

A. Introduction to acyl lipids (fatty acids):

Why study plant fatty acids?

- provide energy storage in seeds, and are important in the human diet as essential nutrients
- are key plant body components: plant cuticles and membranes are acyl lipids
- plants make unique many fatty acids, and combined with genetic engineering, have great potential as 'green chemistry'
- there are lipid-derived signaling molecules and hormones

Lecture 6 & 7 Outline:

1. Structure and diversity of acyl lipids and fatty acids
2. Biosynthesis of fatty acids and triacylglycerol (brief)
3. Modification of seed oils via plant biotechnology

Some Definitions:

lipid: cellular constituents insoluble in water but soluble in non-polar organic solvents

acyl lipid: fatty-acid containing lipid (found in both membranes and storage oils)

fatty acid (FAs): carboxylic acids attached to a long (hydrophobic) hydrocarbon chain.

degree of unsaturation: the number of double bonds (i.e. saturated with H)

FAs in plants are not found as free acids:

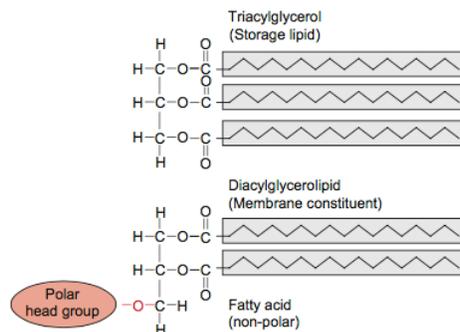
- found as **esters**: = fatty acid esterified to **alcohol** (-OH)
 i.e. glycerol, or to **thiol** (-SH) in **Coenzyme A** (CoA), or **acyl carrier protein** (ACP)
[Coenzyme A = small molecule (coenzyme) used in enzymatic transfer of acyl groups.]

i) Glycerolipids are the common plant lipids (glycerol esterified with one or more fatty acids]

- i) **Triacylglycerols (TAG)** - Glycerol esterified to 3 fatty acids
 - Seed oils are TAGs, very important economically.
- ii) **Glycolipids** - glycerol plus two fatty acids, and one or two galactose units:
monogalactosyl diacyl glycerol (MGDG) and digalactosyl diacyl glycerol (DGDG)
- iii) **Phospholipids** - glycerol plus 1 or 2 fatty acids, plus phosphate ester linking a polar head group.

ii) Waxes and cutin are essential plant tissue components

- wax:** ester of saturated fatty alcohol with saturated fatty acid.
- cutin:** fatty acid with hydroxyls on chain, esterified to carboxyl carbon.



B. Fatty acid structure and diversity:

Basic features

- monocarboxylic, unbranched
- unsaturation is critical: note position, *cis* or *trans* configuration of double bond
- nomenclature: Carbons and desaturation positions (linolenic acid = 18:3 *cis* Δ^{8,12,15})
- note also the 'omega-3, omega-6' naming system
- types of FAs are based on lengths: medium , regular, long chain, very long chain

Structure and melting point depends on: i) **chain length** and ii) the degree and type of **desaturation**

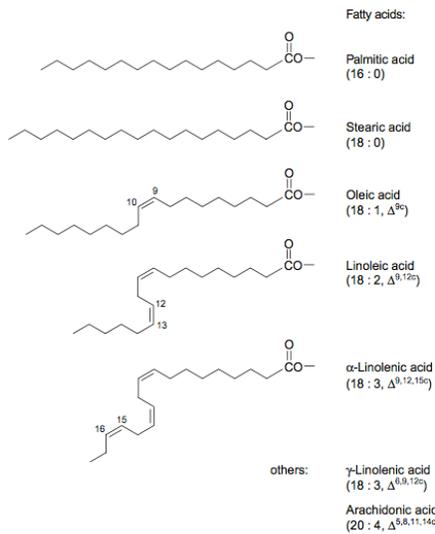


Table 15.1: Influence of chain length and the number of double bonds on the melting point of fatty acids

Fatty acid	Chain length: double bonds	Melting point
Lauric acid	12:0	40°C
Stearic acid	18:0	70°C
Oleic acid	18:1	13°C
Linoleic acid	18:2	-5°C
Linolenic acid	18:3	-11°C

Plants have a diversity of FAs (especially in seed oils)

- leaf FA profiles are similar** (see table), reflecting a highly conserved photosynthetic function.
 - 80 % of leaf FAs are in thylakoid membranes, highly polyunsaturated (18:2, 18:3)
 - fluidity of membranes depends on polyunsaturated FA, especially in cold temperature
- TAG (seed) FA profiles can be very distinct**, reflecting fewer constraints as long as they store C
 - six most common FAs to know

Table 15.3: World production and fatty acid composition of the most important vegetable oils

	World production 10 ⁶ t 2005	% of fatty acid content						
		C 12:0	C 14:0	C 16:0	C 18:0	C 18:1	C 18:2	others
Soybean	30	0	0	8	4	28	53	7
Palm	25	0	2	42	5	41	10	0
Rape seed	13	0	0	4	1	60	20	15
Sunflower	9	0	0	6	4	28	61	1
Peanut	5	0	0	10	3	50	30	3
Coconut	3	48	17	9	2	7	1	16
Palm kernel	3	50	15	7	2	15	1	10
Total production plant fats	98							

Table 6.3 The fatty acid composition of some plant leaves

Plant	Fatty acid composition (% total)				
	16:0	18:1	18:2	α-18:3	Others
Barley	13	6	6	64	11
Pea	12	2	25	53	8
Rape ^a	13	4	16	50	17
Soybean	12	7	14	56	11
Spinach ^a	13	5	14	54	14
Wheat	18	5	15	55	7

^aThese species are '16:3-plants' which have a distinctive pathway of lipid metabolism which involves the desaturation of palmitate to hexadecatrienoate (16:3) within the chloroplast.

Human Uses of FAs

i. FAs are common in food but (some) have potential negative health effects

- saturated FAs (palmitic, stearic acids)- margarine, butter (vs. unsaturated)
- polyunsaturated FAs (linolenic, linoleic acids) are essential, but less stable (oxidize)
- monounsaturated FAs (oleic acid) are favored for healthful eating (olive, canola)
- hydrogenation of oils leads to *trans* FAs (linked to poor health outcomes)

ii. Plant FAs have industrial uses as detergents, lubricants, feedstocks

- medium chain length saturated FAs (8-14Cs) (i.e. lauric acid - soaps, detergents (SDS))
- polyunsaturated: linolenic (18:3), linoleic (18:2) - paints, linoleum, "drying oils"
- specialized **erucic acid** (22:1) - lubrication, stable at high temperatures
ricinoleic acid (18:1 15OH) lubrication, synthesis of nylon + plastics

Table 15.4: Industrial utilization of fatty acids from vegetable oils

	Main source	Utilization for
Lauric acid (12:0)	Palm kernel, coconut	Soap, detergents, cosmetics
Linolenic acid (18:3)	Flax seed	Paints, lacquers
Ricinoleic acid (18:1, Δ9, 12-OH)	Castor bean	Surface protectants, lubricant
Erucic acid (22:1, Δ13)	Rape seed	Tensides Foam control for detergents, lubricant, synthesis of artificial fibers

C. Biosynthesis of Fatty Acids and Triacylglycerol (oil)

Overview of Biosynthesis

- occurs in both plastids and endoplasmic reticulum (ER)
- enhanced by light (requires lots of ATP, NADPH)
- two major routes and products: membrane lipids or TAGs

Stages of Biosynthesis *NB: most steps occur while FA is on Acyl Carrier Protein (ACP)*

i) Make malonyl-CoA from acetyl-CoA and HCO₃⁻

- Enzyme: *Acetyl-CoA carboxylase (ACCase)*
- committed step, light regulated, takes ATP
- prokaryotic and eukaryotic forms

ii) Elongate: 2 C's added per cycle (third C lost as CO₂)

- 1 acetyl-CoA + 7 x malonyl-ACP --> palmitoyl-ACP (16:0)
- Enzyme complex: *β-ketoacyl ACP synthase III (KAS III & KAS I)* (iterative cycle, 7 rounds)

iii) Add 2 more Cs & desaturate at C-9

- Palmitoyl-ACP --> Stearoyl-ACP --> Oleoyl-ACP (18:1)
- Enzymes: - *KAS II*
- *Δ9 stearoyl-ACP desaturase (Δ9 DES)* (soluble)
(soluble Fe⁺⁺ containing enzyme)

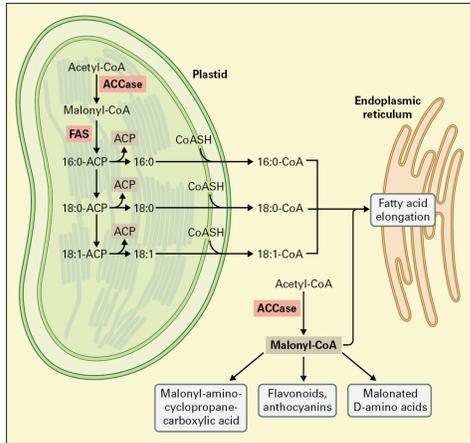
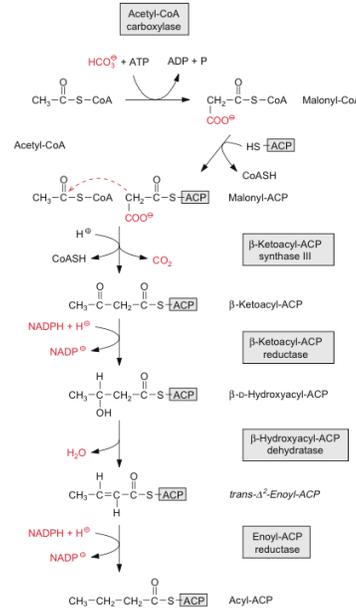


FIGURE 8.11 Multiple fates of malonyl-CoA. Malonyl-CoA produced by the ACCase reaction enters several pathways in plants. Within the plastid, malonyl-CoA is used exclusively for the production of fatty acids. In the cytosol, malonyl-CoA is the carbon donor for fatty acid elongation, producing the precursors for surface waxes and certain seed lipids. Condensation of three molecules of malonyl-CoA produces a diverse range of flavonoids and their derivatives (see Chapter 24). In many plant tissues, the major form of the caffeine precursor, 1-aminocyclopropane-1-carboxylic acid is the inactive malonated derivative, produced by reactions with malonyl-CoA. Finally, many D-amino acids and other secondary metabolites react with malonyl-CoA to form malonylated derivatives. CoASH, coenzyme A.

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iv) Release of FAs from ACP (two routes):

- a) **acyltransferase** - transfer to glycerolipid in plastid, where further desaturations can occur.
- b) **acyl-ACP thioesterase** - release as acyl-CoA, export to ER (where fatty acid can go to glycerolipid, also for further desaturations).
 - Thioesterase **specificity** determines acyl chain length.
 - The two routes represent **plastid** ('prokaryotic-type') and **ER** (eukaryotic-type) pathways

v) Plant fatty acids are usually desaturated further: Desaturation at Δ12, Δ15 (fatty acid desaturases; FADs)

- Δ12 **oleate desaturase (Δ12 DES)** --> linoleic a.
- Δ15 **linoleate desaturase (Δ15 DES)** --> linolenic a.
- occurs within membrane as a phospholipid, and the enzymes are membrane-bound
- occurs in both ER and plastid (different FADs)

