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Nano-encapsulation competitiveness of omega-3 fatty acids and correlations of thermal analysis and Karl Fischer water titration for European anchovy (*Engraulis encrasicolus* L.) oil/β-cyclodextrin complexes

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ABSTRACT

European anchovy (*Engraulis encrasicolus* L.) is one of the most important oily fish that provide valuable omega-3 containing fish oil. The aim of the study was to protect the labile fatty acids from anchovy oil by β-cyclodextrin complexation. The competitiveness to molecular encapsulation of anchovy oil components were also studied.

Anchovy oil/β-cyclodextrin complexes at molar ratios of 1:1 and 1:3 were obtained by crystallization and kneading methods with very good recovering yields (74–78% and 85–99%, respectively). The most concentrated fatty acids in the raw anchovy oil were PUFAs at a relative concentration of 65.5 g/100 g. Higher content of EPA and DHA of 28.2 and 22.3 g/100 g had determined. Molecular encapsulation competitiveness conduct to a decrease of the PUFAs (even by five to seven times for EPA and DHA) and a significant increase of saturated fatty acids in complexes. Thermogravimetry and differential scanning calorimetry parameters well correlate with Karl Fischer titration parameters. They also supports the formation of inclusion compound by means of lowering the water content that is replaced by anchovy oil components. As a conclusion, valuable anchovy oil/β-cyclodextrin complexes as well as omega-3 concentrated anchovy oil (non-encapsulated "residue") can be obtained in one step for food applications.
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1. Introduction

Fish oils in general, and European anchovy (*Engraulis encrasicolus* L.) oil especially, are a cheap and valuable essential fatty acids source, both omega-3 and omega-6 fatty acids (Boran, Boran, & Karaçam, 2008; Kaya & Turan, 2008). The main omega-3 fatty acids, named (all-*Z*)-5,8,11,14,17-eicosapentaenoic acid, EPA and (all-*Z*)-docosa-4,7,10,13,16,19-hexaenoic acid, DHA are very important in human health. EPA is present in the grey matter from brain while DHA is contained by the nerve tissue. As a consequence, they are related to brain and cardiovascular functions and have implications in the treatment of many neuronal and cardiovascular diseases (He, 2009). EPA and DHA (as glycerides) are the most important fatty acids in anchovy oil. Their content varies in a large range, depending on the season and place of growing (Boran et al., 2008; Zlatanos & Laskaridis, 2007). According to Zlatanos and Laskaridis (2007) these variations are in the range of 2.5–12.4 g/100 g for EPA and 12.2–32.5 g/100 g for DHA. The higher content was determined in spring for both omega-3 fatty acids. Monounsaturated fatty acids (MUFAs) are also important in anchovy oil

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(especially oleic acid), as well as other polyunsaturated fatty acids (PUFAs) such as linoleic and linolenic acids (Kaya & Turan, 2008). Palmitic acid is the most concentrated saturated fatty acid (SFA) in anchovy oil (Üstün, Güner, Arer, Türkay, & Erciyes, 1997).

The presence of higher content of PUFAs in fish oils conduct to a higher susceptibility to lipid oxidation (Gokoglu, Topuz, & Yerlikaya, 2009; Huang & Weng, 1998). Oxidation of fatty acids involves radical reactions and conduct to harmful free radicals as well as disagreeable odoriferous compounds (e.g. propanal, hexanal, (*E*,*Z*)-2,4-heptadienal, 1-penten-3-one and 1-penten-3-ol having rancid, metallic, green, and burnt sensory attributes (Serfert, Drusch, & Schwarz, 2010)). The oxidation rate of PUFAs increases by several thousand times in comparison with SFAs (Belitz, Grosch, & Schieberle, 2009). Various conditions such as light, the presence of heavy metal ions, or some proteins and enzymes (e.g. heme proteins and superoxide radical anion-generating enzymes) can enhance the initiation and oxidation rate of MUFAs and PUFAs (Carvajal, Mozuraityte, Standal, Storrø, & Aursand, 2014; Walker, Decker, & McClements, 2015). Studies related to the stability and degradation of various fish oils had performed (for example on anchovy oil by means of unsaponificable matter, peroxide, acid, ester, and thiobarbituric acid values (Boran et al., 2008), on red and pink salmon oil by means of peroxide and free fatty acid values (Bower, Hietala, Oliveira, & Wu, 2009; Huang & Weng, 1998)).

In order to reduce the oxidation level of lipids and to enhance the bioactive properties of compounds, nano-encapsulation methods are widely used. Various shell material can be used. Natural (such as unsaturated soy phosphatidyl choline liposomes (Frenzel & Steffen-Heins, 2015), soybean soluble polysaccharide and maltodextrin (Anwar & Kunz, 2011), fucoidan (Chang & McClements, 2015), sardine and horse mackerel protein hydrolysates (Morales-Medina, Tamm, Guadix, Guadix, & Drusch, 2016), culled banana resistant starch-soy protein isolate (Nasrin & Anal, 2015) and even yeast cells (Czerniak, Kubiak, Białas, & Jankowski, 2015)) and semi-synthetically modified polymers (e.g. *N*-stearoyl *O*-butylglyceryl- or *N*-lauroyl-chitosan (Chatterjee & Judeh, 2015, 2016), methylcellulose in combination with maltodextrin and Arabic gum (Tirgar, Jinap, Zaidul, & Mirhosseini, 2015)) were used for nano-encapsulation of fish oils. Emulsifying of fish oils can also improve the physical and oxidative stability of unsaturated fatty acid glycerides (Walker et al., 2015; Zhang et al., 2015).

Among these shell materials, naturally or chemically modified cyclodextrins (CDs) are often used for molecular encapsulation of bioactive compounds (Giordano, Gazzaniga, Bettinetti, & Manna, 1990; Hırayama & Uekama, 1999; Santos, Kamimura, Hill, & Gomes, 2015; Szejtli, 1988). They are cyclic oligosaccharides with architecture such as truncated cone having hydrophilic exterior and hydrophobic inner cavities (Loftsson & Duchêne, 2007). These structures are capable to molecular encapsulate geometrically compatible and mostly hydrophobic compounds. CDs are extensively used in medicine and food fields (Astakhova & Demina, 2004; Hunt, Tonelli, & Balik, 2008; Sliwa & Girek, 2005). Powdery formulations with higher water solubility, protecting capacity, and controlled release properties could be obtained (Avcı & Dönmez, 2010; Marques, 2010). As a result, it is possible to obtain more stable, useful and healthy fish oils using cyclodextrins. Fatty acids from fish oils possess thin and hydrophobic moieties (Kaya & Turan, 2010; Üstün et al., 1997), which could be proper molecular encapsulated in cyclodextrins (Choi, Ruktanonchai, Min, Chun, & Soottitantawat, 2010; Choi, Ruktanonchai, Soottitantawat, & Min, 2009). No literature data on anchovy oil/cyclodextrin complexation with enhanced oxidative stability was found.

The aim of the study was to evaluate the β-cyclodextrin complexation behaviour of anchovy oil in order to enhance the oxidative stability of omega-3 containing fatty acid glycerides. Furthermore, the competitiveness of anchovy oil components to β-cyclodextrin molecular encapsulation and possible applications of nano-encapsulated and "residual" (non-encapsulated) anchovy oils in food and pharmaceutical fields were also evaluated.

2. Materials and method

2.1. Materials

European anchovy (*E. encrasicolus* L.) was used as research material. This material was supplied from Samsun, Turkey, Black Sea region of local fish markets in spring of the year 2014. The cold chain was provided by the Fisheries Processing laboratory from the Faculty of Fisheries (Akdeniz University) without delay. In this study a total amount of anchovies of 12 kg were used. The following reagents have been used: hexane (GC grade, Sigma–Aldrich), Supelco™ 37 Component FAME mix (Sigma–Aldrich), anhydrous sodium sulphate (*p.a.*, Merck & Co.), C_8–C_{20} alkane standard solution (Fluka Chemie AG), β-cyclodextrin hydrate (>98%, CycloLab, Budapest, Hungary), ethanol 96 mL/100 mL solution (Chimopar, Bucharest, Romania), Hydranal®-Titrant 5, Hydranal®-Solvent and Hydranal®-Water Standard 10.0 (Sigma–Aldrich, Buchs, Switzerland).

2.2. Fish oil extraction

Oil extraction was made by pressing method (with cooking). Fish was boiled at a temperature of 100 °C for approximately 20 min. The fish:water ratio was 1:2. The boiled fish was cooled, filtered, the solid portion or raw fish was pressed in the strainer pressing tool and whole raw oil was separated from aqueous layer. The raw oil was centrifuged for 20 min at 9600× *g*, at 4 °C for the separation of oil. Crude oil, based on upper aggregated from centrifuge tubes were collected in the vacuum liners (350 g of oil) (Rubio-Rodríguez, Jaime, de Diego, Sanz, & Carballido, 2010).

2.3. Obtaining of anchovy oil/β-cyclodextrin complexes

The anchovy oil/β-cyclodextrin complexes have been obtained using two different methods: (1) controlled crystallization of the complex from ethanol–water mixture, and (2) kneading method. Two fish oil:β-cyclodextrin molar ratios of 1:1 and 1:3 have been used (~887 g/mol mean molar mass for fish oil (Kaya & Turan, 2010) and 1314 g/mol for β-cyclodextrin hydrate (Hădărugă, Hădărugă, Bandur, & Isengard, 2012; Hădărugă, Hădărugă, & Isengard, 2012, 2013; Isengard & Heinze, 2003)).

Crystallisation from ethanol–water mixture have been performed in double walled 20 mL glass reactors, equipped with reflux condenser and dropping funnel. One or three mmol of β-cyclodextrin were suspended in 12 mL of distilled water and heated at 50 °C using a Julabo ED heating immersion circulator (Labortechnik GmbH, Germany) under vigorously magnetically stirring. The dropping funnel that was attached to the top of the reflux condenser have been filled with 4 mL ethanolic solution containing one mmol of anchovy oil and slowly added to the β-cyclodextrin suspension at 50 °C during 15 min under magnetically stirring. The complexation process was perfected at the same temperature for another 30 min. The temperature was then decreased to the room temperature in about three hours (cooling rate 8 °C/h). The crystallisation of the complex was perfected at 4 °C over night. Anchovy oil/β-cyclodextrin complex crystals were then filtered under vacuum, washed with 2 mL of ethanol, dried at room temperature in a desiccator using molecular sieves as drying agent, and stored at 4 °C. All fish oil/β-cyclodextrin complexes were obtained in duplicate.

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