

2013 Annual Meeting Abstracts

Lipid Oxidation and Quality

MONDAY

AFTERNOON

ANA 1/LOQ 1.1: Marine Oils - Analytical and Stability

Chair(s): J. Reuther, Eurofins Central Analytical Labs, USA; V. Barthet, Canadian Grain Commission, Canada

Quantitation of Fatty Acids in Marine Oils by Comprehensive gc-online Hydrogenation x Gc.

P. Delmonte⁽¹⁾, A. Fardin Kia⁽²⁾, J. Rader⁽³⁾

⁽¹⁾US Food and Drug Administration, United States of America ⁽²⁾US Food and Drug Administration, United States of America ⁽³⁾US Food and Drug Administration, United States of America

In this study, the separation of fatty acid methyl esters (FAME) prepared from marine oils provided by an SLB-IL111 capillary column is enhanced by adding a second dimension of separation in a comprehensive GCxGC design. After elution from the first column, the FAME are reduced to their fully saturated form by passing through a capillary tube coated with palladium in the presence of hydrogen carrier gas. The products of reduction are then separated by the secondary high polarity capillary column. The two dimensional separations obtained using this technique can be easily interpreted based on the principle that all the saturated FAME lie on a straight line bisecting the separation plane, while the FAME with the same carbon skeleton but differing in the number, geometric configuration or position of double bonds lie on lines parallel to the D1 time axis. This methodology provides the quantitation of the FAME with different chain lengths that are not separated by mono-dimensional chromatography and it also provides valuable structural information without use of a mass spectrometer. The ease of interpretation of the two dimensional chromatograms and the higher separation capability make this technique far superior to the most refined mono-dimensional separations of FAME.

Determination of Trans Polyunsaturated Fatty Acid Content in Fish oil Supplements Available in the U.S. Market

C. Tyburczy⁽¹⁾, J. Rader⁽²⁾

⁽¹⁾U.S. Food and Drug Administration, United States of America ⁽²⁾U.S. Food and Drug Administration, United States of America

The health effects of dietary trans polyunsaturated fatty acids (PUFA), specifically those of the trans isomers of eicosapentaenoic acid (EPA; 20:5n-3) and docosahexaenoic acid (DHA; 22:6n-3), remain to be fully determined. The present study evaluated the content of trans PUFA in fish oil (FO) supplements available in the U.S. market. FA methyl esters (FAME) from 48 FO supplements were prepared according to Official Method Ce 2-66 of the American Oil Chemists' Society and separated by gas chromatography on a 200 m SLB-IL111 ionic liquid column using a combined ramped temperature and flow program. FAME standards for the trans isomers of EPA and DHA were prepared by isomerization with p-toluenesulfonic acid and fractionated by silver ion thin layer chromatography according to the number of trans double bonds. Across all FO samples, the combined content of trans EPA and trans

DHA (0.1 ? 1.3% of total fat) was unrelated to the total content of all-cis EPA and DHA. Additionally, the content of total trans EPA (0.3 ? 4.8% of all-cis EPA; i.e., the degree of isomerization) was highly correlated with that for DHA ($R^2 = 0.95$). Taken together, these results suggest that processing is the major source of trans PUFA in FO supplements. Our findings demonstrate that the production of FO supplements with low levels of trans PUFA (~1% of total fat) is possible and that the 200 m SLB-IL111 column serves as an important analytical tool for the quantitation of trans PUFA in samples of marine origin.

Microalgae: a Potential Source to Enrich Eggs With Omega-3 Fatty Acids

C. Lemahieu⁽¹⁾, C. Bruneel⁽²⁾, R. Termote-Verhalle⁽³⁾, K. Muylaert⁽⁴⁾, J. Buyse⁽⁵⁾, I. Foubert⁽⁶⁾

⁽¹⁾KU Leuven University Kulak, Belgium ⁽²⁾KU Leuven University Kulak, Belgium ⁽³⁾KU Leuven University Kulak, Belgium ⁽⁴⁾KU Leuven University Kulak, Belgium ⁽⁵⁾KU Leuven University, Belgium ⁽⁶⁾KU Leuven University Kulak, Belgium

The long chain omega-3 polyunsaturated fatty acids (n-3 LC-PUFA), EPA and DHA, are associated with several health benefits. Unfortunately, the average daily intake of n-3 LC-PUFA is below the recommended level, raising interest in food enrichment. To that end, the objective of this study was to increase the level of these n-3 LC-PUFA in eggs by feed adaptation using microalgae. Laying hens were fed with four different n-3 PUFA rich autotrophic microalgae (*Phaeodactylum tricornutum*, *Nannochloropsis oculata*, *Isochrysis galbana* and *Chlorella fusca*). Depending on the amount of algae used and on the algae species, egg yolk could be enriched with different levels of n-3 LC-PUFA, ranging from 50 to 120 mg per egg. This experiment pointed out that *Isochrysis* was the most appropriate alga to use for further research. In a second experiment, a dose response study was performed in which nine different n-3 LC-PUFA doses of *Isochrysis* were fed to laying hens. Taking into account the n-3 LC-PUFA enrichment and the efficiency of n-3 LC-PUFA incorporation, supplementation of 120 mg algal ALA+SDA+EPA+DPA+DHA / 100 g feed was the most optimal dose. This dose gave rise to the highest efficiency of n-3 LC-PUFA incorporation (60%) and an enrichment of 84.5 mg n-3 LC-PUFA/egg.

Analysis of Poly Aromatic Hydrocarbons in Seafood and Fish Oil by GC-MS and GC-MS/MS

A. Pradhan⁽¹⁾

⁽¹⁾Eurofins Central Analytical Laboratories, United States of America

Many Polycyclic Aromatic Hydrocarbons (PAHs) are known to be toxic to humans, and some are carcinogenic. PAHs persist in the environment for long periods of time, increasing the chances of exposure to humans through the food chain. Our laboratory has developed fast and accurate testing methods for PAHs and aliphatic hydrocarbon (AHCs) residues in various types of seafood matrices (e.g. crab, fish, oyster, shrimp) and fish byproducts like fish oil for government agencies and commercial buyers and sellers. We play a major role in implementing high-throughput analysis of PAHs using a saponification/alumina cleanup method for fish oil as well as an ASE method for edible seafood. GC-MS and GC-MS/MS quantitative methods has been developed to analyze both PAHs and AHCs at the same time. Discussion of proper quality control measures that ensure the reliability of data will be presented.

Rapid Analysis of In-process Marine Oil by Quality Trait Analysis (QTA) Infrared Spectroscopy

K. Ma⁽¹⁾, K. Kramer⁽²⁾, C. Teng⁽³⁾

⁽¹⁾Eurofins QTA, Inc., United States of America ⁽²⁾Eurofins QTA, Inc., United States of America ⁽³⁾Eurofins QTA, Inc., United States of America

Recent studies have indicated that consumption of omega 3 fatty acids, particularly eicosapentaenoic acid (EPA) and docosahexanoic acid (DHA), can result in numerous health benefits. EPA and DHA are most abundantly found in the oils of fatty fish. To provide consumers with EPA/DHA dietary supplements, fish oils are refined to increase the EPA and DHA content. It is desirable to have a rapid test to monitor the process in real time. The current method of analysis, gas chromatography, is slow, expensive, and resource-intensive. We present a rapid and simple test for in-process fish oil that can be performed by an operator with no science background or technical expertise. To ensure product safety and accuracy in labeling, EPA/DHA supplements are subject to the US Food and Drug Administration's current Good Manufacturing Practices. Therefore, an accurate test for EPA, DHA, and Total Omega 3 is important for both in-process and finished product oils. QTA patented IR technology provides easy-to-use, reliable and accurate measurement of EPA, DHA, Total Omega 3, Mono- Di-, and Tri- glyceride, Ethyl Ester, and Oligomer for both in-process and finished product marine oils.

Issues in Fortification and Analysis of Omega 3s in Foods

E. Hernandez⁽¹⁾, M. Rusli⁽²⁾

⁽¹⁾Omega Protein, United States of America ⁽²⁾Omega Protein, United States of America

There is an increasing awareness of the health benefits of omega-3 fatty acids which is reflected by the growth in consumption of omega-3 fats either through dietary supplements or fortified foods. Omega-3 fatty acids, particularly the longer chain fatty acids eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA) have been extensively studied for their health promotion and disease prevention properties. When fortifying foods and beverages omega-3s fats are usually added in relatively small amounts (mg per serving) and these fatty acids can become imbedded in the matrix in the food components (i.e., complexes of protein, carbohydrates and other fats) which makes the analysis of EPA and DHA makes analysis ever more difficult. Sometimes this can result in appreciable differences between the calculated levels of EPA and DHA in the products formulated and the experimental results from the lab. Fortified foods can have as little as 32mg of EPA and DHA in a 250g serving. This presentation will include examples of foods fortified with omega 3s, techniques of sample preparation, methods of analysis and reporting for ALA, EPA and DHA for certificates of analysis, product validation, and for labeling.

Bioimprinting And/or Immobilization of Lipases for Selective Ethanolysis of Fish Oil

D. Kahveci⁽¹⁾, X. Xu⁽²⁾

⁽¹⁾Yeditepe University, Food Engineering Department, Turkey ⁽²⁾Aarhus University, Denmark

Lipases are unique enzymes with their hydrophobic active site buried under an amphiphilic peptidic lid, which goes under a conformational rearrangement upon contact with a water-lipid interface, leading to the exposure of the active site. This phenomenon, called interfacial activation, is the key to bioimprinting strategy, which involves the incubation of lipase with a substrate analogue in aqueous medium, followed by lyophilization. The lipase is activated since it gets caught in action and unable to adopt its former conformation due to its rigid structure in organic solvent. Bioimprinting of lipases not only improve their activity and stability in anhydrous medium, but also can help to modify their selectivity. If the process is designed properly, immobilization has been revealed as a powerful tool to improve enzyme properties, such as stability, activity, specificity and selectivity. Combination of bioimprinting and immobilization has been employed to several lipases in order to improve activity and stability. The present lecture aims to give a brief overview of the use of bioimprinting w/o immobilization to improve activity and selectivity of lipases, followed by the authors' work on enhancement of those of *Candida rugosa* lipase (CRL) and *Candida antarctica* lipase A (CALA) for selective ethanolysis of fish oil. CRL bioimprinted with fatty acids exhibited 8-fold enhanced transesterification activity in hexane. Fatty acid selectivity of CALA was improved by immobilization

combined with bioimprinting, resulting in 5.5-fold lower omega-3 PUFA in ethyl esters fraction.

Accelerated Solvent Extraction of Lipids: A Highly Efficient Method Preferred for Lipid Oxidation Studies

L. Yao⁽¹⁾, K. Schaich⁽²⁾

⁽¹⁾Rutgers University, United States of America ⁽²⁾Rutgers University, United States of America

The handling required in extraction of lipids for oxidation analyses always poses problems with adventitious oxidation. In previous research, we found that Accelerated Solvent Extraction (ASE) extracts lipids from complex matrices such as processed cheese, biological tissues, and extruded food products with high efficiency. This study focused on optimizing ASE extractions from extruded pet foods (mixed meat and grain base) observed that ASE extractions also minimize degradation during extraction. Extruded kibbles ground to 250 micron particle size were ASE extracted with chloroform, chloroform-methanol 2:1, hexane, and hexane:methanol 2:1. Extraction static time and numbers of extraction cycles were varied to optimize lipid yields. Extracts dried under vacuum were analyzed for lipid composition by thin layer chromatography and for oxidation by conjugated dienes (AOCS Ti 1a-64) and hydroperoxides (PeroxySafe™ assay). ASE extraction at 40 °C provided comparable or higher yields than manual or Soxhlet extraction in shorter extraction times (10-40 minutes depending on the matrix) while inducing less oxidation than manual extraction and less thermal degradation than Soxhlet. Oxidation increased with extraction temperature (60 °C max), but remained lower than other methods. Results also demonstrated that ASE can also utilize normally immiscible solvents to advantage. Hexane and methanol injected into extraction cells separately were able to nearly duplicate extractions of chloroform:methanol, providing an option for replacing chlorinated hydrocarbon solvents. However, differences in oxidation for the two solvents were observed, probably resulting from stabilizers in the chloroform. Overall, ASE appears to provide a superior method for lipid oxidation studies.

Oxidative stability of krill (*Euphasia superba*) oil

I. Bruheim⁽¹⁾, A. Oterhals⁽²⁾, B. Haugsgjerd⁽³⁾, G. Vogt⁽⁴⁾, M. Griinari⁽⁵⁾, B. Thomsen⁽⁶⁾, H. Lu Fung Sieng⁽⁷⁾, C. Jacobsen⁽⁸⁾

⁽¹⁾Olympic Seafood AS, Norway ⁽²⁾Nofima, Norway ⁽³⁾Nofima, Norway ⁽⁴⁾Nofima, Norway ⁽⁵⁾Clanet, Finland ⁽⁶⁾Technical University of Denmark, Denmark ⁽⁷⁾Technical University of Denmark, Denmark ⁽⁸⁾Technical University of Denmark, Denmark

Krill oil is a unique source of omega-3 LCPUFA where the omega-3 fatty acids are bound predominantly to phospholipids. Data in the public domain suggests that the oxidative stability of krill oil assessed by peroxide and anisidine values (PV and AV) is extremely good. However, data from controlled experiments using a broad range of analytical methods to study oxidative stability are lacking. We set out to perform an experiment where oxidation of food grade krill oil and fish oil was studied under accelerated conditions (samples incubated at 40 C, exposed to air and stirred). Sampling was performed on day 0, 7 and 21 and the oxidative status was assessed by determination of PV, AV, thiobarbituric acid reactive substances (TBARS), conjugated dienes, volatile secondary oxidation products and volatile Strecker degradation products (both by dynamic headspace GC-MS analysis), tocopherols, astaxanthin, and pyrroles. Increases in PV, conjugated dienes and TBARS as well as decrease in tocopherols were observed in fish oil samples whereas there were no changes in krill oil. AV increased in fish oil and a less pronounced and variable increase was observed for krill oil. This observation was consistent with pronounced increase in volatile secondary oxidation products in fish oil samples and less pronounced response in krill oil samples. Strecker degradation products and hydrophobic pyrroles increased only in krill oil samples and slight decrease in krill oil astaxanthin was also observed. These findings suggest that PV and AV may have limited use in assessment of the oxidative changes in krill oil.

LOQ 1: Algal Oils

Chair(s): S. Kassner, DSM Nutritional Products, USA; K. Miyashita, Hokkaido University, Japan

Evaluation of sensory stability of algae oils by GCxGC-ToF-MS

A. Duesterloh⁽¹⁾, N. Macfarlane⁽²⁾, S. Salisu⁽³⁾, S. Kassner⁽⁴⁾, M. Stefanski⁽⁵⁾

⁽¹⁾DSM Nutritional Products, Switzerland ⁽²⁾DSM Nutritional Products, England ⁽³⁾DSM Nutritional Products, United States of America

⁽⁴⁾DSM Nutritional Product, United States of America ⁽⁵⁾DSM Nutritional Product, United States of America

In the present study we evaluated the effect of various antioxidant combinations (AOX). Samples were stored up to 9 months and the sensory properties were scored by a trained sensory panel. All samples were analysed by SPME-HS-GCxGC-ToF-MS. Volatile off-odor compounds like (E,Z)-2,6-nonadienal, (E,Z)-2,4-heptadienal and (E,Z)-2,4-decadienal or E-4-heptenal were quantified at low ppb levels below the human odor threshold. The scope of the study was to correlate sensory panel data for differently stabilized algae oils with analytical data at levels between 5-20 ppb, i.e. at concentrations where the consumer perception might change from 'not fishy' to 'fishy'. The data sets, including profiling data of up to 70 different compounds analysed by GCxGC-ToF-MS, were evaluated by uni-variate and multi-variate statistical techniques. A group of ca. 20 compounds were highly correlated with the attribute 'fishy?', mainly including unsaturated, aldehydes and ketones. It was possible to correlate other sensory attributes with the changes in the AOX composition in the DOE. The methodology used will help to understand the effect of small changes in the AOX composition on the sensory properties and the stability of algae oils.

The Use of Sensory Data for Shelf-Life Modeling of Algal Oil

S. Lumor⁽¹⁾

⁽¹⁾Delaware State University, United States of America

Shelf-life assessment can be an arduous task, particularly for polyunsaturated oils because several flavor notes are usually produced during oil degradation and it is difficult to pin-point which flavor notes impart oil quality the most. In cases where the flavor note has been identified, it is usually difficult to confidently determine the level of the analyte that corresponds to the end of shelf-life. In this presentation, the use of sensory data for modeling shelf-life of algal oil, which is rich in polyunsaturated fatty acids, will be demonstrated, and the use of the shelf-life model to predict the amount of shelf-life remaining, during storage or distribution, as a function of temperature will be demonstrated as well. Moreover, the integration of analytical and sensory data to determine the level of an analyte responsible for quality loss will be discussed.

Oxidative Characteristics of Algal Lipids

K. Miyashita⁽¹⁾

⁽¹⁾Hokkaido University, Japan

Due to their higher degree of unsaturation, omega-3 polyunsaturated fatty acids (PUFA) such as α -linolenic (LN; 18:3n-3), stearidonic acid (18:4n-3; SDA), and eicosapentaenoic (EPA; 20:5n-3) acids are much more susceptible to oxidation than other PUFA such as linoleic acid (LA; 18:2n-6). On the other hand, a large amount of LN, SDA and EPA is present as glycolipids (GLs) in photosynthetic membranes of seaweeds. These GLs have an important role in the biological systems, while the GL is always exposed to photooxidation in the thylakoid membrane. PUFA of GL in the photosynthetic membrane will be protected by antioxidants such as carotenoids and tocopherols. In addition,

we have suspected that PUFA as GL form might be protective to the oxidation as compared with other lipid forms. The present paper made clear the oxidative stability of PUFA in GL from this viewpoint. The study showed that GL from seaweeds showed the higher oxidative stability than those of fish oil TAG or fish egg phosphatidylcholine (PC), though fish TAG had the same number of average double bonds in the molecule as those of seaweed GL. Seaweed GL showed the same oxidative stability as that of soybean oil TAG.

Oxidative Stability of Microalgal Oils Rich in Omega-3 Lc-pufa

E. Ryckebosch⁽¹⁾, C. Bruneel⁽²⁾, K. Muylaert⁽³⁾, I. Foubert⁽⁴⁾

⁽¹⁾KU Leuven University Kulak, Belgium ⁽²⁾KU Leuven University Kulak, Belgium ⁽³⁾KU Leuven University Kulak, Belgium ⁽⁴⁾KU Leuven University Kulak, Belgium

Numerous studies have shown that the long chain omega-3 polyunsaturated fatty acids (LC-PUFA) EPA and DHA are effective in preventing or treating several diseases. Nevertheless, the current average intake of these LC-PUFA is below the recommended level. This raises interest in food supplements containing LC-PUFA on the one hand and food stuffs enriched with LC-PUFA on the other hand. Currently, the main commercial source of omega-3 LC-PUFA is fish. However, several problems are associated with this source: unpleasant odor, low oxidative stability, geographical and seasonal variation in quality, as well as increasingly stringent regulation of fisheries. The aim of this research was to investigate the oxidative and hydrolytic stability of omega-3 LC-PUFA rich microalgal oils. Therefore, microalgae oils obtained with two 'food grade' extraction solvents (hexane and hexane/isopropanol 3:2) from 5 species (*Isochrysis galbana*, *Nannochloropsis gaditana*, *Nannochloropsis* sp., *Phaeodactylum tricornutum* and *Pavlova* sp.) were stored for 8 weeks. Both primary (PV) and secondary oxidation products (GC-SPME) were followed. The results show that all microalgae oils are more stable than the commercially available fish oil, tuna oil and DHA-S oil. Furthermore, the microalgae oils obtained with hexane/isopropanol seem to be more stable than the ones obtained with hexane.

Antioxidant Effect of Seaweed Extracts in Vitro and in Food Emulsion Systems Enriched With Fish Oil

C. Jacobsen⁽¹⁾, D. Larsen⁽²⁾, S. Farvin⁽³⁾

⁽¹⁾Technical University of Denmark, Denmark ⁽²⁾Technical University of Denmark, Denmark ⁽³⁾Technical University of Denmark, Denmark

Natural antioxidants derived from marine algae have a high content of bioactive components with potential for improving oxidative stability of lipids in food systems. Bioactive components like polyphenols have been identified in marine algae. In this presentation we will discuss results from our ongoing work on the brown algae *Fucus vesiculosus*. This seaweed contains a wide range of polyphenols with potential antioxidant activity. Thus, in vitro antioxidant properties of *F. vesiculosus* extracts have been found to be related to the total polyphenolic content. It has been suggested that the primary antioxidant activity comes from secondary metabolites such as phlorotannins, a dominant polyphenolic compound. However, studies on the effectiveness of seaweed extracts in food model systems are sparse, therefore there is a need to look further into this area. Results obtained in our lab with different extracts of *F. Vesiculosus* in a range of different food models will be presented.

Functionalities of Marine algal Polyphenols, Phlorotannins from brown seaweeds

Y. Jeon⁽¹⁾

⁽¹⁾Jeju National University, Korea, Republic of

Marine algae are popular and abundant food ingredients mainly in Asian countries, and also well known for their health beneficial effects due to presence of biologically active components. The marine algae have been studied for biologically active components and marine polyphenols are one among them. Among marine algae, brown algae have extensively studied for their potential anti-diabetic activities. Majority of the investigations on polyphenols derived from brown algae have exhibited their various anti-diabetic mechanisms such as α -glucosidase and α -amylase inhibitory effect, glucose uptake effect in skeletal muscle, protein tyrosine phosphatase 1B (PTP 1B) enzyme inhibition, improvement of insulin sensitivity in type 2 diabetic db/db mice, and protective effect of diabetes complication. Therefore, it seems likely that polyphenols of brown algae is a promising functional food or pharmaceutical source that will be helpful for the improvement of type 2 diabetes.

Strategies in the stabilization of fish oils and algal oils

W. Indrasena⁽¹⁾, C. Luigart⁽²⁾, J. Kralovec⁽³⁾

⁽¹⁾DSM Nutritional Products, Canada ⁽²⁾DSM Nutritional Products, United States of America ⁽³⁾DSM, Canada

Algal and microbial oils are becoming popular sources for polyunsaturated omega-3 fatty acids (PUFA) such as eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA) in the form of supplements as well as vital components in food products. Flavor volatiles produced from the decomposition of hydroperoxides generated by the rapid oxidation of these fatty acids have low sensory thresholds and potentially have great impact on the odour and flavor of these oils as well as the food products containing them. Antioxidants are commonly used to retard the oxidation and natural antioxidants are preferred over synthetic antioxidants. Phenolic antioxidants with possible synergistic antioxidants were used in the stabilization of food grade fish oil. The antioxidants were added to the oil before or after deodorization and the sensory stability, hydroperoxide levels (PV) and p-anisidine values (p-AV) were monitored weekly. EPA and DHA-rich algal oils were also stabilized with natural phenolic antioxidants and the sensory stability was monitored every week. Phenolic antioxidants considerably decreased not only the production of hydroperoxides and secondary oxidation products but also the level of deteriorative flavor volatiles improving the sensory of the oil. The sensory stability varied according to the type and quantity of antioxidants as well as the type of substrate used. This presentation will be mainly focused on some strategies used to improve the sensory stability of both algal and fish oils using natural phenolic antioxidants.

TUESDAY

MORNING

LOQ 2: Managing Oxidation in Real Foods

Chair(s): R. Nahas, Kalsec Inc., USA; C. Jacobsen, Technical University of Denmark, Denmark

Cancelled-Oxidative Stability of Margarines With Addition of Pecan nut Shell Extracts [*carya Illinoensis* (wangenh) c. Koch]

J. Block⁽¹⁾, P. Engler⁽²⁾, A. Dal Bó⁽³⁾, R. Luchtenberg⁽⁴⁾

⁽¹⁾UFSC, Brazil ⁽²⁾UFSC, Brazil ⁽³⁾Bunge, Brazil ⁽⁴⁾UFSC, Brazil

Protein Oxidation and pet Food

S. Cutler⁽¹⁾, B. Bowen⁽²⁾

⁽¹⁾Kemin Industries, United States of America ⁽²⁾Kemin Industries, United States of America

High protein, grain free extruded kibble diets have become popular among pet food customers. This study was undertaken to determine the extent of oxidation of protein sources in pet food raw materials and their effect on diet stability. The most common outcomes of protein oxidation are formation of carbonyls, loss of sulfhydryl groups, peroxide formation, and cross-linking. The classic method of carbonyl determination is performed by acid-derivation reaction of extracted proteins to 2,4-dinitrophenylhydrazine, measured colorimetrically. When sulfhydryl groups present in methionine, cysteine, and taurine are oxidized, the loss of thiol groups may be quantified by reaction with Ellman's reagent (5,5 dithiobis 2 nitrobenzoic acid). Lipid oxidation measures were tracked with peroxide value formation by FOX-2 method. Rendered meals with acceptable and poor quality as determined by peroxide value (PV) were tested for carbonyls and loss of thiols. For chicken meal, a higher peroxide value was correlated with a higher level of carbonyls/mg and an inverse relationship existed for thiols. Chicken meal treated with an antioxidant product had lower carbonyl values than untreated chicken meal ($p < 0.05$). Pet food kibbles made with oxidized meal showed higher levels of carbonyls after extrusion when compared to treated meal. Protein oxidation measures may be an additional tool to measure pet food quality and the relationship between protein oxidation and lipid oxidation in the extruded matrix warrants additional study.

Oxidation Rates of Triacylglycerol and Ethyl Ester Fish Oil

J. Sullivan Ritter⁽¹⁾, S. Budge⁽²⁾

⁽¹⁾Ascenta Health, Canada ⁽²⁾Dalhousie University, Canada

Fish oil dietary supplements are sold as both triacylglycerols (TAG) and ethyl esters (EE). The high levels of the polyunsaturated fatty acids eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA) contained in fish oil supplements makes these products prone to rapid oxidation. Though it is generally assumed that TAG products are more stable than EE product, there is little published evidence to support this. In this study, the stability of TAG and EE oils with the same levels of EPA and DHA were evaluated at 5°C, 15°C, 30°C, 45°C and 60°C to determine if rates of oxidation differed between the two products. Fatty acid profile and peroxide value (PV) were measured and used as indicators of oxidation. This study found that PV increased much more rapidly in fish oil EE than in TAG, suggesting that fish oil supplements containing TAG were more resistant to oxidation than products containing EE.

Managing Oxidation in Fish and Fish Products

I. Medina⁽¹⁾

⁽¹⁾Spanish National Council of Research CSIC, Spain

Fish and Seafood have been a part of the human diet for millennia. The perception of fish as a healthy food especially due to this high content on n-3 PUFA, is now used for fishing enterprises to stimulate consumption. However, fish products are a very perishable material. Oxidation of their long chain PUFA provokes the development of off-flavors and rancidity which continues to be the main objection in the exploitation and commercialization of products based on fish muscle. Moreover, the biological functionality attributed to their lipids can decrease. The first defense of fish

muscle against oxidation is related to the presence of lipophilic and hydrophilic antioxidants such as α -tocopherol, ascorbic acid and others. These compounds are subsequently lost during postmortem storage. In addition, prooxidants as hemoproteins and metal catalyzers are affected by the decrease of pH and other postmortem changes resulting in high prooxidant activities. Fish rancidity can not be totally avoided, but some procedures considering the dynamism of fish tissues can minimize the rate of oxidation. This work reviews different aspects of the use of natural antioxidants aimed to retard or minimize lipid oxidation in fish and fish products. Considering the oxidative mechanism occurring in fish muscle, natural compounds are proposed for acting at different levels of the oxidative reactions. Their effects as scavengers of free radicals or reductants of the fish muscle pro-oxidants are studied. The influence of the physical location of the antioxidants or the synergistic effects with other endogenous antioxidants of fish tissues are intensely stressed.

The use of Delivery Emulsions for Fish oil Addition to Dairy Products

A. Horn⁽¹⁾, U. Andersen⁽²⁾, N. Nielsen⁽³⁾, C. Jacobsen⁽⁴⁾

⁽¹⁾Technical University of Denmark, Denmark ⁽²⁾Arla Foods a.m.b.a., Denmark ⁽³⁾Technical University of Denmark, Denmark ⁽⁴⁾Technical University of Denmark, Denmark

Healthy fish oil enriched food products are highly susceptible to lipid oxidation, which might lead to a loss of the beneficial long chain n-3 fatty acids, and potential off-flavour formation. One possible strategy to avoid lipid oxidation is to protect the oil in a delivery emulsion in which the oil droplets are shielded from possible pro-oxidative surroundings by an emulsifier. The antioxidative properties of milk proteins make them an obvious choice as emulsifiers in delivery emulsions. Previous studies have furthermore shown that a combination of proteins and phospholipids may increase the thickness of the interfacial layer in an emulsion to confer additional protection. This presentation will include results from studies on milk and cream cheese, which have been added fish oil-in-water delivery emulsions prepared with different milk proteins or combinations of milk proteins and phospholipids. The addition of delivery emulsions has been compared to the addition of neat fish oil or no oil addition to these two food products. Lipid oxidation was studied during storage for 11 days in milk and 20 weeks in cream cheese. In cream cheese, the choice of emulsifier for the delivery emulsion affected the resulting oxidative stability, whereas in milk, this was not the case.

Understanding and Reducing Lipid Oxidation in Low-moisture Foods

L. Barden⁽¹⁾, E. Decker⁽²⁾

⁽¹⁾University of Massachusetts Amherst, United States of America ⁽²⁾University of Massachusetts Amherst, United States of America

Little systematic research has been conducted on rancidity in low-moisture foods, such as those with water activity below 0.5. Since low moisture foods account for large percentages of consumers' saturated fat intake, these products could be improved by replacing the saturated fats with polyunsaturated oils. However, this approach is limited by increased lipid oxidation rates. Thus, there is great incentive to understand how to stabilize unsaturated fats in low moisture foods. In this study, a cracker model system was utilized using interesterified soybean oil (ISO) as the lipid source. The total polyunsaturated fatty acid composition of the ISO was 39%. Rosmarinic acid and rosmarinic acid esters of varying alkyl chain lengths were added to the crackers to determine the effect of antioxidant hydrophobicity on partitioning, functionality, and efficacy in the low-moisture cracker system. Efficacy was determined by measuring both peroxides and hexanal evolution over time. Results suggest that esters of intermediate polarity?e.g. 12 carbons in fatty acid chain?were most effective. The antioxidants, lipid, and protein were visualized using confocal laser scanning microscopy. Imaging showed that lipid often partitioned around air bubbles. Strategic addition of antioxidants rather than haphazard selection shows promise for reducing lipid oxidation in low-moisture foods.

Phenolipids as Antioxidant in Omega-3 Enriched Food Products

A. Sørensen⁽¹⁾, M. Alemán⁽²⁾, E. Durand⁽³⁾, P. Villeneuve⁽⁴⁾, R. Bou⁽⁵⁾, F. Guardiola⁽⁶⁾, C. Jacobsen⁽⁷⁾

⁽¹⁾Technical University of Denmark, National Food Institute, Denmark ⁽²⁾University of Barcelona, Spain ⁽³⁾CIRAD, UMR IATE, France

⁽⁴⁾CIRAD, UMR IATE, France ⁽⁵⁾CSIC, Spain ⁽⁶⁾University of Barcelona, Spain ⁽⁷⁾Technical University of Denmark, Denmark

Foods containing omega-3 PUFA are highly susceptible to oxidation. This causes formation of undesirable flavors and loss of health-beneficial fatty acids. To protect these food products, antioxidant addition may be a solution. Lately, extensive work has been performed on phenolipids and their efficacy in model emulsion systems. Since the polar paradox hypothesis was a simplified statement of the antioxidant efficacy in emulsions, a new term, 'cut-off effect', was introduced. The cut-off effect describes the efficacy of phenolipids in simple emulsions. However, most food products consist of a complex matrix where several factors may influence the oxidative stability, e.g. type and concentration of emulsifier. Thus, a better understanding of the antioxidative effect of phenolipids in complex foods is of great interest. The aim of this study was to evaluate the antioxidative effect of caffeic acid and its esters, caffeates, in two different fish-oil-enriched food products: mayonnaise and milk. Lipid oxidation was evaluated from 3 parameters measured over storage time: peroxide value, volatiles and tocopherol concentrations. The results demonstrate the influence of the complex emulsions on the antioxidant efficacy.

The use of Multi-functional Lipid Oxidation Management Strategies to Successfully Replace Synthetic Antioxidants With Natural Alternatives in Several Complex Food Matrices

J. McKeague⁽¹⁾, L. Burroughs⁽²⁾, M. Wolf⁽³⁾

⁽¹⁾Kalsec, United States of America ⁽²⁾Kalsec, United States of America ⁽³⁾Kalsec, United States of America

Consumers are continuing to demand cleaner and more natural labels. In order to meet this demand, product developers must find natural alternatives for many synthetic ingredients including antioxidants. The first and most imperative step to identify a suitable replacement is to understand the chemistry of oxidation and the role various antioxidants play in the lipid oxidation pathway. Combinations of natural antioxidants with different modes of action were found to be superior to a single compound, highlighting both the complex nature of oxidation, and the shelf-life implications that product developers face as oxidative quality deteriorates, resulting in off-flavors and aromas. Various food models were developed and utilized to screen individual antioxidant components, and to investigate and quantitatively capture synergistic effects. Subsequently, antioxidant formulations were designed and tested in a number of food applications. Both sensory and analytical methods were employed. The analytical methods included headspace SPME GC-MS, peroxide values and thiobarbituric acid values, while sensory methodology included descriptive profiling and difference testing. For the first time, natural antioxidants were found to be as effective or in some cases even exceeded the performance of standard synthetic antioxidants in a number of matrices including meats, oils, dairy products and snacks. Integral steps to successfully replace a synthetic antioxidant included using mixtures with the appropriate natural antioxidant functionality, combining these antioxidants in the right ratios, integrating the antioxidant in the food through the appropriate carrier, and adding the antioxidant at the ideal point in the food production process.

Common industrial practices to prevent lipid oxidation from food formulation to distribution

L. Liu⁽¹⁾

⁽¹⁾Cargill, Inc., United States of America

Lipid oxidation is one major factor in determining sensory preference and shelf life of processed food products. This presentation reviews industrial practices including high stability oils, antioxidants, inerting, temperature control and packaging for minimizing lipid oxidation and ensuring product quality.

AFTERNOON

LOQ 3: Novel Antioxidants

Chair(s): A. Bedford, Bunge Oils Inc., USA; E. Decker, University of Massachusetts, USA

The Functions of Vitamin e Tocotrienol

B. Tan⁽¹⁾

⁽¹⁾American River Nutrition, United States of America

For 90 years, vitamin E research has produced prolific and notable discoveries, including isolation from plants, chemical identifications and total syntheses. In the four decades immediately following the discovery of vitamin E alpha-tocopherol by Drs. Herbert M. Evans and Katherine S. Bishop in 1922, the main vitamin E function studied was its antioxidative properties. Antioxidation research continued through the '70s and '80s, and then diminished in the 1990s while tocotrienol studies picked up. Currently, the main areas of tocotrienol research are in cancer, inflammation, cardiovascular disease and diabetes, while antioxidants are also making a comeback. Most recently, other research groups have sparked interest in tocotrienol's ability to fight aging, counter radiation, decrease and reverse bone loss, and delay cognitive decline. With more than one-third of research published just in the last few years and many previously unknown functions not shared by their tocopherol siblings, tocotrienols are considered to be the 21st century vitamin E. This presentation will cover: ?Introduction to vitamin E tocopherol and tocotrienol ?Alpha-tocopherol interference with tocotrienol functions ?Compositional and unmatched uniqueness of annatto tocotrienol ? Examples of tocotrienol as better antioxidant than tocopherol ?Tocotrienol functions to lower cholesterol ?Tocotrienol functions to inhibit cancer: breast, prostate, pancreas, skin, colo-rectum ?Other emerging functions of tocotrienol

Investigating the Antioxidant Effects of Phosphatidylserine

A. Reid⁽¹⁾, S. Budge⁽²⁾

⁽¹⁾Dalhousie University, Canada ⁽²⁾Dalhousie University, Canada

Commercially, mixtures of phospholipids such as lecithin are used as antioxidants to preserve oil quality. Literature indicates that phospholipids, including phosphatidylserine (PS), have oxidative protective effects however, their effect is primarily thought to be due to synergy with added or naturally occurring tocopherols found in the oxidative system. The effectiveness of PS as an antioxidant on its own and in the presence of tocopherols was investigated by monitoring the formation of primary and secondary oxidation products by measuring the peroxide and p-anisidine values of tocopherol stripped fish oil stored open under ambient conditions. A slight antioxidant effect of PS was noted after the oil was heavily oxidized. Overall, synergy was not found to exist between tocopherols and PS.

The Impact of the Hydrophilic Antioxidants and Tocopherols Combinations on the Oxidative Stability of Algae Oil

B. CHEN⁽¹⁾, D. McClements⁽²⁾, E. Decker⁽³⁾

⁽¹⁾Southwest University, China ⁽²⁾University of Massachusetts Amherst, United States of America ⁽³⁾University of Massachusetts Amherst, United States of America

Water soluble antioxidants such as green tea extract and ascorbic acid has been previous found to prevent the algae oil oxidation effectively. In this study, the impact of those two water soluble antioxidants on the fate of individual tocopherol and mixed tocopherols in the algae oil was investigated through oxidative kinetic study. Meanwhile, the depletion of tocopherols was studied by NF-HPLC. The addition of water soluble antioxidants could potentially delay the depletion of tocopherol and synergize the antioxidants effectiveness in the algae oil system.

Interactions Between alpha-tocopherol and Rosmarinic Acid and its Alkyl Esters in Emulsions

A. panya⁽¹⁾, K. Kittipongpittaya⁽²⁾, M. Laguerre⁽³⁾, C. Bayrasy⁽⁴⁾, J. Lecomte⁽⁵⁾, P. Villeneuve⁽⁶⁾, D. McClements⁽⁷⁾, E. Decker⁽⁸⁾

⁽¹⁾National Center for Genetic Engineering and Biotechnology (BIOTEC), Thailand ⁽²⁾University of Massachusetts Amherst, United States of America ⁽³⁾CIRAD, France ⁽⁴⁾CIRAD, France ⁽⁵⁾CIRAD, France ⁽⁶⁾CIRAD, France ⁽⁷⁾University of Massachusetts Amherst, United States of America ⁽⁸⁾University of Massachusetts Amherst, France

Synergistic antioxidant interaction, another strategy to improve antioxidant activity in foods, can more effectively inhibit lipid oxidation. Besides chemical reactions, different physical locations and environmental pH of antioxidant might impact to overall antioxidant performance in foods. Esterification of rosmarinic acid produces a variety of compounds with different antioxidant activity due to differences in polarity and thus differences in partitioning in oil, water, and interfacial regions of oil-in-water emulsions (O/W). Therefore, rosmarinic acid and rosmarinate esters provide an interesting tool to study the ability of antioxidant to interact in O/W emulsions. In O/W emulsions, rosmarinic acid (R0) exhibited the strongest synergistic interaction with α -tocopherol while butyl (R4) and dodecyl (R12) rosmarinate esters exhibited small synergistic interaction and eicosyl rosmarinate esters (R20) exhibited slightly antagonistic interaction. Fluorescence quenching and electron paramagnetic resonance (EPR) studies showed that water soluble rosmarinic acid (R0) exhibited more interactions with α -tocopherol than any of the tested esters (R4, R12, R20). In addition, regeneration efficiency of α -tocopherol by R0 exhibited strong pH dependence. At pH 7, R0 exhibited the strongest synergy with α -tocopherol observed in the O/W emulsions and the EPR study. However, the synergy was decreased under lower pH environments. Even though the investigated physical and chemical parameters implied that electron transfer mechanism might contribute to the synergistic interaction between α -tocopherol and R0, the further investigation on sparing effect and decomposition of antioxidant during oxidation suggested that electron transfer mechanism could theoretically occur; however, it might be not efficient to promote synergistic effect.

Antioxidant Activity of Extracts Obtained From Different Herbs by Supercritical Carbon Dioxide Extraction

I. Vieitez⁽¹⁾, I. Mailhe⁽²⁾, M. Braun⁽³⁾, I. Jachmanián⁽⁴⁾

⁽¹⁾Facultad de Química (UDELAR), Uruguay ⁽²⁾Facultad de Química (UDELAR), Uruguay ⁽³⁾Facultad de Química (UDELAR), Uruguay ⁽⁴⁾Facultad de Química (UDELAR), Uruguay

It is known the viability of obtaining extracts rich in natural antioxidants from many herbs and spices commonly consumed with potential to be used in the food industry. Furthermore, the utilization of synthetic antioxidants is limited because consumers are increasingly demanding additive-free or natural products. Supercritical fluid extraction with carbon dioxide (SC-CO₂) is considered to be one of the most suitable methods for obtaining natural antioxidants. Carbon dioxide is safe, non-toxic, non-carcinogenic, non-flammable and has mild critical points (31.1°C, 7.38MPa).

This technology provides solvent free extracts and the selectivity of the supercritical CO₂ can be conveniently adjusted by varying temperature and pressure. The aim of this work was to investigate isolation of antioxidant fractions from rosemary (R), oregano (O), marcela (M), and carqueja (C) by SC-CO₂, as well as to determine the antiradical power of the extracts by DPPH and their antioxidant effect when incorporated at different concentration to sunflower oil using the Rancimat method at 100°C. Addition of extracts R, M and O in a concentration of 500ppm to purified sunflower (without any native or added antioxidants) allowed to increase its oxidative stability 8.7, 3.1 and 1.8 times, respectively, while extract C did not produce any significant effect. Addition of synthetic antioxidants TBHQ, BHA and BHT at the same concentration to the oil increased 9.6, 7.8 and 6.4 times the oxidative stability, respectively. The supercritical extracts obtained from the herbs studied are attractive to be used as natural antioxidants, alternatives to the synthetic antioxidants used by the food industry.

Use of Hydrolysable Tannins From Sweet Chestnut (*castanea Sativa Mill.*) to Reduce Tobacco Specific Nitrosamines (tsna) and Improve Antioxidant Content in Plants

E. Bargiacchi⁽¹⁾

⁽¹⁾Consortium INSTM, Italy

Hydrolysable tannins, water-extracted from sweet chestnut biomass (CHT) and membrane concentrated, have several remarkable effects as antioxidant, antimicrobial, and metal complexing agents. To formulate more use-oriented products, several whole water extracts and process streams, obtained by membrane separation technology, were analyzed and characterized, using HPLC/DAD/ESI-MS methods. Individual polyphenols were identified using their retention times, and both spectroscopic and spectrometric data; quantitation was directly performed by HPLC/DAD, using regression curves built with the available standards. Each one of the analyzed fractions was tested for its antioxidant and antiradical activity using in vitro spectrophotometric methods, i.e., respectively, (i) Folin-Ciocalteu reagent assay (measure of the antioxidant activity through an evaluation of polyphenol content, expressed as Gallic Acid Equivalent, GAE) and (ii) test of the stable radical DPPH[•], 1,1-diphenyl-2-picrylhydrazyl (measure of the antiradical activity expressed as the polyphenols concentration which inhibits to 50% the activity of stable radical DPPH[•], EC₅₀). The properties of selected extracts and fractions, their mixtures, also with other tannin sources, were evaluated for direct spraying on crops, to inhibit some biochemical-related spoiling processes, namely the accumulation of TSNA in tobacco, and improve safety and quality characteristics of plant products by increasing their endogenous antioxidant content. Some of the results obtained are patent pending.

WEDNESDAY

MORNING

LOQ 4: Rancidity and Antioxidant Assessment

Chair(s): S. Zhou, Kelloggs North America Co., USA; H.-S. Hwang, USDA, ARS, NCAUR, USA; M. Pietz, Archer Daniels Midland Co., USA

Lipid Oxidation in Dry Pet Food

M. Hu⁽¹⁾, J. Erdmann⁽²⁾

⁽¹⁾DuPont, United States of America ⁽²⁾DuPont, United States of America

The objective of the presentation is to address the composition, structure and oxidative stability of dry pet food (kibbles). The structures of dry pet food are different from those of bulk oil, O/W and W/O emulsions, powder products and various human foods. A kibble is composed of tiny porous core (kibble matrix) and coating surface covering the kibble matrix. The kibble matrix could be the carbohydrate-protein-lipid network structure formed by the interaction mainly among carbohydrate, protein, lipid and water in the extruder. Dry pet food is usually composed of a number of pet food ingredients, in which the main contributors to lipid oxidation are bulk oils and fats, such as chicken fat, vegetable oils, and fish oil, protein meals, such as chicken meal and fish meal. Protein meals are one of the main components of the kibble matrix, while bulk oils and fats are the main components of coating solution. Therefore, oils and fats in the kibbles are distributed on the outer surface and in the kibble matrix. The whole kibble matrix is covered mainly by a layer of oils and /or fats. The characteristics of lipid oxidation in dry pet foods are oxidation of mixed oils and / or fats, and different oxidation rates on the surface of coating and in the core of the kibbles. In short, lipid oxidation of dry pet food is different from other foods, since the composition and structure of the dry pet food are different from others.

Methods to Assess Secondary Volatile Lipid Oxidation Products in Complex Food Matrices

C. Jacobsen⁽¹⁾, B. Yesiltas⁽²⁾

⁽¹⁾Technical University of Denmark, Denmark ⁽²⁾Technical University of Denmark, Denmark

A range of different methods are available to determine secondary volatile lipid oxidation products. These methods include e.g. spectrophotometric determination of anisidine values and TBARS as well as GC based methods for determination of specific volatile oxidation products such as pentanal and hexanal. Different extraction methods for extracting volatiles before GC analysis can be used, e.g static headspace, dynamic headspace and solid phase microextraction. Traditionally, dynamic headspace extraction has been performed manually. However, recently automated dynamic headspace methods have become available. This presentation will briefly discuss advantages and disadvantages of spectrophotometric methods versus GC- based methods. Moreover, the different extraction methods used for GC-based analysis will be discussed and examples on results obtained with SPME, the traditional and the automated dynamic headspace methods on the same food matrices will be presented.

Development of a Method Using Dpph for Determining the Contents of Antioxidants and of Oxidized Lipids in Oils During Lipid Oxidation

J. Lee⁽¹⁾

⁽¹⁾Sungkyunkwan University, Korea, Republic of

A modified method using 2,2-diphenyl-1-picrylhydrazyl (DPPH) in isooctane has been developed to monitor the changes of radical scavenging compounds during lipid oxidation. The modified DPPH method can monitor the changes of free radical scavenging antioxidants (FRSs) during oxidation. Also, the generation of some compounds, which have ability to react with DPPH, were clearly confirmed by using the modified DPPH method. These compounds were named as RSOLS or radical scavenging compounds from oxidized lipids. Generation of RSOLS are reported in thermally-oxidized model systems such as lard and free fatty acids including linoleic acid and oleic acid. Also, presence of RSOLS were observed in stripped lard under methylene blue photosensitization. Aldehydes including pentanal, t-2-heptenal, and t-2-nonanal were reported to be members of RSOLS, which can react with DPPH in isooctane and decrease the absorbance of DPPH. The modified DPPH method can provide information on the content of FRSs and RSOLS. Antioxidant capacities of FRSs including α -tocopherol, sesamol, butylated hydroxyanisole (BHA), and TBHQ were predicted through comparing absorbance changes of DPPH in isooctane. The advantages of the modified DPPH method are real-time monitoring the profiles of FRSs or RSOLS in lipids during oxidation compared to conventional methods like conjugated dienoic acid (CDA) value or p-anisidine value.

Evaluation of antioxidants in fish oil for food and dietary supplements

W. Indrasena⁽¹⁾, J. Kralovec⁽²⁾

⁽¹⁾DSM Nutritional Products, Canada ⁽²⁾DSM Nutritional Products, Canada

Fish oil is added to a variety of food products in the form of powder, emulsion or oil as a source of omega-3 fatty acids such as eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA) for multiple health and nutritional benefits. Deleterious flavour volatiles generated from the oxidation of polyunsaturated fatty acids can be reduced using a variety of antioxidants. Various different methods are used to evaluate the efficacy of antioxidants and the quality of fish oil. Concentrated fish oil with different levels of EPA and DHA as well as steam deodorized natural fish oil samples were stabilized with different types of antioxidants and, oxidation stability index (OSI), peroxide value (PV) and p-anisidine value (p-AV) were monitored every week. Conjugated di-enes and polymers were also monitored in selected samples. Although the oxidation stability index is widely used to evaluate the efficacy of antioxidants there was no positive correlation between the sensory stability with the OSI where as PV and p-AV may correlate depending upon the type of antioxidant and the nature of oil. OSI may be used only as a primary screening method to evaluate the efficacy of certain antioxidants, and other methods such as sensory evaluation by subjective analysis should be used for oils intended for food applications.

Lipid Modification Effects on Stability and Bioactivity

F. Shahidi⁽¹⁾

⁽¹⁾Memorial University, Canada

Lipid modification may be carried out to alter the physical, chemical and /or the bioactivity of the molecules of interest. Thus, lipophilization of polar molecules may alter their activities in different model systems and in foods and as dietary supplements. In this connection, we have prepared a number of acylated derivatives of epigallocatechin gallate (EGCG) and epigallocatechin (EGC) and examined their activities in controlling oxidation processes and rendering health benefits. The acyl donors were different fatty acids including eicosapentaenoic acid (EPA), docosapentaenoic acid (DPA) and docosahexaenoic acid (DHA), among others. These derivatives were found to generally have improved efficacy as antioxidants and some rendered improved health benefits or effects that were not observed for their parent constituent moieties. This presentation will discuss lipid-containing biomolecules to demonstrate the benefits of such structure modifications in expanding their application in foods and in supplements for reducing disease risk and promoting health.

Comparison of the Autoxidative Stability Between High Oleic-linolenic dag oil and tag oil Affected by Extraneous Antioxidants

E. Choe⁽¹⁾, L. Jung⁽²⁾

⁽¹⁾Inha University, Korea, Republic of ⁽²⁾Inha University, Korea, Republic of

This study compared the effects of extraneous antioxidants (catechin and rosemary extracts, α -tocopherol) on the autoxidative stability of diacylglycerol (DAG) oil and its source triacylglycerol (TAG) oil composed of extra virgin olive and perilla oil (6:4, w/w) at 50°C for 10 d. DAG oil was more susceptible to the oxidation than TAG oil determined by oxygen consumption and peroxide values. Addition of antioxidants improved the oxidative stability of

both oils, with lower improvement in DAG oil than in TAG oil. Concentration of tocopherols, among antioxidants considered, was the best fit to monitor the oxidation of DAG oil. Catechin and rosemary extracts showed higher antioxidant activity than tocopherols in TAG oil, however, there was not a big difference in DAG oil. The endogenous and extraneous antioxidants were degraded during the oil oxidation; the degradation rate of polyphenols was higher than that of tocopherols. Degradation of polyphenols was faster in DAG oil added with catechin or rosemary extracts than in the respective TAG oil, however, TAG oil added with α -tocopherol showed faster degradation of polyphenols than the respective DAG oil. The results suggest that the addition of extraneous antioxidants for oxidation-stable oil consider the composition of lipid class as well as endogenous minor compounds.

Interpreting Sensory Quality of Virgin Olive oil by Volatile Markers

D. García González⁽¹⁾, M. Morales⁽²⁾, I. Romero del Río⁽³⁾, R. Aparicio⁽⁴⁾

⁽¹⁾Instituto de la Grasa (CSIC), Spain ⁽²⁾University of Seville, Spain ⁽³⁾Instituto de la Grasa (CSIC), Spain ⁽⁴⁾Instituto de la Grasa (CSIC), Spain

A deviation of the optimal extraction process of virgin olive oil sometimes leads to sensory defects that must be detected before delivering the product to the market. The current olive oil regulations classify the most frequent off-flavours into four groups: Fusty is the characteristic flavour of oils obtained from olives in an advanced stage of fermentation. Mustiness-humidity is the characteristic flavour of oils obtained from olives piled under humid conditions for several days. Winey/vinegary is a sensory note due to the high concentration of acetic acid, ethyl acetate and ethanol. Rancid is a common sensory characteristic of oils undergoing a process of auto-oxidation. The first three defects are due to inadequate fruit preservation before olive oil processing while the last is produced during olive oil storage. The certain subjectivity and the high error rate of the official method for detecting these defects (based on sensory assessment) have turned the attention to the analysis of volatile compounds, which are ultimately the chemical agents responsible for the off-flavours. In this work the volatile composition associated to the main defects of virgin olive oils is characterized by SPME-GC. The odour threshold values and the sensory description of the volatiles compounds served to select those with major impact on aroma, and/or those that are not detected in extra virgin category and characteristic of a specific defect. The selected volatile markers are submitted to a further study of their quality parameters (repeatability, sensitivity, etc.) to select those that showed better performance.

AFTERNOON

LOQ 5: General Lipid and Oxidation Quality

Chair(s): S. Pan, Solae LLC., USA; C. Hall, North Dakota State University, USA

Effect of pH on the Activity of Non-migratory Metal-chelating Packaging Film in Preventing Lipid Oxidation in an Oil-in-water Emulsion System

F. Tian⁽¹⁾, E. Decker⁽²⁾, J. Goddard⁽³⁾

⁽¹⁾University of Massachusetts Amherst, United States of America ⁽²⁾University of Massachusetts Amherst, United States of America

⁽³⁾University of Massachusetts Amherst, United States of America

Lipids are one of the main targets of oxidative reactions, which are a major problem in packaged food products. Transition metals, especially iron, can significantly accelerate lipid oxidation even with very low concentrations. Non-migratory antioxidant packaging offers a unique means to protect packaged foods against lipid oxidation while avoiding use of additives. Herein, we developed a novel non-migratory active packaging film by grafting metal-chelating monomers (acrylic acid, AA) from polypropylene (PP) film surfaces using photoinitiated graft

polymerization. The ability of the poly(acrylic acid) (PAA) grafted PP film (PP-g-PAA) to inhibit lipid oxidation was demonstrated in oil-in-water emulsion systems. The effect of pH (3.0, 5.0, 7.0) on the ability of PP-g-PAA films to inhibit lipid oxidation was evaluated. Emulsions were incubated at 25 °C, and lipid hydroperoxides, hexanal, particle size, and zeta potential were measured during storage. Results of lipid oxidation analyses indicate that the novel metal-chelating film developed herein is capable of controlling lipid oxidation, and its optimum pH is 5.0 or above. The application of such an effective and economical active packaging film represents a very promising approach in removing the usage of synthetic additives (EDTA, etc.) from food formulations while maintaining high food quality.

Impact of Free Fatty Acids and Phospholipids on Reverse Micelles Formation and Lipid Oxidation in Bulk Oil

K. Kittipongpittaya⁽¹⁾, A. Panya⁽²⁾, D. McClements⁽³⁾, E. Decker⁽⁴⁾

⁽¹⁾University of Massachusetts, Amherst, United States of America ⁽²⁾National Center for Genetic Engineering and Biotechnology, Thailand

⁽³⁾University of Massachusetts Amherst, United States of America ⁽⁴⁾University of Massachusetts, Amherst, United States of America

Association colloids such as phospholipid reverse micelles can increase the rate of lipid oxidation in bulk oils. Besides phospholipid reverse micelles, other surface active minor components in commercial oils such as free fatty acids may also impact on lipid oxidation rate of oils and microstructures of reverse micelles. In this study, the effects of free fatty acids on changes in the critical micelle concentration (CMC) of 1,2-dioleoyl-sn-glycero-3-phosphocholine (DOPC) in stripped corn oil were determined by using the TCNQ solubilization technique. Different free fatty acids including myristoleic (14:1), oleic (18:1, cis), eicosenoic (20:1), elaidic (18:1, trans) and linoleic (18:2) were added at 0.5% by wt along with the DOPC (1-2000 µmole/kg oil) into the bulk oils. There was no significant effect of free fatty acids with different chain length, configuration and number of double bonds on the CMC value for DOPC in bulk oil. However, increasing concentrations of oleic acid (0.5, 1, 3 and 5 % by wt) caused the CMC value for DOPC in bulk oils to increase from 400 to 1000 µmole/kg oil. Physical properties of DOPC reverse micelles in the presence of free fatty acids in bulk oils were also investigated by the small angle X-ray scattering technique. Results showed that free fatty acid could impact on the reverse micelle structure of DOPC in bulk oils. The oxidation study revealed that free fatty acids exhibited prooxidative activity in the presence and absence of DOPC. Different types of free fatty acids shared the same prooxidative activity in bulk oil.

Determination of Volatile Carbonyls in Olive Oil using Ultra Performance Liquid Chromatography and Gas Chromatography-Electron Ionization Mass Spectrometry

H. Zhu⁽¹⁾

⁽¹⁾UC Davis, United States of America

Many volatile carbonyl compounds produced through lipoxygenase pathway and oxidation process contribute to the complex flavor of olive oil; some of the carbonyls, such as hexanal and nonanal, have been widely considered as indicators of lipid oxidation. A sensitive Ultra Performance Liquid chromatography (UPLC) method following dynamic headspace sampling and 2,4-dinitrophenylhydrazine (2,4-DNPH) derivatization was established to determine the volatile carbonyls in olive oil. Quantification of 8 characteristic carbonyls (hexanal, E-2-hexenal, octanal, E-2-octenal, nonanal, E-2-nonenal, E,E-2,4-decadienal, and E,E-2,4-nonadienal) was achieved by using isobutyl acetate as internal standard. To assist the identification of unknown compounds, Gas Chromatograph-Electron Ionization Mass Spectrometry (GC-MS) was employed to exam the same samples of derivatized carbonyls (carbonyl (2,4-DNPH)hydrazones), and the peak assignment was performed on the basis of relative retention time and percentage peak area. New harvested extra virgin olive oil and aged unrefined olive oil were tested to have a better understanding on the changes in the volatile carbonyls during room temperature oxidation.

Oxidative Stability of Pastuerized and raw Flaxseed Milled Under Room and Cold Temperatures.

C. Hall III⁽¹⁾, C. Turner⁽²⁾

⁽¹⁾North Dakota State University, United States of America ⁽²⁾North Dakota State University, United States of America

In a previous study, response surface methodology predicted processing variables of 148°C for 16.25 minutes was needed to eliminate the aerobic plate, mold, and yeast counts. However, no oxidation data was collected on the heat treated flaxseed. Therefore, the objectives were to characterize the effects of pasteurization on milled flaxseed quality and oxidative stability and determine if the combination of pasteurization followed by cold temperature milling will affect milled flaxseed quality as compared to milling under ambient milling conditions. As expected, the raw flaxseed milled under either cold or ambient temperatures were oxidized (e.g., peroxide values) less compared to the flaxseed pasteurized prior to milling. After 16 weeks, the oxidation indicators of raw flaxseed milled at 25 °C did not differ from those of the raw samples milled at approximately 10 °C. Milling temperature of heat treated flaxseed did not have a significant impact on the oxidation of flaxseed. The data suggest that the differential in milling temperatures was not sufficient to impact oxidative stability of flaxseed lipids. However, the heat treatment prior to milling appears to be the most significant contributor to increased oxidation of milled flaxseed. The pasteurization of flaxseed at 148°C for 16.25 minutes to eliminate microorganisms is not recommended for flaxseed that is to be milled and packaged without barrier films.

Stability of Chia Oil-in-water Emulsions

M. Tomás⁽¹⁾, L. Julio⁽²⁾, V. Ixtaina⁽³⁾, J. Wagner⁽⁴⁾, S. Nolasco⁽⁵⁾

⁽¹⁾CIDCA, Argentina ⁽²⁾CIDCA, Argentina ⁽³⁾CIDCA/Fac de Ingeniería, Dto. de Ingeniería Química (TECSE), UNCPBA, Argentina ⁽⁴⁾Área Ingeniería en Alimentos - Dto.de Ciencia y Tecnología ? UNQ, Argentina ⁽⁵⁾Fac de Ingeniería, Dto. de Ingeniería Química (TECSE), UNCPBA, Argentina

The chia seed oil contains a high amount of ω -3 fatty acids, especially ω -linolenic (~60%). Because this type of fatty acids plays an important role in the prevention of several diseases, the development of functional emulsions with chia oil is very interesting. Chia O/W emulsions varying in sodium caseinate (NaCas) concentration (2-10% wt/wt) and homogenization pressure (400-600 bar) were investigated in terms of physical and oxidative stability. Physical emulsion stability was evaluated through the evolution of backscattering (BS) profiles, particle size distribution, and mean diameters (D [4,3], D [3,2]), while the oxidative stability was followed by the peroxide value (PV) and p-anisidine. As evidenced by the BS-profile changes with time, emulsions formulated at 400 bar with 2 and 5 wt% NaCas destabilized mainly by creaming, whereas the emulsion with 10 wt% NaCas remained stable. The homogenization pressure influenced the physical stability in different way according to NaCas concentration. At 2 wt% NaCas, emulsion obtained at 600 bar was more stable than those at 400 and 500 bar; however, at 10% NaCas it had little influence on the physical stability during the time studied. Regarding oxidative stability, the different systems recorded an increase of PV since 50 days with the highest values corresponding to 10% NaCas emulsions at 65 days of storage (PV 200 mM).

Electron Paramagnetic Resonance Study of Radical Production during Olive Oil Oxidation

K. Rangelova⁽¹⁾

⁽¹⁾Bruker BioSpin Corporation, United States of America

Oxidative rancidity occurs during storage and is due to the oxidation of unsaturated fatty acids and the subsequent formation of foul odor and taste. The resistance of olive oil to oxidation is related to the high levels of monounsaturated triacylglycerols and the presence of natural phenolic antioxidants. Electron paramagnetic resonance (EPR) was used to detect free radicals and to determine the level of free radical formation in olive oil during forced oxidation at different temperatures. The spin traps phenyl-N-tert-butyl nitron (PBN) and 5,5-dimethyl-1-pyrroline N-oxide (DMPO) were used to trap free radicals during the forced oxidation assay at elevated temperatures (30-70 °C). The end point of radical formation after 60 min assay was compared with the simultaneously measured peroxide value (PV). We found a drastic increase in the radical formation, i.e. EPR intensity, even during the early stage of oil oxidation, while smaller changes were obtained for the peroxide values. The EPR spin trapping studies using another spin trap, DMPO, identified the presence of peroxy, alkoxy, and alkyl radicals. Computer simulations were used to determine the concentrations of each DMPO-radical adduct and their relative contribution to the composite EPR spectra for a variety of experimental conditions. From these data some mechanistic conclusions could be made regarding the free radical oxidation of olive oil. A good correlation was also found between the radical concentration and some sensory data suggesting that EPR is a sensitive method for measuring and improving the resistance of edible oils to rancidity and adulteration.

Oxidative Stability of Sunflower-chia oil Blends With the Addition of Antioxidants

M. Tomás⁽¹⁾, E. Guiotto⁽²⁾, V. Ixtaina⁽³⁾, S. Nolasco⁽⁴⁾

⁽¹⁾CIDCA, Argentina ⁽²⁾CIDCA/ Fac. de Ingeniería, Dto. de Ingeniería Química (TECSE), UNCPBA, Argentina ⁽³⁾CIDCA/ Fac. de Ingeniería, Dto. de Ingeniería Química (TECSE), UNCPBA, Argentina ⁽⁴⁾CIDCA/ Fac. de Ingeniería, Dto. de Ingeniería Química (TECSE), UNCPBA, Argentina

The oxidative stability of sunflower oil, chia oil -rich in ω -3 fatty acids- and their blends (sunflower-chia 80:20 and 90:10 wt/wt) with the addition of ascorbyl palmitate (AP, 2000ppm), rosemary extract (ER, 5000ppm) and AP:ER (2000:2000ppm) was evaluated periodically during their storage (1 year) at two temperatures (4 and 20±1°C). An accelerated test (Rancimat) was carried out at 98 °C with an air flow of 20 L/h using 5 g of oil, and the oil stability was expressed in terms of induction time (ti). Oils stored at 4°C exhibited higher ti than those stored at 20°C. Thus, the temperature is an important parameter in the stability of vegetable oils. Sunflower oil had the highest initial ti value (13.0h) while chia oil recorded the lowest due to its high PUFAs content. The 80:20 and 90:10 wt/wt blends showed initial ti of 7.6 and 9.2h, respectively. The addition of antioxidants increased the ti in all cases. At the initial time, ER produced the best antioxidant effect, increasing the ti values until 18.1 and 22.5 h for sunflower-chia 80:20 and 90:10 wt/wt, respectively. However, AP:ER was the most effective antioxidant during the storage at both temperatures.

Lipid Oxidation and Quality Poster Session

Chair(s): G. List, Retired, Consultant, USA

Antioxidant Activity and Free Radical Scavenging Potential of Rosemary and Green tea Extract in Ghee (butter Oil) During Accelerated Tests.

N. Pawar⁽¹⁾, S. Arora⁽²⁾, S. Chopde⁽³⁾

⁽¹⁾CDT, Udgir, India ⁽²⁾NDRI, Karnal, India ⁽³⁾CDT, Udgir, United States of America

The effect of rosemary and green tea extract on the oxidative stability of ghee was evaluated by instrument test: Rancimat743-measuring the generated carboxylic oxidation products. Induction period (IP) and potential of the antioxidants to quench 1, 1-diphenyl-2-picrylhydrazyl (DPPH) radical were used as major indicators of antioxidative potential of antioxidants used. The most effective antioxidant in stabilizing ghee by the Rancimat test was found to be rosemary extract (IP 45.47±0.43 h) followed by green tea extract (IP 31.55±0.48 h) and synthetic antioxidant, namely,

butylated hydroxyl anisole (IP 20.14±0.28 h). Both, rosemary and green tea extract were significantly ($P < 0.05$) more effective in stabilizing ghee against oxidation than BHA. Capacity in quenching of the DPPH radicals by antioxidants was measured before and when the end of oxidation. Before the accelerated storage of the samples (i.e. on zero day) at 80±10C, the ability to quench free DPPH radicals was in the following order: Rosemary > BHA > green tea > control. After the accelerated storage of 21 days at 80±10C, it was observed that the ability to quench free DPPH radicals followed the same order as on zero day (before oxidation), except green tea extract, which showed significantly ($P < 0.05$) higher radical-scavenging potential as compared with BHA.

Stability of Polyunsaturated Omega-3 Fatty Acids in Salmon by Different Culinary Treating

J. Liang⁽¹⁾, Y. Jiang⁽²⁾, Y. Zhang⁽³⁾, F. Niu⁽⁴⁾

⁽¹⁾Wilmar (Shanghai) biology R&D center Ltd. Co., China ⁽²⁾Wilmar (Shanghai) biology R&D center Ltd. Co., China ⁽³⁾Wilmar (Shanghai) biology R&D center Ltd. Co., China ⁽⁴⁾Wilmar (Shanghai) biology R&D center Ltd. Co., China

Docosahexaenoic acid (DHA) [22:6, n-3] and eicosapentaenoic acid (EPA) [20:5, n-3] were verified to be important for normal visual and brain development. As a result, sea food with high content of DHA & EPA remains a healthy and attractive food. Salmon, possessing high level of EPA and DHA and is regarded as a common dietary source of DHA&EPA. However, consumption of uncooked fish is only popular in Japan and some tropical places. Altering of FAC by culinary treating of fish with heat could not be ignored. Most studies focused on the change of lipid fraction in the fish. No publication investigated the oxidation and stability of PUFA during cooking in both fish and cooking media. Salmon was steamed, pan-fried and deep-fried. Quantification of DHA&EPA kept in cooked salmon, transferred into cooking medium and degraded during culinary treating was conducted. The lipid extracted from cooked salmon was analyzed for both FAC and oxidative stability. It was found after steaming, the lipid in it was as fresh as that in raw fish with only 4.7% DHA&EPA lost. 9.94% and 22.33% DHA&EPA were destroyed during pan-frying and deep-frying respectively. Deep-frying was proved to be the most violent cooking method.

The Transformation of Tbhq During High Temperature Frying (>200?) and its Effects on the Frying Oil

Frying above 200? is widely used in Chinese frying industry when frying some popular Chinese foods like rice cakes and dough sticks and more. High temperature frying normally accelerates the rate of oxidative deterioration much more than that below 180?. Addition of antioxidants is a common method to inhibit or slow down it. This study was to investigate the effects of different content of TBHQ (100, 200, 300ppm) on the frying performance at 210?. Oxidative stability was evaluated by p-anisidine, total polar compounds and total oxidative value. Minor components produced during frying including 2-MCPD, 3-MCPD, glycidols and trans fats (TFA) were measured. Both remaining of tocopherols and TBHQ were also investigated. The results showed TBHQ could protect tocopherols effectively and inhibit the production of MCPDs ($P < 0.05$) at all three TBHQ concentrations. The oxidative stability and inhibition of TFA could be improved only when 300 ppm TBHQ was added. However, addition of TBHQ also brought obvious disadvantages. Glycidols was higher after frying when TBHQ was used. It also deepened the color of frying oil. TBHQ was degraded severely during frying and it could hardly be detected after at the end of frying. This might be the cause of darker color of the frying oil.

Trolox Equivalent Antioxidant Capacity (teac) Assay Might Predict Oxidative Stability of Refined Vegetable Oils.

V. Castelo Branco⁽¹⁾, V. Di Sarli⁽²⁾, A. Torres⁽³⁾

⁽¹⁾Federal University of Rio de Janeiro, Brazil ⁽²⁾Federal University of Rio de Janeiro, Brazil ⁽³⁾Federal University of Rio de Janeiro, Brazil
Total antioxidant capacity (TAC) of vegetable oils represents the integrated action of antioxidants against oxidation, and therefore, might be used to predict oil stability. The aim of the present study was to investigate the association between TAC and traditional quality indices of vegetable oils subjected to thermal oxidation. Refined oils of soybean (SO), maize (MO), sunflower (SUN) and canola (CO) were submitted to thermal oxidation at 180°C (control, 0.5; 1; 2 and 3h) for analysis of peroxide value (PV) and TAC (TEAC assay). The induction period (IP) in the Rancimat test was also determined for the fresh oils. Fresh SO presented the best oxidative stability, with lowest initial PV (0.38±0.08 meqO₂/kg) and the highest IP (13.6±2.47 h). In contrast, CO presented the highest initial PV. Besides, PV of CO at

the end of oxidation (3h) was lower than in control, indicating extensive oil degradation. Additionally, SO and CO presented the highest and lowest TAC values (mmol TE/kg), 4.45 ± 1.18 and 1.73 ± 0.34 , respectively. The TAC value correlated negatively with initial PV ($r = -0.54$; $p = 0.01$) and positively with IP ($r = 0.69$; $p < 0.01$) and with the difference between final PV and initial PV ($r = 0.57$; $p = 0.02$). Therefore, TAC of refined vegetable oils, especially measured through TEAC assay, seemed a valuable index of oils' oxidative stability.

Headspace liquid-phase microextraction (HS-LPME) as a green analytical technique for assessment autoxidation state in soybean oil during shelf-life

M. Enteshari⁽¹⁾, A. Mohammadi⁽²⁾, K. Nayebzadeh⁽³⁾

⁽¹⁾Shahid Beheshti University of Medical Sciences, Iran ⁽²⁾Department of Food Science and Technology, Iran ⁽³⁾Department of Food Science and Technology, Iran

A novel, green and rapid analytical method applying headspace liquid-phase microextraction (HS-LPME) coupled with gas chromatography-mass spectrometry (GC-MS) was expanded for isolation and determination of some autoxidation compounds in soybean oil during 6 months storage at two different temperatures (4 and 25 °C). Autoxidation of soybean oil during storage resulted in formation of some volatile aldehydes such as propanal, pentanal, hexanal and heptanal which can be oxidation markers for assessment oxidation changes. To investigate the performance of proposed method, linearity, repeatability, recovery, limit of detection (LOD) and limit of quantification (LOQ) were investigated under optimized experimental conditions. Plotting calibration curves demonstrated high amounts of linear correlation with R² limits between 0.981 and 0.996 for all mentioned aldehydes in the range of 0.2-200 ng ml⁻¹. The precision of the method was expressed as the relative standard deviation (RSD) and varied between 3.63 % and 5.74 %. The LODs were calculated to be 0.0016-0.008 ng g⁻¹, while the LOQs of the validate method were 0.0053-0.077 ng g⁻¹. Good recoveries for mentioned aldehydes ranged between 91.43 and 116.04 % to confirm high accuracy of the microextraction technique. The applied method was understood to be sensitive, reliable and fast for determining secondary oxidation compounds especially volatile aldehydes in soybean oil.

Development of antioxidants for frying oil

V. Perreault⁽¹⁾, P. Angers⁽²⁾

⁽¹⁾Université Laval, Canada ⁽²⁾Université Laval, Canada

Heating fats and oils results in thermolytic and oxydative processes leading to the formation of degradation products such as cyclic fatty acid monomers, oligomers (polymers), trans and oxygenated fatty acids. The effectiveness of primary and secondary antioxidants in retarding the deterioration of refined commercial canola oil during static heating (120, 135, 150, 165 and 180 °C) was assessed at different concentrations (0.1-1.0% w/v) for up to 48h. The primary antioxidants that were tested include phellandrene, furfuryl octanoate and propionate, and myrcenyl propionate and acetate whereas secondary antioxidants consisted of isopropylphenol, butylated hydroxytoluene (BHT), hexyl vanillate (HV) and coumarate (HC). The results show a significant antioxidant effect of secondary antioxidants, compared to primary antioxidants and control (canola oil), with a highest efficacy for hexyl coumarate and BHT. At 180°C, after 2 h, both HC and BHT (0.1% w/v) kept oleic, linoleic and linolenic acid levels close to their original levels, resulting in FA values that are, on average, 140% higher than control. HC, BHT and HV at 1.0% (w/v) also resulted in higher unsaturated fatty acid content after 24 and 48 h at 120 °C. Under the conditions used, furfuryl octanoate and myrcenyl propionate have accelerated degradation of unsaturated fatty acids and thus acted as prooxidant.

Evaluation of the oxidative stability of cold pressed Hass avocado oils

I. Santana⁽¹⁾, L. Martins Ferreira dos Reis⁽²⁾, A. Guedes Torres⁽³⁾, L. Maria Corrêa Cabral⁽⁴⁾, S. Pereira Freitas⁽⁵⁾

⁽¹⁾Universidade Federal do Rio de Janeiro (UFRJ), Brazil ⁽²⁾Universidade Federal do Rio de Janeiro, Brazil ⁽³⁾Universidade Federal do Rio de Janeiro, Brazil ⁽⁴⁾Embrapa Agroindústria de Alimentos, Brazil ⁽⁵⁾Universidade Federal do Rio de Janeiro, Brazil

Stability of edible oils relies on many factors, inherent or not to the food matrix, that may act to delay or accelerate oxidation. The Rancimat device allows evaluation of Oxidative Stability (OS) in edible oils, where the sample is subjected to an air stream and a high temperature, being the Induction Period (IP) dependent on the balance between antioxidants and pro-oxidants. The aim of this study was to investigate the OS of Hass avocado oils at different stages

of maturation. The unripe and ripe avocados, peeled and unpeeled were dried at 60 °C in convective dryer and then cold pressed (performed in triplicate). The analysis conditions in Rancimat 743 equipment consisted in temperature of 110 °C and air flow of 20 L/h, for each 3 g of sample. The IP (hours) of oil extracted from ripe peeled avocado was 4.89±0.28, while the sample with peel, 20.24±1.29. Maturation process decreased the OS, as the oil from unripe and peeled avocados showed an IP of 14.13±1.25, and that the extraction of oil from the raw material with peel influenced on OS, causing an increase in the IP of the oil extracted from unripe avocado with peel (21.33±0.95), which was similar to the corresponding mature sample. This behavior is probably due to antioxidant components present in highest amounts in the peel, and raises the interest for this type of process because avoids the disposal of a structure that adds value to oil.

Influence of Thermal Treatment on Physicochemical Properties of Maize Germ Oil Bodies

R. Sukhotu⁽¹⁾, S. Guo⁽²⁾

⁽¹⁾China Agricultural University, China ⁽²⁾China Agricultural University, China

Maize germ oil bodies are coated by a layer of phospholipids and oleosin proteins. The objective of this study is to determine the influence of thermal treatment at high temperature (110°C) on oxidation stability and properties of maize germ oil bodies. Maize germ oil bodies were extracted using aqueous extraction. The results showed that peroxide value and iodine value of the heated oil bodies at 110°C for 6 h were 0.42 mequiv. O₂/kg and 115.27 g I₂/100g oil, respectively. However, under the same conditions with the heated oil bodies both values of the heated corn oil were 15.57 mequiv. O₂/kg and 90.52 g I₂/100g oil, respectively. Moreover, acid value of the heated oil bodies was slightly higher than that of the heated corn oil. Zeta potential of the heated oil body suspension increased from -24 mV to -26 mV after the treatment. The means of particle diameter (d₃₂) rapidly declined from initial time to 5 min after the treatment. The oil bodies showed stability against aggregation and creaming during treatment at high temperature from 5 to 20 min. These results suggest that thermal treatment does not affect the oxidation stability. Thus, maize oil bodies may be utilized as emulsifier in food industrial applications in order to avoid oxidation process.

Antioxidant Activity of the Essential Oil and Methanol Extract of Seeds of *Rumexpatientia* L.

S. Yücel⁽¹⁾, P. Terzioglu⁽²⁾, Y. Cetintas⁽³⁾, D. Çolak⁽⁴⁾, M. Öztürk⁽⁵⁾, M. Duru⁽⁶⁾

⁽¹⁾Yildiz Technical University, Turkey ⁽²⁾Mugla Sitki Kocman University, Turkey ⁽³⁾Mugla Sitki Kocman University, Turkey ⁽⁴⁾Yildiz

Technical University, Turkey ⁽⁵⁾Mugla Sitki Kocman University, Turkey ⁽⁶⁾Mugla Sitki Kocman University, Turkey

Recently, there is an increasing interest for the use of naturally occurring antioxidants in cosmetic, food, and pharmaceutical applications. Plants are excellent natural antioxidant sources. *Rumexpatientia* L. is one of the important Turkish medicinal species from the Polygonaceae family. In this study, antioxidant activity of the methanol extract and the essential oil from the seed of *Rumexpatientia* L. were evaluated by using DPPH free radical and ABTS cation radical scavenging assays. The essential oil from the seed of *Rumexpatientia* L. was obtained by hydrodistillation by using Clevenger apparatus according to the European pharmacopeia. As expected, methanolic extract showed better antioxidant activity than the essential oil. In the ABTS+? scavenging activity assay, the methanol extract (IC₅₀ = 3.02±0.05 µg/ml), demonstrated two times higher activity than that of BHA (butylatedhydroxyanisole) (IC₅₀ = 6.04±0.03µg/ml). In the same conditions, it also proved superior to essential oil (IC₅₀=274.1±0.07 µg/ml). The methanol extract showed comparable levels of ABTS+? scavenging activity against the antioxidant standard ?-tocopherol (IC₅₀ = 2.38± 0.02 µg/ml). Similarly, the methanol extract (IC₅₀= 9.87 µg /ml) showed the highest DPPH? scavenging activity which was comparable to those of BHA (IC₅₀ = 8.80 ± 0.01 µg /ml) and ?-tocopherol (IC₅₀ = 8.39 ± 0.09 µg /ml). In conclusion, the results showed the antioxidant importance of *Rumexpatientia* L. which is commonly consumed in Anatolia as well as in some parts of the whole world with its delicious taste.

Lipid Co-oxidation of Proteins in Peanut Butter

W. WANIBADULLAH⁽¹⁾, K. SCHAICH⁽²⁾

⁽¹⁾RUTGERS UNIVERSITY, United States of America ⁽²⁾RUTGERS UNIVERSITY, United States of America

Lipid oxidation is the major failure mode during storage of peanut butter, producing off-flavors, reducing nutritional value, and changing texture and color by reactions of lipid oxidation products with peanut proteins. To elucidate

reactions underlying this protein co-oxidation, peanut butter samples in MRE (Meals Ready to Eat) laminate packaging were incubated at 25, 40, and 60 °C for 12 weeks. Total soluble protein, albumin, globulin and SDS-mercaptoethanol fractions were separated by differential solvent extraction, then analyzed for tryptophan oxidation, formation of Schiff base and Michael adducts, fragmentation and crosslinking, fraction rearrangements, surface and charge modifications, and formation of protein carbonyls. Browning and hardness increased with incubation time and temperature. Although some peptide crosslinking and scission was evident, the most striking behavior observed was modification of surface residues, resulting in altered Coomassie blue and silver dye binding and unique variations in structural organization. Formation of protein carbonyls, fluorescent adducts or crosslinks, and degradation of side chains altered net protein charge. These changes and formation of low mol wt polymers (<250 kDa) likely contribute to the hardening observed in peanut butter. All lipid oxidation products decreased as protein oxidation developed, establishing a presumptive causal relationship between lipid oxidation and protein damage.

Evaluation of HBr, nitrobenzyl pyridine, diethyl dithiocarbamate, and hydrogen NMR methods for quantitating lipid epoxides

K. Schaich⁽¹⁾, C. Liao⁽²⁾

⁽¹⁾Rutgers University, United States of America ⁽²⁾Rutgers University, United States of America

Epoxides have long been recognized as lipid oxidation products but are seldom analyzed in routine analyses of oxidative degradation, at least in part because there are few established analytical procedures. To identify assays of use with lipid oxidation, four epoxide assays -- AOCs standard HBr titration of epoxides, nitrobenzylpyridine (NBP) reaction with colorimetric endpoint, diethyl dithiocarbamate (DETC) complexation with high pressure liquid chromatography (HPLC) separation and quantitation of adducts, and ¹H nuclear magnetic resonance (NMR) -- were evaluated for accuracy, sensitivity, stoichiometry, reproducibility, and handling requirements using epoxybutane, epoxyhexene, and epoxydecene as standards. The HBr assay was too insensitive (detects 0.0075-0.1M) for quantitating lipid epoxides in foods and biological materials. The HBr degrades so rapidly that frequent restandardization is necessary. The nitrobenzylpyridine assay detects 0.5 mM epoxides, but the reaction response varied considerably with time and temperature of reaction and increased with epoxide chain length. Hence, a different standard must be used for each epoxide analyzed, and selection of an appropriate standard for epoxides of unknown structure is problematic. The DETC reaction response was linear from 1 μM to 1 mM for all three epoxide standards and oxidized methyl linoleate, and but reactivity increased with epoxide chain length. HPLC separates and quantitates individual epoxides, so can provide important information about oxidation chemistry. NMR analyzes oils and extracts directly, detects micromolar epoxides, and clearly distinguishes epoxides from other oxidation products in lipids. The DETC-HPLC and NMR assays hold the greatest promise for routine analysis of epoxides in oxidized lipids.

A New and Green Method to Synthesis Epoxidized Soybean Oil

G. LIU⁽¹⁾

⁽¹⁾SOUTH CHINA UNIVERSITY OF TECHNOLOGY, China

Epoxidized soybean oil (ESO) is a new, biodegradable, non-toxic and environmental- friendly plasticizer. This research chose surfactant PEG as phase transfer catalyst to accelerate and promote the phase transfer reaction. The influence of various parameters such as amount of PEG, H₂O₂ catalyst and reaction time on the epoxidation of soybean oil was examined. Under optimized conditions, high epoxy value and yield were obtained. The present work has clearly illustrated that this method was a new environment-friendly process to produce epoxidized soybean oil, whose reaction condition was mild and reaction time was shorter.

Influence of extraction solvent on content of Vitamin E in Soybean Germ Oil

x. wang⁽¹⁾

⁽¹⁾Henan University of Technology, China

This article studied the influence of extraction solvent on content of vitamin E in soybean germ oil using butane as extracting solvent and mixture of soybean germ as raw-material by subcritical extraction technology. The results showed that the optimized number of extraction was 5 times, extracting time was 10 minutes, extracting temperature was at 40 °C, the rate of raw-material / solvent was 1:2. Under the optimized technological conditions, the residual oil

content in extracted soybean germ meal was 0.98%. Vitamin E in butane extracted soybean germ oil is at the highest level, it riched at 259.59mg/100g. Comparing with other solvents, the Vitamin E contents in extracted soybean germ oils were 159.60 mg/100g and 167.07mg/100g in hexane and ether, respectively.

Optimization of headspace-liquid phase microextraction followed by gas chromatography-mass spectrometry for determining some of volatile oxidation compounds (VOCs) in mayonnaise by response surface methodology

M. Enteshari⁽¹⁾, A. Mohammadi⁽²⁾, K. Nayebzadeh⁽³⁾

⁽¹⁾Shahid Beheshti University of Medical Sciences, Iran ⁽²⁾Department of Food Science and Technology, Iran ⁽³⁾Department of Food Science and Technology, Iran

Headspace liquid phase microextraction (HS-LPME) coupled with gas chromatography-mass spectrometry (GC-MS) as a novel, low-cost and rapid method has been developed and validated in this study. Isolation and quantification of volatile oxidation compounds (VOCs) including hexanal and heptanal in an oxidized mayonnaise (48 h/50 °C) were carried out by HS-LPME/GC-MS. A single drop of n-dodecane containing 2,5-dimethylfuran as an internal standard, suspended from the tip of a microsyringe into a sample vial, was applied for absorbing oxidation compounds from headspace of sample solution. Microextraction conditions were optimized by response surface methodology (RSM) constructed on central composite design (CCD). The most effective independent parameters involved in microextraction procedure consisted of extraction time and temperature, stirring rate and NaCl content. In this way, effectiveness of microextraction parameters was evaluated by a quadratic model. The optimum parameters were selected at extraction temperature 45 °C, 16 min of extraction time, stirring rate at 700 rpm and addition of 2 g NaCl salt to sample solution. Calibration curves demonstrated high amounts of linearity ($R^2 > 0.98$) for volatile oxidation compounds in the range of 0.2-200 ng ml⁻¹. The limits of detection (LOD) and limits of quantification (LOQ) ranged from 0.008 to 0.021 ng g⁻¹ and from 0.027 to 0.071 ng g⁻¹, respectively. The recovery of proposed method was from 91.4 to 107.3 % and repeatability as expressed by relative standard deviation (RSD) varied from 3.68 to 4.04 %. Obtained results suggested the HS-LPME as a reproducible, reliable and quick method for determining volatile oxidation compounds.

Antioxidant Properties of Dogfish Skin Protein Hydrolysates

S. Rajendran⁽¹⁾, S. Faucher⁽²⁾, B. Simpson⁽³⁾

⁽¹⁾McGill University, Canada ⁽²⁾McGill University, Canada ⁽³⁾McGill University, Canada

In this study, dogfish (*Squalus acanthias*) skins were hydrolyzed with three different proteases, α -chymotrypsin, trypsin and papain, and evaluated for antioxidant, antimicrobial and enzyme inhibitory effects. The protein hydrolysates were produced by treating the skins with 1% enzyme for 4 h at 37°C, followed by ultrafiltration using 10 kDa ultra filtration membranes. The antioxidant capacity of the hydrolysates based on their IC₅₀ values for the α -Chymotrypsin treated protein hydrolysate (CPH) were calculated as 0.095 mg/mL, 0.116 mg/mL and 0.349 mg/mL, for superoxide anion scavenging, hydroxyl radical scavenging and metal ion chelating power, respectively; the corresponding values obtained with the trypsin treated protein hydrolysate (TPH) were 0.198 mg/mL, 0.186 mg/mL and 0.211 mg/mL; and the values for the papain treated protein hydrolysate (PPH) were 4.388 mg/mL, 0.096 mg/mL and 0.286 mg/mL, respectively. A reducing power of 0.5 was achieved with 0.940 mg/mL PPH, 1.083 mg/mL CPH and 3.70 mg/ml TPH. The present study shows that enzymatically produced protein hydrolysates from dogfish skin have antioxidant properties. Further studies are needed to explore the antimicrobial and enzyme inhibitory effects, and to characterize the individual peptides in the hydrolysates to verify their potential as food processing aids.

Canolol from canola seeds, meal and canola oil deodistillates: Extraction, evaluation of its antioxidant activity and protective effects on oxidation of canola oil

A. Appukuttan⁽¹⁾, K. Schwarz⁽²⁾, G. Hatfield⁽³⁾, M. Eskin⁽⁴⁾, U. Thiyam-Hollander⁽⁵⁾

⁽¹⁾University of Manitoba, Canada ⁽²⁾University of Kiel, Germany ⁽³⁾Bunge Limited, Canada ⁽⁴⁾University of Manitoba, Canada ⁽⁵⁾University of Manitoba, Canada

Increasing the concentration of canolol (CAN) or 4-Vinylsyringol, a minor component with potent antioxidant and lipid-peroxyl radical scavenger activity, would enhance the food value of canola oil. In our earlier studies, canola seeds and meals were subjected to Accelerated Solvent Extraction at a high pressure (1500 psi) employing hexane and

methanol. The canola seeds and meals produced approximately 8500 μ g and 6900 μ g of CAN per gram substrate, which is the highest level of CAN report so far (HPLC-DAD at 270 nm). Elevated pressure appears to be one of the main factors for the observed increase in the extractability/content of CAN. As a continuation of this research, efforts were made to extract CAN from canola oil deodistillates. A new method was developed and the results of this novel method were compared with the existing extraction methods for canola phenolics from the oil. The DPPH scavenging assay and reducing power potential of CAN, and the concentration of hydroperoxides, hexanal and propanal produced during oxidation of oil (40 °C for 14 days) indicated that CAN exhibited considerable inhibition of hydroperoxide formation at both concentration levels tested (100 and 300 μ Mol). The effectiveness of canola phenolics to inhibit lipid oxidation was: CAN>sinapic acid extract>whole extract>standard sinapic acid>standard sinapine>Control. Differences between canola phenolics may be ascribed mainly to the different chain attached to the phenolic ring, which results in different polarity. We propose that CAN, based on its antioxidative efficacy, can be utilized as an inhibitor of lipid oxidation in various lipid food systems.

Properties and oxidative stability of fish oil emulsion systems containing added bioactive components

S. Quek⁽¹⁾, Q. Chen⁽²⁾, F. Zhong⁽³⁾

⁽¹⁾The University of Auckland, New Zealand ⁽²⁾The University of Auckland, United States of America ⁽³⁾Jiangnan University, Wuxi, China, China

In this study, we aim to investigate the role of bioactive components including phytosterol ester (PE) and limonene in preventing fish oil oxidation. Phytosterol has been reported to have good synergistic effects on prevention of cardiovascular diseases and systemic inflammation when taken together with fish oil while limonene is a natural flavor which may mask fishy odor, and deliver health benefits including chemo-preventive activity against cancers. Fish oil emulsions with 0 to 25% PE and/or limonene (in oil phase) were prepared using whey protein isolate (WPI) and sodium caseinate, or WPI and soluble fiber as emulsifiers. The emulsion properties including droplet size and surface protein load were measured. The antioxidant capacities of PE and limonene were determined by DPPH method. Oil phase oxidation was evaluated in an accelerated storage trial (saturated O₂, 45°C, 24 hours) by measuring the peroxide and p-anisidin values, and also by a sensory panel. Results show that partial replacement of fish oil with PE increased the emulsion droplet size while a high concentration of limonene significantly decreased the droplet size and increased the protein load on the droplet surface ($p < 0.05$). The addition of 12.5% and 25% of PE in the oil phase could largely protect the oil phase from oxidation. This may due to its relatively high antioxidant activity. Limonene had the ability to mask the fishy odor but the effect was independent of its concentration. These data provide a basis for formulation of a stable fish oil emulsion with added health benefits.

EFFECT OF TEMPERATURE TIME COMBINATIONS ON THE CRYSTAL MEMORY OF TRIGLYCERIDES

Y. WANG⁽¹⁾, O. Qatami⁽²⁾, A. Alkhudair⁽³⁾, L. Lin⁽⁴⁾, R. LIU⁽⁵⁾, P. Karthik Batchu⁽⁶⁾, M. Gianfranco⁽⁷⁾

⁽¹⁾Dalhousie University, Canada ⁽²⁾Dalhousie University, United States of America ⁽³⁾Dalhousie University, United States of America
⁽⁴⁾Dalhousie University, United States of America ⁽⁵⁾Dalhousie University, United States of America ⁽⁶⁾Dalhousie University, United States of America
⁽⁷⁾Dalhousie University, United States of America

Fats are mainly composed of triglycerides (TAGs) which occur in different polymorphic phases characterized by unique molar heat capacity and enthalpy values. These values vary between the crystalline forms due to the different crystalline structure of each form. The β' form, for instance, has the least crystalline packing and therefore the highest heat capacity and least enthalpy. The opposite characteristics are observed in the β form due to its densely packed arrangement. So far, there is no clear mechanism for this occurrence. We propose that the formation of multimers and compositional gradients, if not avoided by long enough heating, will influence the subsequent crystallization behavior. To ensure that a melted fat sample is homogeneously mixed before starting crystallizing it, one must apply to it an adequate combination of time and temperature. This will ensure that all the crystals are melted and that proper diffusion mixing occurs. We tested our hypothesis determining the combination of time-temperature required to obtain well mixed liquid prior to crystallization of a blend of trilaurin and tristearin. Time-resolved synchrotron x-ray diffraction patterns at small and wide angles were obtained for the liquid, and their characteristic position and width showed the degree of separation of both TAGs in the liquid. These results were compared to thermal measurements conducted with TA Instruments differential scanning calorimeter, DSC Q100.

Program