-hexanoic acids (addition of one and two acetates, respectively), while 2,4-dichlorophenoxybutanoic acid was metabolized by alfalfa to 2,4-dichlorophenoxyhexanoic (one acetate added) and -decanoic acids (three acetates, Linscott et al., 1968). In contrast, CPCA can form metabolite acids resulting from addition of up to seven acetates in rats (this work) or eight acetates in plants (Quistad et al., 1978). Thus, these results suggest that such chain-elongation reactions may play a relatively widespread role, and investigation of animal tissues for similar chain-elongated products of other acidic metabolites, especially substituted cyclopropanecarboxylic acids derived from pyrethroids, could be of considerable importance.

It should be emphasized that the ω-cyclopropyl fatty acids described herein were only minor products in the free state. Instead, they are predominantly present as a unique class of *nonpolar conjugates* (mostly glycerides) which are more slowly eliminated because of their lipophilicity (cf. Quistad et al., 1976). Since these unusual long-chain cyclopropyl acids are essentially identical in physical properties with natural fatty acids, it is readily apparent that with current analytical technology it would be extremely difficult to analyze for trace amounts of these metabolites which are found in the matrix of a relatively enormous biomass unless metabolites were radiolabeled (impractical for field residue samples).

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Environmental Degradation of the Miticide Cycloprate. 2. Metabolism by Apples and Oranges

Gary B. Quistad,* Luana E. Staiger, and David A. Schooley

The degradation of cycloprate (hexadecyl cyclopropanecarboxylate) was studied on the foliage and fruit of dwarf apple and orange trees. The single major metabolite on both fruit and foliage was cyclopropanecarboxylic acid (up to 38% applied dose) with ω-cyclopropyl fatty acids also abundant (up to 14% applied dose). These metabolites were found predominantly as polar conjugates, being relatively unimportant as free acids. The mixture of ω-cyclopropyl fatty acids was resolved into 15-cyclopropylpentadecanoic, 15-cyclopropylpentadecenoic, and, apparently, 17-cyclopropylheptadecenoic acids which contributed up to 8, 4, and 0.3% of the applied dose, respectively. Cycloprate applied to the surface of fruit does not penetrate the outer surface and neither cycloprate nor cyclopropanecarboxylic acid translocated into fruit from treated leaves in significant levels (<0.4%).

Cycloprate (hexadecyl cyclopropanecarboxylate, ZR-856, trademark Zardex) is a new miticide (Staal et al., 1975; Nelson and Show, 1975; Henrick et al., 1976). As part of a comprehensive investigation of the environmental fate of cycloprate we now report its degradation by apples and oranges.

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EXPERIMENTAL SECTION

Treatment. Leaves and fruit were treated at approximately 1 kg/ha (10 μg/cm^2) by painting via sable hair brush with an emulsion of [*carboxyl*-^{14}C]cycloprate (Quistad et al., 1978). The emulsion was prepared by

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diluting an emulsifiable concentrate of the following composition with water (1 mL): alkyl arylsulfonates, 8.0%; aromatic solvent, 64.0%; X-77 surfactant, 0.045%; and [*carboxyl*-^{14}C]cycloprate, 28.0%, 4.91 mCi/mmol, 500 μg. After treatment of leaves and fruit (duplicates per time point), the intact trees (i.e., dwarf Red Delicious apple, dwarf Northern Spy apple, and Navel orange) were maintained in a greenhouse for the duration of the study.

Radioassay and Chromatography. Radioactivity was measured by liquid scintillation counting and total combustion as previously described (Quistad et al., 1974). Thin-layer chromatography (TLC) plates were precoated (silica gel GF, Analtech), and preparation of $AgNO_3$–TLC plates has been reported (Quistad et al., 1975). Metabolite confirmation was made by high-resolution liquid chromatography (HRLC) on μBondapak C_{18} (Quistad et al., 1978).

Metabolite Analysis. At designated intervals fruit and leaves were collected for extraction with $CHCl_3$, followed by methanol (extracts combined). Initial TLC (hexane–ether–acetic acid, 60:20:1) allowed separation of cycloprate and free primary metabolites; quantitation was achieved by liquid scintillation counting of the appropriate eluted TLC zone. The TLC region (from apple leaves) coincident with cyclopropanecarboxylic acid (CPCA) was derivatized by formation of the *p*-phenylphenacyl ester (with <50 mg biomass in extract—25 mg of α-bromo-*p*-phenylacetophenone, 300 mg of $KHCO_3$, 2 mL of dimethylformamide, room temperature, 1 h). This ester was purified by HRLC (25 × 0.2 cm Zorbax-SIL column, pentane–ether, 90:10) for structural confirmation by gas chromatography–mass spectrometry (Schooley et al., 1975): *m/e* (rel intensity), 280 (5), 182 (14), 181 (100), 153 (12), 152 (19), 69 (6).

In order to analyze extractable conjugates (origin zone from initial TLC), the organic extract was concentrated to dryness and adsorbed onto silica gel. The silica was washed with hexane–ether (9:1) to remove cycloprate and primary metabolites, then the conjugates were recovered by rinsing with methanol. Saponification of conjugates (1 M ethanolic KOH, 75 °C, 1 h) yielded CPCA and ω-cyclopropyl fatty acids. The identity and quantity of CPCA was verified by derivatization to its *p*-phenylphenacyl ester which coeluted with authentic standard upon HRLC (methanol–water, 70:30). The mixture of ω-cyclopropyl fatty acids was methylated, and esters were examined by HRLC (methanol–water, 87.5:12.5) or, in the case of some samples, HRLC was preceded by $AgNO_3$–TLC (hexane–ether, 5:1) to separate the esters into classes based on degree of unsaturation. In this separation the cyclopropane ring itself imparts minimal affinity for $AgNO_3$. Thus, fully saturated ω-cyclopropyl metabolite esters comigrated with saturated natural fatty acid esters (e.g., methyl stearate). A homologous series of ω-cyclopropyl fatty acids was provided by the Chemistry Department at Zoecon and included the following acids: 11-cyclopropylundecanoic [14(11cPr):0], 13-cyclopropyltridecanoic [16(13cPr):0], 15-cyclopropylpentadecanoic [18(15cPr):0], and (*E*)-15-cyclopropyl-14-pentadecenoic [18(15cPr):1(14)].

The monounsaturated ω-cyclopropyl esters from 1- and 2-week treated orange leaves were initially purified by HRLC into two zones, one coincident with 18(15cPr):1(14) and the other eluting with the retention volume expected for 20(17cPr):1. The zones were separately treated with ozone (ca. 20 000 dpm methyl ester, 10 mL of CH_2Cl_2, 2 mg of acetic acid, Welsbach Ozonator). The resultant ozonides were cleaved to shorter-chain ω-cyclopropyl fatty acids (10 mg of acetic acid, 2 mL of 30% H_2O_2, reflux 1 h), which were derivatized to *p*-phenylphenacyl esters for examination by HRLC.

Table I. Three-Day Metabolism of Cycloprate by Leaves of Dwarf Red Delicious Apple Tree

	% applied dose
Cycloprate	58.8
CPCA (free)	4.6
ω-Cyclopropyl fatty acids (free)	<1
Conjugates (aglycone after saponification)	32.6
CPCA	11.9
ω-Cyclopropyl fatty acids	2.7
16(13cPr):0	0.1
18(15cPr):0	1.4
18(15cPr):1	1.0
Volatile products (unknown)	0.8
Untreated leaves (near application site)	0.8
Residual solids	3.6
Total identified	78
Total recovery	101

Unextractable radioactivity in the residual plant solids was determined by total combustion of an aliquot prior to liquid scintillation counting. The residual solids were also saponified to release CPCA and ω-cyclopropyl fatty acids which were analyzed as above.

Apple Fruit Treatment with Sodium Cyclopropanecarboxylate. Two Northern Spy apples were treated (2 kg/ha) with an aqueous solution of sodium [*carboxyl*-^{14}C]cyclopropanecarboxylate (0.5 mCi, 54.1 mCi/mmol, 98.5% radiochemical purity by TLC). After 3 weeks the apples were fractionated into peel and pulp, which were separately extracted with $CHCl_3$–CH_3OH for subsequent analysis (vide supra).

Bioavailability of CPCA Metabolites to Rats. The combined peel–pulp extract represented 89% of the total recovered ^{14}C from CPCA-treated apple fruit. A portion of the combined extract was evaporated to dryness and diluted with water for rat treatment (0.47 g of fruit solids, 0.53 g of water, 3.5 μCi/rat). The aqueous solution of total extractable radiolabeled plant metabolites (and natural fruit solids) was administered orally to four male Simonsen albino rats which were maintained for 4 days prior to sacrifice (for details, Quistad et al., 1978).

Autoradiography. Certain treated fruit were sectioned into thin slices which were lyophilized, then exposed to Kodak no-screen medical x-ray film for 1 week prior to development.

RESULTS AND DISCUSSION

Apple Foliage. Preliminary studies with cycloprate utilized newly emerged dwarf Red Delicious apple leaves. The 3-day metabolic products are given in Table I. Free cyclopropanecarboxylic acid (CPCA) was the only detectable primary metabolite (5% applied dose), but conjugated CPCA was two–three-fold more abundant. Conjugates of long-chain ω-cyclopropyl fatty acids represented 3% of the applied radiolabel which was further characterized as 18(15cPr):0, 18(15cPr):1, and 16(13cPr):0 (1.4, 1.0, and 0.1% applied dose, respectively) by $AgNO_3$–TLC and reversed-phase HRLC.

In order to maximize recovery of aglycons the entire crude conjugate fraction was subjected to enzymatic and chemical cleavage (Table II). It is evident that any generalizations concerning the structural identity of intact conjugates would be potentially misleading since all enzymes were fairly effective in releasing organosoluble radioactivity. However, treatment of conjugates with base proved superior and was used routinely in further conjugate analysis. All subsequent apple studies were per-

Table II. Cleavage of Extractable Conjugates from 3-Day Metabolism of Cycloprate by Apple Leaves

Treatment[a]	% recovered ^{14}C		% recovery ^{14}C	% total ^{14}C rendered organo-soluble
	Water soluble	Ether soluble		
Peptidase (hog mucosa)	65	35	88	31
β-Glucuronidase (*Helix pomatia*, contains sulfatase)	30	70	94	66
β-Glucosidase (almonds)	33	67	85	57
Phosphatase (wheat germ with lipase)	35	65	92	60
Sulfatase (*H. pomatia*, contains β-glucuronidase)	26	74	94	70
Cellulase (*Aspergillus niger*)	22	78	94	73
Cellulase and sulfatase	28	72	91	66
NaOH (0.1 M), 37 °C, 20 h	0	100	76	76
HCl (0.1 M), 37 °C, 20 h	62	38	100	38
Blank (buffer only)	88	12	84	10

[a] All enzymatic incubations used citrate-phosphate buffer, pH 4.5, with agitation at 37 °C for 20 h. For additional experimental details, see Quistad et al. (1974).

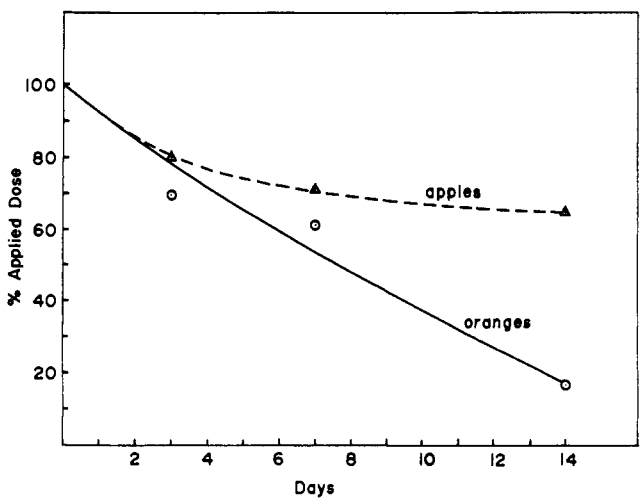

Figure 1. Recovery of unmetabolized cycloprate after application to apple and orange foliage.

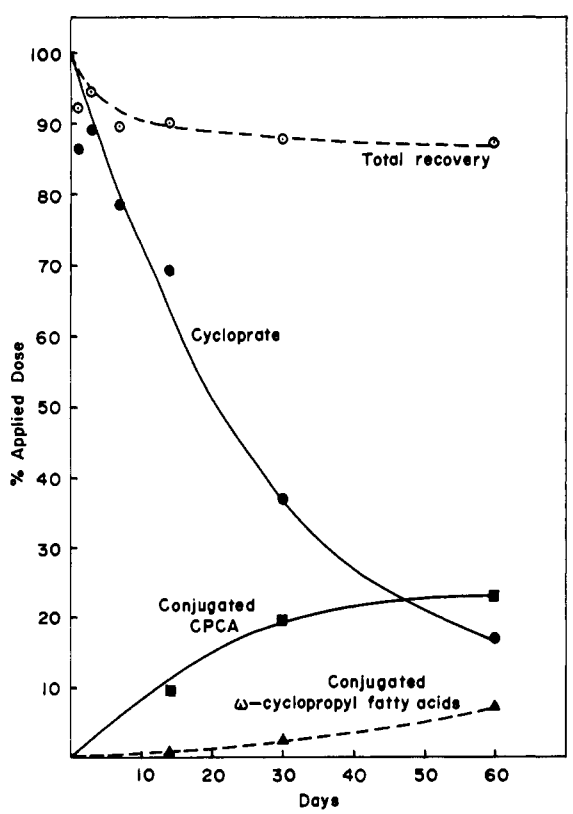

Figure 2. Degradation of cycloprate applied to apple fruit.

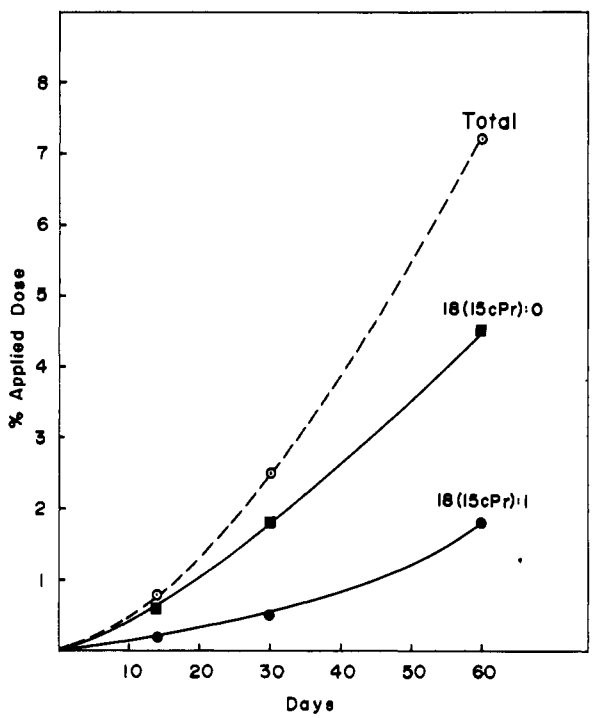

Figure 3. Formation of ω-cyclopropyl fatty acids by apple fruit (as conjugates).

formed with dwarf Northern Spy trees. The degradation of cycloprate on foliage is shown in Figure 1 and by extrapolation the first half-life ($t_{1/2}$) was ca. 28 days. At 3, 7, and 14 days posttreatment more than 90% of the ^{14}C residue was unmetabolized cycloprate while residues of unconjugated CPCA and ω-cyclopropyl fatty acids were <1% of the applied dose. Foliar application resulted in no translocation (<0.1% applied dose) of cycloprate or any metabolite from leaves into adjacent fruit.

Apple Fruit. The degradation products from a 60-day study of cycloprate on Northern Spy apples are summarized in Figure 2. The first $t_{1/2}$ for cycloprate on fruit was ca. 21 days and the second $t_{1/2}$ was ca. 23 days. Unconjugated CPCA and ω-cyclopropyl fatty acids were <1% applied radiolabel for days 3–60 while conjugated CPCA was the most abundant metabolite (23% applied dose after 60 days). Conjugated ω-cyclopropyl fatty acids increased in relative importance with time (Figure 3), but conjugated CPCA was always three–ten-fold more abundant. Analysis of the ω-cyclopropyl fatty acids after 60 days by $AgNO_3$–TLC and reversed-phase HRLC gave 4.5% of the applied dose as 18(15cPr):0 and 1.9% as 18(15cPr):1. No other long-chain ^{14}C fatty acid was present

Table III. Apple Fruit Metabolism of Sodium [*carboxyl*-^{14}C]Cyclopropanecarboxylate

	% total ^{14}C in fruit
Extractable ($CHCl_3$-CH_3OH)	89.4
Nonpolar (ether eluted from silica)	16
Wax esters	≤2
Triacylglycerol	≤0.4
CPCA (free)	<1
ω-Cyclopropyl fatty acids (free)	≤8
Saturated	0.8
Monounsaturated	1.3
Polar (methanol eluted from silica)	74
Ether soluble after acetylation	73
Cleaved by pancreatic lipase	8.1
CPCA	6.9
ω-Cyclopropyl fatty acids	1.2
CPCA-glucose	<1
Saponification released acids	74
CPCA	42
ω-Cyclopropyl fatty acids	32
Saturated	15
18(15cPr):0	12
Monounsaturated	8.1
18(15cPr):1	5.4
20(17cPr):1	1.9
Polyunsaturated	9.0
Residual solids	10.6

in greater than 0.2% applied radiolabel. Autoradiographic analysis showed that cycloprate applied to apple fruit remains on the outer surface, indicating lack of penetration after 3 days. However, when fruit was treated with sodium cyclopropanecarboxylate, 19% of the applied dose had penetrated into the pulp of the apple after 3 weeks.

In order to probe the chemical identity of the ^{14}C metabolites further, certain apples were treated with sodium cyclopropanecarboxylate. The apple metabolites of CPCA (Table III) were similar to those from [^{14}C]-cycloprate, but it was readily evident that in both cases a complex mixture of conjugated ^{14}C acids predominated. Although little structural information was obtained for the conjugated metabolites from CPCA, saponification released only CPCA and three major ω-cyclopropyl fatty acids (Table III). Considering the known complexity of apple fruit lipids (Mudd and Garcia, 1975), it is not surprising that a multitude of ^{14}C residues was found.

Bioavailability of Apple Metabolites. Although we could not structurally characterize the *conjugated* metabolites from CPCA treatment, the collective mixture of ^{14}C metabolites was administered to rats in order to assess potential bioavailability (Table IV). The profile of excreted and tissue-retained ^{14}C, as well as the identified metabolites, was quite similar to that found for rats dosed with [^{14}C]cycloprate (Quistad et al., 1978). Hence, rats metabolize both cycloprate and its apple metabolites (equivalent to CPCA metabolites) to very similar products.

Orange Foliage. The first $t_{1/2}$ for cycloprate on leaves was ca. 8 days (Figure 1). Individual primary metabolites were only minor ^{14}C constituents in leaves examined at 3, 7, and 14 days. Extracts of leaves 1 week after treatment were analyzed by TLC, and the primary metabolite zone (the region between cycloprate R_f and origin after elution with hexane–ether–acetic acid, 60:20:1) contained 3% of the applied dose. Further analysis characterized this radiolabel as free CPCA (0.4% of the applied dose), free ω-cyclopropyl fatty acids (0.5%), and triacylglycerols (containing CPCA and ω-cyclopropyl fatty acids, 0.4%). Saponification of the entire "primary metabolite zone" gave only CPCA (1.4% applied dose) and ω-cyclopropyl fatty acids (1.6%).

Table IV. Bioavailability of Apple Fruit Metabolites of Sodium [*carboxyl*-^{14}C]Cyclopropanecarboxylate to Male Rats

	% applied dose
Urine	69 ± 14[a]
CPCA-gly[b]	33
CPCA[b]	3.0
CPCA-carnitine[b]	2.5
Feces	14 ± 4
Extractable (CH_3OH)	8
Residual solids	6
Carcass	12 ± 3
Extractable ($CHCl_3$-CH_3OH)	9.9
Ether soluble	7.5
Triacylglycerol	6.4
ω-Cyclopropyl fatty acids (total transesterified)	7.4
14(11cPr):0	0.3
16(13cPr):0	3.8
18(15cPr):0	2.7
Water soluble	2.4
CPCA-carnitine	1.8
Residual solids	2.5

[a] Average and standard deviation for four rats. [b] Calculated for 4 days using percent in 1-day urine only.

Table V. Conjugated Metabolites in Oranges

	% applied dose		
	Treated leaves		Treated fruit
	1 week	2 weeks	30 days
Total conjugates	18.1	22.9	59.1
CPCA	1-7[a]	6-16[a]	35
ω-Cyclopropyl fatty acids	4.8	2.5	14.2
Saturated	2.4	1.2	9.6
18(15cPr):0	1.7	1.0	7.6
Monounsaturated	1.2	0.8	4.4
20(17cPr):1	0.2	0.2	0.3
18(15cPr):1	0.8	0.5	3.7
Polyunsaturated	1.2	0.5	<0.1

[a] Smaller number represents actual CPCA quantitated after derivatization as its *p*-phenylphenacyl ester. Larger number includes correction for losses of radiolabel (presumably CPCA) by volatility during workup.

Conjugated metabolites represented the majority of ^{14}C residue in leaves. Saponification of these polar conjugates gave CPCA and a mixture of ω-cyclopropyl fatty acids which were resolved (as methyl esters) into zones of saturated, monounsaturated, and polyunsaturated esters by $AgNO_3$–TLC. Further analysis by HRLC revealed that the major long-chain aglycon acid was 18(15cPr):0 with about half as much 18(15cPr):1 (Table V). The mixture of polyunsaturated esters was resolved by HRLC into at least three unknown components occurring in similar amounts.

Neither cycloprate nor CPCA translocated from treated leaves into adjacent untreated fruit although progressively more radiolabel was found in such fruit at longer times (0.9% applied dose after 2 weeks). The identity of this radiolabel in untreated oranges was not pursued since cycloprate and CPCA were essentially absent (<0.4% applied dose) and the small amount of ^{14}C residue consisted of polar products.

Orange Fruit. The degradation of cycloprate and appearance of metabolites is given in Figure 4, indicating a $t_{1/2}$ of about 2 days. Primary metabolites in the free state were almost absent with none greater than 2% of the applied dose. The majority of the remaining radioactivity

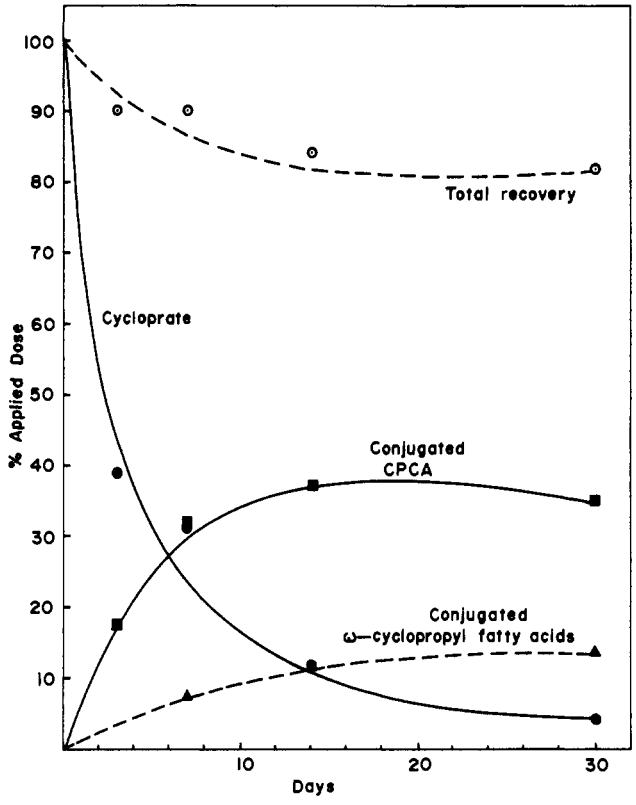

Figure 4. Degradation of cycloprate applied to navel orange fruit.

was contributed by conjugates of CPCA and ω-cyclopropyl fatty acids (some conjugates were extractable with organic solvents, others were bound to residual solids, but released on saponification). Conjugated CPCA alone represented 35% of the applied dose after 30 days. A more exhaustive analysis of the conjugated ω-cyclopropyl fatty acids by $AgNO_3$–TLC followed by HRLC showed that 18(15cPr):0 and 18(15cPr):1 were the most abundant acids (8 and 4% applied dose, respectively) after 30 days (Table V).

An autoradiographic study of orange fruit treated for 3 and 14 days showed no movement of cycloprate or any metabolite into the orange pulp from the peel. The applied radioactivity was found exclusively on the surface of the orange.

Unsaturated ω-Cyclopropyl Fatty Acids. Since monounsaturated long-chain acids represented a significant portion of the ^{14}C residue (1–8% applied dose as conjugates), the isomeric composition of the monounsaturates was explored further in oranges. The monounsaturated zones from $AgNO_3$–TLC were pooled for 7- and 14-day treated leaves. The monounsaturated esters were resolved by HRLC into 18(15cPr):1 and 20(17cPr):1 (Table V) which were separately treated with ozone to determine the positional isomerism. After ozonolysis 20–40% of the product following oxidative workup was identified as CPCA for both 18(15cPr):1 and 20(17cPr):1. Hence, for the monounsaturated ω-cyclopropyl fatty acids about 20–40% of double bonds are α, β to the cyclopropane ring (Figure 5). HRLC of the ozonolysis products (as *p*-phenylphenacyl esters) also suggested the presence of several homologous shorter-chain ω-cyclopropyl fatty acids. Thus, 18(15cPr):1 and 20(17cPr):1 apparently consist of a mixture of positional olefinic isomers.

Radiolabel from polyunsaturated ω-cyclopropyl fatty acids in leaves migrated on $AgNO_3$–TLC with R_f similar

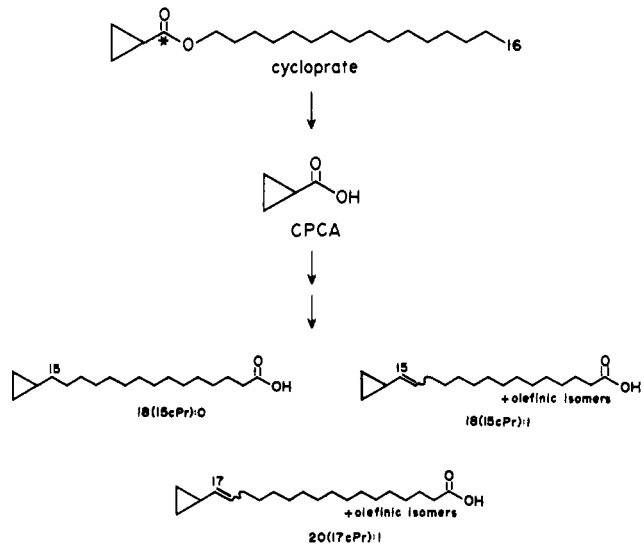

Figure 5. Metabolic products of cycloprate from apples and oranges.

to authentic triunsaturated normal fatty acid methyl ester standards. This apparent triunsaturated zone from $AgNO_3$–TLC consisted of at least three long-chain acids which were resolvable by HRLC and present in similar quantities. Diunsaturated ω-cyclopropyl fatty acids were conspicuously absent by $AgNO_3$–TLC analysis.

Relevance of Metabolites. In contrast to metabolism of cycloprate by rats (Quistad et al., 1978), up to half of the ω-cyclopropyl fatty acids contained one or more sites of unsaturation within the hydrocarbon chain. Plants appear capable of producing a greater variety of long-chain ω-cyclopropyl acids than mammals and the resultant acids are more highly oxidized. Also in sharp contrast to rats, plants store the CPCA and ω-cyclopropyl fatty acids as polar conjugates whereas these same metabolites in rats were found predominantly as nonpolar triacylglycerol conjugates. Similar glyceride conjugates of metabolite acids from cycloprate were less than 2% of the ^{14}C residue in degradation products for plants.

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