

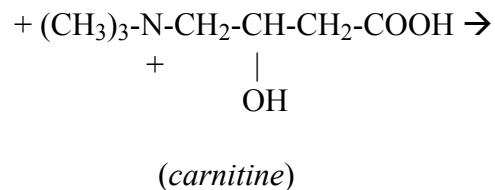
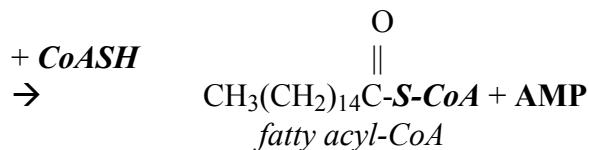
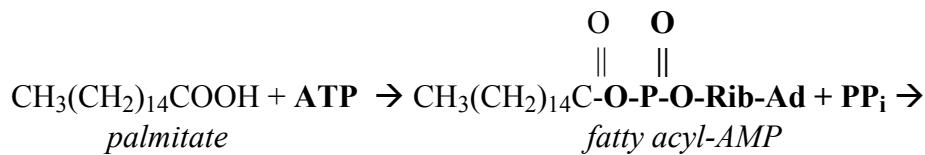
ANSC (NUTR) 618
LIPIDS & LIPID METABOLISM

Fatty Acid Oxidation

I. Enzymatic degradation of fatty acids in eukaryotic cells

A. Activation and transport

1. Activation: fatty acyl CoA synthetase
2. Carnitine palmitoyl transferase I (CPT-I; *carnitine acyltransferase*)
 - a. Exchanges carnitine for CoASH in cytosol
 - b. *Inhibited by malonyl-CoA*
3. Carnitine palmitoyl transferase II
 - a. Exchanges CoASH for carnitine
 - b. Carnitine is transported back to cytosol.



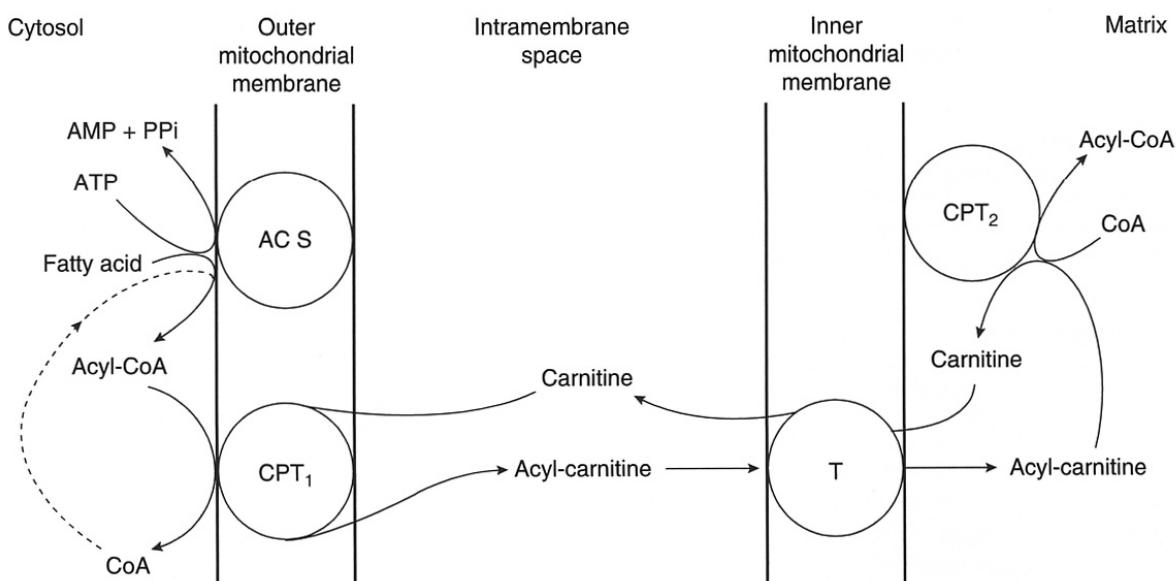
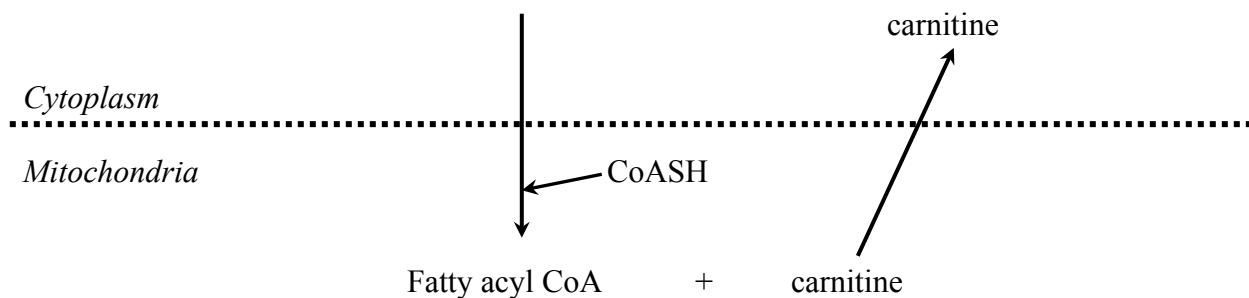
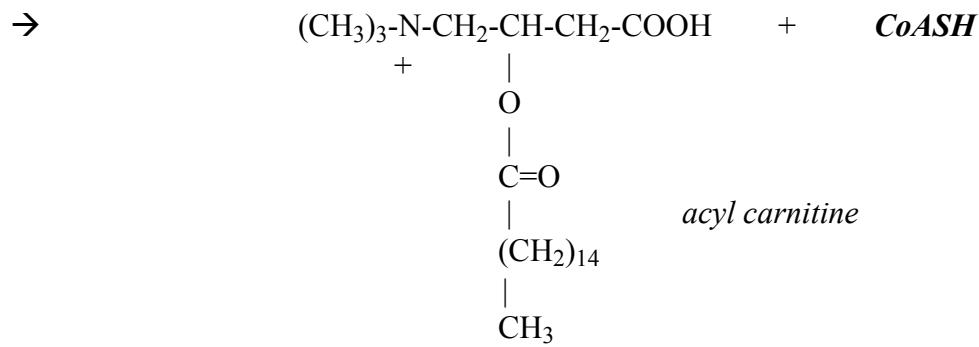
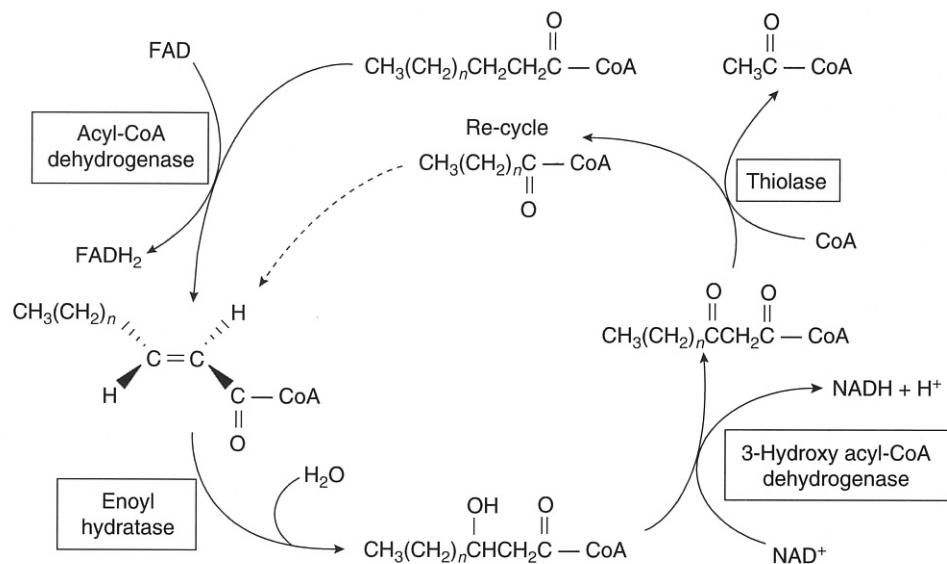


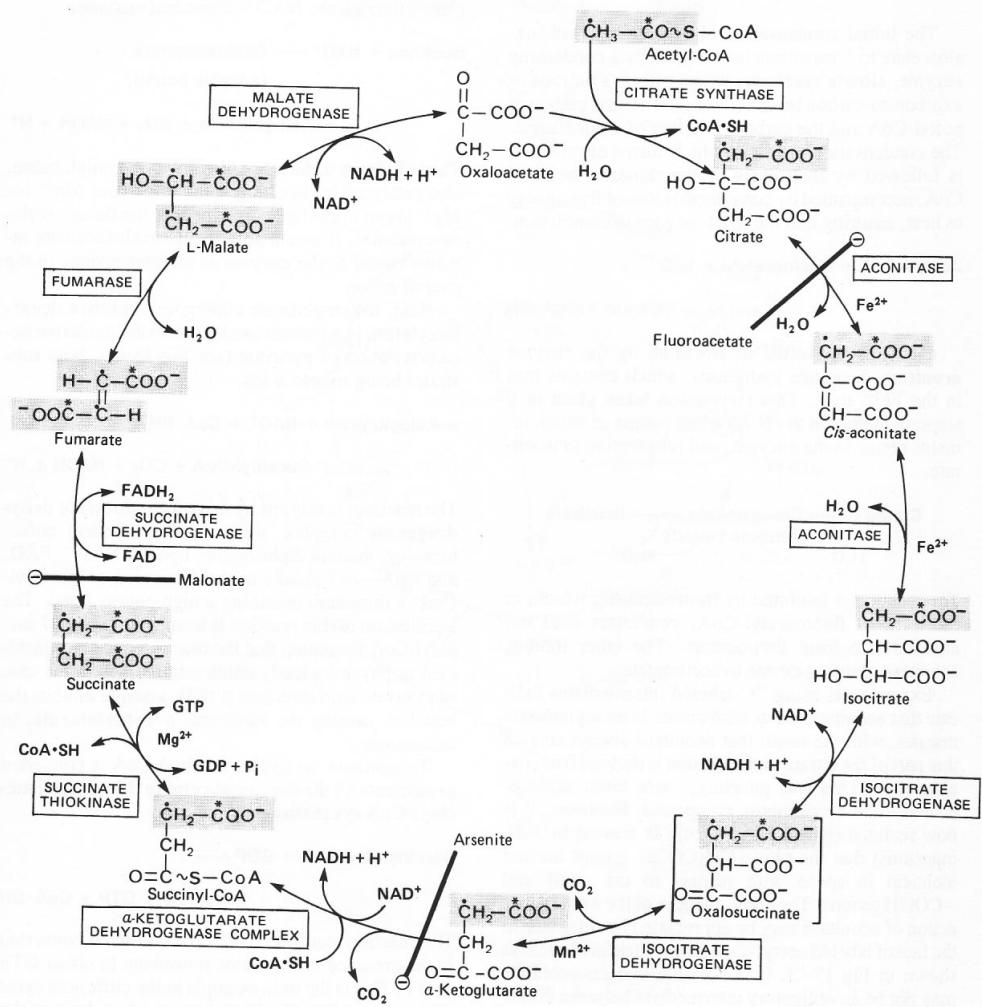
Fig. 2.27 Movement of acyl residues into mitochondria via carnitine. ACS = acyl-CoA synthetase; T = translocase; CPT = carnitine:palmitoyltransferase.

B. β -Oxidation

1. Oxidation of the α -carbon (by FAD) produces a *trans*-double bond.
2. The *trans*-double bond is hydrated, producing a hydroxy-fatty acyl-CoA.
3. The hydroxyl group is oxidized (by NAD^+) to produce a keto-fatty acyl-CoA.
4. The first two carbons are displaced to produce acetyl-CoA.

Fig. 2.28 The fatty acid β -oxidation cycle.

5. Entry of acetyl-CoA into the TCA cycle



6. Comparison to fatty acid synthesis

- Oxidation requires FAD, NAD⁺, synthesis requires NADPH.
- Oxidation requires CoASH derivatives, synthesis requires ACPs.
- Oxidation is multienzyme, synthesis requires just one enzyme complex.

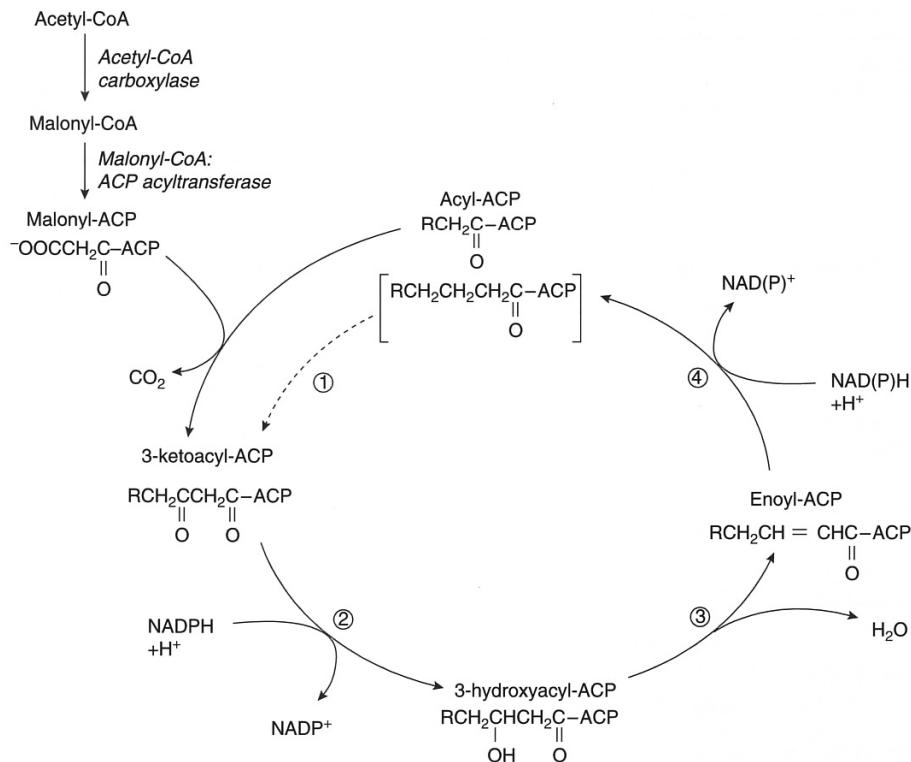


Fig. 2.7 The repeat cycle of reactions for the addition of two carbons by fatty acid synthase. Reactions of the cycle: (1) condensation (3-ketoacyl-ACP synthase); (2) reduction (3-ketoacyl-ACP reductase); (3) dehydration (3-hydroxyacyl-ACP dehydrase); (4) reduction (enoyl-ACP reductase).

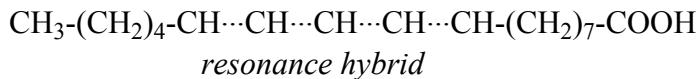
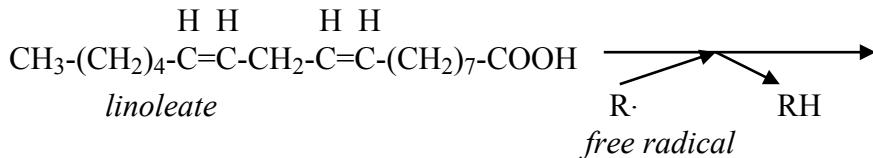
II. Nonenzymatic peroxidation of fatty acids

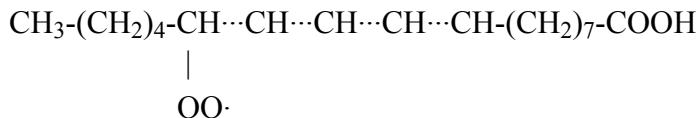
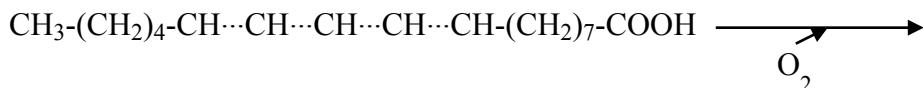
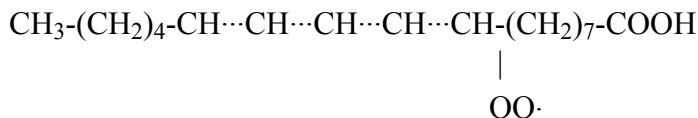
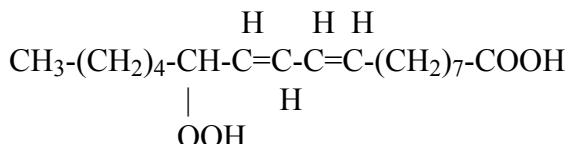
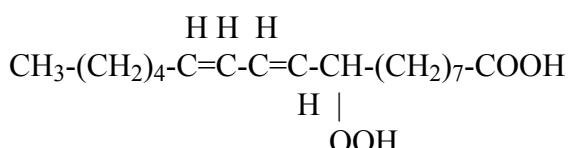
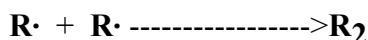
A. General

- Peroxidation = production of peroxides and their degradation products.
- Polyenoic acids (PUFA) are susceptible to peroxidation.

B. Mechanism of peroxidation:

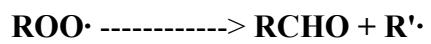
Initiation



Propagation*or**fatty acid free radicals (alkyl radicals; R·)**13-hydroperoxy-9-cis, 11-trans-octadecadienoic acid**or**9-hydroperoxy-10-trans, 12-cis-octadecadienoic acid (hydroperoxides; ROOH)***Termination****C. Decomposition of fatty acid peroxides**

1. Cause of rancidity (warmed-over flavor)
2. Forms aldehydes (homolysis)





(e.g., malonaldehyde)