Review

Phospholipids in foods: prooxidants or antioxidants?

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Abstract

Lipid oxidation is one of the major causes of quality deterioration in natural and processed foods and thus a large economic concern in the food industry. Phospholipids, especially lecithins, are already widely used as natural emulsifiers and have been gaining increasing interest as natural antioxidants to control lipid oxidation. This review summarizes the fatty acid composition and content of phospholipids naturally occurring in several foods. The role of phospholipids as substrates for lipid oxidation is discussed, with a focus on meats and dairy products. Prooxidant and antioxidant mechanisms of phospholipids are also discussed to get a better understanding of the possible opportunities for using phospholipids as food antioxidants.
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INTRODUCTION

Lipids, as one of the major macronutrients required for human growth and maintenance, are important constituents in foods. They provide unique properties of texture, appearance, flavor and caloric density to foods.[1] However, lipids at the same time are prone to oxidation, which negatively impacts not only quality and nutritive values of foods but also consumer health. Thus lipid oxidation is a great concern to both food manufacturers and the general public.

A variety of factors influence lipid oxidation susceptibility. These include water activity, transition metal type and concentration, singlet oxygen, fatty acid composition, presence of antioxidants and environmental conditions such as light, temperature and oxygen concentration.[2] Some of these factors are considered to be prooxidant, which is defined as causing or accelerating lipid oxidation. Prooxidants act by promoting lipid hydroperoxide formation (e.g. singlet oxygen), free radical formation (e.g. irradiation) or hydroperoxide decomposition (e.g. transition metals). In contrast, compounds that can slow down lipid oxidation are known as antioxidants. Antioxidants are classified into primary and secondary antioxidants according to their chemical mechanisms. Broadly speaking, primary antioxidants scavenge the free radicals that promote oxidation, while secondary antioxidants retard lipid oxidation by decreasing other prooxidative factors (e.g. metal chelation) or regenerating primary antioxidants.[3]

The use of antioxidants in foods has been an effective way to inhibit lipid oxidation, because a variety of other methods have shown their limitations. For example, reducing polyunsaturated fatty acid (PUFA) concentrations, partial hydrogenation or exclusion of oxygen from products can be utilized to increase oxidative stability of food products. However, nutritionists do not recommend replacing PUFAs with saturated fatty acids, because dietary PUFAs are linked to many health benefits.[4] Partial hydrogenation would also not be an ideal method to decrease lipid oxidation because it converts PUFAs to *trans* fatty acids, which are more atherogenic than saturated fats because they both increase

low-density lipoprotein (the bad lipoprotein) and decrease high-density lipoprotein (the good lipoprotein). Excluding oxygen can be effective, but these techniques must produce very low oxygen concentrations and are not practical for many types of foods.[5] For all these reasons, the use of antioxidants is widely accepted as a reliable technique to control lipid oxidation in a wide variety of food products. However, primary and secondary antioxidants are not the perfect solution either. One problem is that the most powerful and economical antioxidants are synthetic, e.g. butylated hydroxytoluene (BHT), *tert*-butylhydroquinone (TBHQ) and ethylenediaminetetraacetic acid (EDTA), whose use is contrary to current consumer preference for cleaner and simpler labels. Thus searching for novel natural antioxidants or increasing the antioxidant activity of currently available natural antioxidants is of great importance.

Phospholipids are an essential part of biological membranes and thus are present in all living species from which foods are derived. The concentration and composition of phospholipids endogenous to foods can vary greatly in foods from animal or plant sources and are dependent on the origin of the food and how it is processed. For example, phospholipids from cold water marine animals will be highly unsaturated and high in omega-3 fatty acids compared with warm, fresh water species.[6] Phospholipid concentrations can also be increased during processing operations such as the drying of milk or whey.[7] In addition, phospholipids possessing desirable functional properties such as emulsification, crystallization inhibition, non-stick releasing agent, wetting agent and

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anti-spattering agent, commonly referred to as lecithin, are often added to foods.[8]

Phospholipids are sometimes used as antioxidants in foods. Several mechanisms of how phospholipids could influence lipid oxidation have been proposed. In general, phospholipids could bind prooxidative metals,[9] produce antioxidative compounds through Maillard reactions during lipid oxidation,[10] alter the location of other antioxidants[11] and regenerate primary antioxidants such as tocopherols.[12] However, phospholipids could also serve as oxidation substrates themselves. Owing to their high degree of unsaturation, negative charge that attracts prooxidant metals and large surface area when they exist as dispersions, they can be an important substrate for oxidation in foods containing considerable amounts of biological membranes, such as meats.[13] In addition, there were also times when phospholipids showed no antioxidant activity or even acted as prooxidants.[14,15] One possible prooxidant mechanism of phospholipids in bulk oil could be their formation of association colloids such as reverse micelles which can increase metal–lipid interactions.[16]

To best understand the many facets of how phospholipids influence lipid oxidation in food products, a comprehensive review is needed. In this review, the source and composition of phospholipids in foods will be summarized. The impact of phospholipids in different food systems on lipid oxidation and the different anti- and prooxidant mechanisms will be discussed.

PHOSPHOLIPID PROPERTIES AND SOURCES
Properties

Structures
Phospholipids consist of a glycerol backbone and a phosphate head group, which is typically found at the *sn*-3 position (Fig. 1). The simplest phospholipid is phosphatidic acid (PA) and others are named after the group attached to the phosphate group. For example, if the group attached to the phosphate group is choline, this phospholipid is called phosphatidylcholine (PC). Other substitution groups on the phosphate group include ethanolamine, serine and inositol, thus the phospholipids are named phosphatidylethanolamine (PE), phosphatidylserine (PS) and phosphatidylinositol (PI) respectively. Lysophospholipids refer to phospholipids whose fatty acid chain has been removed from either the *sn*-1 or *sn*-2 position. In addition, there is another type of lipids, sphingolipids, which are sometimes considered to be phospholipids because they could contain a phosphatidylcholine or phosphatidylethanolamine group in the molecules. For example, sphingomyelin contains a phosphatidylethanolamine group.[17]

The fatty acid composition of phospholipids varies depending on their origin (Table 1). Moreover, it is worth noting that dietary lipids can influence phospholipid fatty acid composition.[18–20] In general, saturated fatty acids are more often found at the *sn*-1 position, while unsaturated fatty acids tend to be esterified at the *sn*-2 position. A proper ratio of saturated to unsaturated fatty acids of phospholipids is important to living cells, since the saturation degree will determine the physical state (e.g. fluidity) of the cell membrane.

Molecular charge
pK_a is the negative logarithm of the acid dissociation constant K_a. The value of pK_a is the pH at which the molecule is exactly half dissociated. This indicates how acidic a given hydrogen atom in a molecule is at a given pH. For example, if the pH of the environment is above the pK_a, the molecule exists more as the dissociated form, which is the case where a chelating molecule is charged and thus is able to bind metals. The pK_a values vary among major phospholipids (Table 2). The different measurement methods (e.g. indirect calorimetric and turbidity measurements, surface potential measurement by radioactive electrode, transmembrane potential by potential dynamic and proton binding by acid acid–base titration) and physical systems (e.g. dispersions, monolayers, bilayer membranes and vesicles) used contribute to the different pK_a values that are often reported. For example, pK_a values ranging from 2.1 to 4 for the carboxyl group of PS were reported.[21–23] Similarly, the pK_a values of PC range from 0.8 to 4.5.[24–26]

Sources
All foods that originate from living plants/animals contain phospholipids. This is because all living plants/animals have cells, and phospholipids are integral components of cell membranes. The major animal-based sources of phospholipids include eggs, milks, meats and marine phospholipids. Eggs of chicken, duck and turkey all contain considerable amounts of phospholipids. Egg yolks are especially rich sources of phospholipids, with a weight per cent up to 10%, the majority of the phospholipids being PC (66%) and PE (19%).[27] Egg yolks are a common source of non-vegan food-grade lecithin. Raw meats contain large amounts of biological membranes and thus generally contain 0.5–1% phospholipids. In addition to muscle foods, animal organs contain even higher amounts of phospholipids. For example, pig and chicken kidneys contain 2.9 and 2.5% phospholipids respectively.[27] Seafood has similar phospholipid concentrations as warm-blooded animals, but marine phospholipids are much higher in omega-3 fatty acids (Table 1), which makes them a promising functional ingredient in foods.[6] Krill oil is a unique source of marine phospholipids that originate from small marine crustaceans. Krill oil is high in phospholipids and thus is used in highly bioavailable omega-3 supplements.[28] Vegetable seeds and cereal grains are also rich sources of phospholipids. These include soybean, corn, cottonseed, rapeseed, sunflower, peanut and oats, with commercial lecithin being obtained from some of these sources during oil refining (see below). In addition, phospholipids are present in some vegetable-, fruit- and carbohydrate-related food products such as spinach, orange juice, lemon juice and wheat starch (Table 3).

Lecithin
Lecithin refers to a mixture of phospholipids extracted from animal (e.g. eggs) and vegetable (e.g. soybean, sunflower, rapeseed and cottonseed) sources. Soybean has been the primary commercial source of food-grade lecithin because it is economical to produce and can be used in vegan applications. Lecithin is not only an important additive in foods but also in cosmetics and lubricants. In the food industry, lecithin is the most important natural emulsifier, with an estimated world market of 150 000–170 000 t. In addition to the use of lecithin as a food emulsifier, manufacturers often also expect to receive the benefit of its antioxidant activity.

Production
Soybean lecithin is a co-product of soybean oil processing. Figure 2 is a schematic description of the operations for lecithin production. Crude soybean oil contains 1.5–3% phospholipids, which can decrease oil quality owing to their susceptibility to browning during heating and their ability to trap water in the oil to form
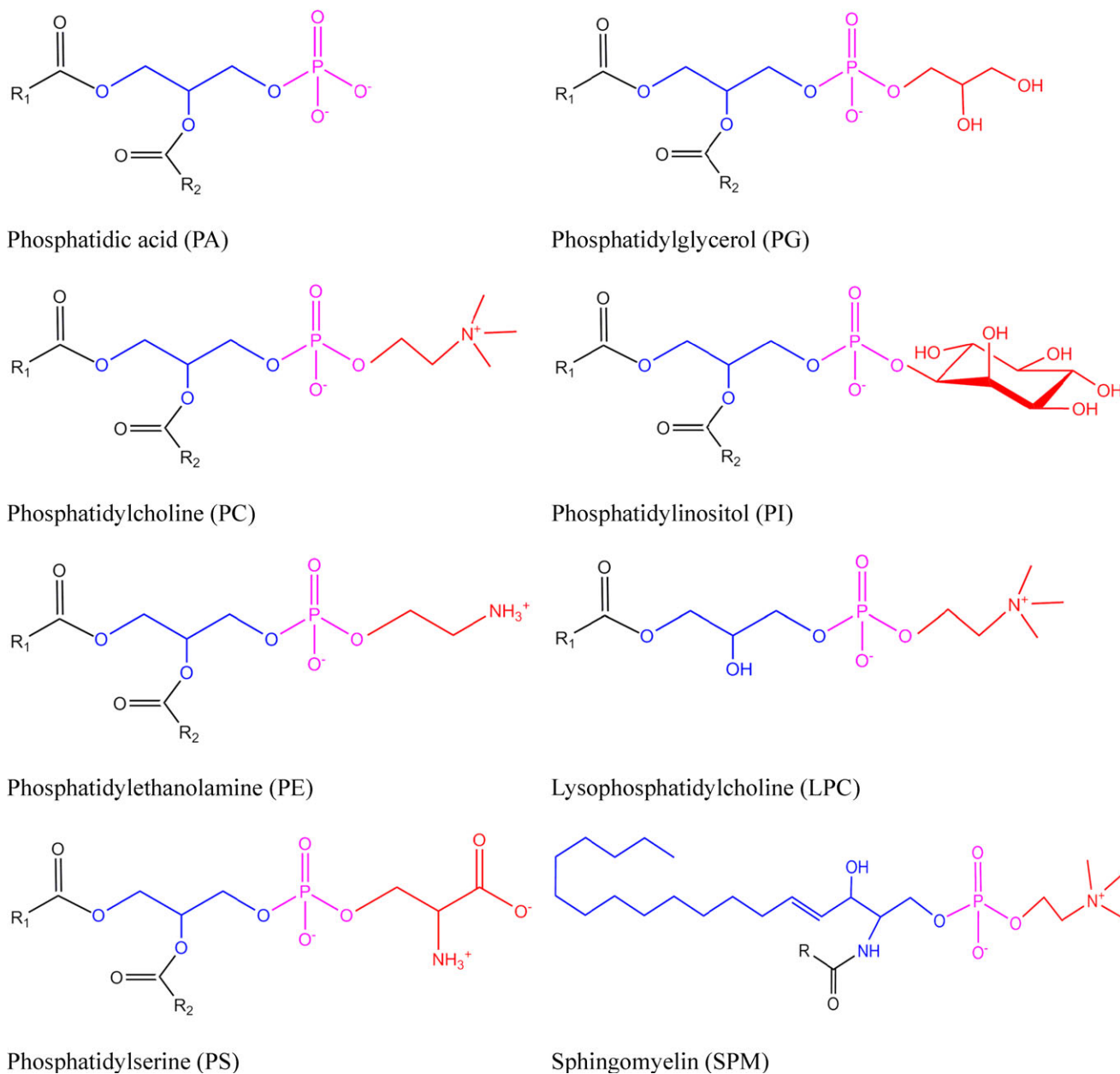
Figure 1. Phospholipid structures.

cloudiness.[29] Phospholipids are removed by the degumming process, which utilizes a weak acid solution to partition out of the oil and into the water fraction. The lecithin fraction would be dried and in some cases bleached to remove the natural brown color of lecithin.

The composition of lecithin can be modified by means of solvent extraction as well as chemical and enzyme modification to produce specialty, value-added products.[8] For example, crude dried lecithin contains 30–40% neutral oil, which can be modified to 2–3% with solvent extraction. The product is called de-oiled lecithin. This is often done with acetone, which can selectively extract neutral oil (triacylglycerides) out of the lecithin. Individual phospholipids have different solubility properties. For example, PC dissolves well in ethanol, while PI does not.[30] Taking advantage of this difference, PC-enriched lecithin can be produced. Increasing the PC content of lecithin results in increased

hydrophilicity, which is preferred in oil-in-water emulsions such as salad dressings. Besides modifications with solvent extraction, chemical modification (e.g. hydrogenation) is used to improve the oxidative stability, color and odor of lecithin. Hydrogenated lecithin is currently used in cosmetics, dyes and lubricants. One example of enzyme-modified lecithin is lyso-lecithin. This product requires phospholipase A_2, which hydrolyzes the fatty acid of phospholipids at the sn-2 position. With the removal of the fatty acid chain from phospholipids, lyso-lecithin exhibits increased hydrophilic and emulsifying properties under lower pH values and a broader range of temperatures and salt concentrations.[30]

Composition

The fatty acid composition of lecithin differs depending on the source (Table 1). However, it is worth noting that lecithins with a variety of phospholipid compositions are commercially available

Table 1. Fatty acid composition (g kg^{-1}) of phospholipids from different sources

Fattyacid	Chicken egg yolk	Bovine whole milk[a]	Chicken breast muscle[b]	Pig	Cattle	Tuna[a, c]	Salmon[d]	Soybean lecithin[a]	Egg lecithin[a]
10:0		4							
12:0		13							
14:0	287	57	8.0	3.0	2.0	14.3	57.8		
14:1			2.0						
14:2			14						
15:0		15				6.8			
16:0	16.5	347	237	166	146	193	130	112	350
16:1		10	18	8.0	8.0	20.9	73.3		
16:2			8.0						
17:0		20				12.3			
18:0	141	95	119	121	110	36	315	119	134
18:1	313	267	211	94	158	129	141	86	304
18:2	163	150	207	314	220	7.0	342	586	180
18:3			8.0	6.0	7.0	4.9	11.2	99	
20:0						4.7			
20:1						6.4	70.9		
20:2							3.5		
20:3		9.0	18				2.9		
20:4	53.8		94	105	100	49.3	11.5		32
20:5		8.0	4.0	10	8.0	57.5	32.2		
21:5							4.4		
22:1							57.2		
22:4							0.6		
22:5			10				20.1		
22:6	26.8		12			416	194		
UnS/S[e]	1.25	0.8	1.66	1.85	1.94	3.09	2.99	3.29	1.07
Ref.	120	121	122	123	123	124	125	126	126

[a] The values are of phosphatidylcholine (PC).
[b] Chickens are 21 days old and fed a diet with no added fat.
[c] The species is yellowfin. The values are in mol%.
[d] The species is anadromous Atlantic salmon and the age is 77 days after hatching.
[e] The ratio of unsaturated fatty acids to saturated fatty acids.

Table 2. pK_a of different functional groups of phosphatidylcholine (PC), phosphatidylethanolamine (PE) and phosphatidylserine (PS)

Phospholipid	pK_a (phosphate)	pK_a (amino)	pK_a (carboxyl)
PC	0.8[a]		
PE	0.5[a]	9.6[c]	
PS	2.6[b]	9.8[c]	3.6[c]

[a] Data from Moncelli et al.[24] A phospholipid monolayer model was used. The values were measured by differential capacity of an electrode coated with phospholipid monolayers.
[b] Data from Petelska and Figaszewski.[25] A phospholipid bilayer membrane model was used. The value was measured by acid–base titration.
[c] Data from Tsui et al.[127] The value for PE was determined by surface potential measurements of PE–PC mixed vesicles. The values for PS were determined by potentiometric titrations and surface potential measurements of PS–PC mixed vesicles.

(such as the different types of lecithin mentioned above) and lecithin mixtures still contain some portion of compounds other than phospholipids (Table 4).

Uses

The molecular characteristics of the phospholipids dictate the application of lecithin. The presence of both hydrophilic and lipophilic groups within a phospholipid molecule makes it surface-active. This surface-active property plus the natural nature of lecithin contribute to emulsification, anti-spattering, wetting, anti-staling, dough-conditioning and antioxidant functions in foods. Emulsifiers are used in many food products owing to their ability to stabilize oil and water dispersions. The emulsification property of lecithin depends on its affinity for oil or water molecules, which can be identified as hydrophilic–lipophilic balance (HLB). The HLB ranges from 0 to 20, with a higher value representing higher hydrophilic affinity. By modifying lecithin composition (e.g. de-oiled, PC-enriched and enzyme-hydrolyzed lyso-lecithin), different HLB values can be created for different applications. For example, standard crude lecithin and de-oiled lecithin with 45% PC have HLB values of 3.5 and 6.5 respectively.[30] Another use of lecithin that directly relates to its emulsification property is anti-spattering. In margarine, which is a water-in-oil emulsion, spattering happens when water droplets coalesce during heating. Lecithin surrounds water particles to slow down this coalescence and thus reduce spattering. Lecithin also serves as a

Table 3. Phospholipid content of common foods[a]

Food	PL	PC	PE	PS	PI	SPM	LPC	LPE	CL	PG	Ref.
Chicken whole egg	34.9	770	166			24	16				27
Bovine whole milk	0.2	327	285	141[b]		230	18				121
Beef	7.0	493[c]	180	139[d]	46	64					27
Pork	6.0	429	267	49	68	75	29		83		128,129
Chicken breast	4.0	610	194	40	67	55					130
Chicken thigh	6.0	500	228	50	73	77					130
Salmon (head)	5.4	547	140	104	25	83	14				131
Tuna	6.0	379	210	54	85	40	215				27,124
Soybean	20	450	263	50[e]	141				35[f]		132
Corn germ	11	307	142	271[e]	187		7.0				133
Rapeseed	15	487	83		184						134
Peanut	6.0	435	81	40[e]	242						27
Lemon juice	0.3	387	355	55[e]	161						135
Orange juice	0.3	323	387	130[e]	65						135
Wheat starch	7.0						809	106			136
Spinach	2.0	236	229	89[e]	70					312	27
Soybean lecithin		386	164	06	192					12	137
Egg lecithin		754	183			19	25	12			138

Abbreviations: PL, total phospholipids; PC, phosphatidylcholine; PE, phosphatidylethanolamine; PS, phosphatidylserine; PI, phosphatidylinositol; SPM, sphingomyelin; LPC, lysophosphatidylcholine; LPE, lysophosphatidylethanolamine; CL, cardiolipin; PG, phosphatidylglycerol.
[a] The values of total phospholipids are in g kg^{-1} total food. The values of individual phospholipids are in g kg^{-1} total phospholipids.
[b] The value includes PI.
[c] The value includes LPC.
[d] The value includes phosphatidic acid (PA) and CL.
[e] The values include PA.
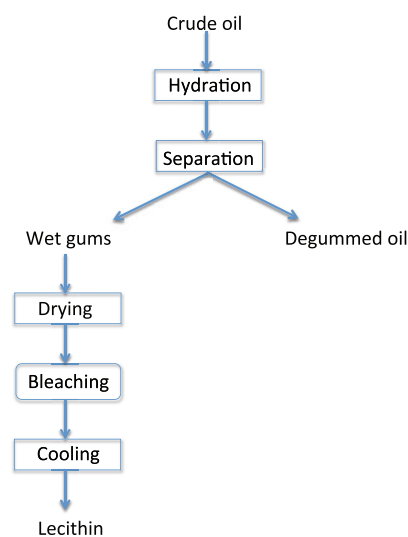[f] The value includes PG.

Crude oil
↓
Hydration
↓
Separation
↙ ↘
Wet gums / Degummed oil
↓
Drying
↓
Bleaching
↓
Cooling
↓
Lecithin

Figure 2. Schematic description of lecithin production.

Table 4. Composition of different types of soybean lecithin (g kg^{-1})[a]

Component	Crude lecithin	De-oiled lecithin	PC-enriched fraction
Phospholipids (total)	470	740	510
PC[b]	319	324	745
PE[b]	234	230	157
PI[b]	213	216	59
PA[b]	85	81	20
Others[b]	149	149	20
Triacylglycerides	370	30	370
Glycolipids	110	170	90
Carbohydrates	35	55	25
Water	<10	<10	<10

Abbreviations: PC, phosphatidylcholine; PE, phosphatidylethanolamine; PI, phosphatidylinositol; PA, phosphatidic acid.
[a] Adapted from van Nieuwenhuyzen and Tomás.[8]
[b] The values are in g kg^{-1} total phospholipids.

wetting agent in powdered or granular products. For example, the addition of lecithin helps cocoa powder disperse easily in water. Another advantage of lecithin is its ability to form complexes with starch and protein. One example is the ability of lyso-lecithin to form a lipid–amylose complex that decreases wheat starch retrogradation.[33] Also, linking to wheat gluten through hydrogen bonds makes lecithin a good dough conditioner in that it can improve bread elasticity, baking volume and fermentation tolerance.[34] Another attractive trait of lecithin is its antioxidant properties.[35–37] However, application of lecithin for the purpose of inhibiting lipid oxidation is not always successful. This will be discussed in more detail in later sections.

LIPID OXIDATION MECHANISMS

Unsaturated lipids undergo oxidation in the presence of oxygen in a pathway which involves free radical chain reactions (Fig. 3). These reactions can be divided into three stages, namely initiation, propagation and termination.[38] An initiator such as light, heat, transition metal or reactive oxygen species is required to initiate
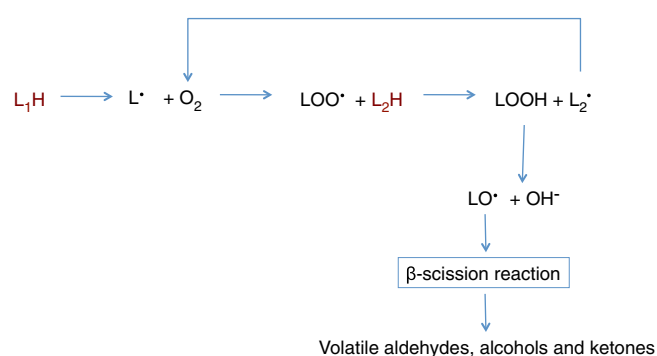
$$L_1H \longrightarrow L^\bullet + O_2 \longrightarrow LOO^\bullet + L_2H \longrightarrow LOOH + L_2^\bullet$$

$$LO^\bullet + OH^-$$

$$\boxed{\beta\text{-scission reaction}}$$

Volatile aldehydes, alcohols and ketones

Figure 3. Schematic description of lipid oxidation chain reaction.

the reaction to convert a fatty acid substrate (L_1H) to a free radical. After the initiation happens, an alkyl radical ($L^\bullet$) is formed and the reaction enters the propagation phase. In the propagation step, the alkyl radical reacts with bi-radical triplet oxygen (O_2) to form a peroxyl radical ($LOO^\bullet$). This reaction is diffusion-limited because it is a radical–radical reaction with minimal activation energy. The peroxyl radical ($LOO^\bullet$) abstracts hydrogen from a new unsaturated fatty acid substrate (L_2H) and thus causes the formation of an additional alkyl radical which can enter a new round of propagation reactions. The peroxyl radical itself forms lipid hydroperoxide ($LOOH$), which is a primary oxidation product. The susceptibility of the fatty acid substrate to lose hydrogen ($LH \rightarrow L^\bullet$) increases with increasing unsaturation, which is why more unsaturated lipids are more easily oxidized. Finally, the reaction will not terminate until two radicals combine to form a non-radical species. However, in food systems, the termination step is not important, because most foods are rancid before there is significant termination.

The development of oxidative rancidity originates from the formation of volatile secondary oxidation compounds resulting from the decomposition of lipid hydroperoxides ($LOOH$), known as β-scission reactions. Lipid hydroperoxides ($LOOH$) decompose in the presence of heat, ultraviolet radiation and transition metals to form alkoxyl radicals ($LO^\bullet$). Alkoxyl radicals are so energetic that they can abstract electrons from the covalent bonds adjacent to the alkoxyl radical to cleave the aliphatic chain, resulting in the formation of low-molecular-weight volatile compounds such as aldehydes and ketones. β-Scission reactions are greatly accelerated by transition metals such as iron and copper, which is why transition metals are so important in lipid oxidation in foods.[39] More details on products from the decomposition of lipid hydroperoxides have been reported.[38]

PHOSPHOLIPIDS IN LIPID OXIDATION
Phospholipids as oxidation substrates
Owing to the presence of unsaturated fatty acids in phospholipids, phospholipids themselves are susceptible to lipid oxidation. In fact, in many foods the phospholipids are more unsaturated than the triacylglycerides since they must provide fluidity in cell membranes. Examples of food systems that involve phospholipid as an oxidation substrate are meats and dried milk products.

Meats are susceptible to lipid oxidation not only because they are exposed to oxygen and contain unsaturated fatty acids, both of which are major substrates of lipid oxidation, but also because they contain prooxidative metals, enzymes and reactive oxygen species. The total lipid content of meats varies depending on

species, animal diet, muscle groups and types of processing, as summarized elsewhere.[27,40] Phospholipids in muscle are very susceptible to lipid oxidation because they are highly unsaturated and are more exposed to prooxidants than triacylglycerides because they are within membranes, which have a very high surface area.[41,42] Generally, the phospholipid content of muscle is about 0.5%.[43] Red meats have greater proportions of phospholipids than white meats, which in part is due to higher levels of mitochondria.[44]

Oxidation in meats leads to negative impacts on flavor[40,43−45] and protein integrity,[46−48] including discoloration.[49,50] Keller and Kinsella[41] observed the loss of unsaturated PC and PE with increasing thiobarbituric acid (TBA) values in raw and cooked beef patties during frozen storage. This was especially true during frozen storage where they found that the total lipids of hamburgers remained constant while the amount of PC and PE decreased. The loss of PC and PE was accompanied by an increase in TBA of ground beef during the first 2 weeks. Igene et al.[46] found that phospholipids oxidized before triacylglycerides during frozen storage of lipid-free muscle fibers where phospholipids and triacylglycerides were added. Igene et al.[53] also reported that PE was associated with high susceptibility to oxidation and was important in the autoxidation of cooked meat. Pikul et al.[54] found that the phospholipid fraction of chicken meat contributed approximately 90% of malonaldehyde during lipid oxidation.

Individual phospholipids have varying degrees of susceptibility to lipid oxidation due to differences in polar head group and level of unsaturation. Pikul and Kummerow[55] found that, in chicken meat, PC and PE produced 70–77% of malondialdehyde, followed by 16–25% from PI and PS. Yin and Faustman[56] found that, in a liposome model system where PC and PE had the same fatty acid composition, PE liposomes oxidized faster than PC liposomes. The rapid loss of PE during oxidation of muscle cell membranes could be due to its higher level of fatty acid unsaturation than PC.[54] In addition, PE loss could also be due to the ability to regenerate α-tocopherol. In general, the fat content of meat does not greatly influence lipid oxidation rates.[57] This further supports that phospholipids are the major lipid substrates rather than triacylglycerides and thus fat concentrations do not impact oxidation rates.

Food products that have low lipid concentrations, such as nonfat dry milk, can also be susceptible to rancidity caused by phospholipid.[58,59] Polar phospholipids are essential components in milk as they, together with proteins, form milk fat globule membranes (MFGMs) that surround the lipid droplets secreted by the mammary gland cells. During processing, the MFGMs can partition into the aqueous phase of milk and are thus present in nonfat dry milk and whey.[60] Two major milk phospholipids, PC and PE, are about one-third polyunsaturated and thus have poor oxidative stability.[61] PC in milk can be hydrolyzed by milk lipase to generate lyso-PC and unsaturated free fatty acids, which can undergo further oxidative deterioration and yield off-flavors.[62] Volatile lipid oxidation compounds, including C_6-C_{14} aldehydes, have been identified in nonfat dry milk,[58,59] whey protein isolate and whey protein concentrate.[61] Hexanal accounted for over 90% of total aldehydes in the latter two products.[63] This high concentration of hexanal was believed to result from the oxidation of linoleic acid of phospholipids. This is because milk fat only contains 2% linoleic acid while the phospholipid from MFGMs contains up to 6%.[63] Again, phospholipids in dried dairy products are unstable owing to their high unsaturation and surface area.

Prooxidant properties of phospholipids

Bulk oil is an example of a food system where phospholipids act as antioxidants and in some situations as prooxidants. Bulk oil is a heterogeneous system that contains more than just triacylglycerides, including 200–800 ppm water and a variety of amphiphilic minor compounds such as monoacylglycerides, diacylglycerides, free fatty acids, phospholipids, phytosterols and oxidation products.[3] The combination of amphiphilic molecules and water in the triacylglycerides will lead to the spontaneous formation of nanostructures. For example, phospholipids in bulk oils form association colloids such as reverse micelles. Gupta et al.[64] found that native soybean phospholipids could form reverse micelles in a mixture of hexane and soybean oil containing less than 3% water. Danino et al.[65] later applied cryo transmission electron microscopy (cryo-TEM) in a similar system (soybean phospholipids/soybean oil/hexane/water) for direct visualization of phospholipid reverse micelles and reported the size of the aggregates to be 5–9 nm. Shtykova et al.[66] reported reverse micelles formed by dilinoleoyl PC (DLPC) and dilinoleoyl PE (DLPE) in hexane. By synchrotron small-angle X-ray scattering, they found spherical aggregates with an outer radius of 1.5 nm. They attributed the smaller size of reverse micelles to the low water content in their system (<0.1%). The authors also found that the amount of reverse micelles increased during the oxidation of phospholipids. Subramanian et al.[67] reported the presence of reverse micelle structures in crude soybean oil and high-oleic sunflower oil containing 245 and 400 ppm water respectively. Recently, evidence of reverse micelles formed by phospholipids in oils stripped of their polar compounds was observed by means of small-angle X-ray scattering.[68,69]

Reverse micelles can act as nano-reactors that can alter chemical reaction rates by bringing hydrophilic and lipophilic compounds into close contact, allowing increased interactions.[70] Kasaikina and co-workers[71–75] used different surfactants in non-aqueous media, including bulk oil, as a simple self-assembling model to investigate the impact of physical structures on lipid oxidation. They indicated that surfactants in heterogeneous systems could spontaneously group into micro/nano-structures such as reverse micelles and that lipid hydroperoxides could act as co-surfactants. The ability of hydroperoxides to reduce interfacial tension and thus be amphiphilic was also confirmed by Nuchi et al.[76] Trunova et al.[71] reported that both cationic reverse micelles formed by cetyltrimethylammonium bromide (CTAB) and anionic reverse micelles formed by sodium dodecyl sulfate (SDS) increased the decomposition of ethylbenzene and limonene hydroperoxides.[70] In another reverse micelle system that used AOT as surfactant (AOT/water/hexadecane), the authors found that lipid oxidation rates of methyl linolenate were altered upon the addition of cumene hydroperoxides, water, oleic acid or PC.[77]

The presence of phospholipid reverse micelles in bulk oils creates oil–water interfaces where hydrophilic (e.g. iron) and amphiphilic (e.g. lipid hydroperoxides) prooxidants and triacylglyceride substrate are driven into close contact with each other, resulting in increased lipid oxidation rates (Fig. 4). Chen et al.[68,78,79] reported the impact of reverse micelles formed by dioleoyl PC on soybean oil oxidation. To minimize the influence of minor components present in commercially refined oil, they used stripped soybean oil so that it contained ultra-low polar lipid (i.e. free fatty acids, phospholipids, monoacylglycerides and diacylglycerides) and antioxidant (i.e. tocopherols) concentrations. They found that dioleoyl PC could spontaneously form reverse micelle structures when its concentration was above its critical micelle concentration and that the reverse micelles would accelerate lipid oxidation. In contrast, when dibutyryl PC was added at the same concentration as dioleoyl PC, no prooxidant effects were observed. They suggested that the lack of prooxidant effect of dibutyryl PC was due to its short fatty acid chains, which were too short and thus not lipophilic enough to form the reverse micelle structures.[68] A similar prooxidant activity of PE was also reported by Cui et al.[80] In their study, they found that dioleoyl PE promoted lipid oxidation of stripped soybean oil by forming reverse micelles, while dihexanoyl PE was unable to form reverse micelles and thus had no impact on lipid oxidation rates. They also reported that the critical micelle concentration of dioleoyl PC and dioleoyl PE decreased with increasing temperature and that the critical micelle concentration decreased when dioleoyl PC and dioleoyl PE were combined to form mixed reverse micelles. Dioleoyl PC and dioleoyl PE mixed reverse micelles were also prooxidant and they decreased the effectiveness of α-tocopherol and trolox upon their addition into stripped oils.[12,78] In addition, prooxidative reverse micelles could be formed in stripped oil by a combination of multiple polar/amphiphilic minor components found in commercial refined oils, such as phospholipids, free fatty acids, phytosterols and diacylglycerides.[98] The prooxidant activity of phospholipids has also been reported in other systems. For instance, Hudson and Mahgoub[81] found that addition of PC and PE to lard promoted oxidation as measured by oxygen absorption induction periods. Yoon and Min[14] found that 300 ppm of phospholipids increased lipid oxidation in stripped soybean oil. Lee and Choe[82] found that chlorophyll b increased oil oxidation as well as chlorophyll b degradation by promoting singlet oxygen production. The addition of PC and PE retarded the decomposition of chlorophyll b. In this way, chlorophyll b could promote more photooxidation of canola oil because chlorophyll b was protected by PC and PE and could contribute to facilitate photooxidation.

Antioxidant properties of phospholipids

The importance of understanding the food system when investigating the antioxidant properties of phospholipids should be emphasized. For example, bulk oils are often treated as homogeneous by many researchers, but this is an incorrect assumption, because different oil systems contain different minor components, which will cause phospholipids to function differently. King et al.[83] reported antioxidant properties of individual phospholipids in a salmon oil model system. However, the salmon oil used in their study contained 280 ppm tocopherols, which made it hard to conclude whether the antioxidant activity of phospholipids came from the phospholipids themselves or from synergism with tocopherols. If the latter was the reason, one would not expect phospholipids to be antioxidant in another salmon oil where tocopherols were depleted. A similar case was where egg yolk phospholipids inhibited lipid oxidation of docosahexaenoic acid (DHA)-rich oil; however, the oil contained 3000 ppm tocopherols.[84] The importance of understanding the food system to learn what roles phospholipids play is also evidenced by Yoon and Min,[14] who reported different activities of phospholipids in different oil environments. The authors found that phospholipids acted as antioxidants when 1 ppm ferrous iron was added into stripped soybean oil which was depleted of tocopherols and other polar compounds. However, in the absence of added iron, the phospholipids exhibited prooxidant activity. This again emphasized the importance of understanding the food system when investigating the antioxidant activity of phospholipids. Reasons for the above differences will be presented in the following subsections.
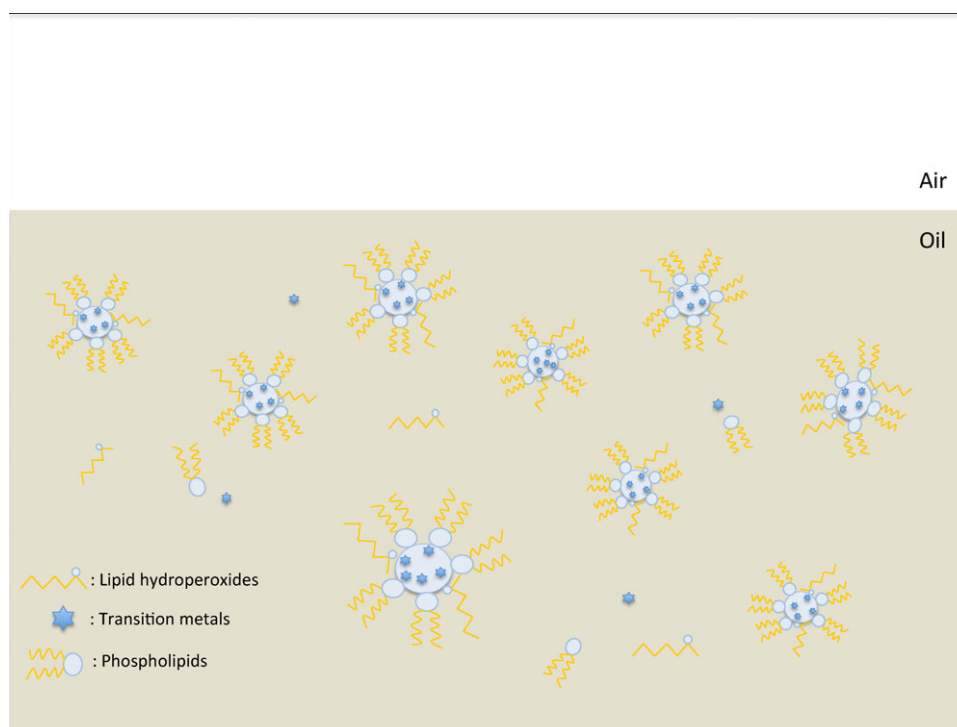
Figure 4. Bulk oil containing phospholipid reverse micelles.

Chelation

Theoretically, phospholipids can bind prooxidative metals through the negative charges present on the phosphate head group and thus inhibit lipid oxidation. A simple test can be conducted to determine the metal-binding ability of phospholipids.[9] Briefly, phospholipid liposomes or microsomes incubated with metals followed by centrifugation to precipitate the liposomes can be a model test. Unbound metals are then determined in the aqueous phase. Using this method, iron was found to bind phospholipid membranes of microsomes and liposomes in the absence of chelators.[85] Zago and Oteiza[86] also reported that ferrous iron bound to PC/PS liposomes and that addition of zinc could displace iron from the membrane. They further suggested that zinc preferentially bound to PS over PC because PS has an additional carboxyl group and thus is more negatively charged. Dacaranhe and Terao[87] reported that the iron-binding capacity of individual phospholipids in egg yolk PC unilamellar liposomes was in the order PA ≥ PS ≥ PG > PE = PC by a method similar to that described earlier. They further determined that iron-promoted decomposition of PC hydroperoxides in unilamellar liposomes was inhibited by the addition of PS. Likewise, Yoshida et al.[9] claimed that both saturated and unsaturated PS protected egg yolk PC liposomes from oxidation by binding free iron. Viani et al.[88] used a PC liposome inserted with arachidonic acid and found that addition of PA significantly retarded iron-induced oxidation. In an oil-in-water emulsion system where sardine oil was stabilized with Triton X-100 in Tris-HCl buffer, the authors found that addition of PA and PS effectively inhibited iron-induced lipid oxidation.[89] Cardenia et al.[15] also believed that the chelating property was responsible for the observed antioxidant activity of PC in stripped soybean oil-in-water emulsion at pH 7 where Tween 20 was used as emulsifier. They reported that at pH 3, which was near or even below the pK_a of PC, PC was not charged and thus unable to chelate metals and consequently its antioxidant activity disappeared. In a bulk oil system where 1 ppm ferrous iron was added, it was found that phospholipids (PC, PE, PI, PA and PG) acted as antioxidants as they chelated iron.[14]

The potential for phospholipids to bind iron does not always guarantee that they will inhibit lipid oxidation. One reason for increased oxidation is based on increased iron solubility. For example, EDTA and organic acids can chelate iron and promote its solubility, which in turn increases metal–lipid interaction and lipid oxidation.[90] Different reactivity of metals bound to chelators could also influence the ability of chelators to act as antioxidants. For example, in a liposome system, EDTA, citrate and adenosine triphosphate (ATP) all removed iron bound to phospholipid membranes, but only EDTA and citrate inhibited lipid oxidation, presumably because the iron bound to ATP was still reactive.[83] It is possible that metals bound to phospholipids are still reactive and can accelerate lipid oxidation. For example, Tampo[91] reported that iron-promoted lipid oxidation was affected by the surface charge of liposomal membranes and that PS was most sensitive to iron-promoted oxidation. Gal et al.[92] also found that increasing the ratio of PS or PA to PC in liposomes produced more negative charges, which resulted in more copper being bound to the membrane surface and more lipid oxidation. Brett and Rumsby[93] reported that PS, PC and PE increased TBA formation in the order PS > PC > PE after exposure to hydroxyl radical. Fukuzawa et al.[94] found that, during lipid oxidation of egg yolk PC induced by a xanthine/xanthine oxidase system, the oxidation was slow in neutrally charged egg yolk PC liposomes and rapid when negatively charged dicetylphosphate was added. Similarly, lipid oxidation of rat liver PC liposomes was accelerated by dicetylphosphate.[94,95]

One reason for the contradicting reports of prooxidant and antioxidant activities of phospholipid-bound metals could be due to different metal types and concentrations in different studies. For example, Gal et al.[92] found that increasing copper concentration decreased the prooxidant activity of PS. They suggested that

copper at high concentrations might cause lateral phase separation of PS and PC in mixed liposomes, where most of the copper bound to PS-rich domains and thus was less available to oxidize PC substrates. Alternatively, copper at low concentrations might bind to both the amine and carboxyl groups of PS to form a 2:1 PS–copper complex, while at higher concentrations it could form a 1:1 complex. In general, chelators such as EDTA are more effective when the chelator concentration exceeds the metal concentration, because the binding of multiple chelators to a metal can tie up all the metal coordination sites and make the metal unreactive.[96]

Antioxidative properties of phospholipid Maillard reaction products

Maillard reactions are very important to the food industry because they can either positively or negatively impact food aroma, taste, color and nutritional attributes. The Maillard reaction occurs in the presence of carbonyls (e.g. reducing sugars, ascorbic acid and lipid oxidation aldehydes) and free amine groups (e.g. lysine).[97] The antioxidant properties of Maillard reaction products from reducing sugars and amino acids have been studied extensively since they can scavenge free radicals[98–100] and act as metal chelators.[101,102]

At first glance, one might not expect Maillard reactions to be important in bulk oils. However, phospholipids such as PE have a primary amine group that can serve as a Maillard reaction substrate. In addition, carbonyls produced from the β-scission reactions of lipid oxidation (e.g. aldehydes and ketones) can provide the other substrate allowing Maillard reactions to occur. One of the reasons why phospholipids are removed during the degumming step of oil refining is to decrease browning. More details of these reactions were described by Zamora and Hidalgo.[103]

Alaiz *et al.*[104] examined the antioxidative property of amine groups in stripped soybean oil, with octylamine, methylheptylamine and dimethylhexylamine representing primary, secondary and tertiary amine groups. The authors found that primary and secondary amines inhibited lipid oxidation while tertiary amine had no effect. They further identified several oxidized lipid/amine reaction products such as pyrrole derivatives that were formed by the reaction between octylamine (primary amine) and 4,5-epoxy-2-heptenal (a lipid oxidation product) in the oil samples and attributed the inhibitory effects of primary and secondary amines to these Maillard reaction products. Similarly to octylamine, PE also contains a primary amine group and was also shown to react with 4,5-epoxy-2-heptenal to generate similar antioxidative Maillard reaction products.[105,106] PC with a tertiary amine group, on the other hand, did not show an inhibitory effect on lipid oxidation in a manner similar to dimethylhexylamine.[10] Since these Maillard products also produced color compounds, the oxidative stability of the oil was correlated with its yellowness index.[10] King *et al.*[107] also reported a relationship between the oxidative stability of salmon oil and its color intensity from Maillard-type reaction products.

Bandarra *et al.*[108] suggested that the synergism between PC/PE and α-tocopherol in sardine oil could be due to Maillard reaction products measured at 430 nm. In a marine phospholipid liposome system, Maillard reaction in the presence of α-tocopherol was again confirmed through measurement of Strecker aldehydes, color changes and pyrrole content and proved to suppress the formation of volatile lipid oxidation.[109] Shimajiri *et al.*[110] reported antioxidant activity of amine-containing phospholipids (PC, PE and SPM) and further suggested that the presence of α-tocopherol

was essential to the reaction that produced antioxidative Maillard reaction products.

Synergism with tocopherols

Many of the antioxidant properties of phospholipids reported in the literature are related to their ability to inhibit lipid oxidation synergistically with primary antioxidants, especially tocopherols. Although many studies reported increased oxidative stability of food products when phospholipids and tocopherols were added together, the evidence of synergism is better demonstrated in studies showing that phospholipids alone do not inhibit lipid oxidation, but when they are in combination with tocopherols a strong antioxidant effect is observed. For instance, in perilla oil that was depleted of mixed tocopherols and stored in the dark at 37 °C, neither 500 ppm PC, PE nor PS affected lipid oxidation. However, when 366 and 866 ppm mixed tocopherols were present, PE and PS prolonged the oxidation lag phase of the oil.[111] When canola oil underwent singlet oxygen-induced lipid oxidation at 10 °C, neither PC nor PE at 50 ppm decreased lipid hydroperoxide formation. Nevertheless, upon the addition of either 50 or 100 ppm α-tocopherol, synergistic activities were observed.[112] Takenaka *et al.*[149] found that 1% unsaturated PE and PC were prooxidative when added alone in stripped bonito oil that was stored in the dark at 40 °C. However, when combined with 500 ppm α-tocopherol, PE exhibited synergistic antioxidant activity, while PC still had no effect. This absence of phospholipid antioxidant activity when used alone but enhanced antioxidant activity when present with α-tocopherol was also supported by the same research group in another study.[105] In stripped soybean oil, PE alone promoted lipid oxidation, but it inhibited lipid oxidation upon the addition of α-tocopherol.[12]

Synergism between phospholipids and tocopherols could be due to the ability of phospholipids to (1) form antioxidative Maillard reaction products in the presence of tocopherols, (2) alter the physical location of tocopherols and/or (3) regenerate tocopherols. As for Maillard reaction mechanism hypotheses, several studies reported increased formation of phospholipid Maillard products in the presence of tocopherols,[10,102–105] which has been discussed above.

Phospholipids can alter the physical location and thus the effectiveness of tocopherols. The physical location of antioxidants is known to influence their activity. For example, Huang *et al.*[113] showed that the distribution of α-tocopherol and trolox was different in different lipid systems (e.g. triacylglycerides, methyl linoleate and linoleic acid in bulk or emulsified form), which resulted in differences in antioxidant activities. Losada-Barreiro *et al.*[114] examined the impact of emulsifiers with different HLB and at different concentrations on the distribution of antioxidants in oil-in-water emulsions. They found that increasing emulsifier concentration and decreasing HLB both promoted the incorporation of α-tocopherol and propyl gallate into the interfacial region of the emulsion. In biological membranes that consist of saturated and unsaturated phospholipids, cholesterol, sphingomyelin and proteins, α-tocopherol is believed to concentrate at a polyunsaturated phospholipid domain.[115]

As both tocopherols and phospholipids have surface activity properties, their combination could influence the physical location of tocopherols as well as other primary antioxidants, and the resulting change in location could impact their antioxidant activity. Koga and Terao[116] examined the impact of α-tocopherol and its phosphatidyl derivative (α-tocopherol conjugated to the head group of PC) on lard oxidation. They found that, while both

Table 5. Synergism between phospholipids and primary antioxidants

Phospholipid(s)	Antioxidant(s)	System	Ref.
PC, PE	Ethoxyquin	Refined menhaden oil	139
PC, PE	α-Tocopherol, quercetin	Lard	81
PC, PE	Polyhydroxyl flavonoids	Lard	140
PC, PE, PI	Mixed tocopherols	Refined soybean oil	141
PE, PS, not PC[a]	Mixed tocopherols	Refined perilla oil	111
SPM, LPC, PC, PE[b, c]	Endogenous mixed tocopherols	Salmon oil	107
PE, ethanolamine, PS, not PC	α-Tocopherol	Sardine and mackerel lipids	142
PS, PE, soybean lecithin, not PC	α-Tocopherol	Methyl linolenate	143
PE, PS, PC[c]	Mixed tocopherols	Fish oil	144
Egg yolk phospholipid	Endogenous mixed tocopherols	DHA-rich oil	83
PE, PC, CL[b, c]	α-Tocopherol	Sardine oil	108
Soybean lecithin	Endogenous mixed tocopherols	Rapeseed, soybean, walnut, palm oil and lard	145
PE, not PC	Endogenous mixed tocopherols	Refined olive oil	10
Soybean lecithin	Endogenous mixed tocopherols	Virgin olive oil	146
PE	Gallic acid, propyl gallate, caffeic acid, α-tocopherol, BHA, BHT, TBHQ	Lard	147
PE	Propyl gallate	Lard	148
PE, not PC[a]	α-Tocopherol	Bonito oil	149
Soybean lecithin	α-Tocopherol	Fish oil	150
PE, PC[a]	α-Tocopherol	Canola oil	112
Soybean lecithin, rapeseed lecithin, sunflower lecithin, not soybean PC	α-Tocopherol	Ethyl linoleate	37
PE, PC, SPM[a]	α-Tocopherol	Fish oil	110
PE, not PC[a]	α-Tocopherol, trolox	Stripped soybean oil	12

Abbreviations: PC, phosphatidylcholine; PE, phosphatidylethanolamine; PI, phosphatidylinositol; PS, phosphatidylserine; SPM, sphingomyelin; LPC, lysophosphatidylcholine; CL, cardiolipin; BHA, butylated hydroxyaniline; BHT, butylated hydroxytoluene; TBHQ, *tert*-butylhydroquinone; DHA, docosahexaenoic acid.
[a] Studies where phospholipids alone had no antioxidant affect but showed synergism with α-tocopherol.
[b] Studies where Maillard reaction products were measured as color index and correlated with oxidative stability.
[c] Studies where the antioxidant activity was ordered and was as the sequence in the table.

chemicals had the same radical-scavenging ability, the phosphatidyl derivative of α-tocopherol had better antioxidant activity than α-tocopherol alone. They suggested that this improvement was due to better accessibility of the functional group of α-tocopherol to the site where iron-dependent oxidation reactions took place. In another study, the same authors monitored the oxidation of methyl linoleate by measuring methyl linoleate hydroperoxides. They found that, in the presence of a water-soluble compound that generates free radicals only in the aqueous phase, PC/PE had no impact alone but increased α-tocopherol antioxidant activity, showing a synergistic activity. In this case, PC/PE increased the consumption of α-tocopherol, meaning more α-tocopherol interacted with free radicals (prooxidants) present only in the aqueous phase. In contrast, when a lipid-soluble compound that generates free radicals only in the lipid phase was used, PC/PE had no impact on the consumption of α-tocopherol, meaning α-tocopherol interaction with prooxidant was minimal. These results together suggested that phospholipids could alter the physical location of α-tocopherol and bring it into close proximity to the site of greatest oxidative stress.[11]

Since oxidized tocopherols (i.e. α-tocopherolquinone, α-tocopherolhydroquinone and epoxy-α-tocopherolquinone) have been reported to accelerate lipid oxidation[117,118] and since oxidized tocopherols cannot scavenge free radicals, regeneration of oxidized α-tocopherol would help inhibit lipid oxidation by (1) eliminating prooxidative oxidized α-tocopherol and (2)

re-forming antioxidative α-tocopherol. Regeneration of α-tocopherol by phospholipids is at least partially responsible for the observed synergism between tocopherols and phospholipids. While many studies mention tocopherol regeneration by phospholipids, few actually explain how this occurs. Oxidation–reduction potential is one potential parameter to determine the possibility that tocopherol can be regenerated by phospholipids. However, direct electron transfer between phospholipid and tocopherol is unlikely since they have a similar reduction potential of around 600 mV (data not shown). In contrast, there are several reports of phospholipids containing a primary amine group, such as PE and PS, interacting with α-tocopherolquinone, an oxidation product of α-tocopherol.[12,37,119] Doert *et al.*[37] monitored the reaction between α-tocopherolquinone and different types of phospholipid (PC, PE, PI, PA and PS) in toluene at 100 °C. They found that all tested phospholipids except PC were able to convert α-tocopherolquinone to α-tocopherol. The authors identified an intermediate PE–α-tocopherone condensation product by examining reaction products of PE and α-tocopherolquinone with mass spectrometry. They further suggested that PE–α-tocopherone would subsequently undergo heterolytic cleavage to form a carbenium ion which regenerated α-tocopherol. This reaction between PE and α-tocopherolquinone was also recently confirmed in a stripped soybean oil and medium-chain triacylglyceride system at a lower temperature of 55 °C.[12] The synergism between

phospholipids and primary antioxidants (mainly tocopherols) reported in the literature is summarized in Table 5.

CONCLUSION

Many foods contain a wide variety of phospholipid combinations. In addition, the commercial phospholipid product lecithin is widely applied to many food products for its wide-ranging functional properties, including antioxidant activity. However, owing to their high degree of unsaturation and large surface area, phospholipids can readily react with prooxidants (e.g. transition metals), thus serving as lipid oxidation substrates and resulting in the development of off-flavors in food products such as meats. This is also the case for food products such as MFGMs in dried nonfat milk and whey products, which have low lipid concentrations but non-negligible phospholipid fractions. Phospholipids can also promote lipid oxidation in bulk oils owing to their surface activity and thus can, alone or together with other polar components present in bulk oils, form association colloids that increase interactions between oxidizable substrates and prooxidative metals. However, phospholipids can also act as antioxidants through one or more combinations of the following activities: chelating prooxidative metals, forming antioxidative Maillard reaction products, changing the location of primary antioxidants or regenerating primary antioxidants. Thus, taking into account all the possibilities of how phospholipids behave in different food environments is essential to understand their antioxidant/prooxidant role before they can be utilized to inhibit lipid oxidation reactions.

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