Discussion

These methods without modification determine 0.1 to 2.5 p.p.m. of 4-dimethylamino-3,5-xylenol, 0.1 to 3.5 p.p.m. of 4-dimethylamino-3,5-xylyl methylcarbamate, or a total of 0.1 to about 3 p.p.m. of mixtures of the "xylenol" and the "carbamate" in peaches and in undelinted cottonseed.

The methods for the residue determinations of 4-dimethylamino-3,5-xylenol and 4-dimethylamino-3,5-xylyl methylcarbamate in peaches, using water as the water-miscible extraction solvent, should be generally applicable to the analysis of agricultural products with a high water content. The methods for the residue determinations in undelinted cottonseed, using benzene as the water-immiscible solvent, can be used on agricultural products containing oils and/or little water. Some modifications, of course, may be necessary.

Table VI. Recovery of Mixtures of 4-Dimethylamino-3,5-xylenol and 4-Dimethylamino-3,5-xylyl Methylcarbamate in Undelinted Cottonseed

Xylenol Added, P.P.M.	Carbamate Added, P.P.M.	Xylenol Found, P.P.M.	Xylenol Recovery, %	Carbamate Found, P.P.M.	Carbamate Recovery, %
0.10	0.10	0.095	95	0.093	93
		0.105	105	0.100	100
0.10	1.00	0.111	111	0.872	87
		0.105	105	0.859	86
1.00	0.10	0.876	88	0.110	110
		0.831	83	0.090	90
0.10	2.00	0.111	111	1.914	96
		0.105	105	1.937	97
2.00	0.10	1.759	88	0.133	133
		1.759	88	0.133	133

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INSECTICIDE RESIDUES IN PROCESSED FOODS

The Effect of Processing on Guthion Residues in Oranges and Orange Products

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The use of Guthion on citrus necessitated a study of the distribution of residues in citrus by-products. A study was conducted on Guthion-treated oranges. It was found that standard washing procedure will remove 30% of Guthion residues from treated oranges. The remaining residue is entirely in the peel. Approximately 75% of the residue is destroyed during the treatment involved in production of citrus cattle feed.

GUTHION (trademark, Farbenfabriken Bayer), *O,O*-dimethyl *S*-4-oxo-1,2,-3,-benzotriazin-3(4H)-ylmethyl phosphorodithioate, is a widely used insecticide. Recently it has been registered for control of a large number of citrus pests including aphids, mites, scales, and brown snails. Extensive residue studies on this product have been conducted both in the authors' laboratories and in the Department of Entomology at the University of California, Riverside, Calif. The latter studies are reported elsewhere (*1*).

As cattle feed prepared from citrus waste is an important agricultural commodity, especially along the east coast of the United States, it was decided that a pilot plant study of the effect of processing on Guthion residues in various citrus by-products should be conducted. This study is reported in this paper. The citrus was processed in the pilot plant equipment at the Citrus Experiment Station, Lake Alfred, Fla. The chemical analyses were all performed in the laboratories of Chemagro Corp., Kansas City, Mo.

Materials and Methods

Spray Treatments. Pineapple oranges were sprayed with Guthion 25% wettable powder at the rate of 8 ounces active per 100 gallons of spray on December 12, 1961, and January 8, 1962. Control and treated fruit were picked January 22, 1962, and processed January 24. Sixty boxes (90 pounds each) of fruit were collected from both the treated and control plots.

Processing Procedure. Processing was carried out according to a standard commercial practice. A flow sheet of the over-all process is given in Figure 1. The washing procedure consisted of a light chlorine rinse, a brushing in a Pacrite Fruit Cleaner G. D. 3A Sudser, a second light chlorine rinse, and a germicidal wash using an 80-pound pressure spray containing Ultrawet 60 L, trisodium phosphate, and a heavy chlorine concentration. The oranges were then put through water-eliminator rolls during which time they were given another light chlorine rinse. A final light chlorine rinse was made when the samples were on the conveyor. Rotten and split fruit were discarded.

Sixty boxes of fruit (approximately 5400 pounds) were used per run, but certain phases of each run were analyzed on a 20-box basis.

Juicing was carried out using a Food Machinery Corporation "In-Line Press" with the following settings: three short strainer tubes and two long strainer tubes, 0.040 and 0.090 inch, respectively; restrictor tubes, $^{7}/_{16}$ inch; cutters, $^{5}/_{8}$ inch long; beam setting, flush; r.p.m., 50. The finisher used was a Food Machinery Corporation Model 35 with screen openings of 0.020 inch and a head clearance of 0.002–0.006 inch.

The crude peel oil emulsion was

Table I. Recovery of Guthion and Guthion Oxygen Analog from Oranges and Orange Products

Sample	Compound	P.P.M. Added	P.P.M. Control	% Recovery
Cattle Feed (Dry)	Guthion	2.0	<0.3	82
	Guthion	2.0	<0.3	85
	Guthion oxygen analog	2.0	<0.3	60
Juice	Guthion	2.0	<0.3	102
	Guthion	2.0	<0.3	114
	Guthion	2.0	<0.3	100
Molasses	Guthion	2.0	0.3	99
	Guthion	2.0	0.3	106
	Guthion oxygen analog	2.0	0.3	86
Oil	Guthion	4.0	0.7	80
	Guthion	4.0	0.7	82
	Guthion oxygen analog	4.0	0.7	76
	Guthion oxygen analog	4.0	0.7	75
Peel	Guthion	2.0	<0.3	77
	Guthion	2.0	<0.3	73
	Guthion	2.0	<0.3	93
Press liquor	Guthion	2.0	<0.3	89
	Guthion	2.0	<0.3	89
	Guthion	2.0	<0.3	95
Pressed peel	Guthion	2.0	<0.3	98
	Guthion	2.0	<0.3	99
	Guthion	2.0	<0.3	96
	Guthion oxygen analog	2.0	<0.3	88
Pulp	Guthion	2.0	<0.3	98
	Guthion	2.0	<0.3	97
	Guthion	2.0	<0.3	73
	Guthion oxygen analog	1.0	<0.3	88

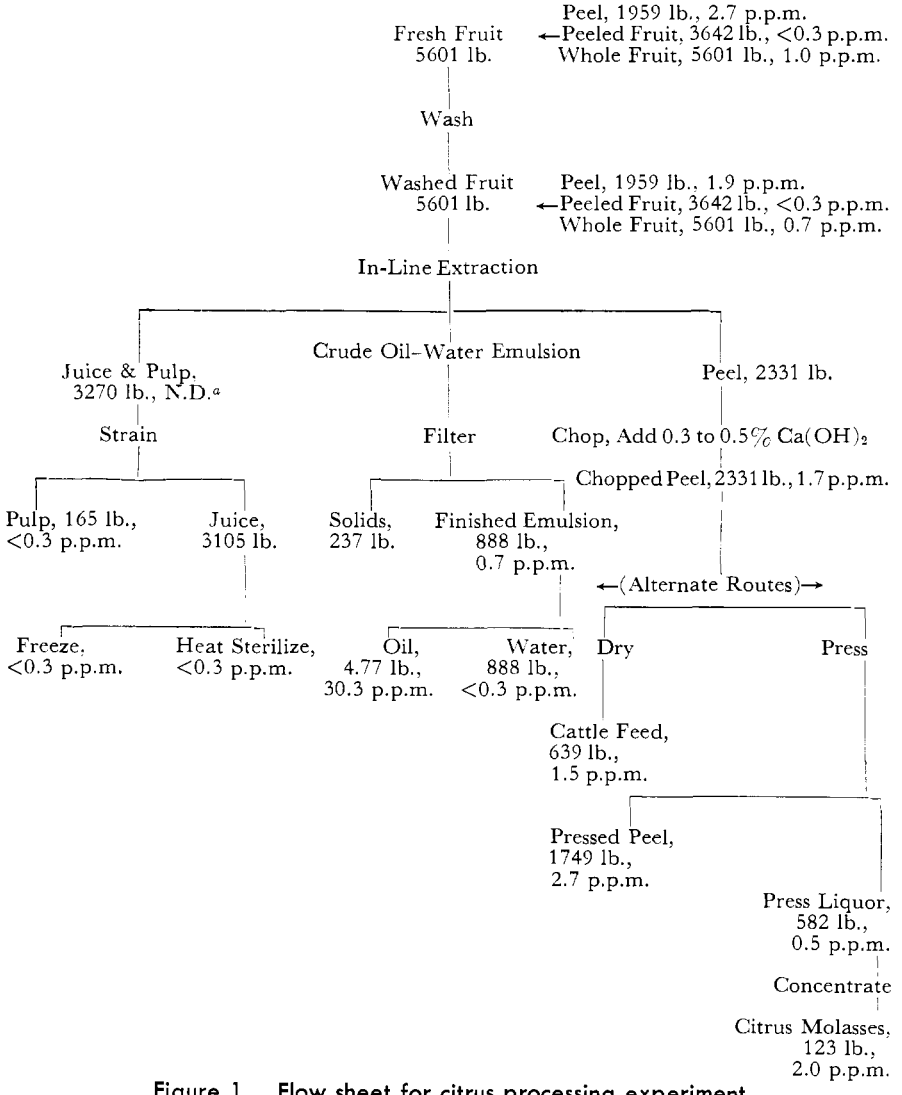

Figure 1. Flow sheet for citrus processing experiment
Samples analyzed 2/12/62 to 2/14/62

[a] None Detectable. All samples with net residue less than that of the untreated control or less than 0.3 p.p.m. are considered to be nondetectable. (All control values were less than 0.3 p.p.m.)

stored in a stainless steel holding tank and immediately pumped through a modified F. M. C. Model 35 finisher having 0.020-inch openings to remove coarse pulp particles and give a finished emulsion. A representative sample of the finished emulsion was taken for analysis. The finished emulsion was allowed to stand for 4 hours, and the concentrated oil emulsion which separated was collected from the top of the tank. The concentrated emulsion was centrifuged to remove fine solid particles, and then put through a Sharples super-centrifuge to give a clear oil.

The ejected citrus peel, pulp, and seeds were chopped in a comminuting machine using a screen with $^3/_4$-inch holes. The chopped peel was mixed thoroughly with calcium hydroxide at the rate of 0.35 pound per 100 pounds of peel and, after a minimum holding period of 20 minutes, was pressed in a hydraulic press at pressures of about 300 pounds per square inch. The press liquor obtained was concentrated to a Brix greater than 68° using a flash evaporator operating at a vacuum between 24 and 27 inches of mercury and a temperature of approximately 160° F. Alternatively, the chopped peel was mixed with calcium hydroxide and dried for cattle feed in a standard commercial drier. The exhaust temperature of the drier gas was 420° F. At each step after picking, samples were removed for analysis. All of the samples except molasses were fast frozen and were held at −10° F. until analyzed. The molasses was stored at room temperature.

Analytical Methods. Peel, peeled fruit, pulp, press liquor, juice, oil-water emulsion, and water from the oil-water emulsion were analyzed by the method described by Meagher *et al.* (*2*) for cole crops. Pressed peel and molasses were diluted with an equal weight of water and then analyzed by the same method. Dry cattle feed was analyzed by blending 100 grams of the powdered material with 400 ml. of acetone in a Waring Blendor, filtering, and reblending with 200 ml. of benzene. The filter cake was washed with an additional 200 ml. of benzene. The combined extracts were evaporated to dryness on a steam bath. The residue was taken up in 100 ml. of Skellysolve B and extracted with 50 ml. of acetonitrile. The acetonitrile extract was, in turn, backwashed with 100 ml. of fresh Skellysolve B. The extraction was repeated with two additional portions of acetonitrile. The combined acetonitrile extracts were then evaporated to dryness and analyzed by the same method as used for peel, etc. Orange oil was analyzed by diluting 25 grams of oil with 220 ml. of Skellysolve B and extracting with three successive 50-ml. portions of acetonitrile, backwashing each acetonitrile extract with 100 ml.

of fresh Skellysolve B. Chromatography and final analyses were the same as for other samples.

Recoveries of Guthion and its oxygen analog from various types of samples are given in Table I. Satisfactory recoveries were obtained in all cases.

Results and Discussion

The weight yields and residue values for the various products are given in Figure 1. Unwashed and washed fruit contained 1.0 and 0.7 p.p.m. Guthion, respectively. These residues are similar to those found for Guthion in oranges in other studies (*1*). Washing, therefore, resulted in a 30% reduction in the residue. Only the peel contained any detectable Guthion. Juice and pulp did not contain detectable residues. The oil-water emulsion from the In-Line extraction contained 0.7 p.p.m. of pesticide which was ultimately separated into an oil fraction containing 30.3 p.p.m. The water did not contain a detectable residue. Cattle feed produced from chopped peel containing a residue of 1.7 p.p.m. had a residue of 1.5 p.p.m. If the concentrating effect of the drying process is taken into account, this corresponds to a 76% destruction of the Guthion. Pressed peel, press liquor, and citrus molasses had residues of 2.7, 0.5, and 2.0 p.p.m., respectively.

From these results, the following conclusions may be drawn. Guthion residues in oranges are entirely in the peel. As washing removes only 30% of the residue, a large portion of the residue is in, rather than on, the peel. The highest concentration of residue is found in peel oil. Production of citrus cattle feed destroys about 75% of the residue, but loss of water approximately compensates for the loss of Guthion so that the resulting cattle feed contains almost as much residue (1.5 p.p.m.) as the chopped peel (1.7 p.p.m.).

Studies to be reported elsewhere have shown that the amounts of Guthion in citrus cattle feed will not cause significant residues in milk.

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INSECTICIDE PERSISTENCE

Persistence of Residues of Guthion on and in Mature Lemons and Oranges and in Laboratory Processed Citrus "Pulp" Cattle Feed

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The insecticide Guthion has been evaluated as a residue on and in mature lemons and oranges. RL_{50} values ("half-life" values) for this insecticide under field conditions are 30 to 38 days for lemons and 340 to 400 days for oranges. Rainfall or simple washing of treated fruits markedly decreases these persisting and largely nonpenetrating residues. The degree of persistence of Guthion residues in dried citrus pulp cattle feed is also demonstrated.

THE COMPOUND *O,O*-dimethyl-*S*-4-oxo - 1,2,3 - benzotriazin-3(4H)-yl methyl phosphorodithioate (Guthion) is promising for the control of insect pests attacking citrus, including California red scale [*Aonidiella aurantii* (Mask)], yellow scale [*A. citrina* (Coq.)], and black scale [*Saissetia oleae* (Bern.)] (*2, 3*). A study of the magnitudes and persistence of Guthion on and in mature lemons and Valencia oranges which were treated in the field to simulate probable commercial practice is presented herein. The feasibility of practicable partial removal of the persisting extrasurface residues that ensue is demonstrated.

Available analytical methods that will respond to microquantities of Guthion include colorimetric tests based on opening the triazine rings followed by coupling with phenyl-1-naphthylamine (*11, 12*), on the chromotropic acid determination of formaldehyde resulting from acid hydrolysis of the parent compound (*4*), on diazotization and coupling of the anthranilic acid resulting from alkaline hydrolysis of the compound (*9*), and on several variations of the many cholinesterase-inhibition procedures. A minor modification of the anthranilic acid method was used for the present study because it alone minimized adequately interference from the other citrus extractives.

Data from this study emphasize the unusually persistent nature of Guthion residues on Valencia oranges in contrast to its much shorter "life" on lemons. Other pesticides which have been studied as residues (*5-7*) on both lemons and either navel or Valencia oranges have not exhibited such grossly different behavior patterns among these citrus varieties. Because this marked difference between the residue behavior of Guthion on lemons versus oranges has not previously been encountered, and also is not reasonably attributable to any known variable not previously encountered and compensated, portions of this study of field residues of Guthion were repeated two successive growing seasons under different weather conditions to help evaluate climatic influences.

Materials and Methods

Fresh Fruit. Mature lemon trees (110 per acre) were sprayed on March 1, 1961 (study *A*), and mature Valencia orange trees (90 per acre) were sprayed April 20, 1959 (study *A*) with a 25% wettable powder formulation of Guthion at the rates of 1 pound and 4 pounds per 100 gallons of water. Applications were made as conventional sprays, using a high-pressure reciprocating pump and manually operated spray guns. Sprays were applied at the rates of approximately 1500 gallons per acre for lemons and 2500 gallons per acre for oranges.

Mature lemon fruit samples and mature orange fruit samples for assay of residues were collected after treatment at the intervals indicated in the figures and tables. Four fruits (one from each quadrant) were picked from each of eight trees in each plot, and the resulting 32-fruit sample was processed as a unit. Three field replicates for each treatment were collected from separate plots and were processed separately.