Chapter 26
Lipids

Lipids

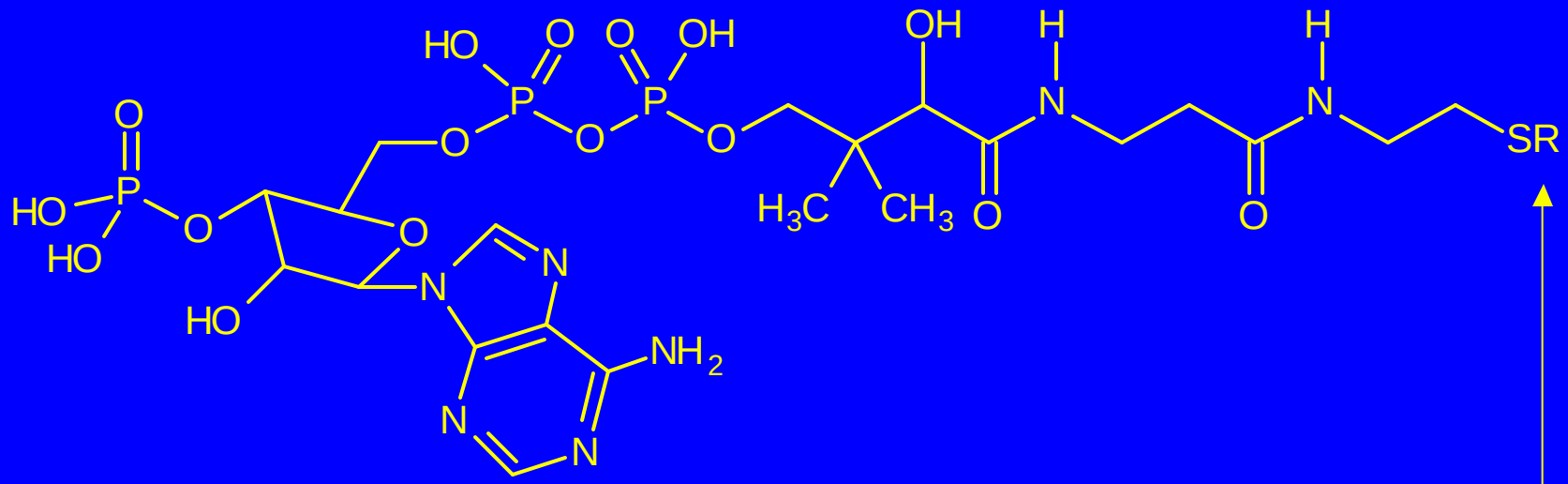
Lipids are naturally occurring substances grouped together on the basis of a common property—they are more soluble in nonpolar solvents than in water.

Some of the most important of them—the ones in this chapter—are related in that they have acetic acid (acetate) as their biosynthetic origin.

In many biosynthetic pathways a substance called *acetyl coenzyme A* serves as the source of acetate.

26.1
Acetyl Coenzyme A

Structure of Coenzyme A



R = H; Coenzyme A

$$R = \overset{O}{\overset{\|}{C}}CH_3;$$ Acetyl coenzyme A

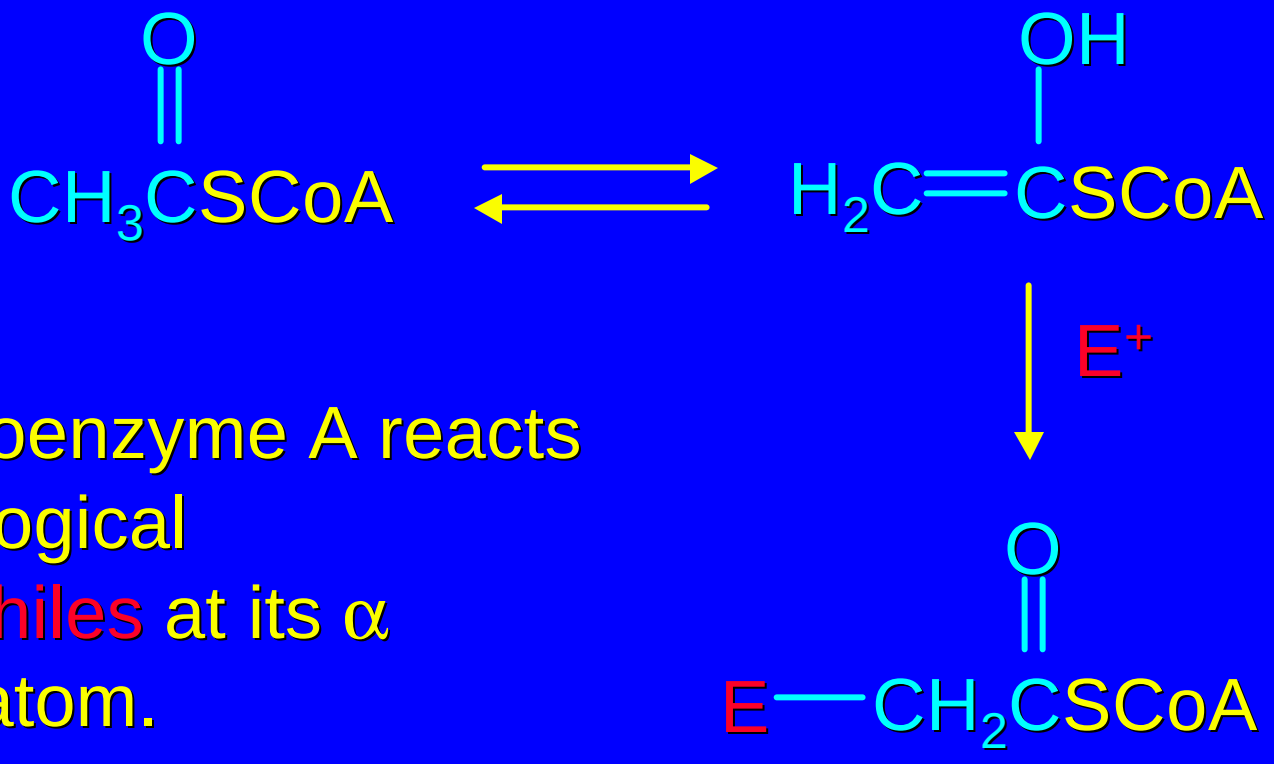
Reactivity of Coenzyme A

Nucleophilic acyl substitution

Acetyl coenzyme A is a source of an acetyl group toward biological nucleophiles; it is an acetyl transfer agent.

Reactivity of Coenzyme A

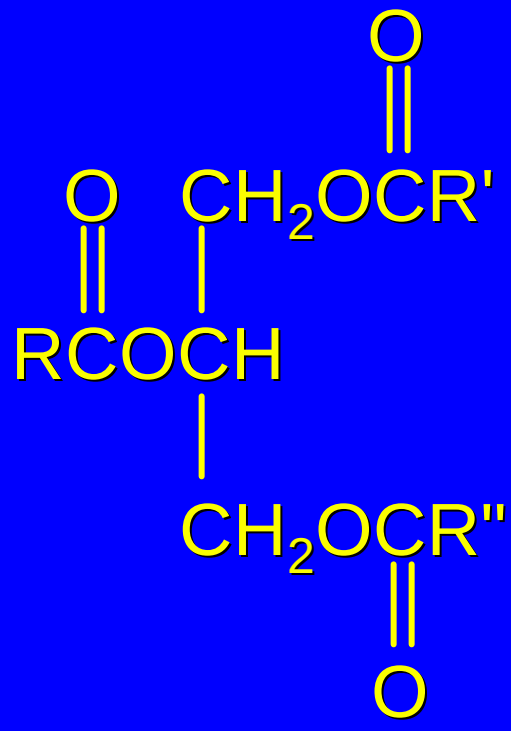
can react via enol



Acetyl coenzyme A reacts with biological electrophiles at its α carbon atom.

26.2
Fats, Oils, and Fatty Acids

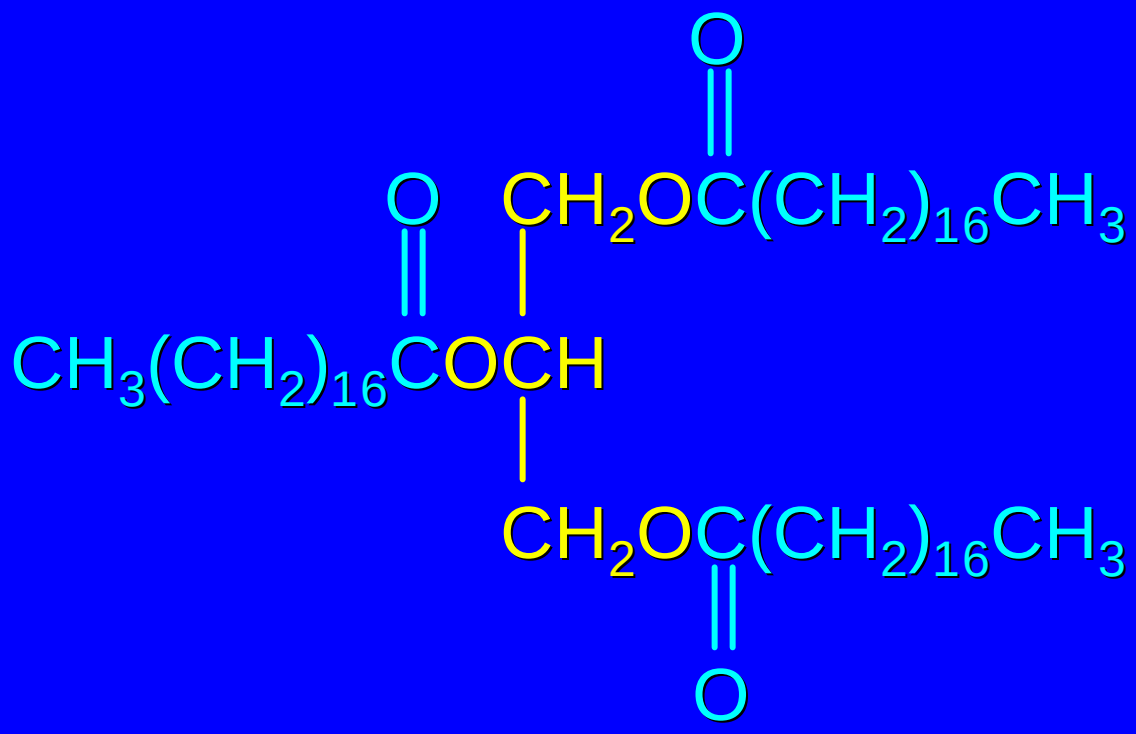
Fats and Oils



Fats and oils are naturally occurring mixture of triacylglycerols (also called triglycerides).

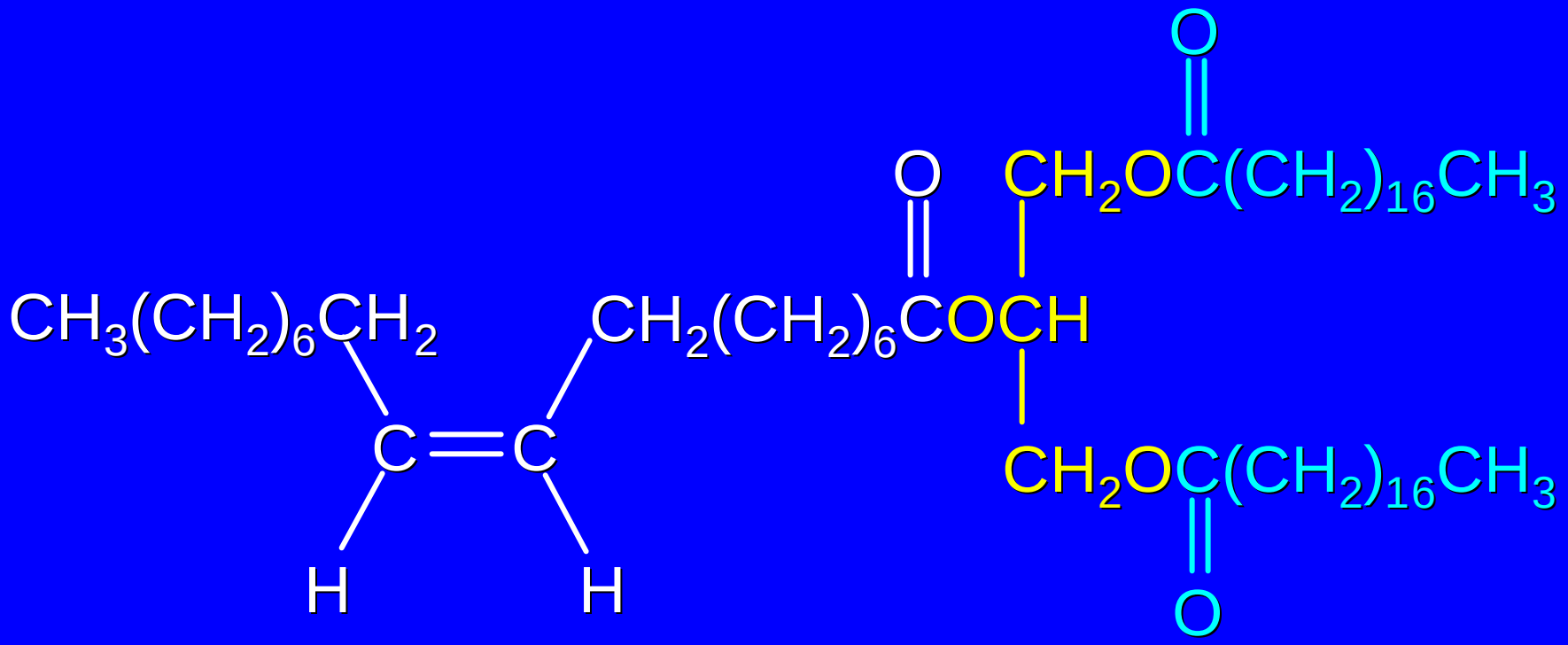
Fats are solids; oils are liquids.

Fats and Oils



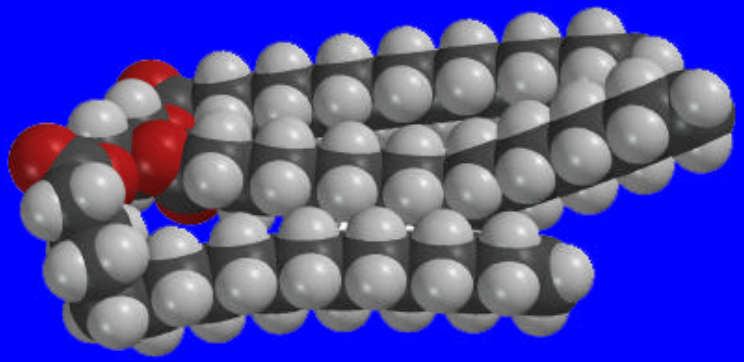
Tristearin; mp 72°C

Fats and Oils



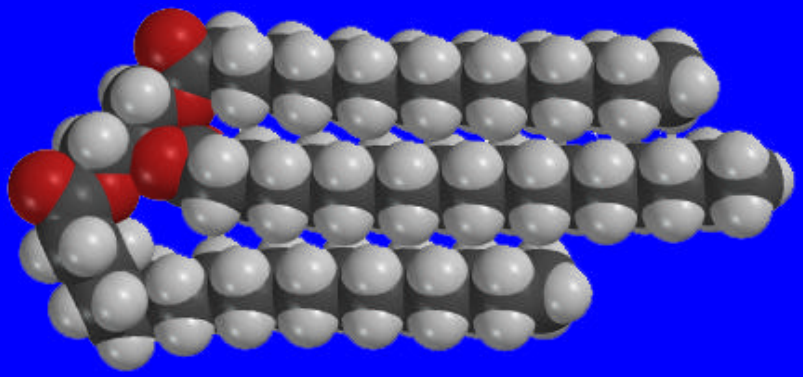
2-Oleyl-1,3-distearylglycerol; mp 43°C

Fats and Oils



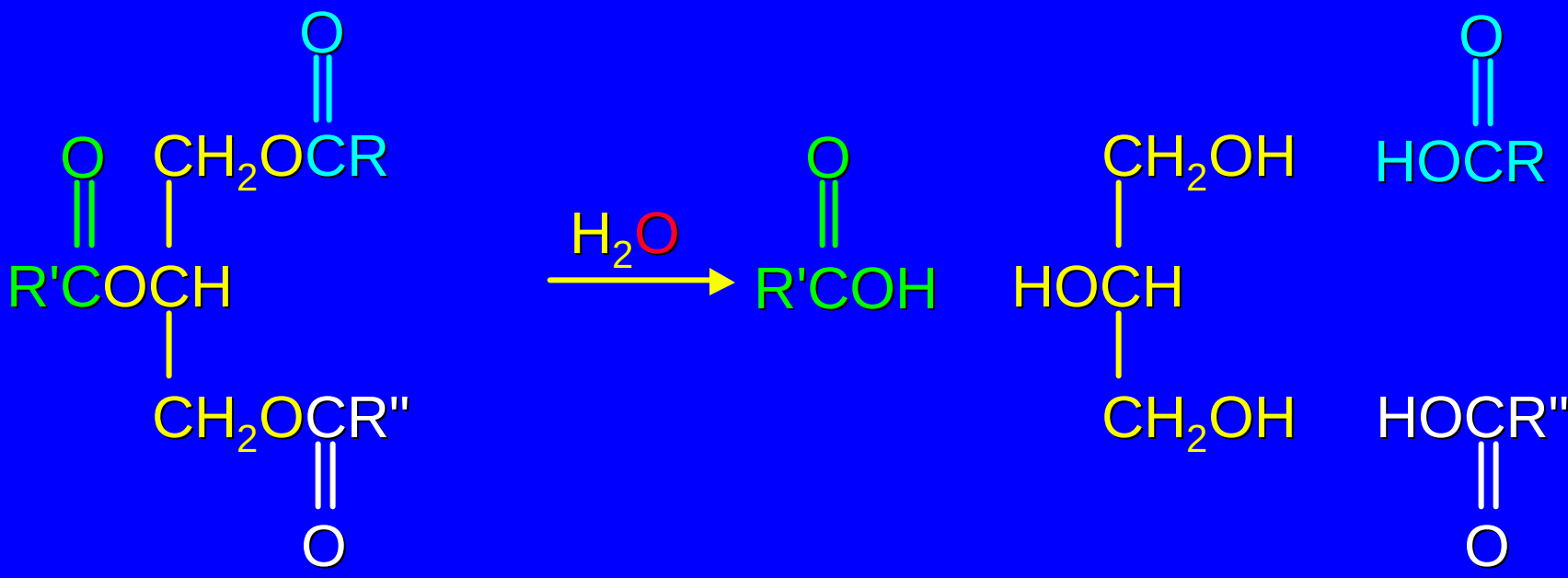
2-Oleyl-1,3-distearylglycerol
mp 43°C

H_2, Pt



Tristearin
mp 72°C

Fatty Acids



Acids obtained by the hydrolysis of fats and oils are called fatty acids.

Fatty acids usually have an unbranched chain with an even number of carbon atoms.

If double bonds are present, they are almost always cis.

Table 26.1 (p 1018)

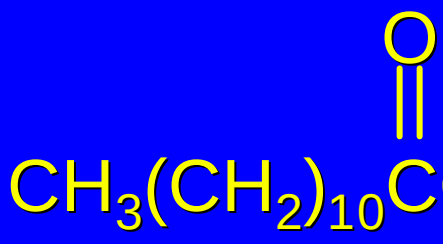
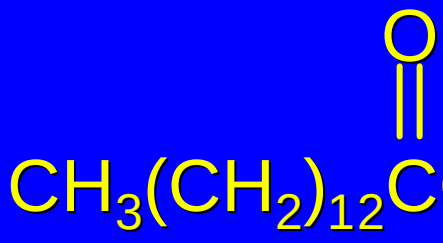
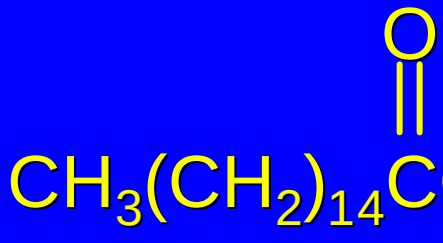
	Systematic name	Common name
	Dodecanoic acid	Lauric acid
	Tetradecanoic acid	Myristic acid
	Hexadecanoic acid	Palmitic acid

Table 26.1 (p 1018)

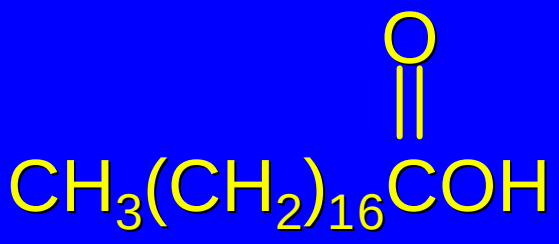
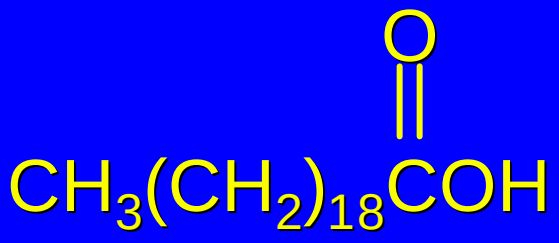
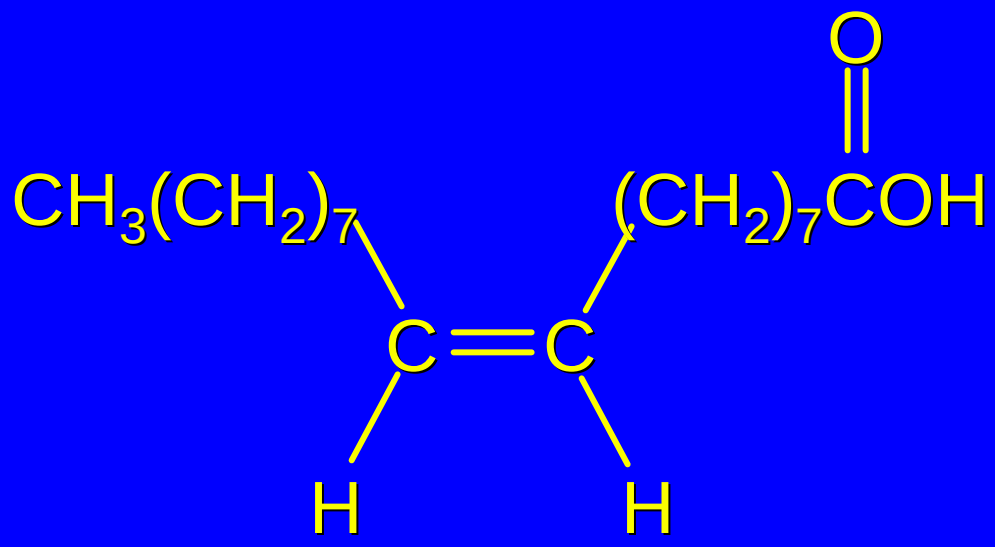
	Systematic name	Common name
	Octadecanoic acid	Stearic acid
	Icosanoic acid	Arachidic acid

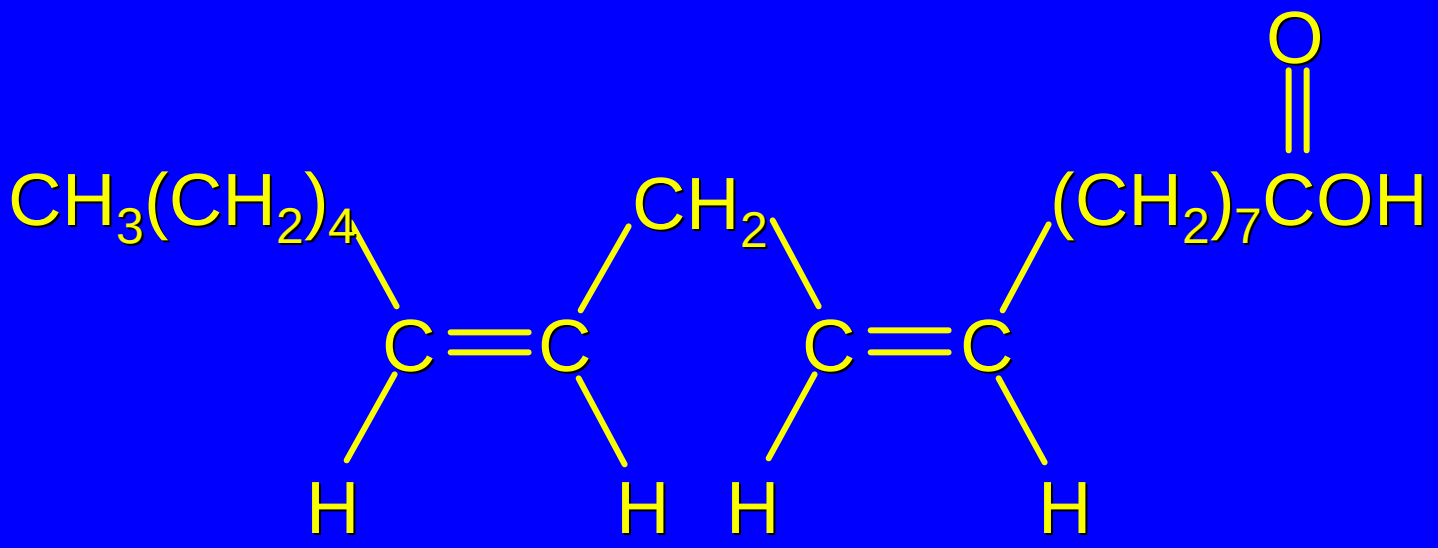
Table 26.1 (p 1018)



Systematic name: (*Z*)-9-Octadecenoic acid

Common name: Oleic acid

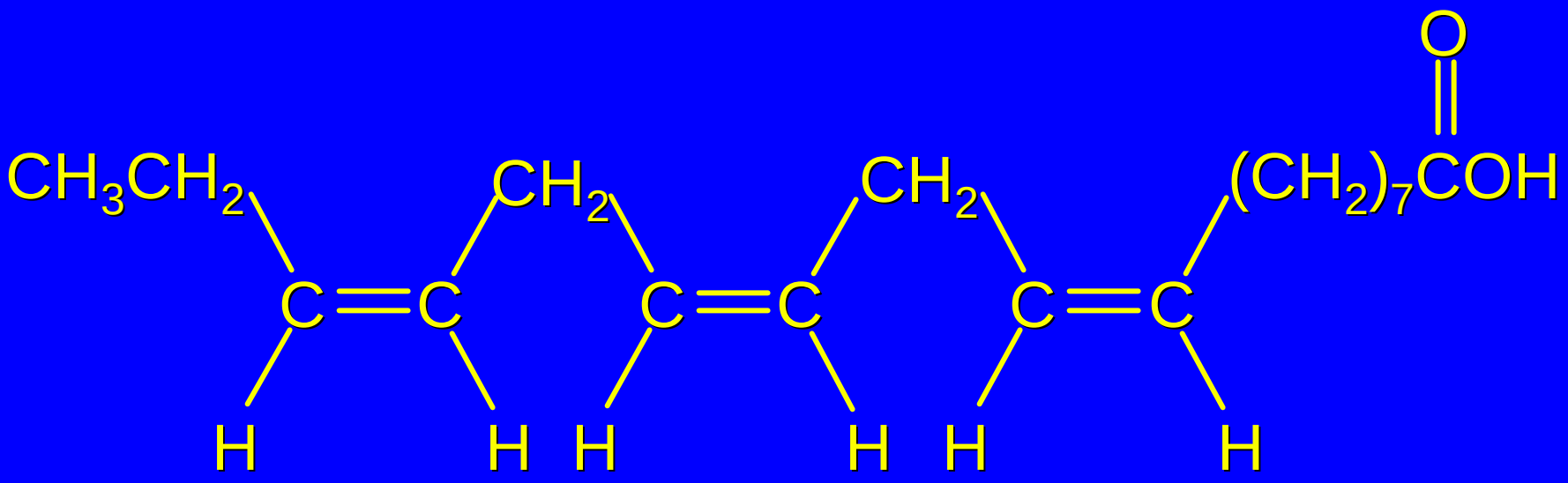
Table 26.1 (p 1018)



Systematic name: (9*Z*, 12*Z*)-9,12-Octadecadienoic acid

Common name: Linoleic acid

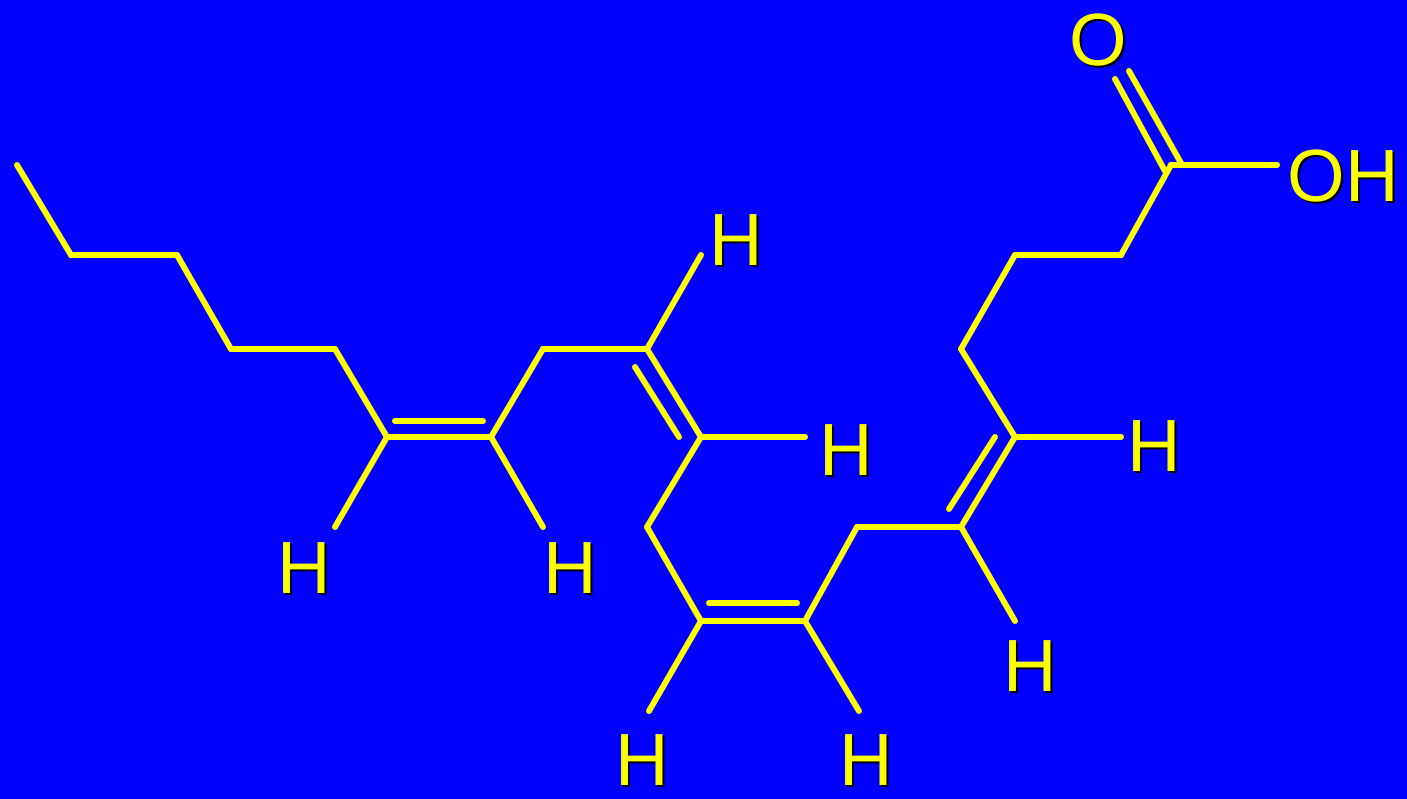
Table 26.1 (p 1018)



Systematic name: (9*Z*, 12*Z*, 15*Z*)-9,12,15-Octadecatrienoic acid

Common name: Linolenic acid

Table 26.1 (p 1018)



Systematic name: (5Z, 8Z, 11*Z*, 14*Z*)-5,8,11,14-Icosatetraenoic acid

Common name: Arachidonic acid

26.3
Fatty Acid Biosynthesis

Fatty Acid Biosynthesis

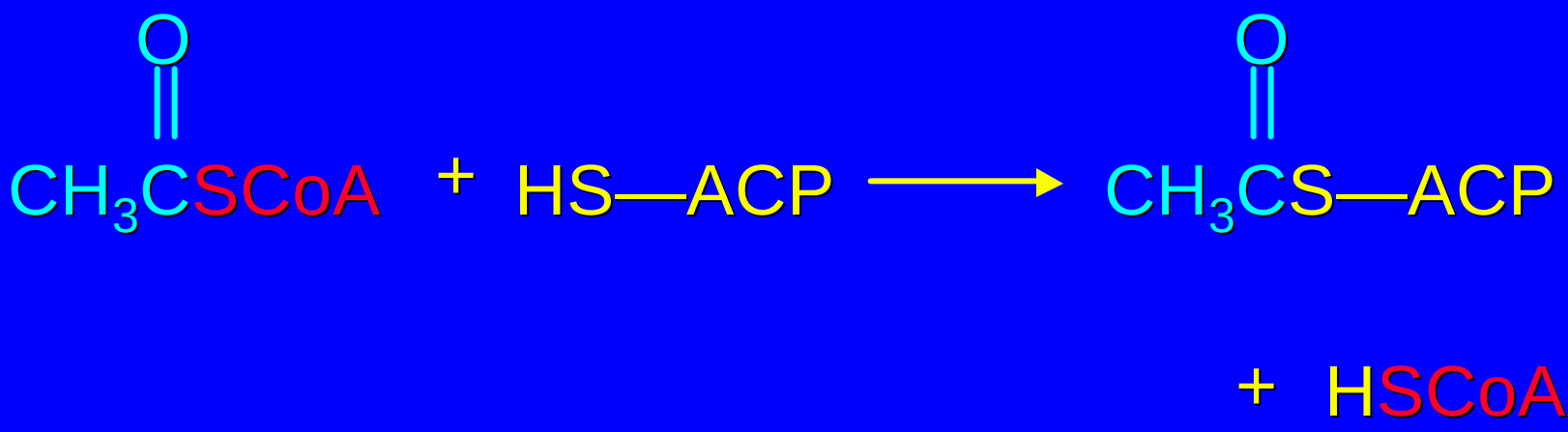
Fatty acids are biosynthesized via acetyl coenzyme A.

The group of enzymes involved in the overall process is called *fatty acid synthetase*.

One of the key components of fatty acid synthetase is *acyl carrier protein* (ACP—SH).

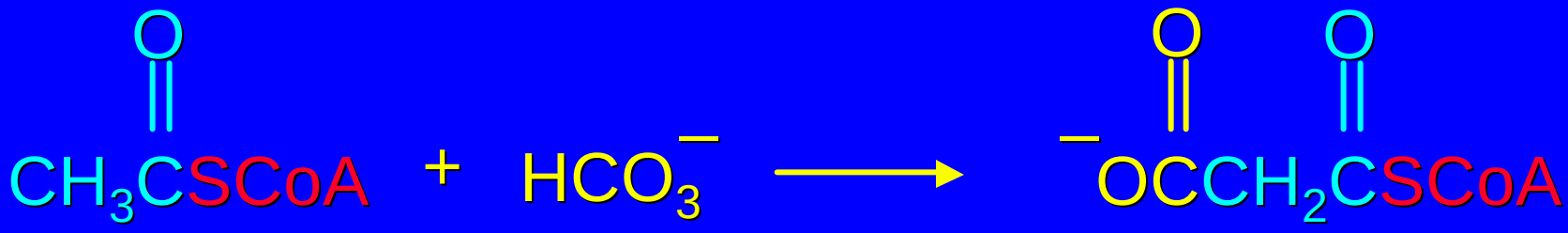
Fatty Acid Biosynthesis

An early step in fatty acid biosynthesis is the reaction of acyl carrier protein with acetyl coenzyme A.



Fatty Acid Biosynthesis

A second molecule of acetyl coenzyme A reacts at its α carbon atom with carbon dioxide (as HCO_3^-) to give malonyl coenzyme A.

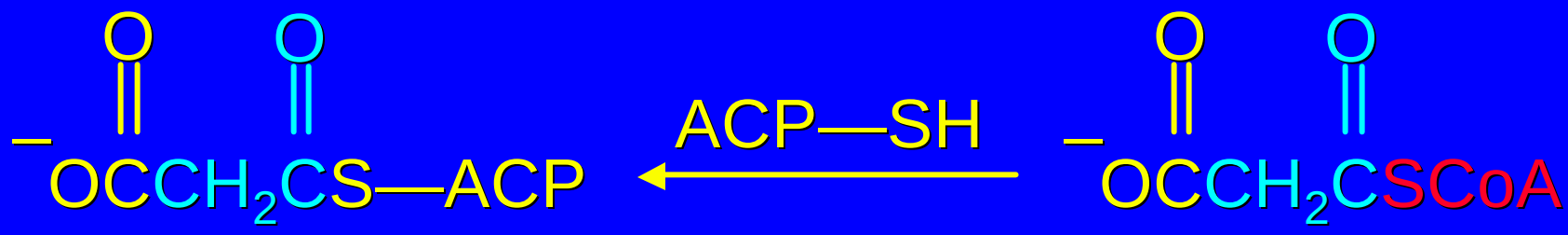


Acetyl coenzyme A

Malonyl coenzyme A

Fatty Acid Biosynthesis

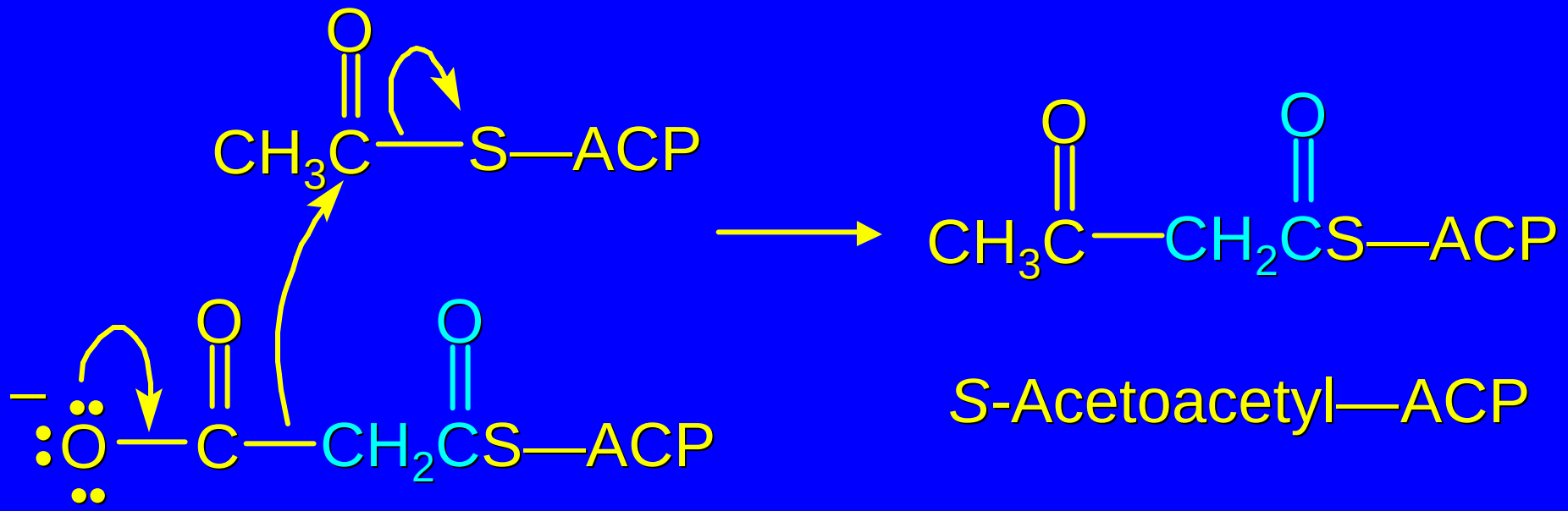
Malonyl coenzyme A then reacts with acyl carrier protein.



Malonyl coenzyme A

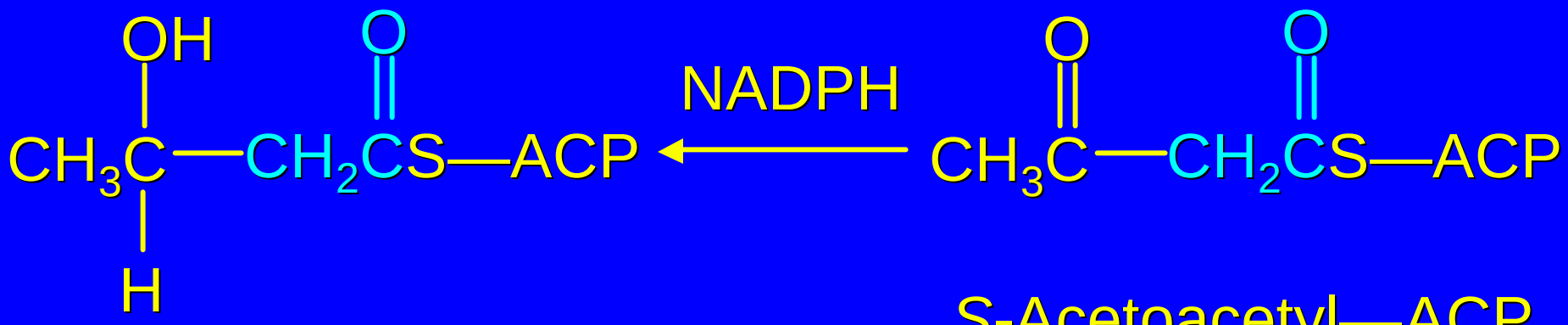
Fatty Acid Biosynthesis

Malonyl—ACP and acetyl—ACP react by carbon-carbon bond formation, accompanied by decarboxylation.



Fatty Acid Biosynthesis

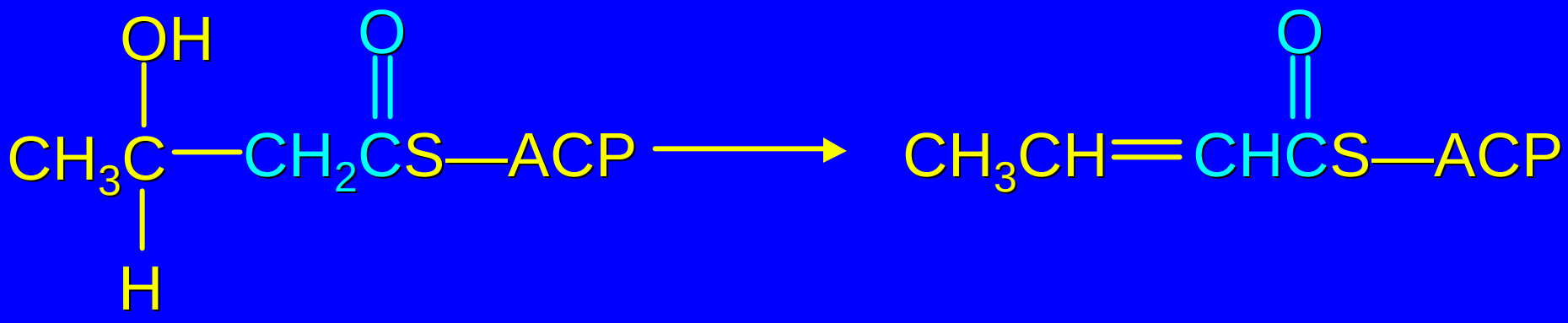
In the next step, the ketone carbonyl is reduced to a secondary alcohol.



S-Acetoacetyl—ACP

Fatty Acid Biosynthesis

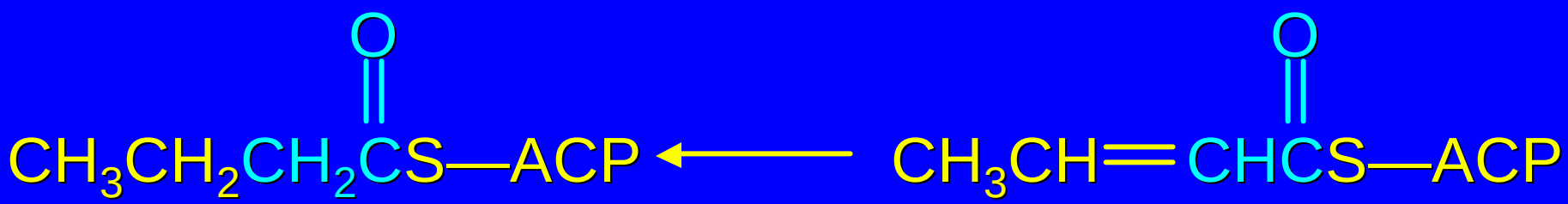
The alcohol then dehydrates.



Fatty Acid Biosynthesis

Reduction of the double bond yields ACP bearing an attached butanoyl group.

Repeating the process gives a 6-carbon acyl group, then an 8-carbon one, then 10, etc.

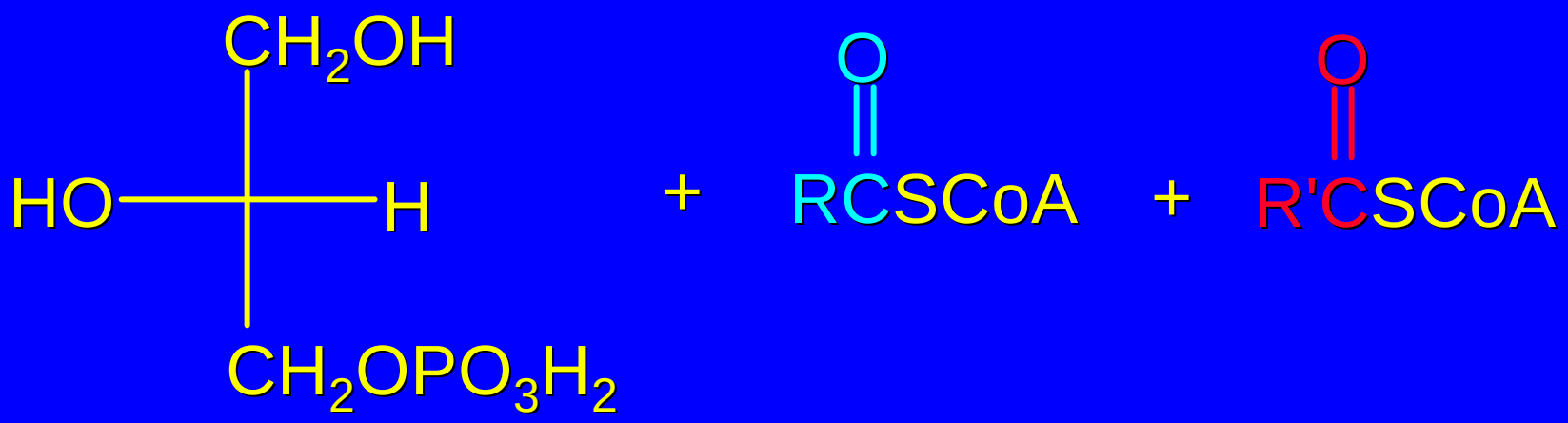


26.4
Phospholipids

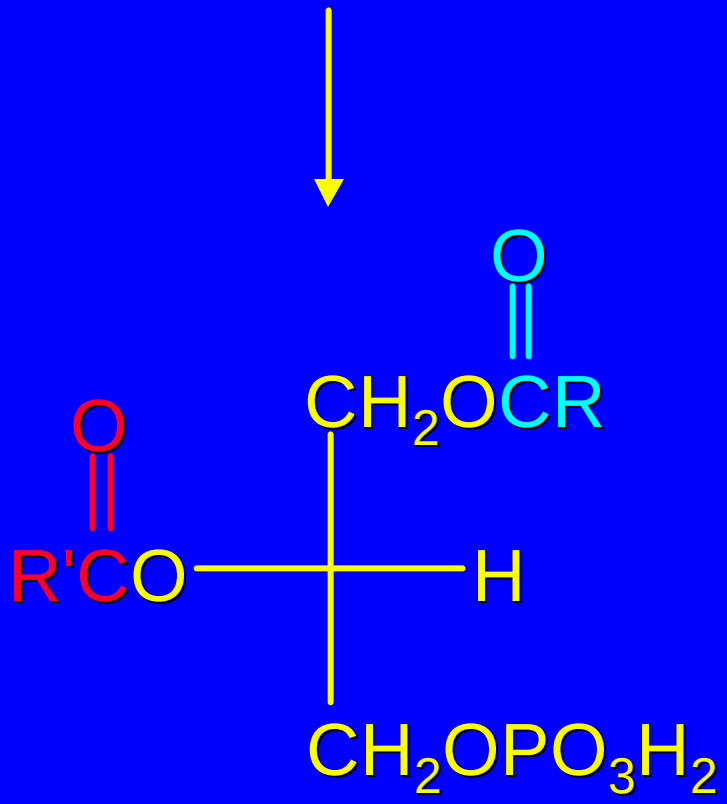
Phospholipids

Phospholipids are intermediates in the biosynthesis of triacylglycerols.

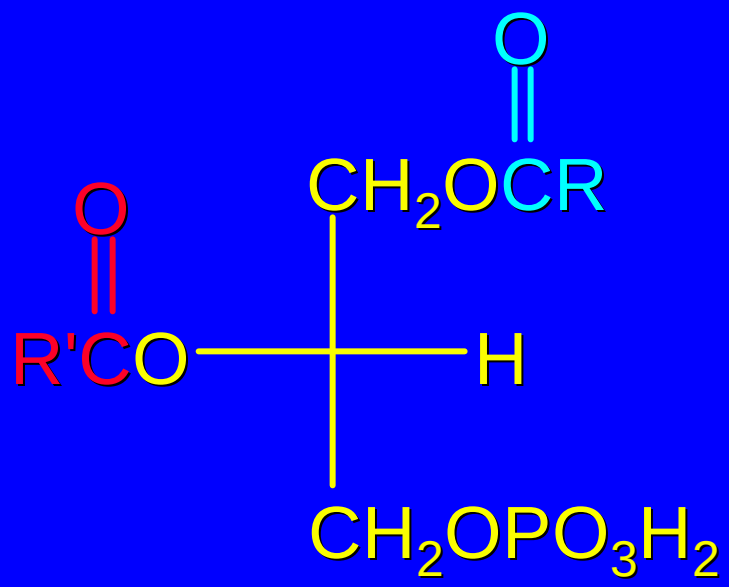
The starting materials are L-glycerol 3-phosphate and the appropriate acyl coenzyme A molecules.

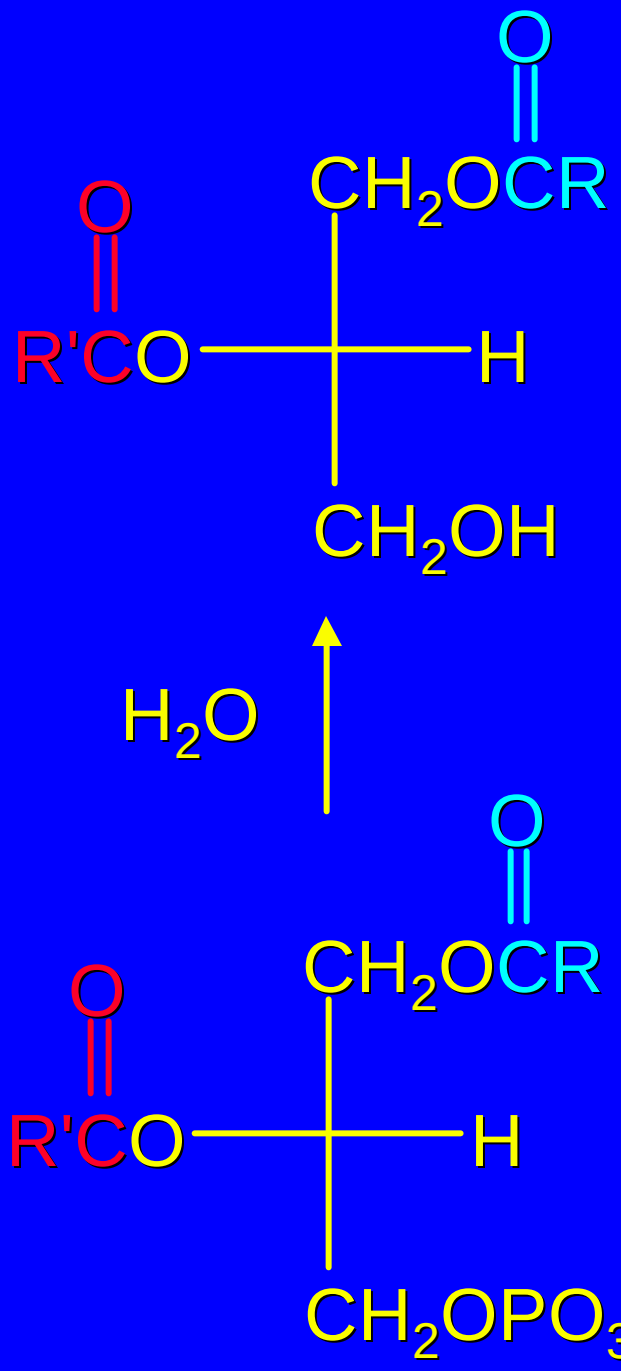


The diacylated species formed in this step is called a *phosphatidic acid*.

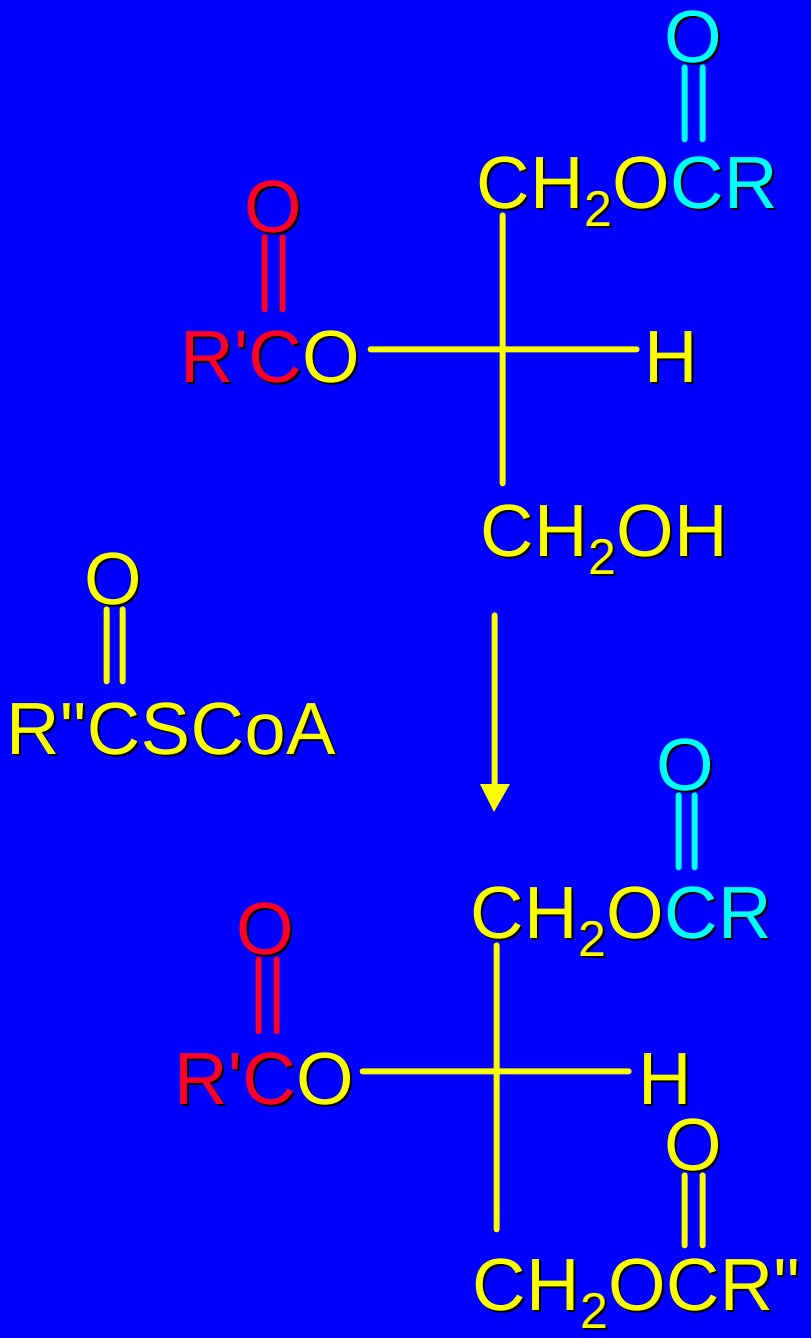


The phosphatidic acid then undergoes hydrolysis of its phosphate ester function.





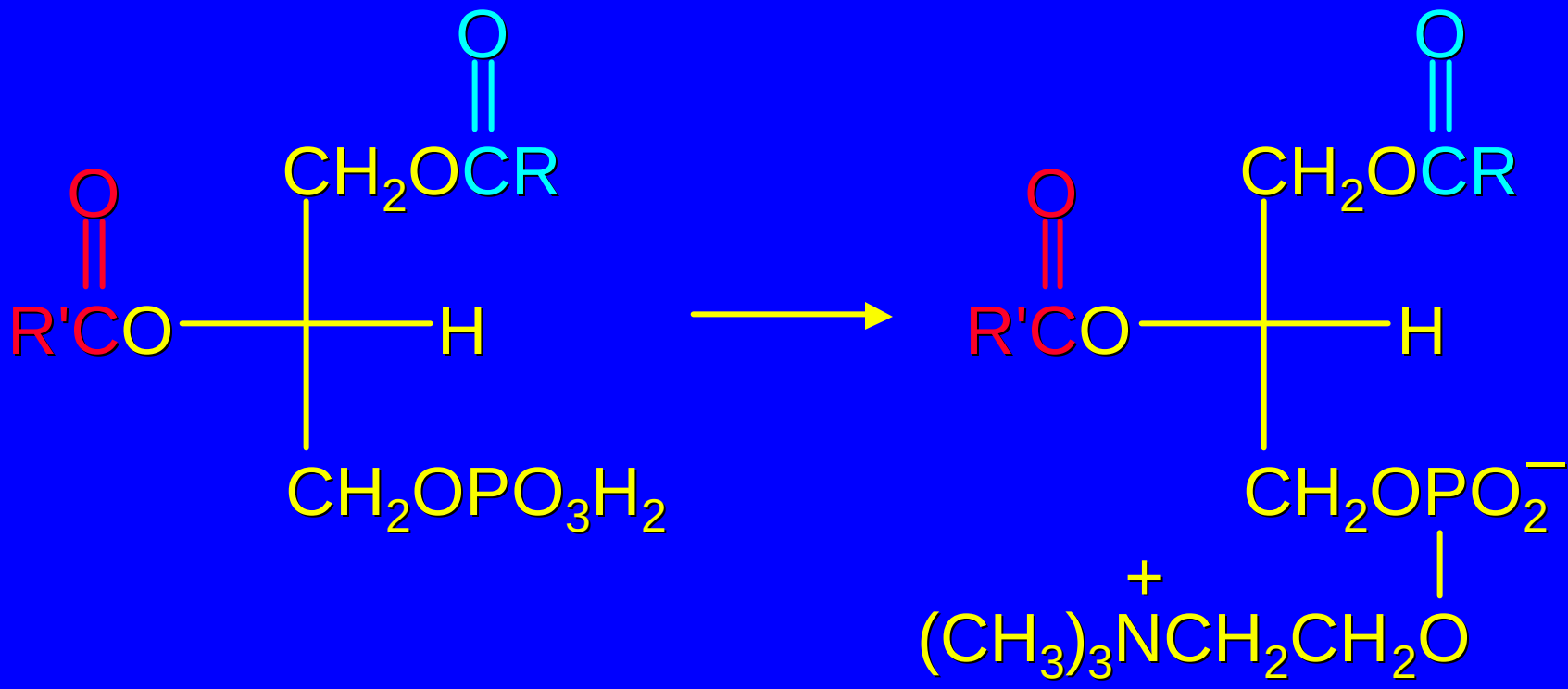
Reaction with a third acyl coenzyme A molecule yields the triacylglycerol.



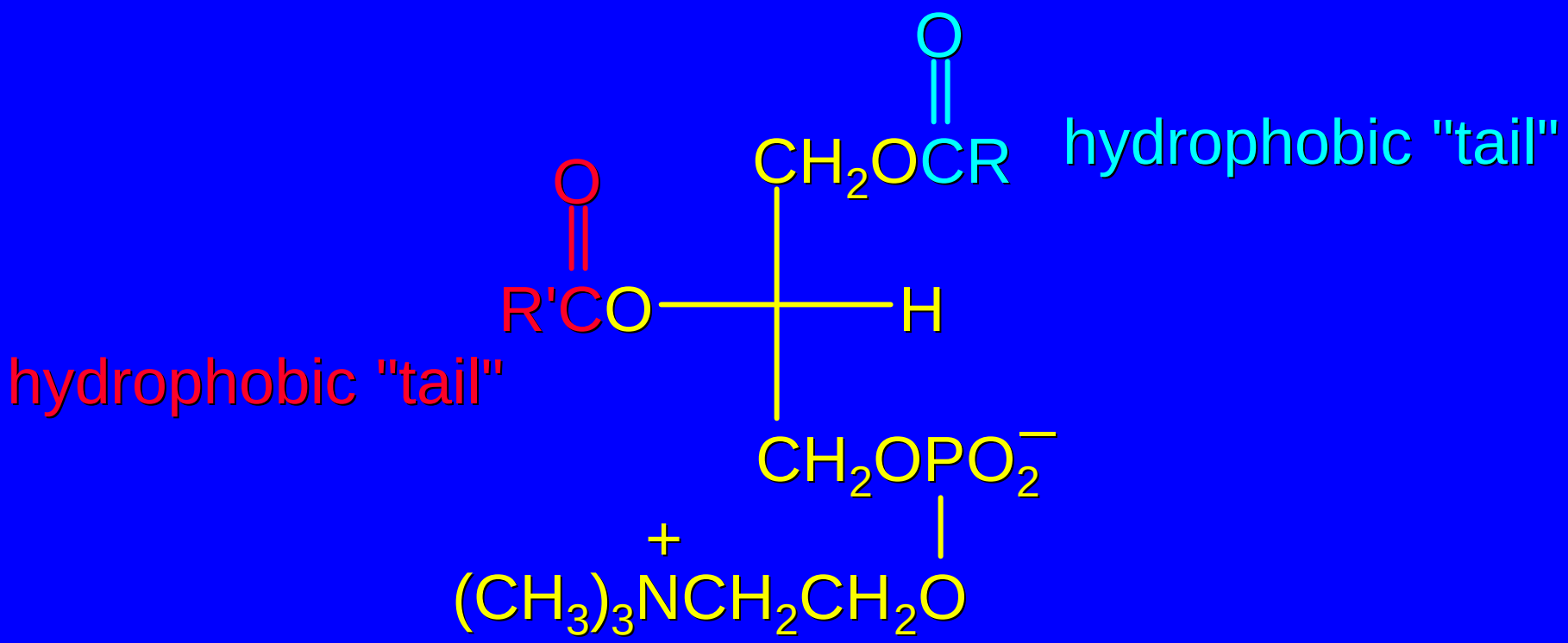
Reaction with a third acyl coenzyme A molecule yields the triacylglycerol.

Phosphatidylcholine

Phosphatidic acids are intermediates in the formation of *phosphatidylcholine*.

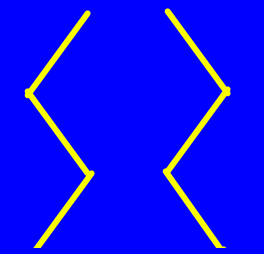


Phosphatidylcholine

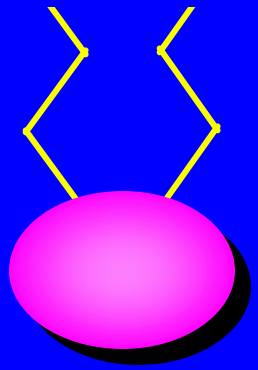


polar "head group"

Phosphatidylcholine



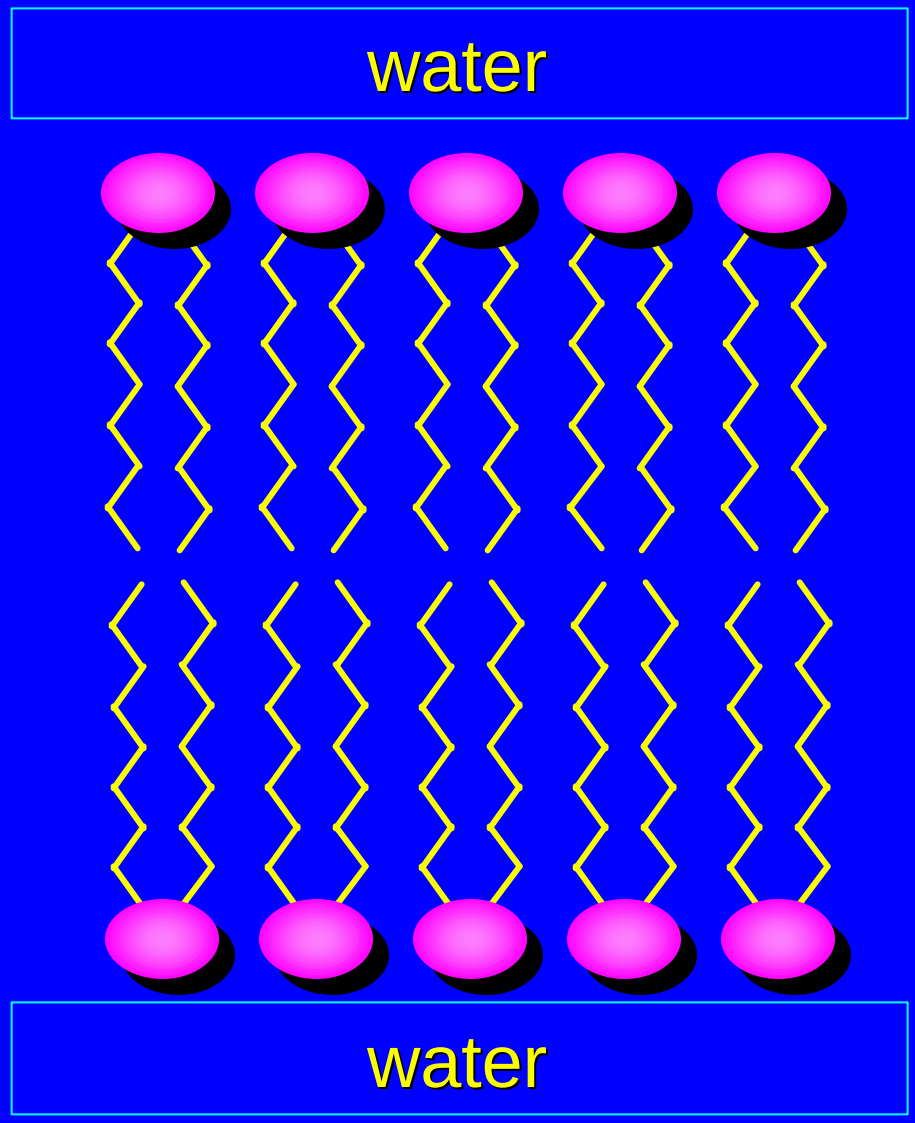
hydrophobic
(lipophilic) "tails"



hydrophilic "head group"

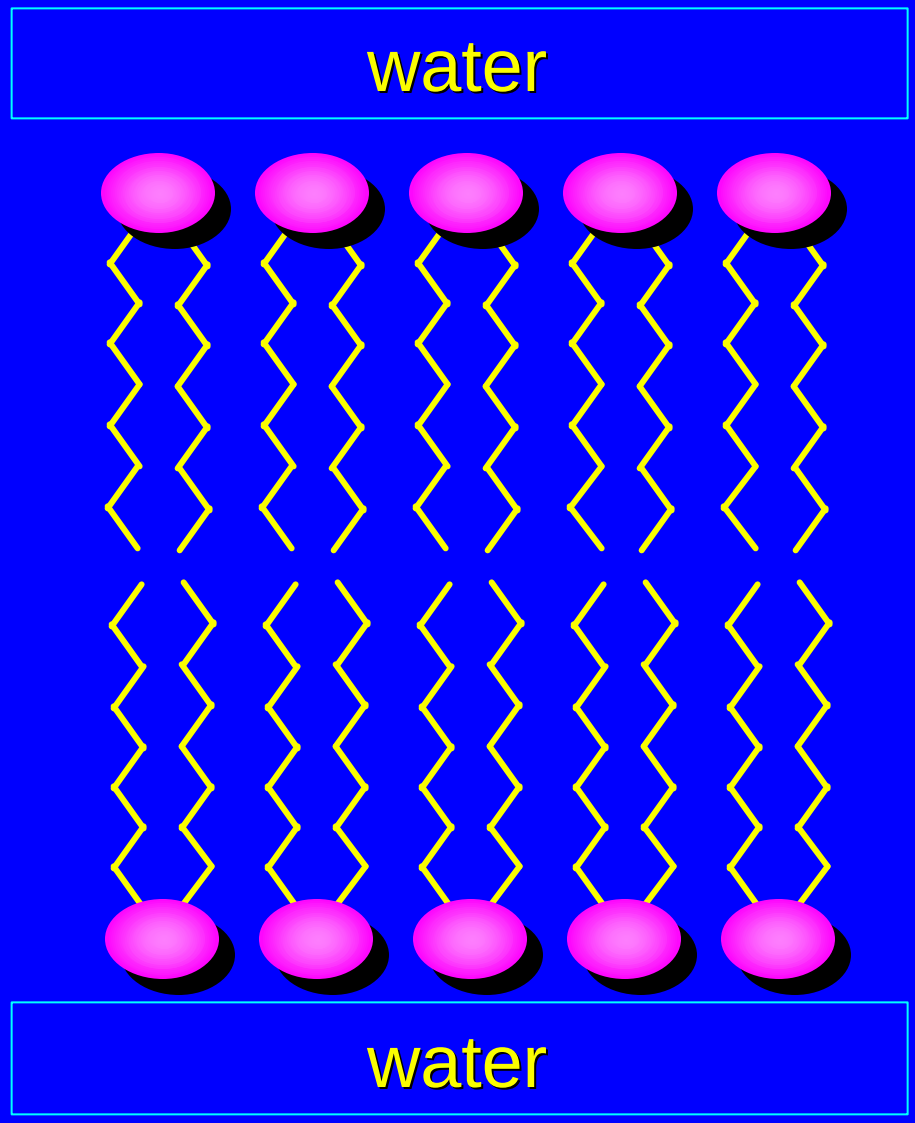
Cell Membranes

Cell membranes are "lipid bilayers." Each layer has an assembly of phosphatidyl choline molecules as its main structural component.



Cell Membranes

The interior of the cell membrane is hydrocarbon-like. Polar materials cannot pass from one side to the other of the membrane.



26.5
Waxes

Waxes

Waxes are water-repelling solids that coat the leaves of plants, etc.

Structurally, waxes are mixtures of esters. The esters are derived from fatty acids and long-chain alcohols.

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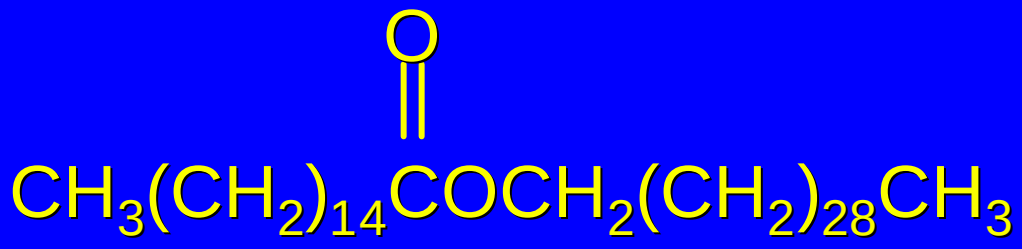


Triacontyl hexadecanoate: occurs in beeswax

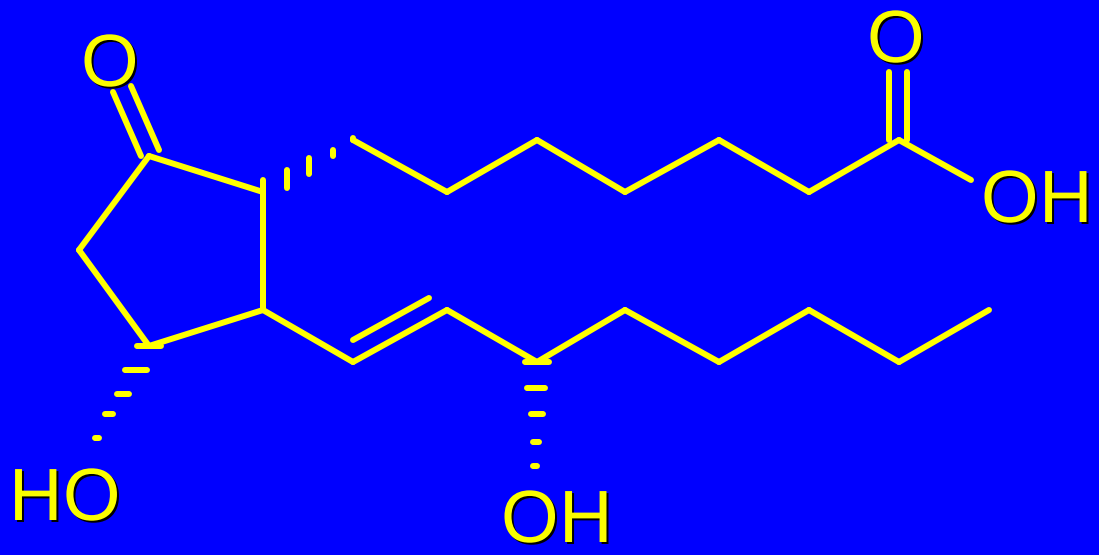
26.6
Prostaglandins

Prostaglandins

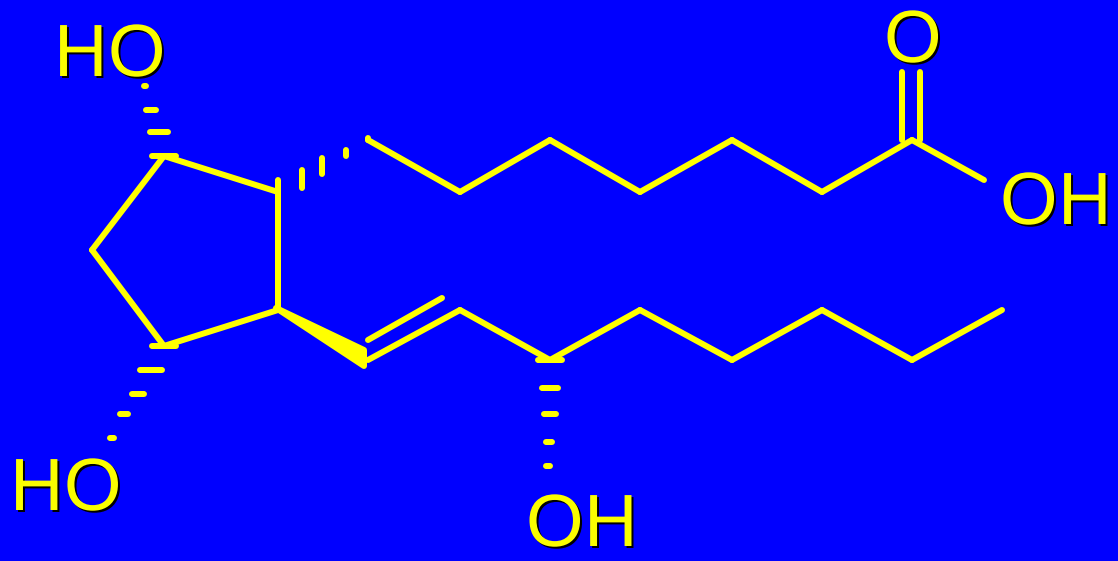
Prostaglandins are involved in many biological processes.

Are biosynthesized from linoleic acid (C_{18}) via arachidonic acid (C_{20}). (See Table 26.1)

Examples: PGE_1 and PGF_{1a}



PGE_1



$PGF_{1\alpha}$