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Comparative human-sensory evaluation and quantitative comparison of odour-active oxidation markers of encapsulated fish oil products used for supplementation during pregnancy and the breastfeeding period

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ABSTRACT

Three different commercial encapsulated fish oil supplements were evaluated by orthonasal sensory evaluation of the encapsulated oil samples, and were rated according to characteristic odour qualities and hedonic impact. The potent odourants of the fish oil samples were obtained by solvent extraction followed by high vacuum transfer of the volatiles, and were evaluated by means of high resolution gas chromatography–olfactometry (HRGC–O). Comparative aroma extract dilution analysis of the solvent extract samples revealed 40 odourants. Most of these were identified based on their respective retention indices on two capillaries of different polarities, their mass spectral data, as well as their odour characteristics during HRGC–O, in comparison with the respective reference compounds. Thereby (poly)unsaturated fatty acid oxidation products were demonstrated to play a significant role in the volatile fraction of the fish oil supplements. Quantification of selected oxidation marker substances confirmed predominant presence of these compounds in the investigated samples, but also major quantitative differences between samples with regard to specific compounds. These data may be used as the basis for future evaluation of sensory quality of encapsulated fish oil supplements, and might relate to the degree of acceptance or rejection by the mothers being supplemented with the respective products.

1. Introduction

Supplementation of fish oil or vegetable oil preparations, either direct or in an encapsulated form, is nowadays a commonly recommended strategy for pregnant and breastfeeding women to ensure optimum supply with the respective long-chain polyunsaturated fatty acids (LC-PUFAs) (Boris, Jensen, Salvig, Secher, & Olsen, 2004; Koletzko et al., 2001; Lauritzen, Jørgensen, Hansen, & Michaelsen, 2002). LC-PUFA supplementation during this critical period of early life development has been shown to reveal better outcomes with regard to, for example, visual and cognitive parameters of the offspring (Birch, Garfield, Hoffman, Uauy, & Birch, 2000; Fleith & Clandinin, 2005). Supplements containing high amounts of LC-PUFAs, especially docosahexaenoic acid (DHA), are generally provided together with other vitamin and mineral preparations as separate capsules that are consumed at regular time intervals, usually once a day.

On the other hand, there are recurring reports that mothers reject such supplements based on fish oil origin, due to negative sensory effects during (Wesson, Lindsay, & Stuiber, 1979) or after consumption of the supplements (own observations with breastfeeding mothers). Specifically, there are complaints about eructation being associated with fishy off-odours some time after swallowing. This obviously occurs when the non-enteric coated capsules open up in the stomach. However, these effects do not regularly occur and seem to be related to specific fish oil products (own observations based on maternal reports).

Based on these observations, the aim of the present study was to sensorically evaluate the overall odour impressions of three encapsulated fish oil supplements. Additionally, the potent odour compounds in the respective samples should be characterised using a combination of modern aroma-analytical and human-sensory techniques, namely one- and two-dimensional high resolution gas chromatography (1D/2D-HRGC)–olfactometry, as well as the main odour triggers should be identified using a series of analytical parameters such as mass spectrometry (MS), retention indices and odour evaluation parameters (odour quality and intensity).

Following identification, a comparative quantitative evaluation of selected oxidation marker substances should be carried out in

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the three fish oil products. Therefore, stable isotope dilution assays in combination with 2D-HRGC–MS were applied to achieve high selectivity and sensitivity in the respective determinations.

2. Materials and methods

2.1. Chemicals

Reference compounds with the stated purities (and supplier in parentheses) were as follows 4-hydroxy-3-methoxybenzaldehyde (vanillin) 99% (ABCR (Karlsruhe, Germany)), 2-aminoacetophenone 98%, δ-decalactone 98%, decanal 99%, decanoic acid 98%, dodecanoic acid 98%, (*Z*)-hept-4-enal 98%, hexanal 98%, 3-hydroxy-4,5-dimethyl-2(5*H*)-furanone (sotolone) 97%, 2-methoxyphenol (guaiacol) 98%, 2-methylbutanoic acid 98%, 3-methylbutanoic acid 99%, (*E,E*)-nona-2,4-dienal 85%, (*E,E*)-nona-2,6-dienal 95%, (*E,Z*)-nona-2,6-dienal 95%, γ-nonalactone 98%, (*E*)-non-2-enal 97%, octanal 99%, octanoic acid 98%, (*E*)-oct-2-enal 94%, oct-1-en-3-one 50%, phenylacetic acid 99%, 4-(2,6,6-trimethyl-1-cyclohexenyl)-3-buten-2-one (β-ionone) 96% (Aldrich, Steinheim, Germany), (*E,E,Z*)-nona-2,4,6-trienal 98%, (*Z*)-octa-1,5-dien-3-one 99% (Aromalab, Freising, Germany), γ-octalactone 95% (EGA Chemie, Steinheim, Germany), (*E,E*)-deca-2,4-dienal 85%, (*E*)-dec-2-enal 95%, (*E*)-hex-2-enal 97%, nonanal 95%, pentanoic acid 99%, *tr*-4,5-epoxy-(*E*)-dec-2-enal 95% (Fluka, Steinheim, Germany), γ-dodecalactone 97%, (*E,E*)-hepta-2,4-dienal 88%, (Z)-hex-3-enal 50% (SAFC, Hamburg, Germany), dichloromethane p.a., sodium sulphate p.a. 98.5% (Th. Geyer GmbH & Co. KG, Renningen, Germany). (*E,Z,Z*)-Trideca-2,4,7-trienal was kindly provided by Dr. Imre Blank (Nestle, Switzerland).

The following stable isotope labelled standards (Fig. 1) were obtained from aromaLAB AG (Freising, Germany):

[5,6-$^2H_2$]-hexanal, [7,8-$^2H_2$]-octanal, [6,7-$^2H_2$]-nonanal, [9,10-$^2H_2$]-decanal, [2,3-$^2H_2$]-(*E*)-hex-2-enal, [3,4-$^2H_2$]-(*Z*)-hex-3-enal, [4,5-$^2H_2$]-(*Z*)-hept-4-enal, [2,3-$^2H_2$]-(*E*)-non-2-enal, [2,3-$^2H_2$]-(*E*)-dec-2-enal, [4,5-$^2H_2$]-(*E,E*)-deca-2,4-dienal, [8,9-$^2H_2$]-γ-nonalactone, [9,10-$^2H_2$]-δ-decalactone, [11,12-$^2H_2$]-γ-dodecalactone, [1,2-$^2H_{2-3}$]-1-octen-3-one, [5,6-$^2H_2$]-(*Z*)-octa-1,5-dien-3-one, 4-(2,6,6-Trimethyl-1-cyclohexenyl)-[1-$^2H_3$]-but-3-en-2-one (β-ionone).

2.2. Samples

The three evaluated fish oil products were specifically produced for the supplementation of $n-3$-PUFAs during pregnancy and lactation period, and were purchased from the respective suppliers. All products were common supplements and were specifically enriched with regard to docosahexaenoic acid (DHA): Femibion Schwangerschaft 2 (Merck, KGaA, Darmstadt, Germany), containing 143 mg DHA and 9 mg Vitamin E per g concentrated fishoil; Marinol D-40 produced by Lipid Nutrition (Loders Croklaan, Wormerveer, The Netherlands), which contained 360 mg DHA (and 55 mg eicosapentaenoic acid (EPA)) and 3 mg mixed natural tocopherols per 1 g fish oil (encapsulated by Ayanda GmbH & CO. KG, Falkenhagen, Germany); and Orthomol natal (Orthomol GmbH, Langenfeld, Germany) containing 61 mg DHA (and 10 mg EPA) and 10 mg Vitamin E per g fish oil.

The oil samples were withdrawn from the capsules using a syringe and evaluated by means of orthonasal aroma profile analysis (APA) (see below), and analysed by HRGC–O and 2D-HRGC–MS for identification or quantification.

2.3. Panellists for sensory evaluation

Panellists aged between 24 and 42 (mean age 31.1), were trained volunteers from the University of Erlangen (Erlangen, Germany) and Fraunhofer-IVV (Freising, Germany), exhibiting no known illness at the time of examination and with audited olfactory and gustatory function. Eight assessors (two males, six females) were recruited in preceding weekly training sessions and orthonasally and retronasally trained for at least half a year in recognising about 90 selected odourants at different odourant concentrations according to their odour qualities, and in naming these according to an in-house developed flavour language.

2.4. Aroma profile analysis (APA) and hedonic rating

Sensory analyses were performed in a sensory panel room at 21 ± 1 °C. Fish oil samples (1 g) were presented to the sensory panel in covered glass vessels (capacity 140 ml) for orthonasal evaluation.

The panellists were first asked to describe the samples (collection of sensory attributes). Then, the panellists were asked to score the intensities of these attributes as well as the overall odour intensities on a seven-point scale from 0 (no perception) to 3 (strong perception) with 0.5 intermediate steps.

For the hedonic rating the panellists were asked to rate pleasantness of the fish oil samples on a scale from 0 (dislike extremely) over 1.5 (neither like nor dislike) to 3 (like extremely).

2.5. Solvent assisted flavour evaporation (SAFE)

Solvent assisted flavour evaporation (SAFE) (Engel, Bahr, & Schieberle, 1999) was applied for the fast and careful isolation of the fish oil volatiles from 1.2 g to 5.0 g of fish oil with 5 ml of freshly purified dichloromethane, stirred for 30 min, and immediately applied for distillation at 50 °C. The residue was taken up in

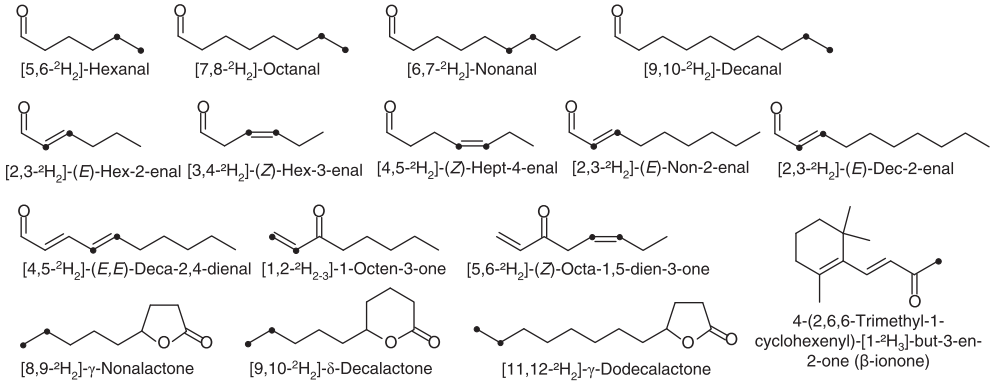

Fig. 1. Chemical structures of the stable isotope labelled standards used for quantification of the target odourants in the fish oil supplements.