Degradative Reactions of Decadienoate Esters[1]

D. E. HEINZ[2] and W. G. JENNINGS, Department of Food Science and Technology, University of California, Davis, California

Abstract

Methyl and ethyl esters of decadienoic acid, which are normal constituents of the Bartlett pear, react with oxygen in the presence of light to produce n-hexanal, and the methyl or ethyl 4-oxybutenoate. The products were separated by gas chromatography, and identified by melting points, infrared spectroscopy, and/or the formation of derivatives. Possible reaction mechanisms are discussed.

Introduction

Because of their association with off-flavors, the oxidative reactions producing carbonyl compounds in lipid systems are of considerable interest. Fatty acid hydroperoxides have been cited as intermediates in some of these reactions (8). Lillard and Day (12) and Cobb and Day (2) pointed out that a number of carbonyl compounds derived from fatty acids and reported in the literature could not be satisfactorily accounted for by fatty acid hydroperoxide decomposition mechanisms. In studies of the continued oxidation of carbonyl compounds initially produced by oxidation of lipid hydroperoxides, these authors found propanal the principal monocarbonyl, and 2-butendial the principal dicarbonyl resulting from the oxidation of 2,4-heptadienal. Their results can be explained by postulating that the autoxidation involved oxygen attack of the double bond furthest removed from the carbonyl group, followed by cleavage to the aldehydes.

This study concerns the autoxidation of certain volatile components of Bartlett pear essence, the 2-4-decadienoate esters, to produce hexanal and the appropriate 4-oxybutenoate ester.

Methods and Procedure

Decadienoate Esters

The methyl and ethyl esters of *trans*:2-cis:4-decadienoic acid were isolated by gas chromatography from adsorption essences of Bartlett pear (5,7). Their structure was confirmed by comparing their infrared spectra with previously reported spectra (3) and synthesis (9).

Gas Chromatography

Initial separations employed an 18 ft x ¼ in. column containing 10% Triton X-305 on 60–80 mesh Gas Chrom Q. Fractions isolated from this column were resolved to single compounds using 10 ft x ⅛ in. columns containing 15% Apiezon L on 60–80 mesh HMDS treated Chromosorb W, and/or 10% Carbowax 20 M on 40–60 mesh Gas Pack F. Equipment and techniques of collection were the same as described previously (6).

Spectrometric Analyses

Infrared spectra were determined with a Beckman Model IR 5 spectrophotometer utilizing a Beckman beam condenser. Spectra were taken on thin films between two NaCl plates, in CIC type C micro cavity cells (0.05 mm pathlength), or on solutions in spectral grade CCl_4.

Ultraviolet spectroscopy utilized a Beckman DB spectrophotometer, and 10 mm silica cells containing spectral grade isooctane solutions.

Derivatives

2,4-Dinitrophenylhydrazone (DNPH) derivatives of the aldehydic oxidation products were prepared by passing the eluant gas from a chromatograph through an aqueous solution of 1 N HCl saturated with 2,4-dinitrophenylhydrazine. The crystals were collected by centrifugation and recrystallized from ethanol-water. Acid derivatives of the aldehydes were obtained by exposing thin films of the aldehyde to air at room temperature. The resulting acids were separated by gas chromatography.

Results and Discussion

Figure 1 compares the chromatographic pattern of a fresh Bartlett pear essence (bottom) and an essence exposed to air and light for one week at room temperature (top). The major differences evidenced by the sample exposed to air and light are increases in the peaks 21 and 24, and the appearance of a large, new peak (attenuation X8) between 9 and 10. When the isolated peak 37, which contains methyl *trans*:2-*trans*:4-decadienoate and ethyl *trans*:2-cis:4-decadienoate (5,6) is chromatographed after exposure to light and air, these same three products appear, indicating that their formation is related to cleavage of the 2,4-decadienoates. Two of these same aldehydic oxidation products are formed by exposing peak 36 (methyl trans:2-cis:4-decadienoate) or peak 39 (ethyl *trans*:2-*trans*:4-decadienoate) to air and light. The decadienoates do not degrade at room temperature if either air or light is excluded.

The oxidation product which appears between peaks 9 and 10 has a retention which agrees with that of n-hexanal, and the acid produced by its oxidation has a retention and infrared spectrum in agreement with those of n-hexanoic acid. The DNPH of the aldehyde exhibited a melting point of 102–102.5C; that of the authentic n-hexanal prepared in the same manner melted at 103C.

Peaks 21 and 24 are methyl and ethyl 4-oxy-*trans*-butenoate, respectively. The white solid methyl oxy-ester, λ_{max} 215 mμ in methanol, melted at 36–39C; the DNPH melted at 196–197C. Remband and Vessiere (15) reported a melting point of 32C for the ester, and 197–198C for the DNPH. Bohlman and Inhoffen reported a λ_{max} of 230 mμ, and melting points of 41C for the ester, and 194–196C for the DNPH. The difference in the melting points of the methyl oxy-ester may be due to the crystal structure, as that from pear was solidified from the outlet of a gas chromatograph. The ethyl 4-oxy-*trans*-butenoate was a liquid, λ_{max} 215 mμ, whose DNPH melted at 161–163C. Bohlman and Inhoffen (1) reported a λ_{max} of 230 mμ for the ester, and a melting point of 161–163C for the DNPH; Remband and Vessiere (15) reported that the DNPH melted at 164C.

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[2] Present address: Department of Chemistry, Ventura College, Ventura, California.

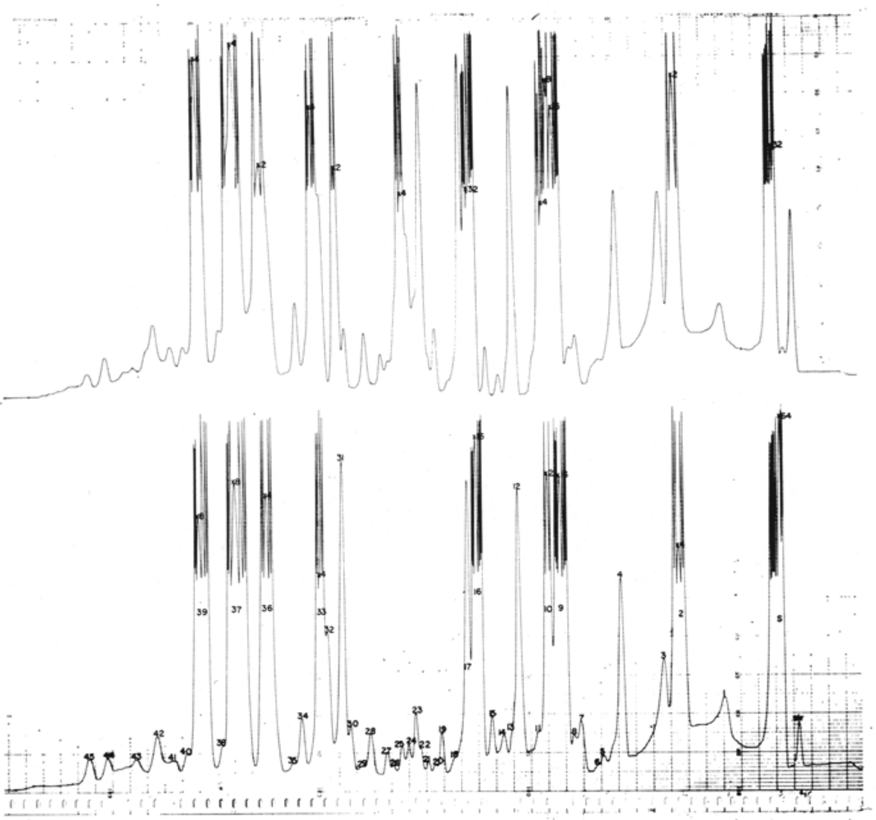


FIG. 1. Chromatograms of fresh Bartlett pear essence (bottom) and essence exposed to light and oxygen for 1 week (top). 10% Triton X-305 on 60–80 mesh Gas Chrom Q, temperature programmed 60–220C.

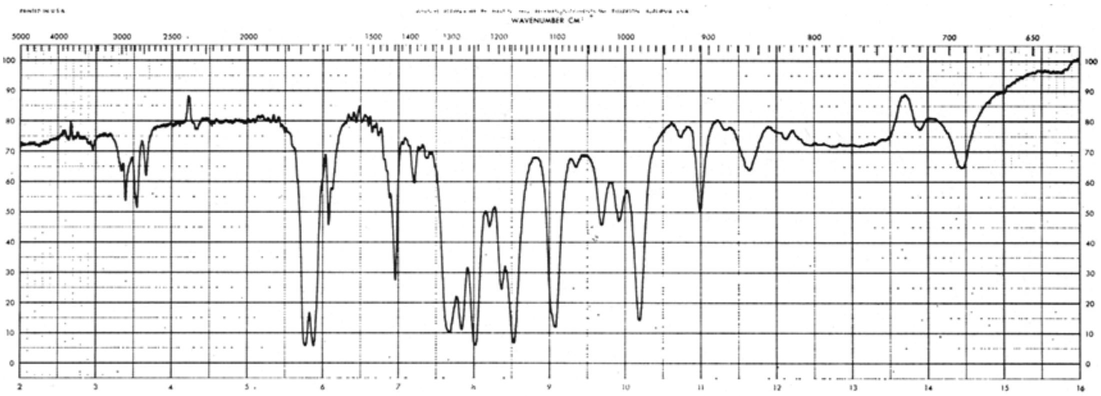


FIG. 2. Infrared spectrum of methyl-4-oxybutenoate. Ca. 2% solution in CCl_4.

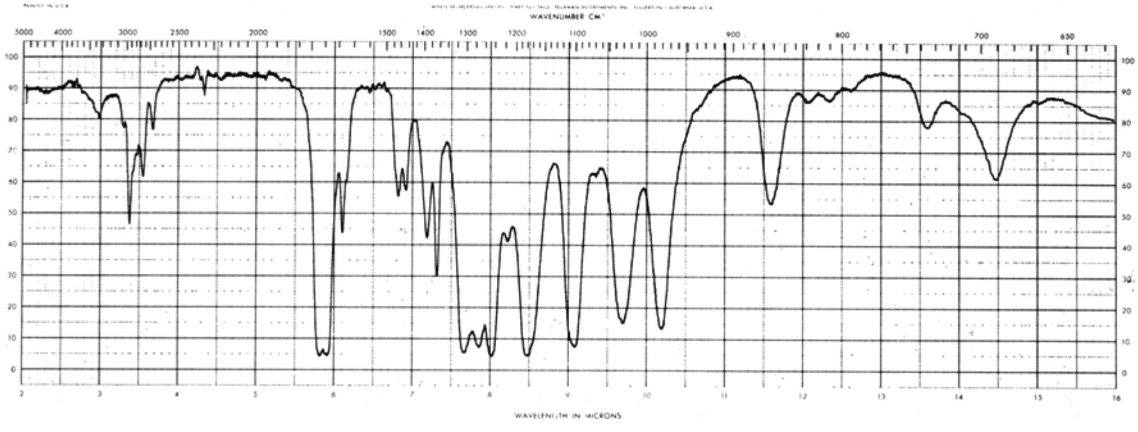


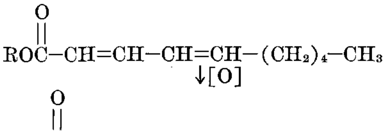
FIG. 3. Infrared spectrum of ethyl-4-oxybutenoate. Thin film.

These differences in λ_{max} can probably be attributed to the ether solvent used by Bohlman and Inhoffen. An unsubstituted double bond in conjugation with two carbonyl groups should, by calculation, absorb at 215 mμ (4).

Infrared spectral studies substantiate the structural assignments of these esters. The infrared spectrum of the methyl oxyester in CCl_4 (Fig. 2) shows absorption at 2725 cm^{-1}, indicating an aldehydic proton, and two carbonyl bands at 1725 and 1695 cm^{-1} (14). Absorptions at 1440, 1356 and 1170 cm^{-1} suggest this is a methyl ester (14). The absorptions at 1645 and 982 cm^{-1} are consistant with the *trans* double bond in a conjugated system (14). The infrared spectrum of the ethyl 4-oxy*trans*butenoate (Fig. 3) also shows the two carbonyl absorptions at 1725 and 1965 cm^{-1} and the aldehyde hydrogen at 2752 cm^{-1}. The absorption at 1642 cm^{-1} is present, indicating unsaturation, and the strong band at 983 cm^{-1} is due to the conjugated *trans* double bond. A band at 1470 cm^{-1} is consistent with the CH_2 scissor (14) of the ethyl moiety.

Air oxidation of the methyl oxy*trans*butenoate yielded a white solid which melted at 144C when collected from Apiezon L. A sample of monomethylfumaric acid, collected from Apiezon L with the same retention, melted at 144.5C.

These products of air oxidation are consistent with the following reaction sequence:



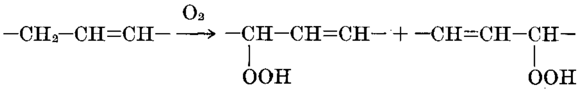
$$\begin{array}{l} RO\overset{\overset{O}{\|}}{C}-CH=CH-CH=CH-(CH_2)_4-CH_3 \\ \qquad\qquad\downarrow[O] \\ R-O\overset{\overset{O}{\|}}{C}-CH=CH-CH=O + O=CH-(CH_2)_4-CH_3 \end{array}$$

where R is CH_3- or $CH_3CH_2^-$.

The decomposition of peaks 36, 37, and 39 into the appropriate methyl and ethyl unsaturated oxyesters and hexanal is also consistent with the *trans* structure of the oxybutenoate esters, since all of the major diunsaturated esters in these peaks contain the more stable *trans*:2 double bond.

The mechanism of this reaction is not clear. The reaction requires light and oxygen, and the products resemble those of ozonolysis. However, both peaks 36 and 37 include hydroxyl esters which persist unchanged through the reaction. Peak 39 contains neither an alcohol nor water, but the aldehyde products are still formed, indicating that the alcohol moiety is not necessary to the reaction. In each case, the aldehydes cited are the only products of the reaction. These facts would appear to preclude involvement of ozone or other powerful oxidizing agents.

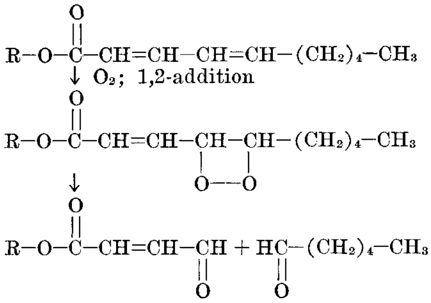
The autoxidation reaction



$$-CH_2-CH=CH- \xrightarrow{O_2} -\underset{\underset{OOH}{|}}{CH}-CH=CH- + -CH=CH-\underset{\underset{OOH}{|}}{CH}-$$

appears important to oxidative rancidity in unsaturated fats (13). Autoxidation of the active allylic methylene group of the 2,4-decadienoate esters would not lead to the oxyester products observed. This classical mechanism would oxidize the wrong carbon in the dienoate ester chain, since the allylic methylene group is in the same oxidation state in the product as it is in the starting material.

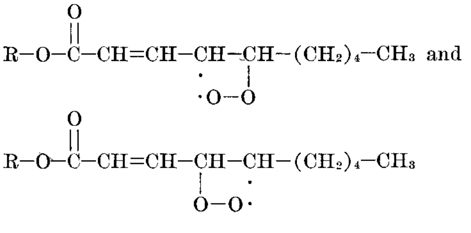
Kern and co-workers (10,11) and Privett (15) have shown that oxidation of conjugated hydrocarbons occurs by addition of oxygen to the diene systems. They suggest that both 1,2- and 1,4-addition can occur, depending upon the diene hydrocarbon. In the case of these diunsaturated, triconjugated esters, any 1,4-addition must interrupt resonance energy due to conjugation with the carbonyl group. However, 1,2-addition produces a product which posesses residual conjugation. It may be that product of 1,2-addition undergoes decomposition to form the respective aldehydes as:



$$\begin{array}{l} R-O-\overset{\overset{O}{\|}}{C}-CH=CH-CH=CH-(CH_2)_4-CH_3 \\ \downarrow O_2;\ 1,2\text{-addition} \\ R-O-\overset{\overset{O}{\|}}{C}-CH=CH-\underset{|}{CH}-\underset{|}{CH}-(CH_2)_4-CH_3 \qquad [I] \\ \qquad\qquad\qquad\qquad\quad O—O \\ \downarrow \\ R-O-\overset{\overset{O}{\|}}{C}-CH=CH-\underset{\underset{O}{\|}}{CH} + \underset{\underset{O}{\|}}{HC}-(CH_2)_4-CH_3 \end{array}$$

[I]

To account for the appearance of ketonic compounds in their system, Lilard and Day (12) proposed two diradicals, of the type



$$\begin{array}{l} R-O-\overset{\overset{O}{\|}}{C}-CH=CH-\dot{C}H-\underset{\underset{\cdot O-O}{|}}{CH}-(CH_2)_4-CH_3 \text{ and} \\ R-O-\overset{\overset{O}{\|}}{C}-CH=CH-\underset{\underset{O-O\cdot}{|}}{CH}-\dot{C}H-(CH_2)_4-CH_3 \end{array}$$

These could be produced from [I], above, by cleavage of the carbon-oxygen bond under their higher temperature conditions. In the present study, which utilized lower reaction temperatures, no ketonic products were observed.

ACKNOWLEDGMENT

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