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Antioxidative effect of lipophilized caffeic acid in fish oil enriched mayonnaise and milk

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ABSTRACT

The antioxidative effect of lipophilized caffeic acid was assessed in two different fish oil enriched food products: mayonnaise and milk. In both emulsion systems, caffeic acid esterified with fatty alcohols of different chain lengths (C1–C20) were better antioxidants than the original phenolic compound. The optimal chain length with respect to protection against oxidation was, however, different for the two food systems. Fish oil enriched mayonnaise with caffeates of medium alkyl chain length (butyl, octyl and dodecyl) added resulted in a better oxidative stability than caffeates with shorter (methyl) or longer (octadecyl) alkyl chains. Whereas in fish oil enriched milk emulsions the most effective caffeates were those with shorter alkyl chains (methyl and butyl) rather than the ones with medium and long chains (octyl, dodecyl, hexadecyl and eicosyl). These results demonstrate that there might be an optimum alkyl chain length for each phenolipid in each type of emulsion systems.

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1. Introduction

In the last years, several studies have aimed at enriching food products with $n-3$ polyunsaturated fatty acids (PUFA) of marine origin (Jacobsen, Let, Nielsen, & Meyer, 2008) due to the low intake of $n-3$ PUFA's in the industrialised world and their known nutritional benefits. However, unsaturated $n-3$ PUFA's are highly susceptible to oxidation, leading to the development of unhealthy free radicals, reactive aldehydes, and off-flavours with a consequent decrease in the shelf life of the enriched product (Jacobsen et al., 2008; Let, Jacobsen, Sørensen, & Meyer, 2007). In order to tackle this problem different strategies such as antioxidant addition are necessary.

Food products are complex systems containing different phases and constituents (air, water, lipids, proteins, etc.). Heterophasic food systems, such as milk and mayonnaise, are widely consumed. Milk and mayonnaise are oil-in-water (o/w) emulsions, which are composed of three phases: oil phase, water phase and an interface between the oil and water phases. The effectiveness of an antioxidant is highly influenced by its interactions with other components (i.e. emulsifier) and its ability to be located in the environment where lipid oxidation takes place. This is known to be at the interface i.e. between the oil and water phases (Coupland & McClements, 1996). In this regard, the so-called polar paradox theory states that lipophilic antioxidants are more effective in oil-in-water emulsions than hydrophilic antioxidants, whereas hydrophilic antioxidants are more effective in oils (Porter, 1993). Based on this theory, phenolic compounds such as caffeic acid, should work better in bulk oils than in emulsions. The lipophilization of phenolic compounds with different alkyl chain lengths will reduce their polarity and thus change their distribution between the different phases in the emulsion. Hence, lipophilization is expected to improve the antioxidant efficacy of polar phenolic compounds.

However, recently several publications have shown that the polar paradox does not accurately predict the behaviour of antioxidants and therefore the polar paradox hypothesis needs to be revisited (Laguerre, López Giraldo, Lecomte, Baréa, et al., 2009, et al., 2010; Panya et al., 2012; Sørensen et al., 2012). Laguerre et al. (2009) evaluated the antioxidant capacity of different chlorogenate esters in a stripped tung o/w emulsion stabilized with Brij 35 (CAT assay). A non-linear tendency of the antioxidant capacity was observed. These authors reported an increased antioxidative

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effect with increasing alkyl chain length up to 12 carbon atoms, whereas further increments in the alkyl chain length led to a collapse in the antioxidant effectiveness. This observation was termed "the cut-off effect" by these authors. The same non-linear tendency was observed with lipophilized rosmarinates; however, for this lipophilized phenolic the maximal antioxidant capacity was obtained with octyl rosmarinate (Laguerre et al., 2010). Later on, Panya et al. (2012) studied the antioxidant efficiency of a homologous series of rosmarinate alkyl esters (C4, C8, C12, C18 and C20) in Tween 20-stabilized stripped soybean o/w emulsion in a storage experiment. In their study, the rosmarinates with shorter fatty alkyl chains (C4, C8 and C12) were much better antioxidants than rosmarinic acid and its octadecyl (C18) and eicosyl (C20) esters.

It is important to note, that several studies have been published assessing different esterified phenolic compounds in simple o/w emulsions. However less attention has been paid to their effectiveness in real food matrices. Sørensen et al. (2012) studied the effect of lipophilized rutin and dihydrocaffeic acid in fish oil enriched milk by comparing the native phenolic compounds with medium and long alkyl chain esters. The lipophilized esters evaluated were rutin laurate, rutin palmitate, octyl dihydrocaffeate and oleyl dihydrocaffeate. It was concluded that for both types of compounds, the medium chain esters were better antioxidants than the long chain esters and the non-lipophilized phenolics. Besides, they pointed out the necessity of further studies in order to understand the antioxidant capacity of the lipophilized compounds regarding their chain length esterified to the phenolic compound and the type of food emulsion system.

Therefore, the aim of the present study was to evaluate the antioxidant effect of caffeic acid and its esters (caffeates) in fish oil enriched mayonnaise and milk emulsions. In mayonnaise caffeic acid and caffeates C1–C18 and in milk caffeic acid and caffeates C1–C20 were evaluated as antioxidants during storage.

2. Materials and methods

2.1. Materials

Rapeseed oil and fish oil were supplied by Maritex A/S a subsidiary of TINE, BA (Sortland, Norway). Rapeseed oil, used in the mayonnaise preparation, had a peroxide value (PV) of 0.3 meq peroxides/kg oil and a tocopherol content of 205 mg α-tocopherol/kg, 68 mg β-tocopherol/kg and 292 mg γ-tocopherol/kg. Finally, the fatty acid composition was as follows: 16:0, 4.5%; 18:0, 1.5%; 18:1$n-9$, 57.2%; 18:1$n-7$, 2.5%; 18:2$n-6$, 20.1% and 18:3$n-3$, 10.2%.

The fish oil, used in both milk and mayonnaise productions, had a PV of 0.3 meq peroxides/kg oil and tocopherol content of 249 mg α-tocopherol/kg, 98 mg γ-tocopherol/kg and 47 mg δ-tocopherol/kg. The fatty acid composition was as follows: 14:0, 3.5%; 16:0, 9.9%; 16:1$n-7$, 8.8%; 18:0, 2.0%; 18:1$n-9$, 16.3%; 18:1$n-7$, 4.9%; 18:2$n-6$, 1,8%, 18:3$n-3$, 2.6%, 18:4$n-3$, 2.6%, 20:1$n-7$, 12.6%; 20:5$n-3$ (EPA), 9.16%; 22:1$n-9$, 5.8%, 22:5$n-3$, 1.1% and 22:6$n-3$ (DHA) 11.1%. The total percentages of $n-3$ and $n-6$ PUFA in this oil were 24.0% and 1.8%, respectively.

Potassium sorbate used was purchased from Merck (Dramstadt, Germany). Grindsted FF DC stabilizer (guar gum and sodium alginate) was donated by Dupont, Danisco Ingredients (Brabrand, Denmark). Fresh milk (0.5% and 1.5% fat content), salt (sodium chloride), sugar, lemon juice, estragon vinegar and egg yolk were purchased in a local market.

Caffeates were synthesized in an acid catalyzed reaction (sulphuric acid) with caffeic acid and fatty alcohols as described elsewhere (Sørensen et al., 2014). Caffeic acid and fatty alcohols were purchased from Sigma Aldrich (Steinheim, Germany).

All other chemicals used were of HPLC grade and purchased from Lab-scan (Dublin, Ireland). The external standards used for the identification and quantification of the secondary oxidation compounds were from Sigma Aldrich.

2.2. Experimental design and production of mayonnaise and milk

Fish oil enriched mayonnaise and milk were produced according to the experimental design in Table 1. Caffeic acid and lipophilized derivatives of caffeic acid (caffeates) were assessed as antioxidants in fish oil enriched mayonnaise and milk. In the mayonnaise experiment, the different caffeates selected were: methyl, butyl, octyl, dodecyl and octadecyl caffeates, and in the milk experiment, the selected caffeates were: methyl, butyl, octyl, dodecyl, hexadecyl and eicosyl caffeates.

All antioxidants were tested at 100 μM. To evaluate the effect of antioxidant concentration in mayonnaise, one additional treatment was included; octyl caffeate added at 200 μM. Octyl caffeate was selected based on earlier results in o/w emulsion (CAT assay), where this ester was most efficient (Sørensen et al., 2013).

Mayonnaise batches of 500 g were prepared under vacuum using a Stephan Universal mixer (Stephan UMC5, Hameln, Germany). The production of mayonnaises at these conditions assures physical stable emulsions as has been probed in previous studies (Jacobsen, Adler-Nissen, & Meyer, 1999; Let et al., 2007). Each batch contained by weight 64% rapeseed oil, 16% fish oil, 9.25% water, 4% estragon vinegar, 4% egg yolk, 1.2% lemon juice, 1.0% sugar, 0.3% salt (sodium chloride), 0.15% Grindsted FF DC and 0.1% potassium sorbate. All antioxidants were dissolved in 1 mL methanol and thereafter added in the water phase before mayonnaise production to give a final concentration of 100 μM and for mayonnaise with octyl caffeate also 200 μM. In the mayonnaise without antioxidant (Mayo_CONTROL), 1 mL methanol was added.

Mayonnaises were stored in 100 mL brown bottles, at 20 °C for 4 weeks in darkness. Samples were taken at day 0, 3, 6, 9, 12, 15, 21 and 28 and subdivided into 50 mL brown bottles, flushed with N_2 and stored at −40 °C until analyses.

Milks with 0.5% and 1.5% fat were mixed (1:1, w/w) to obtain a total fat content of 1%. Subsequently, the milk was heated to 72 °C for 15 s and the fish oil (0.5%, w/w) and the antioxidant were added. This mixture was then homogenised using a two valve table homogenizer from GEA Niro Soavi Spa (Parma, Italy). The pressure was set at 250 bar with four circulations of the emulsion. Using these conditions, stable milk emulsions are achieved as has been

Table 1
Experimental design.

Antioxidant applied	Sample code	Concentration (μM)
Mayonnaise experiment		
Control	Mayo_CONTROL	–
Caffeic acid	Mayo _CA	100
Methyl caffeate	Mayo _CAC1	100
Butyl caffeate	Mayo _CAC4	100
Octyl caffeate	Mayo _CAC8	100
Octyl caffeate	Mayo _CAC8 200	200
Dodecyl caffeate	Mayo _CAC12	100
Octadecyl caffeate	Mayo _CAC18	100
Milk experiment		
Control	Milk_CONTROL	–
Caffeic acid	Milk _CA	100
Methyl caffeate	Milk _CAC1	100
Butyl caffeate	Milk _CAC4	100
Octyl caffeate	Milk _CAC8	100
Dodecyl caffeate	Milk _CAC12	100
Hexadecyl caffeate	Milk _CAC16	100
Eicosyl caffeate	Milk _CAC20	100

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