Table II. Effect of Casein on Oxygenation Rates in Suspensions of Some Legumes and Cereal Grains

source of enzyme[a]	rate of oxygen consumption, nmol/min		casein/meal at I_{50}, % (w/w)	
		linoleate supplemented (0.4 μmol)		linoleate supplemented (0.4 μmol)
green pea	58	93	2.0	3.2
wheat	19	494	0.06	1.6
barley	28	28	0.2	1.6
oats	35	36	1.8	2.7
rye	15	108	0.2	1.2
turnip rape	9	33	*b*	2.5
soybean	77	200	0.4	1.2

[a] For each assay 100 mg of meal without defatting was used in a 3.0-mL reaction mixture. [b] Reaction rates at I_{50} were below the detection limit of the assay.

as a lipoxygenase inhibitor is considered. Table II enables the comparison of different plant meals with respect to casein content required at I_{50}. The use of skim milk in quantities corresponding to the content of casein reproduced the inhibition within experimental error (approximately 15%).

As a conclusion from these observations it is suggested that milk casein offers an alternative to the use of antioxidants and heat treatments in the stabilization of essential unsaturated fatty acids in plant materials.

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Comparative Degradation of the Pyrethroids Tralomethrin, Tralocythrin, Deltamethrin, and Cypermethrin on Cotton and Bean Foliage

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Residues on cotton and bean foliage up to 20 days after treatment with nonstabilized formulations of tralomethrin and tralocythrin consist of the parent pyrethroids and various ester photoproducts, i.e., significant amounts of deltamethrin and (1R,αS)-*cis*-cypermethrin from debromination and *trans*-deltamethrin and -cypermethrin from 1*R*-cis → 1*RS*-cis,trans isomerization and minor levels of 1′-bromodeltamethrin and 1′-bromocypermethrin from dehydrobromination. Small amounts of the α*R* enantiomers of deltamethrin and (1*R*)-*cis*-cypermethrin are also detected. The acid moiety of tralomethrin undergoes rapid debromination on cotton foliage. Additional products include polar conjugates and compounds not readily recovered on extraction with chloroform–acetonitrile. With the exception of the initial debromination and dehydrobromination reactions, the degradation processes and ultimate residues of tralomethrin and tralocythrin appear to be essentially the same as those of deltamethrin and (1*R*,α*S*)-*cis*-cypermethrin.

Tralomethrin and tralocythrin with 3-tetrahaloethyl substituents (Roussel-Uclaf, 1978a) are readily debrominated to deltamethrin and (1*R*,α*S*)-*cis*-cypermethrin with 3-dihalovinyl substituents in insects (Ruzo et al., 1981) and rats (Cole et al., 1982) and upon photolysis (Ruzo and Casida, 1981) (Figure 1). Deltamethrin and cypermethrin are degraded on or in plants primarily by photoisomerization, ester cleavage, and conjugation reactions (Roberts, 1981; Ruzo and Casida, 1979; Wright et al., 1980). The present study compares the degradation of tralomethrin, tralocythrin, deltamethrin, and (1*R*,α*S*)-*cis*-cypermethrin on cotton and bean leaves with emphasis on modification occurring in the acid moiety.

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MATERIALS AND METHODS

Chemicals. Figure 1 gives the structures, names, and abbreviations for the compounds under investigation. It also indicates the labeling positions for the [^{14}C]pyrethroids examined (40–60 mCi/mmol; supplied by Roussel-Uclaf, Paris, France; Cole et al., 1982). Cypermethrin as used here refers to the 1*R*,α*S*-cis isomer unless indicated otherwise.

Treatment of Plants. Cotton leaves (0.3–0.5 g) on greenhouse-grown plants (20–22 cm high) were individually treated with each [^{14}C]pyrethroid (~0.3 μg/leaf) by using cold ether (30 μL) to apply the samples in the shade and

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Table I. Thin-Layer Chromatographic Properties of Tralomethrin, Tralocythrin, and Some of Their Isomers and Derivatives

compound	TLC, R_f[a,b] CT	HA	CAA
(1'*R*)-tralomethrin	0.37 (0.41)[c]	0.51 (0.57)	0.52 (0.54)
(1'*S*)-tralomethrin	0.49 (0.52)	0.60 (0.63)	0.60 (0.60)
(1'*S*)-*trans*-tralomethrin	0.35	0.47	
1'-bromodeltamethrin	0.36 (0.38)	0.56 (0.60)	0.55 (0.56)
deltamethrin	0.44 (0.46)	0.62 (0.66)	0.60 (0.62)
(αR)-deltamethrin	0.44 (0.46)	0.67 (0.71)	0.66 (0.68)
trans-deltamethrin	0.36 (0.39)	0.59 (0.63)	0.58 (0.58)

[a] Silica gel F_{254} chromatoplates, 0.25-mm gel thickness, developed with solvent systems as follows: CT = carbon tetrachloride-toluene (1:1), two developments; HA = hexane-acetone (7:2), two developments; CAA = cyclohexane-acetone-acetonitrile (16:3:1), two developments. [b] Separation of Br_4CA, Br_2CA, and *trans*-Br_2CA was accomplished with chloroform-acetone (9:1) (CA), giving R_f values of 0.58, 0.52, and 0.46, respectively, and with toluene (saturated with formic acid)-ether (10:3), two developments (TFE), giving R_f values of 0.74, 0.73, and 0.65, respectively. Methyl esters in the TFE system give R_f values of 0.81, 0.80, and 0.76, respectively. [c] R_f values for corresponding tralocythrin derivatives are given in parentheses. The tralomethrin and tralocythrin derivatives are not compared simultaneously.

give a deposit of ~0.05 μg/cm². A July–Aug 1980 experiment with the Stoneville 7A variety compared tralomethrin and deltamethrin preparations and the tetrabromo acid moiety of tralomethrin, Br_4CA (Figure 1). An Aug 1981 experiment with the Acala SJ variety compared tralocythrin and cypermethrin. Treated plants were held outdoors in Berkeley, CA, for up to 20 days before harvest of leaves for analysis.

Bean leaves (0.3–0.4 g) on greenhouse-grown Contender variety plants (20–30 cm high) were treated with the ^{14}C-labeled preparation [(1'*S*)-tralomethrin, (1'*S*)-tralocythrin, deltamethrin, and cypermethrin] as above and harvested after up to 4 days of exposure outdoors or in the dark.

Analyses. Each leaf immediately after harvest was cut into small pieces that were extracted twice with diethyl ether (peroxide free), first with 10 mL for 6 h by using mild sonication and then with 5 mL for 18 h. The leaf residue was then extracted with 10 mL of acetonitrile–chloroform (2:1) by soaking for 18 h followed by a 2-mL rinse. Radiocarbon in the extracts was determined by liquid scintillation counting (LSC) and in the residue by combustion and LSC.

The combined ether extracts (apolar fraction) were concentrated under nitrogen and subjected to thin-layer chromatography (TLC) using the solvent systems shown in Table I for both quantitation and tentative ^{14}C-labeled product identification by cochromatography with authentic standards (Ruzo and Casida, 1981; Ruzo et al., 1978). Radiolabeled and unlabeled compounds were detected as previously reported (Ruzo et al., 1978; Ueda et al., 1975). Ether extracts of pyrethroid-treated leaves were chromatographed in two different two-dimensional systems (CT

Table II. [^{14}C]Pyrethroids and Their Labeled Derivatives Recovered Up to Twenty Days after Treatment of Cotton Leaves with Acid-^{14}C- and Alcohol-^{14}C-Labeled Preparations of (1'*RS*)-Tralomethrin, Deltamethrin, (1'*RS*)-Tralocythrin, and Cypermethrin

compound recovered	radiocarbon recovery, %,[a] at indicated day 0	2	5	10	20
	(1'*RS*)-Tralomethrin Applied (1980 Experiment)				
(1'*RS*)-tralomethrin	95 (95)	12 (18)	0 (0)	0 (0)	0 (0)
deltamethrin	4 (4)	27 (20)	33 (29)	29 (15)	8 (8)
(αR)-deltamethrin	0 (0)	3 (3)	3 (1)	2 (2)	1 (1)
trans-deltamethrin[b]	0 (0)	27 (19)	26 (22)	16 (25)	11 (15)
apolar unknowns	0 (0)	16 (24)	6 (10)	5 (11)	7 (7)
polar unknowns	0 (0)	10 (9)	10 (11)	13 (9)	25 (22)
residue	0 (0)	3 (2)	3 (6)	7 (6)	14 (15)
loss	1 (1)	2 (5)	19 (21)	28 (32)	34 (32)
	Deltamethrin Applied (1980 Experiment)				
deltamethrin	99 (99)		50 (34)	26 (24)	15 (15)
(αR)-deltamethrin	0 (0)		0 (0)	1 (2)	0 (0)
trans-deltamethrin	0 (0)		14 (20)	29 (25)	13 (15)
apolar unknowns	0 (0)		4 (9)	3 (1)	1 (5)
polar unknowns	0 (0)		27 (29)	17 (16)	34 (46)
residue	0 (0)		5 (2)	8 (7)	11 (9)
loss	1 (1)		0 (6)	16 (25)	26 (10)
	(1'*RS*)-Tralocythrin Applied (1981 Experiment)				
(1'*RS*)-tralocythrin	95 (94)	21 (15)		0 (0)	0 (0)
cypermethrin	5 (6)	28 (36)		27 (24)	9 (15)
trans-cypermethrin[b]	0 (0)	9 (15)		22 (23)	11 (14)
apolar unknowns	0 (0)	0 (0)		10 (6)	10 (7)
polar unknowns	0 (0)	13 (7)		13 (14)	24 (21)
residue	0 (0)	3 (7)		11 (11)	18 (20)
loss	0 (0)	26 (20)		17 (22)	28 (23)
	Cypermethrin Applied (1981 Experiment)				
cypermethrin	99 (97)	44 (41)		15 (37)	10 (16)
trans-cypermethrin	0 (0)	22 (30)		15 (15)	11 (16)
apolar unknowns	0 (0)	0 (0)		6 (10)	6 (10)
polar unknowns	0 (0)	6 (5)		9 (12)	17 (19)
residue	0 (0)	3 (3)		14 (17)	16 (26)
loss	1 (3)	25 (21)		41 (9)	40 (13)

[a] Recoveries are given first for acid-^{14}C-labeled preparations and in parentheses for alcohol-^{14}C-labeled preparations and in each case are the averages of six replicates. [b] Includes ~10% 1'-bromodeltamethrin from tralomethrin and 0.1–1% 1'-bromocypermethrin from tralocythrin.

Table III. [^{14}C]Pyrethroids and Their Labeled Derivatives Recovered Up to Four Days after Treatment of Bean Leaves with Acid-^{14}C-Labeled Preparations of (1'*S*)-Tralomethrin, Deltamethrin, (1'*S*)-Tralocythrin, and Cypermethrin

compound recovered	radiocarbon recovery, %,[a] at indicated day 0	1	2	3	4
(1'*S*)-Tralomethrin Applied					
(1'*S*)-tralomethrin	97	8	0	0	0 (63)[b]
deltamethrin	1	35	18	36	18 (9)
(α*R*)-deltamethrin	0	4	0	0	0 (2)
trans-deltamethrin[c]	0	16	27	17	21 (0)
apolar unknowns	0	30	8	20	16 (2)
polar unknowns	0	2	20	5	13 (7)
residue	0	3	7	6	12 (8)
loss	2	2	20	16	20 (9)
Deltamethrin Applied					
deltamethrin	99	80	75	55	51 (68)
(α*R*)-deltamethrin	0	2	0	0	0 (3)
trans-deltamethrin	0	7	3	9	8 (0)
apolar unknowns	0	3	6	5	10 (1)
polar unknowns	0	2	4	10	9 (10)
residue	0	2	2	4	6 (4)
loss	1	4	10	17	16 (14)
(1'*S*)-Tralocythrin Applied					
(1'*S*)-tralocythrin	99	15	22	17	17 (91)
cypermethrin	0	29	40	25	38 (6)
(α*R*)-cypermethrin	0	2	0	0	0 (2)
trans-cypermethrin[c]	0	14	11	10	21 (0)
apolar unknowns	0	10	10	6	8 (1)
polar unknowns	0	12	6	10	3 (0)
residue	0	9	5	12	4 (0)
loss	1	9	6	20	9 (0)
Cypermethrin Applied					
cypermethrin	100	63	81	64	48 (53)
(α*R*)-cypermethrin	0	1	0	0	0 (1)
trans-cypermethrin	0	28	13	10	9 (0)
apolar unknowns	0	6	5	5	5 (13)
polar unknowns	0	1	0	6	13 (7)
residue	0	1	1	5	9 (8)
loss	0	0	0	10	16 (18)

[a] Average of duplicate experiments. [b] Recoveries for plants held in the dark. [c] Includes ~10% 1'-bromodeltamethrin from tralomethrin and 0.1–1% 1'-bromocypermethrin from tralocythrin.

× HA and CT × CAA) to separate all relevant esters and leave apolar unknowns at or near the origin. Ether extracts of Br_4CA-treated leaves were chromatographed in the TFE solvent system (direct analysis and following diazomethane treatment) and in the CA solvent system (Table I), moving all materials free of the origin.

The acetonitrile–chloroform extract (polar fraction) was chromatographed in the BAW TLC solvent system [silica gel F254, 0.25 mm, butanol–acetic acid–water (6:1:1)]. Individual products recovered by extracting the silica gel with acetone were subjected to possible hydrolysis with β-glucosidase [method of Gaughan and Casida (1978)] or 6 N hydrochloric acid (6 h, 70 °C) with product identification by TLC in the TFE solvent system.

Terms used to describe various fractions are as follows: apolar = recovered in ether extracts; apolar unknowns = remaining at or near the origin on TLC of ether extracts; polar unknowns = recovered in chloroform–acetonitrile extract; residue = remaining in the residue after the ether and chloroform–acetonitrile extracts; loss = portion not accounted for in the fractions analyzed.

RESULTS

Recovery of Tralomethrin and Tralocythrin. Under the experimental conditions the residues of (1'*RS*)-tralomethrin and -tralocythrin are rapidly degraded on cotton leaves (Table II) and of (1'*S*)-tralomethrin and -tralocythrin on bean leaves (Table III). Tralocythrin appears to be somewhat more stable than tralomethrin (Table III). Light is essential for rapid degradation of tralomethrin and tralocythrin based on recoveries after 4 days of exposure on bean leaves in the light and in the dark (Table III). TLC of the recovered tralomethrin and tralocythrin revealed no isomerization to the corresponding trans esters.

Debromination of Tralomethrin to Deltamethrin and of Tralocythrin to Cypermethrin. The initial disappearance of tralomethrin and tralocythrin is attributable primarily to debromination to deltamethrin and cypermethrin, respectively, which are the major products for at least 10 days on cotton leaves (Table II) and 3 days on bean leaves (Table III). The ease of debromination is indicated by the ~5% conversion values to deltamethrin and cypermethrin in the "zero-time" samples from cotton (Table II).

Dehydrobromination of Tralomethrin to 1'-Bromodeltamethrin and of Tralocythrin to 1'-Bromocypermethrin. Dehydrobromination is a minor reaction of tralomethrin (2–3%) and an almost insignificant reaction of tralocythrin (Tables II and III). Quantitation is difficult because of the similar TLC properties of the 1'-bromo compounds and the corresponding trans isomers of deltamethrin and cypermethrin (Table I).

1*R*-Cis → 1*RS*-Cis,Trans and α*S* → α*RS* Isomerizations. The cis/trans isomerization is a major reaction of deltamethrin and cypermethrin applied directly or derived from debromination of tralomethrin and tralocythrin (Tables II and III). Both the debromination and isomerization reactions are primarily photochemical processes. Isomerization at the benzylic position occurs very slowly and is probably not a photochemical reaction (Tables II and III).

Fate of Tralomethrin Acid Moiety on Cotton Leaves. Br_4CA undergoes rapid debromination to Br_2CA with subsequent isomerization to *trans*-Br_2CA, which in turn is converted to more polar materials (Figure 1; Table IV).

Unknowns and Other Fractions. The apolar unknowns, polar unknowns, and residue and loss fractions generally increase with time after treatment and show no consistent differences between tralomethrin and tralocythrin (Tables II and III), the tetrahaloethyl and dihalovinyl compounds (Tables II and III), and the acid-^{14}C- and alcohol-^{14}C-labeled preparations (Table II). The polar unknown fraction is particularly large with Br_4CA application (Table IV).

The polar unknowns are separated in the BAW solvent system (R_f 0.36 from each of [*acid*-^{14}C]- and [*alcohol*-^{14}C]tralomethrin and [^{14}C]Br_4CA and 0.30 from the latter two compounds). These polar products appear to consist at least in part of Br_2CA, *trans*-Br_2CA, and PBacid (3-phenoxybenzoic acid, Figure 1) conjugates since these acids are liberated on HCl hydrolysis but not on β-glucosidase treatment. Low yields and inefficient conjugate cleavage precluded their characterization. Similar radiocarbon losses occur with each ester and each labeling position examined.

DISCUSSION

Figure 1 gives the products detected on cotton and/or bean foliage treated with tralomethrin, tralocythrin, deltamethrin, cypermethrin, and Br_4CA. Degradation involves photochemical, chemical, and metabolic processes and a variety of reactions, i.e., debromination, dehydro-

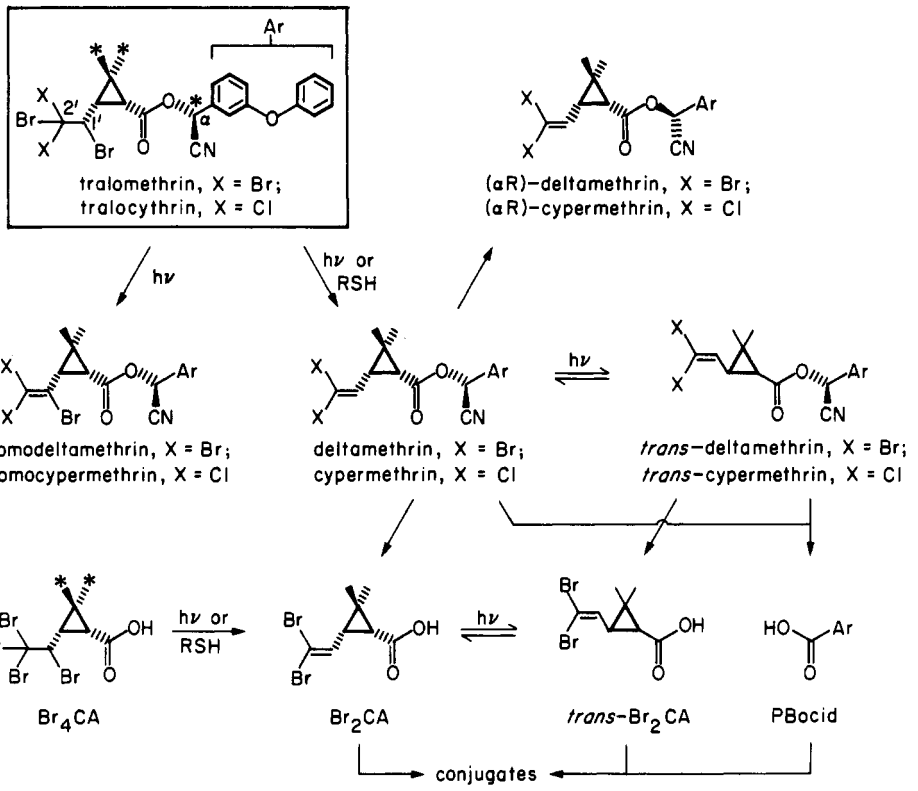

Figure 1. Degradation products from tralomethrin and tralocythrin on cotton and bean foliage and from the acid moiety of tralomethrin on cotton foliage. Asterisks designate positions of ^{14}C labels.

Table IV. Recovery of [^{14}C]-*cis*-2,2-Dimethyl-3-(1,2,2,2-tetrabromoethyl)cyclopropanecarboxylic Acid and Its Labeled Derivatives Up to Twenty Days after Application to Cotton Leaves

	radiocarbon recovery, %,[a] at indicated day			
compound recovered	0	5	10	20
Br_4CA	99	0	0	0
Br_2CA	0	12	5	2
trans-Br_2CA	0	8	3	1
polar unknowns	0	32	19	35
residue	0	6	7	6
loss	1	42	66	56

[a] Recoveries and yields are the average of duplicate treatments.

bromination, isomerization, ester cleavage, oxidation, and conjugation.

Photochemical reactions are the primary mechanism for degradation of tralomethrin and tralocythrin on plant foliage. These compounds undergo much more rapid debromination on bean leaves in the light than in the dark, and dehydrobromination and trans-isomer formation do not occur in the dark [see also Ruzo and Casida (1981)]. Br_4CA quickly debrominates to Br_2CA, which isomerizes to *trans*-Br_2CA, probably as photochemical processes. The finding of similar losses from each ester and labeling position suggests that a major mechanism of residue dissipation involves debromination where applicable and then volatilization of deltamethrin or cypermethrin per se.

The present study examines tralomethrin and tralocythrin without stabilizers and is therefore not directly applicable to formulations with added dyes or other stabilizers (Martel, 1980). Photostabilizers should retard the rate of debromination and dehydrobromination and subsequent reactions dependent on these photoprocesses.

The $\alpha S \rightarrow \alpha RS$ isomerization of deltamethrin and cypermethrin is very minor on cotton and bean foliage (this study) as previously noted with the $\alpha R \rightarrow \alpha RS$ conversion of fenvalerate on dry leaf residue or in insects (Nakayama et al., 1978). This isomerization of deltamethrin and cypermethrin is probably not a photochemical or metabolic reaction since it occurs in both the light and the dark and the benzylic methine proton exchanges readily in basic solutions (Roussel-Uclaf, 1978b) and slowly in methanol (Ruzo et al., 1977).

Although photodebromination is the most significant process in degradation of tralomethrin and tralocythrin on plants, metabolic or thiol-mediated processes are probably also involved (Ruzo et al., 1981). The ester-cleavage and conjugation reactions probably parallel those previously defined with deltamethrin (Ruzo and Casida, 1979), cypermethrin (Wright et al., 1980), and related pyrethroids in plants (Roberts, 1981).

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Synthesis of Homologues of 4,5-Dihydroxy- and 4-Hydroxy-5-oxohexanoic Acid γ-Lactones

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Several substituted γ-lactones have been found in wines. Synthesis of higher molecular weight homologues of these lactones was necessary for verification of their presence in fermentation systems. The reaction of allylic acetates, $RCHOAcCH{=}CH_2$, with manganic acetate in acetic acid and acetic anhydride to form γ-substituted γ-butyrolactone acetates, where R was methyl, ethyl, isopropyl, isobutyl, or *sec*-butyl, is described. The reaction was not successful with allylic ketones, with allylic alcohols, or when R was benzyl. Basic hydrolysis of the lactone acetates gave hydroxy lactones that were oxidized with Collins reagent to keto lactones. The lactone acetates and hydroxy lactones were separable by GC into diastereomeric pairs. The hydroxy lactones, where R = benzyl, were prepared by cis and trans hydroxylation of 6-phenyl-*trans*-4-hexenoic acid. Tentative assignments of *R* and *S* configurations in the diastereomeric pairs were made by comparison of spectral data and relative GC retention data with previously obtained data for the stereospecifically synthesized hydroxy lactones where R was methyl.

In earlier investigations in our laboratories two optically active diastereomers of 4,5-dihydroxyhexanoic acid γ-lactone (Figure 1: **1a**, 4*R*,5*R* or 4*S*,5*S*; **2a**, 4*R*,5*S* or 4*S*,5*R*) (Muller et al., 1969) and 4-hydroxy-5-oxohexanoic acid γ-lactone (Figure 1: **3a**) (Augustyn et al., 1971) were identified as constituents of various wines. We have proposed (Muller et al., 1973) a biochemical pathway for the formation of these lactones from glutamic acid. This pathway also predicts the likely presence in fermentation systems of the additional lactones **1b–f**, **2b–f**, and **3b–f**, shown in Figure 1, from condensations involving α-keto acids known to be present in such systems. The identification of some of these additional lactones from wines would lend support to the validity of the proposed pathway. So that any of these additional γ-lactones could be detected and identified, the synthesis of the lactones indicated in Figure 1 was necessary. In this paper we report the preparation and characterization of these compounds.

γ-Lactones have been identified as important constituents of the aromas and flavors of many natural substances. γ-Heptalactone, which has a strong coconut-like odor, has been identified in sherry wine (Fagan et al., 1982), peach (Sevenants and Jennings, 1964), passion fruit (Winter and Klöti, 1972), and strawberries (Drawert et al., 1973). γ-Octalactone, which also has a coconut-like odor, has been found in sherry (Fagan et al., 1982), apricots (Tang and Jennings, 1967), peaches (Sevenants and Jennings, 1964), passion fruit (Murray et al., 1972), and grapes (Ramshaw and Hardy, 1969). γ-Nonalactone was identified in sherry (Fagan et al., 1982) and in other wines (Brander et al., 1980; Schreier and Drawert, 1974; Schreier et al., 1976). The synthesis and characterization of the substituted γ-lactones indicated in Figure 1 made possible the identification as sherry constituents of 4-hydroxy-5-oxoheptanoic acid γ-lactone (Figure 1: **3b**) and the tentative identification of an additional 4,5-dihydroxy acid γ-lactone with an MS extremely similar to that of 4,5-dihydroxyheptanoic acid γ-lactone (Figure 1: **1b**) (Fagan et al., 1982).

In 1968, Heiba et al. and Bush and Finkbeiner reported that substituted alkenes reacted with manganic acetate to produce substituted γ-lactones. The reaction conditions utilized by the two groups were very similar. Manganic acetate dihydrate and the alkene were dissolved in acetic acid and refluxed until the dark brown color of the Mn(III) disappeared. Heiba et al. (1968) added potassium acetate to raise the reflux temperature to 135 °C, while Bush and Finkbeiner (1968) reported that the addition of acetic anhydride dramatically shortened reaction times and increased yields. We were successful in preparing most of the γ-lactones indicated in Figure 1 using essentially the conditions of Bush and Finkbeiner.

EXPERIMENTAL SECTION

Infrared spectra were measured with a Beckman IR-8 on neat compounds. The ^1H NMR spectra were determined with either a Varian EM-360 or a Varian A-60A spectrometer by using tetramethylsilane as an internal standard. Mass spectra were determined on a Finnigan 3200 quadrupole instrument connected with a Finnigan 6000 data system and accurate masses on a Du Pont 21-492B sector mass spectrometer.

Preparative GLC separations were made on a Loenco Model 70 dual column, dual thermal conductivity chromatograph containing two 3 m × 6.35 mm o.d. stainless steel columns, one packed with 10% FFAP on 80–100-mesh Gas-Chrom Q and the other with 5% SE-30 on 60–80-mesh Gas-Chrom Q. Helium was used as the carrier gas at 75 mL/min on the FFAP column and 55 mL/min on the SE-30 column. The injector temperature was 240 °C and the detector temperature was 250 °C. Samples were trapped from the GLC in 30-cm glass capillary tubes cooled with dry ice. Samples for spectral analyses were purified by one or two passes through the SE-30 column.

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