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Moisture evaluation of β-cyclodextrin/fish oils complexes by thermal analyses: A data review on common barbel (*Barbus barbus* L.), Pontic shad (*Alosa immaculata* Bennett), European wels catfish (*Silurus glanis* L.), and common bleak (*Alburnus alburnus* L.) living in Danube river

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ABSTRACT

The moisture content of β-cyclodextrin/Danube fish oils complexes (common barbel, Pontic shad, European wels catfish, common bleak) was evaluated by thermal methods. Saturated and monounsaturated fatty acids were the most concentrated in fish oils (25.3–30.8% and 36.1–45.0%). ω-3 And ω-6 fatty acids were identified in low concentrations of 2.8–12.1% and 4.1–7.1%. The moisture content was significantly lowered after β-CD complexation, as revealed by thermogravimetric (TG) analysis (13.3% for β-CD, 2.5–6.5% for complexes). These results are consistent with the differential scanning calorimetry (DSC) data for the peaks corresponding to dissociation of water (calorimetric effect of 536 J g^{-1} for β-cyclodextrin and 304–422.5 J g^{-1} for complexes). Furthermore, both TG and DSC results support the formation of inclusion complexes. This is the first study on the nanoencapsulation of Danube fish oils in β-cyclodextrin.

1. Introduction

Fish oils are valuable food products due to their high content of polyunsaturated fatty acids (PUFAs), especially of ω-3 fatty acids (FAs). Among these, (all-*Z*)-5,8,11,14,17-eicosapentaenoic acid (EPA) and (all-*Z*)-docosa-4,7,10,13,16,19-hexaenoic acid (DHA) are the most valuable ω-3 FAs in fish oils (Rubio-Rodríguez et al., 2010). They are involved in human health, being important in neuronal and cardiovascular diseases, dyslipidemias, diabetes, and even in inflammatory diseases, cancer and osteoporosis (Benatti, Peluso, Nicolai, & Calvani, 2004). Moreover, DHA influences the vasodilator mechanism and lowers the blood pressure in overweight men, more than EPA (Mori et al., 2000). Furthermore, they cannot be synthesized by humans and must be taken from diet (Singh, 2005).

There are many sources of fish oils having various ω-3 FA contents, even from natural environment (e.g. seas and oceans) or from aquaculture (Rubio-Rodríguez et al., 2010; Vasconi et al., 2015). Fish species from natural environment, having both economical and health regional impact, become important. Danube river is one of the most important source of such species in Europe. They belong to Actinopterygii class (especially to Cyprinidae, Siluridae, Clupeidae, Esocidae and Percidae families). Common barbel (*Barbus barbus* L.), Pontic shad (*Alosa immaculata* Bennett), European wels catfish (*Silurus glanis* L.), and common bleak (*Alburnus alburnus* L.) are some of the most common species that are fished in Danube river (Davodi, Esmaili-Sari, & Bahramifarr, 2011; Deutschmann et al., 2016; Hallier, Serot, & Prost, 2007; Mancini et al., 2011; Mengden, Röhner, Sudhaus, & Klein, 2015; Misir, Tufan, & Köse, 2016; Simić et al., 2016; Visnjic-Jeftic et al., 2010). Only few studies related to these species exist, some of them discussing the fatty acid profile (Hallier et al., 2007; Küçükgülmez,

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Kadak, & Celik, 2010; Mancini et al., 2011; Merdzhanova, Dobreva, & Makedonski, 2016; Misir et al., 2016). A study on fatty acid composition of common barbel roe reveals that arachidonic acid, EPA and DHA were the most abundant PUFAs (Mancini et al., 2011). Some studies on the fatty acid content of the muscle, liver, and roes of Pontic shad from the Black Sea region indicate a higher content of DHA in comparison with EPA of an average ratio of 3.5 (Misir et al., 2016). Heavy metal and trace element accumulation in Pontic shad from the Daunbe river were also evaluated (Visnjic-Jeftic et al., 2010). The fatty acid profile of lipids extracted from European wels catfish revealed a higher content of DHA comparing with EPA (Küçükgülmez et al., 2010). Common bleak was widely studied for their habitats and invasive effects, as well as for the toxic compound's content; however, no information on fatty acid composition was published (Almeida, Stefanoudis, Fletcher, Rangel, & da Silva, 2014; Deutschmann et al., 2016; Jürgens, Johnson, Jones, Hughes, & Lawlor, 2013).

The health benefit of fish oil components is well known. On the other hand, these compounds have lower stability (especially PUFAs). Furthermore, the increases of double bonds in fatty acid chain increases the susceptibility to degradation and oxidation (Hadaruga et al., 2016; Hădărugă et al., 2006) and the formation of unhealthy radicalic compounds as well as undesirable off-flavor odorants. Consequently, the protection of fish oil glycerides against degradation by oxidation or by other environmental-related processes can be performed using encapsulation. Among many methods and matrices used for fish oil encapsulation (Anwar & Kunz, 2011; Morales-Medina, Tamm, Guadix, Guadix, & Drusch, 2016), such as starch, other polysaccharides and derivatives, protein hydrolysates, by spray granulation, spray-drying or freeze-drying, cyclodextrins (CDs) are widely used (Hădărugă et al., 2016; Vestland, Jacobsen, Sande, Myrset, & Klaveness, 2015; Ünlüsayin et al., 2016). CDs are natural or semi-synthetically modified cyclic oligosaccharides having particular structure. Natural CDs comprise of six to eight α-(1→4)-linked glucopyranose units (corresponding to α-, β- and γ-CD, respectively) in a macrocyclic structure like truncated cone. Consequently, they possess many hydroxyl groups on the exterior that enhance the water solubility. On the other hand, the inner cavity of CDs is more hydrophobic and allows to molecular encapsulates geometrically compatible hydrophobic molecules or moieties (Kurkov & Loftsson, 2013). FAs and their glycerides are appropriate molecules for CD complexation (Hădărugă et al., 2006; Szente & Fenyvesi, 2017). There are various methods for CD complexation, such as cocrystallization or coprecipitation, cogrinding by slurry, dump, paste, and kneading, coevaporation, spray-drying, freeze-drying and sealed-heating (De Marco, & Reverchon, 2008; Duchêne, 2011; Hedges, 1998; Hădărugă, Hădărugă, Bandur, & Isengard, 2012; Hădărugă et al., 2016; Kfoury, Auezova, Greige-Gerges, & Fourmentin, 2015; Ünlüsayin et al., 2016). Complexation using supercritical carbon dioxide or microwave methods were also used. They are applicable at laboratory and/or industrial scale. Solid CD complexes are generally analyzed by chromatographic, thermal, spectroscopic and microscopic methods (Cabral Marques, 2010; López-Nicolás & García-Carmona, 2008; Menezes et al., 2013; Mura, 2015). These analytical methods allows confirming the formation of host-guest molecular inclusion complex. Water behavior indirectly demonstrates the formation of inclusion complexes by replacing of water molecules from the inner cavity of CD by hydrophobic guest molecules. Consequently, methods for water analysis of CD complexes (e.g., Karl Fischer water titration) have also been used (Hădărugă, Hădărugă, & Isengard, 2012; Hădărugă, Hădărugă, & Isengard, 2013; Hădărugă, Hădărugă, Bandur, et al., 2012). CD complexation of fish oil glycerides and FAs provides powdery complexes having enhanced water solubility and reduced olfactory properties, enhanced thermal and oxidative stability, as well as controlled release properties (Szejtli & Szente, 2005; Szente & Fenyvesi, 2017).

The goal of this first study on β-CD/Danube fish oils complexation was to evaluate the complex formation through the behavior of water/moisture molecules, determined by thermal analyses, named thermogravimetry (TG) and differential scanning calorimetry (DSC). Moreover, the influence of FAs profile on the moisture content of β-CD/fish oils complexes was also evaluated.

2. Materials and methods

2.1. Fish samples and oils extraction

Four fish species living in Danube river were selected for the study: common barbel, *Barbus barbus* L. (code "Brb", length 30 cm, weight 1480 g; mean values for five fish samples), Pontic shad, *Alosa immaculata* Bennett (code "Psh", length 18 cm, weight 360 g; mean values for six fish samples), European wels catfish, *Silurus glanis* L. (code "Ewc", length 50 cm, weight 3766 g; mean values for two fish samples), and common bleak, *Alburnus alburnus* L. (code "Blk", length 7 cm, weight 9.7 g; mean values for one hundred fish samples). All fish samples were fished out (September 2015 for "Brb" and "Psh", March–April 2016 for "Ewc" and "Blk") from the Danube river, Mehedinţi County, Romania, transported and handled using proper equipment (suitable tanks with clean water that met the temperature and dissolved oxygen parameters) in order to avoid stress and physical damage, the welfare being maintained. The managing of fish samples were carried out according to EU legal frameworks on the protection of animals (Council Regulation (EC) N° 1099/2009 of 24 September 2009 on the protection of animals at the time of killing and Directive 2010/63/EU of the European Parliament and of the Council of 22 September 2010 on the protection of animals used for scientific purposes, which allows manual percussive stunning by a hand-held wood club for minimizing the pre-slaughter stress, spared any avoidable pain, distress or suffering during the corresponding operations, and causing an immediate loss of consciousness that lasts until death by bleeding; however, fishes were kept in fresh water until the stunning process). The fish slaughtering was according to the Regulations (EC) N° 853/2004 and N° 854/2004 of the European Parliament and of the Council of 29 April 2004 laying down specific hygiene rules for on the hygiene of foodstuffs, and for the organization of official controls on products of animal origin intended for human consumption, as well as the Commission Regulation (EC) N° 889/2008 of 5 September 2008 laying down detailed rules for the implementation of Council Regulation (EC) N° 834/2007 on organic production and labelling of organic products with regard to organic production, labelling and control. Fish muscle samples was immediately separated after stunning/killing process in an appropriate space, temperature and light conditions, avoiding contamination and degradation. The whole fish muscle samples were frozen until the fish oil separation. At least duplicates fish oil samples were obtained by heating-pressing method. Thus, fish muscle was manually separated and grounded in a mortar. Fish muscle sample of 900–2500 g, corresponding to the fish muscle:distilled water ratio of 1:2, were heated at 110 °C (pressure of ~0.15–0.16 MPa) for 90 min in a 6 L aluminum pressure cooker (Tefal Classic 6L, Rumilly, Haute-Savoie, France). After cooling, the mixture was filtered at normal pressure and the fish muscle was pressed using a strainer-pressing equipment (Naumann NM-120, SC SFR Home Equipment SRL, Bucharest, Romania). The crude fish oil was then centrifuged (15 min, 3200 rpm, 20 °C, Heraeus AG, Hanau, Germany); the clear oil was dried over anhydrous sodium sulphate (p.a., Merck & Co., Inc., Kenilworth, NJ, USA) and stored at 4 °C until β-CD complexation and derivatization.