Disappearance of *N′*-(4-Chloro-*o*-tolyl)-*N*,*N*-dimethylformamidine from Six Major Fruit Crops

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Samples of six major fruit crops which had been treated with varying amounts of *N′*-(4-chloro-*o*-tolyl)-*N*,*N*-dimethylformamidine (chlordimeform) were analyzed at various intervals to determine the total residue of this new insecticide they contained. At harvest, apples which had been treated with 48, 72, and 96 oz a.i./acre had residues of 0.06, 0.13, and 0.27 ppm, respectively. Pears treated with 48 and 96 oz a.i./acre had residues of 0.24 and 0.94 ppm, respectively. Plums treated with 48 oz a.i./acre had residues of 1.03 ppm. Cherries treated with 64 and 128 oz a.i./acre had residues of 0.23 and 0.74 ppm, respectively. Peaches treated with 32 and 64 oz a.i./acre had residues of 0.89 and 1.92 ppm, respectively. Strawberries treated with 8 oz a.i./acre had residues of 0.04 ppm. These findings reveal that the amount of total residue of chlordimeform on the various fruit was directly related to the amount of chemical applied, an inverse function of the number of days the fruit was sampled after the last application and was influenced by the nature of the fruit surface.

The acaricidal properties of *N′*-(4-chloro-*o*-tolyl)-*N*,*N*-dimethylformamidine were first described by Dittrich in 1966 (1966a). Early in its research and development program the chemical was tested under the code numbers of Schering-36268, EP-333, and C-8514, and subsequently to the proposed common name of chlorphenamidine. The latter name has since been disapproved, but chlordimeform has been accepted recently as its common name. Commercial formulations of this insecticide are produced under the trade names of Galecron and Fundal by the CIBA Agrochemical Co. and NOR-AM Agricultural Products, Inc., respectively. Emulsifiable concentrates manufactured by both firms utilize the free base form of the active ingredient, whereas the soluble powder formulations contain its hydrochloride salt. Subsequent reference to this chemical in this report will be to its common name, chlordimeform.

In his first report Dittrich (1966a) stated that the acaricidal effects of chlordimeform were both ovicidal and adulticidal and that the chemical kills adult carmine spider mites (*Tetranychus telarius* L.) and two-spotted spider mites (*T. urticae* Koch) when it is applied either as a vapor or a spray. Systemic action in bean plants was demonstrated on the adult carmine spider mite, as well as on its eggs (Dittrich, 1967b). Promising synergistic effects between the vapors of chlordimeform and dichlorvos against the carmine spider mite were reported by Dittrich (1966b). This chemical is equally effective against organophosphorus-tolerant carmine spider mites and two-spotted spider mites (Dittrich, 1966a, 1969).

More recently it also has been reported that chlordimeform effectively controls the two-spotted mite on hops (Cone, 1968), cotton (Furr and Davis, 1969), apples (Asquith, 1968; Batiste and Berlowitz, 1969), and pears (Batiste *et al.*, 1970). Effective control against *Panonychus ulmi* Koch, European red mite, on apples has been reported by Asquith (1968), Batiste and Berlowitz (1969), and Dittrich (1967b), and on pears by Batiste *et al.* (1970). Jeppson *et al.* (1969) found this chemical to be effective against the citrus red mite, *Panonychus citri* (McGregor). Stafford (1968) reported on the effectiveness of chlordimeform for the control of the Pacific spider mite, *Tetranychus pacificus* McGregor, on grapevines and Westigard (1969) and Westigard and Berry (1970), respectively, found chlordimeform to control pear rust mite, *Epitremerus pyri* (Nalepa) and yellow spider mite, *Eotetranychus carpini borealis* (Ewing) on pears. Excellent control of the apple rust mite, *Aculus schlechtendali* (Nalepa), with this compound was obtained by Dittrich (1967b). Wilson and Oliver (1969) reported on the effectiveness of chlordimeform for the control of the southern red mite, *Oligonychus ilicis* (McGregor) on holly, the two-spotted spider mite on roses, and the green mite, *Eotetranychus clitus* (Pritchard and Baker), privet mite, *Brevipalpus obovatus* Donnadieu, and the southern red mite on azaleas. Chlordimeform was found to be highly toxic to the southern tick, *Boophilus microplus* (Canestrini) (M strain), by Shaw *et al.* (1968).

Chlordimeform also has shown high ovicidal effects against a number of insect species. The eggs of the Egyptian cotton leafworm, *Prodinia lituria* F., were especially sensitive to chlordimeform (Dittrich, 1967a; Zeid *et al.*, 1968; Mitri and Kamel, 1970). The cotton leaf perforator, *Bucculatrix thurberiella* Busck, is likewise readily affected by chlordimeform (Harding, 1970). Other insects which succumb readily to the ovicidal activity of chlordimeform are the corn earworm, *Heliothis zea* (Boddie) (Klostermeyer, 1968), the cabbage looper, *Trichoplusia ni* (Hubner) (Harris and Svec, 1970a; Judge and McEwen, 1970), the imported cabbageworm, *Pieris rapae* (L.) (Judge and McEwen, 1970), and the cabbage aphid, *Brevicoryne brassicae* (L.) (Harris and Svec, 1970b).

Chlordimeform is a member of a class of organic chemicals, formamidines, not previously used for agricultural pest control. In addition to its relatively low mammalian toxicity (acute LD_{50} to rats 340 mg/kg) (CIBA, 1967) and short persistence in the soil (half-life of approximately 30 days in Hagerstown silt loam soil) (Ercegovich, 1971), it is not toxic to the honeybee. This pesticide is not very toxic to the ladybird beetle, *Stethorus punctum*, and thus can be used in an integrated control program in orchards (Colburn and Asquith, 1970). These characteristics, along with its effectiveness against organophosphorus resistant mites, suggested its potential usefulness as an acaricide in Pennsylvania fruit orchards. This study, therefore, was conducted to determine the residual persistence of chlordimeform on six major fruit crops: apples, cherries, peaches, pears, plums, and strawberries.

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Table I. Recovery of Chlordimeform from Fortified Whole Fruit Macerates

Sample	μg added 60 g tissue	Chlordimeform recovered	Number of analyses
Apples	5–150	95 ± 13	16
Cherries	100	98 ± 2	5
Peaches	100	95 ± 2	6
Pears	10–100	102 ± 4	5
Plums	100	97 ± 8	5
Strawberries	100	97 ± 7	6

Table II. Total Chlordimeform Residue in Apple Tissue in Relation to Interval After and Rate of Application

	ppm at days after last application				
Tissue	30	45	60	90	107
			48 oz a.i./acre		
Whole apple	0.34	0.30	0.07	0.08	0.06
Apple peel	0.76	0.60	0.51	0.22	0.19
Apple pulp	0.01	0.06	0.03	0.05	0.02
			72 oz a.i./acre		
Whole apple	0.53	0.43	0.24	0.22	0.13
Apple peel	1.04	0.94	0.76	0.64	0.60
Apple pulp	0.11	0.17	0.15	0.13	0.09
			96 oz a.i./acre		
Whole apple	0.82	0.63	0.52	0.33	0.27
Apple peel	1.77	1.21	0.89	0.87	0.84
Apple pulp	0.32	0.43	0.38	0.30	0.20

Table III. Total Chlordimeform Residue in Pear Tissue in Relation to Interval After and Rate of Application

	ppm at days after last application		
Tissue	30	45	60
		48 oz a.i./acre	
Whole pear	0.90	0.59	0.24
Pear peel	3.90	0.48	0.21
Pear pulp	0.52	0.68	0.31
		96 oz a.i./acre	
Whole pear	1.70	1.02	0.94
Pear peel	5.46	0.93	0.55
Pear pulp	1.00	1.21	1.16

MATERIALS AND METHODS

Source and Nature of Samples. All applications were made with the required amounts of an emulsifiable concentrate formulation containing 4 lb/gal of active ingredient (Galecron 50 EC), supplied by the CIBA Agrochemical Co., as indicated below. In each case the spray was applied by conventional high pressure or hydraulic orchard sprayers by thoroughly covering the crop plants to run off. All fruit samples were placed in a large freezer immediately after collection and stored in a frozen state at -20 ± 5 °C until they were analyzed.

Apples. Galecron 50 EC was applied at three different rates of 8, 12, and 16 oz/100 gal of water at three separate intervals. An equivalent of 400 gal/acre of spray was applied each time. Therefore, the respective plots received a total of 48, 72, or 96 oz a.i./acre. These applications were made in an apple orchard in the area of Biglerville, Pennsylvania. Five-pound samples from unsprayed controls and from each experimental replicate were collected at 30, 45, 60, 90, and 107 days after the final application of chlordimeform. Other pesticides applied to these apples included Cyprex, Guthion, captan, carbaryl, dieldrin, ferbam, phosphamidon, and zineb.

Peaches. Chlordimeform was applied at two different rates of application, 8 and 16 oz of Galecron 50 EC/100 gal of water at two different intervals. An equivalent of 400 gal was applied per acre each time. Therefore, totals of 32 and 64 oz a.i./acre were applied to the respective plots. These applications were made in the area of Sodus, New York. Two- to five-pound samples from the unsprayed controls and from each experimental plot were supplied at 14, 28, 56, and 70 days after the final application. Other chemicals applied to these peach trees included captan and parathion.

Pears. Galecron 50 EC was applied at the rate of 8 and 16 oz/100 gal of water at three different intervals. An equivalent of 400 gal was sprayed per acre each time. Thus these plots at Geneva, New York, received a total of 48 and 96 oz a.i./acre during the season. Three- to five-pound samples from unsprayed controls and from each experimental treatment were supplied at 30, 45, and 60 days after the final application. Guthion, Kelthane, captan, malathion, and sulfur were also used for pest control on these trees.

Plums. Galecron 50 EC was applied at the rate of 16 oz/100 gal of water at two different intervals. Three hundred gallons of spray were applied per acre each time; therefore, a total of 48 oz a.i./acre was applied to these plots at Biglerville, Pennsylvania. Two- to three-pound samples from the unsprayed controls and from the experimental plots were supplied at 0, 14, 21, 28, 32, and 51 days after the last application. These trees were also treated with Guthion, Kelthane, captan, carbaryl, ferbam, and sulfur at various times during the season.

Cherries. Galecron 50 EC was applied at the rate of 16 and 32 oz/100 gal of water at two different intervals. A total volume of 400 gal of spray was used each time, thus having exposed these cherries at Sodus, New York, to a total of 64 and 128 oz a.i./acre. One- to two-pound samples from the unsprayed controls and each experimental treatment were supplied at 0, 14, 21, 28, and 35 days after the last application. Other chemicals applied to these trees included captan and carbaryl.

Strawberries. Galecron 50 EC was applied at the rate of 16 oz/100 gal of water once as a preharvest treatment to green fruit at Buddtown, New Jersey. A total of 100 gal/acre was used for this purpose, thus resulting in an exposure of 8 oz a.i./acre. One- to two-pound samples of the untreated controls and of the experimental plots were supplied at intervals of 3, 7, 14, and 21 days after this application was made.

Analytical Procedure. The method of analysis used to determine the total residues of chlordimeform in this investigation was essentially the same as the procedure recently reported by Geissbühler *et al.* (1971). Slight modifications were made for operational convenience and efficiency. The principle of this method involved the hydrolysis of chlordimeform to 4-chloro-*o*-toluidine by successive treatment with acetic acid and sodium hydroxide. The hydrolysis product was recovered into isooctane by steam distillation in a Bleidner apparatus. The 4-chloro-*o*-toluidine, which was extracted from the isooctane with acidified water, was then subjected to diazotization followed by coupling of the diazonium compound with *N*-ethyl-1-naphthylamine. 4-Chloro-*o*-toluidine formed a stable dye when coupled to the chromophore and was separated from interfering azo dyes, derived from plant amines and other pesticides, by cellulose column chromatography. The amount of color in the final eluate was determined colorimetrically.

This method determined the total amount of 4-chloro-*o*-toluidine present in the sample in the free or bound form as chlordimeform or its metabolic products. The smallest amount of 4-chloro-*o*-toluidine which was routinely detected by this method, using a Bausch & Lomb Spectronic 600 spectrophotometer with a 1-cm light path, was 2 μg, or equivalent to 0.04 ppm of chlordimeform in a 60-g sample.

Appropriate controls were included daily with each series of analyses. These included the respective untreated fruit samples, check samples fortified with technical grade chlordimeform within the expected range of residue, and a 4-chloro-*o*-toluidine standard to monitor the efficiency of the colorimetric reaction and separation of dyes on the cellulose column. Data illustrating the efficiency of recovery of chlordimeform obtained during the course of this investigation are listed in Table I.

SAMPLE PREPARATION. The peel and the pulp of apples and pears were analyzed separately, as well as the whole fruit, for total residues of chlordimeform. For the whole fruit, just prior to analysis, one-quarter of each apple and pear of the respective sample was removed, while still frozen and composited. The remaining three-quarters were immediately returned to the freezer for storage until ready for the analysis of the peel and pulp. The composites of quarters were then ground in a Hobart food mill, mixed, and subdivided.

Peel samples were obtained by peeling the remaining three-quarters of the frozen fruit samples, while still frozen, with an Ekco Slip Pru Nee Action, stainless steel paring knife. The thickness of the apple peel, taken longitudinally across the center, averaged 1.3 ± 0.2 mm; while the pear peels had an average thickness of 0.9 ± 0.2 mm. The weight ratios of apple peel to pulp and of pear peel to pulp were approximately 1:5.53 and 1:5.40, respectively.

Pulp samples refer to the portion of the apple or pear devoid of the peel. After removal of the fruit peel, the three-quarter sections were composited, ground in a Hobart food mill, mixed, and subdivided. These macerates were stored in a freezer for several days until after the analyses of the respective peels were completed.

Peaches, plums, and cherries were prepared for analysis by first removing their pits; then they were ground, mixed, etc., in the same manner as were the whole apple and pear samples. All of the respective strawberry sample was macerated in a Waring Blendor. Sixty-gram aliquots of these macerates were taken for a series of two duplicate analyses.

RESULTS AND DISCUSSION

Total Residue on Fruit. The results of the analyses for total chlordimeform residue in apples, pears, plums, cherries, peaches, and strawberries are listed in Tables II through VII, respectively. The values appearing in these tables are the average of two sets of duplicate determinations. All residue values have been corrected for recovery efficiency and for any apparent ppm of chlordimeform found in the controls of the respective analyses. Most frequently the controls showed no absorption at the wavelength at which the colorimetric readings were taken. In the few instances in which some absorption occurred, these values were subtracted from the values of the experimental sample. The separation of the chlordimeform dye from interfering dyes, derived from plant amines or possibly other chemicals to which the crop may have been exposed, was very efficient. In most cases no correction was necessary; but when the controls showed some absorption, it was usually in the range equivalent of 1 to 3 μg of chlordimeform.

The values reported in Tables II through VII are not specific for chlordimeform. The analytical procedure that was used measured the total amount of aniline derivatives which may have been derived from the parent compound. These values, therefore, represent the amount of undegraded chlordimeform and its major degradation products.

Table IV. Total Chlordimeform Residue in Plums at Various Intervals After A Total Application of 48 oz a.i./Acre

Interval, days	ppm
0	4.77
14	3.38
21	2.71
28	1.50
32	1.42
51	1.03

Table V. Total Chlordimeform Residue in Cherries in Relation to Interval After and Rate of Application

	ppm at days after last application				
Rate	0	14	21	28	35
64 oz a.i./acre	1.85	0.48	0.29	0.26	0.23
128 oz a.i./acre	3.65	1.32	1.14	0.80	0.74

Table VI. Total Chlordimeform Residue in Peaches in Relation to Interval After and Rate of Application

	ppm at days after last application			
Rate	14	28	56	70
32 oz a.i./acre	2.63	2.24	1.08	0.89
64 oz a.i./acre	7.99	6.96	2.15	1.92

Table VII. Total Chlordimeform Residue in Strawberries at Various Intervals After an Application of 8 oz a.i./Acre

Interval, days	ppm
3	5.72
7	4.02
14	3.56
21	2.60
41	0.04

Table II shows that apples at harvest, 107 days after the last of three applications in which totals of 48, 72, and 96 oz a.i./acre were applied, contained total chlordimeform residues of 0.06, 0.13, and 0.27 ppm, respectively, in whole fruit. The amount of chemical in the apple fruit pulp of the respective samples was slightly less, *i.e.*, 0.02, 0.09, and 0.20 ppm, while the chemical appears to be concentrated on or at the surface of the apple as evidenced by the three and four times higher concentration in the apple peel, 0.19, 0.60, and 0.84 ppm, respectively.

The data in Table III show that at harvest, 60 days after an exposure of 48 and 96 oz a.i./acre, there were 0.24 and 0.94 ppm of chlordimeform residue in whole pears. Unlike apples there was a significantly higher amount of residue in pear pulp treated with comparable rate of chlordimeform. The residue of 0.31 and 1.16 ppm in pear pulp should be compared with the residues at 60 days in apple pulp, which were 0.03 and 0.38 ppm. The converse was true of the residue of chlordimeform in the peel of pear. Thirty days after the last application of the 4-oz rate, the residual level dropped from 3.90 to 0.21 ppm, and from 5.46 to 0.55 ppm for the 8-oz rate. These decreases of twentyfold and tenfold compared to a fourfold and twofold decrease in apples.

The data in Table IV show that immediately after the last of two applications of 8 oz a.i./100 gal of water, there were 4.77 ppm of chlordimeform residue in plums and that this level constantly decreased over a 50-day period, at which time there remained a residual amount of 1.03 ppm.

The data in Table V show that the concentration of chlordimeform in cherries treated with a total of 64 oz a.i./acre de-

Table VIII. Total Residues of Chlordimeform in Whole Fruit at Harvest as Related to Amount of Active Ingredient Applied per Acre and Interval After Last Application

Crop	Interval, days	ppm per total oz applied						
		8	32	48	64	72	96	128
Cherries	35				0.23			0.74
Strawberries	41	0.04						
Plums	51			1.03				
Pears	60			0.24			0.94	
Peaches	70		0.89		1.92			
Apples	107			0.06		0.13	0.27	

creased from 1.85 to 0.23 ppm in a 35-day period after the last application. When a total of 128 oz of the chemical was applied, there were 3.65 ppm immediately after application, but only 0.74 ppm at harvest 35 days later. These data show that there was a rapid disappearance of chlordimeform from cherries during the first 14 days after the last application, but a much slower rate over the ensuing 21-day period before harvest.

The data in Table VI clearly show that residues of chlordimeform persist longer and higher concentrations in peaches than in any of the other fruit crops. At the lower rate of application, a total of 32 oz a.i./acre, 2.63 ppm of chlordimeform residues were found 14 days after the last application; this quantity had decreased to 0.89 ppm at harvest. At the higher rate of application, 64 oz a.i., 7.99 ppm were found at the first sampling interval, and 1.92 ppm remained at harvest.

The data in Table VII show that 3 days after an application of 8 oz a.i./acre to strawberries, 5.72 ppm of chlordimeform were found and that there was a uniform disappearance of the chemical so that it was barely detectable (0.04 ppm) at harvest 41 days later.

These data were of interest because they revealed that the amount of chlordimeform residue was in direct relation to the amount of the chemical applied and in inverse relation to the number of days after the fruit was sampled after the last application of the chemical.

The difference in the persistence of chlordimeform in the various fruit crops was more readily seen by inspecting the data in Table VIII, which is a summary of the preceding six tables. It is readily apparent that the persistence of chlordimeform was of the same magnitude in cherries, strawberries, apples, and pears, while its disappearance from plums and peaches was more similar in nature and occurred at a much slower rate. The persistence of chlordimeform in peaches appeared to be of considerably greater duration than that in any of the other fruit considered in this investigation. Since the peel and pulp of plums and peaches were not analyzed separately, it is not possible to state that the chemical adheres more tenaciously to the peel or that it is translocated through the peel into the pulp and there stored. The longer persistence of chlordimeform in peaches may be due to the inherent nature of the fruit surface. The hairy structure of the peach skin presents a much greater surface area to which the chemical can adhere, a phenomenon that may account for the higher levels found in this fruit.

The results of this investigation reveal that when chlordimeform is applied according to recommended practices for effective pest control on apples, pears, peaches, plums, cherries, and strawberries, it will disappear quite readily from these fruits. Chlordimeform appears to adhere to the outer surface of apple and peach fruit (CIBA, 1970) and does not appear to translocate readily into its fleshy parts. The converse appears to be true for pear fruit. Nonetheless, the residual amounts of total chlordimeform residue remaining at harvest on all of the fruit crops examined in this investigation are of low magnitude.

LITERATURE CITED

Asquith, D., *J. Econ. Entomol.* **61,** 1044 (1968).
Batiste, W. C., Berlowitz, A., *J. Econ. Entomol.* **62,** 779 (1969).
Batiste, W. C., Berlowitz, A., Olson, W. H., *J. Econ. Entomol.* **63,** 1457 (1970).
CIBA Agrochemical Co., Res. Bull. No. 20, Vero Beach, Fla. (1967).
CIBA Agrochemical Co., Vero Beach, Fla., personal communication (1970).
Colburn, C., Asquith, D., *J. Econ. Entomol.* **63,** 1686 (1970).
Cone, W. W., *J. Econ. Entomol.* **61,** 1685 (1968).
Dittrich, V., *J. Econ. Entomol.* **59,** 889 (1966a).
Dittrich, V., *J. Econ. Entomol.* **59,** 893 (1966b).
Dittrich, V., *J. Econ. Entomol.* **60,** 13 (1967a).
Dittrich, V., *J. Econ. Entomol.* **60,** 558 (1967b).
Dittrich, V., *J. Econ. Entomol.* **62,** 44 (1969).
Ercegovich, C. D., Pesticide Research Laboratory, Penn State Univ., unpublished data (1971).
Furr, R. E., Davis, L. B., *J. Econ. Entomol.* **62,** 732 (1969).
Geissbühler, H., Kossmann, K., Baunok, I., Boyd, V. F., J. AGR. FOOD CHEM. **19,** 365 (1971).
Harding, J. A., *J. Econ. Entomol.* **63,** 1364 (1970).
Harris, C. R., Svec, H. J., *J. Econ. Entomol.* **63,** 666 (1970a).
Harris, C. R., Svec, H. J., *J. Econ. Entomol.* **63,** 665 (1970b).
Jeppson, L. R., Jesser, M. J., Complin, J. O., *J. Econ. Entomol.* **62,** 975 (1969).
Judge, F. D., McEwen, F. L., *J. Econ. Entomol.* **63,** 862 (1970).
Klostermeyer, E. C., *J. Econ. Entomol.* **61,** 1022 (1968).
Mitri, S. A., Kamel, A. A., *J. Econ. Entomol.* **63,** 676 (1970).
Shaw, R. D., Cook, M., Carson, R. E., *J. Econ. Entomol.* **61,** 1590 (1968).
Stafford, E. M., *J. Econ. Entomol.* **61,** 1641 (1968).
Westigard, P. H., *J. Econ. Entomol.* **62,** 1158 (1969).
Westigard, P. H., Berry, D. W., *J. Econ. Entomol.* **63,** 1433 (1970).
Wilson, N. L., Oliver, A. D., *J. Econ. Entomol.* **62,** 1400 (1969).
Zeid, M., Saad, A. A., Ayad, A. M., Tantawi, G., Eldefrawi, M. E., *J. Econ. Entomol.* **61,** 1183 (1968).

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