

In 1961 a total of 35,174 tons of red ripe pimiento fruits were processed in the southeastern U.S. These fruits contained approx 1,456 tons of seeds (fresh wt). From the data in the present report and others (2,4), meal from the dried seeds would be expected to contain approx 20% oil while the remaining dry matter would contain approx 29% protein, 29% fiber, 36% NFE and 6% ash.

## ACKNOWLEDGMENTS

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## Degradation of Monocarboxyls from Autoxidizing Lipids<sup>1</sup>

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### Abstracts

In an attempt to account for carbonyls found in oxidized lipid systems, but not theoretically predicted from the decomposition of lipid hydroperoxides, a member from each of the monocarbonyl classes commonly observed in oxidizing lipids was oxidized at 45°C in a Warburg apparatus and the carbonyl products studied. The carbonyl compounds used were *n*-nonanal, *n*-non-2-enal, *n*-hepta-2,4-dienal and *n*-oct-1-en-3-one. Nonanal was relatively stable to oxidation and was oxidized to nonanoic acid. Oct-1-en-3-one did not absorb oxygen during a 52-hr period; however, the unsaturated aldehydes oxidized at faster rates than methyl linoleate or linolenate. Non-2-enal upon absorption of 0.5 mole of oxygen was oxidized almost quantitatively to non-2-enoic acid. Hepta-2,4-dienal was polymerized at 0.5 mole of oxygen uptake. In addition both of the unsaturated aldehydes produced shorter chain mono- and dicarbonyls as oxidative degradation products. The identification of these compounds helps to explain the presence of carbonyls in oxidizing lipids and model systems that are not accountable through the decomposition of theoretically predictable isomeric hydroperoxide esters. The relatively large yield of malonaldehyde from the oxidized dienal suggests that these carbonyls may serve as a major source of malonaldehyde in oxidizing diene esters. Significant quantities of malonaldehyde are not observed in methyl linoleate until late stages of oxidation, and the dienals formed through degradation of primary hydroperoxides may in turn oxidize to give malonaldehyde.

### Introduction

THE LIST OF CARBONYL compounds derived from autoxidizing lipids and model systems has become extensive. In attempting to explain their origin, most investigators have repeatedly referred to fatty acid hydroperoxides as immediate precursors (1-5). However, there are a number of carbonyl compounds reported in the literature whose origin from oxidized lipid systems cannot be explained by generally accepted fatty acid hydroperoxide decomposition mechanisms. In attempting to account for these compounds, some of which are found in relatively high concentration it seemed feasible to examine other possible substrates that are readily oxidized and that might account for some of the carbonyls observed in autoxidizing lipids.

The findings reported herein deal with the monocarbonyls which are themselves initial degradation products of lipid hydroperoxides.

### Experimental

A member from each of the major monocarbonyl classes that are commonly observed in oxidizing lipids was selected for the study. Those compounds selected were *n*-nonanal, *n*-non-2-enal, *n*-hepta-2,4-dienal and *n*-oct-1-ene-3-one. Oxidation rates, peroxide formation, 2-thio-barbituric acid reactants and carbonyl production were studied and compared with methyl esters of linoleic and linolenic acids oxidized under identical conditions.

**Materials.** Nonanal and non-2-enal were obtained commercially. The purity of nonanal was >98% as determined by gas chromatography. Non-2-enal was purified to 99.5% by preparative scale gas chromatography. Hepta-2,4-dienal was synthesized by the procedure of Pippen and Nonaka (6) and purified by fractional distillation at 4 mm Hg. Purity by gas chromatography was 94%. Oct-1-en-3-one was prepared from oct-1-en-3-ol by the method of Brown and Carg (7). Oct-1-en-3-ol was prepared according to Crabalona (8). The vinyl ketone contained 12% of the alcohol after fractional distillation and was not purified further. Methyl linoleate and methyl linolenate were obtained from the Hormel Foundation and used without further purification.

Ethylene chloride was distilled and stored over potassium carbonate. Celite 545 was dried for 24 hr at 160°C. Seisorb 43 was activated for 49 hr at 400°C. Nitromethane and chloroform were made carbonyl free according to the method of Schwartz and Parks (9).

**Autoxidation of Carbonyls.** Duplicate samples of 0.2-0.5 g of the aforementioned carbonyls were weighed into Warburg flasks. After connecting the flasks to manometers, the samples were equilibrated for 15 min at 45°C in a nitrogen atmosphere and then oxidized in an oxygen stream. Oxygen uptake was measured at 15-min intervals and the rates of oxygen uptake vs. time were plotted on regular graph paper. Measurement of the areas under the resulting curves enabled calculation of total oxygen uptake. Manometric techniques as described by Umbreit et al. (10) were employed. The peroxide values (11), 2-thio-barbituric acid (TBA) reactants (12), and equivalents of acid were determined when oxygen uptake reached approximately 0.25 and 0.5 mole/mole of carbonyl.

**Analysis of Carbonyl Products.** Samples of the oxidized carbonyls (0.01-0.02 g) were added to 50 ml 5N HCl saturated with 2,4-dinitrophenylhydrazine (re-

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TABLE I  
 Analysis of Autoxidizing Monocarbonyl Compounds

Compound oxidized	Oxygen uptake moles/mole compound	Malonaldehyde moles x 10 <sup>2</sup> /mole compound	Peroxides equiv./mole compound	Acid equiv./mole compound
Non-2-enal	0.35	0.18	0.08	0.70
Non-2-enal	0.46	0.17	0.05	1.00
Hepta-2,4-dienal	0.26	0.92	0.09	0.37
Hepta-2,4-dienal	0.53	1.18	0.56	0.07
Oct-1-en-3-one	0.00	0.00	0.00	0.00
n-Nonanal	0.18	0.00	0.01	0.28

ferred to as DNP) and 50 ml carbonyl-free ethanol. After 24 hr, the DNP-hydrazine derivatives were extracted with five 20-ml aliquots of chloroform and the extracts were pooled. Chloroform was removed at reduced pressure to yield a dry residue of derivatives. The derivatives were separated into classes according to Schwartz et al. (13). After elution of the monocarbonyl classes, the DNP-osazones were eluted with nitromethane-ethylene chloride (1:4). Each monocarbonyl class was separated by the hexane-nitromethane-Celite partition column of Day et al. (14). Chain lengths of the monocarbonyl derivatives in each class were determined by paper (15) and thin layer chromatography (TLC) (16).

The DNP-osazones of dicarbonyls were separated by procedures described by Schwartz (17). Identity of derivatives was ascertained by co-chromatography of the unknown and authentic on the Schwartz column and by TLC (18). Melting points and IR spectra from micro-KBr pellets were used as additional evidence when sample size permitted.

The quantity of individual carbonyl derivatives was estimated by measuring the absorbance of chloroform solutions at 358, 373, 390 and 393  $\mu$  for alkanals, alk-2-enals, alk-2,4-dienals and  $\alpha$ -keto alkanals, and calculating the moles of derivatives from previously reported molar absorptivity values of Wyatt and Day (19).

*Autoxidation and Analysis of the Methyl Esters.* Methyl linoleate and linolenate were oxidized according to the procedures used for the carbonyls. The volatile monocarbonyls were isolated and characterized by procedures described previously (19).

### Results and Discussion

The oxygen uptake, and the corresponding amount of malonaldehyde, peroxides and acid equivalents for the oxidized monocarbonyls are given in Table I. Of interest is the low yield of malonaldehyde from non-2-enal, as compared to the dienal. The acid equivalents shown in the Table indicated that the enal was oxi-

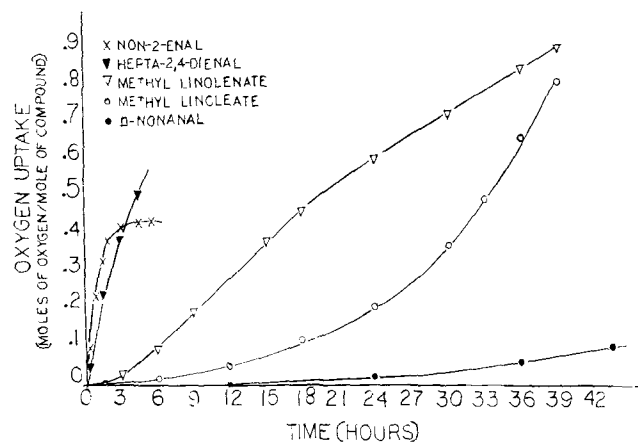


Fig. 1. Rate of oxygen uptake during autoxidation at 45°C of monocarbonyls and methyl esters of linoleic and linolenic acids.

 TABLE II  
 Carbonyl Compounds in Autoxidized Non-2-enal and Hepta-2,4-dienal

Compound	Non-2-enal		Hepta-2,4-dienal	
	Sample A <sup>a</sup> moles x 10 <sup>2</sup>	Sample B <sup>b</sup> moles x 10 <sup>2</sup>	Sample C <sup>c</sup> moles x 10 <sup>2</sup>	Sample D <sup>d</sup> moles x 10 <sup>2</sup>
Ethanal	1.50	2.80	2.70	1.97
Propanal	0.65	0.19	4.19	2.85
Butanal			0.75	0.56
Heptanal	1.20	0.55		
Octanal	3.00	0.24		
Total monocarbonyls	6.35	3.78	7.65	5.38
Glyoxal	0.70	0.09	0.22	0.30
$\alpha$ -Ketopentanal			0.17	0.31
$\alpha$ -Ketoheptanal			0.05	0.06
$\alpha$ -Ketoheptanal	0.05	0.04	0.04	0.04
$\alpha$ -Ketoheptanal	0.62	0.43		
$\alpha$ -Ketononanal	0.08	0.04		
<i>trans</i> -but-2-en-1,4-dial			0.36	0.96
Malonaldehyde	0.02	0.02	0.09	0.12
Total carbonyls	7.82	4.40	8.58	7.17

<sup>a</sup> 0.35 M oxygen uptake/mole aldehyde.

<sup>b</sup> 0.46 M oxygen uptake/mole aldehyde.

<sup>c</sup> 0.26 M oxygen uptake/mole aldehyde.

<sup>d</sup> 0.53 M oxygen uptake/mole aldehyde.

dized, almost quantitatively, to non-2-enoic acid. This was confirmed by comparison of the gas chromatographic properties of the oxidation product with authentic non-2-enoic acid, by comparison of IR spectra and by preparation of the *p*-bromophenacyl esters; mp 74–75°C, unknown; 74.5–75.5, authentic.

Oxygen uptake for non-2-enal was virtually zero after 0.5 mole was absorbed (see Fig. 1). Hepta-2,4-dienal had reached a stage of polymerization by the time 0.5 mole of oxygen was absorbed. In the case of hepta-2,4-dienal, the observed decrease in acid equivalents is difficult to explain unless one can assume the carboxyl group was not titratable in the polymers. The vinyl ketone showed no signs of oxygen uptake during 52 hr oxidation. Nonanal also was relatively stable and required 52 hr to absorb 0.18 mole of O<sub>2</sub>. The saturated aldehyde, when oxidized, appears to yield mainly the acid.

The relative susceptibilities of the three classes of aldehydes to oxidative attack and their comparison to the oxidation rates of the methyl esters is illustrated in Figure 1. No induction periods were noted for the  $\alpha,\beta$ -unsaturated aldehydes and it is noteworthy that these compounds are significantly less stable than the saturated aldehyde and the esters. Most quantitative studies (19,20,21) on oxidizing lipids have shown the alkanal class to predominate. The foregoing data suggests that the alkanals accumulate due to their high stability and to the rapid degradation of unsaturated aldehydes to give saturated aldehydes, acids, etc. (see Table II). Such conditions could explain the rather peculiar quantitative distribution of carbonyls observed by Wyatt and Day (19) during the oxidation of salmon oil.

The resistance of oct-1-en-3-one to oxidation may explain its prominence in the early stages of autoxidation of certain lipid systems (22). Since the conen of the various carbonyls will depend upon both formation and degradation rates, the vinyl ketones could make their most significant contribution during early stages of oxidation. The metallic defect attributed to these compounds in dairy products usually is observed at early oxidation stages, (22).

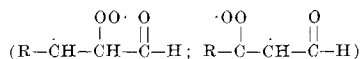
Previous investigators (23,24) have reported that oxidized alk-2-enals and alk-2,4-dienals react with TBA to form the malonaldehyde pigment. The quantitative data in Table I show that the dienal yields approx ten times as much malonaldehyde as the enal. These data suggest that the dienal, in particular, could serve as a malonaldehyde precursor in oxidized lipids and that it may be the major source of malon-

aldehyde in the case of diene esters that give a significant TBA reaction only at late stages of oxidation (25).

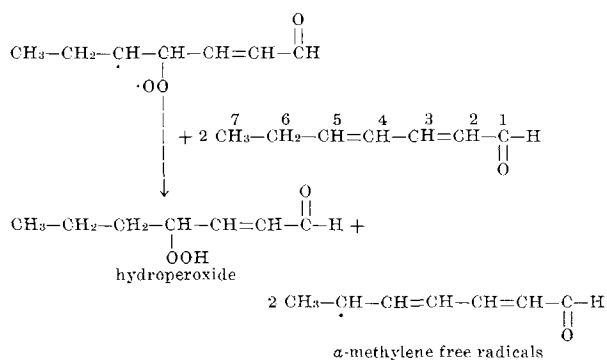
The qualitative and quantitative composition of the carbonyls from oxidized non-2-enal and hepta-2,4-dienal is given in Table II. All of the alkanals that were identified have been isolated from oxidized lipids or fatty acids. Among those listed, *n*-butanal and *n*-heptanal are difficult to rationalize from the more common unsaturated acids by generally accepted oxidation mechanisms. *n*-Butanal has been found in oxidized linolenate (21,26) and its origin would appear to be hepta-2,4-dienal; the latter is a hydroperoxide degradation product of the ester. Similarly, where *n*-heptanal has been observed, non-2-enal also is found (21) and it could serve as the precursor. Analogous mechanisms for the oxidation of other unsaturated aldehydes will yield similar compounds.

Glyoxal and  $\alpha$ -keto octanal were the major dicarbonyls isolated from oxidized non-2-enal while *cis*-but-2-en-1,4-dial was in highest concn in hepta-2,4-dienal. The dicarbonyl fraction from oxidized lipids has not been extensively studied. Schepartz and Daubert (27) reported *cis*-but-2-en-1,4-dial in oxidized soybean oil and Forss et al. (28) obtained tentative evidence for  $\alpha$ -keto octanal in oxidizing milk fat. Many workers (27,29) have postulated dihydroperoxides of unsaturated esters as precursors of dicarbonyls; however, our data show that the dicarbonyls can be derived through oxidation of the initially formed unsaturated monocarbonyls.

Probably a key mechanism in the oxidation of hepta-2,4-dienal is one similar to that proposed by Allen and Kummerow (30) for eleostearate. This involves oxygen attack at the double bonds to give two diradicals:



Polymerization is a major reaction of the radicals and this was observed for heptadienal. To explain the observed monomeric compounds the diradical initially formed probably abstracts hydrogen from two other molecules of heptadienal as follows:



According to the above scheme, hydroperoxides are formed on carbons two, three, four, five and six. Decomposition of the hydroperoxides would yield: carbon 2 = hex-3-enal or glyoxal; carbon 3 = pent-2-enal or malonaldehyde; carbon 4 = butanal or but-2-en-1,4-dial; carbon 5 = propanal or pent-2-en-1,5-dial; carbon 6 = ethanal or hex-2,4-diene-1,6-dial. Additionally, chain cleavage at the indicated carbon would give free radicals which would be proton seekers and  $\alpha$ -methylene chain propagators. In the course of the reaction, the free radicals would yield carbonyls or hydrocarbons. The reaction scheme shown above would account for the compounds isolated from hepta-2,4-

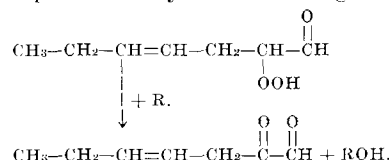
TABLE III  
Theoretically Predictable and Identified Monocarbonyls from Autoxidized Methyl Linoleate and Linolenate

Carbonyl compound	Methyl linoleate	Methyl linolenate
<i>n</i> -Alkanals		
C <sub>2</sub> .....	I <sup>a</sup>	T <sup>b</sup> I
C <sub>3</sub> .....	I	TI
C <sub>4</sub> .....		T
C <sub>5</sub> .....	TI	.....
C <sub>6</sub> .....	TI	.....
C <sub>7</sub> .....	I	.....
Alk-2-enals		
C <sub>1</sub> .....	.....	TI
C <sub>3</sub> .....	.....	TI
C <sub>5</sub> .....	.....	TI
C <sub>7</sub> .....	TI	I
C <sub>8</sub> .....	TI	I
C <sub>9</sub> .....	TI	.....
Alk-2,4-dienals		
C <sub>1</sub> .....	.....	I
C <sub>7</sub> .....	.....	TI
C <sub>8</sub> .....	.....	TI
C <sub>9</sub> .....	I	I
C <sub>10</sub> .....	TI	.....
C <sub>11</sub> .....	T	.....

<sup>a</sup> I—identified.

<sup>b</sup> T—theoretical (see ref. 5).

dienal, except for the C<sub>5</sub>, C<sub>6</sub> and C<sub>7</sub>  $\alpha$ -keto-alkanals. These compounds appeared in low concn, which limited the evidence for their identification to UV spectra and chromatographic behavior. Neither criterion would readily distinguish an isolated double bond so that the aforementioned compounds could exhibit such structure. These compounds could result from heptadienal by the following mechanism:



In the case of non-2-enal, the same mechanism would yield octanal, glyoxal,  $\alpha$ -ketononanal, heptanal and malonaldehyde from hydroperoxides on carbons 2 and 3. Rearrangements and dihydroperoxide formation are required to account for  $\alpha$ -keto-octanal and  $\alpha$ -keto-heptanal.

Table III lists the monocarbonyl compounds that can be predicted from the decomposition of the isomeric hydroperoxides of methyl linoleate and methyl linolenate as well as those carbonyls that were identified from the autoxidized esters. All of the identified monocarbonyls unaccountable by ester hydroperoxide decomposition, except oct-2-enal and the alk-2,4-dienals, can result from oxidation of the theoretically predicted unsaturated aldehydes.

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# Identification of Surface Active Agents in Admixture by Thin Layer Chromatography<sup>1</sup>

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## Abstract

The qualitative identification of the surface active agents commonly used in household detergent formulations is possible using thin layer chromatography (TLC). Successful separations have been made when the samples are spotted on Aluminum Oxide G and developed with isopropanol. A variety of specific reagents may be used to color the spots and thereby supplement the R<sub>f</sub> values as a means to identify the surfactants. The analysis can be made semi-quantitative if the separations are made using an aluminum oxide column and collecting the fractions eluted with isopropanol and methanol.

## Introduction

THE SEARCH for a quicker method of identification for the surfactants present in detergent formulations is a continuing project. Currently the analysis of a detergent is centered around the alcohol soluble portion of the formulation. This portion is subjected to instrumental and chemical testing and further separated by ion exchange chromatography to isolate the nonionic surface active agents. IR analysis of the nonionic portion will indicate the presence or absence of fatty amides by an absorption band near 6  $\mu$  which is characteristic of the amide carbonyl vibration and the presence of alkylphenol ethoxylates will be indicated by a series of bands which includes the strong C—O—C band near 9  $\mu$ . It may be possible to determine the relative concn of an alkylphenol ethoxylate by UV spectroscopy if the assumption is made that the surfactant is a particular adduct of *n* moles of ethylene oxide to a particular alkylphenol. The IR spectrum of the alcohol soluble portion is sometimes useful, but at other times limited in value because of the overlap of absorption bands of the multicomponent system. The more components present, the less positive any identification can be. Therefore, a definite need exists for a procedure which will separate completely, and give identity to, the components in a detergent mixture.

Gas chromatography, which has become a very useful analytical tool, does not lend itself to the complete separation of surface active species. However, paper chromatography has been used by Drewry (1)

in England for the qualitative identification of detergents. The anionic, cationic and nonionic agents, soaps and hydrotropes have been identified on a single chromatogram by a method of consecutive spraying. The sprays, when applied in a definite sequence, develop specific colors with the particular surfactants and thereby make their identity known. This work of Drewry's looked very promising but it required 16-18 hr for the solvent front to rise the necessary 20 cm to develop the chromatogram (solvent system of *t*-butanol-ammonium hydroxide-water).

Separations of a variety of mixtures had been reported in 30 min time when TLC (2-7) was used. In addition to speed, an additional advantage of this technique is that a TLC chromatoplate could be sprayed with sulphuric acid and heated to char any organic material on the plate. This would give a rapid indication of the success of the separation and give an idea as to the number of components in a mixture.

Since TLC, where applicable, gives a rapid separation of multicomponent systems and, since techniques used with paper chromatograms to develop colors with various components of detergent formulations were known, we decided to attempt the separation and identification of detergent formulations by thin layer chromatography.

## Qualitative Identification

### Reagents

- Aluminum Oxide G (according to Stahl)
- Isopropanol
- Pinacryptol Yellow (K & K Laboratories, Inc., 177-10 93rd Avenue, Jamaica, N.Y.)
- Iodine
- Surface Active Agents (commercial samples)

### Apparatus

- Comprehensive TLC Apparatus (Brinkman Instruments, Inc., 115 Cutter Mill Road, Great Neck, Long Island, N.Y.)
- UV Light

*Preparation of Plates.* Both 5 x 20 cm and 20 x 20 cm glass plates were cleaned with concd chromic acid, rinsed with water and then wiped dry. A 1:2 slurry of Aluminum Oxide G and water was prepared and stirred until it was uniform and free of entrapped air. A Desaga applicator was used to draw down a 0.25-mm layer of the aluminum oxide on the plates. The

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