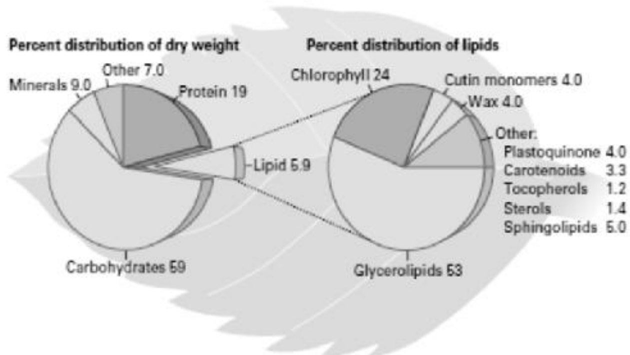
http://smtom.lecture.ub.ac.id/
Password:

https://syukur16tom.wordpress.com/
Password:

Plant Biochemistry
Lecture 08: PLANT LIPID



Lipids are molecules that contain hydrocarbons and make up the building blocks of the structure and function of living cells.

GRADING POLICY

Grading Point	Grade	Weight	Final Grade
Task 1	N1	5%	0.05N1
Quiz 1	N2	5%	0.05N2
Mid Term Exam	**N3**	**25%**	**0.25N3**
Task 1	N4	5%	0.05N4
Quiz 1	N5	5%	0.05N5
Final Term Exam	**N6**	**25%**	**0.25N6**
Lab. Exercise	N7	30%	0.30N7
TOTAL			

WELCOME TO THE COURSE OF PLANT BIOCHEMISTRY

Who am I?: Prof. Dr. S.M. Sitompul

These are my rules

- Come on time (± 10') with a proper dress
- Get into the lecture room, don't hang around
- Use English in my lecture and exam (75-99%)

- These are my philosophies
  - Turn your enemies to be your friends
  - Turn your useless time to be useful time
  - Make big problems to be small problems
  - Simplify the systems or problems

STRUCTURED TASK

1. English Presentation
   - ~~Every student has to make English Presentation~~
2. Dictionary
   - Take your English dictionary every time I give my lecture
3. My Dictionary
   - Buy a writing book (100-pages) and name it MY DICTIONARY
   - Write down all English words with Indonesian meanings that you do not know yet

4. Literature Study
   - **Every student has to undertake literature study to obtain more and detail information as to the lecture materials**
5. Study Groups
   - Organize your study group, 5 member each to discuss the lecture materials
6. Paper (NO COVER, NO COVER, NO COVER,)
   - *Write a paper about Plant Biochemistry or an extended summary of* a published papers in international Journal (internet)
   - ***One (1) page only***, *(single space) arranged in several paragraphs (4-5 sentences/ paragraph), font (Times New Roman 12)*

PAPER TOPICS

COMPOUNDS	9. Jasmonic acid
Chemical Structure, Function and Synthesis	10. Anthraquinones
1. Cathecin	11. Diosgenin
2. Theaflavins	12. Rosmarinic acid
3. Capsaicinoids	13. Saponin
4. Berberine	14. Scopoletin
5. Capsidiol	15. Anthocyanin
6. Hyoscyamine	16. Kinobeon
7. Codeine	17. Methoxymellein
8. Rishitin	18. Salidroside
	19. Shikonin

LEARNING OUTCOMES

Students, after mastering materials of the present lecture, should be able

1. to explain the meaning of lipid and its importance for plant life.
2. to explain major lipids produced by plants.
3. to explain the function and structure of lipids in plants.
4. to explain the classification of lipids.
5. to explain the biosynthesis of fatty acids and glycerolipids.

LECTURE OUTLINE

1. INTRODUCTION

1. Definition
2. Plant Lipids

2. LIPID FUNCTION AND STRUCTURE

1. Lipids have diverse roles in plants
2. Lipid Classification
3. Most lipids contain fatty acids esterified to glycerol

3. LIPID BIOSYNTHESIS

1. Fatty Acid Biosynthesis
2. Glycerolipids Biosynthesis

COURSE PLAN

NO.	TOPICS	Subject
1.	INTRODUCTION	
2.	ENZYME I	Introduction
3.	ENZYME II	Kinetics
4.	ENZYME II	Mechanism & Inhibitor
5.	CARBOHYDRATE I	Introduction
6.	CARBOHYDRATE II	Classification
7.	NUCLEOTIDE BIOSYNTHESIS	
8.	MID SMESTER EXAM	
9.	LIPID	
10.	BIOLOGICAL N FIXATION	
11.	AMINO ACID METABOLISM I	
12.	AMINO ACID METABOLISM II	
13.	PROTEIN SYNTHESIS I	
14.	PROTEIN SYNTHESIS II	
15.	SECONDARY METABOLITES	
16.	END SMESTER EXAM	

REFERENCES

1. Buchanan, B.B., Gruissem, W. and Jones, R.L. (eds.) (2015). Biochemistry & Molecular Biology of Plants. Second Edition. Wiley Blackwell. 1283 pp.
2. Heldt, H-W et al., 2011. Plant Biochemistry. Translation of the 4th German edition. Academic Press
3. Berg, J.M., Tymoczko, J.L. and Stryer, L., 2002. Biochemistry. 5th edition: W.H. Freeman and Co,. New York
4. Buchanan, B.B., Gruissem, W. and Jones, R.L., 2000. Biochemistry and Molecular Biology of Plants. American Society of Plant Biologists
5. Conn, E.E. & Stumpf, P.K., 1976. Outlines of Biochemistry. John Wiley & Sons, New York.
6. Goodwin, T.W. & Mercer, E.I., 1990. Introduction to Plant Biochemistry. Pergamon Press, Oxford.
7. Stryer, L., 1975. Biochemistry. W.H. Freeman and Company, San Francisco
8. Wood, W.B., Wilson, J.H., Benbow, R.M., & Hood, L. E., 1981. Biochemistry A Problems Approach.

1. INTRODUCTION

A. Definition

1. The term lipid refers to a structurally diverse group of molecules that are preferentially soluble in such organic solvents (in a nonaqueous solvent) such as hydrocarbons, chloroform, benzene, ethers and alcohols.
2. It should be asserted that no definition of lipid is widely accepted, and other definitions as follows.
   - Lipids are “fatty acids and their derivatives, and substances related biosynthetically or functionally to these compounds”.
3. Lipids include a wide variety of fatty acid-derived compounds, as well as many pigments and secondary compounds that are metabolically unrelated to fatty acid metabolism.

4. Triacylglycerols (triglyceride, $C_{55}H_{98}O_6$) is an example of simple lipids which is an unsaturated.

Glycerol moiety

Fatty acid moiety

Left part: glycerol moiety; right part, from top to bottom: the moiety of palmitic, oleic, α-linolenic acid.

5. Triglycerides are an important measure of heart health.

   Normal — $<$150 mg/dL

   Borderline high — 150 to 199 mg/dL

   High — 200 to 499 mg/dL

   Very high — 500 mg/dL

B. Plant Lipids

1. Each plant cell contains a diverse range of lipids, often located in specific structures. Furthermore, different plant tissues contain different lipids.
2. The pathways of lipid metabolism in plants are complex and some are not yet well understood.
3. The complexity arises primarily from cellular compart-mentalization of the pathways and the extensive inter-mixing of lipid pools between these compartments (Fig. 8.1).
4. Fatty acids, the simplest of the lipids, are highly reduced compounds with a hydrophilic (water soluble) carboxylic acid group and a hydrophobic hydrocarbon chain.

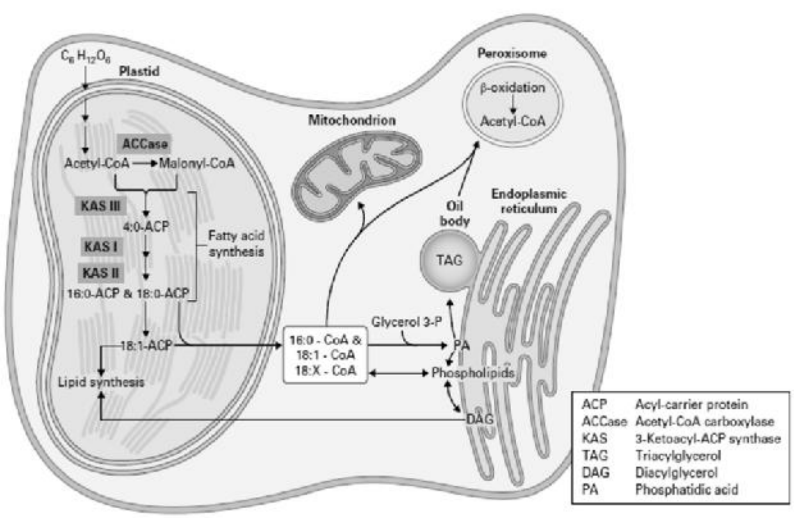


Fig. 8.1 Lipid synthesis and metabolism take place in various organelles, and in many cases involve movement of lipids from one cellular compartment to another.

5. Plants collectively accumulate more than 200 different fatty acids that raise many questions about the nature of the enzymes involved in the synthesis of these compounds.
6. Because plants cannot control their temperatures, they contain much more oil than fat so their membranes will be fluid at ambient temperatures.
7. The most common mono unsaturated fatty acid is oleic acid, while the most common polyunsaturated fatty acids are linoleic acid and linolenic acid.
8. Some plants have a high proportion of saturated fats, containing such fatty acids as palmitic acid, the most common saturated fatty acid found in plants.
9. Plants also contain lesser amounts of other saturated fatty acids, such as lauric and myristic acid.

2. LIPID FUNCTIONS AND STRUCTURE

1. Lipids have diverse roles in plants

- Lipids serve various functions in plants that may be divided into 11 groups;.
  1. Membrane structural components: Glycerolipids, Sphingolipids & Sterols.
  2. Storage compounds: Triacylglycerols & Waxes.
  3. Compounds active in electron transfer reactions: Chlorophyll and other pigments, Ubiquinone & plastoquinone.
  4. Photoprotection: Carotenoids (xanthophyll cycle)
  5. Protection of membranes against damage from free radicals: Tocopherols.
  6. Waterproofing and surface protection: Long-chain and very-long-chain fatty acids and their derivatives (cutin, suberin, surface waxes) Triterpenes.

7. Protein modification
   - Addition of membrane anchors
     - Acylation: Mainly 14:0 and 16:0 fatty acids
     - Prenylation: Farnesyl and geranylgeranyl pyrophosphate
     - Other membrane anchor components: Phosphatidylinositol, ceramide
   - Glycosylation: Dolichol
8. Signaling
9. Internal: Abscisic acid, gibberellins, brassinosteroids 18:3 Fatty acid precursors of jasmonate Inositol phosphates Diacylglycerols
10. External: Jasmonate & Volatile insect attractants
11. Defense and antifeeding compounds: Essential oils, Latex components (rubber, etc.) & Resin components (terpenes)

- Lipids as the major components of biological membranes, for instance, form a hydrophobic barrier that is critical to life.
  - The membranes of chloroplasts, in which the light reactions of photosynthesis take place, primarily contain galactolipids.

- Lipids, however, make up a relatively small proportion of the total mass of plant tissue despite a single gram of leaf tissue may contain as much as 1 m^2 of membrane, (Fig. 8.2).

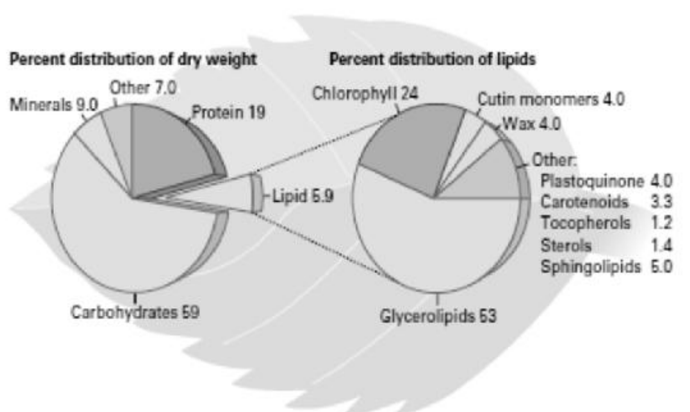


Fig. 8.2 Approximate distributions of cellular constituents (as a percentage of total dry weight) and lipid types (as a percentage of total lipids by weight) in Arabidopsis leaf tissues. Some values were extrapolated from results obtained with other species.

- Lipids also represent a substantial chemical reserve of free energy. Because fatty acids are substantially more reduced organic molecules than carbohydrates, fatty acid oxidation has a higher potential for producing energy.

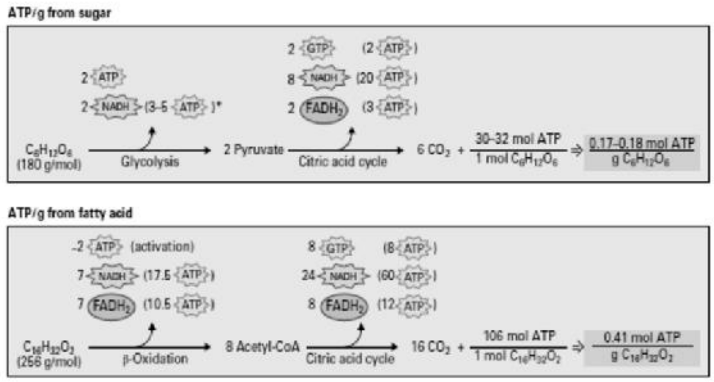
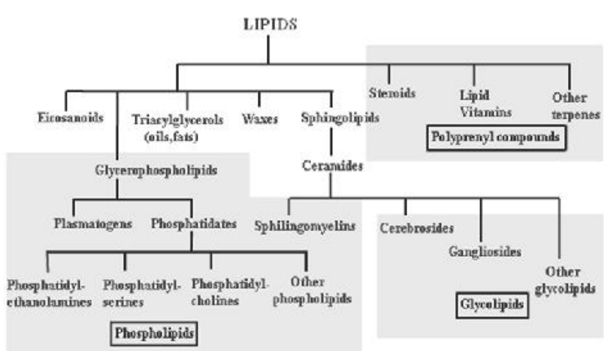


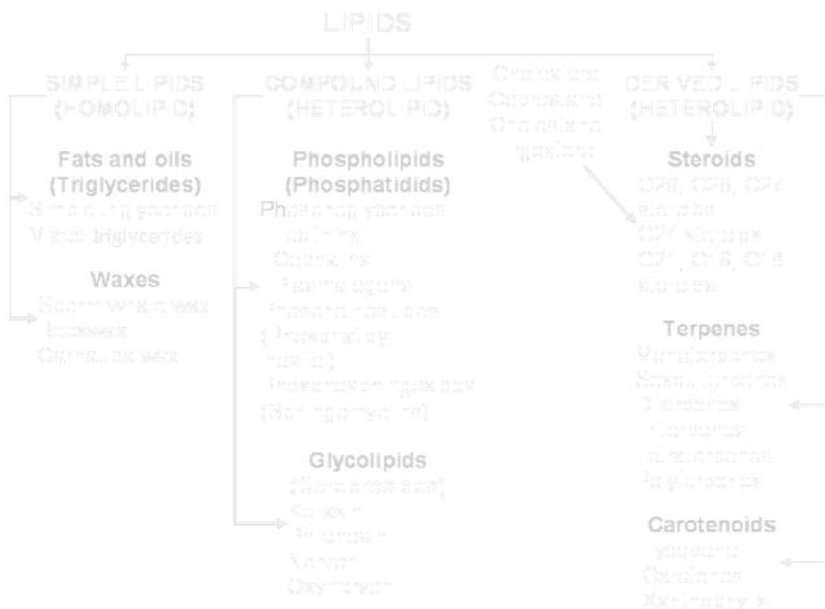
Fig 8.3 Comparison of energy yield in animals from metabolism of fatty acids and carbohydrates to CO_2 and H_2O. Metabolism of fatty acids produces 0.41 mol of ATP per gram of fatty acid, whereas metabolism of carbohydrate yields 0.17 to 0.18 mol/g.

2. Lipid Classification

- Lipids can be classified on the basis of their structures or functions, and are mainly classified into five types:
  Fatty acyl (FA), Glycerolipids (GL), Glycerophospholipids (GP), Sterol lipids (ST) & Sphingolipids (SP).
- The relation between different types of lipids is as follows.



http://chemistry.tutorvista.com/biochemistry/types-of-lipids.html



- The LIPID MAPS classification system is based on the concept of 2 fundamental “building blocks”: ketoacyl groups and isoprene groups (Fahy *et al*., 2011).
- This classification divides lipids into eight categories:
  1. Fatty acyls (Fatty acids attached to something else)
  2. Glycerolipids
  3. Glycerophospholipids
  4. Sphingolipids
  5. Saccharolipids
  6. Polyketides (derived from condensation of ketoacyl subunits)
  7. Sterol lipids and
  8. Prenol lipids (derived from condensation of isoprene subunits) (Fig. 3).
- Each category is further divided into classes, subclasses and, in the case of some subclasses of prenol lipids, 4^{th}-level classes.

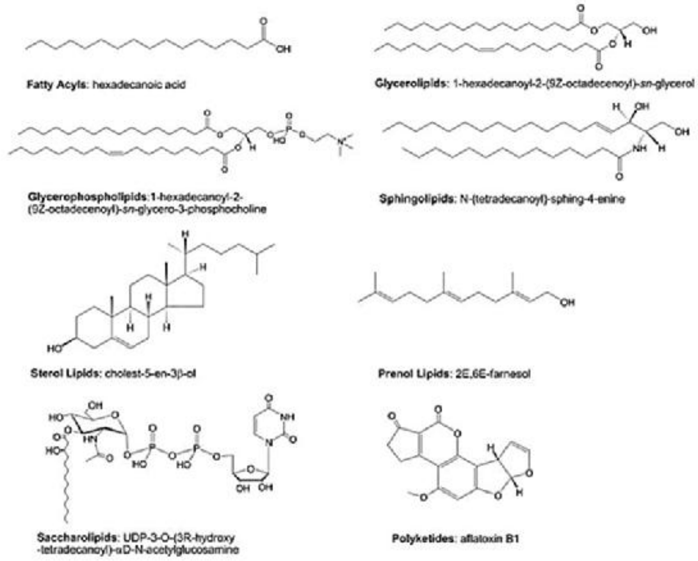
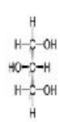


Fig. 3 Examples of lipid categories. Representative structures from each of the 8 LIPID MAPS lipid categories.

3. **Most lipids contain fatty acids esterified to glycerol**



- Fatty acids are carboxylic acids of highly reduced hydrocarbon chains such as palmitic acid (hexadeca-noic acid) and oleic acid (*cis*-9-octadecenoic).
  - Palmitic acid (saturated fatty acid), and oleic acid (monounsaturated fatty acid) is designated successively 16:0 and $18{:}1^{\Delta 9}$ respecetively.
  - The first value, 16 or 18, represents the number of carbon atoms, and the second value, 0 or 1, indicates the number of double bonds.
  - The Δ9 superscript designates the position of the single double bond, counting the carboxyl group as carbon atom number 1.
  - The abbreviation of sn-3 (stereospecific nomenclature-3) indicates the terminal hydroxyl that is phosphorylated in glycerol 3-phosphate, sn-2 refers to the central hydroxyl, and sn-1 is the terminal hydroxyl that is not phosphorylated.

- The typical fatty acids found in the membranes of plants contain 16 or 18 carbons (Table 8.2). Some unusual fatty acids are found typically to accumulate only in the storage triacylglycerols of seeds.
- A major fraction of the fatty acids in plants are the polyunsaturated fatty acids linoleic acid ($18{:}2^{\Delta 9,12}$) and α-linolenic acid ($18{:}3^{\Delta 9,12,15}$).
  - Only a few plants accumulate fatty acids with double bonds closer to the carboxyl group than the Δ9 position.
- In addition to the C_{16} and C_{18} common fatty acids, some plants also produce fatty acids of 8–32 carbons in length that usually accumulate in storage lipids or epicuticular wax.
- The fatty acid composition of lipids can be determined using gas chromatography to separate the methylated derivatives of the fatty acids.

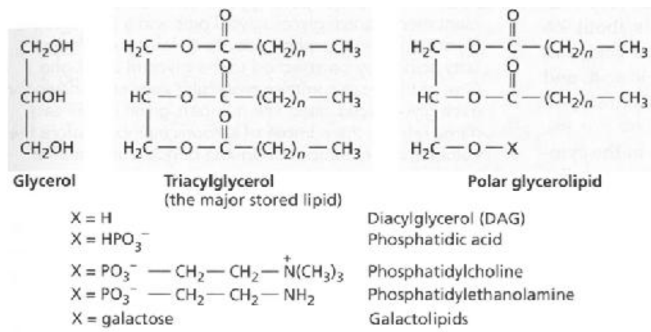
Table 8.2 Selected fatty acids present in plants

Common name	Systematic name	Structure	Abbreviation[a]
Saturated fatty acids			
Lauric acid	n-Dodecanoic acid	$CH_3(CH_2)_{10}COOH$	12 : 0
Palmitic acid[b]	n-Hexadecanoic acid	$CH_3(CH_2)_{12}CH_2CH_2COOH$	16 : 0
Stearic acid[b]	n-Octadecanoic acid	$CH_3(CH_2)_{12}CH_2CH_2CH_2CH_2COOH$	18 : 0
Arachidic acid	n-Eicosanoic acid	$CH_3(CH_2)_{12}CH_2CH_2CH_2CH_2CH_2CH_2COOH$	20 : 0
Behenic acid	n-Docosanoic acid	$CH_3(CH_2)_{12}CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2COOH$	22 : 0
Lignoceric acid	n-Tetracosanoic acid	$CH_3(CH_2)_{12}CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2COOH$	24 : 0
Unsaturated fatty acids			
Oleic acid[b]	cis-9-Octadecenoic acid	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$	$18:1^{\Delta 9}$
Petroselenic acid	cis-6-Octadecenoic acid	$CH_3(CH_2)_{10}CH{=}CH(CH_2)_4COOH$	$18:1^{\Delta 6}$
Linoleic acid[b]	cis,cis-9,12-Octadecadienoic acid	$CH_3(CH_2)_4CH{=}CH{-}CH_2{-}CH{=}CH(CH_2)_7COOH$	$18:2^{\Delta 9,12}$
α-Linolenic acid[b]	all-cis-9,12,15-Octadecatrienoic acid	$CH_3CH_2CH{=}CH{-}CH_2{-}CH{=}CH{-}CH_2{-}CH{=}CH(CH_2)_7COOH$	$18:3^{\Delta 9,12,15}$
γ-Linolenic acid	all-cis-6,9,12-Octadecatrienoic acid	$CH_3(CH_2)_4CH{=}CH{-}CH_2{-}CH{=}CH{-}CH_2{-}CH{=}CH(CH_2)_4COOH$	$18:3^{\Delta 6,9,12}$
Roughanic acid[b]	all-cis-7,10,13-Hexadecatrienoic acid	$CH_3CH_2CH{=}CH{-}CH_2{-}CH{=}CH{-}CH_2{-}CH{=}CH(CH_2)_5COOH$	$16:3^{\Delta 7,10,13}$
Erucic acid	cis-13-Docosenoic acid	$CH_3(CH_2)_7CH{=}CH(CH_2)_{11}COOH$	$22:1^{\Delta 13}$

[b]These five fatty acids are commonly found as the principal constituents of membrane lipids. The others are found principally in storage lipids.

3. LIPID BIOSYNTHESIS

- The discussion of lipid biosynthesis will be confined to glycerolipids consisting of:
  - the triacylglycerols (the fats and oils stored in seeds) and
  - the polar glycerolipids (which form the lipid bilayers of cellular membranes) (Figure 11. 14).



Structural features of triacylglycerols and polar glycerolipids in higher plants

- The main structural lipids in membranes are the polar glycerolipids (Figure 11.14), in which the hydrophobic portion consists of two 16-carbon or 18-carbon fatty acid chains esterified to positions 1 and 2 of a glycerol backbone.
- The biosynthesis of triacylglycerols and polar glycerolipids requires the cooperation of two organelles: the plastids and the endoplasmic reticulum.
- Triacylglycerols in most seeds are stored in the cytoplasm of either cotyledon or endosperm cells in organelles known as oil bodies (also called spherosomes or oleosomes).
- Chloroplast membranes, which account for 70% of the membrane lipids in photosynthetic tissues, are dominated by glyceroglycolipids; other membranes of the cell contain glycerophospholipids (Table 11.4).

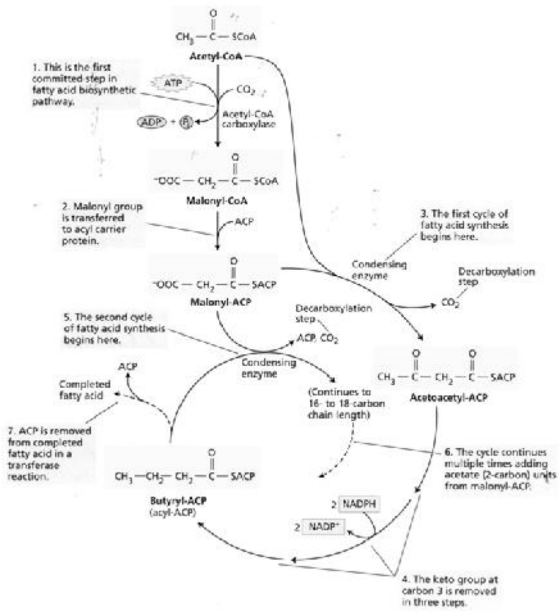
TABLE 11.4
Glycerolipid components of cellular membranes

Lipid	Lipid composition (percentage of total)		
	Chloroplast	Endoplasmic reticulum	Mitochondrion
Phosphatidylcholine	4	47	43
Phosphatidylethanolamine	—	34	35
Phosphatidylinositol	1	17	6
Phosphatidylglycerol	7	2	3
Diphosphatidylglycerol	—	—	13
Monogalactosyldiacylglycerol	55	—	—
Digalactosyldiacylglycerol	24	—	—
Sulfolipid	8	—	—

- In nonphotosynthetic tissues, glycerophospholipids are the major membrane glycerolipids.

1. Fatty acid biosynthesis

- Fatty acid biosynthesis in plants, similar to that in bacteria and consists of cycles of two-carbon addition, involves the **cyclic condensation of two-carbon units derived from acetyl-CoA**.
- In plants, fatty acids are synthesized exclusively in the **plastids**; in animals, fatty acids are synthesized primarily in the cytosol.
- The enzymes of the biosynthesis pathway are thought to be held together in a complex that is collectively referred to as ***fatty acid synthase***.
- The first committed step in the pathway (i.e., the first step unique to the synthesis of fatty acids) is the synthesis of malonyl-CoA from acetyl-CoA and CO_2 by the enzyme *acetyl-CoA carboxylase* (Fig 11. 16) (Sasaki *et al*. 1995).



Cycle of fatty acid synthesis in plastids of plant cells

2. Glycerolipids Biosynthesis

- The fatty acids synthesized in the chloroplast are next used to make the glycerolipids of membranes and oil bodies.
- The first steps of glycerolipid synthesis are two acylation reactions that transfer fatty acids from acyl-ACP or acyl-CoA to glycerol-3-phosphate to form **phosphatidic acid**.
- The action of a specific phosphatase produces **diacylglycerol** (**DAG**) from phosphaticlic acid.
- Phosphatidic acid can also be converted directly into phosphaticlylinositol or phosphatidylglycerol; DAG can give rise to phosphatidylethanolamine or phosphaticly1choline (Figure 11.17).

- In simple terms, the two pathways are referred to as the prokaryotic (or chloroplast) pathway and the eukaryotic (or ER) pathway (Ohlrogge and Browse 1995):

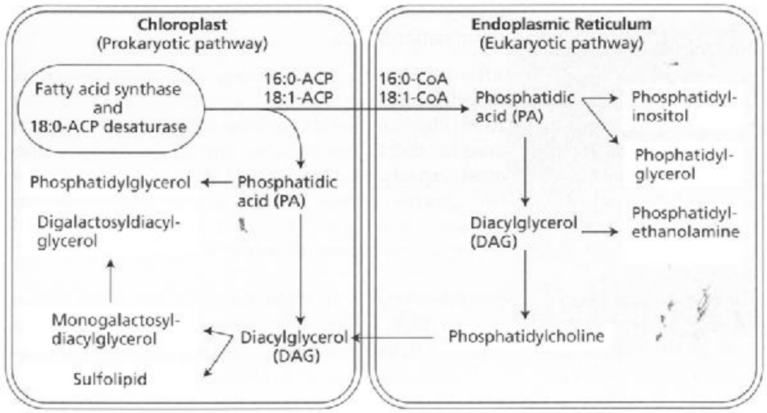


FIGURE11.17 The two pathways for glycerolipid synthesis in the chloroplast and encloplasmic reticulum of Arabiclopsis leaf cells.