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Residues and Half-Life Times of Pyrethrins on Peaches after Field Treatments

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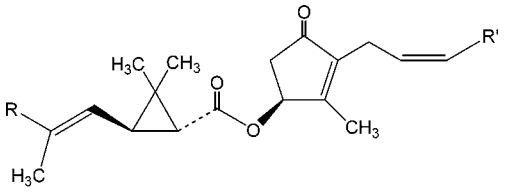
The behavior of pyrethrins and piperonyl butoxide (PB) on peaches has been studied after field treatment. Three experiments were carried out at 1, 5, and 10× the concentration recommended by the manufacturer. In all experiments, the initial deposition was below the maximum residue level (MRL), and the half-life time calculated in the 10× experiment for total pyrethrins within 2.3 days was in agreement with the preharvest interval (PHI) recommended. In a model system, the photodegradation rates of the pyrethrins in three commercial products were compared with pyrethrum pale (PP), with and without the presence of peach waxes. The pyrethrins in formulations containing PB showed higher half-life times but were not influenced by the presence of waxes, whereas in the case of PP that does not contain any PB, photodegradation was significantly affected by the presence of waxes.

KEYWORDS: Pyrethrins; peaches; photodegradation; HPLC−MS

INTRODUCTION

Pyrethrum is the extract from the flowers of *Tanacetum cinerariaefolium*, a species of the *Crysanthemum* plant family (*1*). The insecticide properties of the flowers were first reported in the early 1800's, and thus far, pyrethrum is the most important botanical pesticide. The actual volume of dry flower products worldwide is about 25 000 tons, with the main producer being Kenya, followed by Australia (Tasmania), Rwanda, Tanzania, and Ecuador (*2*, *3*).

The refined commercial product from flowers contains 45−55% of pyrethrins, 20−25% of light isoparaffins, and 23−25% of phytochemical extracts (*4*). The AOAC method (*5*) is the official method used worldwide for determining pyrethrins in pesticide formulation. The active ingredient consists of six esters called pyrethrins and identified as pyrethrin I and II, cinerin I and II, and jasmolin I and II, which are obtained from the combination of chrisanthemic acid and pyrethric acid with three alcohols: cinerolone, pyrethrolone, and jasmolone (*6*) (**Figure 1**). Because the relative amounts of each compound vary depending on the plant type and the region where the plants are grown, the ratio between these two groups ranges from 0.7 in Guinea to more than 2.0 in Rwanda. The ratio is also affected by the period of harvest, and in particular, it decreases during maturation, because pyrethrins I undergo biochemical transformation to pyrethrins II. This ratio is important because pyrethrins have two different types of action against insects: pyrethrins I have a lethal effect, whereas pyrethrins II have a knockdown effect (*1*, *7*−*9*).



Pyrethrins	R	R'
pyrethrins I – esters of chrysanthemic acid		
pyrethrin I	CH_3	$CH{=}CH_2$
cinerin I	CH_3	CH_3
jasmolin I	CH_3	CH_2CH_3
pyrethrins II – esters of pyrethric acid		
pyrethrin II	$CH_3OC(O)$	$CH{=}CH_2$
cinerin II	$CH_3OC(O)$	CH_3
jasmolin II	$CH_3OC(O)$	CH_2CH_3

Figure 1. Chemical structures of pyrethrins I and II.

Pyrethrins are rapidly degraded by the combination of sunlight and air and, therefore, have a low impact on the environment but require frequent applications in field conditions. For this reason, synergists, like piperonyl butoxide (PB) and *N*-octylbicycloheptene dicarboximide (MGK264), are usually added to pyrethrum formulations (*10*). Today, the majority of pyrethrum formulations are synergised by the addition of PB (*11*).

The analysis of pyrethrins has been widely discussed by scientists both in terms of extraction and determination steps

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(*12*−*15*); however, relatively few papers deal with the fate of pyrethrins in field conditions (*16*, *17*).

In this paper, we report the study of the initial deposition and behavior of pyrethrins 1 and II and PB on peaches under field conditions at three different application rates. Moreover, we use a model system to investigate the photodegradation rates of three different commercial formulations of pyrethrins and pyrethrum pale (PP), a commercial concentrate extract containing 50% of pyrethrins.

MATERIAL AND METHODS

Field Trials. Field trials were carried out on a peach orchard (cv. Guglielmina) located at Uta, near Cagliari, Italy, planted in 1999 with a plant spacing of 4.5 × 4 m (550 plants/ha). A random block scheme was used, with four replications for each test, and each block contained four plants.

Treatments were carried out on September 7, 2004, using an AM 150 (Oleo-Mac, Reggio Emilia, Italy) portable motor sprayer. Pyros (Serbios) containing 4% pyrethrins (36.6 g/L) and 12.8% PB (117 g/L) was the commercial formulation applied at 1, 5, and 10× the dose recommended by the manufacturer (44 g/ha, 12 hL/ha). Sampling (on dry plants) started about 1 h after treatment and was repeated after 1, 3, 6, and 10 days, randomly collecting 3 kg of samples from each plot. Because of the low stability of pyrethrins when exposed to UV light, all samples were collected in dark plastic bags and analyzed immediately after harvest. During the experiment, the total rainfall was 54.2 mm in 2 days (September 16 and 17, 22.6 and 31.6 mm, respectively), and the maximum and minimum average temperatures were 32 and 18 °C.

Chemicals. Analytical standards of pyrethrins (pyrethrins technical mixture, Pestanal) at 10.35% pyrethrin I, 7.26% pyrethrin II, 1.51% cinerin I, 1.40% cinerin II, 0.69% jasmolin I, 0.54% jasmolin II, and 21.75% PB were from Sigma−Aldrich (Milan, Italy). Water was distilled and filtered through a Milli-Q apparatus (Millipore, Milan, Italy). Hexane, ethyl acetate, trifluoroacetic acid, and acetonitrile were HPLC solvents (Carlo Erba, Milan, Italy). Sodium chloride was analytical-grade (Carlo Erba, Milan, Italy). Stock standard solutions of the active ingredients were prepared in methanol. Working standard solutions for HPLC analyses were prepared daily by diluting the stock solutions with the mobile phase (water/acetonitrile, 50:50, v/v).

Apparatus and Chromatography. *HPLC−Diode Array Detector (DAD) Analysis*. An Agilent Technologies (Waldbronn, Germany) model 1100 liquid chromatograph was used, fitted with a DAD UV6000LP (TermoQuest, San Jose, CA). An XTerra RP_{18} 5 μm Waters (4.6 × 250 mm) column was employed. The gradient profile for the separation of the pyrethrins and PB was as follows: initial mobile phase water/acetonitrile (50:50, v/v) hold for 3 min, reaching water/acetonitrile (20/80; v/v) in 15 min and hold for 5 min. After each injection, a post time of 15 min was set, at the initial conditions. The injection volume was 50 μL, and the flow rate was 1 mL/min. The analysis was performed at the wavelength of 230 nm according to the pyrethrins maximum in the UV spectra. Calibration graphs for the active ingredients were plotted reporting peak height versus concentration. Good linearities for pyrethrins were achieved in the range of 0.03−3.0 mg/kg and between 0.03 and 6.0 mg/kg for PB, with correlation coefficients between 0.9995 and 0.9998, respectively.

HPLC−MS Analysis. An HPLC system (Shimadzu, Milan, Italy) equipped with an SPD11 Avp DAD detector, an SIL 11 AD vp auto injector, and a LC 10 AD binary pump coupled on line with an MS2010 mass spectrometer (Shimadzu, Milan, Italy) was used. UV and MS data were acquired and processed using Shimadzu "LCMS solution" software. Gradient development was with 0.1% aqueous acetonitrile/99% trifluoroacetic acid (30:70, v/v) at 0 min to 0.1% aqueous acetonitrile/99% trifluoroacetic acid (100:0, v/v) at 40 min. The used column was a 150 × 2.1 i.d. 3.5 μm Waters Symmetry C18. The injection volume was 20 μL, and the flow rate was 0.2 mL/min. MS conditions were as follows: APCI(+) source probe, 350 °C; CDL, 300 °C; block, 290 °C; flow gas (N_2), 2.5 mL/min; probe voltage, 4.5 kV; scan, 200−500 amu.

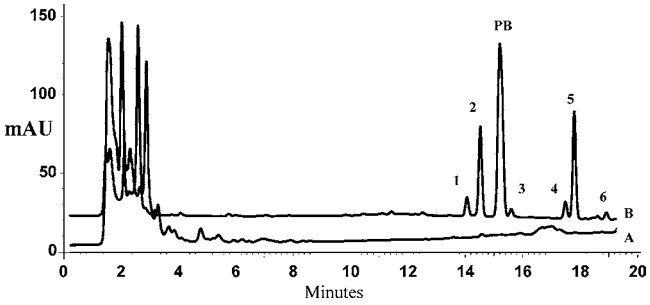

Figure 2. Representative HPLC chromatograms of (A) a blank of peaches and (B) a blank fortified with (1) cinerin II, (2) pyrethrin II, (3) jasmolin II, (4) cinerin I, (5) pyrethrin I, and (6) jasmolin I (total pyrethrins, 0.92 mg/kg) and PB (3 mg/kg).

Extraction Procedure from Peaches. A 5 g aliquot of homogenized sample was weighed in a 30 mL screw capped tube; 2 g of NaCl and 10 mL of ethyl acetate/hexane mixture (50:50, v/v) were added. The tube was then agitated for 30 s in vortex and for 20 min in a rotatory shaker. The phases were allowed to separate, and 2 mL of the organic phase was evaporated to dryness under a gentle nitrogen stream. The residue was dissolved with 1 mL of the water/acetonitrile (50:50, v/v) mobile phase and injected for HPLC analysis.

Recovery Assay. Samples of untreated peaches were fortified with pyrethrins and PB standard solutions to reach concentrations of 0.05, 0.5, 1.0, and 2.0 mg/kg and 0.1, 0.5, 1.0, 2.0, and 4.0 mg/kg, respectively. Prior to the extraction step, the fortified samples were allowed to settle for 30 min. Afterward, they were processed according to the above extraction procedure. Four replicates for each concentration were analyzed, and recoveries ranged between 84 and 97%, with a maximum coefficient of variation (CV) of 12%.

Sunlight Photodegradation Experiments in a Model System. These trials were carried out on three different commercial formulations A, B, and C and on PP. Formulation A and B were both at 4% pyrethrins and 12.8% PB, formulation C and PP were without PB and at 2 and 50% pyrethrins, respectively. A portion of formulation solution dissolved in water and a volume of peach wax extract dissolved in acetone (the appropriate volume to reach the same concentration as on the fruit and vegetable surface) were poured into Petri quartz dishes of 5 cm diameter. To have a uniform film on the dish surface, the solvent was evaporated at room temperature, keeping the dishes one night in the dark at room temperature. The dishes were then exposed to sunlight at 39° 14′ latitude north and 3° 20′ longitude west from the Rome Monte Mario meridian and removed at prefixed intervals (5, 10, 20, 40, and 60 min). Control samples were stored in the dark at room temperature. The residues in the dishes were taken up with 5 mL of the mobile phase and analyzed by HPLC. Every trial was conducted in four replicates.

Extraction of the Waxes from Peaches. The extraction of epicuticular waxes from peaches was carried out as described by McDonald et al. (*18*). Untreated peaches of a known surface were dipped in an exact amount of chloroform for 1 min. The total quantity of wax/cm^2 on peaches, calculated by evaporating to dryness 10 mL of the chloroform extract, was 7.2 μg/cm^2.

Statistical Analysis. Analysis of variance ANOVA was performed by "MSTAT-C" (1991), when appropriate ($p < 0.05$); analysis was followed by the Duncan post hoc test.

RESULTS AND DISCUSSION

An HPLC−DAD chromatogram of a standard of pyrethrins and PB, together with the blank is reported in **Figure 2**. No interfering peaks were detected at the retention time of the analytes; therefore, no clean up was necessary. The HPLC−DAD method allows the separation of all compounds, and the use of the detection wavelength at 230 nm, which was chosen because this value agrees with the λ_{max} (between 227 and 235 nm) of all analytes, revealed to be successful. The limits of

Table 1. LC/MS (APCI+) Characteristics of Pyrethrins, Their Candidate Photoproducts, and PB

compound	log P[a]	HPLC t_R (min)	molecular weight	LC/MS (APCI) *m/z* (amu) (percent relative abundance)
cinerin I	3.61	33.42	316	317 $[M + H]^+$ 100, 358 $[M + H + CH_3CN]^+$ 19
pyrethrin I	3.76	34.45	328	329 $[M + H]^+$ 100, 370 $[M + H + CH_3CN]^+$ 10
jasmolin I	4.03	37.39	330	331 $[M + H]^+$ 100, 372 $[M + H + CH_3CN]^+$ 10
cinerin II	2.94	26.40	360	361 $[M + H]^+$ 100, 378 $[M + 18]^+$ 55, 402 $[M + H + CH_3CN]^+$ 33
pyrethrin II	3.09	27.25	372	373 $[M + H]^+$ 100, 390 $[M + 18]^+$ 25, 414 $[M + H + CH_3CN]^+$ 15
jasmolin II	3.36	29.90	374	375 $[M + H]^+$ 100, 392 $[M + 18]^+$ 49, 416 $[M + H + CH_3CN]^+$ 15
PB	3.85	28.85	338	356 $[M + H_2O]^+$ 100
photoproduct I	3.76	33.77	328	329 $[M + H]^+$ 100, 370 $[M + H + CH_3CN]^+$ 16
photoproduct II	3.09	26.87	372	373 $[M + H]^+$ 100, 390 $[M + 18]^+$ 18, 414 $[M + H + CH_3CN]^+$ 10

[a] Log P values were calculated with CS ChemDraw Pro Cambridge Software Corporation, Cambridge, MA.

Table 2. Residues (mg/kg ± SD) and Half-Life Time ($t_{1/2}$) of Pyrethrins and PB after Field Treatments[a]

1X

time (days)	PB	cinerin II	pyrethrin II	jasmolin II	cinerin I	pyrethrin I	jasmolin I	sum of pyrethrins
0	0.146 ± 0.032	nd	nd	nd	nd	0.020 ± 0.008	nd	0.020
1	0.199 ± 0.035	nd	nd	nd	nd	nd	nd	nd
3	0.211 ± 0.085	nd	nd	nd	nd	nd	nd	nd
6	0.184 ± 0.006	nd	nd	nd	nd	nd	nd	nd
10	0.125 ± 0.010	nd	nd	nd	nd	nd	nd	nd
$t_{1/2}$ (days)	25.9							

5X

time (days)	PB	cinerin II	pyrethrin II	jasmolin II	cinerin I	pyrethrin I	jasmolin I	sum of pyrethrins
0	0.515 ± 0.228	0.026 ± 0.009	0.087 ± 0.040	0.015 ± 0.004	0.011 ± 0.004	0.104 ± 0.048	0.005 ± 0.002	0.248
1	0.475 ± 0.019	0.015 ± 0.004	0.057 ± 0.014	0.010 ± 0.005	0.008 ± 0.005	0.074 ± 0.023	nd	0.164
3	0.479 ± 0.090	0.013 ± 0.007	0.048 ± 0.028	0.007 ± 0.001	0.007 ± 0.001	0.041 ± 0.018	nd	0.116
6	0.510 ± 0.105	nd	nd	0.008 ± 0.002	nd	0.021 ± 0.004	nd	0.029
10	0.354 ± 0.085	nd	nd	nd	nd	nd	nd	nd
$t_{1/2}$ (days)	23.4	3.3	3.8	7.4	5.0	2.6		

10X

time (days)	PB	cinerin II	pyrethrin II	jasmolin II	cinerin I	pyrethrin I	jasmolin I	sum of pyrethrins
0	1.161 ± 0.487	0.053 ± 0.016	0.201 ± 0.085	0.025 ± 0.010	0.023 ± 0.009	0.247 ± 0.100	0.013 ± 0.006	0.562
1	1.115 ± 0.556	0.038 ± 0.022	0.142 ± 0.090	0.014 ± 0,008	0.009 ± 0.001	0.092 ± 0.035	0.005 ± 0.002	0.300
3	0.728 ± 0.148	0.024 ± 0.005	0.101 ± 0.025	0.015 ± 0,007	0.008 ± 0.004	0.062 ± 0.010	nd	0.210
6	1.217 ± 0.522	0.017 ± 0.008	0.102 ± 0.029	0.016 ± 0.004	0.007 ± 0.004	0.033 ± 0.004	nd	0.175
10	0.778 ± 0.276	nd	nd	nd	nd	nd	nd	nd
$t_{1/2}$ (days)	26.6	3.8	6.6	5.5	2.2	2.3		

[a] nd = not detectable.

detection (*19*) for pyrethrins, in matrix, was very low: 3 μg/kg for jasmolin I and II, 6 μg/kg for cinerin I and II, 16 μg/kg for pyrethrin I, and 33 μg/kg for pyrethrin II. The half-life times were calculated as pseudo-first-order kinetic (*20*).

Retention time values (t_R) and APCI fragmentation patterns were the criteria used for compound identification, using the commercially available standard mixture for comparison. Compounds belonging to the pyrethrin II series gave $[M + H]^+$, $[M + 18]^+$, and $[M + H + CH_3CN]^+$ LC/MS adducts; on the other hand, those belonging to the pyrethrin I series gave $[M + H]^+$, and $[M + H + CH_3CN]^+$ adducts (**Table 1**). The ion $[M + 18]^+$ cannot be ascribed to the $[M + NH_4]^+$ adduct because the eluent mixture did not contain ammonium salts.

The formulation used had a higher content of pyrethrin I than pyrethrin II (43 and 36%, respectively), while the concentrations of cinerin I and II were 6 and 8%, respectively, and the concentrations of jasmolin I and II were 3%. Because the size of the fruits did not change during the experiment, the decrease of the pesticides because of a dilution effect can be ruled out.

Table 2 reports the residues of pyrethrins and PB on peaches after treatment.

With the 1× treatment at the doses recommended by the manufacturer, only the concentration of pyrethrin I was detectable at $T = 0$; but already 1 day after treatment, it was not detectable on peaches. Further information on the behavior of pyrethrins was obtained by the 5 and 10× treatment experiments.

PB showed the same behavior in the three experiments with a half-life time of about 1 month. These results do not agree with the data of Antonius et al. (*16*, *17*) who have observed that the deposition of PB on potato leaves was of about 1 ppm and the half-life time was about 3 days, while in pepper and tomato, they found 0.162 and 0.045 mg/kg and a half-life time of 2.3 and 6.1 h, respectively. After treatment, the PB concentration was always found to be below the MRL (3 mg/kg), and its deposition was on average proportional to the concentration of the solution used for the treatment, 0.15, 0.52, and 1.16 mg/kg for the 1, 5, and 10× treatment, respectively.

Table 3. Residues (mg/kg) and Half-Life Time of Pyrethrin I and II Series after 10× Field Treatment[a]

time (days)	pyrethrins I	pyrethrins II
0	0.283	0.279
1	0.106	0.194
3	0.070	0.140
6	0.033	0.135
10	nd	nd
$t_{1/2}$ (days)	1.6	3.1

[a] (nd = not detectable).

The MRL for pyrethrins (expressed as the sum of pyrethrin I and II) is 1 mg/kg with a safety interval of 2 days. Immediately after treatment, the sum of detectable pyrethrins in the 1× experiment was 0.02 mg/kg, clearly below the MRL. The total content of pyrethrins in the 5 and 10× experiments were 0.248 and 0.562 mg/kg, respectively (see **Table 2**). When the concentration of pyrethrin I is taken into account for the three experiments, the pesticide deposition was proportional to the treatment. When the concentration of all compounds at $t = 0$ were compared for the 5 and 10× experiments, there was for each one of them a direct correlation between the two treatments. Besides the concentration of the single compounds at $t = 0$ for the experiment, 5× was too small and after 3 days was no longer detectable. The experiment performed does not allow any conclusion in regard to the distribution of the residues within the different parts of the fruit, because the entire fruits were used for residue analysis. Because the experiment at 10× was the only one that allowed a complete understanding of pyrethrin behavior in peaches after field treatment, it was the one considered in the Discussion. Pyrethrin I showed a half-life time of 2.3 days, while pyrethrin II showed a half-life time of 6.6 days. Also, the concentration of cinerin I decreased more rapidly than cinerin II ($t_{1/2} = 2.2$ versus 3.8 days), which was also reported in the literature (*20*). Interestingly, in the 10× experiment, cinerin I decreased rapidly, during the first day after treatment and remained more or less constant during the rest of the experiment. Jasmolin I decreased rapidly, and already after 1 day, its concentration was below the detection limit, while jasmolin II has a constant decrease with a half-life time of 5.5 days. The data on pyrethrins are often reported separately for pyrethrin I and pyrethrin II series. For comparison with the data reported in the literature, the data of the 10× experiment is shown in **Table 3**. In the formulation employed, pyrethrin I and II series had similar concentrations of about 0.28 mg/kg in the peaches. The half-life times, however, were different, being double for pyrethrin II (3.1 versus 1.6 days). The trend of dissipation observed in our experiment is similar to that reported by Antonius et al. in tomatoes but not in pepper (*16*). The determined half-life times found do not agree with those of Antonius et al. (*16*, *17*) that were in the hour interval, while in our studies, they are in the day interval.

Sunlight Photodegradation Experiment Using a Model System. Pyrethrins expressed as the sum of the pyrethrin I and II were reported to degrade under sunlight with a half-life time of 10−12 min (*21*). According to Kawano and Dickinson, the main photodegradation pathway is the isomerization of the pyrethrolone side chain from a *cis*-(Z) to a *trans*-(E) configuration (*22*, *23*). On the other side, Ruzo and Bullivant suggest the isomerization of the cyclopropane ring (*24*, *25*). Chen and Casida (*26*) have isolated 14 photoproducts derived from pyrethrin I, both from the alcoholic and acidic side of the molecule. Pyrethrins gave two significant photoproducts analyzed by LC/MS with retention times of 26.87 and 33.77 min, giving $[M + H]^+$, $[M + 18]^+$, $[M + H + CH_3CN]^+$, and $[M + H]^+$ and $[M + H + CH_3CN]^+$ adducts, respectively, and tentatively attribute to the photoisomerization of pyrethrins II and I. **Table 4** shows the half-lives of pyrethrins upon sunlight exposure in the three commercial formulations and in PP, with and without waxes. The data obtained with these tests confirm the half-life time of about 14 min for total pyrethrins I and II in PP (*21*), without waxes, while in the presence of waxes, the half-life time is about 22 min. The photodegradation trend is similar to that observed in peaches, with pyrethrins I showing a half-life time lower than pyrethrins II. The photodegradation of the pyrethrins in the formulations A and B, which contain PB, is not influenced by the presence of waxes, and their half-life times are doubled compared to that of formulation C, while their half-life times are slightly higher compared to that of PP without waxes. The half-life time of PP photodegradation is dramatically affected by the presence of the waxes. Considering the single pyrethrin, in the formulations, the presence or absence of waxes do not influence the behavior of the photodegradation, while in PP, the presence of waxes affected in particular pyrethrin I and II, slowing down their decrease.

Table 4. Half-Life Time ($t_{1/2}$, min) of Pyrethrins with Different Formulations, with and without Peach Waxes[a]

	A		B		C		PP	
compound	without	with	without	with	without	with	without	with
				Peach Waxes				
pyrethrin I	12.8	12.8	14.0	13.5	5.8	8.8	7.8	17.2
cinerin I	43.0	31.5	70.4	66.0	9.3	6.0	20.8	26.8
jasmolin I	6.3	5.8	11.8	11.6	7.1	7.6	15.6	15.3
total	16.8	13.6	19.5	18.7	5.6	8.5	11.0	22.7
pyrethrin II	24.0	29.4	22.6	20.7	29.9	29.3	8.7	19.4
cinerin II	38.3	33.4	23.4	19.5	19.6	20.9	34.7	31.6
jasmolin II	32.8	32.4	28.1	31.7	38.5	42.7	24.1	30.8
total	26.4	30.2	23.0	21.2	29.3	29.4	14.2	21.9

[a] The standard deviation obtained ranged between 6 and 11%.

Treatments with pyrethrins showed very low levels of residues after spraying, mostly under the detection limits. Their half-life time was in the day's interval, and their use is not expected to cause any toxicological problem upon the consumption of treated fruits. The degradation of pyrethrins follows the same trend in field as in the model system, with half-life times lower for the pyrethrin I series. In the model system, the degradation of the pyrethrin I series components was slower in the formulations containing PB than those not containing PB. On the other hand, in the case of pyrethrin II series, PB showed no significant influence. Only in PP, the stability of pyrethrins was influenced by the presence of peach waxes.

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