Kömives, T.; Casida, J. E. *Pestic. Biochem. Physiol.* **1982**, *18*, 191.
Kunert, K. J.; Böger, P. *Weed Sci.* **1981**, *29*, 169.
Lagercrantz, C.; Yhland, M. *Acta Chem. Scand.* **1962**, *16*, 1043.
Lambert, R.; Kroneck, P. M. H.; Böger, P. *Z. Naturforsch., C: Biosci.* **1984**, *39C*, 486.
Lambert, R.; Sandmann, G.; Böger, P. *Pestic. Biochem. Physiol.* **1983**, *19*, 309.
Liberti, A.; Brocco, D.; Allegrini, I.; Bertoni, G. In "Dioxin—Toxicological and Chemical Aspects"; Cattabeni, F.; Cavallaro, A.; Galli, G., Ed.; Spectrum Publications: New York, 1978; Chapter 20.
Matsunaka, S. *J. Agric. Food Chem.* **1969**, *17*, 171.
Orr, G. L.; Hess, F. D. *Plant Physiol.* **1982**, *69*, 502.
Stier, A.; Clauss, R.; Lücke, A.; Reitz, I. *Xenobiotica* **1980**, *10*, 661.
Sullivan, A. B. *J. Org. Chem.* **1966**, *31*, 2811.
Suzuki, T.; Uchiyama, M. *Chem. Pharm. Bull.* **1975**, *23*, 2175.
Ward, R. L. *J. Chem. Phys.* **1963**, *38*, 2588.
Wettermark, G. *J. Am. Chem. Soc.* **1962**, *84*, 3658.

Received for review April 19, 1984. Accepted October 17, 1984.

Gas Chromatographic Analysis of the Herbicide Bentazon in Leeks

Allan Cessna

A gas chromatographic method for determining residues of the herbicide bentazon [3-isopropyl-1*H*-2,1,3-benzothiadiazin-4-(3*H*)-one 2,2-dioxide] in leeks (*Allium porrum* L.) has been developed using a nitrogen-specific flame ionization detector. Bentazon residues in leeks that had been treated with two postemergence applications of bentazon (1.0 kg/ha) were less than 30 ppb, the limit of detection of the analytical method based on a 5 g fresh weight equivalent. Recoveries of bentazon as its *N*-methyl derivative were in the order of 70% at the 30-ppb fortification level.

Bentazon [3-isopropyl-1*H*-2,1,3-benzothiadiazin-4-(3*H*)-one 2,2-dioxide] is currently registered in Canada for broad-leaved weed control in soybeans, peanuts, corn, and several bean crops. Crop tolerance and weed efficacy studies (Dion, 1979, 1980) have shown that a broad spectrum of broad-leaved weeds can also be controlled with postemergence applications of bentazon to leeks (*Allium porrum* L.) with no damage to the seedling leeks. Leeks are an onion-like crop with the same culinary uses as onions and are grown commercially in Eastern Canada. When this study was initiated, no registered herbicide uses were available in Canada for weed control in leeks.

The present paper describes a sensitive method of analysis for the gas chromatographic determination of bentazon in leeks as its *N*-methyl derivative (Gaynor and MacTavish, 1981). On the basis of a previously published method ("Pesticide Analytical Manual", 1978), the *N*-methylbentazon was detected by using a nitrogen-specific flame ionization detector. The method was used to determine bentazon residues in leeks that had been treated with postemergence applications of bentazon. These residue data were made available to the regulatory agencies for registration purposes.

MATERIALS AND METHODS

Herbicide Treatments. Leek samples for residue analysis were collected from two locations in Eastern Canada. At each location, both the treated and check plots were replicated 4 times.

Leeks, variety Giant Musselburg, were seeded on May 20, 1980, into 1.5 m × 7.7 m plots near the Agriculture Canada Research Station at Kentville, Nova Scotia. Prior to seeding, the plots were fertilized with 17–17–17 at 748 kg/ha. On May 30, a preemergence application of DCPA (dimethyl tetrachloroterephthalate) at 13.0 kg/ha was applied to the plots mainly for annual grass control. This was followed by an application of the insecticide permethrin [3-phenoxybenzyl (±)-*cis,trans*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate] on June 6 for cutworm control. Two postemergence applications of bentazon at 1.0 kg/ha were then applied: the first on July 18, when the crop was approximately 12 cm high (four- to five-leaf stage), and the second on August 14, when the crop was 25–30 cm high. The herbicide treatments were applied by using a hand-held boom equipped with 8004 nozzles and operated at 186 kPa. Both DCPA and bentazon were applied in 500 L/ha water.

At the Station de Researche en Defense des Cultures, L'Assomption, Quebec, leeks, variety Helvetia, were seeded into 40-m^2 plots that had been previously fertilized with 10–10–10 at 400 kg/ha. A preemergence application of DCPA at 13.0 kg/ha was applied on May 13, followed by a postemergence application of bentazon at 1.2 kg/ha when the crop was at the three- to four-leaf stage (June 20). Both herbicide treatments were applied in 600 L/ha water by using a small plot bicycle-type sprayer equipped with 8003 nozzles and operated at 200 kPa.

Sampling. The plots were randomly sampled at both locations until the sample size (0.25 kg at Kentville; 0.75 kg at L'Assomption) was obtained. Prior to freezing, the leeks were prepared as if for table use or cooking. Roots were removed and the leaves trimmed prior to washing and then the samples were immediately frozen in polyethylene freezer bags. The replicate samples were not pooled. The samples were packed in dry ice when shipped to Regina and upon arrival were stored in a freezer at −10 °C until extraction. Samples were collected on Sept 23 at L'Assomption and on Aug 29 and Oct 10 at Kentville.

Chemicals. All solvents were pesticide grade (Caledon Laboratories, Ltd., Georgetown, Ontario, Canada). Florisil (Fisher Scientific Co.), 60–80 mesh, was heated at 600 °C

Agriculture Canada, Research Station, Regina, Saskatchewan S4P 3A2, Canada.

0021-8561/85/1433-0108$01.50/0 Published 1985 by the American Chemical Society

for 24 h and then deactivated by the addition of 5% water. Sodium sulfate was heated at 600 °C for 48 h. **Caution:** Diazomethane is very toxic and should be prepared and used in a well-ventilated fume hood. Contact of ground glass apparatus with diazomethane, which is also explosive, should be avoided. *N*-Methyl-*N'*-nitro-*N*-nitrosoguanidine, a precursor of diazomethane, is a cancer suspect agent and a very potent mutagen.

Sample Extraction. Chopped leek tissue (25 g) was blended at high speed for 5 min in 125 mL of methanol. The blended sample was filtered through a fritted glass Büchner funnel (coarse porosity) under reduced pressure, and the filter cake was washed with 30 mL of methanol. The filtrate was then taken to volume (200 mL) with methanol.

The methanol extract (40 mL, equivalent to 5 g of leek tissue) was transferred to a 250-mL separatory funnel and 0.5 mL of 4 N H_2SO_4 was added, followed by 100 mL of 5% sodium sulfate solution. The mixture was extracted twice with 50 mL of methylene chloride, with each methylene chloride extract being passed through 30 mL of anhydrous sodium sulfate (contained in a 9 cm diameter, long-stemmed funnel on top of a glass wool plug) into a 250-mL round-bottom flask and followed by a 25-mL methylene chloride wash of the sodium sulfate. The combined methylene chloride extracts were then concentrated just to dryness by using a rotary evaporator.

Diazomethane Derivatization. Diazomethane was prepared from *N*-methyl-*N'*-nitro-*N*-nitrosoguanidine (MNNG) by using the MNNG-diazomethane generation apparatus with Clear-Seal joints (Aldrich catalog no. Z10, 159-1) according to the procedure of Fales et al. (1973). The methylene chloride extract residue was transferred to a 50-mL centrifuge tube with three 1.5-mL diethyl ether rinses of the 250-mL round-bottom flask. Diazomethane solution (2 mL) was added using a fire-polished Pasteur pipet, and the reaction mixture was left at room temperature for 30 min. The reaction mixture was then evaporated just to dryness by using a gentle stream of nitrogen gas.

Florisil Column Cleanup. Florisil (4 mL) was added to 8 mL hexane in a 10 mm i.d. × 200 mm column and topped with 2 cm of anhydrous sodium sulfate, and the hexane was drained to the surface of the sodium sulfate. The methylated residue was transferred to the Florisil cleanup column with three 1.5 mL of 0.5% acetone in hexane rinses of the centrifuge tube and the column eluted at 1 mL/min with an additional 25.5 mL of 0.5% acetone in hexane and the eluate discarded. The column was then eluted at 1 mL/min with 25 mL of 2% acetone in hexane. The last 20 mL eluate was collected, concentrated to approximately 0.5 mL by using a rotary evaporator, and then taken to volume (1 mL) with hexane for gas chromatographic analysis of *N*-methylbentazon.

Fortification. Recoveries of bentazon were determined by the extraction of leek tissue fortified at 150 and 30 ppb. Bentazon (0.75 or 3.75 μg in 1.0 mL of methanol) was added to 25 g of chopped untreated leek tissue in a 50 mL beaker and the beaker placed in a fume hood. After the methanol had evaporated, the beaker was sealed with parafilm and placed in a refrigerator in the dark at 6 °C for 48 h prior to extraction. Six replicates were analyzed at each fortification level.

Gas Chromatography. A Hewlett-Packard Model 5733A gas chromatograph, equipped with a Model 18789A nitrogen–phosphorus detector, was used with a Honeywell Electronik 194 1-mV recorder. A 1.8 m × 4 mm i.d. coiled glass column packed with 0.5% Dexsil 300 on 80–100-mesh Chromosob W, HP, gave a retention time of 4.5 min for *N*-methylbentazon under the following conditions: helium (carrier gas), 35 mL/min; injector and column, 170 °C; detector, 350 °C. The detector voltage was set at approximately 16 V to give an offset of a 20% recorder deflection at attenuation ×32. Detector flow rates were hydrogen 3 mL/min and air 50 mL/min. Under these conditions, 1.2 ng of *N*-methylbentazon gave a full-scale recorder deflection at attenuation ×2, range 1. A linear response was observed over the range 0.1–10.0 ng of *N*-methylbentazon.

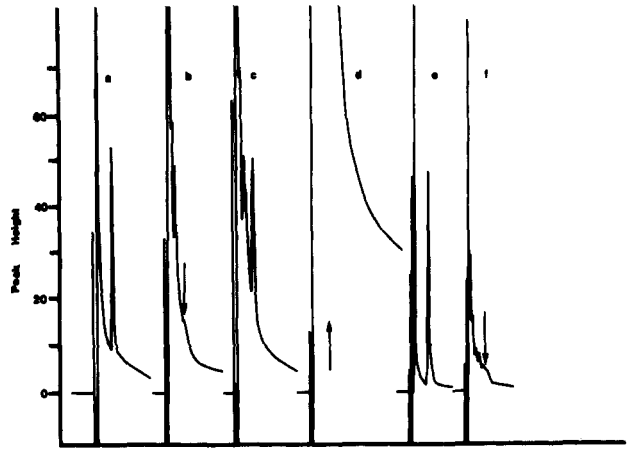

Figure 1. Chromatogram a, 0.6 ng of *N*-methylbentazon in hexane at attenuation ×2 (equivalent to 30 ppb); chromatogram b, leek check methylated with diazomethane prepared with the MNNG–diazomethane generator (attenuation ×2); chromatogram c, recovery from 30-ppb fortification of a leek check (attenuation ×2); chromatogram d, leek check methylated with diazomethane prepared by the method of Rivers et al. (1970) (attenuation ×2); chromatogram e, 3.0 ng of *N*-methylbentazon in hexane at attenuation ×16 (equivalent to 150 ppb); chromatogram f, leek check at attenuation ×16.

RESULTS AND DISCUSSION

A flame photometric detector, operated in the sulfur mode, was used in the previously published method ("Pesticide Analytical Manual", 1978) to detect the *N*-methyl derivative of bentazon. Because of its sensitivity and selectivity for sulfur-containing compounds, this would be the detector of choice. However, since our laboratory is not equipped with this detector, it was decided to take advantage of the presence of two nitrogen atoms in the bentazon molecule and adapt the method for use with a nitrogen-specific flame ionization detector (N-FID). Providing sufficient cleanup could be achieved, the sensitivity of this detector was adequate, as 1.2 ng of *N*-methylbentazon gave a full-scale recorder deflection.

Because of convenience of preparation, diazomethane was initially prepared by the method of Rivers et al. (1970) with the modification that diethyl ether rather than hexane was used for the diazomethane solution. However, interferences from the reagent, which coeluted with the *N*-methylbentazon from the Florisil column, made analysis with the N-FID impossible (Figure 1, chromatogram d). These interferences were effectively removed by using the MNNG–diazomethane generator, which produced an ether solution of relatively pure diazomethane. The resulting analyses of the leek checks showed little interference with the *N*-methylbentazon peak either at attenuation ×16 (Figure 1, chromatogram f) or attenuation ×2 (Figure 1, chromatogram b). However, at attenuation ×2, the *N*-methylbentazon appeared on a steeply downward sloping base line (Figure 1, chromatogram c). The limit of de-

tection of the method was 30 ppb.

Recoveries of bentazon from fortified leek check tissue were determined from a standard calibration curve constructed by plotting nanograms of *N*-methylbentazon against peak height. Six replicates were analyzed at each fortification level, and the percent recoveries, expressed as the mean ± standard deviation, were 68.7 ± 1.6 and 71.6 ± 6.2 at the 150- and 30-ppb fortification levels, respectively.

None of the leek samples from L'Assomption showed bentazon residues greater than 30 ppb. For these samples the time interval between the single postemergence application and sample harvest was 95 days. At Kentville, two postemergence applications of bentazon were made as well as two sample harvests. The time intervals between the second postemergence application and the first and second harvests were 15 and 55 days, respectively. Bentazon residues in these samples were also less than 30 ppb. The disappearance of bentazon residues to less than 30 ppb in only 15 days suggests a rapid metabolism of bentazon by the bentazon-tolerant leeks. Rapid metabolism of bentazon has been observed in other tolerant species such as rice, corn, soybean, and barnyardgrass (Mine et al., 1975) and soybean and navy bean (Mahoney and Penner, 1975).

The registrations of postemergence applications of bentazon for broad-leaved weed control in crops (soybean, corn, peanuts, and bean) in Canada were based on bentazon residues in the mature grain of these crops being less than 100 ppb (Bennett, 1983). The bentazon residues observed in leeks in the present study, which were representative of leaks prepared either for table use or cooking, were much less than that level.

ACKNOWLEDGMENT

I thank E. A. Mulatz for her technical assistance and K. Jensen, Agriculture Canada Research Station, Kentville, Nova Scotia, and A. Dion, Station de Researche en Defense des Culture, L'Assomption, Quebec, for conducting the field treatments and collecting and shipping the leek samples to Regina.

Registry No. Bentazon, 25057-89-0.

LITERATURE CITED

Bennett, P., Health and Welfare Canada, Health Protection Branch, Additivies and Pesticides Division, Ottawa, Ontario, Canada, personal communication, 1983.

Dion, A. "Research Report: Expert Committee on Weeds (Eastern Section)"; Agriculture Canada, Research Branch: Ottawa, Ontario, Canada, 1979; p 239 (abstract only).

Dion, A. "Research Report: Expert Committee on Weeds (Eastern Section)"; Agriculture Canada, Research Branch: Ottawa, Ontario, Canada, 1980; p 263 (abstract only).

Fales, H. M.; Janouni, T. M.; Babashak, J. F. *Anal. Chem.* **1973**, *45*, 2302.

Gaynor, J. D.; MacTavish, D. C. *J. Agric. Food Chem.* **1981**, *29*, 626.

Mahoney, M. D.; Penner, D. *Weed Sci.* **1975**, *23*, 265.

Mine, A.; Miyakado, M.; Matsunaka, S. *Pestic. Biochem. Physiol.* **1975**, *5*, 566.

"Pesticide Analytical Manual". U.S. Department of Health, Education and Welfare: Washington, DC, 1978; Vol. II.

Rivers, J. B.; Yauger, W. L., Jr.; Klemmer, H. W. *J. Chromatogr.* **1970**, *50*, 334.

Received for review June 4, 1984. Accepted November 6, 1984.

Novel Insecticidal-Miticidal Cyclic Dithiacarbamoyloximes

Themistocles D. J. D'Silva,* John A. Durden, Jr., Anthony A. Sousa, and Mathias H. J. Weiden

A series of novel dithiacyclic carbamoyloximes that have a readily oxidizable sulfide linkage and a thiohydroximate group in the same molecule has been synthesized and its insecticidal and miticidal profile determined. The biological properties of these materials reflect the activities of both aldicarb- and methomyl-like compounds. The most active compounds are 4-[(methylcarbamoyl)oximino]-1,3-dithiolanes with one or two methyl substituents at the C_5 position, compounds **12** and **13**, respectively. Compound **16**, 2-[(methylcarbamoyl)oximino]-1,4-dithiane, although slightly less effective against Lepidoptera, is safer to rats than are the other molecules of comparable pesticidal activity.

Many methyl carbamoyloximes are potent inhibitors of acetylcholinesterase and some exhibit a broad spectrum of insecticidal activity. During the last two decades this class of toxicants has been the subject of extensive investigation (Weiden et al., 1965; Addor, 1965; Weiden, 1968; Felton, 1968). These efforts have resulted in the successful commercialization of aldicarb by Union Carbide (Weiden et al., 1965) and methomyl by Du Pont and Shell (Felton, 1968). Oxamyl (British Patent, 1970), thiofanox (Magee, 1975), and experimental compounds such as Tirpate (Fridinger et al., 1971) and Talcord (Breese, 1970) have also shown promising activity.

A study on thiophan-3-one *O*-(methylcarbamoyl)oximes, the cyclic analogues of aldicarb and thiofanox (Durden and Weiden, 1974), has shown that these materials are also similar to the acyclic analogues in their pesticidal properties.

The carbamoyloximes studied thus far may be broadly classified into two groups on the basis of their structural features and biological properties (shown below). One group is comprised of compounds such as aldicarb, thiofanox, and Tirpate, which are derived from aldoximes or ketoximes, and the other group is comprised of com-

Union Carbide Agricultural Products Company, Research and Development Department, Research Triangle Park, North Carolina 27709.

0021-8561/85/1433-0110$01.50/0