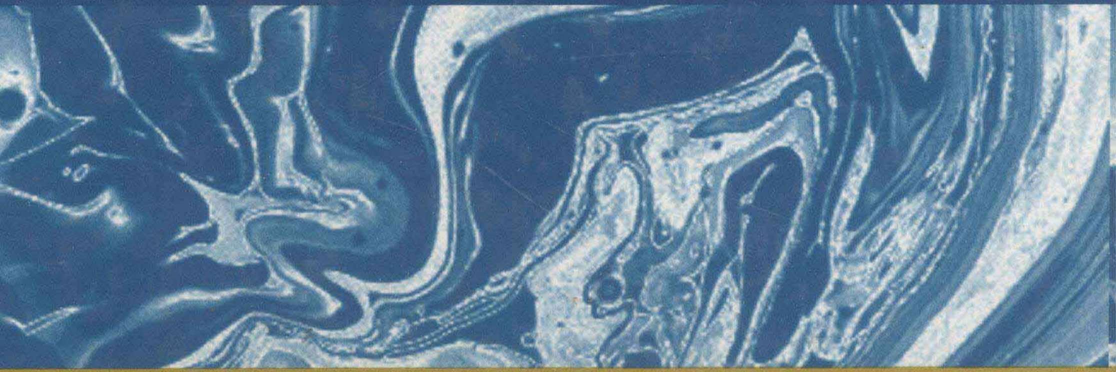
FATTY ACID AND LIPID CHEMISTRY



Frank Gunstone

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Fatty Acid and Lipid Chemistry

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Fatty Acid and Lipid Chemistry

Preface

This book has a pedigree. It has developed from earlier publications by the author and from his experience over 50 years in reading, writing, thinking, and working with lipids and fatty acids. The earlier publications are:

(i) *An Introduction to the Chemistry of Fats and Fatty Acids*, Chapman and Hall, 1958.
(ii) *An Introduction to the Chemistry and Biochemistry of Fatty Acids and their Glycerides*, Chapman and Hall, 1967.
(iii) *Lipids in Foods: Chemistry, Biochemistry, and Technology* (with F.A. Norris), Pergamon Press, 1983.
(iv) *The Lipid Handbook* (with J.L. Harwood and F.B. Padley), Chapman and Hall, first edition 1986, second edition 1994.
(v) *A Lipid Glossary* (with B.G. Herslof), The Oily Press, Dundee, 1992.
(vi) Lecture notes for a course on *Fatty Acids and Lipids* designed for those entering the oil and fat industry and given on over 20 occasions since 1977.

The book is dedicated to the next generation of lipid scientists. The study of lipids now involves many disciplines, all of which require a basic knowledge of the chemical nature and properties of these molecules, which is what this book is about. It is written particularly for those who, with some knowledge of chemistry or biochemistry, need to know more about the nature of lipids and fatty acids. I expect that many of my readers will be employed in the food industry since 80% of the world production of oils and fats is eaten by humans and another 6% goes into animal feed. They will need to understand the materials they handle; their origin, their chemical nature, the effects of processing, and their physical, chemical, biochemical, and nutritional properties. Another group of readers will be employed in the oleochemical industry, modifying the material produced by nature for the benefit of human kind. They will have to understand the constraints of production and of chemistry within which they work and they will have to be aware of the present state of knowledge of these materials. Another group may consider themselves to be academic researchers but they cannot escape from the real world of marketplace availability, and will need to know something about sourcing, about the changes which occur on refining oils and fats and how these materials can be modified on a commercial scale.

For the most part, I have given only general references at the end of each chapter. These will furnish detailed information for those who need it. Not surprisingly, my first port of call would be *The Lipid Handbook* which, in its second edition, has 722 pages of text and an extensive selection of dictionary entries with references, abstracted from the *Dictionary of Organic Compounds* (551 pages).

In preparing a book of this limited size, I have had to be selective and although some less common fatty acids and some of the less useful chemistry of the acids has not been completely ignored, I have nevertheless emphasized throughout the most common and the useful features of fatty acid and lipid chemistry. My appreciation of these matters is based on long experience, wide reading, attendance at many conferences and frequent contact with those who work in the food and oleochemical industry. Apart from a few historical comments I have dwelt on things as they now are. There are, of course, new developments but it is too soon to fully appreciate their significance. Some research reports will gather dust on library shelves and become archive material; others will be the seed from which there will be significant growth. I have had to use my own judgement in deciding between these; if I have got it right more often than I have got it wrong I have done well.

The book is divided into ten chapters. It is necessary first to describe the fatty acids (chapter 1) and the lipids (chapter 2) and to discuss their nomenclature, structure, biosynthesis, and chemical synthesis. This is followed by an account of the major sources of oils, fats, and other lipids (chapter 3), a description of the processes by which such materials are made available and are modified (chapter 4), and then the analytical procedures used for their investigation (chapter 5). The physical and chemical properties of the fatty acid and lipids are covered in the next three chapters and the final two chapters are devoted to nutrition and to the major food and non-food uses of lipids.

The book has been read in an earlier draft form by Dr F.B. Padley (Unilever) and by Dr H. Eierdanz (Henkel) and I acknowledge the assistance they have given me in weeding out errors and pointing out omissions. The book is better for their contributions but they hold no responsibility for any remaining errors.

F.D.G.

Contents

1 Fatty acids – Nomenclature, structure, isolation and structure-determination, biosynthesis, and chemical synthesis 1

2 Lipids – Nomenclature, structure, biosynthesis, and chemical synthesis 35

9 Dietary fats and nutrition 223

10 Practical applications of oils and fats 229

1 Fatty acids – Nomenclature, structure, isolation and structure determination, biosynthesis and chemical synthesis

There is no generally accepted definition of the class of natural products designated as lipids and the author continues to use his earlier definition that "lipids are compounds based on fatty acids or closely related compounds such as the corresponding alcohols and the sphingosine bases". On this basis it is reasonable to start this book with a discussion of the fatty or long-chain acids which are an essential part of most lipids. The chemical structures of these acids and their physical, chemical and biological properties are basic to the understanding of the physics, chemistry, and biochemistry of lipids. In a few lipids the acids are replaced by related long-chain compounds such as alcohols, aldehydes, or amines.

1.1 Fatty acid nomenclature

Fatty acids are designated in several different ways. Despite the alternative descriptions set out here many trivial names are still widely used and have therefore to be known. These names were originally given before the chemical structure of the acid was elucidated and were often chosen to indicate the source of the acid. Examples include: palmitic (from palm oil), oleic (from olive oil, *Olea europea*), linoleic and linolenic (from linseed oil), ricinoleic (from castor oil, *Ricinus communis*), and arachidic acid (from groundnut oil, *Arachis hypogea*). Less often the name is linked with the scientist who first described the acid or some significant property of that acid, e.g. Mead's acid (20:3 *n*-9). Sometimes an acid had more than one trivial name until the identity of the material from different sources was established. Thus 9-hexadecenoic acid was earlier designated palmitoleic acid and also zoomaric acid. A trivial name may also be assigned or may continue to be used because the systematic name is cumbersome as for example with α-eleostearic acid which is simpler than 9c11*t*13*t*-octadecatrienoic acid. Trivial names are easy to use but they are not, in themselves, indicative of structure; that has to be remembered as well as the name.

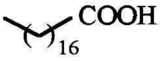
Systematic names are based on internationally accepted rules agreed by organic chemists and biochemists. Those who know the rules can interconvert systematic names and structures. As a simple example oleic acid is *cis*-9-octadecenoic acid. This is a carboxylic acid (oic) with 18 carbon atoms (octadec) and one olefinic centre (en) which lies between carbon 9 and 10 (counting from the carboxyl end) and has *cis* configuration, i.e.

$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$

which may also be represented by the line drawing:

Representations like this are increasingly popular. They are more useful when the number of double bonds and/or other functional groups is larger and the saturated sections of the molecule are short. The structure shown below is not easily recognizable as stearic acid (octadecanoic) as the number of carbon atoms represented in this structure is not immediately apparent and has to be carefully counted:

This difficulty is overcome in the alternative formulation:



Even though the line forms of these structures are useful because of their immediate visual impact, they are not convenient for tabulated data or for insertion into lines of text. Because the word form can be complex and clumsy, systematic or trivial names are sometimes abbreviated to two or three capital letters as in the following examples:

gamma-linolenic acid	GLA
arachidonic acid	AA
eicosapentaenoic acid	EPA
docosahexaenoic acid	DHA

The third way of designating fatty acids involves the use of numbers such as 18:2. This symbol describes an acid such as linoleic with 18 carbon atoms (assumed to be straight-chain) and two unsaturated centres (assumed to be *cis*-olefinic). Since there are many isomeric compounds which could be represented by this symbol additional descriptors may be added thus:

18:2 (9,12), 18:2 (9*c*,12*c*), 18:2 (9*Z*,12*Z*), 18:2 (*n*-6)

All these refer to the same acid. The first indicates the position of the two unsaturated centres in the C_{18} chain with reference to COOH = 1. The second and third formulations confirm the *cis* or *Z* configuration of the double bonds. The symbol Δ is sometimes added to show that numbering is with respect to the acid function. The fourth designation introduces a further concept in fatty acid nomenclature.

Sometimes it is useful to designate double bond positions with respect to the end CH_3 group and this is done with symbols such as ω6 or *n*-6 which indicate that the first double bond is on carbon 6 counting from the methyl group. In the absence of other information it is assumed that double bonds are methylene-interrupted and have *cis* (*Z*) configuration. Symbols such as *c*, *t*, *e* are used to show *cis*, *trans*, and ethylenic unsaturation (where configuration is not known or does not apply) and *a* (acetylenic) or *y* (ynoic) is used to show a triple bond.

All of these systems of nomenclature will be used as appropriate throughout this text and the lipid scientist must expect to meet them all.

1.2 Fatty acids – main structural features

The number of known natural fatty acids exceeds 1000 although only a relatively small number – perhaps 20–50 – are of common concern. Based on a survey of these 1000 structures, and noting particularly the structures of those acids produced most commonly in nature, it is possible to make four general statements. Each of these is generally true but there are exceptions to all four. The exceptions are frequently trivial but sometimes they are significant. Though originally based on a survey of chemical structures it is now clear that these statements also reflect the underlying biosynthetic pathways by which the acids are produced in nature (section 1.15).

(i) Natural fatty acids – both saturated and unsaturated – are straight-chain compounds with an even number of carbon atoms in their molecules. This is true for the great majority of structures and for the more abundant acids. Chain lengths range from two to over 80 carbon atoms although they are most commonly between C_{12} and C_{22}. Despite the validity of this statement, acids with an odd number of carbon atoms (e.g. heptadecanoic, C_{17}) occur as do those with branched chains (e.g. isopalmitic, ante-isononadecanoic) or with carbocyclic units (e.g. sterculic, chaulmoogric).

(ii) Acids with one unsaturated centre are usually olefinic compounds with *cis* (*Z*) configuration and with the double bond in one of a limited number of preferred positions. This is most commonly Δ9 (i.e. nine carbon atoms from the carboxyl group as in oleic) or *n*-9 (i.e. nine carbon atoms from the methyl group as in oleic or erucic acid). But double bonds occur in other positions (e.g. petroselinic, 6*c*-18:1), or have *trans* configuration (e.g. elaidic 9*t*-18:1), or can be replaced by an acetylenic unit (e.g. tariric 6*a*-18:1).

(iii) Polyunsaturated acids are mainly polyolefinic with a methylene-interrupted arrangement of double bonds having *cis* (*Z*) configuration. That is, *cis* double bonds are separated from each other by one CH_2 group as in arachidonic acid:

The 1,4-pattern of unsaturation is characteristic of natural fatty acids and differs from that in acyclic isoprenoids which is usually 1,3 (conjugated) or 1,5. Polyunsaturated acids occur in biosynthetically related families. The most important are the *n*-6 acids based on linoleic and the *n*-3 acids based on α-linolenic acid. In contrast to this very common pattern of unsaturation some acids have conjugated unsaturation which may be *cis* or *trans* (e.g. eleostearic, calendic, parinaric acids), some have mixed en/yne unsaturation which may be conjugated (e.g. isanic) or non-conjugated (e.g. crepenynic), and some have non-conjugated unsaturation which is not entirely methylene-interrupted. These are known as non-methylene-interrupted polyenes (e.g. columbinic, pinolenic).

(iv) Fatty acids rarely have functional groups apart from the carboxyl group and the various types of unsaturation already discussed. Nevertheless acids are known which also contain a fluoro, hydroxy, keto, or epoxy group. Two important examples are ricinoleic (12-hydroxyoleic acid) and vernolic acid (12,13-epoxyoleic).

These generalizations have a biosynthetic basis and even some of the exceptions are accommodated into the general biosynthetic scheme with only minor modifications.

Based on the annual production of commercial vegetable oilseeds it has been estimated that eight acids account for about 97% of the total production: lauric (4%), myristic (2%), palmitic (11%), stearic (4%), oleic (34%), linoleic (34%), α-linolenic (5%), and erucic (3%). The level of linolenic would rise if all green tissue were taken into account. The major acids in animal fats and in fish oils are myristic, palmitic, palmitoleic, stearic, oleic, eicosenoic, arachidonic, EPA, docosenoic and DHA.

1.3 **Saturated acids** (Table 1.1)

1.3.1 Short- and medium-chain saturated acids (C_4–C_{14})

Members of this group of acids occur in milk fats and in some vegetable oils known as the lauric oils. Cow milk fat, for example, contains butanoic (butyric, C_4) acid at a level of about 4% (wt). This may not seem very much but because of the low molecular weight of the C_4 acid compared

Table 1.1 Names and selected physical properties of some alkanoic acids

Chain length	Systematic name	Trivial name	Acid		Methyl ester		Mol wt
			mp (°C)	bp (°C)[a]	mp (°C)	bp (°C)[a]	
4	butanoic	butyric	–5.3	164	–	103	88.1
6	hexanoic	caproic	–3.2	206	–69.6	151	116.2
8	octanoic	caprylic	16.5	240	–36.7	195	144.2
10	decanoic	capric	31.6	271	–12.8	228	172.3
12	dodecanoic	lauric	44.8	130^{1}	5.1	262	200.3
14	tetradecanoic	myristic	54.4	149^{1}	19.1	114^{1}	228.4
16	hexadecanoic	palmitic	62.9	167^{1}	30.7	136^{1}	256.4
18	octadecanoic	stearic	70.1	184^{1}	37.8	156^{1}	284.5
20	eicosanoic	arachidic	76.1	204^{1}	46.4	188^{2}	312.5
22	docosanoic	behenic	80.0	–	51.8	206^{2}	340.6
24	tetracosanoic	lignoceric	84.2	–	57.4	222^{2}	368.6

[a] bp at 760 mm or at 1 or 2 mm as indicated by superscript.
Adapted from *The Lipid Handbook*, 2nd edition (1994) p. 1.

with the more common C_{18} acids this represents about 8.5% on a molar basis, which means that it could be present in up to 25% of milk fat glycerides. Also present are lower levels of the C_6–C_{12} acids. The short-chain acids are retained in butter and in other products made from milk fat.

Some seed oils contain very high levels of lauric acid (C_{12}, about 50%) with significant levels of caprylic (C_8), capric (C_{10}) and myristic acids (C_{14}) also. The best known of these oils are coconut oil and palm kernel oil. At the present time there is interest in other sources of these medium-chain acids (section 3.7.1). Among these are the *cuphea* oils which show great promise but still need to be fully domesticated before they produce an easily cultivated crop. A transgenic rapeseed has also been developed which produces a lauric-rich oil.

1.3.2 Palmitic and stearic acids

Palmitic acid (16:0) is the most widely occurring saturated acid. It is present in fish oils (10–30%), in milk and body fats of land animals (up to 30%), and in virtually all vegetable fats at a range of levels between 5 and 50%. Useful sources of palmitic acid include cottonseed oil (15–30%), palm oil (30–60%), Chinese vegetable tallow (60–70%), lard (20–30%), and tallow from sheep and cattle (25–35%).

Despite popular impression, stearic acid (18:0) is much less common than palmitic acid. It is a major component of the tallows of ruminant animals (5–40%) and a significant component in a number of vegetable tallows (solid fats of vegetable origin) including cocoa butter (30–35%), Illipe or Borneo tallow (40%), and shea butter (45%). Stearic acid is also easily made by hydrogenation of readily available oleic, inoleic and linolenic acid.

Since many population groups in the world have scruples about animal products vegetable sources of palmitic acid and stearic acid are preferred. These are used in food and non-food products (surfactants, cosmetics, personal hygiene products) to obtain products which find general acceptance.

1.3.3 Long-chain acids

Saturated acids of chain length greater than 18 carbon atoms are present at low levels in a few seed oils and at higher levels only in a few uncommon sources. The C_{20}–C_{30} members are often present in waxes. A convenient source of some of these acids is groundnut oil which contains 5–8% of long-chain acids including arachidic (20:0), behenic (22:0), and lignoceric (24:0) acids. Rarer but richer sources include rambutan tallow (*Nephelium lappaceum*, about 35% of 20:0), kusum (*Schleichera trifuga*, 20–30% of 20:0), *Lophira alata* (15–30% of 22:0), and *L. procera* (around 20% of 22:0) seed fats. Long-chain acids can also be made from more readily available shorter chain acids (C_{12}–C_{18}) by appropriate chain-extension procedures. These reaction sequences are not confined to adding one or two carbon atoms at a time since methods exist for adding five or six carbon atoms in one cycle of reactions.

1.4 Monoene acids (Table 1.2)

Over 100 monoene acids have been described. These fall almost entirely in the range C_{10}–C_{30} with C_{16}, C_{18}, and C_{22} members the most common. Most have *cis* (*Z*) configuration and the most important are either Δ9 or *n*-9, i.e. the double bond is nine carbon atoms from the carboxyl (Δ9) or the methyl group (*n*-9).

9-hexadecenoic acid (palmitoleic, zoomaric) is a minor component (<1%) of many seed oils and animal fats. It is more significant in fish oils where it may attain a level around 10% and is a major component of a few seed oils. Macadamia oil is a useful source of this acid at around the 20% level. It is also a significant component in *Saccaromyces cerevisiae* (30–50%) and other yeasts.

9-octadecenoic acid (oleic) is the most widely distributed and the most extensively produced of all fatty acids (see section 1.2). It is the prototype of all monoene acids and serves as the biological precurser of other *n*-9 monoene acids and of the *n*-9 family of polyene acids. Olive oil (60–80%) and almond oil (60–70%) are rich sources of this acid and it is also present at high levels (55–75%) in several nut oils (filbert, cashew, pistachio,