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Progress in natural emulsifiers for utilization in food emulsions

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There is growing demand in the food industry for natural ingredients to fabricate 'clean label' products. This article provides a review of recent studies on the identification, characterization, and utilization of natural food-grade emulsifiers, such as proteins, polysaccharides, phospholipids, and saponins. Particular emphasis is given to relating the structural properties of these emulsifiers to their ability to form and stabilize emulsions. The influence of environmental stresses, such as pH, ionic strength, and temperature, on the performance of natural emulsifiers is discussed. This information should facilitate the rational selection of natural emulsifiers for applications in emulsion-based food, beverage, cosmetic, and pharmaceutical products.

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Introduction

One of the most critical aspects in the formation of successful emulsion-based products is the selection of an appropriate emulsifier [1••]. Emulsifiers are surface-active substances that play two key roles in the creation of emulsions: first, they facilitate emulsion formation; second, they promote emulsion stability. In general, there are numerous kinds of synthetic and natural emulsifiers that can be utilized in the food industry, including proteins, polysaccharides, phospholipids, and surfactants [2]. Nevertheless, consumers are increasingly demanding 'clean' labels on food and beverage products, and so the food industry is trying to replace many synthetic surfactants with natural alternatives, or to formulate new products entirely from natural ingredients.

This article highlights recent research on the identification, characterization and utilization of natural emulsifiers suitable for application in the food industry, and highlights the molecular features required for their functional performance. This information should aid in the identification of new types of natural emulsifiers for use in foods and beverages.

Overview of natural food-grade emulsifiers

Proteins

Many proteins are surface active because they contain a mixture of hydrophilic and hydrophobic amino acids along their polypeptide chains [3••]. Consequently, they can adsorb to oil–water interfaces and coat the oil droplets formed during homogenization. They may also stabilize droplets from aggregation because they contain amino acids that possess negative (–COO^-) or positive (–NH_3^+) charges, and can therefore generate an electrostatic repulsion [4,5]. In addition, they may inhibit aggregation through steric repulsion by forming thick interfacial layers or by having carbohydrate moieties attached [6]. There has been considerable interest in identifying and characterizing glycoproteins that naturally have these carbohydrate moieties [7], or in attaching carbohydrate moieties to proteins, for example, by the Maillard reaction [8,9].

Currently, the most commonly used natural protein-based emulsifiers in the food industry are derived from bovine milk: caseins and whey proteins [10]. Caseins are a group of amphiphilic proteins with flexible structures (α_{s1}, α_{s2}, β, and κ-caseins), whereas whey proteins are a group of globular proteins with fairly rigid structures (α-lactalbumin, β-lactoglobulin, BSA, and immunoglobulins). Gelatins extracted from cow, pig, or fish also have flexible structures and exhibit surface activity, but they are typically not good at stabilizing emulsions [11]. One of the most interesting areas of current research is the identification of protein-based emulsifiers from plant sources [3••]. This research is largely driven by the desire to replace animal proteins in vegetarian or vegan products, as well as to improve food sustainability and security [12]. Numerous plant-based proteins have been shown to be promising emulsifiers, including pea proteins [13], lupin proteins [14], soy proteins [15•], and corn germ proteins [16]. The major challenges in this area are first, identification of economically viable protein sources; second, establishment of effective methods for protein isolation, fractionation and purification; third, characterization of emulsifier functionality in terms of emulsion formation and stability.

Polysaccharides

Most polysaccharides are highly hydrophilic molecules that are not particularly surface-active, and are therefore not good emulsifiers [17]. Instead, they tend to stabilize emulsions by increasing aqueous phase viscosity and thereby inhibiting droplet movement [1••]. These types of polysaccharides can often be made surface-active by chemically or enzymatically attaching non-polar groups or protein molecules to their hydrophilic backbones, but then the resulting emulsifier would not be considered natural. The main examples of this kind of molecule are modified starches [18•] and Maillard complexes of proteins and carbohydrates [19•].

Some natural polysaccharides have good emulsifying properties because they already have non-polar groups or proteins attached to their hydrophilic carbohydrate chains [17]. The most common examples of this type of surface-active polysaccharide are gum arabic, pectin, and galactomannans. Currently, gum arabic is by far the most widely used natural polysaccharide-based emulsifier in the food industry [20], particularly in beverage emulsions [21•]. However, the major disadvantage of gum arabic is that a relatively high emulsifier-to-oil ratio ($\approx$1:1) is required to form stable emulsions [22•,23•]. Recent studies have shown that citrus pectins can also be used as emulsifiers, with their efficacy at forming and stabilizing emulsions depending on their molecular weight and degree of methoxylation [24]. Other studies have shown that polysaccharides isolated from basil seed were good emulsifiers, with the surface activity being attributed to the presence of protein moieties and non-polar groups on the carbohydrate backbone [25]. Corn fiber gum has also been shown to have good emulsifying properties also attributed to the presence of protein moieties [26,27]. As with proteins, there is need for more research on identifying, isolating, and characterizing the properties of polysaccharide-based emulsifiers from natural sources in an economic manner [28].

Phospholipids

Phospholipids are natural amphiphilic molecules found in the cell membranes of animal, plant, and microbial species [29]. These phospholipids can be isolated, purified, and utilized as surface-active ingredients in the food industry, where they are typically referred to as lecithin [2]. The lecithin used in the food industry is usually extracted from soybeans, egg yolk, milk, sunflower kernels, or rapeseeds [30•]. Lecithin ingredients are typically mixtures of different phospholipids, with the most common being phosphatidylcholine (PC), phosphatidylethanolamine (PE) and phosphatidylinositol (PI). Phospholipids are surface active because they have hydrophobic fatty acid tail groups and hydrophilic head groups containing phosphoric acid esterified with glycerol and other substitutes [2,30•]. Despite being surface-active, phospholipids are often not good emulsifiers because they form interfacial layers that are prone to coalescence [31]. Nevertheless, certain types of lecithin do appear to be effective at forming and stabilizing emulsions depending on the blend of phospholipids they contain [30•]. Lecithin may also be used in combination with other natural emulsifiers to form emulsions, for example, proteins [32]. Research on the emulsification properties of lecithin is likely to continue as fractions with more well-defined and novel phospholipid blends are introduced commercially.

Saponins

Saponins are water-soluble small amphiphilic molecules that can be isolated from various natural sources [33]. The surface activity of saponins is due to the fact they contain hydrophilic sugar groups attached to non-polar agylcone groups. Recently, a food-grade ingredient (Q-Naturale, Ingredion) has become commercially available that consists of saponins isolated from the bark of the *Quillaja saponaria* tree [34]. These quiillaja saponins have been shown to be particularly effective at forming emulsions with small droplets that are stable to a wide range of environmental stresses [35,36], and are therefore likely to find increasing use in the food industry.

Emulsion formation

Factors affecting emulsion formation

An effective emulsifier must have a number of physicochemical characteristics if it is going to be effective at forming small droplets during homogenization [1••]:

(i) *Surface-activity*: Emulsifiers must be capable of adsorbing to oil-water interfaces, which means that they must have an appropriate ratio of polar and non-polar groups on their surfaces.
(ii) *Adsorption kinetics*: Emulsifiers must rapidly adsorb to droplet surfaces during homogenization so they can quickly reduce the interfacial tension and prevent droplet aggregation.
(iii) *Interfacial tension reduction*. Adsorbed emulsifiers should effectively decrease interfacial tension as this facilities droplet disruption within homogenizers.
(iv) *Stabilization:* Adsorbed emulsifiers should protect droplets from aggregating during droplet–droplet encounters by generating strong repulsive interactions, such as steric or electrostatic repulsion.
(v) *Surface coverage:* The amount of emulsifier required to stabilize an emulsion depends on the surface load, which is the mass of emulsifier per unit surface area at saturation. The higher the surface load, the more emulsifier required to stabilize a given emulsion.

Natural emulsifiers vary considerably in the above characteristics, which means that there are large differences in their ability to form emulsions.