	0,31	0,16	0,05	0,006
Cauliflower	0,59	0,21	0,11	0,07	0,02	0,004
White Cabbage	0,61	0,42	0,17	0,06	0,02	0,008
Leek	0,60	0,21	0,08	0,06	0,01	0,002
Red Cabbage	0,84	0,52	0,20	0,15	0,05	0,004
Cucumbers	0,36	0,11	0,06	0,04	0,02	0,002
Tomatoes	0,28	0,17	0,16	0,08	0,06	0,02
Beans	0,66	0,22	0,17	0,10	0,07	0,007

Injection of larger volumes of extract solution or more concentrated extracts to increase detectability led to overloading of the detector, resulting in poor recorder responses.

The response was linear as far as it was tested up to 10 ng-μl^{-1}. The reproducibility (standard deviation) of the results for the total assay was usually within $\pm$ 10% of the man values.

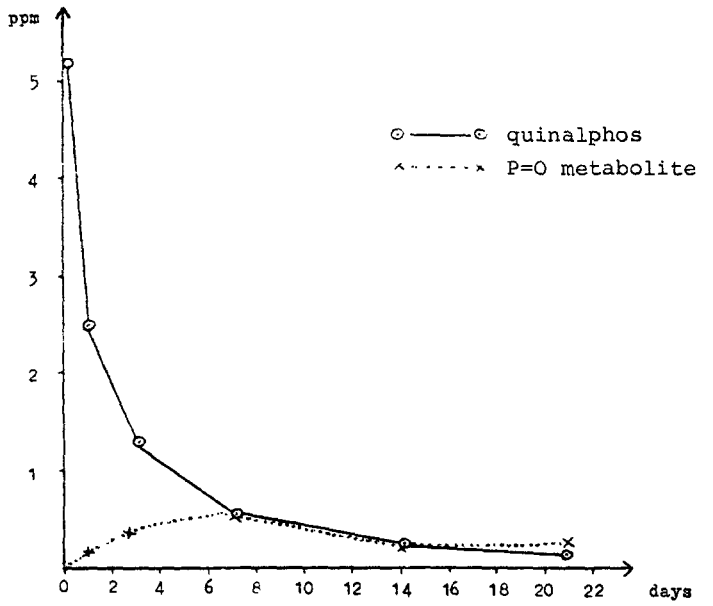


Figure 2: Residues of quinalphos and its P = O metabolite in cherries, treated with 0,2% of Ekalux 25

TABLE 2

Residues (ppm) of quinalphos and its P = O metabolites in various crops, treated with 0,2% of Ekalux 25

Sample	Days after treatment																							
	0		1		3		4		7		9		14		16		21		24		28		35		50	
	Q	M	Q	M	Q	M	Q	M	Q	M	Q	M	Q	M	Q	M	Q	M	Q	M	Q	M	Q	M	Q	M
Cherries		n.d.[a]	2,5	0,15	1,3	0,40			0,58	0,56			0,23	0,20			0,14	0,25								
Rice	0,85	n.d.	0,23	n.d.	0,16	n.d.			0,02	n.d.			0,02	n.d.			0,01	n.d.			0,004	n.d.				
Wheat[b]	5,67	n.d.	3,34	n.d.	0,21	0,01					0,01	0,07			0,004	0,08			0,002	0,01						
Wheat[b]	2,31		0,88	n.d.			0,13	n.d.	0,08	n.d.			0,03	0,02			0,005	0,07			0,003	0,09	0,003	0,02	0,002	0,006

[a] n.d. = not detected

[b] samples from two different sites

Q = quinalphos (I)

M = P=O metabolite (II)

The method was used to investigate the dissipation of Ekalux residues from various plant materials grown in the field.

As indicated in tables 1 and 2, quinalphos dissipates rather fast from the treated crops. The initial deposits shortly after treatment, according to good agricultural practice, varied from 0.28 ppm on tomatoes to 5.67 ppm on wheat plants. Already 10 days after treatment the residue level of quinalphos in all tested crops with the exception of cherries dropped below 0.1 ppm, with the highest level of 0.07 ppm in beans and the lowest of 0.01 ppm in leek. The cherries still contained 21 days after treatment 0.14 ppm of the a.i. (see also figure 2).

In most samples the P = O metabolite was not detectable. Only in cherries and wheat plants could it's occurrence be demonstrated. As shown in figure 1, one day after treatment 0.15 ppm were detected increasing to 0.56 ppm after 7 days and dropping to 0.25 ppm after 21 days. In wheat plants the P = O metabolite was found after 3 days up to the last sampling (Table 2) with a maximum residue level of 0.09 ppm after 28 days.
No additional peak besides the peaks described for quinalphos and it's P = O metabolite did ever show up in the gas chromatograms of the various samples under investigation.
We, therefore, conclude that no further P containing metabolites, stable under the conditions of the described procedure, did occur.

REFERENCES

DRAGER, G.: Pflanzenschutz-Nachrichten Bayer, 22, 218 (1969).

STORHERR, R.W. and WATTS, R.R.: J. Assoc. Offic. Anal. Chemists, 48, 1154 (1965).

STORHERR, R.W., MURRAY, E.J., KLEIN, I. and ROSENBERG, L.A.: J. Assoc. Offic. Anal. Chemists, 50, 605 (1967).