Solubility of Parathion in Orange Leaf Wax[1]

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Parathion is an effective scalicide in citriculture. On and in citrus fruit rind, however, it may persist for long periods in the natural waxes and oils (GUNTHER and BLINN 1955, GUNTHER 1969). Purified citrus oils have long been known to be superior solvents for parathion, but the evidence for its high solubility in citrus waxes has been indirect residue-analytical data for the existence of persisting extrasurface and surface residues ("A" and "B" residues) embedded and dissolved in *in situ* fruit waxes (GUNTHER and BLINN 1955). In connection with the possible friction transfer of parathion-bearing citrus leaf waxes to fruit pickers' arms, hands, and clothing as a factor in "reentry safety" it became of interest to establish the solubility, at realistic temperatures, of parathion in citrus leaf wax.

If highly soluble, such contaminated waxes could indeed represent a possible hazard to pickers. For example, at 10 lb a.i./A about 50 g of parathion would be applied/tree. With approximately 100,000 leaves of 25 cm^2 upper surface area each, the initial deposit could and does (GUNTHER and BLINN 1955, GUNTHER 1969) attain about 20 μg of parathion/cm^2, large portions of which may be long-lived under field conditions (GUNTHER *et al.* 1976). van DYK and GUNTHER (unpublished) have shown that appreciable quantities of citrus leaf waxes are transferred to pickers' hands, arms, and clothing during a few hours of picking activity.

Materials and Methods

Leaf wax. Gentle rubbing of freshly picked, unsprayed, mature navel orange leaves with fine steel wool was laborious, frequently ruptured oil sacs, and afforded wax contaminated with particles of steel wool. The biochemically acceptable method of RICHMOND and MARTIN (1959) was therefore used. Fifty leaves at a time, in cheesecloth bags, were dipped 10X in 2 L of diethyl ether, with drainage into the bath. Fresh ether was used for each group of 1,000 leaves. The ether was allowed to partially evaporate in a hood, the water layer was separated and washed 3X

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with fresh ether, and the combined ether strippings were dried over anhydrous $MgSO_4$ and filtered; the filter cake was rinsed with extra ether. Removal of solvent on a rotary evaporator at room temperature afforded 0.72 g of gray wax from 4,000 leaves.

Solubility of Parathion in Leaf Wax by GLC

The MC REYNOLDS (1970) constants for a 3-ft column of 10% leaf wax on Chromosorb W AW/DMCS were determined to see if a commercially available gas chromatographic liquid phase would match and serve as a readily available source of citrus wax-like material. However, the constants for the citrus wax column appeared to be significantly different from any liquid phase measured by MC REYNOLDS (see Tables I and II).

TABLE I

Characterizations and polarities of 10% columns of citrus wax and two reference materials in terms of MC REYNOLDS constants[a/].

	Liquid phase			
			Citrus wax (10%)[b/]	
Solvent	Beeswax	Apiezon W	Before parathion	After parathion
Benzene	43	82	52	47
1-Butanol	110	135	168	142
2-Pentanone	61	99	98	78
1-Nitropropane	88	155	118	109
Pyridine	122	154	152	116
Av. polarity	424	625	588	492

[a/] At 120°C; valid to ±5.
[b/] Absolute retention volume of n-octane = 5.20 ml before and 3.28 ml after parathion run; weight of packing 1.011 g before and 0.994 g after parathion run, or 1.7% loss if due only to citrus wax.

TABLE II

Comparison of 1% and 10% citrus wax columns in terms of MC REYNOLDS constants[a/].

	1% column		
Solvent	Before parathion run	After parathion run	10% column[b/]
Benzene	42	32	42
1-Butanol	192	187	203
2-Pentanone	89	83	93
1-Nitropropane	123	108	108
Pyridine	146	136	167
Av. polarity	592	546	613

[a/] At 56°C; valid to ±10.
[b/] At 75°C; before parathion run.

The temperature was then increased until, with a flame ionization detector, parathion could be seen coming off the column with repeated 10 μl injections of a 1 mg/ml solution of analytical parathion in hexane. Data were taken at column temperatures of 177.4°, 188.9°, and 195.2°C. The column was cooled and the MC REYNOLDS constants were remeasured, the absolute retention volume of n-octane was determined, and the column was re-weighed to establish heating losses. Results, shown in Tables I and II, indicate that the column had changed significantly during the heating process, perhaps due both to loss of citrus wax and perhaps also to chemical reactions that lessen its polarity.

To lower the column temperature necessary for elution of parathion, a 1-ft 1% citrus wax on Chromosorb W column was prepared. MC REYNOLDS constants were obtained, then parathion was chromatographed at 114.6° and at 124.5°C; after cooling, the MC REYNOLDS constants and absolute retention volume of n-octane were checked and found not to have changed significantly. Also, the MC REYNOLDS constants of the 1% column were not significantly different from those of the 10% column. When the log V_g^T values for the 5 temperatures are plotted vs. $\frac{1}{T}$(°K) a straight line of absolute slope 2.47(log V_g^T/T^{-1}) is obtained. This is surprising due to the changes noted in the 10% column, but the latter probably also are a function of $\frac{1}{T}$ and thus are corrected for in the process of graphing the data.

The solubility of parathion in the leaf wax, V_g^T, is equal to the absolute retention volume at temperature T divided by the weight of the liquid phase in grams. These data and calculations are collated in Table III.

TABLE III

Data and calculations[a/] for the solubility of parathion in citrus wax at 25° C.

Citrus wax column (%)	T (°C)	$\frac{1}{T}$ (X 10^3) (°K)	V_g^T	Log V_g^T
10	177.4	2.220	4.91 X 10^3	3.691
	188.9	2.165	2.68 X 10^3	3.428
	195.2	2.135	1.93 X 10^3	3.286
1	114.6	2.579	2.38 X 10^5	5.377
	124.5	2.515	1.18 X 10^5	5.070

[a/] Slope = 4.667 X 10^3(±0.019 X 10^3) for log V_g^T vs. ($\frac{1}{T}$)
Intercept = −6.675 (±0.043)
At 25°C, 1/T in °K = 3.355 X 10^{-3} = x
When $y = mx + b$, y = (4.667 X 10^3·3.355 X 10^{-3}) + (−6.675)
$y = \log V_g^{25.0°C}$ = 8.98±0.08
$V_g^{25.0°C} \cong 9.55 \times 10^8 \pm 20\% = \dfrac{\text{g parathion/g citrus wax}}{\text{g parathion/cc of gas at column temperature}}$

At 24°C, the vapor pressure of parathion is 0.03 μ (ZWEIG 1964).
$PV = g/MW \cdot RT$, or $g = \dfrac{MW \cdot PV}{RT}$

$$g = \frac{291.3 \cdot 0.03 \times 10^{-3} \cdot 1.0 \times 10^{-3}}{0.0821 \cdot 298.1} = 4.70 \times 10^{-10} \text{ g parathion/cc gas}$$

g parathion/g wax = 9.55 X 10^{-8}·4.70 X 10^{-10} = 0.45

Conclusion

The solubility of parathion in orange leaf wax at 25°C is therefore 0.5 g/g of wax, which is equivalent to approximately a 30% solution. This high solubility and previously demonstrated in-wax-solution stability clearly demonstrate that citrus leaf waxes may be an important factor in citrus picker "reentry safety."

References

GUNTHER, F. A.: Residue Reviews 28, 1(1969).

GUNTHER, F. A., and R. C. BLINN: Analysis of Insecticides and Acaricides. New York: Interscience (1955).

GUNTHER, F. A., Y. IWATA, and G. E. CARMAN: In preparation (1976).

MC REYNOLDS, W. O.: J. Chrom. Sci. 8, 685(1970).

RICHMOND, D. V., and J. T. MARTIN: Ann. Appl. Biol. 47, 583 (1959).

ZWEIG, G.: Analytical Methods for Pesticides, Plant Growth Regulators, and Food Additives, Vol. II, p. 321. New York: Academic Press (1964).