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REPORT

Naturally Occurred Fats and Oils: A Review

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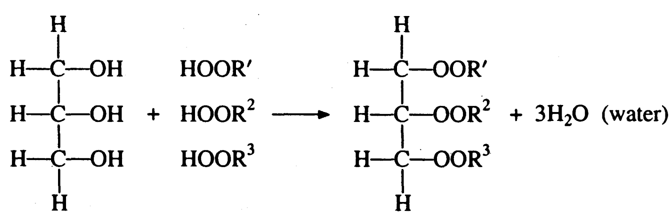
Fats and oils are categorized under the wide term lipids. They are found in abundance in vegetable and animal sources. They are glyceral esters of fatty acids. Both act as heat insulators and as reserve sources of energy.

The term lipid is applied to a group of naturally occurring substances characterised by their insolubility in aqueous media and their solubility in fat solvents, being found in all vegetable and animal sources. Lipids are chemically either esters of fatty acids or substances capable of forming such esters. Lipids act as heat insulators and are reserve suppliers of energy.

Fats and oils are predominantly glyceryl esters of fatty acids or triglycerides which are the condensation products of one molecule of glyceral with three molecules of fatty acids to yield three molecules of water and one molecule of triglycerides. When the fatty acids are same, they are called simple triglycerides and when the fatty acids are different they are called mixed triglycerides. Glycerol is a trihydric alcohol, $CH_2OH{\cdot}CHOH{\cdot}CH_2OH$, each hydroxyl (OH) group joined to a fatty acid to form a triglyceride. If only one hydroxyl is esterified, a monoglyceride is formed; if two, a diglyceride; and if three, a triglyceride. Fats are usually solid or semi-solid at ordinary temperature whereas oils are liquid in the same conditions.

A triglyceride is the condensation product of one molecule of glycerol with three molecules of fatty acids to yield one molecule of triglyceride and three molecules of water as shown below:



Fatty acid Triglyceride

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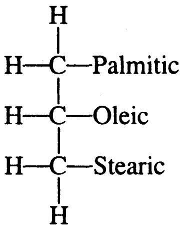
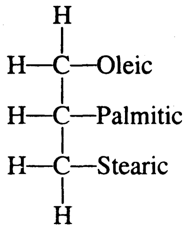
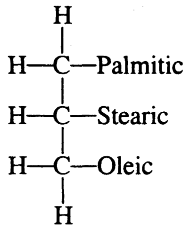
A mixed triglyceride which contains three different fatty acids has three isomeric forms depending on which fatty acid is in the middle β or 2 position and which fatty acids in the α or 1 and α′or 1′ position.



Oleopalmitostearian



Palmitooleicstearian



Stearopalmitoolein

The molecular weight of the glycerol position (C_3H_5) of a triglyceride molecule is 41. The combined molecular weights of the fatty acid radicals (RCOO) with different oils vary from 650 to 970. Thus the fatty acids contribute from 94 to 96% of the total weight of the molecule and thus fatty acids greatly influence the character of the glycerides.

Fatty acid consists of a paraffinic chain coupled to a carboxylic group; unsaturated acid is oleic acid $CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$ with just one double bond but there are acids with two, three or four double bonds to be found in plant and animal fats and even more in marine fats.

The naturally occurring fatty acids are monobasic aliphatic compounds having a single straight chain with some exceptions; most acids are found to contain an even number of carbon atoms. The individual fatty acids differ from one another due to the number of carbon atoms and double bonds which occur between the carbon atoms in the chain. The fatty acids which do not have any double bond are designated as saturated fatty acids whereas the fatty acids which contain double bonds, one or more, are termed as unsaturated fatty acids and the degree and reactivity of unsaturation depends on the number of double bonds.The most common saturated fatty acids occuring in fats and oils are listed in Table-1.

The unsaturated fatty acids are characterised by the presence of one or more double bonds in the molecules. They have been classifed in accordance with the number of double bonds and the position of the bonds in the carbon chain being indicated by a number referred to the carboxyl carbon atom as number one. Because of the presence of double bond the unsaturated fatty acids are much more reactive than the saturated fatty acids, the reactivity increases with increase in the number of double bonds. The most common unsaturated fatty acid found in nature is the monounsaturated fatty acid, oleic acid (9-octadecenoic acid). Other common unsaturated fatty acids include: (1) double bond unsaturated linoleic acid, (2) linolenic acid which is having three double bonds found largely in vegetable fats, (3) arachidonic acid (four double bonds).

Fatty acid chains are of two types: non-conjugated and conjugated. Non-conjugated are those in which double bonds in the carbon chain are separated by at least two carbon atoms and conjugated acids are those in which single and double bonds alternate between certain carbon atoms.

Mono-unsaturated fatty acids exist in either the *cis-* or *trans-* form, according to the spatial arrangements of the two positions of the molecule on either side of the double bond. The average degree of unsaturation of a fat or mixture of fatty acids is measured by the iodine value; the average molecular weight is measured by saponification number or saponification value. In addition to the more common fatty acids described, some natural fatty acids have different structures such as triple bond, hydroxyl or ketone groups or epoxy and cyclopropane rings.

TABLE-1

Common name	Chemical name	Structure	Occurrence
Butyric	Butanoic	$CH_3(CH_2)_2COOH$	Butter fat
Caproic	Hexanoic	$CH_3(CH_2)_4COOH$	Butter fat, coconut oil
Caprylic	Octanoic	$CH_3(CH_2)_6COOH$	Butter fat, coconut oil
Capric	Decanoic	$CH_3(CH_2)_8COOH$	Butter fat, coconut oil
Lauric	Dodecanoic	$CH_3(CH_2)_{10}$-COOH	Laurel kernel oil, butter fat, coconut oil
Myristic	Tetradecanoic	$CH_3(CH_2)_{12}COOH$	Nutmeg fat, butter fat, vegetable fats
Palmitic	Hexadecanoic	$CH_3(CH_2)_{14}COOH$	Most vegetable and animal fats
Stearic	Octadecanoic	$CH_3(CH_2)_{16}COOH$	Most vegetable and animal fats
Arachidic	Eicosanoic	$CH_3(CH_2)_{18}COOH$	Peanut oil
Behenic	Docosanoic	$CH_3(CH_2)_{20}COOH$	Rapeseed oil, peanut oil
Lignoceric	Tetracosanoic	$CH_3(CH_2)_{22}COOH$	Cerebrosides, sphingomyelin, peanut oil

A large number of unsaturated fatty acids occur naturally which usually contain an even number of carbon atoms. In most cases the double bonds have the *cis-* configuration and a preferred position for a double bond is between the 9th and 10th carbon atoms. Fatty acids with as many as seven double bonds have been reported as components of fats. Those containing one, two and three double bonds and 18 carbon atoms are the most important unsaturated fatty acids of vegetable and animal fats, those with four or more double bonds and 20 to 24 carbon atoms are found principally in marine oils. Acids with one double bond are called monounsaturated fatty acids containing 2 less carbon atoms than the corresponding saturated fatty acids and have the empirical formula $C_nH_{2n-2}O_2$. Diunsaturated fatty acids contain 4 less hydrogen atoms than the corresponding saturated fatty acids and have empirical formula $C_nH_{2n-4}O_2$. Triunsaturated fatty acids have the empirical formula $C_nH_{2n-6}O_2$.

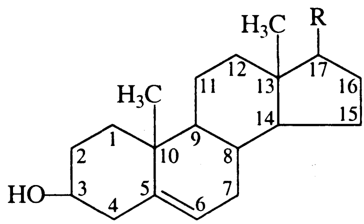
One plant acid of particular biological importance to humans is linoleic acid $CH_3(CH_2)_4(CH{=}CH{\cdot}CH_2)_2(CH_2)_6COOH$, that is, two specifically sited double bonds. It is called an essential fatty acid because although the body needs it, a key enzyme for synthesizing it is missing from the body and so the acid must be present in the fat of the diet. So quite apart from the hazards of taint formation, this acid must be protected from oxidation because linolenic acid is a precursor within the body of two physiologically important acids: γ-linolenic acid

$CH_3(CH_2)_4(CH{=}CH{\cdot}CH_2)_3(CH_2)_3COOH$ with three doubles, arachidonic acid $CH_3(CH_2)_4(CH{=}CH{\cdot}CH_2)_4(CH_2)_4COOH$ with four double bonds. Arachidonic acid is needed for the lipid component of biological membranes, lipid being a generic term applied to all fatty compounds, of which glycerides form a coherent sub-group. It is implicit in this, of course, that the diet should be arranged to contain sufficient essential fatty acids.

All fats and oils contain small amount of non-glyceride components of those which persist; some are without pronounced flavour, odour and relatively inert from a chemical standpoint. These may be considered of minor importance, since their presence is neither objectionable nor desirable. Certain other components, however, particularly those which have pro- or antioxidant properties, or are strongly flavoured or highly coloured, may considerably affect the character of the fat, even though they are present in traces.

The collective name sterols has been assigned to crystalline, neutral, unsaponifiable alcohols of high melting points with properties resembling those of cholesterol. The sterols are ordinarily of little concern as they are relatively inert and do not contribute to any property of the oil. Sterols occur in fats and oils in the free form, as esters of the fatty acids and as glucosides. The characteristic and predominant sterol of animal fats is cholesterol, $C_{27}H_{46}O$. It is also the best known and most plentifal sterol. The sterols of vegetable oils consist of a mixture. The vegetable oil sterols are known collectively as phytosterols. Two of the most common phytosterols are β-sitosterol, $C_{29}H_{50}O$, and stigmasterol, $C_{29}H_{48}O$. The former is widely distributed and is the principal sterol of cottonseed oil; the latter is a principal sterol of soyabean oil.

The structure of sterol is represented as follows:



In the respective cases of the three sterols mentioned, R is:

$—CH(CH_3)(CH_2)_3CH(CH_3)_2$; (Cholesterol)

$—CH(CH_3)CH_2CH_2CHCH(CH_3)_2$ with C_2H_5 on the CH (Sitosterol)

$—CH(CH_3)CH{=}CHCH(CH_3)_2$ with C_2H_5 on the =CH (Stigmasterol)

The sterols provide a means of distinguishing between fats of animal and vegetable origin since the melting point of cholesterol acetate (114°C) is substantially lower than that of the acetates of any of the phytosterols (126–137°C).

Causes of fats and oils being coloured are not entirely known; one of the best known classes of pigments is the carotenoids which are largely responsible for the yellow to red colours of most fats. These pigments are fat-soluble. Their colour ranges from yellow to deep red depending on their structure. One of the most important carotenoids is β-carotene. About 70 carotenoids have been discovered; the best known are the isomeric hydrocarbons α-, β- and γ-carotenes and lycopene $C_{40}H_{56}$. The carotenoids are widely distributed in crude animal and vegetable fats in low concentration. Most of the colours of crude oil and cotton seed oil are attributed to gossypol type pigments. Another pigment is chlorophyll present in olive oil, soyabean oil, etc.

It has been observed that because oils and fats contain minute amount of substances capable of strongly inhibiting oxidation, natural oils and fats are much more resistant to oxidative deterioration. These are due to naturally occurring antioxidants. Tocopherols, the most important and almost universally distributed antioxidents, constitute fat-soluble vitamin E. Tocopherols were designated as α-, β- and γ-. Tocopherols differ from α-tocopherol in having one less methyl group in the aromatic ring. In β-tocopherol the methyl groups are in the 5 and 8 position and in γ-tocopherol they are in 7 and 8 position.

Tocopherols are light yellow to colourless and are fat-soluble as a result of their long side chains. Like other antioxidants, the tocopherols are themselves readily oxidizable. Although the tocopherols are the chief antioxidants of vegetable oils, there are other antioxidants. Sesame oil contains about 0.3–0.5% sesamoline, a glucoside of the phenolic compound sesamol and it is a powerful antioxidant. Sesamol is formed during the processing of sesame oil. Another compound, gossypol, a complex phenolic substance which has strong antioxidant properties, occurs in crude but not in refined cottonseed oil. Phosphatides are not antioxidants when present alone in oil but some phosphatides are capable of reinforcing the action of tocopherols or other antioxidants of the phenolic type.

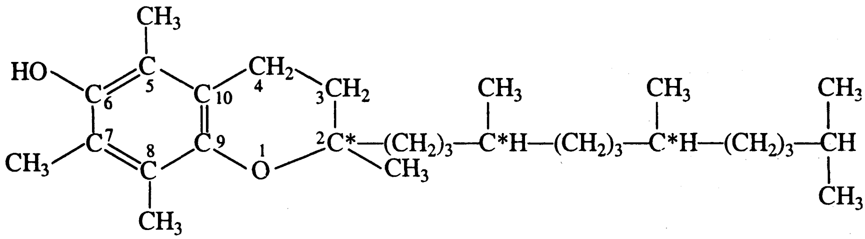
Oxidation proceeds in two stages: initiation and propagation. Initiation involves the formulation of a free radical, that is a compound made unstable and reactive by the removal of a hydrogen atom at one or other of the carbon atoms adjacent to a double bond. There can then be interchange as shown below to produce a total of four free radicals.

$$
\begin{array}{c}
—CH^*—CH{=}CH—CH_2— \\
\| \\
{=}CH^*—CH{=}CH—CH_2—
\end{array}
$$

and

$$
\begin{array}{c}
—CH_2—CH^*{=}CH—CH_2— \\
\| \\
—CH_2—CH^*{=}CH—CH^*—
\end{array}
$$

In the absence of antioxidant, propagation will proceed in two stages. First a peroxide being formed and then a new free radical being produced. Without intervention, the chain reaction would terminate only by fortuitous interaction of free radicals. A good antioxidant will mop up the free radicals as they are formed. Antioxidants are used to limit oxidative spoilage, particularly of fats



α-Tocopherol

Phosphates are a class of naturally occurring substances—some related to the glycerides that are widely involved in biological system when two immersible phases have to be kept in close proximity. When they first came under scientific scrutiny, they were called lecithins and the name is still in use today. Soyabean lecithin, for example, is one of the most commonly used emulsifiers.

From the triglycerides given below:

CH_2OOCR'

R^2OOCH

CH_2OOCR^3

wherc R', R^2 and R^3 are the paraffinic chains $CH_3(CH_2)_n$— of the fatty acid radicals. If two radicals are removed, it is left with a monoglyceride

CH_2OOCR'

HOCH

CH_2OH

This will act as an emulsifier because of the two hydrophilic OH groups and the hydrophobic R' group. If only one of the radicals had been removed there would have been a diglyceride with weaker emulsifying powers.

If one of the fatty acid radicals of a triglyceride reacts with a phosphoric acid radical, it would give a phospholipid or phosphatide, of the general form:

CH_2OOCR'

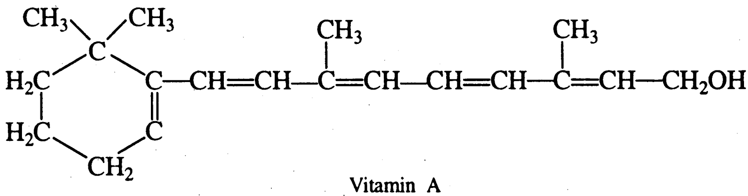
R_2COOCH

CH_2O—P—OX

O—

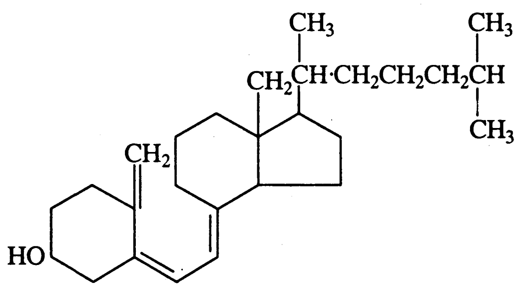
In this OX most commonly choline, $HOCH_2CH_2OHN(CH_3)_3$ and less commonly ethanolamine, $HOCH_2CH_2NH_2$ are attached.

Fats and oils are important sources of the fat-soluble vitamin A, vitamin D and vitamin E. Vitamin A may be considered to be derived from carotin by clearage of a molecule of the latter in the middle of the hydrocarbon chain and the addition of one molecule of water to each fragment. The conversion of β-carotine to vitamin A occurs in the body of man and other animals; hence β-carotone is designated as pro-vitamin A.



Vitamin A

The vitamins D are related to and derived from sterols. Vitamin D or calciferol has the following formula:



Vitamin D_3

The body oils of most fish and marine animals contain a considerable amount of vitamins A and D. Certain fish liver oils are extremely rich in these vitamins.

Most of the world's produced fats are consumed as food; they are an important source of energy in the diet of many of the world's people. Fats are the most concentrated of all food materials, furnishing about 9 calories of energy per gram in comparison to 4 calories each furnished by carbohydrates and proteins. Oils and fats have the highest calorie density of any foodstuff because they are usually consumed in a relatively water-free condition whereas proteins and carbohydrates often occur with large quantities of water. Fat delays the digestion of food and thus prevents premature sensation of hunger after consumption.

More than half of the fat is obtained as "invisible" fat from meat eggs, dairy products (other than butter), cereals, nuts, grains and miscellaneous sources. The remainder is consumed as "visible" fat such as butter, margarine, lard, shortenings and edible oils. Oils and fats are essential constituents of all forms of plant and animal life. A large source of oil at present is the seeds of animal plants.

Fats serve as a storage of food in plant and animal organisms and one of great importance for the cellular process, evidently along with other lipids. Fats can serve as a source of energy and are especially important dietary constituents when the bulk of a diet must be controlled, since they yield approximately 0.9 calories per gram as compared to 0.4 for both proteins and carbohydrates. In addition to providing flavour and satiety to the diet, fats serve as vehicles for the fat-soluble vitamins A, D, E and K. The poly-unsaturated fatty acids (PUFA), linoleic in particular, are necessary for the proper functioning of many metabolic processes. Because of the inability of the animal to synthesize linoleic acid in quantities sufficient for its requirement, linoleic acid is a necessary dietary constituent.

REFERENCES

1. B.L. Oser (Ed.), Hawk's Physiological Chemistry, 14th Edn., Tata Mcgraw-Hill, New Delhi.
2. R.S. Kirk and Ronald Sawyer (Eds.), Pearson's Composition and Analysis of Foods, 9th Edn., Longman Scientific and Technical, U.K.
3. Daniel Swern (Ed.), Bailey's Industrial Oil and Fat Products, 4th Edn., Interscience, New York-U.K.-Sydney.
4. J.C. Allen and R.S. Hamilton (Eds.), Rancidity in Foods, Applied Science Publishers, London-New York.
5. E.B. Uvarov and D.R. Chapman, A Dictionary of Science, 5th Edn., English Language Book Society and Penguin Books.

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