WHAT IS A LIPID?

From FST 515
, University of Tennessee ~ 2000
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http://web.utk.edu/~jmount/Classes/515/

- group of naturally occurring compounds, which have in common a ready solubility in such organic solvents as hydrocarbons, chloroform, benzene, ethers and alcohols. They include a diverse range of compounds, like fatty acids and their derivatives, carotenoids, terpenes, steroids and bile acids.

WHAT IS A LIPID?

- fatty acids and their derivatives, and substances related biosynthetically or functionally to these compounds

Classification of Lipids

- Fatty acids
  - Saturated
  - Monounsaturated
  - Polyunsaturated
- Glycerides
  - Neutral
  - Phosphoglycerides
- Nonglycerol Lipids
  - Sterolids
  - Waxes
  - Sphingolipids
- Complex Lipids
  - Lipoproteins
  - Glycolipids

Fatty acid structure

Long chain monocarboxylic acids

$$CH_3(CH_2)_nCOOH$$

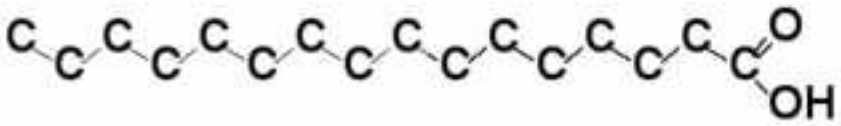
Size Range: C_{12} - C_{24}

Always an even number of carbon.

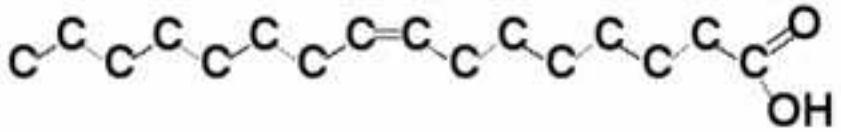
Saturated - no double bonds.
Unsaturated - one or more double bonds.

Fatty acid structure

Saturated fatty acid



Unsaturated fatty acid



Fatty acids

Trivial name	Shorthand designation	Molecular wt.	Melting point (°C)
butyric	4:0	88.1	-7.9
caproic	6:0	116.1	-3.4
caprylic	8:0	144.2	16.7
capric	10:0	172.3	31.6
lauric	12:0	200.3	44.2
myristic	14:0	228.4	53.9
palmitic	16:0	256.4	63.1
stearic	18:0	284.4	69.6
arachidic	20:0	412.5	75.3
behenic	22:0	340.5	79.9

Fatty acids

- Fatty acids with 4 to 12 carbon atoms are found mainly in milk fats (mainly butyric acid in cow and decanoic acid in sheep) but those with 10 and 12 carbon atoms are found also in certain seed oils such as coconut and other kernel fats of the palm family.

- **Butyric acid** (4:0) is the lowest member of the acetic acid series found in natural fats. It occurs (2 to 4%) as a component of milk fats. It gives a rancid odor to butter when triglycerides are hydrolyzed and is present in fermentation products of carbohydrates.

- **Caproic acid** (6:0) occurs in milk fats to the extent of about 2%. It was first isolated from butter in 1816 by Chevreul. It has a characteristic odor of goats, hence its name (from the Latin *caper*, goat).

- **Caprylic acid** (8:0) is widely distributed in animal and vegetable fats but rerely exceeding 8% of the total fatty acids. It occurs to an extent of 1 to 4% in milk fats, and 6 to 8% in coconut and palm oils.

- **Capric acid** (10:0) occurs as a minor component in the same fats that contain caprylic acid but also in the head oil of the sperm whale, and in wool and hair fats. It is a major constituent of certain seed oils (50% in elm and 37% in California bay tree)

Fatty acids

- **Lauric acid** (12:0) is one of the three most widely distributed saturated fatty acids found in nature (14:0, 16:0, and 18:0). It occurs extensively in cinnamon oil (80-90%), coconut oil (40-60%). The recent uses of lauric acid are in the manufacture of soaps, shampoos and other surface active agents, including special lubricants. Lauric acid as a monoglyceride is known to the pharmaceutical industry for its good antimicrobial properties.

- **Myristic acid** (14:0) is present in major amounts in seeds of the family *Myristicaceae* (nutmeg oil - or oil of mace). Coconut and palm kernel oils are also convenient sources of C8-C14 fatty acids which are isolated in a pure form by distillation. It is also present in milk fats (8-12%) and in the head oil of the sperm whale (15%).

- **Palmitic acid** (16:0) is the most common saturated fatty acids in plant and animal lipids. It was purified first by Chevreul in his researches on butter and tallows, but was first characterized by Fremy E (*Ann 1840, 36, 44*), who prepared it in pure form from palm oil, from which he named it. Despite its wide distribution, it is generally not present in fats in very large proportions. It usually forms less than 5% of the total fatty acids, sometimes as much as 10% in common vegetable oils (peanut, soybean, corn, coconut) and in marine-animal oils. Lard, tallows, cocoa butter palm oil contain 25 to 40% of this component.

Fatty acids

- **Stearic acid** (18:0) was described by **Chevreul** (1823) in the course of his researches on fats. It is the highest molecular weight saturated fatty acid occurring abundantly in fats and oils. It occurs in small quantities in seed and marine oils. Milk fats (5-15%), lard (10%), tallows (15-30%), cocoa and shea butters ((30-35%) are the richest sources of stearic acid. It is the principal constituent of hydrogenated fats and oils (about 90%).

- **Arachidic acid** occurs in appreciable quantities in groundnut oil (3%). It is also found in the depot fat of some animals and in milk fats.

- **Behenic acid** was first reported as a constituent of ben (behen) oil (seeds of *Moringa oleifera*). Except for the seed oils of the *Crucifereae* (between 0.5 and 3.4%), this fatty chain does not occur in the principal oils. Large amounts are found in hydrogenated animal and vegetal oils (8-57%).

Solubility in water at 20°C (in grams acid per liter)

Carbon number	Solubility
2	infinite
4	infinite
6	9.7
8	0.7
10	0.15
12	0.055
14	0.02
16	0.007
18	0.003

Mono & Poly unsaturated f.a.

Systematic name	Trivial name	Shorthand designation	Molecular wt.	Melting point (°C)
cis-9-hexadecenoic	palmitoleic	16:1(n-7)	254.4	0.5
cis-9-octadecenoic	oleic	18:1(n-9)	282.4	16.2
cis-13-docosenoic	erucic	22:1(n-9)	338.6	33.4

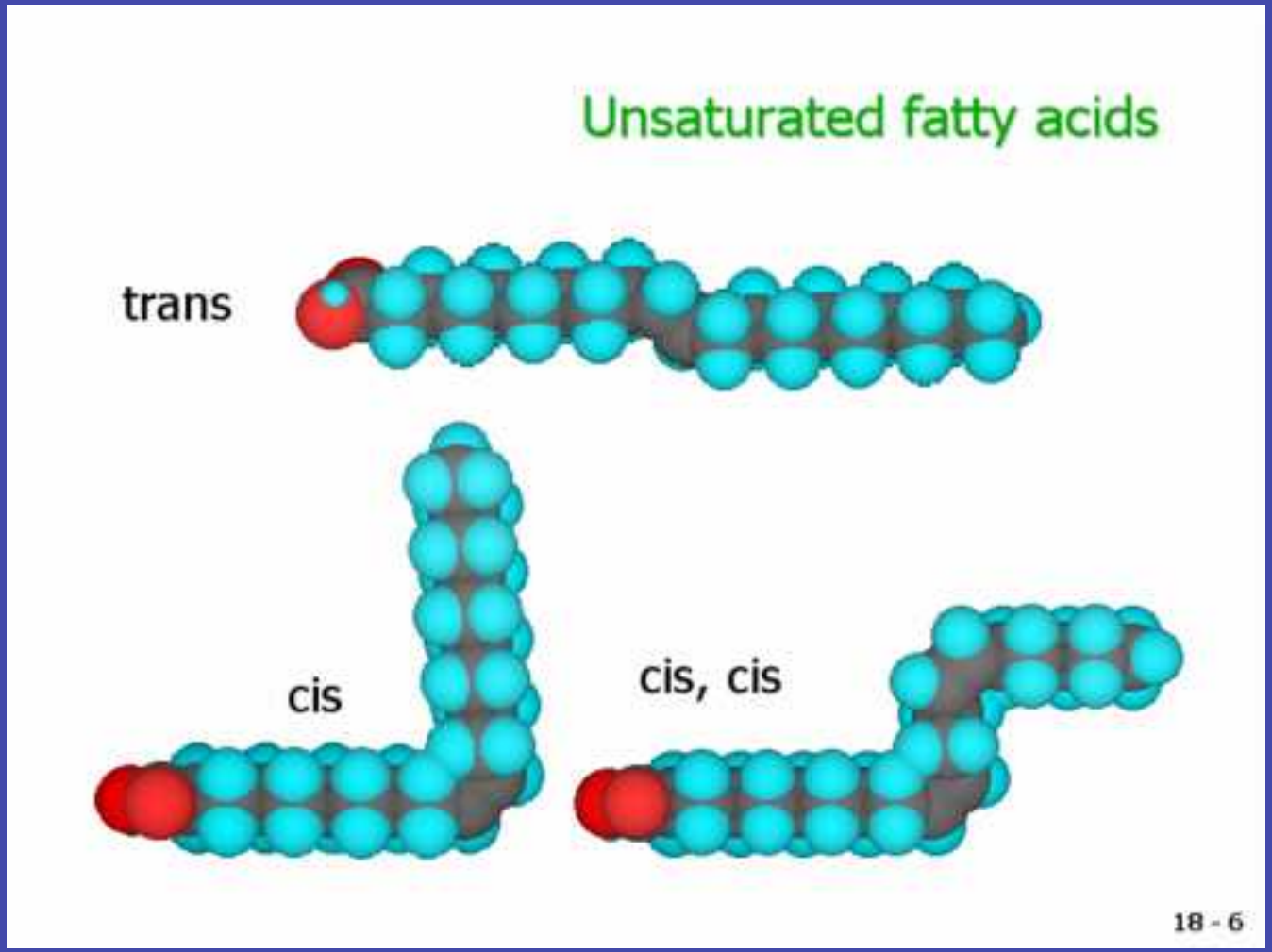
Systematic name	Trivial name	Shorthand designation	Molecular wt.	MP °C
9,12-octadecadienoic	linoleic	18:2(n-6)	280.4	-5
5,8,11,14-eicosatetraenoic	arachidonic	20:4(n-6)	304.5	-50
9,12,15-octadecatrienoic	α-linolenic	18:3(n-3)	278.4	-11
5,8,11,14,17-eicosapentaenoic	EPA	20:5(n-3)	302.5	-54
4,7,10,13,16,19-docosahexaenoic	DHA	22:6(n-3)	328.6	-44

Monounsaturated fatty acids

- **Oleic acid** is probably the most common fatty acid (olive oil has a high content of this acid: about 60-70%, but it is also found in a large range of nuts).

- **Palmitoleic acid** is found mainly in animal fats, particularly in fish and marine mammals. This acid was first noticed in 1854 in sperm whale oil and named physetoleic acid.

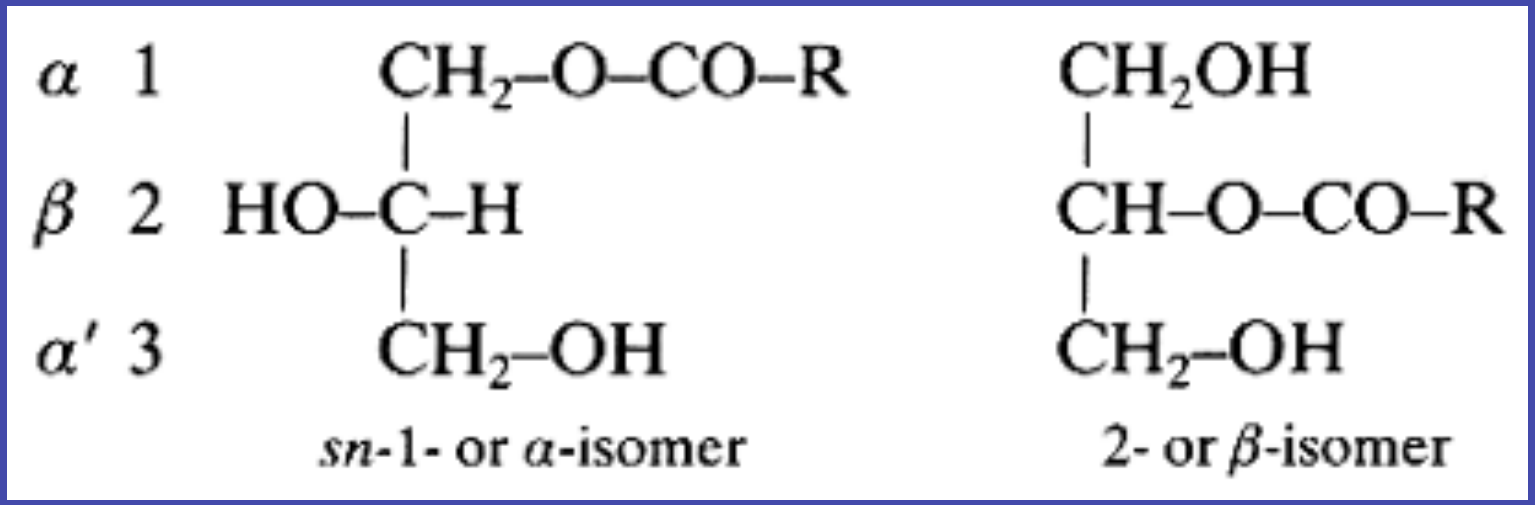
- **Erucic acid**, with 22 carbon atoms, is found in high amounts (up to 50%) in seed oils of the *Cruciferae* such as *Nasturtium*, rape, mustard, *Lunaria* (38-48%) and of the *Tropaeolaceae*.


Unsaturated fatty acids
trans
cis
cis, cis
18 - 6

ACYLGLYCEROLS
OR
GLYCERIDES

- These important constituents are known also as acylglycerols and most commonly as neutral fats.
- The IUPAC-IUB commissions on biochemical nomenclature have recommended that the names triacyl-, diacyl- and monoacylglycerol should replace the terms triglyceride, diglyceride and monoglyceride.

MONOACYLGLYCEROLS



MONOACYLGLYCEROLS

- Monoacylglycerols are the most polar components of simple lipids (they have only one hydrocarbon chain and 2 alcohol groups) and, thus, need care to prevent their loss in hydrophilic solutions and on chromatographic columns. Furthermore, they have detergent properties, hence they easily form micelles in water solutions.

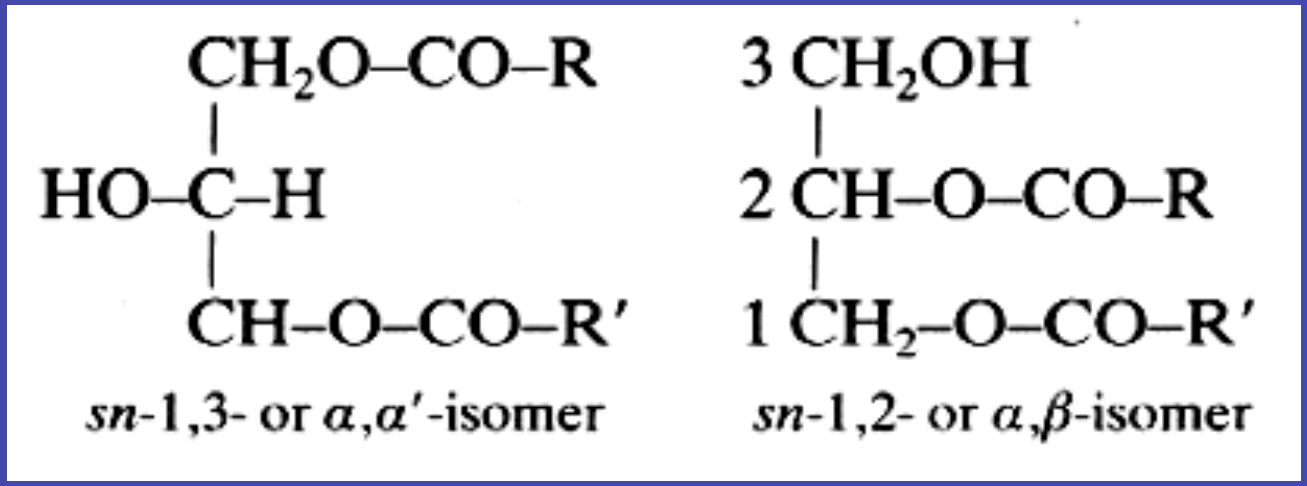
MONOACYLGLYCEROLS

- Monoacylglycerols with saturated or unsaturated fatty acids are by far the most commonly used food surfactants.
- Surfactants are used in the food industry to prepare food products and increase their shelf life. They give to emulsions their stability and the required viscosity.
- The first use on an industrial scale was, more than 50 years ago, for making margarine where they emulsify the water phase in oil and fat phase.
- They are now currently included in low-calorie spreads, peanut butter, ice cream to control their texture, starch-base food (macaroni, noodles, potato products...) and baking industry.

MONOACYLGLYCEROLS

- Monoacylglycerols are used also as raw materials for making more lipophilic or more hydrophilic molecules utilized in food industry.
- Esters are made with acetic, lactic, succinic and citric acids to emulsify commercial products.
- These food additives are permitted for use in foods after they have been tested in toxicological studies and are assigned a GRAS number after regulation by the US Food and Drug Administration or an E number by a EEC Council Directive.
- In the US, only monoacylglycerols are generally recognized as safe. No established acceptable daily intakes are defined for these surfactants.

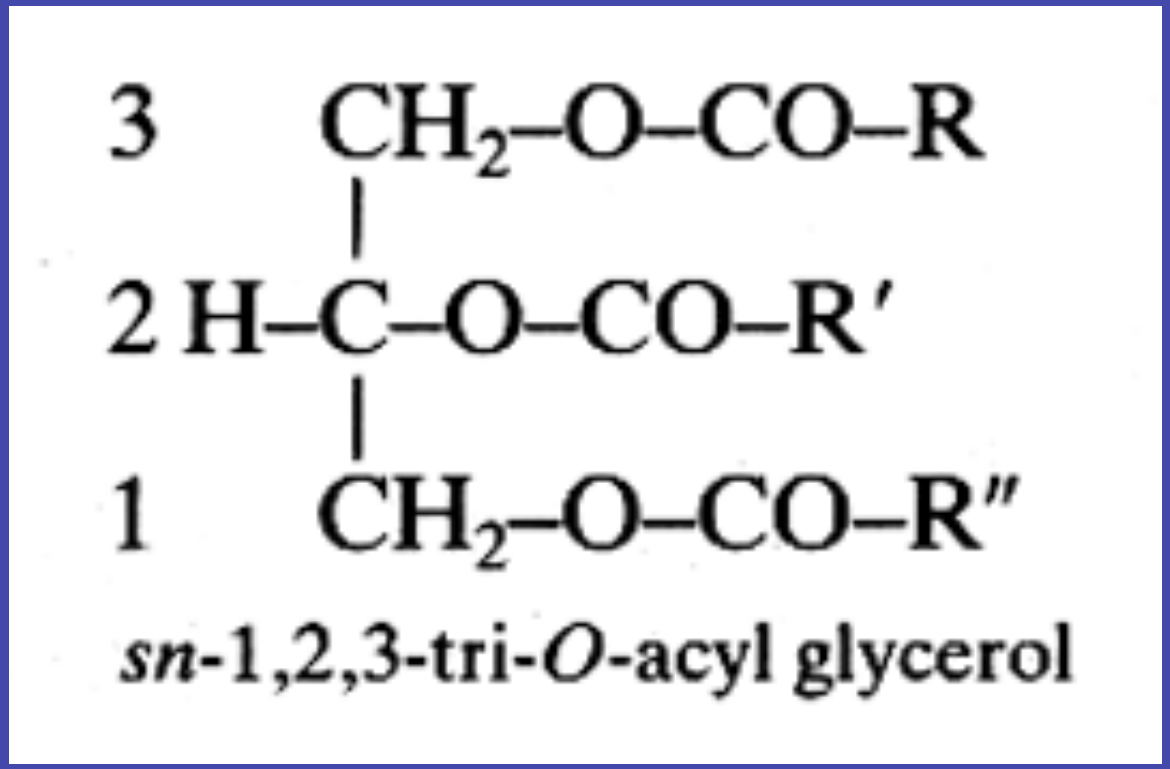
DIACYLGLYCEROLS



DIACYLGLYCEROLS

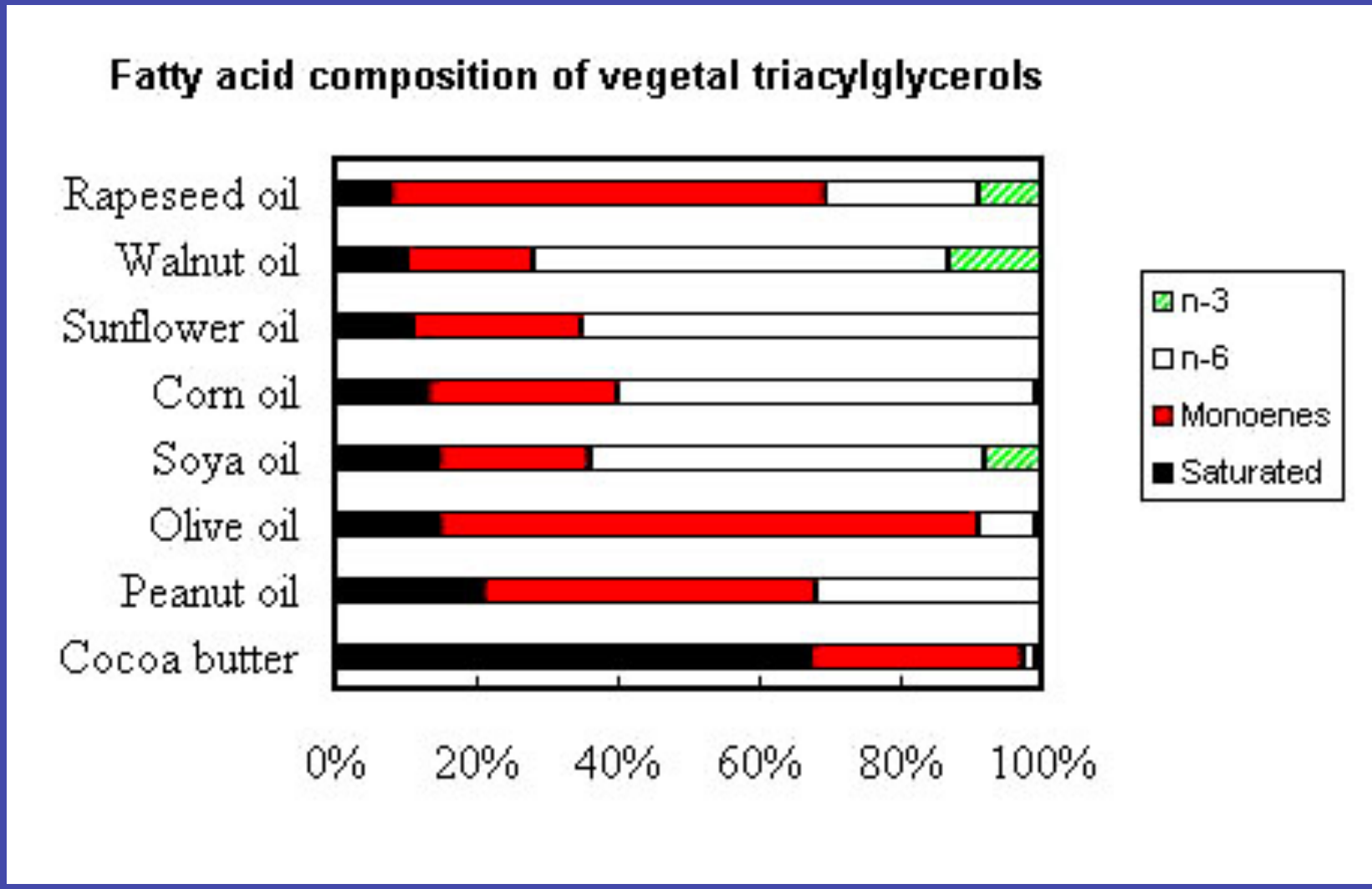
- Diacylglycerols are the main components of new cooking oils (ex: Econa, Kao corp.). These oils are proposed to slow the increase of blood triglycerides to help prevent the accumulation of body fat and high blood cholesterol levels.

TRIACYLGLYCEROLS



sn-1,2,3-tri-*O*-acyl glycerol

Fats and Oils



Fats and Oils

- From a world production of about 20 million tons in 1939, about 77 million tons were produced in 1989 whose 74% were of vegetal origin. In 1999-2000 the global production of fats and oils was 113 million tons with 82% of vegetal origin.
- The global vegetable oil consumption has more than doubled between 1980 and 2000, reaching about 76 million tons.

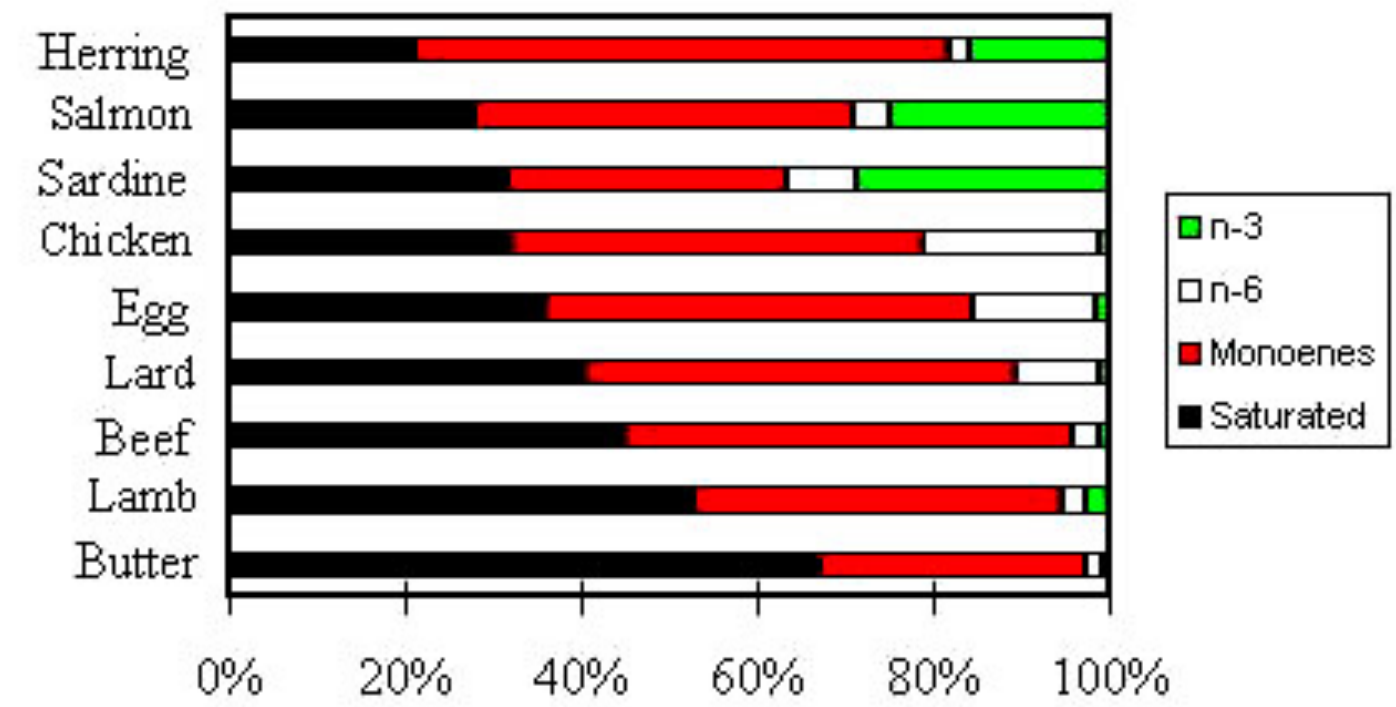
Fats and Oils

- All plants contain oils (ex. olive oil) or fats (ex. cocoa butter) and mainly in their seeds. Vegetal oils are frequently classified in two main groups, according to their source: pulp oil (palm, olive, avocado) and seed oil (other sources). The amount of lipids in plant parts varies from as low as 0.1% in potatoes to about 70% in pecan nuts. Some vegetal products are fat poor (1% in lentils, 3% in mushrooms), some seeds have a middle range amount (about 10% in wheat germ, 20% in soybeans) while some are very oily (44% in peanuts, 55% in almonds, 65% in walnuts).

ANIMAL FATS

- Animal fats can be found in various products such as by-products of meat (carcass fat of cattle and pigs, tallow, lard), by-products of fish caught (fish oil), milk (milk fat, butter fat) and accessorily poultry and eggs. In contrast with oil plants no livestock is bred particularly for fat production.

ANIMAL FATS


Fatty acid composition of animal triacylglycerols
Herring
Salmon
Sardine
Chicken
Egg
Lard
Beef
Lamb
Butter
0%
20%
40%
60%
80%
100%
n-3
n-6
Monoenes
Saturated

Lipid functions

Cell membrane structure

- Creates a barrier for the cell.
- Controls flow of materials.

Energy storage

- Fats stored in adipose tissue.

Hormones and Vitamins

- Hormones - communication between cells.
- Vitamins - assist in the regulation of biological processes.

Classification of lipids

- **Fatty Acids.** A fatty acid consists of a long nonpolar chain of carbon atoms, with a polar carboxylic acid group at one end. Most natural fatty acids contain an even number of carbon atoms. They may be saturated, unsaturated, or polyunsaturated (containing two or more double bonds). Fats and oils are simple lipids that are esters of glycerol and fatty acids. The difference between fats and oils is the melting point, which is essentially a function of the fatty acids in the compound.

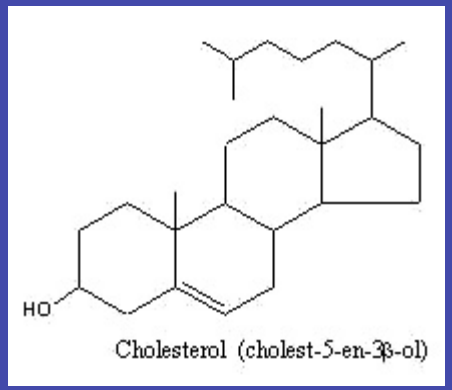
- **Chemical Properties of Fats and Oils.** Fats and oils can be hydrolyzed in the presence of acid to produce glycerol and fatty acids. When the hydrolysis reaction is carried out in the presence of a strong base, salts of the fatty acids (soaps) are produced. During hydrogenation, some multiple bonds of unsaturated fatty acids contained in fats or oils are reacted with hydrogen and converted to single bonds.

Classification of lipids

- **Waxes.** Waxes are simple lipids composed of a fatty acid esterified with a long-chain alcohol. Waxes are insoluble in water and serve as protective coatings in nature.

fatty acid long-chain alcohol

- **Steroids.** Steroids are compounds that have four rings fused together in a specific way. The most abundant steroid in humans is cholesterol, which serves as a starting material for other important steroids such as the bile salts, adrenocorticoid hormones, and the sex hormones.



Melting point

18:0 stearic	70 C
18:1 oleic (cis)	13
18:1 (trans)	44
18:2 linoleic (cis-cis)	-5
18:2 (trans-trans)	28

Melting point

Trisaturated	S-S-S	72
	P-P-P	65
	S-P-P	62
Disaturated	P-O-P	37
	O-P-P	34
	S-O-P	35
	S-P-O	39
	P-S-O	36
Diunsaturated	O-O-P	19
	O-O-S	23
Triunsaturated	O-O-O	5
	E-E-E	42
	L-L-L	-10

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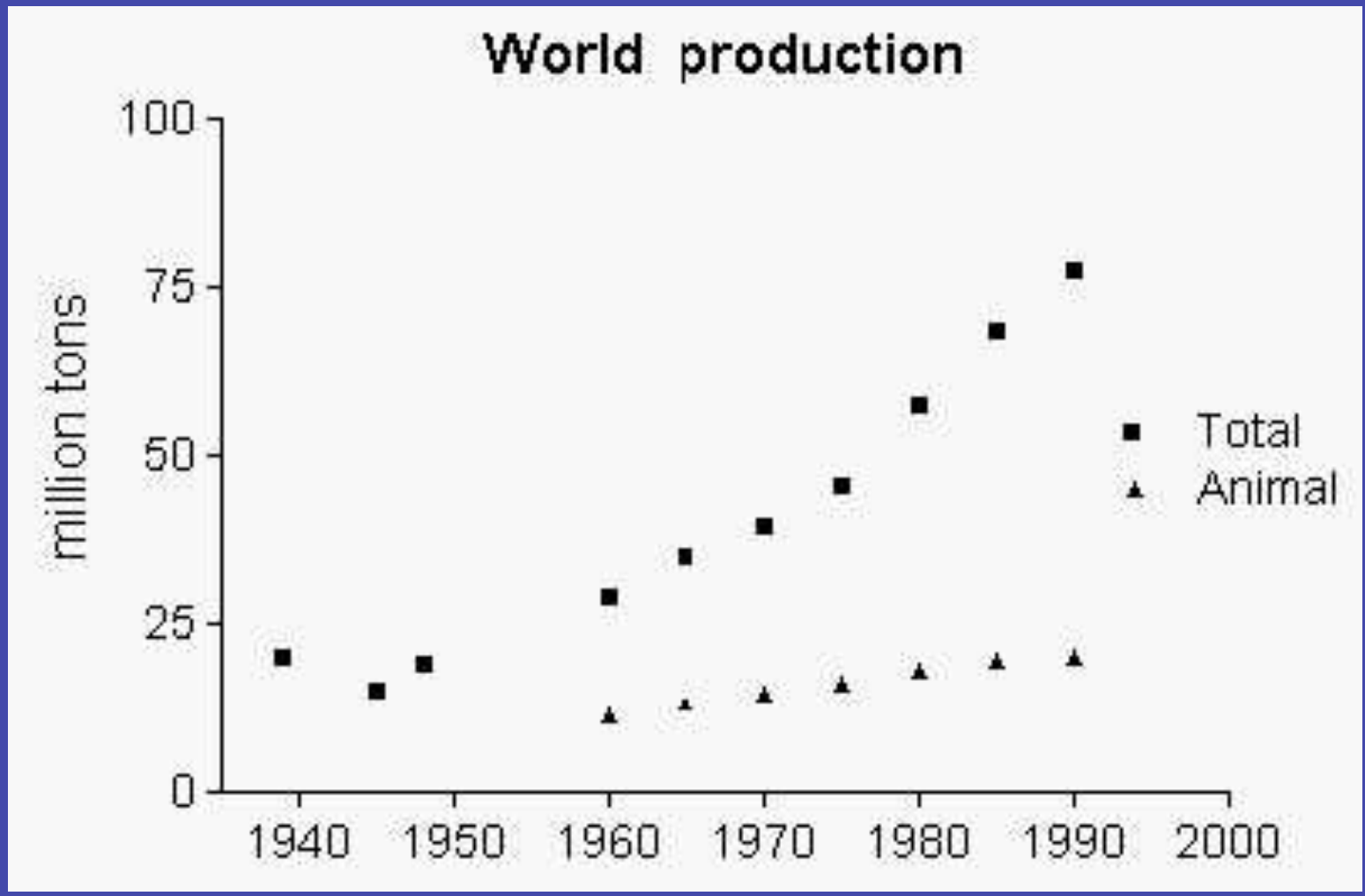
Fats and Oils



MAIN WORLD SOURCES OF OILS

- about 70 million tons of vegetal oils are produced per year and that about 70% of that production are accounted for four vegetal species:
  - 1 - **Soya oil**, about 26% of the world production, in USA, Argentina, Brasil and China
  - 2 - **Palm oil**, about 18% of the world production, in Malaysia, Indonesia and Africa
  - 3 - **Rape oil**, about 12% of the world oil production (for 2000-01), in China (32%), EEC (26%), India (11.3%), Canada (9.3%), and Japan (6.6%).
  - 4 - **Sunflower oil**, about 13% of the world production, in EEC, Russia and Argentina

MAIN U.S. SOURCES OF OILS

Soybean oil
Cottonseed oil
Corn oil
Peanut oil
Palm oil
Cocoanut oil
Canola oil
Sunflower oil
Safflower oil

Fatty acid	Soy	Cotton	Maize	Palm	Coconut
8:0		-			9-10
10:0		-			5-10
12:0		-			40-54
14:0	-	<1	-	0-15	15-23
16:0	8-13	17-31	8-13	22-46	6-11
16:1	-	<1	<1	0-2.5	<2
18:0	2-5	1-3	1-4	0.5-5	1-4
18:1	17-26	13-21	24-32	36-68	4-11
18:2(n-6)	50-62	34-60	55-62	2-20	1-2
18:3(n-3)	4-10	<1	<2	<1	-
20:0	<1	-	<1	<0.5	
20:1	<0.4		<0.5	-	
22:0	<0.5		<0.5	-	
22:1	-			-	-

Fatty acid composition of monounsaturated and high polyunsaturated oils

Fatty acid	Peanut	Olive	Canola	Sunflower
8:0	-	-	-	
10:0	-	-	-	
12:0	-	-	-	
14:0	-	-	-	-
16:0	8-13	8-21	5	5-7
16:1	<0.3	1-4	-	<0.5
18:0	1-4	1-6	2	4-6
18:1	35-66	53-80	55-61	15-25
18:2	14-41	2-24	20-21	62-70
18:3	<0.3	1-2	8-11	-
20:0	<2	<0.5		<1
20:1	<2	<0.5		<0.5
22:0	2-5	<1		<1

ANIMAL FATS

- Animal fats can be found in various products such as by-products of meat (carcass fat of cattle and pigs, tallow, lard), by-products of fish caught (fish oil), milk (milk fat, butter fat) and accessorily poultry and eggs. In contrast with oil plants no livestock is bred particularly for fat production.

LIPIDS OF LAND ANIMALS

- ## Lard

  This fat is obtained from cutaneous adipose tissue of pork. Its fatty acid composition depends on the diet. As an example, linoleic acid content is low (about 2%) when pork is fed with rice but high (about 30%) when soja is used as main food.
  The dressed weight of pigs contains about 30% fat but very fat pigs can contain up to 50% fatty matter. The world production of lard is about 5 million tons per year.

- ## Beef tallow

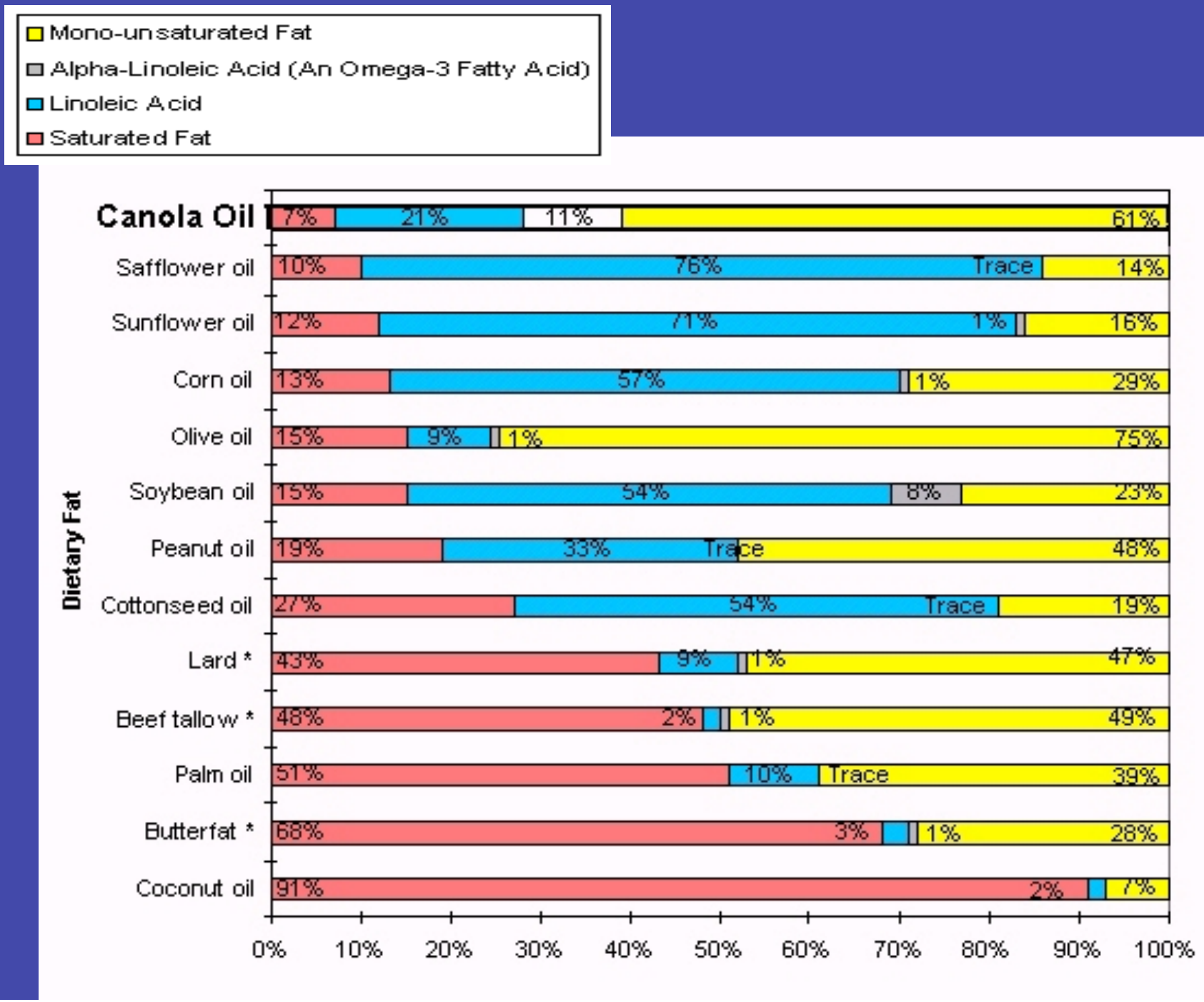
  This fat is extracted from beef adipose tissue. By definition, tallow is fat rendered primarily from cattle, but it also is fat from sheep and goats. Its fatty acid composition depends on the tissue location more than on the food ingested. As lipids are partially hydrogenated in the rumen, 6-8% elaidic acid and traces of conjugated dienes and trienes are detected in beef tallow.
  The proportion of fat in the dressed weight varies from 8% up to 25% in fat beef. The world production of beef tallow was about 8.2 million tons in 1999-2000 (about 7% of the global fats and oils production).
  Accounts of the use of tallow in soapmaking extend back thousands of years (traditional soap is made of about 85% tallow and 15% coconut or palm kernel oil). Tallow was also a part of the world's first surviving art since prehistoric cave paintings were most probably made using animal tallow mixed with pigments.
  While amounts of tallow used for edible purposes in human show slight decline, its use is increasing in animal feeds.
  Inedible tallow gives numerous and various derivatives from plastics, lotions, soaps and detergents, tires, candles, paints and varnishes, lubricants and several pharmaceuticals. Tallow is an important factor in the global fatty acids market. These fatty acids play an important role in the formulation of pesticides, herbicides, emulsifiers, and dispersing agents. Several derivatives are produced from tallow : fatty alcohols, amines, amides, esters and glycerol.

Animal fatty acids

	Lard	Tallow	Poultry
14:0	1-2	3-4	0.2-1.3
15:0	-	<0.6	-
16:0	22-26	23-27	22-28
16:1	1.5-3	2-4	2-9
17:0	<0.5	1-1.5	-
17:1	<0.4	<1	-
18:0	13-18	15-23	6-11
18:1	39-45	36-43	37-53
18:2	8-15	1.5-4	9-25
18:3	0.5-1.5	0.3-1	<2
20:0	<0.3	<0.2	-
20:1	<1.3	<0.5	-
isoC15-18	<0.3	1-2.5	-

Animal fatty acids

	sn	14:0	16:0	16:1	18:0	18:1	18:2	20:1	22:1	20:5	22:5	22:6
Pig	**1** **2** **3**	2 4 1	16 **59** 2	3 4 3	21 3 10	**44** 17 **65**	12 8 24					
Chicken	**1** **2** **3**	2 1 1	25 15 24	12 7 12	6 4 6	**33** **43** **35**	14 23 14					
Herring	**1** **2** **3**	6 10 4	12 17 7	13 10 5	1 1 1	16 10 8	3 3 1	**25** 6 **20**	14 5 50	3 **18** 4	1 3 1	1 13 1
Cod	**1** **2** **3**	6 8 4	15 16 7	14 12 14	6 1 1	**28** 9 **23**	2 2 2	12 7 17	6 5 7	2 12 13	1 3 1	1 20 6


Mono-unsaturated Fat
Alpha-Linoleic Acid (An Omega-3 Fatty Acid)
Linoleic Acid
Saturated Fat
Dietary Fat
Canola Oil
7%
21%
11%
61%
Safflower oil
10%
76%
Trace
14%
Sunflower oil
12%
71%
1%
16%
Corn oil
13%
57%
1%
29%
Olive oil
15%
9%
1%
75%
Soybean oil
15%
54%
8%
23%
Peanut oil
19%
33%
Trace
48%
Cottonseed oil
27%
54%
Trace
19%
Lard *
43%
9%
1%
47%
Beef tallow *
48%
2%
1%
49%
Palm oil
51%
10%
Trace
39%
Butterfat *
68%
3%
1%
28%
Coconut oil
91%
2%
7%
0%
10%
20%
30%
40%
50%
60%
70%
80%
90%
100%

Fat content in food

		Butter	80%
Sausage (raw)	50%	Margarine	80%
Hotdogs	30%	Peanut Butter	53%
Hamburger (raw)	30%	Cheddar Cheese	34%
Hamburger,cooked	17.5	Semi-sweet chocolate	30%
Ham, cooked	18%	Mozzarella Cheese	17%
Herring	12.5%	Cream of Chix Soup	9%
Beef	8-25%	Whole Milk	3.3%
Chicken	4-17%	Whole Wheat Bread	3%
Cod	0.4%	Chicken Noodle Soup	1.5%

Functions of fat in food

- Texture
  - Tenderization
    - Bakery products – interferes with gluten (protein) development
    - Less mixed products form layers between dough to make flaky products
    - Smoothness in candies, frozen desserts by retard crystallization
    - Juiciness of meat

Functions of fat in food

- Aeration
  - Increased viscosity of batter
- Heat transfer
  - Rapid heat transfer