material and carries the oil up into the condenser. The condenser oil collects on the surface of the condensed water in the lower section of the graduated column. The plant material is distilled for 1.5 h even though most of the oil distills over in 20 min. If the volume of oil collected is less than 1 mL, the level of water in the column may be raised by connecting a water reservoir to the lower outlet of the 3-way stopcock forcing the oil into the calibrated 1-mL section. This permits measurement of the oil volume to 0.01 mL and estimation to 0.005 mL. For oil volumes greater than 1 mL the lower 10-mL section must be used. This results in some loss in precision as graduations are only to 0.1 mL. This lack of precision can be overcome by calibrating individually the junctions of the two calibrated regions for each distillation unit and using both the 10-mL and 1-mL sections. Alternatively a column with continuous graduations between the 1 mL and 10 mL may be used in the original construction. Such columns with continuous graduations were not available at the time of fabrication of our units.

Weight of oil obtained is calculated by multiplying the oil volume by the specific gravity measured for the oil type under determination. Spent plant material is removed after distillation for dry weight determination.

## RESULTS

Accuracy and reproducibility of the distillation units in the determination of the essential oil content of mint plants was ascertained by distilling known quantities of mint oil and measuring the quantity of oil collected.

A mean recovery of 89.9 ± 1.1% was obtained on five determinations.

Yields of mint oil varied considerably depending on the species of *Mentha* and the condition of growth of the individual plants. Table I indicates the yields of individual plants of several species and varieties of *Mentha*. This information is provided only as an indication of yields obtained with this apparatus. A more comprehensive account of yields from some of these species will be published in due course.

## ACKNOWLEDGMENT

The authors are grateful to the Glassblowing Services, University of Queensland, for fabricating the distillation units and to D. Page-Hanify, Department of Agriculture, for assistance in designing and fabricating the frame and generator.

## LITERATURE CITED

Association of Official Analytical Chemists, "Official Methods of Analysis", 11th ed, Washington, D.C. 1970.
Clevenger, J. F., *J. Am. Pharm. Assoc.* 17, 346 (1928).
Howe, K. J., Ph.D. Thesis, Cornell University, Ithaca, NY, 1956.

**Graham L. Kerven***
**Wendy Dwyer**
**Soonthorn Duriyaprapan**
**Edward J. Britten**

Department of Agriculture
University of Queensland
St. Lucia, Queensland, Australia 4067

Received for review May 15, 1979. Accepted September 4, 1979. This work was in support of a project funded by the Australian Freedom From Hunger Campaign to whom special thanks are extended.

# Residues of Fensulfothion in Selected Vegetable Crops

Fensulfothion, *O,O*-diethyl *O*-[*p*-(methylsulfinyl)phenyl] phosphorothioate, and three of its metabolites—the oxygen analogue, the sulfone, and the oxygen analogue sulfone—were determined collectively by a simplified method in spinach, table beets, cabbage, and carrots grown in treated soils. Fensulfothion and its metabolites were oxidized with *m*-chloroperbenzoic acid to the single product—the oxygen analogue sulfone. The sulfone was then analyzed as total fensulfothion by gas chromatography using a NP thermionic detector with a nonvolatile rubidium glass bead as the alkali source. Field-treated samples of spinach, table beets, and cabbage had residue levels of <0.01 ppm total fensulfothion. Residues in carrots ranged from 0.15 to 0.60 ppm, depending on the nematicide formulation and rate of application to the soil.

Fensulfothion, *O,O*-diethyl *O*-[*p*-(methylsulfinyl)phenyl] phosphorothioate, known as Dasanit, has been registered for use as an insecticide and nematicide on onions, pineapples, pea forage, bananas, sugar cane, sugar beets, peanuts and hulls, rutabagas, tomatoes, and several meat products. Its three metabolites—the oxygen analogue, the sulfone, and the oxygen analogue sulfone—were first detected in cotton plants by Katague and Anderson (1967). Fensulfothion and its three metabolites have also been detected in carrots, cauliflower, and potatoes (Williams et al., 1971) and in corn, grass, and milk (Bowman and Hill, 1971). Fensulfothion and its sulfone have also been detected in muck soil (Williams et al., 1972). Previously the residues of this organophosphate and its metabolites were extracted; the extract was fractionated on a silica gel column; and each fraction was analyzed by gas chromatography with flame photometric detection, Anderson (1973) simplified the determination of fensulfothion and its metabolites by oxidizing with *m*-chloroperbenzoic acid to form one product—the oxygen analogue sulfone. The sulfone was then analyzed by gas–liquid chromatography. This method has been successfully applied to fenthion, disulfoton, and phorate and their metabolites (Bowman and Beroza, 1969).

We undertook to determine the total residue of fensulfothion and its metabolites in selected vegetable crops grown in soils treated for the control of nematodes and evaluate the level of this toxic nematicide.

## EXPERIMENTAL SECTION

**Solvents and Reagents.** Fensulfothion and its oxygen analogue sulfone of 93.8 and 96.0% purity, respectively, were kindly supplied by the Chemagro Corporation, Kansas City, MO. Acetone and chloroform were pesticide-grade solvents from Fisher Scientific, *m*-chloroperbenzoic acid was from Eastman Kodak Co., Hyflo Supercel

from Johns-Manville, and isopropyl ether AR from Mallinckrodt.

**Field Plot Treatment.** Spinach, table beets, cabbage, and carrot seed cultivars were planted in soil designated as sandy clay loam at Weslaco, TX. Each experiment was arranged as a randomized complete block, with each treatment replicated four times. Plots were 9.1 m long with two rows per plot. Cultivars were planted in single rows on beds with centers 1.02 m apart.

The nematicide was applied as a spray on designated plots with a two-row conventional sprayer at 4.44 and 8.88 kg/hectare. A 15% granular formulation was applied on remaining plots with a Gandy Applicator at rates of 4.44 and 8.88 kg/hectare. The chemicals were incorporated to a depth of 10.2 cm with a tractor-driven rotary hoe. Each formulation was applied once at seed planting time. Untreated control plots were included in the experimental design.

**Field Sampling.** Samples of each crop at the earliest stage of maturity were obtained for residue analysis and represented the two formulations. Controls were also taken on the same dates as field-treated samples. The samples from each plot treatment were washed with water to remove adhering soil, mixed, and reduced by quartering. A 0.454-kg sample from each plot treatment was frozen with dry ice and stored at −20 °C for no longer than 10 days.

**Extraction.** The samples were prepared and extracted by Method I in the Pesticide Analytical Manual (1973), except that they were chopped with hand knives. The extracts were cleaned, oxidized, and then analyzed on the gas chromatograph.

**Gas Chromatographic Analysis.** A Perkin-Elmer Model 900 equipped with NP detector was used for the analysis. A glass column filled with 80/100 mesh Gas-Chrom Q coated with 1.5% OV-17/1.95% OV-210 was used. The conditions for GC analysis were column oven temperature, 205 °C; injection port temperature, 205 °C; helium carrier gas, 35 mL/min; hydrogen, 60 mL/min; air, 280 mL/min; chart speed 1.3 cm/min. The NP detector was in the phosphorus mode.

**Thin-Layer Chromatography.** The method used is essentially Method I as it appears in the Pesticide Analytical Manual (1973) with the following modifications for carrot extracts: oxidized extracts were pooled and concentrated to 1.0 mL; 100 μL of each sample and a standard were spotted onto silica gel GF plates; the chromatograms were developed in ethyl acetate, the solvent front travelling 14 cm from the origin. Development of the TLC plates a second time with 10/90 benzene–acetone was not necessary.

**Recovery.** Experiments were run to test the extraction procedure and determine whether fensulfothion degrades during 10 days of storage at −20 °C. Thus samples of spinach, table beets, and cabbage were fortified with the nematicide at 0.1 ppm, stored frozen for designated periods and extracted.

## RESULTS AND DISCUSSION

Figure 1 is a chromatogram of a standard mixture of fensulfothion and its oxygen analogue sulfone. The peak with a retention time of 5.5 min is due to fensulfothion. Typical gas chromatograms of extracts from spinach (A), beets (B), and cabbage (C) grown in fensulfothion-treated soils are shown in Figure 2. The peak with a retention time of 7.4 min is due to the oxygen analogue sulfone; and no interfering peaks are evident. The peak of an unidentified compound with a retention time of 5.4 min appears in the chromatograms for treated and untreated control samples. A chromatogram of an extract from field-treated carrots is shown in Figure 3. Evidently

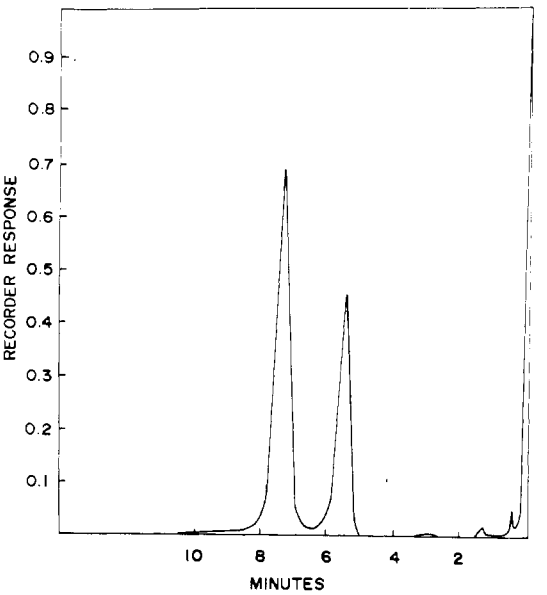


**Figure 1.** Typical gas chromatogram of a standard mixture of fensulfothion and its oxygen analogue sulfone. Each peak represents 10 ng of compound. Ordinate figure × 100 represents percentage of full-scale deflection.

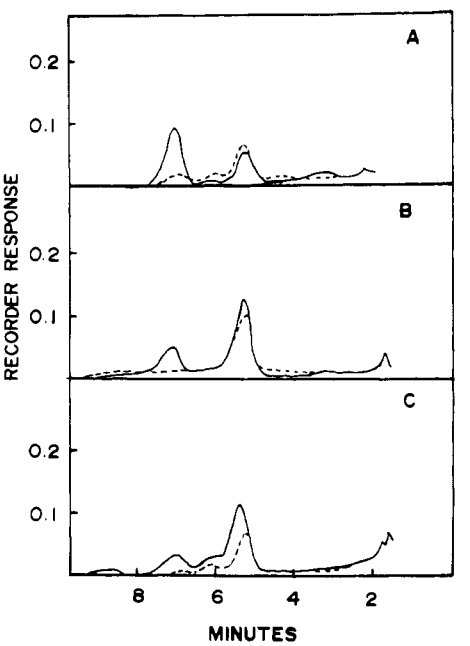


**Figure 2.** Typical gas chromatograms of the oxygen analogue sulfone of fensulfothion in extracts of field-treated (—) and untreated (- -) spinach 1A, table beets 1B and cabbage 1C. The peak with a retention time of 7.4 min represents less than 0.01 ppm of the sulfone. Ordinate × 100 denotes percent of full-scale deflection.

Table I. Recovery of Total Fensulfothion as the Oxygen Analogue Sulfone in Fortified Crop Samples[a]

| crop | fortif level, ppm | ppm 0 days | 3 days | 7 days | 10 days |
|---|---|---|---|---|---|
| spinach | 0.10 | 0.11 | 0.11 | 0.08 | 0.13 |
| table beet | 0.10 | 0.10 | 0.09 | 0.07 | 0.11 |
| cabbage | 0.10 | 0.11 | 0.09 | 0.11 | 0.09 |

[a] Values are the averages of two replications at each time.

Table II. Levels of Total Fensulfothion as the PO Analogue of Dasanit Sulfone[a]

| treatment | spinach | | table beets | | cabbage | | carrots | |
|---|---|---|---|---|---|---|---|---|
| | PO analogue of dasanit sulfone, ppm | days after treatment | PO analogue of dasanit sulfone, ppm | days after treatment | PO analogue of dasanit sulfone, ppm | days after treatment | PO analogue of dasanit sulfone, ppm | days after treatment |
| 4.44 kg/ha granular | <0.01 | 105 | <0.01 | 123 | <0.01 | 161 | 0.23 (SD ± 0.09) | 133 |
| 8.88 kg/ha granular | <0.01 | 105 | <0.01 | 123 | <0.01 | 161 | 0.56 (SD ± 0.13) | 133 |
| 4.44 kg/ha spray | <0.01 | 105 | <0.01 | 123 | <0.01 | 161 | 0.15 (SD ± 0.05) | 133 |
| 8.88 kg/ha spray | <0.01 | 105 | <0.01 | 123 | <0.01 | 161 | 0.43 (SD ± 0.10) | 133 |
| control (untreated) | | 105 | | 123 | | 161 | | 133 |

[a] All values are the averages of four replications, two samples per replication.

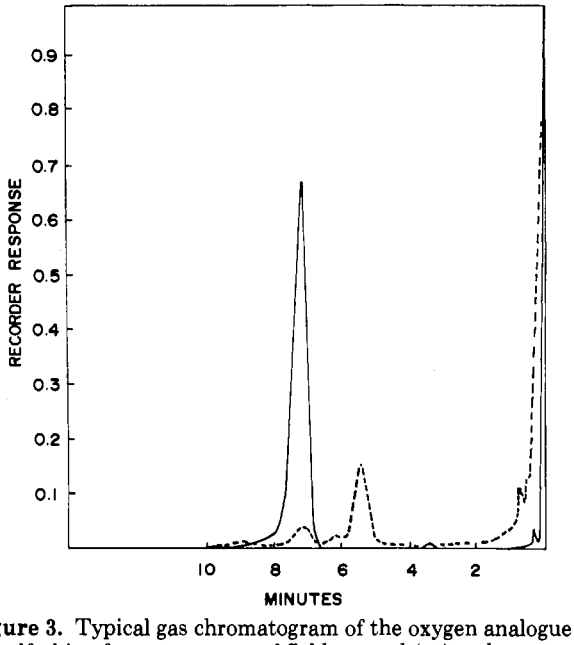


**Figure 3.** Typical gas chromatogram of the oxygen analogue of fensulfothion from an extract of field-treated (—) and untreated (- -) carrots. The peak with a retention time of 7.4 represents 0.23 ppm of the sulfone. Ordinate × 100 denotes precent of full-scale deflection.

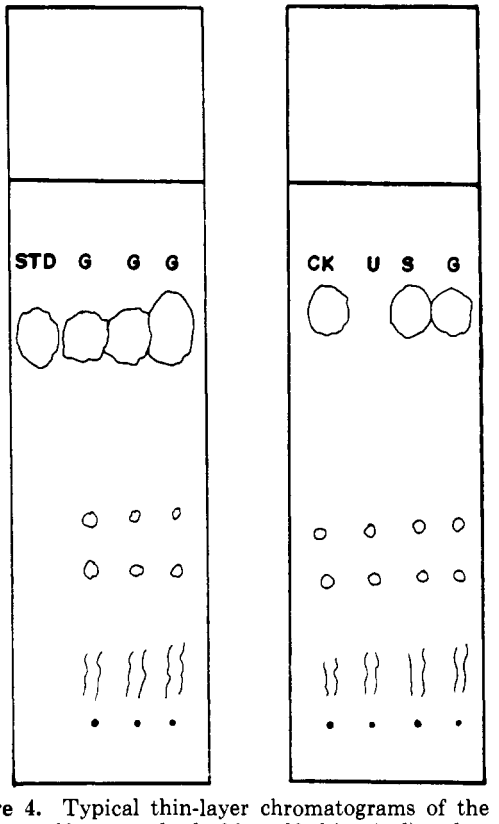


**Figure 4.** Typical thin-layer chromatograms of the oxygen analogue sulfone standard of fensulfothion (std) and pooled extracts from carrots grown in soils treated with granular (G) and spray formulations (S), untreated controls (U), and fortified samples (CK).

carrots unlike spinach, beets and cabbage absorb and retain some of the fensulfothion from the soil.

Table I shows the recovery of fensulfothion and its metabolites (ppm), as the analogue sulfone (total fensulfothion) in fortified field samples over a 10-day storage period—the maximum number of days field samples were stored after harvest. There was no observable degradation

of fensulfothion in the samples stored at −20 °C. These data also illustrate the effectiveness of the acetone and the *m*-chloroperbenzoic acid as extracting and oxidizing agents, respectively.

Table II shows the levels of total fensulfothion in four crops grown on treated soils. The levels suggest that this organophosphate is only slightly absorbed by spinach, beets, and cabbage or that these three crops, but not carrots, can effectively degrade fensulfothion. Our results on carrots are consistent with the findings of Williams et al. (1971) that fensulfothion, its sulfone and oxygen analogue sulfone were present in field-treated carrots. Thin-layer chromatography of our carrot extracts confirmed the presence of the oxidized fensulfothion (Figure 4). Yellow spots with the same retention as the pure oxygen analogue sulfone appeared on the plate after it was sprayed with 2,6-dibromo-*N*-chloro-*p*-quinonimine (DCQ).

Evidence from this investigation is that vegetable tissues can differ in retention of fensulfothion. Therefore, new crops grown in soils treated with this organophosphate should be evaluated for the presence of residual amount of this toxic material.

LITERATURE CITED

Anderson, C. A., in "Analytical Methods for Pesticides and Plant Growth Regulators", Vol. VII, Zweig, G., Ed., Academic Press, New York, 1973, Chapter 10.

Bowman, M. C., Beroza, M. J., *J. Assoc. Off. Anal. Chem.* **52**, 31 (1969).

Bowman, M. C., Hill, K. R., *J. Agric. Food Chem.* **19**, 342 (1971).

Katague, D. B., Anderson, C. A., *Bull. Environ. Contam. Toxicol.* **2**, 228 (1967).

McMahon, B. M., Sawyer, L. D., Ed., in "Pesticide Analytical Manual", Vol II, Sec. 180.234 Method 1, U.S. Department of Health, Education and Welfare, Food and Drug Administration, Washington, DC, 1973.

Williams, I. H., Brown, M. J., Finlayson, D. B., *J. Agric. Food Chem.* **20**, 1219 (1972).

Williams, I. H., Kore, R., Finlayson, D. G., *J. Agric. Food Chem.* **19**, 456 (1971).

**Eduardo R. Stein***
**Charles M. Heald**
**Amelia T. Murray**

U.S. Department of Agriculture
Science and Education Administration
Agricultural Research, Southern Region
Food Crops Utilization Research Laboratory
Weslaco, Texas 78596

Received for review May 15, 1979. Accepted August 22, 1979. Mention of a trademark, proprietary product, or vendor does not constitute a guarantee or warranty of the product by the U.S. Department of Agriculture and does not imply its approval to the exclusion of other product or vendors that may also be suitable.