Chemistry in Industry

Fats, Oils and Waxes

Peter Tooley

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Peter Tooley BSc MSc ARIC MIBiol

Head of Department of Chemistry
St Osyth's College, Clacton

John Murray Albemarle Street London

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Preface

The rapid and often revolutionary advances in applied chemistry since World War II have made it increasingly difficult for the hard-pressed teacher to keep abreast of events and bridge the gap between school and industry. In addition the pupil, in daily contact with novel materials forged by the chemists' skill, and keen to discuss the related problems of scientific advance such as pollution and the misuse of knowledge, is unlikely to be satisfied by a narrow academic approach to the subject. In tracing the origin, current development and socio-economic implications of a score or so branches of chemical technology, the present series aims at providing the teacher with relevant background material. Emphasis has been placed upon changing patterns of industry such as the transition from batch to continuous production and other problems of large-scale manufacture. An attempt has also been made to show how the properties of substances are related to their structure and how these properties can be modified by molecular tailoring.

Two complementary volumes, *Techniques* and *Handbook of Experiments*, contain suggestions for related practical work and a survey of modern preparative and analytical techniques.

Although the text has been written primarily as a source-book for science teachers it should also prove useful to students at universities and colleges as well as senior pupils carrying out project work. Bearing in mind the wide spectrum of the chemical industry covered it is inevitable that certain errors and omissions will have occurred but every effort has been made to give a concise and accurate account of the chosen topics.

Acknowledgments

It is a pleasure to acknowledge the ready help of many colleagues and friends in industry and Government departments who provided valuable advice, statistics and other material. I have also had to draw upon the published works of many authors who are too numerous to mention individually, but to whom my thanks are also due.

I am grateful for the help afforded by the staff of John Murray who have successfully steered the book through the hazards of production. Mention must also be made of the loyal assistance of my senior technician, Miss Sandra Fairbairn, who has not only deciphered and typed the MS but given freely of her time and technical expertise.

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Chapter 1

Introduction

> 'It is an excellent thing to shew the diversity of ways to make Oyl. That if Olives should ever be scarce, yet we might know how to draw Oyl from many kinds of fruits and seeds.'
>
> *Natural Magick—Book 4,* John Baptista Porta, 1658

At the present time the human race uses an estimated 40 million tonnes a year of fats and oils derived from both animal and vegetable sources. This reflects both their nutritional and industrial importance, and yet curiously the fats and waxes have remained for many years a neglected chapter in organic chemistry. More recently, however, interest has been stimulated by the advances which have been made in the manufacture of such materials as detergents, polishes, cosmetics and edible fat blends. In addition the unravelling of the complex chemistry of the essential oils has led to the development of technical perfumes and synthetic flavouring agents.

The true fats (glycerides) belong to a large group of natural organic polar compounds known as lipids, which also includes the waxes, lecithins and phospholipids. These are widely distributed in foods and are of great nutritional value. Fats provide fatty acids which are necessary to animal metabolism and represent a concentrated reserve of energy, yielding about 37 kJ (9 Calories) per gramme. This compares with corresponding values of 16·5 kJ (4 Calories) and 22·75 kJ (5·5 Calories) per gramme for carbohydrate and protein respectively. Although animal foods contribute a considerable proportion of our dietary fats some plant materials—especially seeds and nuts—are rich in lipids. Thus soya bean, groundnut, cottonseed, sunflower seed, coconut and palm kernel are all important sources of edible oils. Certain fruits such as the avocado and olive also have an unusually high fat content.

Animal fat is mainly located in adipose tissue cells. These are distended with oily droplets which solidify on death in warm-blooded

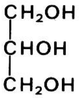
Palm kernels from which palm oil is extracted

Source	*Fat content %*	*Source*	*Fat content %*
Pecans	73	Safflower	30
Copra	69	Avocado	20
Walnuts	64	Cottonseed	20
Castor seed	50	Olive	19
Palm kernel	50	Soya	18
Sesame seed	50	Oatmeal	7·5
Groundnuts	45	Yam	4
Rapeseed	40	Maize	2
Linseed	36	Barley	1

animals. In the human body, fat forms about 12% of its total weight. At least half of this fat forms a protective heat insulating subcutaneous layer, which is part of the depot fat available to the body as a food. Smaller amounts are to be found in the intermuscular connective tissue, bones, and as a protective layer around nervous tissue, kidneys, heart and other organs. Fats and oils derived from water-living animals usually contain a greater variety of fatty acids than those obtained from land animals and plants. A substantial proportion of these fatty acids are unsaturated, the marine oils being mainly in the C_{20}–C_{22} range and the fresh water oils from C_{16}–C_{18}.

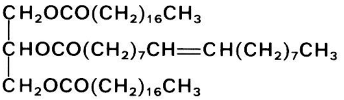
Commercial fats and oils consist almost entirely of true fats which are the glyceryl esters of fatty acids. The fatty acids are so-called because many were first discovered as the result of hydrolysing the glyceryl esters occurring in fats. As glycerol is a trihydric alcohol it can react with one, two or three molecules of monobasic fatty acids to produce monoglycerides, diglycerides or triglycerides respectively. Only triglycerides are found naturally in undecomposed fatty material. A simple triglyceride contains only one type of fatty acid radical. Thus an important component of olive oil is triolein which is the triglyceride of oleic acid. The majority of naturally occurring triglycerides are mixed, however, containing two or three different fatty acid radicals. The structure of a triglyceride is often represented by the initials of its component fatty acid radicals. In this way 2-oleo 1,3-distearin would be identified as SOS.

Most fats are themselves mixtures of triglycerides and the proportions of these which are present determine their physical characteristics. The oils, which are fats with low melting points, contain predominantly unsaturated fatty acids. Castor oil, for example, contains about 90% unsaturated ricinoleic acid. The presence of double bonds in the fatty acid chain permits the formation of isomers, which also affects the melting point. For example, (*cis*) oleic acid has a melting point of 16·3 °C while its isomeric form (*trans*) elaidic acid has a melting point of 43·7 °C.



$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$$

glycerol



$$\begin{array}{l} CH_2OCO(CH_2)_{16}CH_3 \\ | \\ CHOCO(CH_2)_7CH{=}CH(CH_2)_7CH_3 \\ | \\ CH_2OCO(CH_2)_{16}CH_3 \end{array}$$

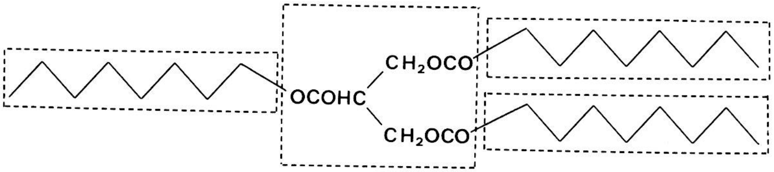
2-oleo 1,3-distearin (SOS)
(a mixed triglyceride)

Another factor which determines whether a fat is a solid or an oil is the molecular weight of the fatty acids involved. Thus hydrolysis of coconut oil produces a mixture including saturated fatty acids with low molecular weights, whereas the hydrolysate of beef 'dripping' yields long chain saturated fatty acids such as stearic acid and palmitic acid.

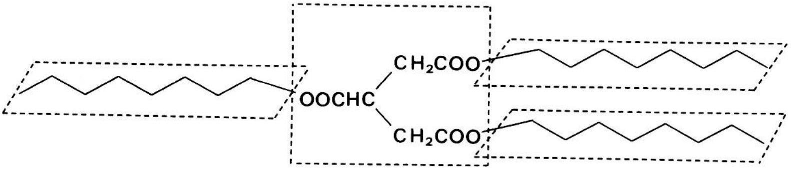
	Saturated fatty acids				*Unsaturated fatty acids*			
	Myristic	*Palmitic*	*Stearic*	*Arachidic*	*Oleic*	*Linoleic*	*Butyric*	*Caproic*
Corn oil	—	5	2	2	36	55	—	—
Olive oil	1	8	2	1	80	8	—	—
Lard	1	27	9	—	55	6	—	—
Beef dripping	2	33	14	—	48	3	—	—
Butter	10	23	11	—	31	3	10	2

Approximate percentage distribution of a range of fatty acids in some common edible fats

When glycerides solidify they exhibit differences in their crystalline packing structure (polymorphism). This is due to the inability of the atoms to rotate around single bonds as in the liquid state and a consequent 'freezing' of the molecular form as solidification occurs. Three principal forms have been identified by X-ray diffraction techniques, an unstable alpha form produced by rapid cooling and two relatively stable beta forms (beta—β, and beta prime—β'). These molecular patterns in solid fats represent different orientations of the fatty acid chains with relation to the plane of the glyceride molecule. This is thought to be shaped like a tuning fork. Interconversion of one



(*a*) Possible beta crystalline form

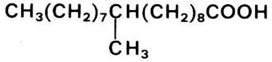


(*b*) Possible beta prime crystalline form

( represents a fatty acid chain) crystalline form into another can be followed by noting the small associated heat changes which occur during cooling (differential thermal analysis).

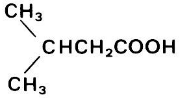
When pure, the glycerides and the fatty acids are colourless and usually almost odourless. The colour and smell of fats are due to the presence of small quantities of non-fatty materials. Thus the yellowish colour of some fats originates from fat soluble pigments such as carotenoids, and the characteristic smell of palm oil is largely due to small quantities of β-ionone.

The fatty acids which are found as esters of glycerol and other alcohols in the fats and waxes are usually straight chain compounds with an even number of carbon atoms in the molecule. An interesting and isolated exception is iso-valeric acid which is a C_5 acid found in the hydrolysate of dolphin oil. In addition to having an odd number of carbon atoms, iso-valeric acid has a branched chain. Some of the waxes found in bacilli also have branched chain fatty acids.



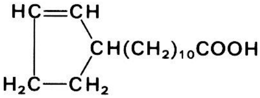
$CH_3(CH_2)_7\underset{\underset{CH_3}{|}}{C}H(CH_2)_8COOH$

tuberculostearic acid
(found in
Mycobacterium tuberculosis)

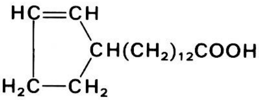


iso-valeric acid

Three fatty acids of plant origin (gorlic, hydnocarpic and chaulmoogric acids) have a hydrocarbon chain which terminates in a cyclopentene ring. Since these acids possess an asymmetric carbon atom they are able to form optical isomers.



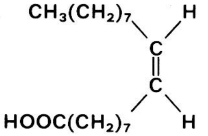
hydnocarpic acid



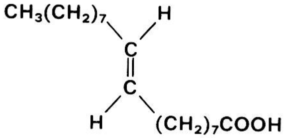
chaulmoogric acid

The lower fatty acids are soluble in water but as the chain length increases solubility falls rapidly. The higher members of the series are insoluble in water although readily soluble in the usual organic solvents. All the fats are insoluble in water, and, with the exception of castor oil, are only sparingly soluble in ethanol. The ready solubility of fats in most organic solvents is utilized in solvent extraction techniques.

The double bonds present in the hydrocarbon chain of the unsaturated fatty acids enable stereoisomeric forms to exist. This is due to the restriction on free rotation around the double bonds which allows the formation of different molecular structures. Thus oleic acid and elaidic acid are geometrical isomers, the naturally occurring oleic acid having both hydrocarbon chains on the same side of the double bond (*cis* form), elaidic acid having them on opposite sides (*trans* form). Only the *cis* isomers occur naturally.

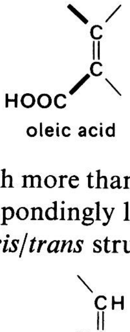


oleic acid (*cis* form)

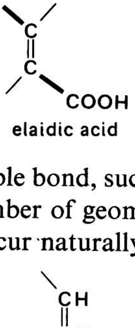


elaidic acid (*trans* form)

This may be shown in diagrammatic form for convenience, the thick lines representing hydrocarbon chains.

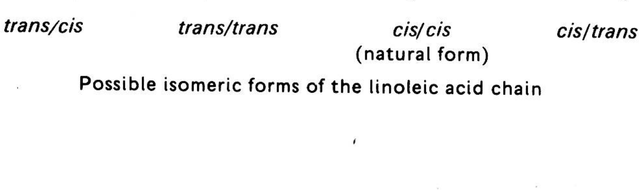


oleic acid



elaidic acid

A fatty acid with more than one double bond, such as linoleic acid, can form a correspondingly larger number of geometric isomers, although only the *cis/trans* structures occur naturally.



trans/cis *trans/trans* *cis/cis* (natural form) *cis/trans*

Possible isomeric forms of the linoleic acid chain

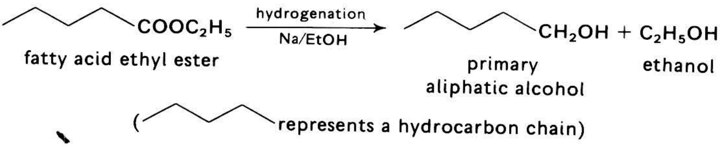
Other types of stereoisomerism also occur with unsaturated fatty acid structures. Position isomers such as linolenic acid and eleostearic acid have their double bonds located at different points along the hydrocarbon chain.

The chemical properties of the fats and fatty acids may be thought of in terms of the reactions of the carboxyl group and its attached hydrocarbon chain which can be either saturated or unsaturated. Although it is convenient to consider the reactions of these two parts of the molecule separately, it is important to remember that they exert a powerful influence on each other.

The carboxyl group of the fatty acids is involved in a number of reactions, perhaps the most important of these technologically being esterification and reduction. Some interesting synthetic fatty esters have been prepared for use mainly in cosmetics. Thus by treating long chain fatty acids such as myristic or palmitic acid with boiling methanol in the presence of a little concentrated hydrochloric acid, the methyl ester separates out as an oily layer. Iso-propyl myristate and iso-propyl palmitate are especially useful in reducing the viscosity and greasiness of other cosmetic fats. Similarly, synthetic glyceryl esters such as glyceryl monostearate have become widely used in the preparation of cosmetic emulsions.

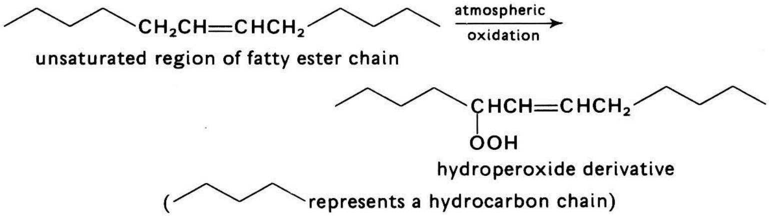
Interesterification is often carried out in order to alter the characteristics of a fat. Heating to about 100 °C in the presence of a small amount of catalyst (0·2% sodium ethoxide) promotes interchange of the fatty acid radicals among the component glycerides. This random distribution affects properties such as melting point, grain structure and plasticity and is often used to improve the characteristics of edible fats.

Reduction of fatty acids using catalytic hydrogenation, or increasingly by the use of sodium in alcohol (Beauveault-Blanc reaction), is a valuable industrial route for the production of the synthetic long chain aliphatic alcohols required in the manufacture of synthetic detergents.



Fats can be hydrolysed using water or steam to reform free fatty acids and glycerol (fat-splitting). If the hydrolysis is carried out using a caustic alkaline solution, water soluble soaps are formed. Fats are also decomposed at high temperatures (pyrolysis) to yield hydrocarbons. This process was used at one time in China for the production of motor fuel.

Saturated hydrocarbon chains are relatively inert, but the unsaturated chains are affected by both oxidizing and reducing agents. A certain amount of oxidation occurs when unsaturated fats and oils are exposed to the air (autoxidation). This is responsible for the 'drying' of oils such as linseed oil used in the manufacture of linoleum and paints, and for the rancid taste and smell which develop in fats. It has been shown that autoxidation involves attack by atmospheric oxygen at methylene groups adjacent to the double bonds.

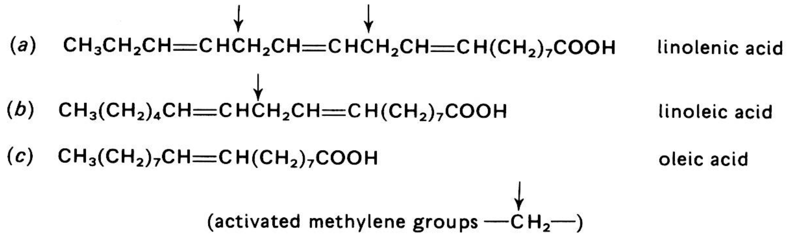


Oxidation of unsaturated fatty acids and fats with oxidizing agents such as potassium permanganate, hydrogen peroxide and the halogens is mainly of analytical rather than commercial interest.

Prior to the onset of rancidity certain flavour changes are detectable in most oils and fats. The bland pleasant taste produced during processing often reverts to the original undesirable flavour of the crude oil. This phenomenon is known as *reversion* and is especially noticeable in fish oils. It has been found that reversion is particularly likely in fats such as soya bean oil which are rich in linolenic acid. The development of reversion is also influenced by short-wave light, temperature, oxygen tension and traces of metals such as copper and chromium which catalyse the reaction. For this reason metal 'scavengers' such as EDTA (ethylenediamine tetra-acetic acid) are often used during fat processing.

The catalytic hydrogenation of unsaturated oils is of great industrial importance in the manufacture of solid edible fats. The catalyst which is commonly used industrially is finely divided nickel, which forms an intermediate compound with the fat and gaseous hydrogen. This technique was first used commercially in 1906 after successful experiments carried out by Norman four years earlier. It is interesting to note that selective hydrogenation occurs across double bonds separated by activated methylene groups. Thus a linolenate with two activated methylene groups is preferentially hydrogenated over a linoleate with only one. Both are hydrogenated before oils such as oleates which possess only a single double bond, or oils with double bonds separated by more than one methylene group, neither of which have such highly active structures.

In addition to fatty acid esters and small amounts of free fatty acids the commercial oils and fats invariably contain other lipid substances. Crude seed oils contain quite appreciable quantities of phospholipids such as lecithins and cephalins, and sterols such as cholesterol. These are mostly removed during purification.

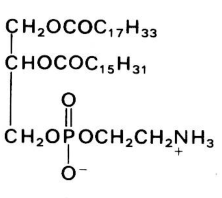


(*a*) $CH_3CH_2CH{=}CH\overset{\downarrow}{C}H_2CH{=}CH\overset{\downarrow}{C}H_2CH{=}CH(CH_2)_7COOH$ linolenic acid

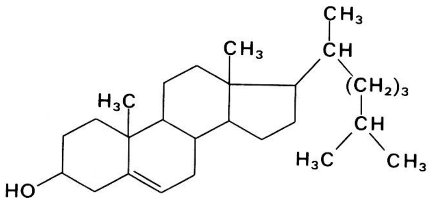
(*b*) $CH_3(CH_2)_4CH{=}CH\overset{\downarrow}{C}H_2CH{=}CH(CH_2)_7COOH$ linoleic acid

(*c*) $CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$ oleic acid

(activated methylene groups $—\overset{\downarrow}{C}H_2—$)



lecithin
(a phosphoglyceride)



cholesterol (an animal sterol)

Occasionally unsaturated hydrocarbons such as squalene ($C_{30}H_{50}$) and pristane ($C_{18}H_{28}$) are also present. The darkening of oils during heating or storage is partly due to destruction of the tocopherols (vitamin E) which when present inhibit atmospheric oxidation. Thus the stability of coconut oil at room temperature (5 mg tocopherol/100 g) is very much less than cottonseed oil (110 mg tocopherol/100 g). Other antioxidants are also thought to be present in natural fats since some relatively stable oils have a very low tocopherol content.

The formation of vegetable fats and oils is still shrouded in mystery. It appears that part of the carbohydrate material produced by photosynthesis is converted into saturated fatty acids which then react with glycerol to form saturated fats. It has been suggested that a further series of reactions then occurs producing unsaturated fats and oils and free fatty acids. Other evidence suggests that the saturated and unsaturated fats are formed quite independently.

Animal fat can originate from ingested carbohydrate, or be formed from dietary fat or protein. Experiments with rats and pigs have shown that certain 'essential fatty acids' such as linoleic and arachidonic acids can only be produced from ingested fat.

Animal and vegetable waxes also contain fatty acid esters, but these differ from those present in the fats in being formed from the higher monohydric alcohols such as cetyl alcohol ($C_{16}H_{33}OH$) and myricyl alcohol ($C_{30}H_{61}OH$) instead of glycerol. The vegetable waxes occur as deposits on the surface of certain plant leaves, stems and fruits, protecting them from excessive water loss. Thus candelilla wax is obtained from the stems of a species of Mexican weed, and carnauba wax, which is the hardest of all the commercial waxes, is recovered from the leaves of the Brazilian palm.

The majority of the animal waxes are obtained from marine sources, especially from the sperm and bottlenose whales. Beeswax and wool-fat are also commercially important. The purification of the crude waxes is usually carried out by melting in boiling water, and then bleaching the skimmed product.

ANALYSIS OF FATS

Physical Characteristics

Fats and oils can often be identified by their physical properties such as melting point, refractive index and density. Because of their complex nature and the existence of different crystalline forms the determination of melting point is not as precise as in the case of pure organic compounds. Most fats tend to supercool and soften over a range of temperatures and may even exhibit a double melting point because of conversion from one crystalline polymorph to another. The *slip point* is often measured by noting the temperature at which a plug of fat rises in a capillary tube or metal cylinder suspended in a heating bath.

Although there is generally an increase of specific gravity with chain length, differences are so small that refractive index is a more useful physical constant for identifying fats. Using a refractometer at constant temperature (25 ° or 40 °C is usual) the purity of samples can be rapidly estimated and their identification is possible. For cooking fats the temperature at which hazing occurs (*smoke point*), and vapour ignition point (*flash point*) are obviously of importance. If an oil is dissolved in a warm solvent in which it is sparingly soluble turbidity

		m.p. °C
Saturated fatty acids		
Myristic	$C_{13}H_{27}$ COOH	54
Palmitic	$C_{15}H_{31}$ COOH	63
Stearic	$C_{17}H_{35}$ COOH	70
Arachidic	$C_{19}H_{39}$ COOH	75
Benenic	$C_{21}H_{43}$ COOH	80
Lignoceric	$C_{23}H_{47}$ COOH	84
Unsaturated fatty acids		
Oleic	$CH_3(CH_2)_7CH{=}CH(CH_2)_7$ COOH *cis*-9-octadecenoic acid	16
Linoleic	$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7$ COOH *cis-cis*-9,12-octadecadienoic acid	−5
Linolenic	$CH_3CH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_7$ COOH *cis-cis-cis*-9,12,15-octadecatrienoic acid	−11

Melting points of common fatty acids in most stable crystalline form