# Wheat and Rice Bran as Natural Additives for the Protection of Fish Oil from Oxidation

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Article

# Wheat and Rice Bran as Natural Additives for the Protection of Fish Oil from Oxidation

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**ABSTRACT:** Fortification of food products with omega-3 polyunsaturated fatty acids (ω-3 PUFAs) is difficult due to their high oxidative susceptibility. Use of synthetic antioxidants in food products to extend shelf life is challenged by the growing demand for natural ingredients from consumers. In this study, the stabilization effect of wheat and rice bran on fish oil oxidation was investigated. Five, 10, and 20 g of fish oil were added to 95, 90, and 80 g of cereal brans, respectively. The obtained powders were homogenized and stored for accelerated oxidation study at 38 °C up to 30 days (to avoid dramatic changes of the oxidation reaction pathways compared to those at room temperature). Secondary oxidation products were analyzed by both solid phase microextraction-gas chromatography−mass spectrometry and liquid chromatography−high resolution mass spectroscopy. Wheat bran showed a better protection effect on fish oil oxidation. That could be explained by its phytochemical and physical stabilization effect. Heat and enzymatic treatments did not improve antioxidant capacity of wheat or rice bran. Fine wheat bran water extract protected the fish oil from oxidation to the same extent as the whole wheat bran.

**KEYWORDS:** *Wheat bran, rice bran, lipid oxidation, fish oil, PUFAs, volatiles*



## 1. INTRODUCTION

Regular consumption of omega-3 polyunsaturated fatty acids (PUFAs) such as α-linolenic acid (ALA; C18:3), eicosapentaenoic acid (EPA; C20:5), and docosahexaenoic acid (DHA; C22:6) are reported to have several health benefits. These include lower risk of cardiovascular,[1] neuropsychiatric,[2] and neurodegenerative[3] diseases, colorectal, breast, and prostatic cancer,[4−6] and preventing inflammation.[7] DHA plays an important role in brain growth and development in infants and is essential for normal brain functions. The daily adequate intake recommended by the EFSA is 250 mg EPA + DHA for adults and 100 mg of DHA for children 6−24 months.[8] EPA and DHA are essential PUFAs and can be synthesized from ALA (present in plant source) through limited conversion (ALA-EPA < 8%, ALA-DHA < 0.1%).[9] In adults, for ALA the mean intakes varied between 0.7−2.3 g per day.[8] Therefore, conversion from ALA to EPA and DHA is insufficient to reach the DAI recommendation. The richest dietary source of EPA and DHA are oily fishy and marine sources. For people who eat little or no fish, it is challenging to consume these doses through ordinary diet. A single lean fish meal (cod) could provide 200−300 mg EPA, DPA, and DHA, while a single oil fish meal (tuna, salmon, sardine, and mackerel) could provide 1.5−3 g these fatty acids.[7] Therefore, food enrichment with ω-3 PUFAs is an alternative solution to increase their daily intake. Examples of fortified foods are cereals, dairy products, infant formulas, and ready-to-drink beverages. Unfortunately, PUFAs are very sensitive to oxidation and their oxidative instability increases with their degree of unsaturation (multiple double bonds). The oxidation of PUFAs results from complex mechanisms in nonvolatile and volatile oxidation products including hydroperoxides, epoxides, aldehydes, ketones, alcohols, and carboxylic acids. Among them, aldehydes and ketones have a low odor threshold and are known to be responsible for rancidity and unacceptable fishy off-flavor in oxidized foods.[10] To protect oils rich in PUFAs from oxidation, synthetic antioxidants such as butylated hydroxytoluene (BHT), butylated hydroxyanisole (BHA), tertiary butylhydroquinone (TBHQ), and propyl gallates (PG) have been used. However, the use of synthetic antioxidants is increasingly challenged by the growing demands for natural ingredients and the safety concerns about these synthetic chemicals. Some strategies for the stabilization of long chain ω −3 PUFA-enriched foods have been reviewed.[11]

Cereal-based products constitute a large part of our daily diet. Besides the use of cereal flours, their byproducts (e.g., bran) are well-known for their water- and fat-adsorption properties.[12] In addition to their inexpensive price and nutritional value (e.g., rich in dietary fibers, vitamins, minerals), cereal brans are rich in phytochemicals, such as tocopherols, tocotrienols, polyphenols, lutein, cryptoxanthin, zeaxanthin, β-carotene, and phenolic acids (e.g., ferulic, vanillic, caffeic, syringic, sinapic, and *p*-coumaric acids).[13,14] Phenolic acids are present in either soluble form (conjugated to mono- or oligosaccharides), insoluble bound form (ester-linked with polysaccharides) or free form. Bound phenolics

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were reported to play a major role in bran antioxidant activity by a surface reaction mechanism.[13]

In wheat bran, ferulic acid (acting as a radical scavenger) is the predominant phenolic acid which accounts for about 46−67% of total phenolic acids on a weight basis,[14−16] and constitutes about 0.5% (w/w) of the wheat bran.[17] About 75% of ferulic acid in wheat bran is present in bound form, esterified to cell wall hemicelluloses (arabinoxylans).[18] Dehydrodiferulates are concentrated in the outer pericarp layers and cross cells, while ferulic acid is abundant in the aleurone layer.[19] Different batches of cereal bran can differ in phenolic content depending on variety, geographical region, crop conditions, and extraction methods.[20−24] This variation is even higher for the antioxidant capacity, which is significantly affected by the method used for analysis.

Rice bran constitute 8−10% of the rough rice weight and contains up to 13−21% fat.[25] Crude rice bran oil consists of neutral lipids, glycolipids, and phospholipids (phosphatidylcholine, phosphatidylethanolamine, and phosphatidylinositol). Rice bran oil is reported to contain significant amounts of γ-oryzanol (0.9−2.9%) and vitamin E (0.10−0.14%).[26] Gamma-oryzanol is a mixture of ferulic acid esters of phytosterols and triterpene alcohols.[27] Both γ-oryzanol and vitamin E showed chain-breaking antioxidant properties.[26] It has been reported that rice bran contains higher free phenolics but lower bound phenolics than wheat bran.[18]

The objective of the present investigation is to evaluate the potential of wheat and rice bran as a natural, affordable, and consumer friendly replacement of synthetic antioxidants for the stabilization of ω-3 PUFAs in fish oil. Different treatments such as grinding, defatting, enzymatic, and thermal treatments have been applied to wheat and rice bran. Oxidation study was carried out by spiking 5, 10, and 20 g of fish oil in 95, 90, and 80 g, respectively, of the brans. A negative control sample was added using maltodextrin (without antioxidant activity) as amatrix to form a powder mixture with fish oil. A commercially available and chemically stabilized fish oil powder was used as a positive control. This stability study was performed under accelerated oxidation conditions. Secondary oxidation metabolites were analyzed by solid phase microextraction−gas chromatography−mass spectrometry (SPME-GC-MS) and liquid chromatography−high resolution mass spectroscopy (LC-HRMS). The odors (rancid, fishy, metallic, and so forth) of the samples were evaluated by an expert panel of five people, and the results were used as complementary information to the chromatography analyses.

## 2. MATERIALS AND METHODS

**2.1. Materials.** Fish oil (20−26% DHA) and high DHA fish oil powder stabilized (positive control, 32.5% DHA) were provided by Sofinol (Manno, Switzerland). Coarse wheat bran and coarse and fine rice bran were purchased from Group Minoteries (Granges-près-Marnand, Switzerland) and Herba Ricemills (Sevilla, Spain), respectively. The approximate composition of the brans used in this study are shown as Supporting Information (supplementary 1). Maltodextrin (M) (21 dextrose equivalent DE) was provided by Roquette (Lestrem, France). Pentopan 500 BG was from Novozymes (Bagsværd, Denmark). All chemicals and solvents used were from Sigma-Aldrich (Buchs, Switzerland). Brans used in prescreening study are coarse wheat/rice bran (CWB/CRB), fine wheat/rice bran (FWB/FRB), enzymatically treated wheat/rice bran (EWB/ERB), defatted fine wheat/rice bran (DWB/DRB), and fine wheat bran thermally treated (FWBΔT). Thermally treated rice bran was not included in this study because the rice bran has been thermally treated by the supplier prior to commercialization. On the basis of the outcome of the prescreening, wheat bran showed stronger antioxidant effect than rice bran, therefore only fine wheat bran and fine wheat bran water extract (FWBWE) were further included in the accelerated shelf life study.

**2.2. Methods.** *2.2.1. Bran Treatment. 2.2.1.1. Particle Size Reduction and Measurement.* The CWB was milled by Ultra Centrifugal Mill ZM 200 through 80 μm sieve Retsch (Haan, Germany) to get FWB. The particle size of CWB/FWB and CRB/FRB was measured by Camsizer XT Retsch with an applied pressure of 120 kPa.

*2.2.1.2. Defatted Wheat and Rice Bran.* The prepared FWB and commercially available FRB were mixed with hexane (1/5, m/v) and stirred for 30 min to remove the free lipids[28] (e.g., monoacylglycerides (MAG), diacylglycerides (DAG), triacylglycerides (TAG), and free fatty acids). The extraction was repeated twice. After Büchner filtration, the brans were dried overnight at room temperature and manually homogenized in a mortar. The quantity of extracted lipids was weighted after evaporation of hexane in rotary evaporator.

*2.2.1.3. Enzymatic Hydrolysis.* FWB and FRB were added separately to water (20%, w/v). For wheat bran, the bran-water suspensions were heated at 90 °C for 10 min under magnetic stirring (500 rpm) to inactivate endogenous enzymes and to induce starch gelatinization. When cooled down to 40 °C, Pentopan 500 BG was added (0.5%, w/w dry basis) and the mixtures were stirred for 2 h. The Pentopan 500 BG, which is an enzymatic preparation commercialized as 1,4-beta xylanase, contains an esterase side activity (108 U/g). Xylanase and feruloyl esterase are necessary for the release of ferulic acid from bound form (bound to arabinoxylans) into free ferulic acid. The enzymes were then inactivated by a heating step (10 min, 90 °C), and the mixture was freeze-dried (Alpha 2-4 LSC freeze-dryer; Martin Christ (Osterode am Harz, Germany) and grounded in a lab scale mill A11 basic; IKA (Staufen, Germany). For FRB, the bran−water suspension was adjusted to pH to 5.5, Ban 800 (alpha-amylase) and Depol 740 (feruloyl esterase) were added respectively at 0.07 and 0.13% w/w on dry basis. The enzymatic hydrolysis was run at a different heating step: 10 min at 55 °C, 5 min at 85 °C, and 10 min at 70 °C. Finally, a 10 min heating step at 90 °C to inactivate the enzyme, then the mixture was freeze-dried as described above.

*2.2.1.4. Thermal Treatment of Wheat Bran.* The same thermal process used for the enzymatic treatment (Section 2.2.1.3) was applied to wheat bran but without adding enzyme. The aim was to evaluate the impact of the thermal treatment on the antioxidant activity of the bran in the absence of enzyme. FWB (20%) was weighed in mill-Q water and the mixture was heated up to 90 °C and kept 10 min under stirring. The temperature was then cooled down to 40 °C, and the mixture stirred for 2 h. The temperature was then increased to 90 °C, and the mixture stirred for 10 min. The sample was freeze-dried in an alpha 2-4 LSC freeze-dryer Martin Christ (Osterode am Harz, Germany), and the resulting powder was ground in an analytical mill A11 IKA (Staufen, Germany).

*2.2.1.5. Preparation of Fine Wheat Bran Water Extract.* The water extract of wheat bran (FWBWE) was produced by dissolving FWB in Milli-Q water (10%, w/v). The slurry was stirred for 1 h at room temperature. After centrifugation (20 min, 12000×*g*), the supernatant was collected. This extraction was performed a second time with fresh water, and the supernatants were combined, freeze-dried, and the resulting powder was ground in an analytical mill A11 basic (IKA, Staufen, Germany).

*2.2.2. Prescreening of Bran Matrices.* For prescreening, 5, 10, and 20 g of high DHA fish oil (w/w) were added respectively to 95, 90, and 80 g of the different bran matrices: CWB/CRB, FWB/FRB, DWB/DRB, EWB/ERB, and FWBΔT. The concentrations of fish oil were selected based on the processability of the mixture's bran-fish oil. Beyond 20% fish oil (20 g fish oil + 80 g bran), the mixture became difficult to process, not homogeneous (formation of lumps), and some of the oil was floating on the surface of the bran. This is due to limited oil binding capacity of the bran. The obtained powders were homogenized. Powder mixtures of maltodextrin-fish oil were used as negative control. For prescreening, all powder mixtures spiked with


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fish oil were stored in an oven at 38 °C[29] (without control of humidity) to induce an accelerated oxidation. At each time point (0, 7, and 15 days), one bottle from each sample was withdrawn, odors were evaluated by experienced panel, and volatiles were analyzed by LC-HRMS and SPME-GC-MS.

*2.2.3. Measurement of Oxygen Radical Absorbance Capacity (ORAC) Values in Wheat Brans.* The ORAC value was measured by an external laboratory (Institute Prof. Kurz GmbH, Germany), following a reported method.[30] Trolox was used as an internal control and tryptophan as a positive control. These values were expressed as micromoles of Trolox equivalent (TE) per 100 g of sample.

*2.2.4. Accelerated Oxidation Study of Fish Oil with Fine Wheat Bran and Fine Wheat Bran Water Extract.* Maltodextrin and chemically stabilized high DHA fish oil powder were used as negative and positive control. Five, 10, and 20 g of high DHA fish oil were added respectively to 95, 90, and 80 g of FWB. Mixtures were homogenized in a Multi Lab mixer Caleva (Dorset, England) at 100 rpm for 3 min. Samples were stored at 38 °C in an oven (without control of humidity). One bottle of each sample was withdrawn after 0, 1, 3, 7, 10, 15, and 30 days, odors were evaluated by experienced panel, and volatiles were analyzed by LC-HRMS and SPME-GC-MS. For 90 g of FWBWE, 10 g of high DHA fish oil was added (limited oil binding capacity), and the mixture was stored at 38 °C for 0, 7, and 15 days. All experiments were performed in duplicates. The volatiles were analyzed, and the odors were evaluated as mentioned above.

*2.2.5. Analysis of Secondary Oxidation Products by LC-HRMS.* Secondary oxidation products were analyzed following a reported method[31] with minor modifications. The samples (matrix-fish oil, 2 g) were dissolved in 10 mL chloroform/methanol (1/2, v/v), stirred mechanically (10 min, 2500 rpm), and centrifuged (10 min, 2500 rpm/1272 g). In an Eppendorf vial, 100 μL of supernatant was added with 5 μL of internal standard (hexanal-$d_{12}$, 10 μg/mL, in acetonitrile), and 100 μL of derivatizing agent, 7-(diethylamino)-coumarin-3-carbohydrazide (CHH) solution (8 mM, in acetonitrile). The mixtures were then stirred for 1.5 h in an Eppendorf thermomixer (Comfort, Germany) (37 °C, 1400 rpm). After derivatization, acetonitrile was added to make up to 500 μL end volume. Samples were vortexed, centrifuged (2500 g, 20 °C, 2 min), and supernatants were analyzed by Q-Exactive Plus system coupled with an UPLC Dionex UltiMate 3000 system from Thermo Fisher Scientific (MA, U.S.A.). The identification of analytes was based on exact mass, retention time and MS/MS fragmentation using software Xcalibur (version 2.2).

The following secondary oxidation products (aldehydes and ketones) were monitored by LC-HRMS: hexanal, (*E*)-2-hexenal, (*E*)-2-heptenal, (*Z*,*Z*)-3,6-nonadienal, 1-octen-3-one, octanal, 2-nonanone, propanal, (*E*)-2-nonenal, (*E*,*E*)-2,4-decadienal, (*E*)-2-decenal, (*E*)-2-pentenal, (*Z*)-3-hexenal, (*E*,*E*)-2,4-heptadienal, (*Z*)-4-heptenal, 2,4-octadienal, 2,4,7-decatrienal, 3,6,9-dodecatrienal, (*E*)-4,5-epoxy-(*E*,*Z*)-2,7-decadienal, (*E*)-4,5-epoxy-(*E*)-2-decenal, 2,4,7,10-tridecatetraenal, 3,6,9,12-pentadecatetraenal, 2,4,7,10,13-hexadecapentaenal, and 2,4,7,10,13,16-nonadecahexal.

*2.2.6. Analysis of Secondary Oxidation Products by SPME-GC-MS.* To avoid an additional transfer of sample and loss of volatiles through sampling, mixtures (bran-fish oil, 1 g) were placed directly in 10 mL glass vials used for SPME-GC-MS analyses and closed by a magnetic seal with septa during the storage time. The extraction of volatiles was performed using a Gerstel MPS2 auto sampler equipped with a 65 μm polydimethylsiloxane/divinylbenzene SPME fiber from Sigma-Aldrich Chemie GmbH (Buchs, Switzerland). The vials were incubated at 40 °C for 10 min, then the volatiles were extracted by the fiber from the headspace for 30 min at 40 °C and subsequently injected for analysis on a 6890A gas chromatograph coupled with a 5973N quadrupole mass detector from Agilent Technologies (Santa Clara, U.S.A.). For the desorption/injection into the GC-column, the SPME fiber remained in the GC inlet for 3 min at 240 °C in splitless mode and then the inlet purge was open at a flow rate of 50 mL/min to clean the fiber. Compounds were separated on a DB-FFAP column (30 m length, 0.25 mm i.d., 0.25 μm film thickness, Agilent Technologies (Santa Clara, U.S.A.)). Helium was used as carrier gas at a constant flow rate of 1 mL/min. The oven temperature was held at 40 °C for 5 min, raised to 230 °C at 4 °C/min, and then held at 230 °C for 10 min. MS acquisitions were achieved with a mass range from $m/z$ 29 to 300 amu at 5.08 scans/sec.

The volatiles were identified by comparison of their mass spectra with those contained in an internal database (Oceane and CRN141) or a commercial library (W11N14). The identification was further confirmed by the linear correlation between retention index (RI) and the retention time (RT). For the determination of the response of volatiles, a method was applied based on a quantitative ion and qualitative ion which were selected based on the best compromise between selectivity and sensitivity (Supporting Information, supplementary 2). Hexanal-$d_{12}$ (Pointe-Claire, Canada) was used as internal standard (1 ppm). For other analytes, the relative responses were determined by the peak area ratio of the analyte to the internal standard (hexanal-$d_{12}$).

The volatiles monitored by SPME-GC-MS were hexanal, (*E*,*Z*)-2,4-heptadienal, (*E*,*E*)-2,4-heptadienal, (*E*,*E*)-2,4-decadienal, (*E*)-2-pentenal, 1-penten-3-ol, (*E*)-2-hexenal, (*Z*)-4-heptenal, (*E*)-2-penten-1-ol, (*E*,*Z*)-3,5-octadien-2-one, (*E*,*Z*)-2,6-nonadienal, and (*E*,*Z*)-2,4-decadienal.

*2.2.7. Analysis of Total and Free Ferulic Acid by UPLC.* Total ferulic acid in wheat bran was determined by alkaline hydrolysis. NaOH (2 M, 50 mL) was added to 1.5 g of wheat bran in a dark Erlenmeyer flask. The mixture was heated up to 40 °C for 2 h under nitrogen and then cooled down to 20 °C. The pH was reduced to 2.0 with HCl (4 M), the mixture centrifuged (10 min, 4500 rpm), and the liquid phase filtered (2 μm). Ethyl acetate (150 mL) was added to the filtrate in 250 mL dark Erlenmeyer flask and the mixture shaken with a magnet stirrer (300 rpm) at room temperature for 15 min. The organic phase was vacuum evaporated, and the concentrated extract was analyzed by reverse-phase ultraperformance liquid chromatography. A C18-column Acquity UPLC BEH C18 1.8 μm, 2.1 mm × 150 mm Waters AG (Baden-Dättwil, Switzerland) was used. The system consisted of an UPLC-PDA system with binary gradient pump, a degassing system, a sample injector with an injection loop >5 μL, and a Photodiode Array detector (PDA) Waters AG (Baden-Dättwil, Switzerland). Column temperature was controlled at 35 °C and injection volume was 2 μL. Elution flow rate was set at 0.5 mL/min, solvent A (water) and B (acetonitrile) were both acidified with 0.1% phosphoric acid. The gradient started with 3% of solvent B, maintained for 1.8 min and followed by linear increase of solvent B to 15% within 5 min, to 21% within 3 min and finally to 90% within 0.1 min, the 90% solvent B was maintained for 2 min before returning to initial condition within 0.1 min and equilibrating in 3% solvent B for 4 min. The detection was monitored with PDA set at 280 nm.

## 3. RESULTS AND DISCUSSION

### 3.1. Prescreening of Bran for Fish Oil Stabilization.

Wheat and rice are two of the most widely produced grains worldwide, therefore wheat and rice brans are accessible byproducts which can be valorized. Different bran treatments, such as particle size reduction, defatting, heat treatment or enzymatic hydrolysis, have been applied to improve the technical, physical and chemical characteristics of the bran.

The stabilization effect of bran was assessed by odor evaluation by an experienced internal panel and volatiles were analyzed by LC-HRMS and SPME-GC-MS. The volatile markers were selected from compounds originating from fish oil oxidation based on literature.[31] Hexanal and propanal are the most often cited markers for ω-6 and ω-3 PUFAs oxidative degradation, respectively. While hexanal has green, grassy, and fishy odor, propanal does not have much flavor impact. Two additional volatiles from ω-3 PUFAs oxidation, (*Z*)-4-heptenal and (*E*,*E*)-2,4-heptadienal, were selected as markers for fishy, fatty, and pungent off-flavors.[32,33] Using maltodextrin (the negative control) as reference, the peak area ratios (%) of bran


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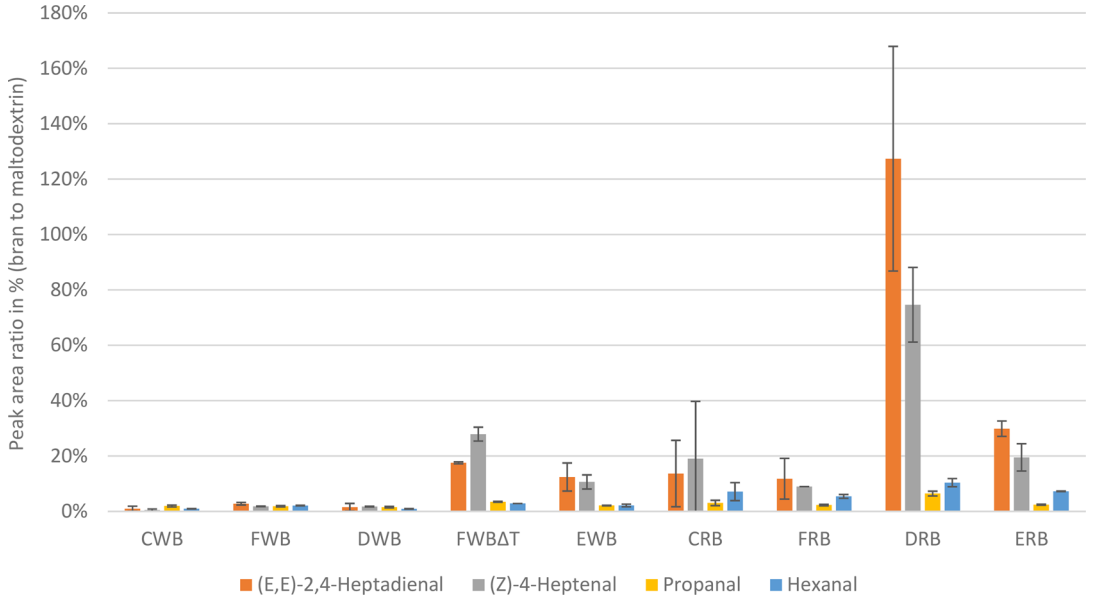


**Figure 1.** Peak area ratio in percentage (brans to maltodextrin) of hexanal, propanal, (*E*,*E*)-2,4-heptadienal, and (*Z*)-4-heptenal measured by LC-HRMS after 15 days of storage at 38 °C in prescreening study. Ten grams of fish oil (10%) was added to 90 g of M, DRB/DWB, ERB/EWB, FRB/FWB, CRB/CWB, and FWBΔT. Error bars indicate SD of duplicate measurements ($n$ = 2).

to maltodextrin of selected volatiles are reported (Figure 1). Absolute quantification was not possible without isotopic labeled standard for each analyte. All of the bran-based matrices significantly ($P < 0.05$) inhibited the formation of volatiles related to oxidation of fish oil (except for (*E*,*E*)-2,4-heptadienal and (*Z*)-4-heptenal in DRB).

Overall, wheat bran showed a better protecting effect on fish oil than rice bran. It might be due to the higher phytochemicals, such as tocopherols, total phenolics, flavonoids, and ferulic acid (free and bound forms) content in wheat bran.[18] Beside, tannins are more abundant in wheat than in rice bran,[34] and tannins are reported to be strong antioxidants due to strong capabilities to donate hydrogen atoms or electrons, to chelate metal, and to inhibite cyclooxygenase.[35] Amphiphilic phenolipids such as alkylresocinols homologues are found in the bran layer of wheat, rye, and barley and showed antioxidant activity in bulk oils and heterogeneous system.[36] Wheat bran contains considerable level of phytic acid which strongly chelates minerals, hence enhances the oxidative stability. Besides chemical protection, physical properties (e.g., entrapment, encapsulation, and capillary attraction of oil or oil binding capacity) might also contribute to the antioxidant capacity of the bran. The physicochemical characterization of wheat and rice bran shown that wheat bran has a four times higher oil binding capacity than rice bran.[38]

Particle size is an important physical parameter which determines the specific surface area and the surface properties of the bran.[37] In coarse bran, ferulic acid will be mainly embedded in the bran matrix and may therefore display minimal reactivity. Our hypothesis is that with particle size reduction, ferulic acid may become more accessible, and therefore might improve the oxidative stability of PUFAs in bran structure. In addition, it has been hypothesized in the literature that reduced particle size might lead to liberation of active components due to cell breakage.[39] However, these hypotheses cannot be proven. The reduction of the particle size of wheat bran (CWB/FWB; 429/117 $\mu$m) and rice bran (CRB/FRB; 170/68 $\mu$m) used in this study had no significant impact on the generation of volatiles (Figure 1). It may be that the particle size of the "coarse" bran used in this study is already relatively small and can be considered as medium or even fine size depending on definition. Furthermore, the increased contact surface caused by particle size reduction may also increase contact with oxygen and therefore increase oil oxidation.

Bran lipids could play a role in the stability of fish oil due to the presence of lipid soluble active components. In this study, while defatting of wheat bran showed no significant effect on the stability of fish oil, DRB resulted in a significant increase of the volatiles when compared to a nondefatted one (Figure 1). Rice bran lipids are composed of multiple phytochemicals such as tocopherols and tocotrienols, squalene, phytosterols, polyphenols, $\gamma$-oryzanol, and phospholipids (e.g., phosphatidylethanolamine, phosphatidylcholine, phosphatidylinositol). Among them, $\gamma$-oryzanol (0.9−2.9%) and tocopherols (0.1−0.14%) are most abundant and play a key role in the stabilization of fish oil.[26] In addition, rice bran lipids contain 3% wax, which has been reported to protect PUFAs from oxidation.[40] Because wheat bran has a lower oil content (2−5%) than rice bran 13−21% fat,[25] defatting affects less wheat bran than rice bran. In addition, the defatting solvent hexane has stronger impact on rice bran than on wheat bran. Rice bran contains predominantly free lipids (triacylglycerols, diacylglycerols, monoacylglycerols, free fatty acids[41]), while wheat bran contains more bound lipids.[38] To conclude, defatting in both rice and wheat bran did not improve its antioxidant capacity, which is our primary aim, therefore further optimization of the defatting process was not pursued.

Ferulic acid is used as a food preservative because it can absorb UV or inhibit fatty acid peroxidation.[16] It is also an important constituent of the plant cell wall, implicated in cell adhesion.[42] Bound ferulic acid (through covalent ester bonds to polysaccharides, for example, arabinoxylans) found in byproducts such as sugar beet pulp, brewer's spent grain, wheat, and maize bran can survive certain agri-food processing


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activities.[43] Because ferulic acid in wheat bran is mainly present in bound form, esterified to hemicelluloses (arabinoxylans) of the cell walls, enzymatic hydrolysis is needed to release free ferulic acids. However, the antioxidation effect of free ferulic acid was not demonstrated by this experiment. Enzymatic treatment of wheat (EWB) and rice (ERB) bran resulted in increased volatile products when compared to nonhydrolyzed ones (FWB and FRB). The total ferulic acid content of the wheat bran used in this study was 450 mg/100 g when analyzed by UPLC after alkaline hydrolysis. The concentration of free ferulic acid was 1.1 mg/100 g (~0.24%). After enzymatic treatment of wheat bran, the concentration of free ferulic acid was 270−300 mg/100 g with a reaction yield of 57−62%. On the contrary, the alkaline and enzymatic treatment of rice bran used in this study did not result in any significant increase of the concentration of free ferulic acid (data not shown), because ferulic acid exists in rice bran mainly in the form of γ-oryzanol through esterification with phytosterols and triterpene alcohols. Surprisingly, the release of free ferulic acid through enzymatic hydrolysis of wheat bran decreased the oxidative stability of fish oil, suggesting that in fish oil bound ferulic acids may have a stronger antioxidant effect than free ones. This is aligned with a previous study showing in 10% oil-in-water emulsion that bound ferulic acid inhibited more hydroperoxides formation than free ones, although in the DPPH and TEAC assays free ferulic acid showed much stranger antioxidant capacity than the bound ones.[44] In another study, the esterification of ferulic acid with oligosaccharides reduced the antioxidant capacity of ferulic acid up to 55% when measured by TEAC and ORAC assays.[45]

The strong in vitro antioxidant capacity of free ferulic acids can be confirmed by the ORAC results of the selected wheat brans (Table 1). EWB showed the highest ORAC value that is probably due to the higher concentration of free ferulic acid and derivatives (e.g., diferulic acid) released by enzymatic treatment (degradation of the aleurone layer of the cell wall by xylanases).[46] Then FWB followed with higher ORAC value than CWB. This may be explained by a larger particle surface area and therefore a better exposition of the antioxidant compounds in FWB. DWB displayed the lowest ORAC value because fat removal partially eliminated compounds with antioxidant potential. Regarding antioxidant capacity of ferulic acid, both our findings and literature showed misalignment between volatiles/hydroperoxides and in vitro assays. This may be explained by the fact that antioxidants in lipid partitioning is not considered in in vitro assays.[47] In addition, the ORAC assay measures only the antioxidant capacity to scavenge peroxyl radicals (through hydrogen donation and chain-breaking)[48] but not for metal chelating, electron transfer, potential reduction, or carbonyl scavenging capacities.[49] Furthermore, the physical protection effect of bran cannot be evaluated by ORAC assay and the solvent used to extract the antioxidants from bran matrices may bring variability to the ORAC assay.

**Table 1. Oxygen Radical Absorbance Capacity[a]**

| wheat bran matrices | ORAC value [μmol TE/100 g] |
|---|---|
| enzymatically hydrolyzed wheat bran (EWB) | 13990 |
| fine wheat bran (FWB) | 7610 |
| coarse wheat bran (CWB) | 6270 |
| fine wheat bran thermally treated (FWBΔT) | 6230 |
| defatted wheat bran (DWB) | 4700 |

[a]Expressed as μmol of Trolox Equivalent (TE) per 100 g of fine/coarse wheat bran (FWB/CWB), enzymatically hydrolyzed wheat bran (EWB), fine wheat bran thermally treated (FWBΔT) and defatted wheat bran (DWB).

Rice bran with high fat content was heat treated by the supplier prior to commercialization to inactivate lipase and lipoxygenase (LOX). Lipase breaks down fats to free fatty acids, while LOX initiates enzymatic oxidation of ω-3 PUFAs, and both cause rancidity in rice bran. No further thermal treatment on FRB was carried out in this study. Unlike rice bran, the wheat bran used was not heat stabilized by the supplier, therefore to be experimentally consistent a heat treatment was applied. As result, a significant increase of the volatiles was observed for the heat treated sample (Figure 1). The in-house heat treatment probably modified the physical and chemical structure of the bran, promoting oxidation and off-flavors development.

Additionally, odor evaluation could be well correlated with LC-HRMS results. The freshly prepared fish oil mixtures with wheat and rice bran (day 0) were described as cereal-like (distinct flavor of cereal bran), while the samples with maltodextrin were odorless. The fish oil-EWB was described as caramel-like, which could be linked to the presence of carbonyl-amine adduct (for example pyrazines, compounds associate with baked, roasted, caramel aromas found in fish oil[32]). After 15 days of incubation, all of the wheat bran samples were perceived as cereal-like, while rice bran samples were slightly fishy and the maltodextrin sample was rancid, oxidized (such as (*E*,*E*)-2,4-heptadienal, and (*Z*)-4-heptenal), metallic (for instance, (*E*)-4,5-epoxy-(*E*,*Z*)-2,7-decadienal and (*E*)-4,5-epoxy-(*E*)-2-decenal[33]), plastic, painty, and pungent flavor (like (*E*,*Z*)-3,5-octadien-2-one and 1-penten-3-ol).[31]

**3.2. Fish Oil Stabilization with Fine Wheat Bran during Storage.** Identified as the most promising bran matrix from prescreening, FWB was submitted to accelerated oxidation storage. FWB samples containing 0, 5, 10, and 20% fish oil (Section 2.2.4) were stored at 38 °C for 30 days and the volatiles were measured by LC-HRMS and SPME-GC-MS. During the storage (*Z*)-4-heptenal and (*E*,*E*)-2,4-heptadienal demonstrated a strong inhibition of the oxidation in wheat bran samples containing 5, 10 and 20% fish oil compared to maltodextrin (Figure 2). By SPME-GC-MS, (*E*,*Z*)-3,5-octadien-2-one and 1-penten-3-ol were also strongly inhibited in the presence of FWB (Figure 2). EPA oxidation product (*E*,*Z*)-3,5-octadien-2-one is strongly related to fatty, hay green, plastic, and synthetic odors. 1-Penten-3-ol is formed during fish oil oxidation and has a chemical-like, painty, and green smell. A fish oil concentration-dependent formation of volatiles was observed by LC-HRMS. With a shorter induction period (7 days vs 15 days by LC-HRMS) and signal saturation in the sample containing ≥5% of fish oil, SPME-GC-MS showed strong sensitivity to these volatiles. Signal suppression in SPME-GC-MS was due to fiber saturation caused by the highly intense compounds present in the samples.

The odors of stored samples were evaluated by an experienced panel of five people. Maltodextrin with fish oil samples were described as fishy and rancid after 15 days of storage. This rancidity and metallic notes became very strong after 30 days. All FWB samples were described as cereal-like, and no fishy/rancid odor notes could be perceived up to 30


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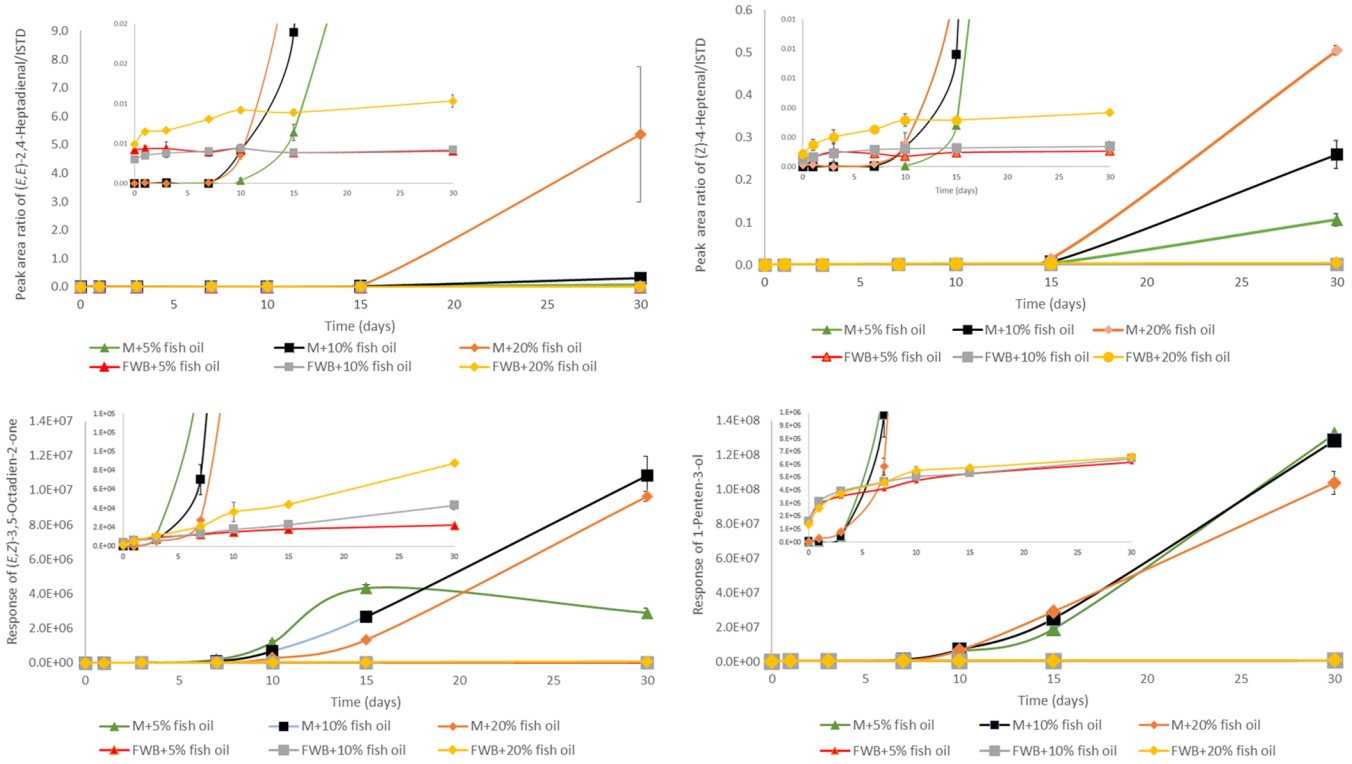


**Figure 2.** Relative responses of (*E*,*E*)-2,4-heptadienal and (*Z*)-4-heptenal measured by LC-HRMS and absolute responses of (*E*,*Z*)-3,5-octadien-2-one and 1-penten-3-ol measured by SPME-GC-MS during 30 days accelerated oxidation storage at 38 °C in M and FWB with the addition of 10% and 20% fish oil. Error bars indicate SD of duplicate measurements ($n$ = 2).

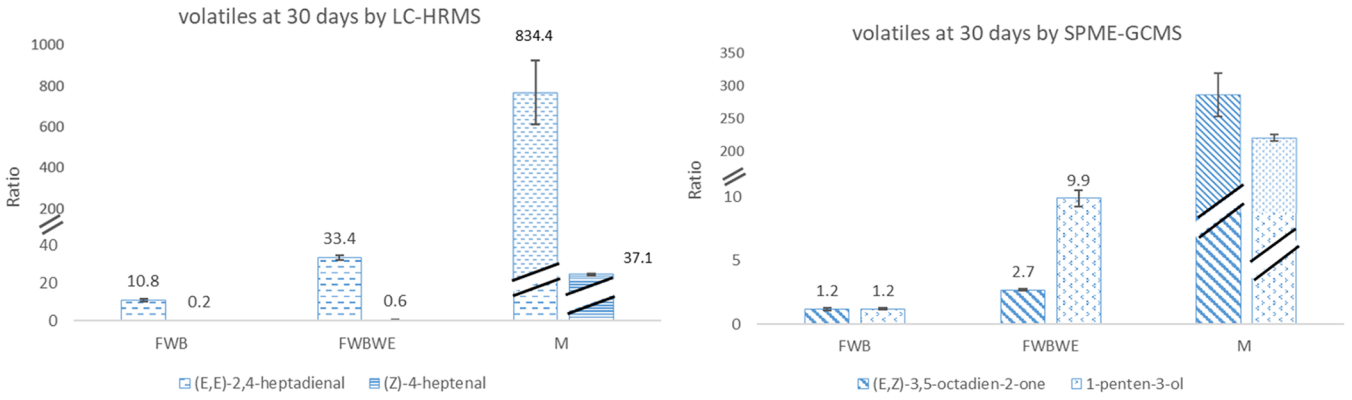


**Figure 3.** Peak area ratio (FWB/FWBWE/M to high DHA fish oil powder) of (*E*,*E*)-2,4-heptadienal and (*Z*)-4-heptenal measured by LC-HRMS and (*E*,*Z*)-3,5-octadien-2-one and 1-penten-3-ol measured by SPME-GC-MS after 30 days accelerated oxidation storage at 38 °C. Commercial high DHA fish oil powder (positive control as reference) was stabilized with 1500 ppm tocopherols. Error bars indicate SD of duplicate measurements ($n$ = 2).

days. The odor descriptions correlated well with the analytical results obtained by LC-HRMS and GC-SPME-MS.

**3.3. Impact of Wheat Bran Water Extract on the Stability of Fish Oil.** The aim of this water extraction was to evaluate the impact of bran water-soluble compounds on the stability of fish oil, because wheat bran hydrophilic fractions were reported to contribute to more than 80% of the total bran (hydrophilic + lipophilic fraction) antioxidant activity.[50] To prepare the accelerated oxidation study, 90 g of FWBWE was mixed with 10 g of fish oil (10% fish oil) and the powder mixture was incubated at 38 °C for 0, 15, and 30 days. The formation of volatiles was monitored. FWBWE and FWB showed comparable inhibition effect on fish oil oxidation when compared with the positive control (high DHA fish oil powder), while maltodextrin did not protect fish oil from oxidation (Figure 3). This result was demonstrated by the peak area ratio (FWB/FWBWE/M to positive control) of (*E*,*E*)-2,4-heptadienal and (*Z*)-4-heptenal by LC-HRMS, and (*E*,*Z*)-3,5-octadien-2-one and 1-penten-2-ol by SPME-GC-MS after 30 days accelerated oxidation.

In this study, we used only water to extract wheat bran hydrophilic fraction. No organic solvents were used in the perspective of application to food products. The optimization of the extraction yield was not targeted here, but it may be interesting for future study. From 1 kg of FWB, 76 g of FWBWE was extracted, which corresponds to an extraction yield of 7.6% w/w of the FWB dry weight. The composition of this water extract was analyzed, and it mainly contains 58.5%


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carbohydrates including 8.59% total dietary fiber, 26.42% proteins, 3.86% lipids, and 10.32% ash (Table 2). The

**Table 2. Composition Analyses of Fine Wheat Bran Water Extract**[a]

| composition | values | units |
|---|---|---|
| total carbohydrates (including fiber) | 58.5 | % |
| total dietary fiber | 8.59 | % |
| protein ($f$ = 6.25) | 26.42 | % |
| nitrogen | 4.23 | % |
| total fat as triglycerides (%) | 1.98 | % |
| total fat as fatty acids (%) | 1.88 | % |
| ash | 10.32 | % |
| total solids | 97.21 | % |
| moisture | 2.79 | % |
| total phenolic content (TPC) | 1.74 | g gallic acid eq/100 g |
| ferulic acid | 72.5 | mg/100 g |
| cichoric acid | 66.0 | mg/100 g |
| sinapic acid | 25.6 | mg/100 g |
| vanillic acid | 6.55 | mg/100 g |

[a]The analytical results were provided by Nestlé Quality Assurance Center Dublin, Ohio, U.S.A.).

FWBWE also contains small quantities of water-soluble phytochemicals such as phenolics. The total phenolic content (TPC) as determined by Folin Ciocalteu was 1.74 g of gallic acid eq/100 g of FWB extract, which is equivalent to 7.64 $\mu$mol of gallic acid eq/g of FWB. The most abundant phenolic acids found in the water extract are ferulic, cichoric, sinapic, and vanillic acids (Table 2).

The samples were also odor evaluated. At time 0, the FWBWE smelt buttery, caramel, and cookielike, while the FWB was cereal-like. Maltodextrin and the positive control were perceived as fresh fishlike and neutral. After 30 days of incubation, no significant changes were detected in the odors of FWB, FWBWE, and the positive control. On the contrary, the sample containing maltodextrin was described as fishy, metallic, or strongly rancid. The caramel-like odor of the FWBWE sample could be explained by Maillard reaction products or carbonyl-amine adducts that could occur during storage in the presence of reducing sugars, amino acids, and carbonyl lipid oxidation products in FWBWE-fish oil mixture. Maillard reaction was reported to occur under mild temperature (37 °C) and low water activity (0.3−0.6) in milk powder.[51] In addition, both Maillard reaction products and carbonyl-amine adducts exhibit antioxidant activities in food products through radical and hydrogen scavenging and metal chelating mechanisms.[52] Besides chemical antioxidant properties of Maillard reaction products, physical protection effect has also been reported by forming an impermeable, thick, and viscoelastic interface layer around oil-in-oil encapsulation.[52,53] These results are very promising for future applications because the FWBWE not only stabilized the PUFAs but also masked the flavor of the fish oil.

In summary, fish oil is very sensitive to oxidation and causes off-flavor in food products during shelf life. The use of byproducts from industrial side-streams (e.g., cereal brans) is a sustainable and consumer friendly approach. In this study, we showed the potential of wheat and rice bran to protect fish oil from oxidation under accelerated oxidation conditions. The formation of off-flavor volatiles was significantly inhibited when fish oil was mixed with cereal bran compared to maltodextrin. Wheat bran had relatively higher protection effect on fish oil than rice bran. The enzymatic hydrolysis and heat treatment of wheat bran did not improve the stability of fish oil despite the increase of ORAC values. The stabilization of PUFAs by bran could be due to chemical (phytochemicals) and physical protection (e.g., entrapment, encapsulation, and capillary attraction of oil). The water-soluble fraction of wheat bran masked the fishy notes and brought pleasant caramel and buttery-like flavor. However, more research is needed to fully understand the antioxidant mechanisms of the cereal bran and the water extract.

To conclude, wheat and rice bran are potential, promising, and cost-affordable natural ingredients for the protection of fish oil from oxidation. These cereal brans are also a good source of dietary fibers, resistant starch, and oligosaccharides which are important for gut health.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsfoodscitech.1c00054

Supplementary 1: The approximate composition of wheat and rice bran. Supplementary 2: List of analytes detected by SPME-GC-MS with their identification information and odor description (PDF)

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### Notes

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