Biosynthesis of Food Constituents: Lipids. 2. Triacylglycerols, Glycerophospholipids, and Glyceroglycolipids – a Review

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Abstract

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This review article gives a survey of the principal biosynthetic pathways that lead to the most important food glycerolipids, i.e. triacylglycerols, glycerophospholipids, and glyceroglycolipids as reported in recently published papers. Glycerophospholipids are further subdivided to phosphatides, lysophosphatides, and plasmalogens. The subdivision of the topics is predominantly via biosynthesis. Reaction schemes, sequences, and mechanisms with the enzymes involved are extensively used as well as detailed explanations based on chemical principles and mechanisms.

Keywords: biosynthesis; lipids; homolipids; heterolipids; glycerolipids; triacylglycerols; glycerophospholipids; phosphatides; lysophosphatides; plasmalogens; glyceroglycolipids

In food lipids, fatty acids are mainly found as esters in the form of triacylglycerols (fats and oils) and glycerophospholipids. Fats and oils represent a storage form of energy for most organisms (in animal adipose tissue and plant seeds), being subjected to oxidative metabolism as required. Triacylglycerols and partial fatty acid esters of glycerol (di- and monoacylglycerols) belong to the group of lipids known as homolipids, while glycerophospholipids are classified as heterolipids, being esterified with both fatty acids and phosphoric acid. Homolipids derived from glycerol, glycerophospholipids, and glyceroglycolipids together constitute one class of lipids known as glycerolipids.

The second class of lipids, sphingolipids, comprises fatty acid amides derived from the nitrogen-containing alcohols sphingosines[1]. These lipids include homolipids (*N*-acylsphingosines

[1]Sphingosines are long-chain bases, 2-amino-1,3-dihydroxyalkanes, carrying a *N*-acylated fatty acid of 14–26 carbon atoms. In mammals, the long-chain base moiety is mostly (*E*)-sphing-4-enine or (2*S*,3*R*,4*E*)-2-aminooctadece-4-ene-1,3-diol (sphingosine, C18:1), whereas in the yeast *Saccharomyces cerevisiae*, the predominant long-chain base is 4-hydroxysphinganine or (2*S*,3*S*,4*R*)-2-amino-1,3,4-octadecanetriol (phytosphinganine, C18:0). In contrast, the sphingoid base composition of plants is more variable, being composed of up to eight different C18-sphingoid bases derived from D-*erythro*-sphinganine or (2*S*,3*R*)-sphinganine. Due to an additional *cis*- or *trans*-desaturation at C-8, the predominating regioisomers are (*E*/*Z*)-sphing-8-enine (C18:1), (4*E*/8*E*/*Z*)-sphinga-4,8-dienine (18:2), and (8*E*/*Z*)-4-hydroxysphing-8-enine (Sperling & Heinz 2003).

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or ceramides), and heterolipids (sphingophospholipids and sphingoglycolipids) exemplified in Figure 1. Glycerophospholipids, glyceroglycolipids, and sphingolipids together represent structural lipids that occur in biological membranes. Sphingolipids are not dealt with in this review as they are of marginal importance to foods. A selection of recent review articles, however, provides the necessary information (Ohlrogge & Browse 1995; Munnik *et al*. 1998; Dickson & Lester 1999; Levade *et al*. 1999; Liu *et al*. 1999; Merrill *et al*. 2000; Van Meer & Holthuis 2000; Buccoliero & Futerman 2003; Cinque *et al*. 2003; Meijer & Munnik 2003; Menaldino *et al*. 2003; Sperling & Heinz 2003; Colombaioni & Garcia-Gil 2004).

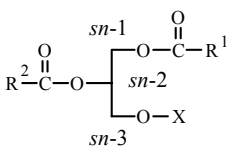
For example, wheat flour contains 1.5–2.5% lipids, depending on the milling extraction rate. Part of these lipids (75% of total lipids) are non-starch lipids, while the rest are starch lipids. Non-starch lipids and starch lipids significantly differ in their composition. In non-starch lipids, the major constituents are triacylglycerols (46.7%) followed by glyceroglycolipids (26.9%) and glycerophospholipids (14.7%), while in starch-bound lipids, the major constituents are phospholipids (89.4%). Glyceroglycolipids (5.0%) and triacylglycerols (1.4%) represent the minor constituents of starch-bound lipids (Belitz *et al*. 2004).

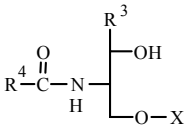
Biosynthesis of an extensive group of compounds accompanying lipids (formerly called lipoids), as well as of other lipophilic compounds (such as various terpenoids, carotenoids, and some lipophilic vitamins), starts with isoprene. Numerous of the lipophilic compounds generated in this way, even if counted among lipids[2], are not the object of this review, and neither are the changes of lipids during foods storage and processing.

1 TRIACYLGLYCEROLS

In all cells, triacylglycerols are mostly synthesised from glycerol in the endoplasmic reticulum and in the mitochondria. Fatty acids bound in triacylglycerols are stored for the future use, primarily in adipocytes of adipose tissue in animals and in plant seeds. Adipocytes synthesise triacylglycerols from 1,3-dihydroxyacetone phosphate (1,3-dihydroxypropan-2-one phosphate or glycerone phosphate). Glycerone phosphate can also serve as a backbone precursor for triacylglycerols synthesis in tissues other than adipose tissue, however, to a much lesser extent than glycerol.

Glycolysis pathway produces as an intermediate the three-carbon D-aldonic acid, (*R*)-glyceric acid 3-phosphate or (*R*)-3-phosphoglyceric acid, which is hydrolysed by glycerate kinase (EC 2.7.1.31) to (*R*)-glyceric acid. Oxidation of glyceric acid by the





	glycerolipids	sphingolipids	
homolipids	1,2,3-triacyl-*sn*-glycerols		X = acyl
	1,2-diacyl-*sn*-glycerols	*N*-acylsphingosines (ceramides)	X = H
heterolipids	glycerophospholipids	sphingophospholipids	X = phosphoric acid ester
	glyceroglycolipids	sphingoglycolipids	X = glycosyl

Figure 1

[2]Recently, lipids have been defined as hydrophobic or amphipathic small molecules that may originate entirely or in part by carbanion-based condensations of thioesters (fatty acids, polyketides, etc.) and/or by carbocation based condensations of isoprene units (prenols, sterols, etc.). Additionally, lipids have been broadly subdivided into simple and complex groups, with simple lipids being those yielding at the most 2 types of products on hydrolysis (e.g., fatty acids, sterols, and acylglycerols) and complex lipids (e.g., glycerophospholipids and glyceroglycolipids) yielding 3 or more products on hydrolysis. Lipids have been categorised based on their chemically functional backbone and divided into 8 categories (fatty acyls, glycerolipids, glycerophospholipids, sphingolipids, prenol lipids, saccharolipids, and polyketides) containing distinct classes and subclasses of molecules (Fahy *et al*. 2005).

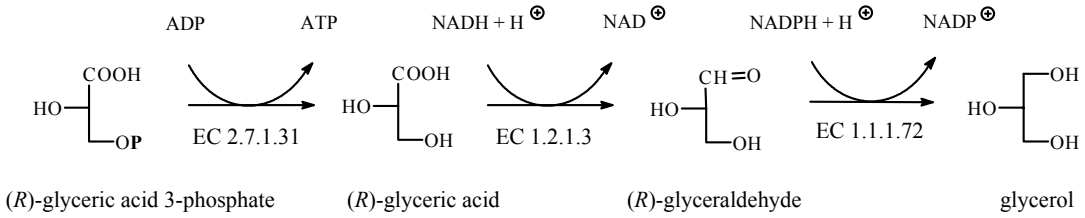


Figure 2

widely specific aldehyde dehydrogenase (NAD^+) (EC 1.2.1.3) yields (*R*)-glyceraldehyde (D-glyceraldehyde or D-*glycero*-triose or D-glyceral), which is reduced by glycerol dehydrogenase ($NADP^+$) (EC 1.1.1.72) to glycerol, the major building block for the synthesis of triacylglycerols (Figure 2). Glycerone phosphate is also produced as a glycolytic pathway product and in plants is also obtained by photosynthesis (Voet & Voet 1990).

The glycerol backbone is activated by phosphorylation (esterified) at the C-3 position by glycerol kinase (EC 2.7.1.30) and forms prochiral glycerol 3-phosphate (Figure 3). Triacylglycerols are produced from *sn*-glycerol 3-phosphate by esterification with fatty acyl-CoA residues. The first step, catalysed by glycerol 3-phosphate *O*-acyltransferase (EC 2.3.1.15) (the enzyme acts only on the derivatives of fatty acids of the chain length above C10), yields 1-acylglycerol 3-phosphoric acid also known as lysophosphatidic acid. This compound is then esterified at the C-2 hydroxyl by 1-acylglycerol 3-phosphate *O*-acyltransferase (EC 2.3.1.51) giving rise to 1,2-diacylglycerol 3-phosphoric acid (commonly identified as phosphatidic acid). The phosphate group is then removed by phosphatidate phosphatase (EC 3.1.3.4) prior to the last esterification of 1,2-diacylglycerol to triacylglycerol, which is catalysed by diacylglycerol *O*-acyltransferase (EC 2.3.1.20, palmitoyl-CoA and other long-chain acyl-CoAs can act as donors). Phosphatidic acid can be also used for the biosynthesis of glycerophospholipids.

The acyltransferases are not quite specific (with the exception of 1-acylglycerol 3-phosphate *O*-acyltransferase, EC 2.3.1.51) for the transfer of fatty acyl groups, thus the majority of fats and oils have a saturated fatty acid (mainly palmitic acid) at the position of *sn*-1 and an unsaturated fatty acid (oleic acid) at the position of *sn*-2 (Akoh & Min 1998).

Adipocytes lack glycerol kinase, therefore, glycerone phosphate is the precursor for the synthesis of triacylglycerols (Figure 4). In the endoplasmic reticulum and in the peroxisomes, glycerone

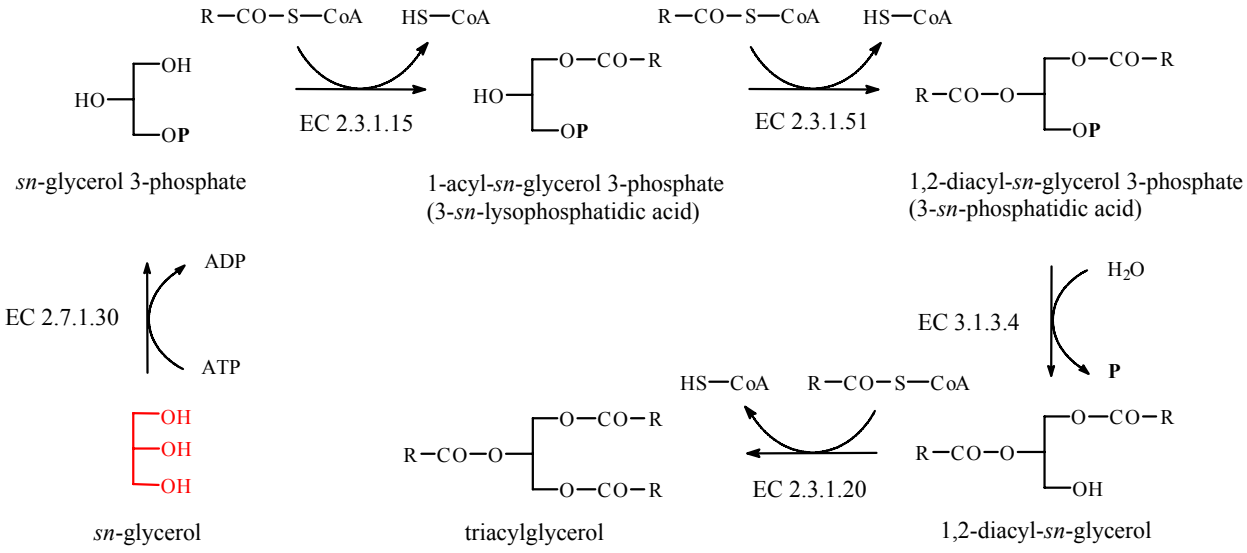


Figure 3

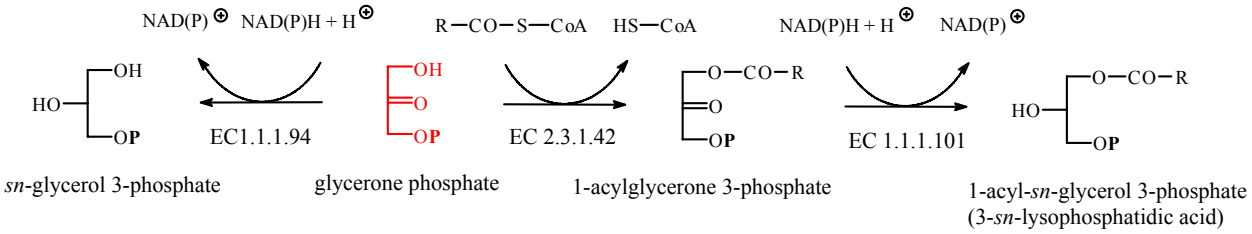


Figure 4

phosphate may be directly reduced to glycerol 3-phosphate by the action of various dehydrogenases, such as glycerol 3-phosphate dehydrogenase (NAD^+) (EC 1.1.1.8) and glycerol 3-phosphate dehydrogenase $NAD(P)^+$ (EC 1.1.1.94), or esterified to 1-acylglycerone 3-phosphate by glycerone phosphate *O*-acyltransferase (EC 2.3.1.42). 1-Acylglycerone 3-phosphate is then reduced to 1-acylglycerol 3-phosphate (3-*sn*-lysophosphatidic acid) by acylglycerone phosphate reductase (EC 1.1.1.101) or used for the biosynthesis of glycerophospholipids.

Alternatively, 2-acylglycerols produced by hydrolysis of dietary fats by lipases[3], can also serve as substrates for the synthesis of 1,2-diacylglycerols[4]. This transformation of 2-acylglycerols to 1,2-diacylglycerols is catalysed by the action of 2-acylglycerol *O*-acyltransferase (EC 2.3.1.22) (Figure 5).

2 GLYCEROPHOSPHOLIPIDS

Glycerophospholipids constitute three groups of fatty acid esters. The first two group representatives are derived from either 3-*sn*-phosphatidic acid (phosphatides) or 3-*sn*-lysophosphatidic acid (lysophosphatides) (Figure 6). The third group of glycerophospholipids are glycerol ether phospholipids or plasmalogens[5]. There are two types of plasmalogens, alk-2-en-1-yl ethers derived from 3-*sn*-plasmenic acid, and 1-alkyl ethers derived from 3-*sn*-plasmanic acid (Figure 7).

In animals and plants, glycerophospholipids are mostly synthesised in the endoplasmic reticulum and in the mitochondria by esterification of an alcohol to the phosphate of phosphatidic acid (1,2-diacyl-*sn*-glycerol 3-phosphate). The most commonly encountered alcohols in phosphatides and

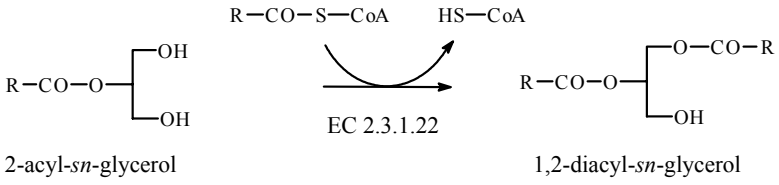


Figure 5

[3]The human fat-digestive enzymes include triacylglycerol- and phospholipases. Triacylglycerol lipase catalyses the hydrolysis of triacylglycerol to free fatty acid, mono- and diacylglycerol. The human lipases include the pre-duodenal lingual and gastric lipase (EC 3.1.1.3) and the extra-duodenal pancreatic, hepatic lipase (EC 3.1.1.3), lipoprotein lipase (EC 3.1.1.34), and the recently described endothelial lipase (EC 3.1.1.3) (Mukherjee 2003).

[4]Various 2-acyl-*sn*-glycerols can act as acceptors. Palmitoyl-CoA and other long-chain acyl-CoAs can act as donors. The *sn*-1 position and the *sn*-3 position are both acylated at about the same rate (KEGG).

[5]The term plasmalogen may be used as a generic term for glycerophospholipids in which the glycerol moiety bears an alk-1-en-1-yl ether group. The term plasmenic acid signifies a derivative of *sn*-glycerol 3-phosphate in which C-1 bears an *O*-(alk-1-en-1-yl) residue, and C-2 is esterified with a fatty acid. The terms plasmanic acid and plasmanyl may also be applied to ethers with an alkyl group bearing a double bond within the chain. In such cases, the proper term alkenyl, if used without the ene locant(s), would be misleading.

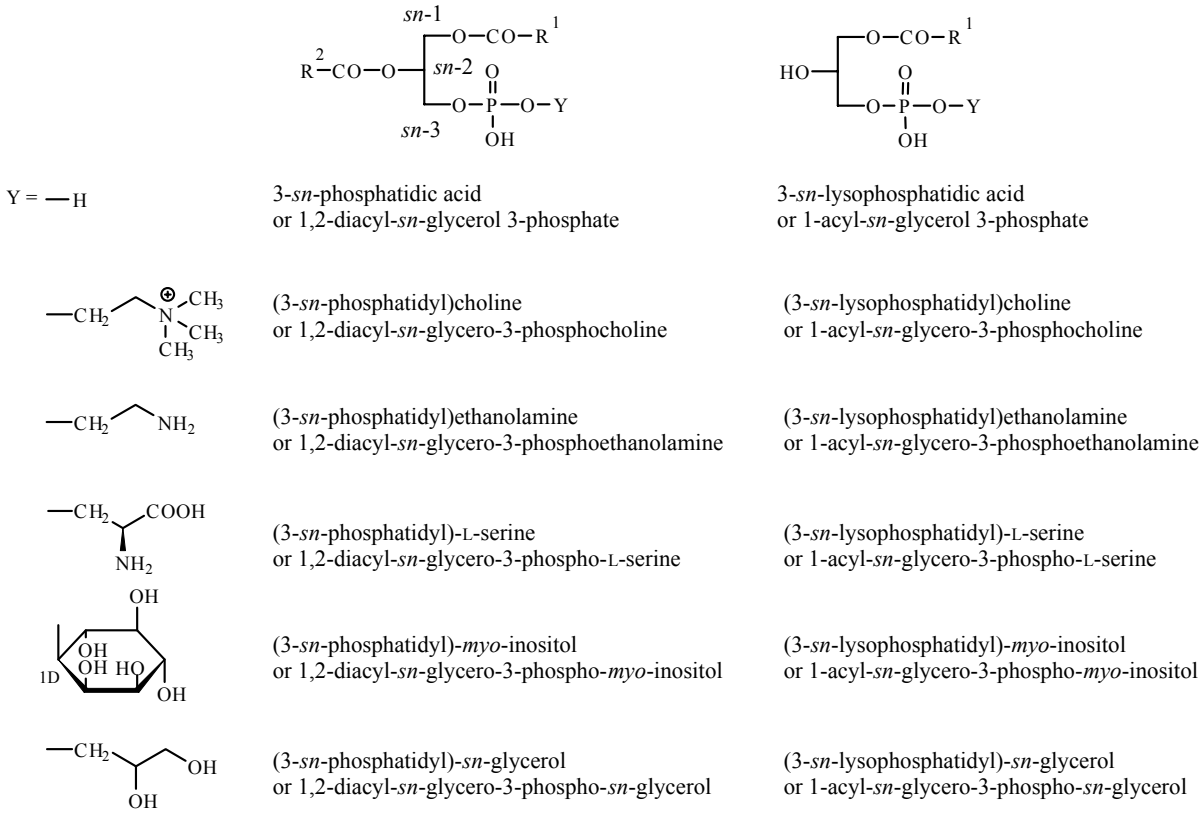


Figure 6

lysophosphatides are choline (*N*,*N*,*N*,-trimethylethanolamine), ethanolamine (2-aminoethanol), L-serine, *myo*-inositol, and glycerol. Plasmalogens are derived from choline, ethanolamine, and serine.

For example, non-starch phospholipids of wheat flour are composed of phosphatidylcholines (4.9%), *N*-acylphosphatidylethanolamines (4.9%), phosphatidylinositols (0.5%), phosphatidylglycerols (1.0%), lysophosphatidylcholines (1.5%), *N*-acyllysophosphatidylethanolamines (1.7%), and lysophosphatidylglycerols (0.3%). Starch phospholipids of wheat flour comprise lysophosphatidylcholines

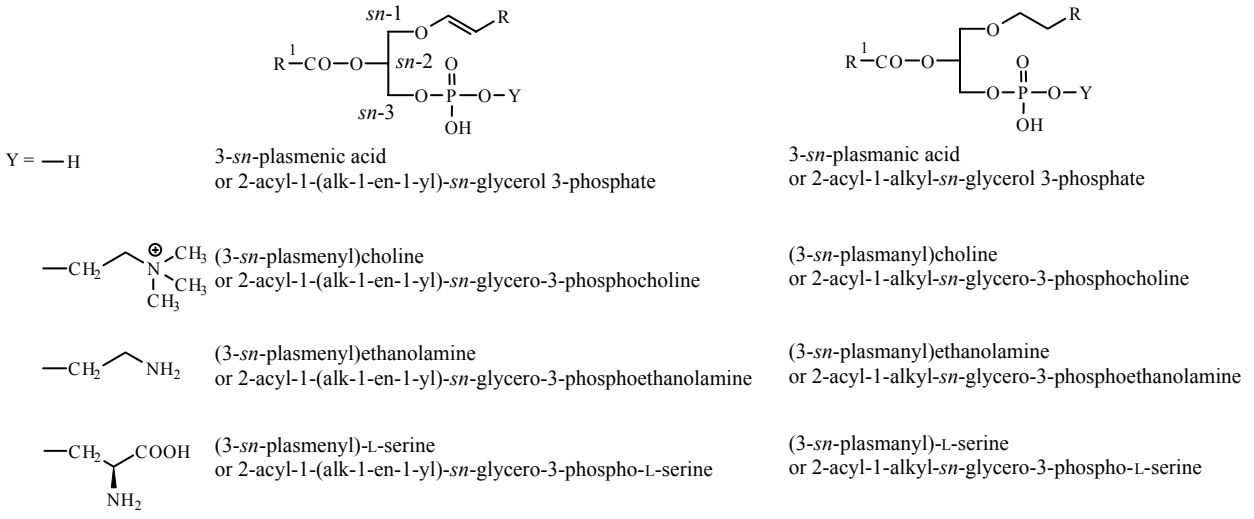


Figure 7

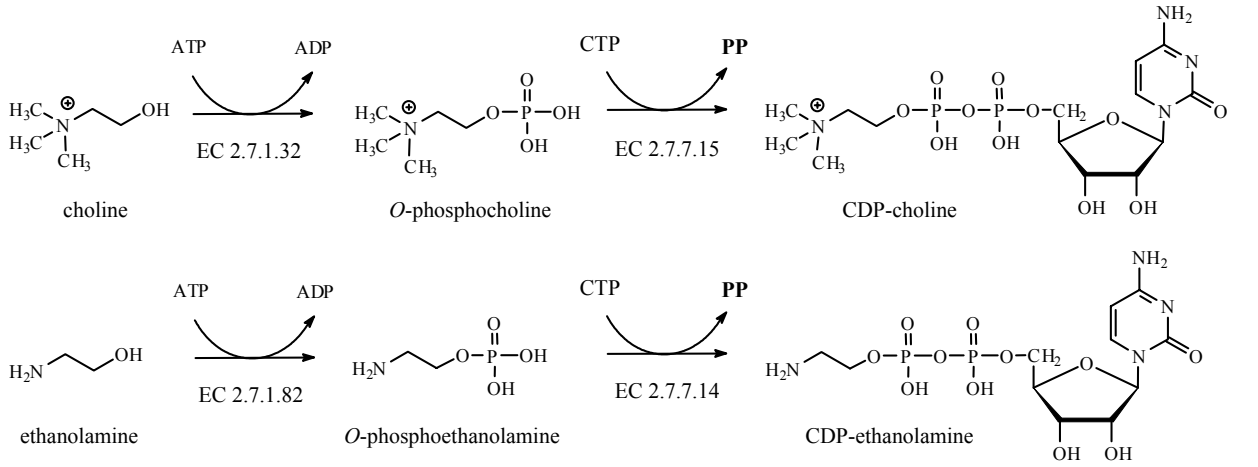


Figure 8

(74.8%), lysophosphatidylethanolamines (9.9%), lysophosphatidylserines/lysophosphatidylinositols (2.5%), and lysophosphatidylglycerols (2.2%) (Belitz *et al.* 2004).

2.1 Phosphatides

Phosphatides can be synthesised by two mechanisms. One utilises a CDP-activated alcohol (choline or ethanolamine) for the attachment to the phosphate moiety of phosphatidic acid. The other utilises CDP-activated 1,2-diacylglycerol and an inactivated alcohol.

The alcohols are transferred to the CDP-activated alcohols in two steps (Figure 8). The first step, the formation of the corresponding *O*-phosphoalcohol, is catalysed by choline kinase (EC 2.7.1.32) and ethanolamine kinase (EC 2.7.1.82), respectively. In the second step, the *O*-phosphoalcohol is transformed to the corresponding CDP-alcohol by the action of CTP-phosphocholine cytidyltransferase (CDP-choline synthetase, EC 2.7.7.15) and CTP-phosphoethanolamine cytidyltransferase (CDP-ethanolamine synthetase, EC 2.7.7.14), respectively.

The CDP-activated 1,2-diacylglycerol is formed from phosphatidic acid in the reaction catalysed by phosphatidate cytidyltransferase (CDP-diacylglycerol synthetase, EC 2.7.7.41) (Figure 9).

Synthesis of phosphatidylcholine (sometimes incorrectly called lecithin) can occur by three pathways. In the first pathway (Figure 10), CDP-choline is attached to diacylglycerol by diacylglycerol cholinephosphotransferase (EC 2.7.8.2). In the second pathway, phosphatidylcholine is also synthesised by the addition of choline to CDP-activated 1,2-diacylglycerol by phosphatidylcholine synthase (EC 2.7.8.24). A third pathway involves the conversion of either phosphatidylserine or phosphatidylethanolamine to phosphatidylcholine (Figure 11). The conversion of phosphatidylserine to phosphatidylcholine first requires decarboxylation of phosphatidylserine by the pyridoxal phosphate protein phosphatidylserine decarboxylase (EC 4.1.1.65) to yield phosphatidylethanolamine; this then undergoes a series of three methylation reactions utilizing *S*-adenosyl-L-methionine (AdoMet, SAM) as the methyl group donor. In the first methylation reaction catalysed

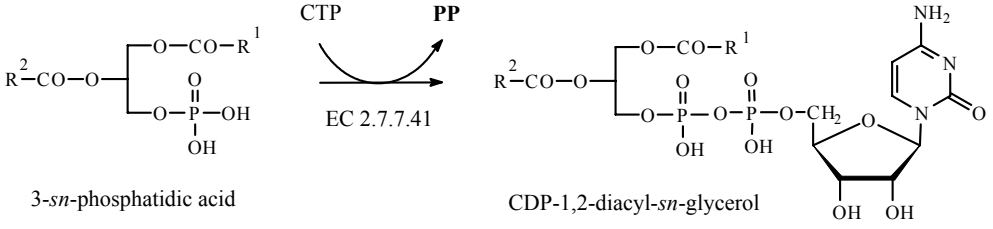


Figure 9

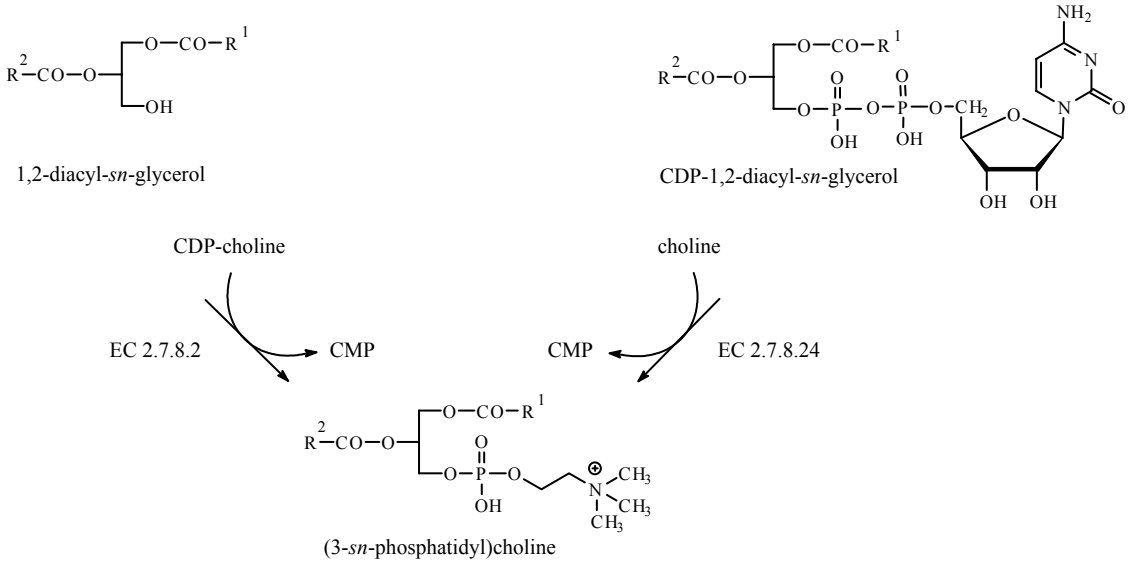


Figure 10

by phosphatidylethanolamine *N*-methyltransferase (EC 2.1.1.17), phosphatidylethanolamine yields phosphatidyl-*N*-methylethanolamine, which is then methylated by phosphatidyl-*N*-methylethanolamine *N*-methyltransferase (EC 2.1.1.71) to phosphatidyl-*N*,*N*-dimethylethanolamine. The enzyme also catalyses the transfer of a further methyl group, producing phosphatidylcholine.

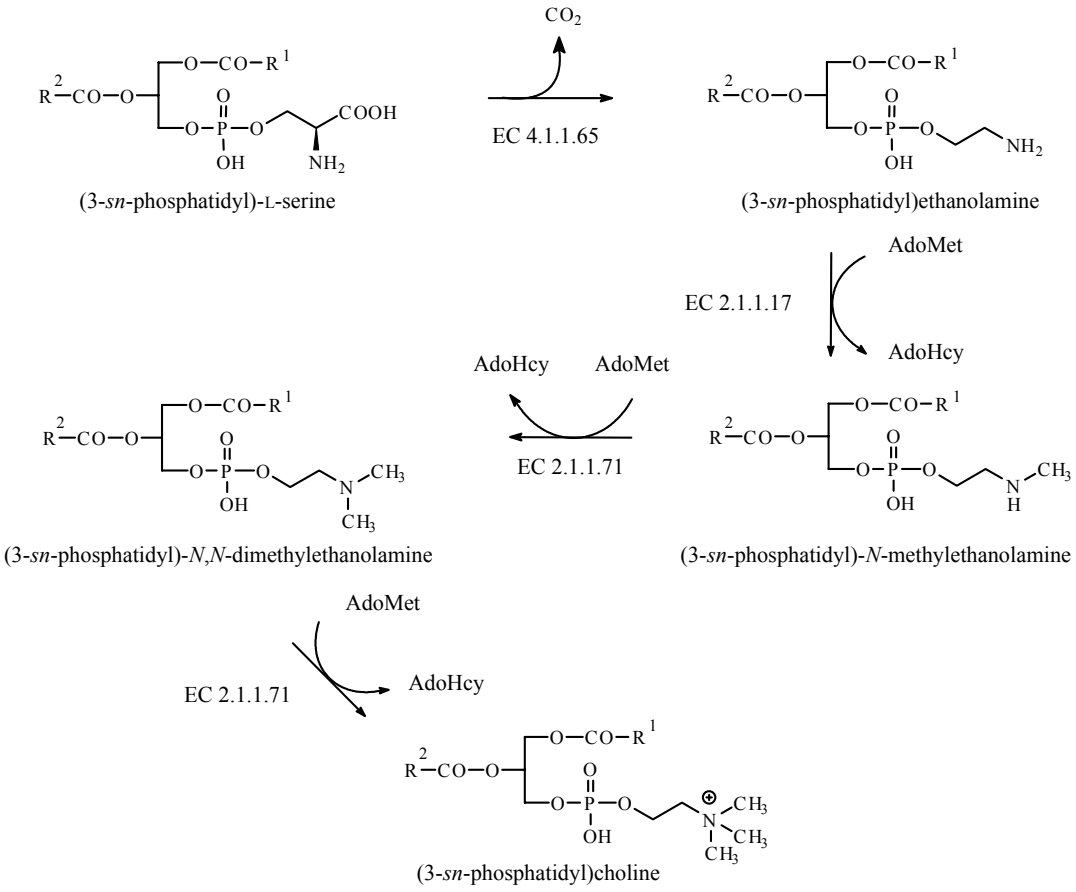


Figure 11

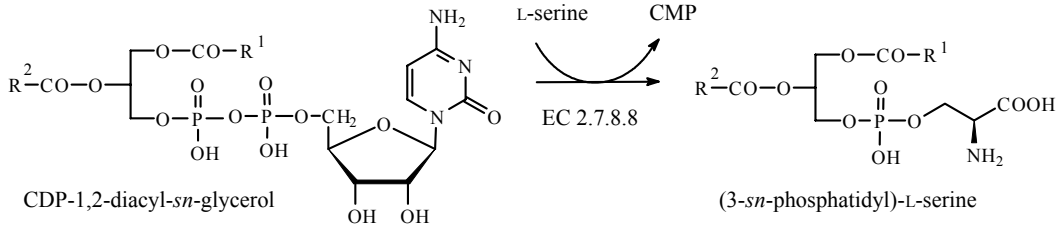


Figure 12

For example, phosphatidylcholine containing at both carbon C-1 and carbon C-2 positions palmitic acid is the major glycophospholipid in the extracellular lipid layer lining the pulmonary alveoli. Phosphatidylcholines are also the major glycophospholipids of milk, egg, and oil seed phosphatides (Velíšek 2002).

Synthesis of phosphatidylethanolamine can occur by two pathways. The first requires that ethanolamine be activated by phosphorylation and then by coupling to CDP. The ethanolamine is then transferred from CDP-ethanolamine to diacylglycerol by diacylglycerol ethanolaminephosphotransferase (EC 2.7.8.1) to yield phosphatidylethanolamine (Figure 12). The second pathway involves decarboxylation of phosphatidylserine (Figure 11).

Animal phosphatidylethanolamines contain primarily palmitic or stearic acid on C-1 and a long-chain unsaturated fatty acid at carbon C-2 (linoleic, arachidonic, DHA). In milk, egg, and oil seeds, phosphatidylethanolamines (together with phosphatidylcholines) represent the major constituents of the phosphatide fraction (Velíšek 2002).

The pathway for phosphatidylserine synthesis involves a reaction of serine with CDP-diacylglycerol catalysed by phosphatidylserine synthase (EC 2.7.8.8) (Figure 13). Phosphatidylserines are composed of fatty acids similar to phosphatidylethanolamines. In milk, egg, and oil seeds, phosphatidylserines are minor components of the phosphatide fraction (Velíšek 2002).

The synthesis of phosphatidylinositol involves CDP-activated diacylglycerol condensation with *myo*-inositol catalysed by phosphatidylinositol synthase (EC 2.7.8.11) (Figure 14). For example, the mammalian phosphatidylinositols contain almost exclusively stearic acid at carbon C-1 and arachidonic acid at carbon C-2. The arachidonic acid released is then the substrate for the synthesis of eicosanoids (Velíšek & Cejpek 2006). Although *myo*-inositol (bound at 1D position) is the predominant form, the presence of *scyllo*-inositol-containing phosphatides has been found in plant cells and *chiro*-inositol-containing phosphatides in animal cells (Loewus & Murthy 2000). Biosynthetic conversion of D-glucose 6-phosphate to *myo*-inositol has been recently described (Velíšek & Cejpek 2005).

Phosphatidylinositols are further phosphorylated by specific kinases to yield phosphorylated phosphatidylinositol derivatives (phosphoinositides). Phosphoinositides exist in animal and plant membranes with various levels of phosphate esterified to the hydroxyls of the *myo*-inositol moiety. Thus, phosphatidylinositol 4-phosphate (1-phosphatidyl-1D-*myo*-inositol 4-phosphate) forms by the action of 1-phosphatidylinositol 4-kinase (EC 2.7.1.67) and phosphatidylinositol 4,5-bisphosphate (1-phosphatidyl-1D-*myo*-inositol 4,5-bisphosphate) by the action of 1-phosphatidylinositol 4-phosphate kinase (EC 2.7.1.68). They represent extremely important membrane phospholipids involved in the transduction of signals for the cell growth and differentiation (Munnik *et al.* 1998). Their levels

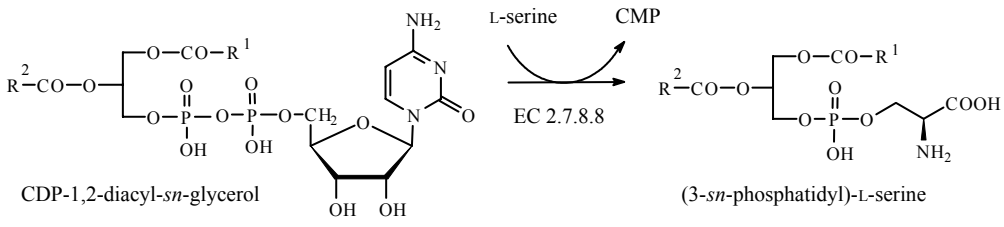


Figure 13

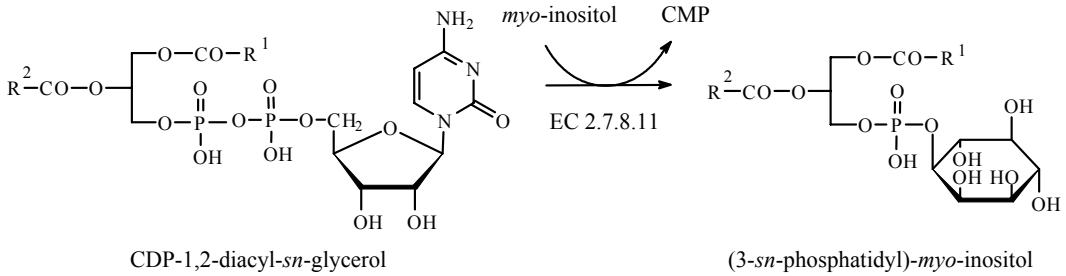


Figure 14

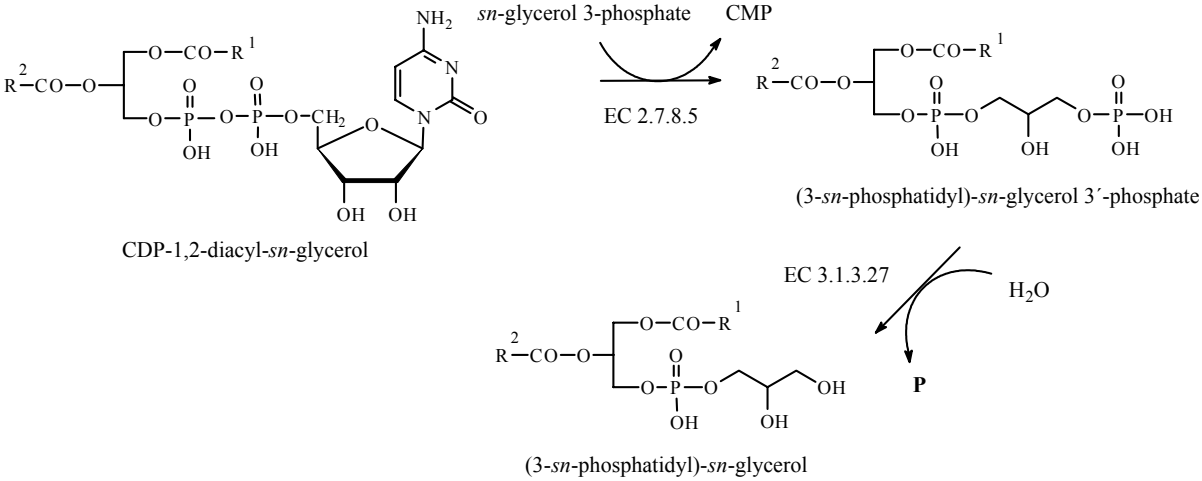


Figure 15

in oil seeds are much higher than those in milk or eggs (Velíšek 2002).

Phosphatidylglycerol is synthesised from CDP-diacylglycerol and glycerol 3-phosphate by the action of phosphatidylglycerol phosphate synthase (EC 2.7.8.5) (Figure 15).

Phosphatidyl glycerols are found in high levels in mitochondrial membranes and as components of pulmonary surfactant. The vital role of phosphatidylglycerols is to serve as the precursors of diphosphatidylglycerols derived from 1´,3´-di-*O*-(*sn*-3-phosphatidyl)-*sn*-glycerol (diphosphatidic acid) (Figure 16).

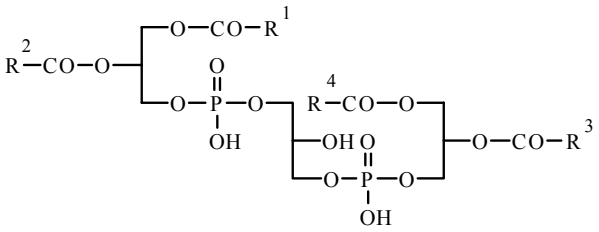


Figure 16

2.2 Lysophosphatides

Lysophoshatidylderivatives (lysophosphatidylcholine, lysophosphatidylethanolamine, lysophosphatidylserine, and lysophosphatidyl-*myo*-inositol)[6] occur naturally in foods of animal (egg yolk) and plant origins (e.g. lipids of cereal starches). The fatty acid distribution at the C-1 and C-2 positions of glycerol within native glycerophospholipids is continually in flux, owing to the glycerophospholipid degradation and the continuous glycero-

[6]The term lyso originated from the fact that these compounds are haemolytic. It is here redefined to indicate a limited hydrolysis of the phosphatidyl derivative (i.e. deacyl).

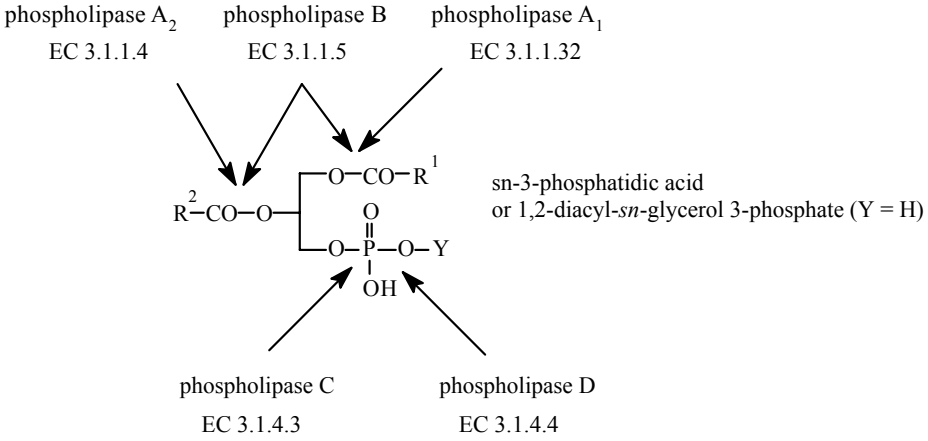


Figure 17

phospholipid remodelling that occurs while these molecules are in membranes. Glycerophospholipid degradation results from the action of phospholipases that exhibit substrate specificities for different positions in glycerophospholipids (Figure 17), i.e. phospholipase A_1 (EC 3.1.1.32), phospholipase A_2 (EC 3.1.1.4), phospholipase B (EC 3.1.1.5), phospholipase C (EC 3.1.4.3), and phospholipase D (EC 3.1.4.4). The products of the phospholipase A_2 action are called lysophosphatides. In many cases the acyl group, which was initially transferred to glycerol by the action of acyl transferases, is different from that present in the glycophospholipid when it resides within the membrane, as the deg-

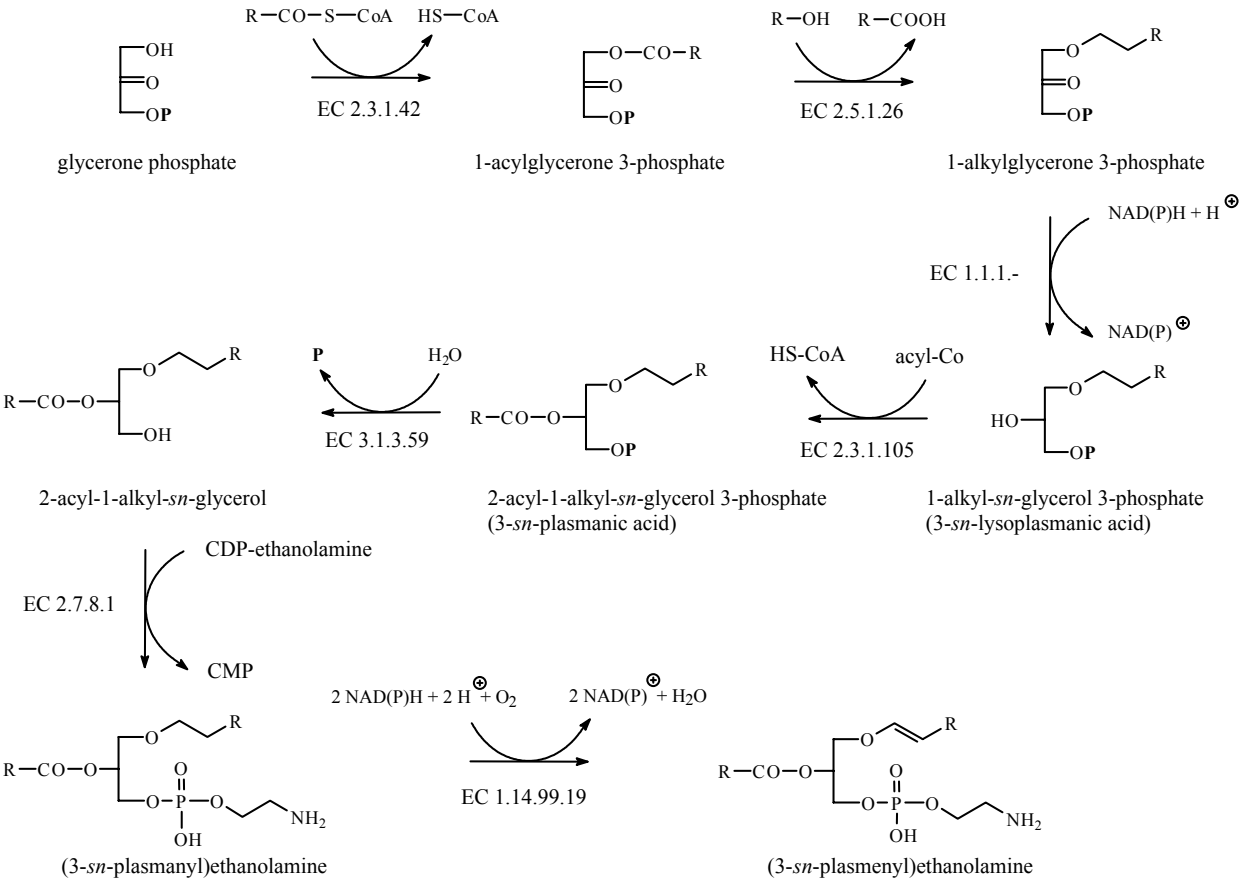


Figure 18

radation products can become substrates for acyl transferases utilising different acyl-CoA groups. Lysophosphatides can also accept acyl groups from other glycerophospholipids in an exchange reaction catalysed by lysolecithin acyltransferase (EC 2.3.1.23).

2.3 Plasmalogens

Choline plasmalogen is especially abundant in cardiac tissue and ethanolamine plasmalogen prevails in myelin within neurons. Glycerone serves as the glycerol precursor for the synthesis of glycerol ether glycophospholipids (plasmalogens). Figure 18 exemplifies the biogenesis of plasmanyl- and plasmenylethanolamine. Glycerone is first esterified to 1-acylglycerone 3-phosphate by glycerone phosphate *O*-acyltransferase (EC 2.3.1.42) as in the case of triacylglycerol synthesis (Figure 4). The ester-linked fatty acid of 1-acylglycerone 3-phosphate is then cleaved by alkyldihydroxyacetone phosphate synthetase (EC 2.5.1.26), replaced by a long-chain alcohol in an ether linkage. 1-Alkylglycerone 3-phosphate is reduced to 1-alkylglycerol 3-phosphate (lysoplasmanic acid) by a reductase (EC 1.1.1.-) and esterified by alkylglycerophosphate 2-*O*-acetyltransferase (EC 2.3.1.105) to yield 2-acyl-1-alkylglycerol phosphate (plasmanic acid). Alkylacetylglycerophosphate phosphatase (EC 3.1.3.59) splits off phosphoric acid to yield 2-acyl-1-alkylglycerol, which reacts with CDP-ethanolamine (diacylglycerol ethanolaminephosphotransferase, EC 2.7.8.1) and forms plasmanylethanolamine. Plasmanylethanolamine is then transferred to plasmenylethanolamine by plasmanylethanolamine desaturase (EC 1.14.99.19, requires NADPH or NADH and Mg^{2+} and ATP as cofactors).

3 GLYCEROGLYCOLIPIDS

Glycerophospholipids and glyceroglycolipids are important components of biological membranes. In photosynthetic organisms (cyanobacteria and plants), however, phosphorus-free galactolipids are the most abundant lipid class. They not only play a crucial role in photosynthesis but are also important for the adaptation of membrane-lipid composition in plants to phosphate-limiting conditions (when phosphate is limiting, phospholipids in plant membranes are reduced but these are replaced, at least in part, by glycolipids). The glycerogalactolipids (monogalactosyldiacylglycerols and digalactosyldiacylglycerols) are the predominant lipids (Kelly & Dörmann 2004). For example, non-starch lipids of wheat flour contain digalactosyldiacylglycerols (16.5%) as the major glyceroglycolipids, which are followed by monogalactosyldiacylglycerols (5.9%), digalactosylmonoacylglycerols (2.7%), and

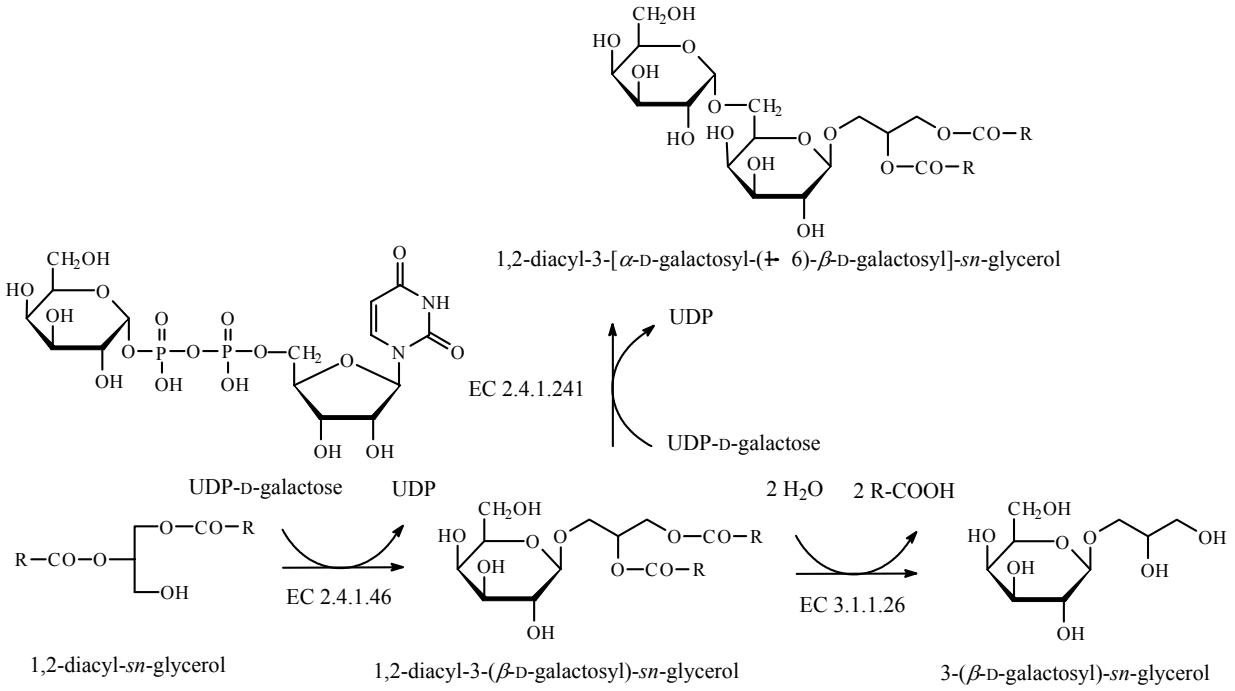


Figure 19

monogalactosylmonoacylglycerols (0.9%). Starch glyceroglycolipids are composed of digalactosyldiacylglycerols (1.1%), monogalactosyldiacylglycerols (0.4%), digalactosylmonoacylglycerols (2.3%), and monogalactosylmonoacylglycerols (1.0%) (Belitz *et al.* 2004).

Galactolipids are derived from either the plastid-located (prokaryotic) or the endoplasmic reticulum-located (eukaryotic) pathway. 1,2-Diacyl-*sn*-glycerol serves as the precursor for the synthesis of 1,2-diacyl-3-(*β*-D-galactosyl)-*sn*-glycerol (monogalactosyldiacylglycerol) that have the galactose head group linked in *β*-configuration to diacylglycerol (Figure 19). In the reaction catalysed by monogalactosyldiacylglycerol synthase (EC 2.4.1.46), 1,2-diacylglycerol reacts with the metabolically active form of D-galactose, uridinediphospho-D-galactose (UDP-D-galactose), yielding monogalactosyldiacylglycerol and uridine-5´-diphosphate (UDP). Under catalysis by the Mg^{2+}-dependent digalactosyldiacylglycerol synthase (EC 2.4.1.241), monogalactosyldiacylglycerol then reacts with the second UDP-D-galactose and forms 1,2-diacyl-3-[α-D-galactosyl-(1→6)-*β*-D-galactosyl]-*sn*-glycerols (digalactosyldiacylglycerol) where, in contrast, the second galactose is bound to the first one by *α*-anomeric linkage. Biosynthesis of UDP-D-galactose from UDP-D-glucose has been already described (Velíšek & Cejpek 2005). Monogalactosyldiacylglycerols can be hydrolysed to 3-*β*-D-galactosylglycerol by galactolipase (EC 3.1.1.26). This enzyme also acts on digalactosyldiacylglycerols and glycerophospholipids.

Alternatively, monogalactosyldiacylglycerol can act as a substrate for galactolipid galactosyltransferase (EC 2.3.1.184) that transforms monogalactosyldiacylglycerol to digalactosyldiacylglycerol (Figure 20). Further transfers of galactosyl residues to the digalactosyldiacylglycerol, trigalactosyldiacylglycerol and tetragalactosyldiacylglycerol[7] also

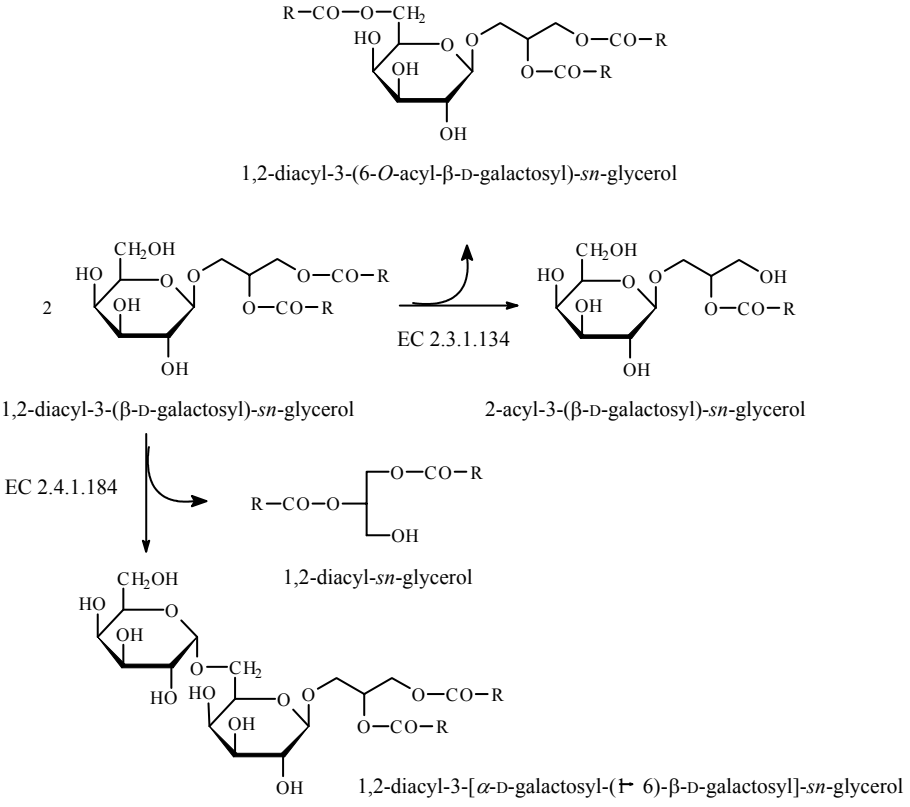


Figure 20

[7]Normal isomers of monogalactosyldiacylglycerols (*β*) and digalactosyldiacylglycerols (*β*,*α*) are found in all higher plants. The activity of galactolipid galactosyltransferase is located in chloroplast envelope membranes, but it does not contribute to net galactolipid synthesis in plants. Three series of unusual oligogalactolipid isomers (e.g. trigalactolipids, *β*,*α*,*β*; *β*,*β*,*β*; *β*,*α*,*α*) exist in some plant species as a result of the galactolipid galactosyltransferase activity (Kelly & Dörmann 2004).

proceed. Monogalactosyldiacylglycerol can also serve as the precursor of monogalactosylmonoacylglycerol and monogalactosyldiacylglycerol containing acylated galactose at the C-6 position. This reaction is catalysed by galactolipid *O*-acyltransferase (EC 2.3.1.134); digalactosyldiacylglycerol can also act as acceptor. Galactosylacylglycerol *O*-acyltransferase (EC 2.3.1.141) then transfers long-chain acyl groups to the *sn*-1 position of the glycerol residue in monogalactosylmonoacylglycerol (KEGG).

EC (Enzyme Commission) numbers and some common abbreviations

EC (Enzyme Commission) numbers, assigned by IUPAC-IUBMB, were taken from KEGG. In many structures, the unionised forms are depicted to simplify the structures, to eliminate the need for counter-ions, and to avoid the mechanistic confusion.

AdoHcy	*S*-adenosyl-L-homocysteine (SAH)
AdoMet	S-adenosyl-L-methionine (SAM)
ADP	adenosine 5´-diphosphate
ATP	adenosine 5´-triphosphate
CDP	cytidine 5´-diphosphate
CMP	cytidine 5´-monophosphate
CoA	coenzyme A as a part of a thioester
CTP	cytidine 5´-triphosphate
DHA	docosahexaenoic acid
NADH	nicotinamide adenine dinucleotide
NADPH	nicotinamide adenine dinucleotide phosphate
P	phosphoric acid
PP	diphosphoric acid
sn	stereospecific numbering
UDP	uridine-5´-diphosphate

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