FRYING OF FOOD

Oxidation, Nutrient and Non-Nutrient Antioxidants, Biologically Active Compounds and High Temperatures

EDITED BY

Dimitrios Boskou
Ibrahim Elmadfa

FRYING of FOOD

Oxidation, Nutrient and Non-Nutrient Antioxidants, Biologically Active Compounds and High Temperatures

EDITED BY

Dimitrios Boskou, Ph.D., D.Sc.

Ibrahim Elmadfa, Ph.D., D.Sc.

TECHNOMIC PUBLISHING CO., INC.

LANCASTER · BASEL

Frying of Food
a **TECHNOMIC**® publication

Technomic Publishing Company, Inc.
851 New Holland Avenue, Box 3535
Lancaster, Pennsylvania 17604 U.S.A.

Printed in the United States of America
10 9 8 7 6 5 4 3 2 1

Main entry under title:
Frying of Food: Oxidation, Nutrient and Non-Nutrient Antioxidants, Biologically Active Compounds and High Temperatures

A Technomic Publishing Company book
Bibliography: p.
Includes index p. 271

Library of Congress Catalog Card No. 99-64542
ISBN No. 1-56676-786-5

FRYING OF FOOD

HOW TO ORDER THIS BOOK

BY PHONE: 800-233-9936 or 717-291-5609, 8AM–5PM Eastern Time

BY FAX: 717-295-4538

BY MAIL: Order Department
Technomic Publishing Company, Inc.
851 New Holland Avenue, Box 3535
Lancaster, PA 17604, U.S.A.

BY CREDIT CARD: American Express, VISA, MasterCard

BY WWW SITE: http://www.techpub.com

Preface

THERE has been global interest, in the last two decades, in the relationship of dietary antioxidants to the possible prevention of a number of diseases, in the etiology of which oxidation mechanisms are involved. As a result, naturally occurring nutritive and non-nutritive antioxidants recently have become a major area of scientific research. In the field of nutrition phytochemicals such as phenols are now examined and discussed as food antioxidants. In addition, changed lifestyles in the modern industrialized world have triggered a growing awareness that particular ingredients in foods may favorably modify diet-related problems. This requires that valuable constituents of foods are preserved during processing. Thus, it is interesting to examine frying of food from the point of view of changes due not only to glycerides, but also to non-glyceride components. Minor constituents either initially present in the oil before frying or formed during the frying process have an important effect on the stability performance and nutritive value of the frying oil and the fried food.

Among the various biologically active ingredients present in oils and fats, antioxidant vitamins and carotenes seem to be important. However, other minor constituents such as phytosterols, phospholipids and hydrocarbons probably affect the performance of a heated oil. Some of these minor constituents, such as phytosterols and squalene, may also be categorized as functional. Finally, polar phenolic compounds, which are naturally occurring in certain oils or can be obtained from herbs, spices or other natural sources, have been shown to have an impact on the stability of oils at high temperatures and may influence the rate of oxidation of nutrients.

This book deals with some chemical, biochemical, physiological and nutritional aspects of frying. When fats and oils are used for frying a wide range of breakdown products is formed. The deterioration of the fat at elevated temperatures is influenced by various factors, such as the nature of the cooking fat, the conditions of frying, the kind of heat transfer, the fryer removal constructions and the use of antioxidants and other additives. The book concentrates mainly on two of these factors, the nature of the heated fat and the presence of oxidation retardants, especially those naturally occurring in oils or obtained from natural sources. Other aspects have been discussed and information can be found in excellent reviews, already available in the literature. It is also the editors' intention to cover some important aspects of the interactions between frying oil and natural components present in the food or substances produced during frying.

In examining the various topics the contributors have tried to discuss as many classes of compounds as possible and to give examples of fried foods which are consumed globally and also examples of local products from many countries, such as Germany, the Czech Republic, Estonia, Yugoslavia, the United Kingdom, Poland, Mediterranean countries, China, Japan, India, Latin American countries and others. This feature, related to the role of minor constituents and their interactions in a variety of fried food products, sets this book significantly apart from others in the field.

Other topics examined in the book are: fat and nutrition, oxidation products and metabolic processes, formation of free radicals and protection mechanisms *in vitro* and *in vivo,* changes of nutrients at frying temperatures, enzymatic methods for the study of thermally oxidized oils and fats, determination of oxidized compounds and oligomers, nutrient and non-nutrient antioxidants and stability of frying oils, phytosterols and their effect on the performance of a frying oil, effects of detrimental components in relation to safety and reliability during frying oils, frying performance of high oleic acid oils such as palm olein and olive oil.

It is hoped that all those interested in frying of food will find this an essential reference book. It is also anticipated that some readers will recognize that the book not only presents current facts about the frying of food but also tracks some lines for future research.

THE EDITORS

List of Contributors

William E. Artz
Department of Food Science and Human Nutrition
382 Agricultural Engineering Science Building
University of Illinois
1304 West Pennsylvania Ave.
Urbana, IL 61801-4726

O. Berdeaux
Instituto de la Grasa (CSIC)
Padre García Tejero
4. 41010 Sevilla, Spain

George Blekas
Laboratory of Food Chemistry and Technology
School of Chemistry
Aristotle University of Thesaloniki
54006 Thessaloniki, Greece

Dimitrios Boskou
Laboratory of Food Chemistry and Technology
School of Chemistry
Aristotle University of Thessaloniki
54006 Thessaloniki, Greece

M. C. Dobarganes
Instituto de la Grasa (CSIC)
Padre García Tejero
4. 41010 Sevilla, Spain

Ibrahim Elmadfa
Institute of Nutritional Sciences
University of Vienna
Althanstrasse 14, A-1090 Vienna

S. P. Kochhar
Good-Fry International, n.v.
Research and Development Centre
48 Chiltern Crescent
Earley
Reading RG6 1AN, U.K.

Christopher R. Lambert
Department of Chemistry
Connecticut College
270 Mohegan Avenue
New London, CT 06323-4196

Symon M. Mahungu
Chemistry Department
Egerton University
Njoro, Kenya

G. Márquez-Ruiz
Instituto de la Grasa (CSIC)
Padre García Tejero
4. 41010 Sevilla, Spain

T. P. Pantzaris
Palm Oil Research Institute of Malaysia
PORIM EUROPE
Brickendonbury
Hertford SG13 8NL, U.K.

Edward G. Perkins
Department of Food Science and Human Nutrition
382 Agricultural Engineering and Science Building
University of Illinois
1304 West Pennsylvania Ave.
Urbana, IL 61801-4726

Jan Pokorný
Prague Institute of Chemical Technology
Department of Food Chemistry and Analysis
Technická 5
CZ-166 28 Prague 6, Czechia

J. M. Sánchez-Montero
Departamento de Química Orgánica y Farmacèutica
Facultad de Farmacia
Universidad Complutense de Madrid
28040-Madrid, Spain

F. J. Sánchez-Muniz
Department de Nutrición y Bromatología (Nutrición)
Sección Lípidos
Facultad de Farmacia
Universidad Complutense de Madrid
28040-Madrid, Spain

J. Velasco
Instituto de la Grasa (CSIC)
Padre García Tejero
4. 41010 Sevilla, Spain

Karl-Heinz Wagner
Institute of Nutritional Sciences
University of Vienna
Althanstrasse 14, A-1090 Vienna

Contents

CHAPTER 1

Fat and Nutrition

IBRAHIM ELMADFA
KARL-HEINZ WAGNER

INTRODUCTION

CHEMICALLY, fats comprise a non homogeneous group of different sub stances which have some physico-chemical characteristics in common. They are insoluble in water and soluble in non-polar solvents like hexane, chloroform or ethers. In the past lipids were assumed to be not essential constituents of the food. The human organism was supposed to remain healthy even if no lipids were supplied, as long as the requirement of food energy was met. Today it is well-known that the polyunsaturated fatty acids are essential and that a balance between unsaturated and saturated fatty acids is important for the normal metabolic function and the primary care. The fact that lipids represent an important constituent of the cell membrane as proteins underlines their essential character.

In nutrition and dietetics a distinction is made between visible and invisible fats. Visible fats are clearly apparent to the consumer (spreads, cooking oils or the fat on meat). Most of the fat in many consumed foods, however, is hidden as a natural component of the raw material, through incorporation during cooking or frying processes (cakes, fried potatoes, french fries) or as a result of the formation of emulsions like mayonnaise. During frying the lipid component may undergo qualitative and quantitative changes.

It is therefore important to understand better the factors affecting the stability of oils and fats at high temperatures as well as the extent to which nutritionally important lipids are deteriorated.

COMPOSITION OF DIETARY FATS

Edible fats usually contain 98–99% triacylglycerols and 1–2% nonsaponifiable components like sterols, fat-soluble vitamins and lipopigments. According to their chemical composition lipids are classified to those which contain fatty acids in their molecules as structural components and lipids which are isoprenoid derivatives. The main characteristics of the fatty acids are chain length (= number of C-atoms) and the position of unsaturation of the molecule. Both features are decisive for the physical characteristics as well as for the biochemical functions of the fatty acids and fats.

The most abundant fatty acids have straight chains of an even number of carbon atoms; the spectrum ranges from 4 (in milk fat) to 22 (plant oils); in some fish oils there are up to 30 carbon atoms in length. Despite the variety of fatty acids in nature, the number of those that are significant for human nutrition in terms of quantity are limited; frequently the fatty acids have eighteen carbons (Table 1).

Fatty acids are saturated or unsaturated with one double bond (monounsaturated) or more double bonds (polyunsaturated). Saturated fatty acids are generally solid at room temperature and are most commonly found in animal products. They increase serum cholesterol and triglyceride levels (review from Dietschy, 1998). Experiments showed that animals fed only saturated fatty acids do not survive (Elmadfa and Leitzmann, 1998).

Medium-chain fatty acids (6–12 C-atoms) are recommended as dietetics because they undergo faster oxidation than long-chain fatty acids. The different time of oxidation explains the "lipid sparing" effects of carbohydrates; the $^{14}CO_2$-concentration of the exhaled air increases with an increasing number of carbon atoms.

Unsaturated fatty acids are subdivided into different classes according to their degree of unsaturation, the distance of the terminal methyl group from the nearest double bond and the essentiality.

- level of unsaturation, number of double bonds: monoene acids—oleic acid (18:1ω9), palmitoleic acid (16:1ω7); diene acids—linoleic acid (18:2ω6); triene acids—α-, γ-linolenic acid (18:3ω3; 18:3ω6); tetraene acids—arachidonic acid (20:4ω6); pentene acids (20:5ω3) and hexaene acids (22:6ω3)
- essentiality of fatty acids: unsaturated, non-essential—oleic acid; unsaturated, essential—ω-3 and ω-6 families

TABLE 1. Characterization of Important Fatty Acids in Foods (CL = chain length, DB = double bonds, MP = melting point).

Common Name	CL	DB	Symbol	Systematic Names	MP	Occurrence
Butyric acid	4	0	C4:0	*n*-Butanoic acid	–8	Milk fat
Caproic acid	6	0	C6:0	*n*-Hexanoic acid	–2	Milk fat
Caprylic acid	8	0	C8:0	*n*-Octanoic acid	16	Milk fat
Capric acid	10	0	C10:0	*n*-Decanoic acid	31	Milk fat
Lauric acid	12	0	C12:0	*n*-Dodecanoic acid	44	Cocos fat
Myristic acid	14	0	C14:0	*n*-Tetradecanoic acid	54	Animal fats
Palmitic acid	16	0	C16:0	*n*-Hexadecanoic acid	63	Animal fats
Palmitoleic acid	18	1	C16:1ω7	*cis*-9-Hexadecenoic acid	1	Animal fats, fish oils
Stearic acid	18	0	C18:0	*n*-Octadecanoic acid	70	Animal fats
Oleic acid	18	1	C18:1ω9	*cis*-9-Octadecenoic acid	13	Fats and oils
Vaccenic acid	18	1	C18:1ω7	*trans*-11-Octadecenoic acid	40	Summer butter
Linoleic acid	18	2	C18:2ω6	all *cis*-9,12-Octadecadienoic acid	–6	Phosphatides
γ-Linolenic acid	18	3	C18:3ω6	all *cis*-6, 9,12-Octadecatrienoic acid		Plant oils
α-Linolenic acid	18	3	C18:3ω3	all *cis*-9,12,15-Octadecatrienoic acid	14	
Arachidic acid	20	0	C20:0	*n*-Eicosanoic acid	76	Animal fats
Gadoleic acid	20	1	C20:1ω9	*n*-11-Eicosenoic acid		
Arachidonic acid	20	4	C20:4ω6	all *cis*-5,8,11,14-Eicosatetraenoic acid	–50	Phosphatides
Timnodonic acid	20	5	C20:5ω3	all *cis*-5,8,11,14,17-Eicosapentaenoic acid		Fish oils, phosphatides
Behenic acid	22	0	C22:0	*n*-Docosanoic acid	80	Cerebrosides
Erucic acid	22	1	C22:1ω9	*cis*-13-Docosenoic acid	35	
Clupandonic acid	22	5	C22:5ω3	all cis-7,10,13,16,19-Docosapentaenoic acid		Fish oils, phosphatides
Docosahexaenic	22	6	C22:6ω3	all cis-4,7,10,13,16,19-Docosahexaenoic		Fish oils, phosphatides
Lignoceric acid	24	0	C24:0	*n*-Tetracosanoic acid	84	Phosphatides
Nervonic acid	24	1	C24:1ω9	*cis*-15-Tetracosenoic acid	40	Cerebrosides, phosphatide
Cerebronic acid	24	0	C24:0	2-Hydroxytetracosanoic acid	100	Cerebrosides
Hydroxynervoic	24	1	C24:1ω9	2-Hydroxy-15-Tetracosenoic acid	6	Cerebrosides

For a long time only the ω-6-linoleic and arachidonic acids were considered as essential fatty acids for human beings. According to more recent investigations ω-3 fatty acids like α-linolenic acid, eicosapentaenoic acid (EPA) or docosahexaenoic acid (DHA), components of membrane phospholipids and the retina in human, are important for the cell integrity, brain development, for the function of nerve cells and the visual effects; thus their essentiality for humans and different animal species is acknowledged (Simopoulos, 1991; Gerster, 1995; Nelson et al., 1997).

The unsaturated fatty acids available in the organism are derived mainly from three fatty acids occurring in the body: oleic acid, linoleic acid and α-linolenic acid. Therefore we can classify them into oleic acid, linoleic acid and a linolenic acid groups (Figure 1). There is also a minor group derived from palmitoleic acid. Oleic acid, in combination with other fatty acids enhances the absorption of saturated fatty acids. Eicosatrienoic acid (C20:3ω9) is formed from oleic acid in considerable amounts in absence of linolenic and linoleic acid and therefore it is an analytical parameter for the deficiency of essential fatty acids in serum and structure lipids. The ratio C20:3ω9/C20:4ω6 also called T/T-ratio describes the status of essential fatty acids and is normally ≤ 0.4.

UNSAPONIFIABLE COMPONENTS AND FATTY ACID PATTERN IN FOODS

Apart from the content of short and medium chain fatty acids and the relation of saturated to unsaturated fatty acids, the content of unsaponifiable fat-attendant substances is important for the evaluation of the quality and physiological effects of dietary fats. Vitamins, antioxidants, taste and flavour substances as well as phytosterols belong to this group. Animal fats, except fish oils, consist predominantly of saturated and monounsaturated fatty acids and contain only small quantities of polyunsaturated fatty acids. A low content of unsaponifable components is common to animal fats such as lard, tallow and butter. Plant oils and fats except coconut oil, palm seed oil and olive oil have a high content of polyunsaturated fatty acids as well as a high content of unsaponifiables. The highest concentrations of unsaponifiables are found in wheat germ oil, rice oil and corn oil (Table 2). The presence of natural antioxidants in the unsaponifable fraction of vegetable oils is an advantage (longer shelf life).

For a long time only the P/S-ratio (polyunsaturated/saturated ratio) was the main indicator to assess effects of fats on plasma triglyceride and cholesterol levels. Today it is known that the ratio of saturated (SFA): monounsaturated (MONO):polyunsaturated (PUFA) is more important to describe the health impact of edible fats and oils. For primary health care