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.

**Table I. Persistence of Guthion Residues in P.P.M. on and in Peel[a] and Pulp[b] of Field-Sprayed Lemons and Oranges**

| Elapsed Days | Rainfall Since Previous Sampling, Inches | Unwashed Fruit, P.P.M. | | | | | | Washed Fruit,[c] P.P.M. (4-Lb. Dosage), | Residue Reduction by Washing, % |
|---|---|---|---|---|---|---|---|---|---|
| | | 1 Lb. 25% W.P./100 Gal. | | 4 Lb. 25% W.P./100 Gal. | | Control, P.P.M. | | | |
| | | Peel[d] | Pulp[e] | Peel[d] | Pulp[e] | Peel[d,e] | Pulp[e] | Peel[d] | |
| | | | | LEMONS, STUDY *A*[f] | | | | | |
| 5 | None | 5.3, 5.1, 4.5 | nil | 11.3, 13.1, 14.4 | nil | <0.3 | nil | .. | .. |
| 12 | None | 3.2, 4.0, 3.9 | nil | 11.0, 12.1, 11.1 | nil | nil | nil | .. | .. |
| 19 | 0.11 | 2.7, 3.4, 3.5 | nil | 8.2, 8.7, 10.4 | nil | <0.5 | nil | .. | .. |
| 33 | 0.37 | 1.8, 2.5, 2.3 | nil | 7.6, 7.1, 8.1 | nil | nil | nil | .. | .. |
| 64 | 0.05 | 1.6, 1.7, 1.6 | nil | 4.8, 3.9, 4.0 | nil | nil | nil | .. | .. |
| | | | | STUDY *B* (3 LB. 25% W.P./100 GAL.) | | | | | |
| 3 | None | ... | .. | 10.0, 10.3, 11.9 | nil | <0.6 | nil | .. | .. |
| 7 | None | ... | .. | 11.5, 9.9, 10.6 | nil | nil | nil | .. | .. |
| 14 | 1.40 | ... | .. | 7.0, 6.6, 6.3 | nil | <0.3 | nil | .. | .. |
| 21 | 0.79 | ... | .. | 3.8, 4.5, 4.0 | nil | nil | nil | .. | .. |
| | | | | VALENCIA ORANGES, STUDY *A*[g] | | | | | |
| 1 | None | 4.0, 4.8, 5.1 | nil | 16.8, 16.6, 19.0 | <0.07 | <0.3 | <0.3 | 0.8, 0.8 | 96 |
| 7 | 0.15 | 3.7, 4.6, 3.3 | nil | 14.6, 15.4, 14.1 | <0.07 | <0.5 | nil | 2.1, 2.8 | 84 |
| 14 | 0.07 | 3.8, 6.3, 4.4 | nil | 14.4, 16.1, 14.1 | nil | <0.2 | <0.04 | 1.9, 2.2 | 86 |
| 22 | None | 3.7, 4.4, 3.4 | nil | 11.2, 12.6, 12.3 | <0.05 | <0.4 | nil | 1.2, 2.6 | 84 |
| 44 | None | 3.9 .. 3.0 | .. | .. .. .. | nil | <0.3 | nil | .. | .. |
| 57 | None | 4.8, 5.8, 5.7 | nil | 14.6, 13.9, 15.6 | <0.05 | nil | nil | 2.7, 2.4 | 83 |
| 91 | 0.01 | 3.5, 3.4, 3.9 | nil | 14.3, 14.9, 13.6 | <0.06 | <0.3 | nil | 3.3, 2.2 | 81 |
| 120 | None | 3.9, 2.9, 3.6 | <0.03 | 11.6, 12.1, 10.5 | <0.13 | <0.2 | nil | 3.7, 3.6 | 71 |
| | | | | STUDY *B* (3 LB. 25% W.P./100 GAL.) | | | | | |
| 3 | None | ... | .. | 6.5, 7.3, 6.5 | nil | <0.4 | nil | .. | .. |
| 7 | None | ... | .. | 6.0, 6.4, 6.8 | nil | <0.2 | nil | .. | .. |
| 14 | 1.40 | ... | .. | 3.0, 3.0, 3.0 | nil | nil | nil | .. | .. |
| 21 | 0.79 | ... | .. | 2.0, 2.1, 2.3 | nil | nil | nil | .. | .. |
| | | | | STUDY *C* (1 AND 3 LB. 25% W.P./100 GAL.) | | | | | |
| 3 | None | 3.0, 3.9, 3.0 | nil | 9.3, 8.2, 10.5 | 0.2 | nil | nil | .. | .. |
| 7 | None | 2.4, 3.9, 3.2 | nil | 10.5, 7.2, 11.9 | nil | nil | nil | .. | .. |
| 14 | None | 4.3, 3.3, 4.2 | nil | .. 11.9, 8.5 | nil | nil | nil | .. | .. |
| 21 | None | 3.3, 3.0, 3.0 | nil | 10.4, 10.3, 6.3 | nil | nil | nil | .. | .. |
| 35 | None | 2.0, 2.7, 3.8 | nil | 9.5, 9.8, 6.7 | nil | <0.3 | nil | .. | .. |

[a] Based on weight of peel only, mature lemons have 30.0 ± 8.5 wt. % peel from 632 measurements; mature Valencia oranges have 18.7 ± 6.3 wt. % peel from 297 measurements. [b] Based on weight of pulp (edible portion) only. [c] Hand washed with dilute Triton X-45 solution before being processed. [d] All values corrected for recovery (lemons, 77 ± 3% from 14 fortified samples prepared at each sampling date over the 9 weeks of the study; oranges, 93 ± 5% from 9 fortified samples over 17 weeks) and for background, except for controls. The value "nil" means the limit of absolute indistinguishableness, by the particular total analytical technique, that has been reached for that particular sample and is less than 11 μg. of Guthion for lemons (0.4 p.p.m.) and less than 5 μg. of Guthion for oranges (0.2 p.p.m.) for 25-gram samples of fruit portion utilized. [e] All triplicated and averaged values corrected for recovery (lemons, 88 ± 4% from 11 fortified samples prepared at each sampling date over the 9 weeks of the study; oranges, 99 ± 6% from 9 fortified samples over 17 weeks) and for background, except for controls. The value "nil" means the limit of absolute indistinguishableness, by the particular total analytical technique, that has been reached for that particular sample and is less than 11 μg. of Guthion for lemons (0.1 p.p.m.) and less than 2 μg. of Guthion for oranges (0.02 p.p.m.) for 100-gram samples of fruit portion utilized. [f] No storage correction because analyzed within 2 weeks of sampling date. [g] Duplicated peel control stripping solutions fortified at 1.0 and 0.5 p.p.m. levels were stored at 10° C. for 92 weeks when they showed apparent increases in Guthion content of 22, 20, 14, and 10%, respectively, with 85% recovery on a current fortified control; clearly an evaporation factor was involved. The 1-, 7-, and 14-day samples were analyzed upon receipt; subsequent stripping solutions were stored at 10° C. as follows: 22-day sample, 3 months; 44-day sample, 4 months; 57-day sample, 4 months; 91-day sample, 2 months; 120-day sample, 1 month.

Subsequently, other mature lemon and Valencia orange trees were sprayed on January 29, 1962 (studies *B*) with the same 25% wettable powder formulation of Guthion at the rate of 3 pounds per 100 gallons of water in the manner previously described. Appreciable rain occurred 10 days later so sampling was abandoned 3 weeks after treatment. In the final study, mature Valencia orange trees were sprayed on June 4, 1962 (study *C*) as previously described at the rates of 1 pound and 3 pounds of the 25% wettable powder formulation of Guthion per 100 gallons of water. There was no rain during the 35-day sampling period utilized.

The unwashed fruits were peeled and processed with *n*-hexane as previously described (*6*) to afford stripping solutions for both the peel and the pulp (edible) portions of the fruit.

To evaluate effects of fruit washing, separate samples of the oranges from the several plots treated at the rate of 4 pounds of the 25% wettable powder per 100 gallons of water were hand washed in dilute Triton X-45 solution, thoroughly rinsed in distilled water, and air dried before being peeled and processed as above.

All stripping solutions were washed three times with 25-ml. portions of 3*N* hydrochloric acid solution prior to analysis to remove any naturally occurring methyl anthranilate which might be present (*1*, *8*). A measured aliquot of each washed stripping solution was evaporated to near dryness in a Kuderna-Danish evaporative concentrator, and the Guthion present was hydrolyzed to anthranilic acid by means of 2 ml. of 1*N* alcoholic potassium hydroxide solution for 30 minutes at 60° C. in the tightly capped Kuderna-Danish tube. The hydrolyzed mixture was strongly acidified with 3 ml. of 3*N* hydrochloric acid solution, extracted with benzene and then with methylene chloride to remove interfering acidic and neutral substances, then reacted with 0.1 gram of zinc dust for 15 minutes to destroy substances present which prevent subsequent color development (*9*) in this procedure. A

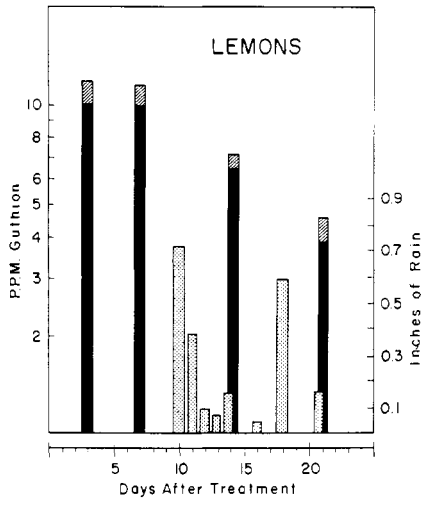


Figure 1. Persistence of Guthion residues on lemons exposed to rain

Striped areas: residue variation among replicates; dotted areas: rainfall

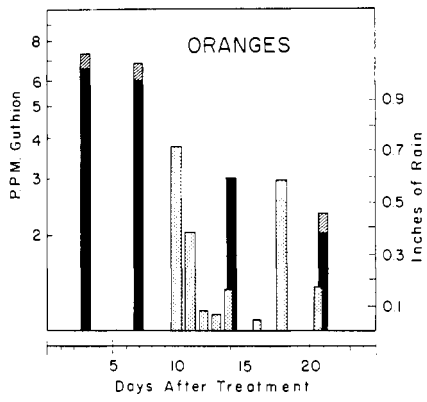


Figure 2. Persistence of Guthion residues on Valencia oranges exposed to rain

Striped areas: residue variation among replicates; dotted areas: rainfall

**Table II. Calculated Initial Deposits of Guthion, on a Whole Fruit Basis, Resulting from the Various Treatments**

| Dosage, Lb./100 Gal. | Calcd. Initial Deposit, P.P.M.[a] | |
|---|---|---|
| | Lemons | Valencia oranges |
| 1 | 1.8, 1.7, 1.5 | 0.8, 1.0, 1.0, 0.8, 1.0, 0.8 |
| 3 | 3.3, 3.4, 3.9 | 1.8, 2.2, 1.8, 2.0, 1.8, 2.2 |
| 4 | 3.8, 4.4, 4.8 | 3.4, 3.3, 3.8 |

[a] Whole fruit basis; see footnote *a*, Table I. From slope values of extrapolated persistence curves.

**Table III. Residues of Guthion during Conversion of Lemon and Navel Orange Peel to Citrus Pulp Cattle Feed 19 and 14 Days, Respectively, after Being Sprayed in the Field**

| Sample | No. of Replicates | Corrected P.P.M.[a] | Per Cent Residue Reduction |
|---|---|---|---|
| LEMON AFTER 0.11 INCH OF RAIN | | | |
| Fresh Peel | | | |
| Unwashed | 6 | 9.4 ± 0.4 | |
| Washed | 6 | 3.5 ± 0.4 | 63 |
| Cattle feed from washed peel | | | |
| Normal wt. | 4 | 5.6 ± 0.7 | |
| Dry wt.[b] | | 6.2 | |
| Wet wt.[c] | | 1.2 | 88 (unwashed) 80 (washed) |
| NAVEL ORANGE AFTER NO RAIN | | | |
| Fresh Peel | | | |
| Unwashed | 3 | 4.3 ± 0.1 | |
| Washed | 3 | 0.7 ± 0.1 | 84 |
| Cattle Feed from Washed Peel | | | |
| Normal wt. | 3 | 1.4 ± 0.0 | |
| Dry wt.[b] | | 1.6 | |
| Wet wt.[c] | | 0.2 | 95 (unwashed) 86 (washed) |

[a] Corrected for recoveries: lemon peel 74 ± 2% from 5 fortified samples, lemon cattle feed 88 ± 14% from 6 fortified samples, orange peel 99 ± 9% from 6 fortified samples, orange cattle feed 85 ± 12% from 3 fortified samples. Corrected for backgrounds from controls: lemon peel nil, lemon cattle feed nil, orange peel nil, orange cattle feed nil. "Nil" mean less than 11 μg. of Guthion present, with from 12.5 to 100 g. of substrate per analytical aliquot.

[b] Residue values corrected from the "normal" oven-dried moisture content (lemons 11%, oranges 10%) to zero moisture content, based on Dean and Stark method with 100 g./samples.

[c] Residue values corrected from "normal" oven-dried moisture content back to the usual moisture content (lemons 82–84%, oranges 79–80%) of freshly ground peel, based on Dean and Stark method with 100 g./samples.

**Table IV. Residues of Guthion from Conversion of Guthion-Fortified Ground Peel to Citrus Pulp Cattle Feed**

| Sample | Moisture Content, % | | Guthion Residue, P.P.M.[a] | | Guthion Reduction,[b] % | |
|---|---|---|---|---|---|---|
| | Lemons | Oranges | Lemons | Oranges | Lemons | Oranges |
| Fresh ground peel | 82, 84 | 79, 80 | 9.9, 8.8 | 9.3 ± 0.5 | . . | . . |
| Dry feed[c] | 11, 11 | 10, 10 | 7.0, 6.0 | 4.8 ± 0.3 | 91[b] | 94[b] |

[a] Corrected for recoveries and background (see footnote *a*, Table II).

[b] Calculated to 80% moisture content: lemons 8.5 p.p.m. lost, oranges 8.7 p.p.m. lost.

[c] From 2500 grams of freshly ground peel, press liquor amounted to lemons 637 grams, oranges 1267 grams.

5-ml. aliquot of this "reduced" filtered solution containing any Guthion-derived anthranilic acid was next diazotized with 1 ml. of 0.25% sodium nitrite solution, the excess nitrite ion was destroyed with 1 ml. of 2.5% ammonium sulfamate solution, and the color was allowed to develop for 30 minutes after the addition of 2 ml. of 1% *N*-(1-naphthyl)ethylenediamine dihydrochloride solution. After being diluted with 5 ml. of 95% ethyl alcohol, the absorbance of the final magenta colored solution was determined at 555 mμ, using a reagent blank to set the instrument. When this procedure was used, a typical daily calibration curve for purified Guthion had a slope of 24 μg. per 0.1 absorbance unit (Beckman model B spectrophotometer).

**Processed Citrus Pulp Cattle Feed.** Mature lemon trees were treated on March 1, 1961, with 4 pounds of the 25% wettable powder formulation of Guthion per 100 gallons of water, and mature navel orange trees were treated on February 1, 1961, with 3 pounds of the 25% wettable powder of Guthion per 100 gallons of water. Applications were made as described in the preceding section.

Mature lemon fruit samples were collected prior to treatment (control) and 19 days after treatment, and mature orange fruit samples were collected prior to treatment (control) and 14 days after treatment. Thirty-two fruits (eight from each quadrant) were picked from each of 16 trees in each plot, resulting in composited 512 fruit samples for both control and treated specimens of each variety. From each composited unwashed sample, three reference 32-fruit samples were selected at random, and processed separately as described above.

The remaining fruits were washed by hand with a 0.5% solution of a typical citrus washing soap powder (50% soap and 50% sodium carbonate) in water, with the fruit submerged at 110° to 112° F. for 2 to 3 minutes, brushed very lightly, then rinsed thoroughly with both tap and distilled water and dried. Each washed fruit was halved

and juiced on a power juicer; juice was discarded. The resulting hemispheres of peel were ground in a Hobart food grinder with a medium plate. Replicated 100-gram portions of ground material were withdrawn by quartering for Dean-Stark moisture determinations. Three 500-gram subsamples were stripped with 2 ml. of *n*-hexane per gram, with equilibration for 1 hour, filtered, and stored at 10° C. awaiting analysis. One 3500-gram subsample of control ground peel was fortified in the usual manner (*5–7*) to contain 10 p.p.m. of purified Guthion, of which 3000 grams was for recovery evaluation during conversion to cattle feed, and 500 grams was for recovery evaluation during reference extraction of the freshly ground peel.

Seven kilograms each of control and of treated ground peel of approximately 80% water content was converted to cattle feed as follows, on the advice of the Research Department of Sunkist Growers, Inc., and of the authors' own experiences. Each subsample was triturated with 9 grams of dry, hydrated lime per kg., allowed to stand at room temperature for 30 minutes to assure adequate enzyme action, then pressed with a Hobart tapered-screw juice extractor, type D, on the Hobart food cutter. The pressed pulp of approximately 40% water content was dried in thin layers at 65° C. in a forced-draft oven to approximately 10% water content. One-hundred-gram subsamples of the resulting dried citrus pulp cattle feed were quartered out for moisture determinations. Three 250-gram subsamples of this dried feed were stripped with 4 ml. of *n*-hexane per gram each, equilibrated for 1 hour as above, filtered, and the stripping solutions were stored at 10° C. awaiting analysis as described in the preceding section.

## Results

Residue values for Guthion on and in the peel and pulp (edible portion) of lemons and Valencia oranges as determined by the anthranilic acid colorimetric procedure resulting from the three consecutive residue studies are collated in Table I. Included in this table are those residue values found in the peel of those oranges which were treated at the rate of 4 pounds of the 25% wettable powder formulation of Guthion per 100 gallons of water and which had been washed prior to being processed. In Table II are listed the slope-calculated initial deposits of Guthion on and in the whole fruit from the various dosages applied to establish repeatability of field application. In Figures 1 and 2 are presented graphically the residue and rainfall data on both lemons and oranges to illustrate the marked effect of rainfall on fresh and aged Guthion residues. In Table III are presented the Guthion residue values in the dried citrus pulp cattle feed prepared in the laboratory from field-treated lemons and navel oranges. In Table IV are listed the recovery values for the Guthion-fortified ground citrus peel before and after being processed by the same laboratory procedure into dried citrus pulp cattle feed.

There was no deterioration of Guthion-containing stripping solutions during refrigerated storage (data are in footnote *g*, Table I).

## Discussion

Calculation of $RL_{50}$ values (time required for 50% of a residue to be dissipated, formerly referred to as "half-life" value) from the data in Table I by the usual means (*6*) afforded values of 30 to 38 days for lemons and 340 to 400 days for Valencia oranges in the absence of rainfall; even a few tenths of an inch of rain decreased these values significantly as shown by study *A*, Table I. Persistence of Guthion on oranges is unusually high compared to the persistence of many other pesticides which have been studied on citrus fruits (*5–8*). However, significant reduction in the residue content of Guthion-treated oranges can be accomplished by rainfall or by simple washing of the fruits, as shown by the data in both Tables I and III. This attritioning effect of rainfall on Guthion deposits and residues agrees with the observations of Williams (*10*), who demonstrated significant losses of Guthion from apple foliage with as little as 0.13 inch of rain.

There is no obvious explanation for the 10-fold higher field persistence of Guthion on oranges as contrasted with lemons, although discrepancies as high as 2:1 are not uncommon (*5*).

Table II also shows that while significant reductions of residual Guthion accompany processing of the peel into dried citrus pulp cattle feed, Guthion concentration actually increases because the water losses from the drying operation exceed the losses of Guthion from fresh peel during conversion to the dried product.


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