Deltamethrin Residues on Saskatoon Berries†

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Following four applications of deltamethrin [(*S*)-α-cyano-3- phenoxybenzyl (1*R*,3*R*)-*cis*-2,2-dimethyl-3-(2,2-dibromovinyl)cyclopropanecarboxylate], saskatoon berries were manually collected 1, 7, 14, 21, 28, and 39 days after the last application. Berries were stored frozen in foil-lined bags pending analysis. An acetone extraction of the berries was purified on Florisil and analyzed on a 50% phenylmethyl silicone megabore capillary column using an electron capture detector. The mean residue on the berries 1 day after the last application was 0.22 ppm and after 7 days had declined to 0.08 ppm. Thirty-nine days after the last application, the mean residue of deltamethrin on the berries was 0.01 ppm.

INTRODUCTION

The saskatoon shrub (*Amelanchier alnifolia* Nutt.) is a common plant of coulees, bluffs, and open woodlands of the Great Plains of North America (Fernald, 1950; Looman and Best, 1987). The saskatoon berry was used by indigenous people as a constituent of pemican. Today, the fruit is used for jams, syrups, pie fillings, and, to a lesser extent, wine, both domestically and commercially. The extent of a commercially cultivated crop is limited, but it has been suggested that 4000 ha may be in commercial production in the future in the Canadian prairies.

As saskatoons became established in commercial orchards, it became evident that a number of insects were or had the potential to become pests. The Provincial Entomologist of Saskatchewan isolated 22 insects that feed on saskatoons (Harris, 1988). Of the insects present, saskatoon bud moth (*Epinotia bicordana* Heinr.), apple curculio (*Tachypterellus quadrigibbus* (Say)), cherry shoot borer (*Argyresthia oreasella* Clem.), and a sawfly (*Hoplocampa* sp.) were of major concern. The apple curculio had been previously identified as a pest of saskatoons (Steeves et al., 1979; Bethune et al., 1979). In the Peace River district of Alberta, 15 insects were found on saskatoons (Davidson, 1986).

Insect damage to saskatoons may reduce both yield and quality of fruit. The magnitude of the losses experienced by the producers is not readily available. Estimates of crop loss range from a low of 5% to as high as 100% (Davidson, 1986; J. L. Harris, Personal communication, 1990). Steeves et al. (1979) reported that in a limited survey, the number of desirable berries was less than 2% of the number of flowers initially present. Much of the loss was attributed to the damage caused by the apple curculio. Examination of branches removed from saskatoon bushes in 1989 found that between 20% and 70% of the bud clusters were infested, mainly by saskatoon bud moth (Harris and Westcott, 1989).

Numerous studies in the province of Alberta demonstrated the efficacy of deltamethrin, a synthetic pyrethroid insecticide, for control of insect pests of saskatoon berries (Davidson, 1987; Davidson and Neighbour, 1983, 1984, 1986, 1987a–d; Howard et al., 1987, 1988). However, no insecticides were registered in Canada, and none could be legally recommended to the producers. In 1989, deltamethrin was again evaluated for the express purpose of obtaining data to support a Minor Use Registration in Canada.

Deltamethrin residues have been determined by methods based on high performance liquid chromatography (Noble et al., 1982; Haddad et al., 1989) and more commonly, and with greater sensitivity, by gas chromatography (L'Hôtellier, 1982; Vaysse et al., 1984; WHO, 1990). The method chosen for the determination of residues of deltamethrin in saskatoon berries was adapted from our earlier determination of deltamethrin residues on wheat and clover herbage (Westcott and Reichle, 1987). This paper describes the determination of residues of deltamethrin on saskatoons.

MATERIALS AND METHODS

Chemicals. All solvents and chromatographic adsorbents were of high purity and suitable for pesticide residue analysis.

Chemical Application. The study sites for this project were located approximately 16 km southwest of Saskatoon along the South Saskatchewan River. Plots measuring 13.5 m × 25 m were established in each of three orchards. Control plots of similar size were also established. Each plot contained four rows of saskatoon bushes. A Turbomist orchard sprayer was calibrated to deliver 480 L/ha of an insecticide mixture at an operating pressure of 700 kPa. Deltamethrin (Decis 5EC, Hoechst Canada Inc.) at 10 g/ha was applied on May 1, 12, and 24 and June 1, corresponding to leaf bud break, inflorescence extension, 90% petal fall, and 8 days after 90% petal fall, respectively.

Samples of immature and mature berries were collected manually from each deltamethrin treatment plot plus check plots. Berries were collected directly into foil-lined paper bags (18 cm × 35 cm, Hoechst Canada Inc.) that were closed for storage by folding the top down several times and stapling it shut. The use of these bags was recommended by Hoechst Canada Inc. to reduce the possibility of deltamethrin residues being absorbed by plastic bags or contaminants being transferred to the berries. Collections were made on June 2, 8, 15, 22, and 29 and July 10. Three samples were collected on each date from each treated plot and one sample from the control plot. Samples were transported back to Saskatoon where they were frozen pending chemical residue analysis which started about 1 month after the final collection.

Analysis of Deltamethrin in Saskatoon Berries. Saskatoon berries (25 g as picked) and Hyflo SuperCel (5 g) in acetone (100 mL) were homogenized in a 250-mL homogenizer flask for 5 min. The macerate was filtered through a 5.5-cm Büchner funnel containing a 6-mm pad of Hyflo SuperCel on a Whatman No. 2 paper filter. The filter cake was washed with acetone (50

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† Financial support by the Saskatchewan Fruit Growers' Association and Saskatchewan Agriculture Development Fund is gratefully acknowledged. Contribution 1089 of the Saskatoon Research Station.

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0021-8561/93/1441-2153$04.00/0 Published 1993 by the American Chemical Society

mL), rehomogenized with acetone (100 mL) for 5 min, and filtered through Hyflo SuperCel as before. The combined filtrates were evaporated under reduced pressure to just dryness on a rotary evaporator with a water-bath temperature not exceeding 35 °C. The extract was transferred to a 500-mL separatory funnel with 10% (w/v) aqueous sodium chloride (300 mL) and diethyl ether:hexane (1:4 v/v, 50 mL). The contents of the separatory funnel were mixed and allowed to separate for 10 min. The aqueous layer was drained off. The organic and emulsion phases were centrifuged at low speed for 2 min. The organic layer was collected. The aqueous layers were combined in the separatory funnel and reextracted twice with diethyl ether:hexane (1:4 v/v, 50 mL). The combined organic extracts were dried over sodium sulfate and filtered through a 6-mm pad of Hyflo SuperCel in a 5.5-cm Büchner funnel. The filter cake was washed with diethyl ether:hexane (1:4 v/v, 50 mL).

The dried organic extract in diethyl ether:hexane (1:4) was transferred to a 12-mm i.d. glass column prepared in diethyl ether:hexane (1:4) and containing a glass wool plug, 5 g of Florisil (activated at 650 °C for 4 h, cooled, and deactivated with 5% v/w water), and topped with 6 mm of sodium sulfate. After all the extract was on the column, the column was eluted with diethyl ether:hexane (1:4 v/v, 50 mL). The total eluent was collected and evaporated under reduced pressure to just dryness on a rotary evaporator with a water-bath temperature not exceeding 35 °C.

The residual was transferred to a 250-mL separatory funnel with hexane (150 mL) and acetonitrile saturated with hexane (50 mL). The contents were shaken vigorously, and the layers were allowed to separate. The acetonitrile layer was transferred to a second separatory funnel containing hexane (150 mL). The contents of the separatory funnel were shaken vigorously, the layers were allowed to separate, and the acetonitrile layer was collected. The original hexane layer was extracted twice more with acetonitrile saturated with hexane (50 mL). The acetonitrile layer was collected each time and used to extract the hexane layer in the second separatory funnel. The three acetonitrile extracts were collected and evaporated under reduced pressure to just dryness on a rotary evaporator with a water-bath temperature not exceeding 35°C.

The residual was transferred to a disposable Pasteur pipet containing a glass wool plug and 0.5 g of silica gel (Davidson 950, deactivated with 1.5% v/w water) with diethyl ether:hexane (1:19 v/v, 3 mL). The silica gel was eluted with diethyl ether:hexane (1:19 v/v, 4 mL). The eluent was evaporated under reduced pressure on a rotary evaporator with a water-bath temperature not exceeding 35°C and transferred to a volumetric flask with acetone for gas chromatographic analysis.

Recovery Efficiency Studies. Known quantities of deltamethrin dissolved in acetone were added to 25-g samples of saskatoon berries. The deltamethrin on the berries was extracted as above and analyzed.

Gas Chromatographic and Analytical Conditions. Instrumentation: Hewlett-Packard (Mississauga, ON) Model 5890 gas chromatograph with ^{63}Ni electron-capture detector Hewlett-Packard Model 7673A autoinjector, and Hewlett-Packard Model 3393 integrator programmed for external standardization using peak area. Column: HP17 cross-linked 50% phenylmethyl silicone, 10 m × 0.53 mm with 2-μm film thickness (Hewlett-Packard, Mississauga, ON). Injector: splitless. Oven temperature: 260°C. Injector temperature: 300°C. Detector temperature: 300 °C. Purge time: 0.75 min. Carrier gas and flow: helium at 2 mL/min (head pressure 23 psi). Detector gas and flow: 5% methane in argon at 60 mL/min. Makeup gas and flow: helium at 25 mL/min. Retention time of deltamethrin: 4.0 min.

RESULTS AND DISCUSSION

Recovery efficiencies of deltamethrin from spiked samples of saskatoon berries were determined over the range 0.01–5 μg/g. Recoveries were greater than 95% (Table I). Check samples from two of the three locations were free of interfering peaks or detectable residues of deltamethrin. The third check sample was accidentally field contaminated and contained detectable residues (not reported) over the entire sampling period.

Table I. Recoveries of Deltamethrin from Triplicate Samples of Saskatoon Berries Spiked at Four Concentrations

	concentration			
	0.01 ppm	0.05 ppm	0.5 ppm	5.0 ppm
% recovery	95.5	97.2	100.4	101.9
	98.3	102.6	98.1	99.6
	96.1	98.8	101.2	98.6
av	96.6	99.8	99.9	100.0

Table II. Mean Residues (N = 3) of Deltamethrin on Saskatoon Berries from Three Orchards and Study Mean Residues of Deltamethrin on Saskatoon Berries following Four Applications of Deltamethrin at 10 g/ha

		deltamethrin (ppm)			
		orchard			
	days after last application	north	west	east	study mean
June 2	1	0.22	0.25	0.18	0.22
June 8	7	0.06	0.09	0.08	0.08
June 15	14	0.04	0.06	0.04	0.05
June 22	21	0.03	0.04	0.03	0.03
June 29	28	0.02	0.02	0.02	0.02
July 10	39	nd[a]	0.02	0.01	0.01

[a] nd, below detection limit of 0.01 ppm.

Residues on collected berries from the three treated locations are reported in Table II. The mean residue detected 1 day after the last of four applications was 0.22 ppm. Seven days after the last application, residues had declined to 0.08 ppm with progressively less residue detected as postapplication time increased. The observed residues in saskatoon berries and their dissipation are comparable to residues of 0.5 and 0.2 ppm on blackcurrant and gooseberries, respectively, 4 days after treatment and that were nondetectable 10 days after treatment (Hoechst, 1983). Residues of 0.1–0.2 ppm were detected in blackcurrants 7 days after treatment (L'Hôtellier, 1982).

The residues detected on the berries most likely resulted from the last application applied at 8 days after 90% petal fall and to a much lesser extent from the second to last application timed at 90% petal fall. The first two applications, while of major importance in controlling insect pests, were applied before significant berry formation. In the 24 h after the last application and before the collection of the first sample, 12 mm of rain was recorded in the study area. A total of 62 mm of rain was received between the last application date and the last collection date. In addition to possible losses to rain and other environmental factors, berry growth would contribute to residue dilution. The diameter of the berries increased from approximately 0.5 cm on the first sampling date to 1 cm by the last sampling date.

CONCLUSIONS

The analytical method described for deltamethrin determination permits detection of residues to the 0.01 ppm level. Deltamethrin dissipation from saskatoon berries is rapid, particularly in the first week. A 21-day postharvest interval is sufficient time to allow for deltamethrin residues to decrease below the 0.1 ppm level on saskatoon berries.

ACKNOWLEDGMENT

The cooperation of Ben Epp, Dan Byblow, and Eldon Neufeld is gratefully acknowledged.

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Received for review March 25, 1993. Accepted August 16, 1993.®

® Abstract published in *Advance ACS Abstracts,* October 1, 1993.