Targeting Interfacial Location of Phenolic Antioxidants in Emulsions: Strategies and Benefits

Claire Berton-Carabin, Pierre Villeneuve

ANNUAL REVIEWS

Annual Review of Food Science and Technology

Targeting Interfacial Location of Phenolic Antioxidants in Emulsions: Strategies and Benefits

Claire Berton-Carabin[1,2] and Pierre Villeneuve[3,4]

[1]INRAE, UR BIA, Nantes, France; email: claire.berton-carabin@inrae.fr

[2]Laboratory of Food Process Engineering, Wageningen University, Wageningen, Netherlands

[3]CIRAD, UMR Qualisud, Montpellier, France; email: pierre.villeneuve@cirad.fr

[4]Qualisud, University of Montpellier, Avignon Université, CIRAD, Institut Agro, IRD, Université de La Réunion, Montpellier, France

Annu. Rev. Food Sci. Technol. 2023. 14:63–83

The *Annual Review of Food Science and Technology* is online at food.annualreviews.org

https://doi.org/10.1146/annurev-food-060721-021636

Keywords

emulsions, lipid oxidation, phenolic antioxidants, oil–water interface, phenolipids, antioxidant reservoirs

Abstract

It is important to have larger proportions of health-beneficial polyunsaturated lipids in foods, but these nutrients are particularly sensitive to oxidation, and dedicated strategies must be developed to prevent this deleterious reaction. In food oil-in-water emulsions, the oil–water interface is a crucial area when it comes to the initiation of lipid oxidation. Unfortunately, most available natural antioxidants, such as phenolic antioxidants, do not spontaneously position at this specific locus. Achieving such a strategic positioning has therefore been an active research area, and various routes have been proposed: lipophilizing phenolic acids to confer them with an amphiphilic character; functionalizing biopolymer emulsifiers through covalent or noncovalent interactions with phenolics; or loading Pickering particles with natural phenolic compounds to yield interfacial antioxidant reservoirs. We herein review the principles and efficiency of these approaches to counteract lipid oxidation in emulsions as well as their advantages and limitations.

1. INTRODUCTION

The use of polyunsaturated lipids in food or cosmetic industries implies associated risks of oxidation upon processing or storage of the final products. Such an oxidative degradation results in off-flavor development, rancidity, loss of essential fatty acids and liposoluble micronutrients, and generation of new oxidized chemical species with potential toxicity (Schaich 2020b, Skibsted 2010). Lipid oxidation is a complex cascaded reaction, generally involving radicals, that leads to the formation of a broad range of primary and secondary oxidation products (Schaich 2020a). Although the oxidative degradation of oils and fats was described early in the nineteenth century (Hammond & White 2011) and the nature of the formed chemical species was described in the twentieth century, the precise chemical pathways are not yet clearly established and are still under scrutiny, especially regarding the ways and methods by which lipid oxidation should be measured and quantified (Schaich 2020a). In addition to the inherent complexity of this chemical reaction, an additional hurdle relates to the complex physical organization of food and biobased systems, as they often consist of multiple immiscible phases (e.g., oil and water), which confers them with a large structural heterogeneity at various length scales (Berton-Carabin et al. 2018). Understanding and, in turn, controlling lipid oxidation in multiphase food systems have therefore been notoriously challenging. A prominent strategy has been to use antioxidants, but it should be pointed out that their application (type of antioxidant chosen, concentration) is often empirical because their activity is intimately dependent on their interactions with other components present in the system and on their location (Laguerre et al. 2007). For instance, it is largely known that antioxidants that tend to locate at the interface between oil and aqueous phases offer superior protection against lipid oxidation compared to largely hydrophilic or lipophilic counterparts (Laguerre et al. 2013, 2015). Yet many naturally occurring food and biocompatible antioxidants do not spontaneously position at this specific locus in multiphase, interface-dominated systems; thus, targeted design strategies have to be carried out. The present review therefore examines various approaches and underlying principles that may be considered to achieve such a build-up, with a specific focus on phenolic antioxidants. The ranges of applications, assets, limitations, and perspectives of these different strategies are discussed, notably in a context of naturalness and clean-label trends.

2. LIPID OXIDATION IN EMULSIONS

2.1. Structure and General Properties of Emulsions

Many foods and other biobased products contain immiscible oil and water phases, which exist as one phase dispersed in the other as colloidal droplets. Such systems may be water-in-oil (W/O) emulsions represented, for instance, by butter and margarine, or oil-in-water (O/W) emulsions, as found in a broad range of beverages, milk, infant formulas and other dairy-based products, mayonnaise, and dressings as well as in various pharmaceutical, cosmetic, and personal care products. Because of the molecular incompatibility between both phases, emulsions tend to physically destabilize to strive to minimize the interfacial area between oil and water, which eventually leads to complete phase separation. Yet it is possible to yield metastable emulsions (i.e., those that retain their physical properties and colloidal structure over periods of time that are relevant compared to typical storage times) by using physical stabilizers such as emulsifiers, which are molecules or structures that are able to adsorb at the oil–water interface. For O/W emulsions, which are the main target of this review, three main categories of food emulsifiers exist (**Figure 1**): (*a*) low-molecular-weight emulsifiers (LMWEs), often referred to as surfactants, which usually have a polar or fully charged hydrophilic headgroup and one or more hydrophobic alkyl chains, represented, for example, by lecithin, polysorbates, mono- and diacylglycerols, or other fatty acid esters (Hasenhuettl & Hartel 2008, McClements 2005); (*b*) amphiphilic biopolymers, which are

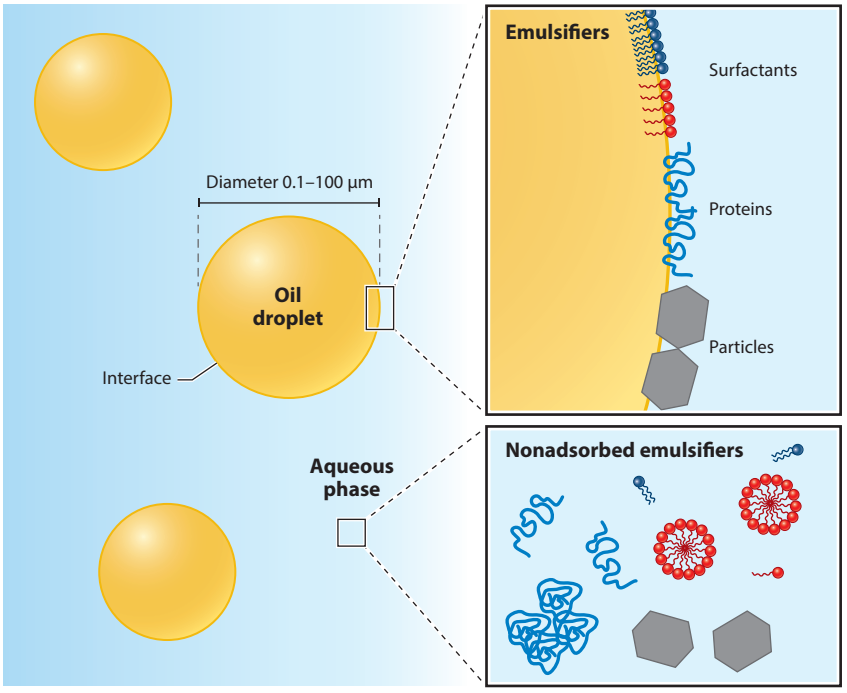

Figure 1

Generic structure of oil-in-water (O/W) emulsions and main categories of food emulsifiers: surfactants, proteins, and colloidal particles.

larger molecules with regular or random distribution of hydrophilic and hydrophobic segments and of which an important representative is proteins (Dickinson 1994); and (*c*) colloidal particles with surface properties conferring them with partial wettability by oil and by water, which allows them to strongly anchor at the oil–water interface, forming so-called Pickering emulsions (Berton-Carabin & Schroën 2015, Dickinson 2012, Pickering 1907).

The selection of a given emulsifier is far from trivial, as the consequences on the properties of emulsions reach far beyond ensuring the physical integrity of individual droplets only. First, the properties of the interfacial layer formed depend greatly on the type of emulsifier (Berton-Carabin et al. 2018, Tcholakova et al. 2008): For LMWEs, the interface thickness is close to the size of the individual molecules (1–3 nm), the surface load (Γ) ranges from <1 to 1–2 mg/m^2, the layer formed is highly mobile and viscous, and the adsorbed molecules have substantial lateral mobility and are subjected to rapid exchange with excess surfactants present in the surrounding aqueous phase (Bos & van Vliet 2001, Lucassen & Van Den Tempel 1972). For proteins, the interfacial thickness may vary between 1 and 15 nm (Atkinson et al. 1995, Dalgleish 1997, Dickinson 2009), which depends on the type and quaternary structure/aggregation state of the protein, its ability to unfold and reorganize after adsorption, and the homogenization conditions (Graham & Phillips 1979). Accordingly, the surface load may range from 1–2 mg/m^2 for monomeric, flexible proteins at a low interfacial concentration to >10 mg/m^2 for interfaces containing aggregates and/or multiple layers (Bos & van Vliet 2001, Walstra 2003). Adsorbed proteins may establish lateral interprotein interactions, forming a network that confers mechanical strength and high elasticity to the interfacial film (Hinderink et al. 2020, Murray & Dickinson 1996). Interfacial reorganization and molecular exchanges with proteins in the bulk aqueous phase may occur but

usually at much longer timescales than with surfactants (Hinderink et al. 2022). Most of the research conducted to assess the interfacial and emulsifying properties of proteins was historically done on animal-derived, well-soluble proteins (e.g., dairy and egg proteins), but in recent years, research on alternative proteins (and, in particular, plant-based proteins) has become more and more prominent. Finally, in the case of adsorbed colloidal particles (Pickering emulsions), the interfacial thickness and surface load are directly linked to the size and density of the adsorbed particles and may be higher than the values usually seen for LMWEs and biopolymers by orders of magnitude (Berton-Carabin & Schroën 2015). This is illustrated by the fact that particle layers may be able to modify the overall density of the droplets, even leading to droplet sedimentation instead of creaming in some cases (Rayner et al. 2012). Such layers are also characterized by strong attractive lateral capillary forces between particles trapped within the interfacial film. These forces result from the deformation of the fluid interface around the particles and confer the interfacial layer with high mechanical stability (Hunter et al. 2008, Tcholakova et al. 2008) and rigidity, leading to a jammed, solid shell at the surface of the droplets at sufficiently high surface coverage (Chevalier & Bolzinger 2013).

A last important point to mention regarding emulsifiers is the fact that food emulsions are often formulated with a large excess of emulsifiers compared to the amount strictly needed to cover and physically stabilize the oil–water interface (Berton-Carabin et al. 2014). Consequently, only a limited fraction of the emulsifier actually stabilizes oil droplets, whereas a large fraction remains in the continuous phase. This excess fraction may not only be present as soluble monomeric molecules, but it can also form various colloidal structures such as micelles [above the surfactant critical micelle concentration (CMC)] or aggregates. This can have crucial implications for the physico-chemical stability of emulsions. For instance, large biopolymer concentrations in the continuous phase are known to induce depletion flocculation (Guzey & McClements 2006), and excess surfactant micelles promote compositional ripening, implying that they actively enhance droplet-to-droplet mass transfer of lipid molecules (Peña & Miller 2006). This ability of emulsifier-based structures in the aqueous phase of emulsions to solubilize and segregate some components is also key when it comes to the chemical reactivity of the system and, in particular, to lipid oxidation, which is detailed in the next section.

2.2. Main Factors Controlling Lipid Oxidation in Emulsions

In complex systems such as O/W emulsions, lipid oxidation reactions and kinetics are governed by many different parameters that range from the physicochemical properties of the emulsified system to the chemical reactivity of the various molecular species present. The influence of these parameters has already been extensively covered in several reviews (Berton-Carabin et al. 2014, Decker et al. 2017, Laguerre et al. 2017, Musakhanian et al. 2022). The oxidative stability of an emulsion depends on the nature of the oil and more specifically on its fatty acid composition (degree of unsaturation and nature and regiodistribution of unsaturated fatty acids), on the presence of impurities such as peroxide traces or free fatty acids, and on the concentration of endogenous antioxidants present in the oil (e.g., tocopherols). The presence of pro-oxidant species, such as metals, in the continuous aqueous phase is also of crucial importance. Furthermore, since the pioneering work by Frankel et al. (1994), it is accepted that lipid oxidation in emulsions is initiated at the oil–water interface, as this is the locus where the oxidizable lipid substrate comes into contact with aqueous phase pro-oxidants. Therefore, the nature and properties of the interface, for example, in terms of thickness or charge, have been suggested to be highly relevant. Regarding the effect of the electrostatic charge, it has been shown that the use of cationic surfactants induces a positively charged interface that repels pro-oxidant metal cations. Conversely, anionic

surfactants attract metal ions to the interface where their pro-oxidant actions are particularly efficient (Mancuso et al. 1999, Waraho et al. 2011). These results suggest that increasing the concentration of pro-oxidant metal cations at the droplet surface increases the lipid oxidation rate, which is well in line with the fact that strong metal chelators such as ethylenediamine tetraacetic acid (EDTA) are particularly efficient at moderating this adverse effect (Frankel et al. 2002). It is worth mentioning that although this effect of the emulsifier's electrostatic charge is very clear when cationic versus anionic surfactants are involved, it has not been systematically found with biopolymers of various charges, such as proteins. This is probably because in that case, other variables (pH, protein partitioning, amino acid composition) have a predominant impact on lipid oxidation compared to that of the droplet surface charge (Berton-Carabin et al. 2014).

It has often been suggested that emulsifiers that are capable of forming a thick layer at the lipid droplet surface could have a protective effect against lipid oxidation, as they would constitute a steric barrier against the action of pro-oxidants. This hypothesis was originally supported by findings such as those of Hu et al. (2003), who found that emulsions stabilized by casein, a protein that is recognized for its ability to form thick and dense interfacial layers, were more oxidatively stable compared to emulsions stabilized with other proteins (in that case, whey or soy proteins). It was also reported that the oxidative stability of soy protein–stabilized emulsions was improved when the protein surface load was increased by means of physical treatments (heat treatment or addition of salt) (Shao & Tang 2014). Yet it should be pointed out that in these studies, the actual interfacial thickness was generally not determined, and thus related effects remain at the level of speculation. As also stressed by McClements & Decker (2018), the experimental approaches aiming to modulate interface thickness often imply other modifications (such as, for proteins, the amino acid composition, conformational changes, distribution of proteins between the interface and the aqueous phase, etc.). In addition, conceptually the molecular size of pro-oxidants (metal ions, reactive oxygen species) is orders of magnitude smaller than that of typical structural elements at the interface (biopolymer loops, pores), making it questionable whether this parameter is decisive for the oxidative fate of emulsions.

The emulsification conditions (type of equipment and energy input) that are used are also important, as they determine the specific droplet size distribution, which directly impacts the capacity of the emulsion to resist oxidation from variations of the total surface area (Neves et al. 2017, Walker et al. 2015). On principle, smaller droplets, and therefore a larger oil–water interfacial area, should favor lipid oxidation. This effect has often been confirmed experimentally, even if some contradictory effects have been reported, which could, again, be due to the practical difficulty of modulating only the droplet size without affecting other properties of the emulsion (Berton-Carabin et al. 2014).

As stated above, the partitioning of emulsifiers between the interface and the continuous phase is a parameter that largely affects the oxidative stability of emulsions. When surfactant micelles are present in the continuous phase, they can modify the partitioning of many species involved in lipid oxidation pathways (Berton-Carabin et al. 2014, Decker et al. 2017, Laguerre et al. 2020, Villeneuve et al. 2021). For instance, as recently reviewed by Villeneuve et al. (2021), micelles can solubilize lipophilic antioxidants such as tocopherols (Inchingolo et al. 2021, Kiralan et al. 2014) and may also trap metal ions (Richards et al. 2002). It has been suggested that surfactant micelles could contribute to physically propagating oxidation in emulsions by transporting lipid oxidation intermediates through the continuous phase (Laguerre et al. 2017, 2020). The likelihood of such a micelle-assisted mass transfer is supported by the well-known compositional ripening phenomena, according to which mixing populations of droplets made of different lipids eventually leads to a system at equilibrium, with droplets having all the same lipid content (McClements et al. 1992). When it comes to lipid oxidation, the nature of the molecules being transported and the

relative importance of such an effect on the overall oxidative fate of the emulsion still need to be investigated. Next to surfactant micelles, excess proteins in the aqueous phase of emulsions are largely recognized for their ability to prevent or at least delay lipid oxidation. This effect seems to be generic among various sources of proteins, ranging from dairy proteins (Berton et al. 2011, 2012; Faraji et al. 2004) to soy (Feng et al. 2021) and other plant-based proteins (Gumus et al. 2017). It is usually explained by the ability of certain amino acid residues to chelate metal ions or scavenge free radicals (Elias et al. 2008).

Finally, the presence of endogenous or exogenous antioxidants has a crucial influence on lipid oxidation kinetics in emulsions. These molecules delay oxidation through different mechanisms such as radical-scavenging activities or metal-chelating properties (Durand et al. 2021, Jacobsen 2015, Laguerre et al. 2007, Schaich 2020a). The following section gives an overview of the general properties of phenolic antioxidants, a prominent category of food antioxidants for which the mechanisms of action and location in multiphase systems have been largely investigated.

3. PHENOLIC ANTIOXIDANTS: GENERAL PROPERTIES AND SPONTANEOUS LOCATION IN EMULSIONS

Phenolic compounds are secondary metabolites that are widely spread in the plant kingdom, especially in fruits, vegetables, spices, and aromatic herbs. They contribute to the defense system of the host species and are known to possess various biological activities such as anti-inflammatory, antimicrobial, anticarcinogenic, and antioxidant properties (Cheynier et al. 2013, Quideau et al. 2011, Shahidi & Ambigaipalan 2015). They represent a wide variety of chemical structures, from simple phenolic acids and their derivatives to more complex molecules such as flavonoids, stilbenes, lignans, and tannins (**Figure 2*a***). Phenolic acids and their derivatives belong to the cinnamic acid or benzoic acid families and are distinguished according to their substituted groups (hydroxy, methoxy) on their aromatic cycle. At the industrial scale, the phenolic antioxidants that are used are mainly pure synthetic molecules such as butylated hydroxytoluene (BHT), butylated hydroxyanisole (BHA), gallate esters, and tertiary-butylhydroquinone (TBHQ). Only a few natural phenolic antioxidant extracts, such as rosemary or tea extracts, are used in foods. Yet, as individual molecules or as plant extracts, phenolic compounds are widely studied as antioxidants to protect unsaturated lipids from oxidation. Their antioxidant activity is attributed to their capacity to scavenge radicals by hydrogen donation or electron transfer or their ability to chelate pro-oxidant metals due to the presence of a catechol group or an ortho-keto-hydroxy group in their structure (Dangles 2012).

In emulsified systems, the efficiency of phenolic antioxidants is dependent on their partitioning in the emulsion and more specifically on their location at the interface. This distribution at the interface not only depends on the chemical structure of the antioxidant itself but can also be modulated by pH, temperature, type, and concentration of the used emulsifiers (Villeneuve et al. 2021). In other words, the efficiency of a given phenolic antioxidant depends on not only its own chemical reactivity or chemical interactions with other compounds present in the system (proteins or synthetic surfactants, pro-oxidants, other antioxidants) but also its partitioning in the emulsion and more specifically its capacity to locate at the interfacial area where lipid oxidation is initiated. Important notions such as the polar paradox theory, the cut-off effect, and the pseudophase kinetic model illustrate the importance of the interfacial location of antioxidants to favor good oxidative stability, as further detailed below. Indeed, Porter et al. (1989) proposed the antioxidant polar paradox, which suggests that nonpolar antioxidants work better in O/W emulsions than their polar counterparts. This was attributed to the capacity of nonpolar antioxidants to locate at the lipid–droplet interface (Frankel et al. 1994, Laguerre et al. 2015).

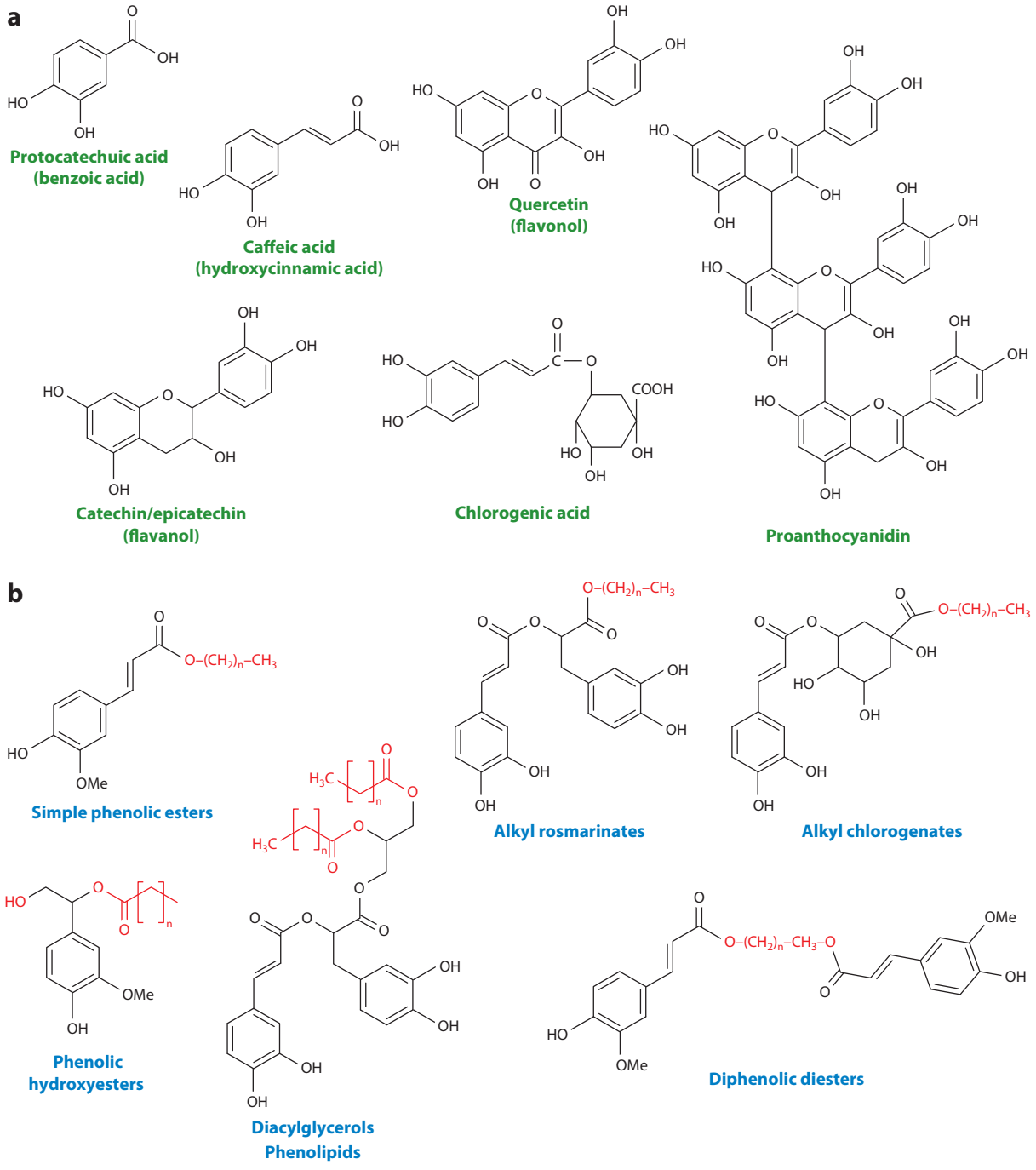

Figure 2

Chemical structures of examples of (*a*) natural plant phenolic antioxidants and (*b*) phenolipids obtained by lipophilization of phenolic acids.

More recently, other authors (Laguerre et al. 2009) using a series of alkyl esters of phenolic acids (phenolipids) postulated that the polar paradox theory was probably not entirely valid and that more complex phenomena than the polarity of antioxidants may impact their efficacy. These authors showed that hydrophobicity and antioxidant activity in emulsions increased up to a certain point (corresponding to the critical length of the alkyl chain), beyond which further lengthening of the alkyl chain drastically reduced antioxidant activity. This phenomenon was called the cut-off effect and later confirmed by many other studies; it constitutes the basis for one of the most prominent strategies to promote the interfacial location of phenolic antioxidants, as detailed in the following section.

4. STRATEGIES TO BRING (AND BIND) PHENOLIC ANTIOXIDANT MOLECULES AT THE OIL–WATER INTERFACE

4.1. Lipophilization of Phenolic Acids: The Cut-Off Effect

Having an antioxidant that is capable of localizing itself at the oil–water interface in an emulsion is a very important parameter to guarantee good resistance against lipid oxidation. One of the strategies to localize a phenolic antioxidant at this interface is to structurally modify the concerned molecule to adjust its hydrophilic/lipophilic balance. For this, lipophilization reactions can be carried out that consist of the covalent grafting of at least one lipophilic moiety to a phenolic molecule to obtain new lipophilized antioxidant molecules (phenolipids) that have surface-active properties (Figueroa-Espinoza & Villeneuve 2005, Figueroa-Espinoza et al. 2013).

Lipophilization procedures correspond to the esterification by a fatty alcohol of the free carboxylic group of phenolic acids and do not affect the chemical reactivity of the concerned molecule because its aromatic hydroxyl groups are not modified. However, a few examples exist in the literature where the lipophilization reaction involves one of the hydroxyl functions. One may speculate that such particular lipophilization may affect the H donation or electron transfer capacity of the resulting phenolipid. Lipophilization can be performed by either chemical or enzymatic catalysis. Typically, chemically catalyzed lipophilization reactions are made using strong acidic catalysts such as hydrochloric acid, sulfuric acid, para-toluene sulfonic acid, or sulfonic resins and are quite efficient in terms of production yields. Enzymatic synthesis, using lipases, may also be performed to obtain phenolipids. Describing in detail all the operational parameters that influence the efficiency of such lipophilization reactions is outside the scope of this review, but we recommend that interested readers consult some recent reviews on the topic (Farooq et al. 2021, Figueroa-Espinoza et al. 2019, Kahveci et al. 2015). The obtained phenolipids are then considered to be synthetic antioxidant molecules, but it is worth mentioning that natural phenolipids are also found in the plant kingdom (Caillol 2018, Crauste et al. 2016, Medina et al. 2022, Saha et al. 1991, Sonar et al. 2017).

A wide variety of phenolipids can be obtained through lipophilization reactions; typical examples are given in **Figure 2*b***. Their activities as antioxidants in O/W emulsions were evaluated in various studies. Using chlorogenic acid and its esters (from methyl to eicosyl chlorogenate esters) in emulsions, Laguerre et al. (2009) observed that the antioxidant capacity of these chlorogenate esters increases as the alkyl chain is lengthened, until the threshold for the dodecyl chain, after which further chain extension leads to a drastic decrease in antioxidant capacity. The authors explained their results in terms of antioxidant location because the dodecyl ester presented the lowest concentration in the aqueous phase. This nonmonotonic influence of the polarity of the antioxidant on its efficiency in emulsions was in contradiction with the polar paradox theory; thus, the authors proposed that this theory was not entirely valid and that more complex phenomena than only their polarity may impact the efficacy of antioxidants. By analogy with the so-called

cut-off effect largely observed in biological studies, the authors proposed that such a cut-off effect occurs for phenolipids in emulsions. A year later, the same group confirmed the occurrence of a cut-off effect for rosmarinate esters (Laguerre et al. 2010). This effect was later reported in a wide range of other studies (Medina et al. 2009, Panya et al. 2012b, Sørensen et al. 2012). It was also found that the precise critical chain length for a given series of phenolipids was strongly affected by the nature of the system (Alemán et al. 2015). Using caffeate esters from C1 to C20 in fish oil–enriched mayonnaise and milk, the authors observed that in both systems, phenolipids were better antioxidants than was nonlipophilized caffeic acid. However, the optimal chain length was different in both emulsions. Sørensen et al. (2015) also observed that methyl and butyl ferulates were more efficient than octyl ferulate in fish oil–enriched milk. Interestingly, they observed that alkyl ferulate from C8 to C12 has a pro-oxidant effect in such a system. Further elongation of the alkyl chain length to C16 and C20 resulted in weak pro-oxidant effects and weak antioxidant effects. A similar tendency was observed with alkyl protocatechuates in O/W emulsions, with short- to medium-chain lengths (from C1 to C6) leading to better antioxidants than the longest chains (Grajeda-Iglesias et al. 2016). In a very recent work, ten Klooster et al. (2022) evaluated the activity of gallic acid and gallate esters (C3 to C16) in dried emulsions and measured lipid oxidation in the surface free fat and encapsulated fat fractions. For both fat fractions, the alkyl chain length had to be relatively long to be effective at delaying lipid oxidation. Natural phenolipids such as alkylresorcinol homologs from rye bran were also evaluated for their efficiency as antioxidants in stripped algae O/W emulsions (Elder et al. 2021). The antioxidant activity of alkylresorcinols increased as the alkyl chain length increased, with an optimal activity at intermediate alkyl chain length (C21) beyond which activity decreased.

In the aforementioned examples, the efficiency of all these phenolipids in emulsions seems to depend on their specific partitioning in the system and, in particular, their location at the oil–water interface. Various studies were thus carried out to evaluate phenolipid location in emulsions. Lucas et al. (2010) synthesized a series of tyrosol and hydroxytyrosol fatty acid esters and studied their surface-active properties. They found a nonmonotonic dependency of surfactant effectiveness with the increase in chain length of the phenolipids, and this tendency fit well with the reported antioxidant activity with the best antioxidant of the series (hydroxytyrosol octanoate) being also a very effective surfactant. Other researchers proposed a pseudophase model to assess the partitioning of phenolipids in emulsions using an interfacial arenediazonium probe (Romsted & Bravo-Díaz 2013). This model is advantageous, as it does not require extraction or phase separation to locate antioxidants. Using this pseudophase model, various studies clearly correlated the efficiency of a given phenolipid with its location at the interface (Costa et al. 2015, Freiria-Gandara et al. 2018, Losada-Barreiro et al. 2013). Costa et al. (2020) also showed that surfactant concentration was the main factor controlling the partitioning of gallate esters at the interface: An increase in the surfactant volume fraction promoted the incorporation of the phenolipids into the interfacial region but concomitantly increased the interfacial volume, leading to a dilution of the antioxidants in that region that decreased their efficiency.

According to various studies, the cut-off effect can indeed be modulated by the interactions of the phenolipids with the emulsifier, as these interactions strongly affect the partitioning (interfacial location) of phenolipids. For example, González et al. (2015) compared a series of alkyl gallates in fish O/W emulsions stabilized by lecithin, sodium dodecyl sulfate (SDS), or Tween 20. In the case of lecithin-stabilized emulsions, a clear cut-off effect was observed, with medium-chain alkyl gallates (C6–C12) being the best antioxidants. Conversely, with Tween 20, no cut-off effect was observed and the behavior of the tested phenolipids followed the polar paradox theory. Sørensen et al. (2017) studied the effect of the nature of the emulsifiers (Citrem and Tween 80) on the efficacy of caffeate esters in O/W emulsions and observed that the concentration of caffeic acid

and its methyl esters in the aqueous phase was much lower with Tween 80 as compared to Citrem. This suggests that interactions between the emulsifier and phenolipids were more important in the case of Tween 80 and that this surfactant was better able to locate these antioxidants at the interface.

This consistent effect of the nature of the emulsifier on the efficiency of phenolipids can be explained by the crucial role of surfactant micelles (Villeneuve et al. 2021). On the one hand, solubilization of phenolipids into surfactant micelles may occur by H-bonding with the OH groups of the antioxidants and the emulsifier (Stöckmann et al. 2000). This not only modifies the partitioning of the phenolipid at the interface but can also lead to a reduction of the antioxidant capacity. On the other hand, in the case of highly lipophilic phenolipids, their activity can greatly be improved when promoting their migration from the oil droplet core to the aqueous or interfacial phases. This was illustrated by Laguerre et al. (2010) using a series of rosmarinate esters (C4–C20). In the absence of surfactant micelles (Brij 35 was used below its CMC), they found that octyl rosmarinate was the best antioxidant because of its optimized partitioning at the interface. In contrast, eicosyl rosmarinate performed as a weak antioxidant because its high hydrophobicity favored partitioning into the oil droplets. Interestingly, these authors showed that increasing quantities of Brij 35 surfactants above its CMC led to solubilization of eicosyl rosmarinate into the aqueous phase. Later on, the same research group (Panya et al. 2012a) found similar effects with Tween 20–based emulsions. When low amounts of surfactant were used, eicosyl rosmarinate was the least efficient antioxidant compared with the other esters. The authors then showed that increasing Tween 20 concentrations resulted in an increase in the concentration of all the esters in the aqueous phase, but the increase was the strongest with eicosyl rosmarinate. Moreover, they demonstrated that partitioning of eicosyl rosmarinate into surfactant micelles was greater than that of butyl and dodecyl esters and that the micellization of eicosyl rosmarinate favored its presence at the interface at concentrations similar to those of butyl and dodecyl esters. Of course, such relocation of long-chain phenolipids at the interface by the action of micelles optimizes its antioxidant activity. Concomitantly, they observed that the efficacy of the polar rosmarinate esters (butyl and dodecyl) was reduced by their relocation into the surfactant micelles. Indeed, although these phenolipids were primarily located at the oil–water interface when the concentration of surfactant micelles was low, addition of surfactant micelles displaced them from the interface to the aqueous phase, thereby reducing their antioxidant activity. Very comparable results were obtained by Ferreira da Silveira et al. (2021), who also observed that the most hydrophobic gallate esters (C16) have better antioxidant efficacy in emulsions when high amounts of SDS micelles are present.

To wrap up, the lipophilization of various antioxidants is an interesting strategy to design new antioxidants with interfacial properties that are particularly efficient in protecting lipids from oxidation in emulsified systems. However, their behavior as antioxidants is system dependent and difficult to anticipate, especially when considering the multitude of potential chemical or physical interactions that may occur with the other compounds present in the emulsion.

4.2. Binding Phenolic Antioxidants to Surface-Active Biopolymers

Biopolymers, and in particular, proteins, are largely used as emulsifiers. Although they may intrinsically have a strong potential to mitigate lipid oxidation in emulsions, their antioxidant properties can be enhanced by targeted interactions with phenolic compounds (McClements & Decker 2018, Quan et al. 2019). Two main routes can be considered for this purpose: complexation (when noncovalent interactions are involved) or conjugation (when the phenolic compound is covalently grafted onto the biopolymer, which can be considered analogic to the aforementioned lipophilization reaction, except that it pertains to biopolymers instead of alkyl chains). Accordingly,

biopolymer–phenolic compound physical complexes can be obtained by simple mixing of aqueous solutions of each component, leading to complex formation by hydrogen bonds, hydrophobically driven interactions, and electrostatic interactions (Karefyllakis et al. 2017, von Staszewski et al. 2012). For covalent conjugation, different preparation methods can be applied, including enzymatic reaction, use of a free radical–generating system (Gu et al. 2017), or alkaline pH (Liu et al. 2017, 2019). In general, such combinations (complexes and conjugates) have been shown not to impair and even to improve the interfacial and emulsifying properties of the biopolymer (Baba et al. 2021, Quan et al. 2019) and may even lead to additional benefits, such as a decreased allergenicity (Li et al. 2021). **Table 1** summarizes a few examples of applications of protein–phenolic compound complexes or conjugates in emulsions to limit lipid oxidation. It should be noted that these examples are far from exhaustive and do not include studies in which the potential antioxidant activity of such complexes or conjugates was evaluated by other means than direct measurements of lipid oxidation in emulsions, such as free radical scavenging activity tests (Parolia et al. 2022, Ren et al. 2022). Overall, these examples tend to consistently point to the fact that these complexes or conjugates are efficient in limiting lipid oxidation in emulsions as compared to control emulsions formulated with the protein constituent only. This effect is generic for various proteins, ranging from traditional dairy or egg proteins (Fan et al. 2018, Feng et al. 2018, Gu et al.

Table 1 Examples of protein-phenolic compound complexes or conjugates used to stabilize emulsions and prevent lipid oxidation

Protein	Phenolic	Type of complexes/ conjugates formed	Type of emulsion	Main findings	Reference
β-Lactoglobulin (BLG)	Gentisic acid	Covalent conjugation by an amine-reactive compound; various phenolic-to-protein molar ratios (grafting numbers)	Stripped hemp O/W emulsion	The conjugates led to better emulsion oxidative stability (compared to nonconjugated BLG) only at the highest grafting number tested; conjugate solubility and interfacial structures seem important to consider	Li et al. 2022
BLG	Green tea polyphenols	Noncovalent complexation in aqueous acidic buffer; various phenolic-to-protein mass ratios	Fish liver O/W emulsion	Strong inhibition of lipid oxidation at all phenolic-to-BLG ratios tested (in comparison with the BLG only–based emulsion)	von Staszewski et al. 2014
Whey protein isolate (WPI)	Epigallocatechin gallate (EGCG)	Free radical–mediated grafting	Fish O/W emulsion	Strong inhibition of lipid oxidation (in comparison with the WPI only–based emulsion); antioxidant effect further enhanced when combined with the WPI-EGCG conjugation with interfacial cross-linking	Fan et al. 2018

(*Continued*)

Table 1 (*Continued*)

Protein	Phenolic	Type of complexes/ conjugates formed	Type of emulsion	Main findings	Reference
Egg white proteins	Catechin polymers (CTPs)	Enzymatic catechin polymerization + free radical–mediated grafting to proteins	Polysorbate 20-linoleic acid-in-water emulsion	The conjugates led to better emulsion oxidative stability compared to the protein only or to nonconjugated protein–CTP mixtures; however, the interfacial location of the conjugates is questionable due to the presence of a surfactant	Gu et al. 2017
Ovalbumin	Catechin (C), epigallocatechin (EGC) or EGCG	Free radical–mediated grafting	Fish O/W emulsion	The conjugates led to better emulsion oxidative stability compared to the protein only, in the order C<EGC<EGCG; this was observed at both acidic and neutral pH. Good correlation with the radical scavenging properties of the conjugates (ABTS assay)	Feng et al. 2018
Bovine serum albumin + poly-arginine	Tannic acid (TA)	Electrostatic interactions	Multilayered (LbL) linseed O/W emulsion	The incorporation of TA in between biopolymer layers at the droplet surface suppresses lipid oxidation	Lomova et al. 2010
Flaxseed protein isolate	Flaxseed polyphenols or hydroxytyrosol	Alkaline conjugation (referred to as complexation)	Flaxseed O/W emulsion	Both types of conjugates are very efficient at preventing lipid oxidation (as compared to an emulsion made with the protein isolate only); however, conjugation decreases protein solubility	Pham et al. 2019
Soy protein isolate	EGCG	Alkaline conjugation (referred to as complexation)	Soybean O/W emulsion, costabilized by tea saponins (TSs) or CTAB	Anionic TSs hamper interfacial location of the conjugates, whereas cationic CTAB promotes it; lipid and protein oxidation occur to a lower extent in the former case (TS) than in the latter (CTAB)	Yan et al. 2022

Abbreviations: ABTS, 2,2′-azinobis(3-ethylbenzothiazoline-6-sulfonic acid ammonium salt); CTAB, hexadecyltrimethylammonium bromide; LbL, layer-by-layer (electrostatic deposition); O/W, oil-in-water.

2017, Li et al. 2022, von Staszewski et al. 2014) to plant proteins (Pham et al. 2019). It is, as well, relatively independent of the type of phenolic used, even though some differences in the degree of protective effect have been seen. For example, Feng et al. (2018) found that ovalbumin-based conjugates all led to a protective effect against lipid oxidation in a fish O/W emulsion, with an efficiency ranking as follows: epigallocatechin gallate (EGCG) > epigallocatechin (EGC) > catechin. In some studies, the phenolic-to-protein ratio seems to be important; for instance, Li et al. (2022) observed that β-lactoglobulin–gentisic acid conjugates had a pronounced antioxidant effect only at the highest grafting number tested, whereas lower ratios even led to pro-oxidant effects. This ratio therefore seems to be a relevant parameter to consider and optimize in such studies. Recently, Yan et al. (2022) investigated the potential of soy protein isolate–EGCG conjugates to prevent lipid oxidation in emulsions. Their study design involved the use of cosurfactants [anionic tea saponins or cationic hexadecyltrimethylammonium bromide (CTAB)], which either competed with the conjugates for interfacial adsorption (tea saponins) or promoted it (CTAB). They found that overall, the emulsions with CTAB oxidized slightly more than the surfactant-free control emulsions (i.e., that contained only the conjugates), whereas the emulsions with the tea saponins were the most oxidatively stable. Interestingly, they also determined that protein oxidation was most likely an important factor explaining their findings because protein oxidation was prevented when the protein–EGCG conjugates were not adsorbed at the oil–water interface because of the competition with saponins. The fact that adsorbed proteins in emulsions may themselves be subjected to extensive oxidation was already well-documented (Berton et al. 2012); this therefore suggests that despite the high potential of protein–polyphenol conjugates or complexes to act as dual emulsifier–interfacial antioxidant compounds, their efficiency may be balanced by oxidative reactions pertaining to the protein moiety, and that the nonadsorbed fraction of these compounds may also hold a substantial antioxidant potential. Finally, an original strategy considered by Lomova et al. (2010) consisted of entrapping tannic acid at the surface of emulsion droplets by electrostatic interactions within biopolymer layers. They observed a high oxidative stability of the system, which could not be achieved with the interfacial architecture of biopolymer multilayers only. However, manufacturing multilayered emulsions requires numerous sequential steps, which largely limits the applicability of this technology.

As described earlier for the phenolipids, it is also worth mentioning that although a large amount of research has been conducted on preparing biopolymer–phenolic complexes or conjugates from distinct ingredients, some amphiphilic polymers naturally contain phenolic residues and could thus be considered for dual physical-oxidative stabilization of emulsions. This was exemplified, for instance, by spruce galactoglucomannans, which are able to act as emulsifiers and endogenously contain covalently bound phenolic residues, ranging from simple free aromatic phenolic acids to polymers (lignin) (Lehtonen et al. 2018). The authors of this work found high oxidative stability of emulsions stabilized with these biopolymers.

Finally, some authors reported that one of the drawbacks of conjugation of proteins with phenolic compounds may be a decrease, which can be quite substantial, in solubility, thereby hampering their interfacial and emulsifying properties (Quan et al. 2019). It is, however, interesting to observe that this apparent pitfall can be converted into an advantage, as the propensity of some conjugates to precipitate can be used as a basis to form colloidal particles. The latter has become increasingly popular for formulating Pickering emulsions, which are examined in the next section. It is debatable whether such structures (which may be soft, deformable protein particles) fully meet the definition of Pickering particles (Murray 2019), and it is even possible that the boundary between conjugated biopolymers (this section) and Pickering emulsions (next section) is a gray area rather than clear and distinct.

4.3. Interfacial Particles as Reservoirs of Antioxidants: Multifunctional Location Pickering Emulsions

Pickering emulsions currently represent one of the most active areas of research in the field of food emulsions. This is illustrated by the fact that in 2021, the number of entries when searching in the Web of Science for the topic "food + emulsion + Pickering" represented 21% of the total number of entries for "food + emulsion" (this proportion was only 3% in 2011), and accordingly the term "neo-Pickering era" has been recently proposed (Dickinson 2020). Most of the research on such systems for food applications has therefore been conducted in the past 5–10 years and has mostly revolved around the identification of biobased particles suitable for the physical stabilization of emulsions (Berton-Carabin & Schroën 2015, Murray 2019, Rayner 2015, Schröder et al. 2018, Tavernier et al. 2016, Wang et al. 2022). Conversely, the impact of interfacial particle layers on lipid oxidation in Pickering emulsions has been less extensively examined so far, even though a rising number of studies has been published in the past two years. As recently reviewed by Berton-Carabin et al. (2021), it does not seem that there is a generic potential of Pickering particles to prevent lipid oxidation in emulsions through a physical barrier effect only, which is probably due to the fact that it is extremely challenging (which is not to say impossible) to create a defect-free interfacial layer at the scale relevant to the compounds involved in the reaction, such as metal ions and reactive oxygen species. Nonetheless, it may still be possible to functionalize Pickering particles to limit lipid oxidation by conferring them with the additional role of antioxidant reservoir. This concept was patented and published by Schröder et al. (2019, 2020), who showed that entrapping α-tocopherol or carnosic acid in high-melting-point colloidal lipid particles (CLPs) that were next used as Pickering stabilizers for O/W emulsions led to a substantially better oxidative stability in comparison with a control Pickering emulsion of similar overall composition and structure, but where the antioxidant was initially dissolved in the liquid to-be-dispersed oil phase (**Figure 3*a***). In the concept emulsion, it was observed that the antioxidant was slowly released from the interfacial particles into the core of the liquid oil droplets, which suggests that CLPs behave as an interfacial reservoir of antioxidants, thereby conferring a substantial residency time at this critical zone of the system. Interestingly, when antioxidant-loaded CLPs were present only in the continuous phase, no antioxidant-enhancing effect was found anymore, confirming the importance of the interfacial location (Schröder et al. 2020). The concept of antioxidant-loaded Pickering particles has also been applied to other combinations of carrier particles and antioxidants (mostly phenolic antioxidants). Protein-based particles seem quite promising for this purpose (Wang et al. 2022); for instance, hydrophobic prolamins such as zein or gliadins and hydrophilic phenolics have been combined to form composite particles by antisolvent precipitation. Using this approach, it was shown that zein–tannic acid particles could lead to Pickering emulsions with a fairly high oxidative stability compared to bulk oil or control protein-stabilized emulsions (Zhou et al. 2020, Zou et al. 2017). In another study, emulsions stabilized by gliadin–proanthocyanidin composite particles were shown to be better protected against lipid oxidation compared to control emulsions stabilized by antioxidant-free particles (Zhou et al. 2018), and similar protective effects were again reported in high internal phase emulsions stabilized by EGCG–soy β-conglycinin particles (Peng & Tang 2020). Another interesting recent example reported the development of dendritic mesoporous silica nanospheres (DMSNs), which can act as both nanocarriers for hydrophilic and hydrophobic antioxidants (proof of concept established for EGCG and resveratrol, respectively) and Pickering stabilizers (Hu et al. 2021) (**Figure 3*b***). Although the system was tested only for the emulsification and stabilization of flavoring essential oil (not for polyunsaturated edible oil), the particles were shown to be efficient at retaining the targeted antioxidant within their internal structure and to significantly protect citral against oxidation.

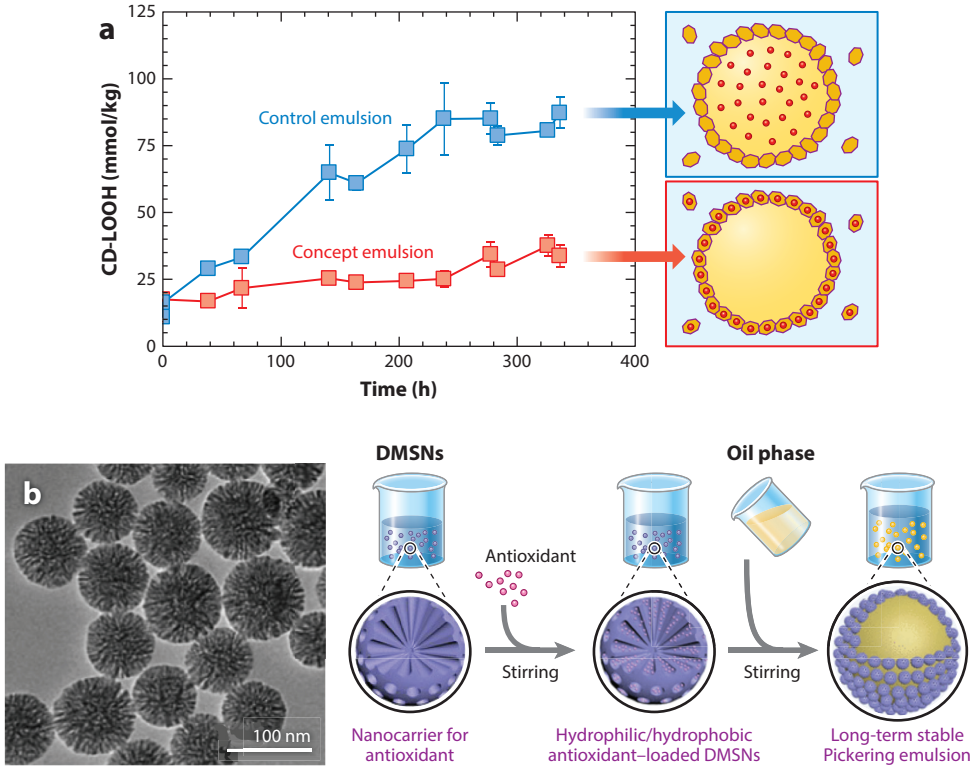

Figure 3

(*a*) Formation of lipid oxidation products [conjugated diene hydroperoxides (CD-LOOH)] during incubation of Pickering emulsions formulated with colloidal lipid particles (CLPs) and containing α-tocopherol (*red squares*, concept emulsion, α-tocopherol in the CLPs; *blue squares*, control emulsion, α-tocopherol in the liquid oil; see also schematic illustrations). Adapted from Schröder et al. (2020), with permission from Elsevier. (*b*) Transmission electron microscopy image of dendritic mesoporous silica nanospheres (DMSNs) (*left*) and schematic representation of their application for antioxidant loading and subsequent Pickering emulsion formation (*right*). Figure adapted from Hu et al. (2021), with permission from ACS Publications.

Such advanced hierarchical designs to yield bifunctional Pickering particles (i.e., with physical + oxidative stabilization potential) have thus been useful to establish the proof of concept of interfacial antioxidant reservoirs and hold the potential to boost the efficiency of natural phenolic antioxidants. Yet a major disadvantage that may limit their widespread application is the fact that such a strategy involves a complex process, is costly, and does not meet the current trends toward natural, clean-label, and mildly transformed food systems. A way to circumvent this while still using the concept of antioxidant-loaded Pickering particles could be to make use of the endogenous antioxidant content of naturally occurring particles (i.e., using a top-down approach instead of a bottom-up one, as in the previous examples), such as food and biobased product side streams. Although the level of control on the composition and structure of such particles will be necessarily lower than for tailor-made composite particles, they would hold great potential in terms of sustainability, naturalness, and interfacial retention of antioxidants (Berton-Carabin et al. 2021). One of the available examples of such a strategy relates to Pickering emulsions stabilized with milled red rice particles containing anthocyanins (Lu & Huang 2020). The authors showed that

these polyphenol-rich particles led to better protection of emulsified oil droplets against oxidation in comparison with white rice starch-stabilized emulsions and with bulk oil. Another recent study from our group dealt with the preparation of Pickering emulsions using different plant-based particles and showed that matcha tea and spinach leaf particle-stabilized emulsions were highly stable to lipid oxidation as compared to reference emulsions stabilized by conventional emulsifiers (Schröder et al. 2021). This protective effect can most likely be explained by the presence of endogenous antioxidants in these fractions, such as free radical–scavenging phenolics and chelatant organic acids. The use of such natural particles seems therefore to be a promising route for the physical and oxidative stabilization of clean-label emulsions. In particular, considering the omnipresence and breadth of phenolic antioxidants in food-compatible plant materials, there are surely many prospective Pickering particle sources to explore.

5. CONCLUSIONS AND OUTLOOK

Various routes and design principles can be considered to locate phenolic antioxidant compounds at the oil–water interface in emulsions. The different strategies described herein consistently point to the fact that interfacial location of such key reactants in the system is in fact a very important lever to tackle lipid oxidation. However, most of the research in this area looks at the location of these components (as well as that of other critical molecules in the system) from a frozen perspective, i.e., overlooking the dynamics of the molecules and structures present. This is certainly an important aspect to consider in the future to bridge the gap between purely spatial considerations and a spatiotemporal approach (Laguerre et al. 2020), which would also include relevant dynamic notions, such as interfacial residency times of antioxidants.

DISCLOSURE STATEMENT

The authors are not aware of any affiliations, memberships, funding, or financial holdings that might be perceived as affecting the objectivity of this review.

ACKNOWLEDGMENTS

C.B.-C. gratefully acknowledges Région Pays de la Loire and Nantes Métropole for financial support (Connect Talent grant, 2021–2025).

LITERATURE CITED

Alemán M, Bou R, Guardiola F, Durand E, Villeneuve P, et al. 2015. Antioxidative effect of lipophilized caffeic acid in fish oil enriched mayonnaise and milk. *Food Chem*. 167:236–44

Atkinson PJ, Dickinson E, Horne DS, Richardson RM. 1995. Neutron reflectivity of adsorbed β-casein and β-lactoglobulin at the air/water interface. *J. Chem. Soc. Faraday Trans.* 91(17):2847–54

Baba WN, McClements DJ, Maqsood S. 2021. Whey protein-polyphenol conjugates and complexes: production, characterization, and applications. *Food Chem*. 365(March):130455

Berton C, Ropers M-H, Guibert D, Solé V, Genot C. 2012. Modifications of interfacial proteins in oil-in-water emulsions prior to and during lipid oxidation. *J. Agric. Food Chem.* 60(35):8659–71

Berton C, Ropers M-H, Viau M, Genot C. 2011. Contribution of the interfacial layer to the protection of emulsified lipids against oxidation. *J. Agric. Food Chem.* 59(9):5052–61

Berton-Carabin C, Schröder A, Schroën K, Laguerre M. 2021. Lipid oxidation in Pickering emulsions. In *Omega-3 Delivery Systems*, ed. PJ Garcia-Moreno, B Yesiltas, AD Sorensen, C Jacobsen, pp. 275–93. Amsterdam: Elsevier

Berton-Carabin CC, Ropers M-H, Genot C. 2014. Lipid oxidation in oil-in-water emulsions: involvement of the interfacial layer. *Compr. Rev. Food Sci. Food Saf.* 13:945–77

Berton-Carabin CC, Sagis L, Schroën K. 2018. Formation, structure, and functionality of interfacial layers in food emulsions. *Annu. Rev. Food Sci. Technol.* 9:551–87

Berton-Carabin CC, Schroën K. 2015. Pickering emulsions for food applications: background, trends and challenges. *Annu. Rev. Food Sci. Technol.* 6:263–97

Bos MA, van Vliet T. 2001. Interfacial rheological properties of adsorbed protein layers and surfactants: a review. *Adv. Colloid Interface Sci.* 91:437–71

Caillol S. 2018. Cardanol: a promising building block for biobased polymers and additives. *Curr. Opin. Green Sustain. Chem.* 14:26–32

Chevalier Y, Bolzinger M-A. 2013. Emulsions stabilized with solid nanoparticles: Pickering emulsions. *Colloids Surf. A* 439:23–34

Cheynier V, Comte G, Davies KM, Lattanzio V, Martens S. 2013. Plant phenolics: recent advances on their biosynthesis, genetics, and ecophysiology. *Plant Physiol. Biochem.* 72:1–20

Costa M, Losada-Barreiro S, Bravo-Díaz C, Vicente AA, Monteiro LS, Paiva-Martins F. 2020. Influence of AO chain length, droplet size and oil to water ratio on the distribution and on the activity of gallates in fish oil-in-water emulsified systems: emulsion and nanoemulsion comparison. *Food Chem.* 310:125716

Costa M, Losada-Barreiro S, Paiva-Martins F, Bravo-Díaz C, Romsted LS. 2015. A direct correlation between the antioxidant efficiencies of caffeic acid and its alkyl esters and their concentrations in the interfacial region of olive oil emulsions. The pseudophase model interpretation of the "cut-off" effect. *Food Chem.* 175:233–42

Crauste C, Rosell M, Durand T, Vercauteren J. 2016. Omega-3 polyunsaturated lipophenols, how and why? *Biochimie* 120:62–74

Dalgleish DG. 1997. Adsorption of proteins and the stability of emulsions. *Trends Food Sci. Technol.* 8:1–6

Dangles O. 2012. Antioxidant activity of plant phenols: chemical mechanisms and biological significance. *Curr. Org. Chem.* 16(6):692–714

Decker EA, McClements DJ, Bourlieu-Lacanal C, Durand E, Figueroa-Espinoza MC, et al. 2017. Hurdles in predicting antioxidant efficacy in oil-in-water emulsions. *Trends Food Sci. Technol.* 67:183–94

Dickinson E. 1994. Protein-stabilized emulsions. *J. Food Eng.* 22:59–74

Dickinson E. 2009. Hydrocolloids as emulsifiers and emulsion stabilizers. *Food Hydrocoll.* 23(6):1473–82

Dickinson E. 2012. Use of nanoparticles and microparticles in the formation and stabilization of food emulsions. *Trends Food Sci. Technol.* 24(1):4–12

Dickinson E. 2020. Advances in food emulsions and foams: reflections on research in the neo-Pickering era. *Curr. Opin. Food Sci.* 33:52–60

Durand E, Beaubier S, Ilic I, Fine F, Kapel R, Villeneuve P. 2021. Production and antioxidant capacity of bioactive peptides from plant biomass to counteract lipid oxidation. *Curr. Res. Food Sci.* 4:365–97

Elder AS, Coupland JN, Elias RJ. 2021. Effect of alkyl chain length on the antioxidant activity of alkylresorcinol homologues in bulk oils and oil-in-water emulsions. *Food Chem.* 346:128885

Elias RJ, Kellerby SS, Decker EA. 2008. Antioxidant activity of proteins and peptides. *Crit. Rev. Food Sci. Nutr.* 48:430–41

Fan Y, Liu Y, Gao L, Zhang Y, Yi J. 2018. Oxidative stability and in vitro digestion of menhaden oil emulsions with whey protein: effects of EGCG conjugation and interfacial cross-linking. *Food Chem.* 265:200–7

Faraji H, McClements DJ, Decker EA. 2004. Role of continuous phase protein on the oxidative stability of fish oil-in-water emulsions. *J. Agric. Food Chem.* 52(14):4558–64

Farooq S, Abdullah, Zhang H, Weiss J. 2021. A comprehensive review on polarity, partitioning, and interactions of phenolic antioxidants at oil-water interface of food emulsions. *Compr. Rev. Food Sci. Food Saf.* 20(5):4250–77

Feng J, Cai H, Wang H, Li C, Liu S. 2018. Improved oxidative stability of fish oil emulsion by grafted ovalbumin-catechin conjugates. *Food Chem.* 241:60–69

Feng J, Schroën K, Fogliano V, Berton-Carabin C. 2021. Antioxidant potential of non-modified and glycated soy proteins in the continuous phase of oil-in-water emulsions. *Food Hydrocoll.* 114:106564

Ferreira da Silveira TF, Laguerre M, Bourlieu-Lacanal C, Lecomte J, Durand E, et al. 2021. Impact of surfactant concentration and antioxidant mode of incorporation on the oxidative stability of oil-in-water nanoemulsions. *LWT* 141:110892

Figueroa-Espinoza MC, Bourlieu C, Durand E, Lecomte J, Villeneuve P. 2019. Lipophilized antioxidants. *Encycl. Food Chem.* 2:193–201

Figueroa-Espinoza MC, Laguerre M, Villeneuve P, Lecomte J. 2013. From phenolics to phenolipids: optimizing antioxidants in lipid dispersions. *Lipid Technol.* 25(6):131–34

Figueroa-Espinoza MC, Villeneuve P. 2005. Phenolic acids enzymatic lipophilization. *J. Agric. Food Chem.* 53(8):2779–87

Frankel EN, Huang S-W, Kanner J, German JB. 1994. Interfacial phenomena in the evaluation of antioxidants: bulk oils versus emulsions. *J. Agric. Food Chem.* 42:1054–59

Frankel EN, Satué-Gracia T, Meyer AS, German JB. 2002. Oxidative stability of fish and algae oils containing long-chain polyinstaurated fatty acids in bulk and in oil-in-water emulsions. *J. Agric. Food Chem.* 50(7):2094–99

Freiria-Gandara J, Losada-Barreiro S, Paiva-Martins F, Bravo-Díaz C. 2018. Enhancement of the antioxidant efficiency of gallic acid derivatives in intact fish oil-in-water emulsions through optimization of their interfacial concentrations. *Food Funct.* 9:4429–42

González MJ, Medina I, Maldonado OS, Lucas R, Morales JC. 2015. Antioxidant activity of alkyl gallates and glycosyl alkyl gallates in fish oil in water emulsions: relevance of their surface active properties and of the type of emulsifier. *Food Chem.* 183:190–96

Graham DE, Phillips MC. 1979. Proteins at liquid interfaces. III. Molecular structures of adsorbed films. *J. Colloid Interface Sci.* 70(3):427–39

Grajeda-Iglesias C, Salas E, Barouh N, Baréa B, Panya A, Figueroa-Espinoza MC. 2016. Antioxidant activity of protocatechuates evaluated by DPPH, ORAC, and CAT methods. *Food Chem.* 194:749–57

Gu L, Peng N, Chang C, McClements DJ, Su Y, Yang Y. 2017. Fabrication of surface-active antioxidant food biopolymers: conjugation of catechin polymers to egg white proteins. *Food Biophys.* 12(2):198–210

Gumus CE, Decker EA, McClements DJ. 2017. Impact of legume protein type and location on lipid oxidation in fish oil-in-water emulsions: lentil, pea, and faba bean proteins. *Food Res. Int.* 100:175–85

Guzey D, McClements DJ. 2006. Formation, stability and properties of multilayer emulsions for application in the food industry. *Adv. Colloid Interface Sci.* 128–130:227–48

Hammond EG, White PJ. 2011. A brief history of lipid oxidation. *J. Am. Oil Chem. Soc.* 88(7):891–97

Hasenhuettl GL, Hartel RW. 2008. *Food Emulsifiers and Their Applications*. New York: Springer

Hinderink EBA, Meinders MBJ, Miller R, Sagis L, Schroën K, Berton-Carabin CC. 2022. Interfacial protein-protein displacement at fluid interfaces. *Adv. Colloid Interface Sci.* 305:102691

Hinderink EBA, Sagis L, Schroën K, Berton-Carabin CC. 2020. Behavior of plant-dairy protein blends at air-water and oil-water interfaces. *Colloids Surfaces B* 192:111015

Hu J, Du P, Xu R, Deng W. 2021. Supersmall dendritic mesoporous silica nanospheres as antioxidant nanocarriers for Pickering emulsifiers. *J. Agric. Food Chem.* 69(49):14893–905

Hu M, McClements DJ, Decker EA. 2003. Lipid oxidation in corn oil-in-water emulsions stabilized by casein, whey protein isolate, and soy protein isolate. *J. Agric. Food Chem.* 51(6):1696–1700

Hunter TN, Pugh RJ, Franks GV, Jameson GJ. 2008. The role of particles in stabilising foams and emulsions. *Adv. Colloid Interface Sci.* 137(2):57–81

Inchingolo R, Bayram I, Uluata S, Kiralan SS, Rodriguez-Estrada MT, et al. 2021. Ability of sodium dodecyl sulfate (SDS) micelles to increase the antioxidant activity of α-tocopherol. *J. Agric. Food Chem.* 69(20):5702–8

Jacobsen C. 2015. Some strategies for the stabilization of long chain n-3 PUFA-enriched foods: a review. *Eur. J. Lipid Sci. Technol.* 117(11):1853–66

Kahveci D, Laguerre M, Villeneuve P. 2015. Phenolipids as new antioxidants: production, activity and potential applications. In *Polar Lipids: Biology, Chemistry & Technology*, ed. MU Ahmad, X Xu, pp. 185–214. Urbana, IL: AOCS Press

Karefyllakis D, Altunkaya S, Berton-Carabin CC, van der Goot AJ, Nikiforidis CV. 2017. Physical bonding between sunflower proteins and phenols: impact on interfacial properties. *Food Hydrocoll.* 73:326–34

Kiralan SS, Doğu-Baykut E, Kittipongpittaya K, McClements DJ, Decker EA. 2014. Increased antioxidant efficacy of tocopherols by surfactant solubilization in oil-in-water emulsions. *J. Agric. Food Chem.* 62:10561–66

Laguerre M, Bayrasy C, Lecomte J, Chabi B, Andrew E, et al. 2013. How to boost antioxidants by lipophilization? *Biochimie* 95:20–26
Laguerre M, Bayrasy C, Panya A, Weiss J, McClements DJ, et al. 2015. What makes good antioxidants in lipid-based systems? The next theories beyond the polar paradox. *Crit. Rev. Food Sci. Nutr.* 55(2):183–201
Laguerre M, Bily A, Roller M, Birtic S. 2017. Mass transport phenomena in lipid oxidation and antioxidation. *Annu. Rev. Food Sci. Technol.* 8:391–411
Laguerre M, Giraldo LJL, Lecomte J, Figueroa-Espinoza M-C, Baréa B, et al. 2009. Chain length affects antioxidant properties of chlorogenate esters in emulsion: the cutoff theory behind the polar paradox. *J. Agric. Food Chem.* 57(23):11335–42
Laguerre M, Lecomte J, Villeneuve P. 2007. Evaluation of the ability of antioxidants to counteract lipid oxidation: existing methods, new trends and challenges. *Prog. Lipid Res.* 46(5):244–82
Laguerre M, López Giraldo LJ, Lecomte J, Figueroa-Espinoza M-C, Baréa B, et al. 2010. Relationship between hydrophobicity and antioxidant ability of "phenolipids" in emulsion: a parabolic effect of the chain length of rosmarinate esters. *J. Agric. Food Chem.* 58(5):2869–76
Laguerre M, Tenon M, Bily A, Birtic S. 2020. Toward a spatiotemporal model of oxidation in lipid dispersions: a hypothesis-driven review. *Eur. J. Lipid Sci. Technol.* 122(3):1900209
Lehtonen M, Merinen M, Kilpeläinen PO, Xu C, Willför SM, Mikkonen KS. 2018. Phenolic residues in spruce galactoglucomannans improve stabilization of oil-in-water emulsions. *J. Colloid Interface Sci.* 512:536–47
Li H, Pan Y, Yang Z, Rao J, Chen B. 2022. Modification of β-lactoglobulin by phenolic conjugations: protein structural changes and physicochemical stabilities of stripped hemp oil-in-water emulsions stabilized by the conjugates. *Food Hydrocoll.* 128:107578
Li X, Li M, Zhang T, McClements DJ, Liu X, et al. 2021. Enzymatic and nonenzymatic conjugates of lactoferrin and (−)-epigallocatechin gallate: formation, structure, functionality, and allergenicity. *J. Agric. Food Chem.* 69(22):6291–302
Liu F, Ma C, McClements DJ, Gao Y. 2017. A comparative study of covalent and non-covalent interactions between zein and polyphenols in ethanol-water solution. *Food Hydrocoll.* 63:625–34
Liu J, Yong H, Yao X, Hu H, Yun D, Xiao L. 2019. Recent advances in phenolic-protein conjugates: synthesis, characterization, biological activities and potential applications. *RSC Adv.* 9(61):35825–40
Lomova MV, Sukhorukov GB, Antipina MN. 2010. Antioxidant coating of micronsize droplets for prevention of lipid peroxidation in oil-in-water emulsion. *ACS Appl. Mater. Interfaces* 2(12):3669–76
Losada-Barreiro S, Bravo-Díaz C, Paiva-Martins F, Romsted LS. 2013. Maxima in antioxidant distributions and efficiencies with increasing hydrophobicity of gallic acid and its alkyl esters. The pseudophase model interpretation of the "cutoff effect." *J. Agric. Food Chem.* 61:6533–43
Lu X, Huang Q. 2020. Nano/submicrometer milled red rice particles-stabilized Pickering emulsions and their antioxidative properties. *J. Agric. Food Chem.* 68(1):292–300
Lucas R, Comelles F, Alcántara D, Maldonado OS, Curcuroze M, et al. 2010. Surface-active properties of lipophilic antioxidants tyrosol and hydroxytyrosol fatty acid esters: a potential explanation for the nonlinear hypothesis of the antioxidant activity in oil-in-water emulsions. *J. Agric. Food Chem.* 58(13):8021–26
Lucassen J, Van Den Tempel M. 1972. Dynamic measurements of dilational properties of a liquid interface. *Chem. Eng. Sci.* 27(6):1283–91
Mancuso JR, McClements DJ, Decker EA. 1999. The effects of surfactant type, pH, and chelators on the oxidation of salmon oil-in-water emulsions. *J. Agric. Food Chem.* 47(10):4112–16
McClements DJ. 2005. *Food Emulsions: Principles, Practices and Techniques*. Boca Raton, FL: CRC Press
McClements DJ, Decker E. 2018. Interfacial antioxidants: a review of natural and synthetic emulsifiers and coemulsifiers that can inhibit lipid oxidation. *J. Agric. Food Chem.* 66:20–35
McClements DJ, Dungan SR, German JB, Kinsella JE. 1992. Oil exchange between oil-in-water emulsion droplets stabilised with a non-ionic surfactant. *Food Hydrocoll.* 6(5):415–22
Medina I, Lois S, Alcántara D, Lucas R, Morales JC. 2009. Effect of lipophilization of hydroxytyrosol on its antioxidant activity in fish oils and fish oil-in-water emulsions. *J. Agric. Food Chem.* 57(20):9773–79
Medina S, Auñón D, Lehoux J, Durand T, Crauste C, Gil-Izquierdo Á. 2022. Hydroxytyrosol fatty acid esters as new candidate markers for detecting olive oil inadequate storage conditions by UHPLC-QqQ-MS/MS. *Microchem. J.* 181:107656

Murray BS. 2019. Pickering emulsions for food and drinks. *Curr. Opin. Food Sci.* 27:57–63
Murray BS, Dickinson E. 1996. Interfacial rheology and the dynamic properties of adsorbed films of food proteins and surfactants. *Food Sci. Technol. Int.* 2(3):131–45
Musakhanian J, Rodier JD, Dave M. 2022. Oxidative stability in lipid formulations: a review of the mechanisms, drivers, and inhibitors of oxidation. *AAPS PharmSciTech* 23(5):151
Neves MA, Wang Z, Kobayashi I, Nakajima M. 2017. Assessment of oxidative stability in fish oil-in-water emulsions: effect of emulsification process, droplet size and storage temperature. *J. Food Process Eng.* 40:12316
Panya A, Kittipongpittaya K, Laguerre M, Bayrasy C, Lecomte J, et al. 2012a. Interactions between α-tocopherol and rosmarinic acid and its alkyl esters in emulsions: synergistic, additive, or antagonistic effect? *J. Agric. Food Chem.* 60(41):10320–30
Panya A, Laguerre M, Bayrasy C, Lecomte J, Villeneuve P, et al. 2012b. An investigation of the versatile antioxidant mechanisms of action of rosmarinate alkyl esters in oil-in-water emulsions. *J. Agric. Food Chem.* 60:2692–700
Parolia S, Maley J, Sammynaiken R, Green R, Nickerson M, Ghosh S. 2022. Structure—functionality of lentil protein-polyphenol conjugates. *Food Chem.* 367:130603
Peña AA, Miller CA. 2006. Solubilization rates of oils in surfactant solutions and their relationship to mass transport in emulsions. *Adv. Colloid Interface Sci.* 123–126(Spec. Iss.):241–57
Peng LP, Tang CH. 2020. Outstanding antioxidant Pickering high internal phase emulsions by co-assembled polyphenol-soy β-conglycinin nanoparticles. *Food Res. Int.* 136:109509
Pham LB, Wang B, Zisu B, Adhikari B. 2019. Complexation between flaxseed protein isolate and phenolic compounds: effects on interfacial, emulsifying and antioxidant properties of emulsions. *Food Hydrocoll.* 94:20–29
Pickering SU. 1907. Emulsions. *J. Chem. Soc.* 91:2001–21
Porter WL, Black ED, Drolet AM. 1989. Use of polyamide oxidative fluorescent test on lipid emulsions: contrast in relative effectiveness of antioxidants in bulk versus dispersed systems. *J. Agric. Food Chem.* 37(3):615–24
Quan TH, Benjakul S, Sae-leaw T, Balange AK, Maqsood S. 2019. Protein-polyphenol conjugates: antioxidant property, functionalities and their applications. *Trends Food Sci. Technol.* 91:507–17
Quideau S, Deffieux D, Douat-Casassus C, Pouységu L. 2011. Plant polyphenols: chemical properties, biological activities, and synthesis. *Angew. Chem. Int. Ed.* 50(3):586–621
Rayner M. 2015. Current status on novel ways for stabilizing food dispersions by oleosins, particles and microgels. *Curr. Opin. Food Sci.* 3:94–109
Rayner M, Timgren A, Sjöö M, Dejmek P. 2012. Quinoa starch granules: a candidate for stabilising food-grade Pickering emulsions. *J. Sci. Food Agric.* 92(9):1841–47
Ren G, Shi J, Huang S, Liu C, Ni F, et al. 2022. The fabrication of novel zein and resveratrol covalent conjugates: enhanced thermal stability, emulsifying and antioxidant properties. *Food Chem.* 374:131612
Richards MP, Chaiyasit W, McClements DJ, Decker EA. 2002. Ability of surfactant micelles to alter the partitioning of phenolic antioxidants in oil-in-water emulsions. *J. Agric. Food Chem.* 50(5):1254–59
Romsted LS, Bravo-Díaz C. 2013. Modeling chemical reactivity in emulsions. *Curr. Opin. Colloid Interface Sci.* 18(1):3–14
Saha MM, Mallik UK, Mallik AK. 1991. A chromenoflavanone and two caffeic esters from *Pongamia glabra*. *Phytochemistry* 30(11):3834–36
Schaich KM. 2020a. Lipid oxidation: new perspectives on an old reaction. In *Bailey's Industrial Oil and Fat Products*, ed. F Shahidi, pp. 337–408. Hoboken, NJ: Wiley & Sons
Schaich KM. 2020b. Toxicity of lipid oxidation products consumed in the diet. In *Bailey's Industrial Oil and Fat Products*, ed. F Shahidi, pp. 599–686. Hoboken, NJ: Wiley & Sons
Schröder A, Corstens MN, Ho KKHY, Schroën K, Berton-Carabin CC. 2018. Pickering emulsions. In *Emulsion-Based Systems for Delivery of Food Active Compounds: Formation, Application, Health and Safety*, ed. S Roohinejad, R Greiner, I Oey, J Wen, pp. 29–67. Hoboken, NJ: Wiley & Sons. 1st ed.
Schröder A, Laguerre M, Sprakel J, Birtic S, Schroën CGPH, Berton-Carabin C. 2019. *Emulsion comprising antioxidant particles*. WO Patent 2020/007885

Schröder A, Laguerre M, Sprakel J, Schroën K, Berton-Carabin CC. 2020. Pickering particles as interfacial reservoirs of antioxidants. *J. Colloid Interface Sci.* 575:489–98
Schröder A, Laguerre M, Tenon M, Schroën K, Berton-Carabin CC. 2021. Natural particles can armor emulsions against lipid oxidation and coalescence. *Food Chem.* 347:129003
Shahidi F, Ambigaipalan P. 2015. Phenolics and polyphenolics in foods, beverages and spices: antioxidant activity and health effects—a review. *J. Funct. Foods.* 18:820–97
Shao Y, Tang C-H. 2014. Characteristics and oxidative stability of soy protein-stabilized oil-in-water emulsions: influence of ionic strength and heat pretreatment. *Food Hydrocoll.* 37:149–58
Skibsted LH. 2010. Understanding oxidation processes in foods. In *Oxidation in Foods and Beverages and Antioxidant Applications*, ed. EA Decker, pp. 3–35. Cambridge, UK: Woodhead Publ.
Sonar VP, Corona A, Distinto S, Maccioni E, Meleddu R, et al. 2017. Natural product-inspired esters and amides of ferulic and caffeic acid as dual inhibitors of HIV-1 reverse transcriptase. *Eur. J. Med. Chem.* 130:248–60
Sørensen ADM, Lyneborg KS, Villeneuve P, Jacobsen C. 2015. Alkyl chain length impacts the antioxidative effect of lipophilized ferulic acid in fish oil enriched milk. *J. Funct. Foods.* 18:959–67
Sørensen ADM, Petersen LK, de Diego S, Nielsen NS, Lue BM, et al. 2012. The antioxidative effect of lipophilized rutin and dihydrocaffeic acid in fish oil enriched milk. *Eur. J. Lipid Sci. Technol.* 114(4):434–45
Sørensen AM, Villeneuve P, Jacobsen C. 2017. Alkyl caffeates as antioxidants in O/W emulsions: impact of emulsifier type and endogenous tocopherols. *Eur. J. Lipid Sci. Technol.* 119:1600276
Stöckmann H, Schwarz K, Huynh-Ba T. 2000. The influence of various emulsifiers on the partitioning and antioxidant activity of hydroxybenzoic acids and their derivatives in oil-in-water emulsions. *J. Am. Oil Chem. Soc.* 77(5):535–42
Tavernier I, Wijaya W, Van der Meeren P, Dewettinck K, Patel AR. 2016. Food-grade particles for emulsion stabilization. *Trends Food Sci. Technol.* 50:159–74
Tcholakova S, Denkov ND, Lips A. 2008. Comparison of solid particles, globular proteins and surfactants as emulsifiers. *Phys. Chem. Chem. Phys.* 10(12):1608–27
ten Klooster S, Villeneuve P, Bourlieu-Lacanal C, Durand E, Schroën K, Berton-Carabin C. 2022. Alkyl chain length modulates antioxidant activity of gallic acid esters in spray-dried emulsions. *Food Chem.* 387:132880
Villeneuve P, Bourlieu-Lacanal C, Durand E, Lecomte J, McClements DJ, Decker EA. 2021. Lipid oxidation in emulsions and bulk oils: a review of the importance of micelles. *Crit. Rev. Food Sci. Nutr.* In press
von Staszewski M, Jara FL, Ruiz ALTG, Jagus RJ, Carvalho JE, Pilosof AMR. 2012. Nanocomplex formation between β-lactoglobulin or caseinomacropeptide and green tea polyphenols: impact on protein gelation and polyphenols antiproliferative activity. *J. Funct. Foods.* 4(4):800–9
von Staszewski M, Pizones Ruiz-Henestrosa VM, Pilosof AMR. 2014. Green tea polyphenols-β-lactoglobulin nanocomplexes: interfacial behavior, emulsification and oxidation stability of fish oil. *Food Hydrocoll.* 35:505–11
Walker R, Decker EA, McClements DJ. 2015. Development of food-grade nanoemulsions and emulsions for delivery of omega-3 fatty acids: opportunities and obstacles in the food industry. *Food Funct.* 6(1):41–54
Walstra PW. 2003. *Physical Chemistry of Foods*. New York: Marcel Dekker
Wang C, Wu J, Wang C, Mu C, Ngai T, Lin W. 2022. Advances in Pickering emulsions stabilized by protein particles: toward particle fabrication, interaction and arrangement. *Food Res. Int.* 157:111380
Waraho T, McClements DJ, Decker EA. 2011. Mechanisms of lipid oxidation in food dispersions. *Trends Food Sci. Technol.* 22(1):3–13
Yan S, Xu J, Zhang S, Zhu H, Qi B, Li Y. 2022. Effect of interfacial composition on the physical stability and co-oxidation of proteins and lipids in a soy protein isolate-(−)-epigallocatechin gallate conjugate emulsion. *Food Hydrocoll.* 130:107720
Zhou B, Gao S, Li X, Liang H, Li S. 2020. Antioxidant Pickering emulsions stabilised by zein/tannic acid colloidal particles with low concentration. *Int. J. Food Sci. Technol.* 55(5):1924–34
Zhou F-Z, Yan L, Yin S-W, Tang C-H, Yang X-Q. 2018. Development of Pickering emulsions stabilized by gliadin/proanthocyanidins hybrid particles (GPHPs) and the fate of lipid oxidation and digestion. *J. Agric. Food Chem.* 66:1461–71
Zou Y, Zhong J, Pan R, Wan Z, Guo J, et al. 2017. Zein/tannic acid complex nanoparticles-stabilised emulsion as a novel delivery system for controlled release of curcumin. *Int. J. Food Sci. Technol.* 52(5):1221–28

Annual Review of Food Science and Technology

Volume 14, 2023

Contents

Errata

An online log of corrections to *Annual Review of Food Science and Technology* articles may be found at http://www.annualreviews.org/errata/food