

## Analysis of Potatoes Treated with Dinoseb and Chlorbromuron Herbicides

Preemergence applications of Sinox PE alone or in sequence with Sinox General and of Maloran in sequence with Sinox General to Netted Gem potatoes left no residues in the tubers at harvest. The two dinoseb formulations were extracted from tubers as 2-*sec*-butyl-4,6-dinitrophenol with hot methanol-sulfuric acid, cleaned up on basic alumina, diazomethane methylated, and then cleaned up on acidic alumina. Chlorbromuron was extracted in methanol and cleaned up on Florisil. Compounds were analyzed on 10% DC-200 or 3% OV-210 columns by using electron capture gas chromatography. Recoveries from potato pulp and peel fortified with 0.05–0.5 ppm of dinoseb or 0.1–0.5 ppm of chlorbromuron were 83% and 88% or 80% and 84.5%, respectively.

The herbicide dinoseb as the amine salt of 2-*sec*-butyl-4,6-dinitrophenol (DNBP) in the commercial formulations Premerge or Sinox PE is applied preemergence to approximately 90% of the potato acreage in New Brunswick, mainly for the control of germinating broad-leaved weeds. Chlorbromuron is also effective and is gaining increased usage in potatoes. Dinoseb as the free phenol in the commercial formulations Sinox General or Dytop is a harvest aid used to reduce the amount of potato vines by desiccation for easier harvesting, to reduce losses from late blight tuber rot, to control tuber size, and to reduce skinning of the tubers. Dinoseb for vine killing is usually applied at least 14 days before harvest.

DNBP was not highly systemic when applied to plants (Barrons and Watson, 1969; Bandal and Casida, 1972).

Although herbicidal and vine-killing treatments have been successfully used, no studies regarding their residues in potatoes have been made in New Brunswick.

The objectives of this paper were to analyze for residues of the two formulations of dinoseb and chlorbromuron in the field-treated potato Netted Gem. High rates of application of dinoseb were included to represent misuse or spray overlapping.

### EXPERIMENTAL SECTION

**Field Experiments.** Four blocks each divided into 8 plots 12 × 1.8 m were established at the Fredericton Research Station, New Brunswick, and planted with seed pieces of Netted Gem potato according to general practices on June 7, 1974. On June 24 when 15% of the potatoes had emerged, plots were treated with either Sinox PE containing 360 g/L dinoseb (Niagara) at 2.2, 4.5, or 9.0 kg of a.i./ha or with Maloran 50 WP containing 50% chlorbromuron by weight (Ciba-Geigy) at 1.7 kg of a.i./ha (Table I). On Sept 5, Sinox General containing 600 g/L dinoseb (Niagara) was applied at either 2.2 or 4.5 kg of a.i./ha to selected plots. The materials were applied with a portable sprayer and delivered in 340 L/ha at 200 kPa. Four random samples each of potato tubers were harvested from each plot on Sept 20 and kept at 4.4 °C for 2 weeks and then analyzed. Notes on the effect of herbicides on potatoes and weeds were made on July 23.

**Apparatus and Reagents.** Analytical-grade standards of dinoseb, 2-*sec*-butyl-4,6-dinitrophenol, Agricultural Products Department, Dow Chemical U.S.A., Midland, MI, and chlorbromuron, 3-(4-bromo-3-chlorophenyl)-1-methoxy-1-methyl urea, Ciba-Geigy, Montreal, were used. Alumina, basic and acidic, activity grade I, Diazald, and all other reagents were as described in Gardner and McKellar (1980). The Hyflo-Super-Cel filtering aid, Johns-Manville, was shaken with methanol and filtered through suction, and the resulting cake was washed with methanol and vacuum-dried. A Tracor Micro-Tek 220 gas chromatograph equipped with a <sup>63</sup>Ni electron capture detector was used. Columns, 10% DC-200 and 3% OV-210, and operating conditions are listed in Table II.

**Analysis of Dinoseb and Chlorbromuron Herbicides in Potato Pulp and Peel.** Potato tubers were washed with water, wiped, and quartered, and subsamples were obtained from two opposite quarters and isolated into peel and pulp.

**Analysis of Dinoseb.** The basic procedure described by Bjerke (1974) and published later by Gardner and McKellar (1980) for the extraction and cleaning up of dinoseb residues in crops and soil and then analysis by gas chromatography was followed. Briefly, each peel or pulp sample was extracted with hot methanol-sulfuric acid, the extract filtered through washed Hyflo-Super-Cel, partitioned into ether, and cleaned up on basic alumina by using sodium bicarbonate for elution. Aliquots were acidified, partitioned into ether, diazomethane methylated, and then cleaned up on acidic alumina by using ether for elution. The resulting dinoseb methyl ether was made to a suitable volume in trimethylpentane and analyzed by electron capture gas chromatography using the 10% DC-200 column (Table II).

**Analysis of Chlorbromuron.** Chlorbromuron was extracted from potatoes in methanol following basically Ragab's et al. (1979) procedure for soil with slight modifications. Subsamples of 25 g of blended potato pulp or peel were shaken mechanically with 50 mL of methanol and 5 g of cleaned Hyflo-Super-Cel in a 200-mL centrifuge bottle for 1 h. The mixture was filtered with suction through a Hyflo-Super-Cel layer in a Büchner coarse fritted disk funnel, the bottle was washed with methanol, and the washings were filtered. The combined filtrate was concentrated in a vacuum evaporator at 35 °C and made to volume in a 25-mL volumetric flask. A 10-mL aliquot was evaporated to dryness (35 °C) and the residue was dissolved in 5 mL of hexane containing 6% ether and cleaned up on Florisil column with 20% ether in hexane as described by Khan et al. (1975) for linuron residues from soils. The eluate was concentrated (35 °C) to 10 mL in a 15-mL centrifuge tube, and 5 µL was injected into the gas chromatograph when the 3% OV-210 column was used (Table II).

### RESULTS AND DISCUSSION

The effect of dinoseb and chlorbromuron herbicides on potato tubers is shown in Table I. The vigor of the Netted Gem potato vines was reduced 10–20% when dinoseb was applied at late ground crack with 15% of the plants emerged. However, none of the treatments affected the yield of tubers. Netted Gems are a long-season potato variety. The vine-killing treatment was applied before the tubers were fully mature, thus the apparent reduction in specific gravity of tubers from the treatments receiving vine killing.

Satisfactory recovery of dinoseb and chlorbromuron from fortified potato pulp and peel at levels of 0.05, 0.2, and 0.5 ppm dinoseb and 0.1 and 0.5 ppm of chlorbromuron is shown in Table III. Table IV shows that no

Table I. Effect of Dinoseb and Chlorbromuron Herbicides on Netted Gem Potato<sup>a</sup>

treatment in 340 L/ha at 200 kPa			yield, cwt/ha			visual estimates on July 23			
herbicide and vine killing	time applied	rate, kg/ha	marketable tubers	small tubers	tuber sp gravity	potatoes		barnyard grass	
						S <sup>b</sup>	V <sup>c</sup>	S <sup>b</sup>	V <sup>c</sup>
dinoseb, herbicidal <sup>d</sup>	June 24	2.2	124.26	62.74	1.083	1	1	6	4
dinoseb, herbicidal	June 24	4.5	153.79	71.60	1.084	1	1	7	4
dinoseb, herbicidal	June 24	9.0	135.47	65.79	1.086	2	1	10	10
chlorbromuron <sup>f</sup>	June 24	1.7							
dinoseb, vine killing <sup>e</sup>	Sept 5	2.2	141.57	20.88	1.080	1	1	10	10
chlorbromuron	June 24	1.7							
dinoseb, vine killing	Sept 5	4.5	171.11	74.86	1.079	0	0	10	10
dinoseb, herbicidal	June 24	4.5							
dinoseb, vine killing	Sept 5	2.2	91.67	73.94	1.078	0	2	8	6
dinoseb, herbicidal	June 24	4.5							
dinoseb, vine killing	Sept 5	4.5	115.10	82.50	1.076	0	1	8	5
check hand weeded no chemicals			169.07	71.40	1.084	0	0	9	7
		L.S.D.: 0.05 0.01	N.S.		0.003 0.005				

<sup>a</sup> Planted June 7 and harvested Sept 20. <sup>b</sup> Stand 0-10; 0 = no effect; 10 = stand reduced 100%. <sup>c</sup> Vigor 0-10; 0 = no effect; 10 = complete kill. <sup>d</sup> Sinox PE containing 360 g/L 2-sec-butyl-4,6-dinitrophenol. <sup>e</sup> Sinox General containing 600 g/L 2-sec-butyl-4,6-dinitrophenol. <sup>f</sup> Maloran 50% WP.

Table II. Electron Capture Gas Chromatographic Data for Dinoseb Methyl Ether and Chlorbromuron on 10% DC-200 and 3% OV-210 Columns

compound	column			inlet temp, °C	gas flow rate, °C mL/min		rel retention time (RRT)	
	type <sup>a</sup>	length <sup>b</sup>	temp, °C		carrier	purge	aldrin	lindane
dinoseb methyl ether	10% DC-200	47	188	210	17.6	11.6	0.62	1.39
dinoseb methyl ether	3% OV-210	33	175	188	14.5	9.6	2.98	3.76
chlorbromuron	10% DC-200	50	175	175	40.5	19.2	1.20	3.00
chlorbromuron	3% OV-210	36	175	200	43.5	19.2	3.60	4.30

<sup>a</sup> On Gas-Chrom Q, 80-100 mesh. <sup>b</sup> 0.4-cm i.d. <sup>c</sup> Argon containing 5% methane.

Table III. Recovery of Dinoseb and Chlorbromuron from Fortified Potatoes

potato part	dinoseb recovery, % <sup>a</sup> from fortified			chlorbromuron recovery, % <sup>a</sup> from fortified	
	0.05 ppm	0.2 ppm	0.5 ppm	0.1 ppm	0.5 ppm
pulp	80	74	95	77	83
peel	83	84	97	80	89

<sup>a</sup> Average of four determinations.

dinoseb from either of the two formulations or chlorbromuron was found in any of the field-treated potatoes. The result was confirmed by using the 3% OV-210 column for dinoseb and 10% DC-200 column for chlorbromuron (Table II). The difference in column length in each case was not a factor; it just happened that the complete analysis was not done at one time. Table II shows the retention times of both compounds relative to those of aldrin and lindane chromatographed on both columns under the same respective parameters and at the same time. This a good means of confirmation of results.

Additional confirmatory tests were obtained by thin-layer chromatography on 20 × 20 cm glass plates coated with 0.5 mm thickness silica gel (Kieselgel DF-0, Camag) with fluorescent binder. Appropriate aliquots of cleaned up extracts were chromatographed as bands, along with reference standards, by using dichloromethane. Dinoseb (as 2-sec-butyl-4,6-dinitrophenol) (without derivatization) and chlorbromuron in a given sample of fortified or reference standard produced dark bands of  $R_f$  0.66 and  $R_f$  0.42, respectively, under a short-wave UV light against a

Table IV. Residues of Dinoseb and Chlorbromuron Herbicides from Field-Treated Potatoes

treatment no.	herbicide <sup>a</sup>	vine <sup>b</sup> killing	rate applied, kg/ha	residue, ppm <sup>c</sup>	
				pulp	peel
1	dinoseb		2.2	<0.01	<0.01
2	dinoseb		4.5	<0.01	<0.01
3	dinoseb		9.0	<0.01	<0.01
4	chlorbromuron		1.7	<0.05	<0.05
		dinoseb	2.2	<0.01	<0.01
5	chlorbromuron		1.7	<0.05	<0.05
		dinoseb	4.5	<0.01	<0.01
6	dinoseb		4.5	<0.01	<0.01
		dinoseb	2.2	<0.01	<0.01
7	dinoseb		4.5	<0.01	<0.01
		dinoseb	4.5	<0.01	<0.01
8	check	check	0.00	<0.01	<0.01

<sup>a</sup> Applied June 24. <sup>b</sup> Applied Sept 5. <sup>c</sup> Average of four determinations.

fluorescent background. Field-treated samples produced no response to the thin-layer chromatographic procedure. Care was taken to ensure that the chlorbromuron extract was not heated above 35 °C or taken to complete dryness because chlorbromuron is decomposed by heat.

The absence of dinoseb from the field-treated potatoes indicates its lack of translocation as was reviewed by Barrons and Watson (1969) and observed by Bandal and Casida (1972) in their metabolism studies in beans. The present study also indicates that dinoseb residues in soil did not come in contact with the potato roots. This is in agreement with Barrons and Watson (1969), who stated that dinoseb had a limited downward movement in soil and only the plant parts contacted by it will show an effect.

Most of chlorbromuron remained in the soil in the 0-2.5-cm depth (Ragab et al., 1979), and probably little or no residues reached potato roots.

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## A Novel Class of Fungicides: (2-Pyridylthio)methyl Benzoate N-Oxides

The reaction of chloromethyl benzoates with sodium pyriithione afforded (2-pyridylthio)methyl benzoate N-oxides having in vitro fungicidal activity on a variety of agriculturally important fungi (e.g., *Alternaria solani* and *Phytophthora infestans*). The title compounds have demonstrated a spectrum of activity similar to that of zinc pyriithione, suggesting that release of the fungicidal 2-mercaptopyridine 1-oxide moiety may be significant. The synthesis of thiomethyl benzoate analogues and their bioevaluation are described.

The role of fungicides in seed storage and in the prevention and cure of systemic plant fungal infections is a significant area of interest to the agricultural scientist and farmer alike. The antifungal and antibacterial properties of 2-mercaptopyridine 1-oxide and its salts have long been known (Ladd, 1954; Albert et al., 1956; Leonard et al., 1956; Sijpesteijn et al., 1958). It was of interest to synthesize derivatives of 2-mercaptopyridine 1-oxide which had the capacity to hydrolytically release the active moiety after application. Such a protecting group was found to be the methyl benzoate system.

#### EXPERIMENTAL SECTION

**Chemistry.** The general synthetic scheme is shown in Figure 1. The acid chlorides (Ia-d) were commercially available (Aldrich Chemical Co.) and were used without further purification. Infrared spectra (IR) were recorded with a Perkin-Elmer Model 727B instrument. All <sup>1</sup>H NMR spectra were obtained with a Hitachi Perkin-Elmer Model R-24B 60-MHz high-resolution spectrometer. NMR samples were prepared in CDCl<sub>3</sub> or Me<sub>2</sub>SO-*d*<sub>6</sub> containing 1% Me<sub>4</sub>Si; chemical shifts are reported in ppm ( $\delta$ ) relative to  $\delta(\text{Me}_4\text{Si}) = 0$ . Melting points were determined with a Thomas-Hoover capillary melting point apparatus and are uncorrected.

The syntheses of IIa-d were accomplished with moderate yields (20-70%) by using anhydrous zinc chloride and paraformaldehyde at 100 °C (Henry, 1901; Descude, 1901) and purified by distillation. The syntheses of the (2-pyridylthio)methyl benzoate N-oxides (IVa-d) were carried out in low yields (8-41%) by using sodium pyriithione (III, sodium omadine, 90%) in a simple displace-

ment reaction. The low yields are apparently a consequence of hydrolysis of the product during the reaction. The procedure for the synthesis of IVa serves as an example.

**(2-Pyridylthio)methyl Benzoate N-Oxide (IVa).** Chloromethyl benzoate (IIa) (distilled: bp 75-77 °C/2.0 mm; 4.8 g, 28.1 mmol) in 10 mL of 2-propanol was added dropwise to a rapidly stirring solution of sodium pyriithione (III, 6.71 g, 45.0 mmol) in 25 mL of 2-propanol under anhydrous conditions and at ambient temperature. After 1 h, the mixture was filtered to remove precipitated sodium chloride and the filtrate concentrated at reduced pressure to yield a white solid. Recrystallization from toluene afforded 1.5 g of IVa (21% yield): mp 124 °C dec; IR (CO)  $\nu$  1750 cm<sup>-1</sup>,  $\nu$  (NO) 840 cm<sup>-1</sup>; <sup>1</sup>H NMR (Me<sub>2</sub>SO-*d*<sub>6</sub>)  $\delta$  5.85 (2 H, s), 7.50 (8 H, m), 8.20 (1 H, d, 6 Hz). Anal. Calcd for C<sub>13</sub>H<sub>11</sub>NO<sub>3</sub>S: C, 59.78; H, 4.25; N, 5.36. Found: C, 59.95; H, 4.36; N, 5.36.

The procedures for the synthesis of IVb-d were identical with that for IVa.

**(2-Pyridylthio)methyl 2-Chlorobenzoate N-Oxide (IVb).** The data are as follows: 41% yield; mp 123 °C; IR  $\nu$  (CO) 1740 cm<sup>-1</sup>,  $\nu$  (NO) 840 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  5.90 (2 H, s), 8.50 (8 H, m). Anal. Calcd for C<sub>13</sub>H<sub>10</sub>ClNO<sub>3</sub>S: C, 52.79; H, 3.38; N, 4.74. Found: C, 52.56; H, 3.28; N, 4.75.

**(2-Pyridylthio)methyl 2-Methylbenzoate N-Oxide (IVc).** The following data were found: 29% yield; mp 123 °C dec; IR  $\nu$  (CO) 1700 cm<sup>-1</sup>,  $\nu$  (NO) 840 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  2.55 (3 H, s), 5.70 (2 H, s), 7.50 (8 H, m), 8.20 (1 H, d, 6 Hz).

**(2-Pyridylthio)methyl 4-Methoxybenzoate N-Oxide (IVd).** The data were as follows: 8% yield; mp 140 °C dec;