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Oat bran extract (*Avena sativa* L.) from food by-product streams as new natural emulsifier

Theo Ralla [a], Hanna Salminen [a], Matthias Edelmann [b], Corinna Dawid [b], Thomas Hofmann [b], Jochen Weiss [a, *]

[a] Department of Food Physics and Meat Science, University of Hohenheim, Garbenstrasse 21/25, 70599 Stuttgart, Germany
[b] Chair of Food Chemistry and Molecular Sensory Science, Technical University of Munich, Lise-Meitner-Strasse 34, 85354 Freising, Germany

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ABSTRACT

Natural emulsifiers have become of increasing interest within the food and beverage industry. Oat bran is a natural side-stream product produced during oat refinement that may be used to obtain amphiphilic extracts. Our hypothesis was that the oat bran extract is rich in surface-active and amphiphilic oat saponins and proteins that can form and stabilize emulsions. For this, we examined the surface activity of oat bran extract at oil-water and air-water interfaces, its ability to form oil-in-water emulsions and their stability against various stress tests. The highly surface-active oat bran extract acted as an ionic emulsifier, forming highly negatively charged submicron-sized emulsion droplets. These emulsions were stable over a wide range of pH (4–9), heat treatment (≤50 °C), and during storage at ≤25 °C up to 42 days. However, the emulsions showed instability at pH 2–3, at high ionic strengths, and during freeze-thawing. The formation and stability of the emulsions is related to interfaces containing oat saponins or oat saponin-protein complexes rather than a protein layer. These findings show that oat bran extract is a highly promising natural emulsifier, providing the food and beverage industry with a viable substitute to traditional emulsifiers.

1. Introduction

Emulsion based food and beverage products are thermodynamically unstable systems that tend to separate into the immiscible phases over time. This inevitable change in spatial distribution can be prolonged by the addition of emulsifiers, typically of synthetic origin. However, 'natural' products that are free of synthetic food additives have aroused increasing interest among consumers (McClements & Gumus, 2016). So far, typical food-grade 'natural' emulsifiers include proteins from plants, (e.g., pea, sunflower) (González-Pérez, Vereijken, Merck, Gruppen, & Voragen, 2005; Liang & Tang, 2014) and animals (e.g., whey) (Demetriades, Coupland, & McClements, 1997), polysaccharides (e.g., pectin, guar gum) (Huang, Kakuda, & Cui, 2001; Leroux, Langendorff, Schick, Vaishnav, & Mazoyer, 2003), and phospholipids (e.g., soy, egg) (Rydhag & Wilton, 1981; Schuh, Bruxel, & Teixeira, 2014). Most of these traditional emulsifiers have been shown to be effective, however, they also have limitations in their techno-functional and physicochemical performance upon changes in pH, ionic strength, and temperature (Kralova & Sjöblom, 2009; Lam & Nickerson, 2013; McClements & Gumus, 2016). For example, protein (whey protein isolate) stabilized emulsions are unstable at pH close to their pI due to them losing their charge, as well as at high temperature where denaturation may occur (McClements, 2004; McClements, Bai, & Chung, 2017). In contrast, polysaccharide (beet pectin) stabilized emulsions are typically stable at varying pH, ionic strength and temperature conditions due to them mainly providing steric repulsion forces after anchoring of protein moieties at interfaces (Bai, Huan, Li, & McClements, 2017; Qian, Decker, Xiao, & McClements, 2011). However there, emulsion stabilization for polysaccharides requires a rather high emulsifier-to-oil ratio (1:1), i.e. 10% polysaccharides are required to stabilize 10% oil-in-water emulsions. Finally, phospholipid (soy lecithin) stabilized emulsions are unstable under highly acidic conditions or at high ionic strengths and temperatures because they form only thin interfaces with low steric repulsion capabilities (Ozturk & McClements, 2016). However, these statements should only be seen as a rough estimate as the performance of emulsifiers highly depend on intrinsic and

* Corresponding author.
E-mail address: j.weiss@uni-hohenheim.de (J. Weiss).

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extrinsic factors such as composition as well as pH, ionic strength, and temperature.

Another recently investigated 'natural' group of bioemulsifiers is the group of amphiphilic saponins that can be extracted from a variety of different plants such as *Quillaja*, sugar beets, and asparagus (Dawid & Hofmann, 2012; Waller & Yamasaki, 1996a, 1996b; Yoshikawa, Murakami, Kadoya, Yamahara, & Matsuda, 1996). These low-molecular weight secondary plant metabolites consist of polar sugar moieties attached to a nonpolar triterpene or steroid backbone, making these amphiphilic molecules highly surface-active (Mitra & Dungan, 1997, 2000). Earlier studies have mostly focused on extracts obtained from *Quillaja saponaria* trees (Yang, Leser, Sher, & McClements, 2013), whereas the latest studies reveal that extracts obtained from other plant sources such as sugar beets and ginseng also show promising techno-functional properties (Ralla et al., 2017a, 2017b, 2017d). Nevertheless, economic (e.g. high price), ecological (e.g. a questionable sustainability because of the increasingly occurring deforestation), and sensory (e.g. an astringent, bitter taste) reasons require that alternative sources for *Quillaja* saponins are found and developed. A potential solution is to exploit common plant-based food by-product streams that are available in abundance, and that currently are not used in other value-added processes. Thereby, a suitable fractionation process could yield extracts that could become valuable and viable alternatives to *Quillaja* saponins.

Oat (*Avena sativa* L.) is one of the main cereal grains with an annual global production quantity of ca. 22 million tons (FAO, 2014), that is mainly used for food and livestock feed (Peterson, 1992). Oat bran is a common by-product of milling oat, which makes up about 50% of the whole grain (based on dry matter content) and is considered to be healthy because of the presence of β-glucans, which exhibit cholesterol-lowering effects (Whitehead, Beck, Tosh, & Wolever, 2014). Oat contains considerable amounts of triterpene saponins such as the monodesmosidic avenacin A1 as well as A2 (Fig. 1a) and steroid saponins such as the bidesmosidic avenacoside A (Fig. 1b) (Oenning, Asp, & Sivik, 1993; Osbourn, 2003; Pecio, Wawrzyniak-Szolkowska, Oleszek, & Stochmal, 2013). In addition, oat contains proteins such as globulins and α- and β-polypeptides that account for ~80% of the total protein content as well as albumins, prolamins, and glutelins (Klose & Arendt, 2012; Ma & Harwalkar, 1984). Consequently, we hypothesized that oat bran extract containing surface-active saponins and proteins may be used as natural emulsifier.

For this purpose, we first extracted and characterized the resulting oat bran extract for its composition and interfacial properties. Second, we investigated the emulsion forming properties of the oat bran extract by generating oil-in-water emulsions at different extract concentrations through high-pressure homogenization at different homogenization pressures. Third, we studied the influence of external stresses (pH, ionic strength, temperature, freeze-thaw, and storage time) on the stability of the generated oil-in-water emulsions.

2. Materials and methods

2.1. Materials

Oat bran (*Avena sativa* L.) was obtained from SchapfenMühle GmbH & Co. KG (Ulm, Germany), Antersdofer Mühle GmbH & Co Vertriebs KG (Simbach am Inn, Germany), and Peter Kölln GmbH & Co. KGaA (Elmshorn, Germany). Medium chain triglyceride oil (Miglyol 812N) was purchased from Cremer Oleo GmbH & Co. KG (Hamburg, Germany). Methanol was purchased from J.T. Baker (Deventer, Netherlands), whereas *n*-pentane (analytical reagent) was obtained from VWR International GmbH (Ismaning, Germany). Water for the oat bran extraction was obtained from a Milli-Q Advantage A10 Water Purification System (Millipore S.A.S, Molsheim, France). Dowex 66 free base, Dowex 50WX4 hydrogen form, sodium phosphate monobasic monohydrate (≥99.0%) and sodium phosphate dibasic (≥99.0%) were obtained from Sigma-Aldrich GmbH (Steinheim, Germany). Carrez I and II solutions, hydrochloric acid, and sodium hydroxide (≥98.0%) and round filter paper, type 111A, Ø 110 mm, were purchased from Carl Roth GmbH & Co. KG (Karlsruhe, Germany). Deionized water from an ELGA LabWater system (PurLab Classic, Bucks, UK) was used for sample preparation throughout the study.

2.2. Solvent extraction

A portion of oat bran (*Avena sativa* L., 100 g) was defatted three times with distilled *n*-pentane (140 mL) at room temperature while stirring for 30 min. After centrifugation (10 min at 10,000 rpm, Avanti J-E, Beckman Coulter GmbH, Krefeld, Germany) and decantation, the residual oat bran was first extracted three times with methanol (340 mL each), and then three times with a mixture of methanol and water (70/30, v/v, 340 mL each) upon stirring for 30 min. The methanol and methanol/water extracts were combined and filtrated by means of a Buechner funnel lined with filter paper (Carl Roth, Germany, 111A, Ø 110 mm). After filtration, the combined filtrates were separated from methanol in vacuum at 40 °C, followed by freeze-drying (yield: 4.2 g/100 g) and stored at −20 °C until they were used. No additional preservatives were added.

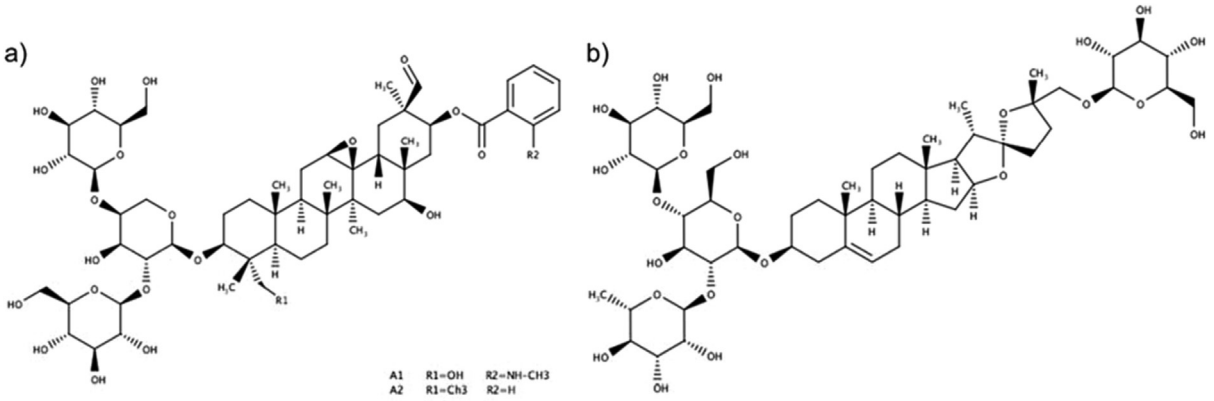

Fig. 1. Chemical structures of saponins found in oat bran: Avenacin A1 and A2 (a) as well as Avenacoside A (b). The presented structures are based on those presented by Osbourn (2003) and Pecio et al. (2012).