LIPIDS IN
FOOD FLAVORS

PT.1

ACS SYMPOSIUM SERIES **558**

Lipids in Food Flavors

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Developed from a symposium sponsored
by the Division of Agricultural and Food Chemistry
at the 205th National Meeting
of the American Chemical Society,
Denver, Colorado,
March 28–April 2, 1993

American Chemical Society, Washington, DC 1994

Library of Congress Cataloging-in-Publication Data

Lipids in food flavors / Chi-Tang Ho, editor, Thomas G. Hartman, editor.

p. cm.—(ACS symposium series, ISSN 0097–6156; 558)

"Developed from a symposium sponsored by the Division of Agricultural and Food Chemistry at the 205th National Meeting of the American Chemical Society, Denver, Colorado, March 28-April 2, 1993."

Includes bibliographical references and indexes.

ISBN 0–8412–2922–8

1. Flavor—Congresses. 2. Lipids—Congresses.

I. Ho, Chi-Tang, 1944– . II. Hartman, Thomas G., 1958– III. American Chemical Society. Division of Agricultural and Food Chemistry. IV. Series.

TP372.5.L57 1994
664'.5—dc20 94–13923
CIP

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PRINTED IN THE UNITED STATES OF AMERICA

Lipids in Food Flavors

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ACS Symposium Series 558

1994 Advisory Board

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Foreword

THE ACS SYMPOSIUM SERIES was first published in 1974 to provide a mechanism for publishing symposia quickly in book form. The purpose of this series is to publish comprehensive books developed from symposia, which are usually "snapshots in time" of the current research being done on a topic, plus some review material on the topic. For this reason, it is necessary that the papers be published as quickly as possible.

Before a symposium-based book is put under contract, the proposed table of contents is reviewed for appropriateness to the topic and for comprehensiveness of the collection. Some papers are excluded at this point, and others are added to round out the scope of the volume. In addition, a draft of each paper is peer-reviewed prior to final acceptance or rejection. This anonymous review process is supervised by the organizer(s) of the symposium, who become the editor(s) of the book. The authors then revise their papers according to the recommendations of both the reviewers and the editors, prepare camera-ready copy, and submit the final papers to the editors, who check that all necessary revisions have been made.

As a rule, only original research papers and original review papers are included in the volumes. Verbatim reproductions of previously published papers are not accepted.

M. Joan Comstock
Series Editor

Preface

FLAVOR, AN IMPORTANT ATTRIBUTE OF FOOD, is of major interest to food scientists and technologists. The public's perception of food taste and quality is dependent upon food flavor. Lipids, proteins, and carbohydrates are the major sources of flavor in foods. Of the three, lipids may play the most important role in flavor. Lipids are involved in the rancidity, oxidized flavors, and stale flavors of many lipid-containing foods and are also thought to be responsible for warmed-over flavor of meat. On the other hand, lipids are responsible for the desirable flavors of many fruits and vegetables, dairy products and deep-fat fried foods.

The past symposium on Lipids as a Source of Flavor (ACS Symposium Series No. 75) was held in 1977. Since then the mechanisms of lipid oxidation have been greatly upgraded, consequences of oxygen chemistry on food quality are better understood, the interaction of lipid oxidation and Maillard reactionhas been discovered, and the analytical methodology for flavor research has advanced. The purpose of the symposium on which this book is based was to bring together scientific leaders in the field to present their latest findings on lipids in food flavors and to stimulate fellow scientists to participate in dialogues on current developments in enhancing food flavors.

We are indebted to the contributing authors for their worthy contributions. Without their dedication, expertise, and hard work, timely publication of this book would not have been possible.

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February 23, 1994

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Lipids in Food Flavors

An Overview

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This article provides a brief introduction outlining the autoxidation, singlet oxygen oxidation and lipoxygenase mediated reaction of lipids. Important flavor compounds derived from lipid oxidation including aldehydes, ketones and furans are discussed. Recent studies on the interaction between the Maillard reaction and lipid degradation leading to the formation of desirable flavor compounds of foods are also discussed.

Lipids, proteins, and carbohydrates, the major structural components of living cells are also the major source of flavor in foods.

Generally, the negative qualitities of food flavor are associated more closely with lipids than with proteins and carbohydrates. Lipids are responsible for rancidity in fats, oils and lipid-containing foods. On the other hand, lipids are also responsible for much of the desirable flavors of vegetables such as tomatoes, cucumbers, mushrooms and peas as well as many deep-fat fried foods such as French fried potatoes and fried chicken.

Formation of volatile flavor compounds from lipids is usually associated with either free radical-initiated or lipoxygenase-mediated oxidation.

Free Radical Autoxidation of Lipids.

The reaction of unsaturated lipids with oxygen to form hydroperoxides is generally a free radical process involving three basic steps (*1-2*).

Initiation:

$$RH \xrightarrow[\text{metal}]{\text{heat, light}} R\bullet + H\bullet$$

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$$\mathrm{ROOH} + \mathrm{M}^{n+} \longrightarrow \mathrm{RO}\bullet + \mathrm{M}^{(n+1)+} + \mathrm{OH}^-$$

$$\mathrm{ROOH} + \mathrm{M}^{(n+1)+} \longrightarrow \mathrm{ROO}\bullet + \mathrm{M}^{n+} + \mathrm{H}^+$$

$$2\,\mathrm{ROOH} \longrightarrow \mathrm{ROO}\bullet + \mathrm{RO}\bullet + \mathrm{H_2O}$$

Propagation:

$$\mathrm{R}\bullet + \mathrm{O_2} \longrightarrow \mathrm{ROO}\bullet$$

$$\mathrm{ROO}\bullet + \mathrm{RH} \xrightarrow{\text{slow}} \mathrm{ROOH}$$

$$\mathrm{RO}\bullet + \mathrm{RH} \longrightarrow \mathrm{ROH} + \mathrm{R}\bullet$$

Termination:

$$\mathrm{R}\bullet + \mathrm{R}\bullet \longrightarrow 2\mathrm{R}$$

$$\mathrm{R}\bullet + \mathrm{ROO}\bullet \longrightarrow \mathrm{ROOR}$$

$$\mathrm{ROO}\bullet + \mathrm{ROO}\bullet \longrightarrow \mathrm{ROOR} + \mathrm{O_2}$$

RH, R•, RO•, ROO•, ROOH and M represent an unsaturated fatty acid or ester with H attached to the allylic carbon atom, alkyl radical, alkoxy radical, peroxy radical, hydroperoxide and transition metal, respectively.

The initiation reaction is the homolytic abstraction of hydrogen to form a carbon-centered alkyl radical in the presence of an initiator. Under normal oxygen pressure, the alkyl radical reacts rapidly with oxygen to form the peroxy radical which reacts with more unsaturated lipids to form hydroperoxide. The lipid-free radical thus formed can further react with oxygen to form a peroxy radical. Hence, the autoxidation is a free radical chain reaction. Because the rate of reaction between the alkyl radical and oxygen is fast, most of the free radicals are in the form of the peroxy radical. Consequently, the major termination takes place via the interaction between two peroxy radicals..

The rate of autoxidation increases with the degree of unsaturation. Linoleate is oxidized 10 times faster than oleate; linolenate 20-30 times faster (*3*).

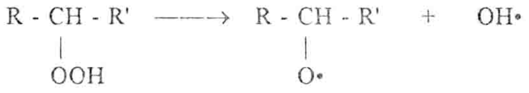
Hydroperoxides of Fatty Acids or Their Esters

It is well-known that the free radical mechanism of hydroperoxy formation involves the abstraction of the hydrogen atom from the α-methylene group of a lipid molecule. This is favored due to the formation of a very stable allyl radical in which the electrons are delocalized over either three carbon atoms such as in the case of oleate, or five carbon atoms such as in the case of linoleate or linolenate. The mechanisms for the formation of isomeric hydroperoxides by autoxidation have been reviewed extensively (*4-5*)

For oleate, the hydrogen abstraction on C-8 and C-11 produces two allylic radicals. These intermediates react with oxygen to produce a mixture of 8-, 9-, 10- and 11-allylic hydroperoxides. Autoxidation of linoleate involves hydrogen abstraction on the doubly reactive allylic C-11, with the formation of a pentadienyl radical. This intermediate radical reacts with oxygen to produce a mixture of conjugated 9- and 13-diene hydroperoxides. In the case of linolenate in which there are two separate 1,4-diene systems, hydrogen abstraction will take place on the two methylene groups, C-11 and C-14. These intermediate free radicals react with oxygen to form conjugated dienes with hydroperoxides on C-9 and C-13, or C-12 and C-16, with the third double bond remaining unaffected.

Decomposition of Hydroperoxides

Hydroperoxides of unsaturated fatty acids formed by autoxidation are very unstable and break down into a wide variety of volatile flavor compounds as well as nonvolatile products. It is widely accepted that (*1*) hydroperoxide decomposition involves homolytic cleavage of the -OOH group, giving rise to an alkoxy radical and a hydroxy radical.



$$R - \underset{\underset{\text{OOH}}{|}}{CH} - R' \longrightarrow R - \underset{\underset{\text{O}\bullet}{|}}{CH} - R' \quad + \quad OH\bullet$$

The alkoxy radical undergoes β-scission on the C-C bond, with the formation of an aldehyde and alkyl or vinyl radical. A general reaction scheme with the formation of volatile aldehyde, alkene, alkane and alcohol is illustrated in Figure 1.

Aldehydes. Of the volatiles produced by the breakdown of the alkoxy radicals, aldehydes are the most significant flavor compounds. Aldehydes can be produced by scission of the lipid molecules on either side of the radical. The products formed by these scission reactions depend on the fatty acids present, the hydroperoxide isomers formed, and the stability of the decomposition products. Temperature, time of heating and degree of autoxidation are variables which affect thermal oxidation (*6*).

Some volatile aldehydes formed by autoxidation of unsaturated fatty acids are listed in Table I. The flavors of aldehydes are generally described as green, painty, metallic, beany and rancid, and are often responsible for the undesirable flavors in fats, oils and lipid-containing foods. Hexanal and 4-heptenal are found to be primarily responsible for the off-flavor in alligator meat (Chapter 13). Hexanal has long been used as an index of oxidative deterioration in foods (Chapters 8 and 18). Some aldehydes, particularly the unsaturated aldehydes, are very potent flavor compounds.

It should be pointed out that extremely low levels of many aldehydes

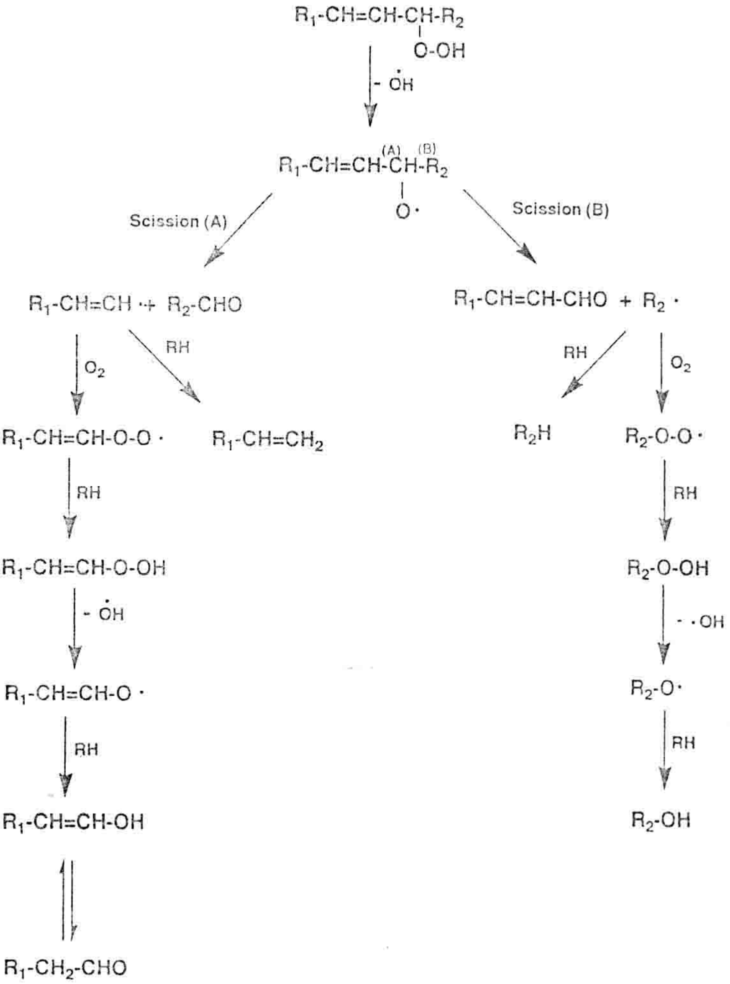


Figure 1. General reaction pathway for the homolytic cleavage of hydroperoxides of unsaturated fats.

Table I. Some Volatile Aldehydes Obtained from Autoxidation of Unsaturated Fatty Acids

Fatty acid	Monohydroperoxides	Aldehydes formed
Oleate	8-OOH	2-undecenal decanal
	9-OOH	2-decenal nonanal
	10-OOH	nonanal
	11-OOH	octanal
Linoleate	9-OOH	2,4-decadienal 3-nonenal
	13-OOH	hexanal,
Linolenate	9-OOH	2,4,7-decatrienal 3,6-nonadienal
	12-OOH	2,4-heptadienal 3-hexenal
	13-OOH	3-hexenal
	16-OOH	propanal
Arachidonate	8-OOH	2,4,7-tridecarienal 3,6-dodecadienal
	9-OOH	3,6-dodecadienal
	11-OOH	2,4-decadienal 3-nonenal
	12-OOH	3-nonenal
	15-OOH	hexanal
Eicosapentaenoate	5-OOH	2,4,7,10,13-hexadecapentaenal, 3,6,9,12-pentadecatetraenal
	8-OOH	2,4,7,10-tridecatetraenal 3,6,9-dodecatrienal
	9-OOH	3,6,9-dodecatrienal
	11-OOH	2,4,7-decatrienal 3,6-nonadienal
	12-OOH	3,6-nonadienal
	14-OOH	2,4-heptadienal 3-hexenal
	15-OOH	3-hexenal
	18-OOH	propanal

contribute to the desirable flavors of many foods. For example, the contributive role of aldehydes in poultry flavor has been well-recognized. Out of 193 compounds reported in the flavor of roasted chicken, 41 of them were lipid-derived aldehydes (*7*). When the aroma components of cooked chicken and cooked papain hydrolysates of chicken meat were qualitatively and quantitatively analyzed, 23 out of 66 compounds reported were lipid-derived aldehydes (*8*). Table II lists the quantitative data of selected aldehydes identified in these two studies. The most abundant aldehydes identified in chicken flavor were hexanal and 2,4-decadienal. In view of the much lower odor threshold of 2,4-decadienal (0.00007 mg/Kg) compared to hexanal (0.0045 mg/Kg) (*9*) the 2,4-decadienal should be the more important odorant for chicken flavor. Hexanal and 2,4-decadienal are the primary oxidation products of linoleic acid. The autoxidation of linoleic acid generates 9- and 13-hydroperoxides of linoleic acid. Cleavage of 13-hydroperoxide will lead to hexanal and the breakdown of 9-hydroperoxide will lead to 2,4-decadienal (*10*). Subsequent retro-aldol reaction of 2,4-decadienal will produce 2-octenal, hexanal and acetaldehyde (*11*). 2,4-Decadienal is known to be one of the most important flavor contributors to deep-fat fried foods (*12*). As shown in Table II, the enzymic hydrolysis of chicken with papain increased the concentration of 2,4-decadienal, as the aroma of cooked meat improved.

2,4-Decadienal can undergo further oxidation to produce *trans*-4,5-epoxy-*trans*-2-decenal. This compound was recently characterized as one of the most potent odorants of the crumb flavor of wheat bread and has a low odor threshold of approximately 1.5 pg/L (air) (*13*).

Ketones. Aliphatic ketones formed by autoxidation of lipids also contribute to the flavor of oils and food products. For example, Cadwallader et al. (Chapter 13) identified 1-octen-3-one as one of the odor-active compounds in the meat of wild alligators. This compound was described as metallic and mushroom-like. The reaction pathway for the formation of 1-octen-3-one from the arachidonate 12-hydroperoxide via the β-scission route is illustrated in Figure 2.

Furans. 2-Pentylfuran has been identified in many fats and oils and lipid-containing foods such as spray-dried dairy products (Chapter 7), mashed potatoes (Chapter 8) and alligator meat (Chapter 13). It is a well-known autoxidation product of linoleic acid and has been known as one of the compounds responsible for the reversion of soybean oil (*14*). Figure 3 shows the probable mechanism for its formation. The conjugated diene radical generated from the cleavage of the 9-hydroxy radical of linoleic acid may react with oxygen to produce vinyl hydroperoxide. The vinyl hydroperoxide will then undergo cyclization via the alkoxy radical to yield 2-pentylfuran (*6*).

Alcohols and Other Compounds. Cleavage of lipid hydroperoxides will also lead to alcohols, alkanes, alkenes and alkynes. The mechanism for the formation of 1-octen-3-ol which has a strong mushroom flavor is also shown in Figure 2.