

ANA 1.1/LOQ 1: Evaluation and Correlation of Sensory and Analytical Methods for Assessing Rancidity

Chairs: M. Collison, Archer Daniels Midland Co., USA; and C. Jacobsen, Technical University of Denmark, Denmark

Using Secondary Oxidation Products to Evaluate the Sensory Stability of Foods with Different Antioxidants.

X. Yang, P. Joseph, L. Burroughs, R. Boyle, J. McKeague, M. Wolf, and R. Nahas, Kalsec, Inc., Kalamazoo, MI, USA.

The most reliable method to evaluate food product quality is real life sensory evaluation, which determines whether a product still has acceptable sensory characteristics in a given time period. However, when there are multiple product formulations to be assessed, for example when different antioxidants need to be tested to improve the product shelf-life, sensory evaluation could be both time and cost-consuming. Therefore, faster analytical methods are favorable in this case. Here, the concentrations of secondary oxidation products measured by headspace SPME GC-MS were found to follow closely the development of oxidized flavors and aromas evaluated by sensory analysis in foods with different antioxidants. The correlation between sensory scores and secondary oxidation product levels revealed that the measurement of the appropriate secondary oxidation marker may serve as a simple, rapid and effective analytical tool to evaluate various antioxidants performance in different food applications.

Can Volatile Lipid Oxidation Products Be Used to Predict Sensory Qualities of Fish Oils?

S.M. Budge and J.C. Sullivan Ritter, Dalhousie University, Halifax, NS, Canada.

Polyunsaturated fatty acids (PUFA) found in fish oil are well known for both their health benefits and oxidative instability. This had led to the development of a number of simple chemical tests, such as peroxide and *p*-anisidine values, to evaluate the extent of lipid oxidation in fish oils. However, these tests rarely agree with the sensory perception of oxidation and a number of alternative approaches to track lipid oxidation have been proposed. The simplest methods measure individual compounds arising from lipid oxidation. More complex methods involve multivariate statistical techniques to allow correlation of concentrations of volatile lipid oxidation products with sensory evaluation. Here we describe a method that uses solid phase microextraction coupled with GCMS to acquire concentrations of lipid oxidation products; principal

component analysis is then used to identify the volatiles that best correlate with the sensory perception of fish oil rancidity.

New Challenges for Evaluation of Oxidative Stability and Shelf Life of Oils/Fats and Oils/Fats Contained Products.

M. Hu and J. Erdmann, DuPont Nutrition & Health, New Century, KS, USA.

In food and pet food industry, a business decision may be made based on oxidative stability data of products. Obviously, a number of analytical methods can be selected to evaluate oxidative stability and shelf life of oils/fats and oils/fats contained products. Also there are advantages and disadvantages for each analytical method. Thus, it is critical to select right analytical method for evaluating oxidative stability of a product and the efficacy of an antioxidant in a specific food system. In the oral presentation, we will use new data to show how to select right analytical method for a target food system and to use the data for a business decision. For instance, we will evaluate oils based on OSI data in high temperature and headspace oxygen levels over ambient storage time, and assess solid samples based on Oxipres at 100°C and PV and hexanal level over ambient storage time. In addition, the following issues will be discussed: 1. how to evaluate heat sensitive antioxidants. 2. how to select accelerated and ambient storage testing. 3. how to compare oxidative stability of different foods with different matrixes, 4. how to avoid pitfall when comparing data from different methods or same method but different pretreatments and analytical procedures as well as different units used.

Thinking Beyond Traditional Theory in Lipid Oxidation: Alternate Pathways that Compete with Hydrogen Abstraction.

K.M. Schaich, B. Bogusz, and J. Xie, Rutgers University, New Brunswick, NJ, USA.

Current attempts to stabilize foods reformulated with polyunsaturated fatty acids as well as to elucidate the role of lipid oxidation in pathology challenge traditional understanding of lipid oxidation mechanisms. For more than 50 years, lipid oxidation has been explained simply as a free radical chain reaction composed of series of hydrogen abstractions, with radical recombinations afterwards leading somehow to products. However,

observed kinetics and distributions of products do not always fit this mechanism. This paper presents evidence for multiple alternate pathways of peroxy and alkoxy radicals, including internal rearrangements, additions to double bonds, and scissions that compete with hydrogen abstraction in lipid oxidation and alter both observed kinetics and products. Questions are raised also about dominance of hydroperoxide positions and a vs b scissions of alkoxy radicals as currently accepted. A concerted mechanism integrating the alternate pathways is proposed to stimulate new research in lipid oxidation mechanisms.

Proton NMR Can Be Used to Measure Epoxides Derived from Lipid Oxidation. W. Xia, S.M Budge, and M. Lumsden, Dalhousie University, Halifax, NS, Canada.

Hydroperoxides and carbonyl compounds are typically viewed as the main products of lipid oxidation. Recently, epoxides have also been suggested as important intermediates but there is a lack of suitable methods for their determination in oxidized oils. Here we describe a method to quantify epoxide yield during lipid oxidation using ¹H NMR. To investigate the chemical shifts of mixed epoxides derived from polyunsaturated fatty acids, fresh fish oil was epoxidized using formic acid and hydrogen peroxide. The chemical shifts of mixed epoxides in epoxidized fish oil were found to be between 2.9-3.3 ppm. The peaks associated with glycerol remained constant during both oxidation and epoxidation of fish oil, allowing them to be used as an internal reference for the quantification of epoxides. Oil samples with different epoxide concentration were made and standardized using the AOCS method for oxirane oxygen. These were analyzed by ¹H NMR under standard conditions to generate a calibration curve. To demonstrate the utility of the method, commercial oils were then oxidized under a variety of conditions and epoxides were determined by ¹H NMR.

Development of Defective Aroma References for Sensory Evaluation of Virgin Olive Oil. H. Zhu¹(Analytical Division Student Award Winner), S. Langstaff², C. Shoemaker¹, and S. Wang², ¹Dept. of Food Science and Technology, University of California Davis, Davis, CA, USA, ²University of California Davis Olive Center, Davis, CA, USA.

Negative flavors and aroma attributes such as rancid, fusty, musty, muddy-sediment, winey-vinegary are sensory attributes of defective virgin

olive oil recognized by the United States Department of Agriculture. Solid phase microextraction-gas chromatography/mass spectrometer (SPME-GC/MS) is employed to establish a flavor profile for each defective oils and the significant compounds in certain concentration are selected for each defective flavor to develop sensory reference standards. For example, E-decenal (120 mg/kg), E-2-octenal (35 mg/kg), E-2-heptenal (10mg/kg), nonanal (120 mg/kg), and E-2-nonenal (30 mg/kg), etc. are identified as significant compounds to reproduce the flavor and aroma of rancidity. The reference standard of each defective flavor can be reproduced with ease in the laboratory and used for sensory panel training. To the best of our knowledge, currently there are no reference samples available for olive oil though they exist for some other foods and beverages such as wine and beer.

Monitoring Lipid Oxidation of Canola Oil Using Surface Enhance Raman Spectroscopy (SERS). M. Driver and L. He, University of Massachusetts, Amherst, MA, USA.

Lipid oxidation is a major challenge in the food industry's attempts to incorporate nutritionally beneficial lipids in food products. However, conventional methods are time consuming and not as sensitive as the human nose in detecting oxidative rancidity. Surface-enhanced Raman spectroscopy (SERS) is combination of Raman spectroscopy and nanotechnology. Raman signals can be enhanced tremendously using gold nanoparticles, thus increasing sensitivity greatly. The objective of this study is to develop and apply a SERS based method for rapid detection of lipid oxidation. Gold nanoparticles fabricated in citrate buffer were firstly modified with alkanethiols to change the hydrophobicity, so that they can be dispersed well in hexane diluted canola oil. The oxidation of canola oil was monitored daily at 55°C for two weeks using conventional methods that measured conjugated dienes, hydroperoxides, and hexanal, conventional Raman spectroscopy and SERS. The significant increase of conjugated dienes, hydroperoxides, and hexanal were observed at day 10, 7, 14 respectively. The conventional Raman spectra of 100% oil didn't change significantly over time, while the SERS spectra of 3% oil changed significantly at day 2 analyzed by principal component analysis. This study demonstrated the potential of the SERS method for rapid and sensitive detection of lipid oxidation.

Improved Gas Chromatography-flame Ionisation

Detector Analytical Method for the Analysis of Epoxy Fatty Acids. E. Mubiru, K. Shrestha, A. Papastergiadis, and B. De Meulenaer, Ghent University, Ghent, Belgium.

In this study an improved method for analysis of epoxy fatty acids is reported. Data obtained from analysis of polar fatty acids has previously been presented, but due to the high number of compounds that co-elute in the polar fraction, the resultant chromatograms are complex which may lead to compromising the accuracy of the data. A three steps separation of fatty acid methyl esters (FAMES) by solid-phase extraction (SPE) on a silica gel column to remove hydroxy fatty acid interferences was proposed. This approach is opposed to a two step separation procedure that has been often used to prevent analytical interferences caused by non-altered fatty acids. A gas chromatograph with a flame ionisation detector (GC-FID) equipped with a polar CP-Sil 88™ column was used. Quantification was based on the use of

methyl nonadecanoate (C19:0), as an internal standard. Individual mono epoxy fatty acids were well separated without co-eluting compounds. The optimised method was finally applied to screen epoxy fatty acids in 37 fresh oil samples. Results obtained for the total epoxy fatty acids were in the range 0.03 – 2 mg g⁻¹ of oil with repeatability coefficient of variation (CV) ranging from 2.8 to 9.9% for duplicate analysis showing that the results obtained are repeatable.

Shelf Stability of Vegetable Oils. A. Syed and M. Evenson*, Dow AgroSciences, Indianapolis, IN, USA.

A 2-year long shelf stability study was conducted on common vegetable oils.

Chemical and sensory analyses were conducted at intermittent time points.

Resulting data suggest that each oil has a characteristic behavior of its own, and that using the one analytical criteria to grade them may not be exactly instructive.

LOQ 2: From Theory into Applications: Investigation of Fundamental Oxidation Mechanisms, Encapsulation, and Unique Antioxidant Functionality

Chairs: D. Berdahl, Kalsec Inc., USA; and F. Shahidi, Memorial University of Newfoundland, Canada

Factors Affecting the Stability and Stabilization of Edible Oils. F. Shahidi (*Alton E. Bailey Award Winner*), Memorial University of Newfoundland, St. John's, NL, Canada.

Edible oils are composed mainly of triacylglycerols (TAGs) with varying fatty acids located in the sn-1, sn-2 and sn-3 positions of the glycerol backbone molecule; the type and location of unsaturated fatty acids in the TAGs is a primary determinant of oil stability. Edible oils also contain a myriad of minor components such as tocopherols / tocotrienols, metal ions, chlorophylls, squalene, and carotenoids, which also can affect oil stability during processing as well as storage. Furthermore, dietary supplements, such as omega-3 concentrates, are in the form of ethyl esters or reconstituted TAGs, and these possess different stability characteristics. The preparation of healthful structured lipids via acidolysis or other techniques leads to the production of oils with modified fatty acids and altered minor components. The presentation will provide a cursory account of different factors that influence the stability of edible lipid-containing foods and supplement oils.

Use of Green Tea Extract as a Natural Shelf-life Solution for Foods. S.P.J. Namal Senanayake, DuPont Nutrition & Health, New Century, KS, USA.

Green tea extract has gained popularity as one of the dietary supplements in the U.S. market in recent years. Green tea extract can also be used in lipid-containing foods to inhibit lipid oxidation and to extend the shelf-life of various food products. The primary antioxidant components in green tea extract are catechins, which comprise epicatechin, epigallocatechin, epicatechin-3-gallate and epigallocatechin-3-gallate. This presentation reviews the chemistry, flavor constituents, antioxidant mechanism, regulatory status, and various applications of green tea extract in food.

Antioxidant Activity of Fat Soluble Green Tea Extracts in Soybean Oil. J. Liang, F. Niu, Y. Zhang, and Y. Jiang, Wilmar (Shanghai) Biotechnology R&D Center Co., Ltd., Shanghai, China.

Green tea extracts has long been used as antioxidant for food. The main function ingredients

in green tea extracts are flavonoids. They are chemically water soluble and also may deepen the color of oils. These limit their application in oils and fats. In this study, green tea extracts were modified by esterification and fat soluble green tea extracts (FSGTE) were obtained. The antioxidant activities of FSGTE in soybean oil during heating at 60°C and storage were tested. The concentration of 0.25, 0.50, 1.00 mg/g FSGTE in soybean oil were studied. Soybean oil without antioxidant added and with 0.08 mg/g TBHQ were used as control. It was found FSGTE can improve the stability of soybean oil during heating at 60°C and during storage. The antioxidant activities of 0.50 mg/g FSGTE were better than that of 0.08 mg TBHQ. This provides a great opportunity to replace TBHQ with more nature and healthy antioxidant. Details of the study will be presented.

Optimizing Antioxidants for Tailored Algal Oils. M. Peitz¹, R. Bond², and T. Tiffany¹, ¹Archer Daniels Midland, Decatur, IL, USA, ²Solazyme, Inc., South San Francisco, CA, USA.

Triglyceride oils from traditional sources such as plant crops have been studied for many decades to optimize their oxidative stability for both food and industrial uses. Recently, unique compositions of triglycerides from Solazyme Tailored Algal Oils have been produced that can be further enhanced by utilizing antioxidants. This paper presents results of studying the impact of synthetic and natural antioxidants on the oxidative stability of Solazyme Tailored Algal Oils via Oven Storage Tests for Accelerated Aging of Oils (AOCS Official Method Cg 5-97). The accelerated storage stability data will provide insight into improving the inherent stability of tailored algal oils to meet the needs for the use of these oils in applications that require long shelf life and greater resistance to oxidative deterioration.

Oxidative Stability of Selected Fruit Seed Oils. Q. Li and F. Shahidi, Memorial University, Biochemistry Department, St. John's, NL, Canada.

Oxidation of edible oils depends on their degree of unsaturation, positional distribution of the fatty acids within the triacylglycerol molecules as well as minor components present and storage conditions. In this connection, presence of phenolic compounds,

including tocopherols and tocotrienols as well as prooxidant metal ions and photosensitizers such as chlorophylls are important contributing factors. Thus, fruit seed oils, namely those of blackberry, black raspberry and blueberry were examined for their autoxidation and photooxidation as such and following stripping of their minor components. The results so obtained demonstrated the importance of chlorophylls as oxidation initiators in the non-stripped oils and that if tocopherols under autoxidation conditions. Details of this work as well as potential use of seed antioxidants in stabilization of lipid-containing foods and biological systems will be presented.

Newer Antioxidants on the Horizon: Mustard Bran, Canola Meal, and Canola Refining By-products as Source of Antioxidants. U. Thiyam-Hollander^{1,2},
¹Richardson Center for Functional Foods, Winnipeg, MB, Canada, ²Dept. of Human Nutrition, Winnipeg, MB, Canada.

Increasing the concentration of canolol (CAN) or 4-Vinylsyringol, a potent antioxidant with lipid-peroxyl radical scavenger activity, would increase the value of canola oil, meal and mustard bran. Recently, we demonstrated that canola seeds, and meals could be used to generate canolol and sinapic acid rich extracts. We translated our work to derive canolol from mustard bran and mustard processing by-products. This paper will discuss and review the potential of mustard bran and canola by-product utilization trend of the food industry supported by recent findings in our laboratory. Fractions of different canola refining by-products were investigated for the content of phenolic compounds, namely sinapic acid, sinapine, and CAN. Sinapine was detected in the spent bleaching clay, while considerable amount of sinapic acid could be recovered from the refining soap stock. Additionally, the water wash was established as a promising source of CAN. CAN can be utilized as an inhibitor of lipid oxidation in various lipid containing food systems and non-food emulsions. A collaborative study with Drs. Matthaus and Pudiel using CAN as antioxidants for deep frying will be presented. A conclusion based on the current status will be presented.

Impact of Phosphatidylethanolamine and Its Combination with Phosphatidylcholine on Lipid Oxidation in Bulk Oils. L. Cui and E. Decker,

University of Massachusetts Amherst, Amherst, MA, USA.

Phospholipids are important minor components in edible oil that play a role in lipid oxidation. Surface active phospholipids have intermediate hydrophilic-lipophilic balance values which allow them to form association colloids such as reverse micelles in bulk oil. These association colloids can influence lipid oxidation since they create lipid-water interfaces where prooxidants and antioxidants can interact with fatty acids. In this study, we examined the formation of reverse micelles in a stripped oil system by dioleoyl phosphatidylethanolamine (DOPE) and the effect of these physical structures on lipid oxidation kinetics. Fluorescence spectrometry showed that the critical micelle concentration (CMC) of DOPE was approximately 800 mmol/kg oil. Oxidation kinetics studies showed that DOPE was prooxidative with 1100 mmol/kg oil DOPE reducing the lag phase from 14 days (control) to 8 days. The addition of combinations of DOPE and dioleoyl phosphatidylcholine (DOPC) resulted in formation of mixed micelles with a CMC of 150 mmol/kg oil. These mixed micelles were also prooxidative, decreasing the lag phase from 14 days to 8 days. These findings provide a better understanding of phospholipids in lipid oxidation of edible oil and could contribute to better antioxidant approaches.

Antioxidant Activity of Sphingoid Bases on PUFA Oxidation. K. Miyashita¹, M. Uemura¹, M. Shiota², and M. Hosokawa¹, ¹Faculty of Fisheries Sciences, Hokkaido University, Hakodate, Japan, ²Megmilk Snow Brand Co. Ltd., Kawagoe, Japan.

Amine containing glycerophospholipids (PLs) such as phosphatidylcholine (PC) and phosphatidylethanolamine (PE) have been well known as synergists in combination with tocopherols. On the other hand, little has been known on the effect of sphingolipids (SLs), although they contain amines in their sphingosyl backbone. In the present study, we reported the effect of SLs and sphingoid base, a basic structural element of SL, on the oxidative stability of triacylglycerol (TAG) in the presence or absence of α -tocopherol. SL and sphingoid base had little effect on the TAG oxidation in the absence of α -tocopherol. On the other hand, they could act synergistically with α -tocopherol. The synergistic activity of sphingoid bases was much higher than those of PLs and SLs. The comparison of changes in α -tocopherol content during the

incubation of fish oil TAG and in tricaprilyn suggested that antioxidant compounds would be formed from the amine group and the lipid oxidation products in a mild oxidation condition controlled by α -tocopherol. Furthermore, the present study demonstrated that the formation of antioxidant from sphingoid bases was more significantly found in the oxidation of omega-3 PUFA but not much in that of omega-6 PUFA.

Development of HPLC 2,4-Dinitrophenylhydrazone Assay for Quantitating Carbonyls from Lipid

Oxidation. L. Yao and K.M. Schaich, Rutgers University, New Brunswick, NJ, USA.

2,4-Dinitrophenylhydrazine (DNPH) reaction with carbonyls to produce dinitrophenylhydrazones monitored at 300-360nm has been a standard assay for quantitating secondary products of lipid oxidation. However, traditional DNPH assays lack stability and sensitivity and provide no information about the carbonyls present. To overcome the limitations, a more accurate and reproducible HPLC

method of analyzing soluble carbonyls was developed to improve quantitation of total carbonyls and identify core aldehydes on phospholipids and triacylglycerols as well as monomer products. Hydrazones generated from monomer carbonyls and oxidized phospholipid and triacylglycerol standards were separated in high resolution on an RP Ultra C18 column with acetonitrile:isopropanol and water gradient elution and DAD detection at 360nm. Short chain aldehydes expected as scission products from lipid oxidation eluted first and were completely separated from core aldehydes in phospholipids and triacylglycerols. Separation of unreacted DNPH from the hydrazones also increased stability of products. Monomer carbonyls can be tentatively identified by comparison with standards; identification of core aldehydes requires mass spectrometry detection. Combining DNPH-HPLC results with hydroperoxide and conjugated diene assays can provide a more complete and accurate picture of lipid oxidation in oil and lipid extracts.

LOQ 3: Frying Oils: Health Impact and Stability

Chairs: M. Peitz, Archer Daniels Midland Co., USA; and J. Moser, USDA, ARS, NCAUR, USA

Mechanisms of Thermal Degradation in Heated Oils: Thermal Scissions Versus Arrhenius-accelerated Oxidation.

K.M. Schaich, X. Tian, and I. Repko Rider, Rutgers University, New Brunswick, NJ, USA.

Unsaturated oils degrade rapidly at frying temperatures. Stabilization approaches based on free radical chain reactions have had limited success, so it is clear some reaction mechanisms are not being considered. To elucidate reactions involved in thermal degradation of lipids, a corn oil-high oleic acid sunflower oil blend was heated in an oxygen bomb at temperatures from 100 to 180°C under 2 bars air for up to three hours. The headspace was vented through a thermal desorption trap and volatiles were analyzed by gas chromatography; oils were analyzed for conjugated dienes, hydroperoxides, aldehydes, and free fatty acids. Results support thermal scissions described by Nawar (Food Chemistry, Fennema, 1986) as the dominant degradative process at high temperatures. Thermal scission radicals add oxygen to form peroxy radicals that initiate radical oxidation chains, which increase in importance as heating is prolonged. A reaction scheme integrating thermal scissions, autoxidation, and heating conditions is proposed.

High Throughput Screening of Treatments for the Stabilization of Frying Oils.

L. Ban, J. Drury, and W. Schroeder, Kemin Food Technologies, Des Moines, IA, USA.

Frying oil stability is one of the crucial factors for the quality and health effect of both fried food and oil. The use of antioxidants to improve oxidative stability of frying oil has been studied extensively. However, questionable conditions and method, like Oxidative Stability Instrument (OSI), often lead to incorrect conclusions of the effectiveness of antioxidants. A frying study, on the other hand, is resource intensive. Realistically, only a limited number of oil types and treatments can be tested. This study aims at developing a rapid method to mimic real frying conditions. It targets at screening large numbers of antioxidants to evaluate their effectiveness in stabilization of frying oil and fried food. The design utilized multi-well heating blocks of conventional OSI. In the frying oil, total polar compounds, color, oxidation products and

acrylamide are measured. In the fried food, oxidation products are monitored. The treatments which give the best, medium and worst performance are subject to actual frying study to validate the screening results. Natural plant extracts including rosemary extract, sage extract, ascorbic acid, citric acid and their derivatives (catechin esters, rosmarinate esters and ascorbyl palmitate) are compared to synthetic antioxidant TBHQ using soybean oil as the frying oil.

Development of a Frying Oil Stability Model.

P. Smith¹, A. Menzel¹, S. Smith², and P. Adhikari³,
¹Cargill R&D Centre Europe, Vilvoorde, Belgium,
²Cargill Inc., Wayzata, MN, USA, ³Cargill Asia Pacific Food Systems, Beijing, China.

The life time of frying oil is determined by its stability against oxidation. National laws in many countries have defined quality parameters which determine whether an oil can still be used or needs to be replaced. At the same time there is a significant push to more healthy oils, which contain higher proportions of unsaturated fatty acids. This causes a risk of reduced oxidative stability of these healthier frying oils. In order to being able to predict relative oxidative stability of different frying oil blends, we have developed a statistical model to serve as a tool that enables a realistic estimation of the relative oxidative stability of a different oil blends prior to intensive frying tests.

The statistical model was built using an accelerated oil oxidation reactor, following fundamental oil oxidation parameters, including peroxide value and anisidine value. The analytical results were all fit into a statistical model by determining the kinetics parameters for many different oxidation equations, in order to achieve a tool enabling realistic predictions.

Effects of Natural Antioxidants and Addition Methods on Oxidative Stability of Fried Instant Noodles.

M. Wolf, L. Burroughs, and R. Boyle, Kalsec, Inc., Kalamazoo, MI, USA.

Over the course of a stability study, sensory and GC-MS headspace evaluations were used to determine the effects of various antioxidants (rosemary extract, green tea extract, mixed tocopherols and ascorbic acid) in slowing lipid

oxidation in fried instant noodles. Additionally, two methods of incorporation of antioxidants were compared: addition to the water phase of the dough and addition to the frying oil. Choice of addition method seems to play a considerable role on the efficacy of the antioxidant. Sensory analysis also explored the effects of antioxidants on noodles in both dry and hydrated states, chosen to represent various stages of the consumer's interaction with the final product. Aroma of dry noodles was chosen to model perception after opening the retail packaging while flavor in hydrated noodles was used to model the consumer experience just prior to consumption. Lipid oxidation was effectively controlled by choosing the right antioxidant system, and optimization of the incorporation method.

Additives Increasing Antioxidant Activity of Sesamol in Soybean Oil at Frying Temperature. H.S. Hwang, J.K. Winkler-Moser, and S.X. Liu, USDA, ARS, NCAUR, Peoria, IL, USA.

Sesamol has drawn a considerable interest as an alternative to synthetic antioxidants due to its excellent radical scavenging ability at room temperature, low cost and additional health-promoting benefits. However, when it was evaluated for its antioxidant activity in soybean oil at frying temperature, it did not show very impressive results. Additives were tested to investigate their effects on the antioxidant activity of sesamol. Twenty two additives were examined and some of them showed remarkable improvements in antioxidant activity of sesamol during heating of soybean oil at 180°C. It is believed that this innovative method can be applied to many other natural and synthetic antioxidants. After a patent application is filed in November, the detailed information will be stated in the updated abstract and the presentation.

Oil-soluble Antioxidant of Bamboo Leaves Promotes the Frying Stability of Palm Oil as well as Controls Acrylamide Formation. L. Liu and Y. Zhang, School of Biosystems Engineering and Food Science, Zhejiang University, Hangzhou, Zhejiang, China.

Oil-soluble AOB (AOB-o) is a novel antioxidant approved by China government. It is an acylation product of bamboo leaf extract (*Phyllostahys Sieb. et Zucc.*) and fatty acid. AOB-o can be directly added to oil and fat or shifted by medium chain fatty acids. It could enhance the oxidative stability of palm oil, lard and fried potato chips by Rancimat evaluation under

130°C, which was of more strong effect than oil-soluble tea polyphenol (OTP) and little weaker than TBHQ. 0.02% AOB-o in palm oil reached about 20% inhibiting rate on acrylamide formation in French fries. The effectiveness of AOB-o on retarding frying oxidation of palm oil was also investigated. The synthesis results showed that AOB-o was more effective to inhibit oil oxidation than BHA, BHT, TBHQ and OTP at the same dosage level of 0.02% after frying 36 hrs at 180±2°C. No significant differences on PV and *p*-AV values were observed between AOB-o and RE, but AOB-o displayed more strong reducing capacity than RE in TBA, AV and FFA values. AOB-o maybe provides a good solution for edible oil and fat to promote frying stability and prolong shelf life as well as reduce health risks.

Linolenic Acid as the Main Source of Acrolein Formed During Heating of Vegetable Oils. S. Nakajima¹ and Y. Endo², ¹Tsuno Food Industrial Co. Ltd., Wakayama, Japan, ²Tokyo University of Technology, Hachioji, Tokyo, Japan.

Acrolein, which was an irritating and off-flavor compound formed during heating of vegetable oils was estimated by the gas-liquid chromatography (GLC). Several vegetable oils such as high-oleic sunflower, perilla, rapeseed, rice bran and soybean oils were heated at 180 degree(C) until 480 min and then the concentration of acrolein in head space gas was determined by GLC. The formation of acrolein was highest in perilla oil among tested oils, while it was very lower in rice bran oil and high-oleic sunflower oil. There was a good correlation between the level of acrolein and linolenate (18:3n-3) in vegetable oils. To investigate the formation of acrolein from linolenate, methyl oleate, methyl linoleate and methyl linolenate were also heated at 180 degree(C), and the level of acrolein formed from them was determined by GLC. The level of acrolein was the highest in methyl linolenate. Acrolein was also formed from methyl linoleate, but not from methyl oleate. It was confirmed that acrolein in vegetable oils was formed from polyunsaturated fatty acids, especially linolenic acid but not from glycerol backbone in triacylglycerols.

Influence of TAG, DAG, and MAG on the Formation of 3-MCPD Esters and Glycidyl Esters in Deep Frying.

T. Zhang, X. Jin, Z. Ma, and Y. Jiang, Wilmar (Shanghai) Biotechnology Research & Development Center Co., Ltd., Shanghai, China.

The formation and reduction methods of 3-monochloropropane-1,2-diol (3-MCPD) during refining was reported widely in the past; however, it was rarely discussed in the field of deep frying. During frying the oil is thermally and oxidatively decomposed to various substances such as diacylglycerols (DAG), monoacylglycerols (MAG), free fatty acids and others. This study found that MAG was strongly related to the formation of 3-MCPD esters(3-MCPDE) while DAG was related to the formation of Glycidyl esters(GE) in frying oil. The relation between 1,3-DAG and 2,3-DAG with the formation of 3-MCPDE and GE was also discussed. Besides, GE was considered to be an important precursor of 3-MCPDE in frying oil for first time. The influence extent of different substances on the formation of 3-MCPDE and GE was presented in the study and the possible mechanisms were discussed. The experiment was based on the addition of variables(DAG, MAG, GE, TAG as blank) into a model oil which was pure triglyceride, gained by removal of impurities by column chromatography filled with adsorbents composed of magnesium silicate, activated clay, activated carbon and silica gel. This study might explain the mechanism of formation of 3-MCPDE and GE in deep frying oil and further studies could be combined with particular foods to investigate detailed methods for reduction.

Detoxification of Deuterium Labeled Isomeric Cyclic Fatty Acid Monomers Fed to Rats.

A. Desmarais¹, E. Pujos-Guillot^{2,3}, J.F. Martin^{2,3}, B. Lyan^{2,3}, J. Arul¹, P. Angers¹, and J.L. Sebedio^{*2,3}, ¹Université Laval, Quebec City, PQ, Canada, ²INRA, UMR 1019, UNH, CRNH Auvergne, Clermont-Ferrand, France, ³INRA, UMR 1019, Plateforme d'Exploration du Métabolisme, UNH, Clermont-Ferrand, France.

Cyclic fatty acid monomers (CFAMs) are mainly formed during frying of edible oils. These fatty acids are mixtures of disubstituted 5 or 6 carbon membered ring structures. Some earlier studies have suggested that some of these molecules could be metabolized and detoxified but so far the detoxification mechanism (s) have not yet been fully elucidated. The objective of the present study was to identify the metabolites resulting from the metabolism and detoxification of CFAMs. For that purpose, the 9-²H-10-(6-propyl-2-cyclohexenyl)-dodecenoic acid was synthesized and fed to animals along with a CHOW diet. Biological fluids were collected, analyzed using an untargeted metabolomic approach by UPLC-QToF and compared to those of rats fed with the same diet without CFAM.

Identifications of CFAMs metabolites in urine of rats fed CFAM indicate that this molecule may be detoxified following two pathways i) β oxidation cycles and ii) hydroxylation in the α position of the ethylenic bond without chain shortening followed by β oxidation, and elimination mostly by glucuronidation. NO₂ derivatives of the metabolites described above were also identified. Increased excretion of medium chain hydroxyl acylcarnitines in the urine of rats fed with CFAM could indicate changes in fatty acid β -oxidation.

LOQ 4a: General Lipid Oxidation and Quality

Chairs: S. Pan, Solae LLC, USA; and C. Hall, North Dakota State University, USA

Reverse Micelles of Multiple Surface Active Minor Components and Their Effect on Lipid Oxidation in Bulk Oil. K. Kittipongpittaya¹ (*Honored Student Award Winner and The Peter and Clare Kalustian Award Winner*), A. Panya², D.J. McClements¹, and E.A. Decker¹, ¹University of Massachusetts, Amherst, MA, USA, ²National Center for Genetic Engineering and Biotechnology, Khlong Luang, Pathum Thani, Thailand.

Association colloids formed by surface active minor components play important role on oxidative stability of bulk oils. In this research, multiple surface active minor components including free fatty acids, phospholipids, diacylglycerols and sterols were used to form nanostructures in stripped corn oil. The critical micelle concentration (CMC) of the mixed components was determined. Moreover, the impact of the reverse micelles formed by these components on oxidative stability of bulk oil was studied. The CMC of the mixed surface active components was as low as 100 $\mu\text{mole/kg}$ oil in the presence of 383 \pm 2 ppm of water in bulk oil. The reverse micelles of mixed components showed prooxidative activity in bulk oil as determined by monitoring the formation of lipid hydroperoxide and hexanal. The impact of mixed minor components at below and above their CMC on antioxidant activity of tocopherols was investigated. This model system closely imitates the nanostructures that could be found in refined oils. Understanding how these complex structures impact on lipid oxidation and on reactivity of antioxidants could provide a new perspective to improve oxidative stability in bulk oils.

The Location of Long-chain n-3 Polyunsaturated Fatty Acids on Phospholipids or Triacylglycerols Modulates the Kinetics of Oxidation in Dietary Sub-micron Emulsions. C. Genot, T.H. Kabri, M. Viau, L. Ribourg, and A. Meynier, Biopolymères Interactions Assemblages, Nantes, France.

Oxidation of long-chain n-3 polyunsaturated fatty acids (n-3 LC-PUFA) depends on the molecular structure of the lipids and their organization in the matrix. This study was aimed at comparing the oxidation of oil-in-water emulsions carrying n-3 LC-PUFA either as triacylglycerols (TAG) or as phospholipids (PL). The emulsions, prepared with food grade oils and designed to respect lipid dietary recommendations, had oil droplet average

diameters lower than 250 nm and good physical stabilities. The emulsifiers were soybean phosphatidyl-choline combined with Tween-80 or a lecithin rich in DHA (PL-DHA).

The emulsions oxidized slowly at 37°C in the dark, with accelerated kinetics in the presence of metmyoglobin, the consumption of oxygen and tocopherols and the formation of hydroperoxydes, malondialdehyde, 4-hydroxy-2-hexenal and 4-hydroxy-2-nonenal being more rapid in one emulsion or in the other depending on the chosen marker and the incubation condition. The emulsion containing LC-PUFA as phospholipids was finally slightly less oxidizable than the other but the results illustrate the complexity of oxidation kinetics.

Oxidative Stability of Conjugated Linoleic Acid Rich Soy Oil Obtained by Heterogeneous Catalysis. S. Lele, A. Proctor, and C. Ruan, University of Arkansas, Fayetteville, AR, USA.

CLA rich soy oil (CLARSO) has been produced using ruthenium heterogeneous catalysis. The objective of this investigation was to determine the oxidative stability of the CLARSO oil, with 4ppm ruthenium, and adsorption treated CLARSO, with 1ppm ruthenium, relative to soy oil. Primary oxidation, secondary oxidation and decline of TAG unsaturated fatty acids, relative to that of a control soy oil was measured. Oxidative stability was determined at 50°C by measuring gravimetric analysis, peroxide value, headspace oxygen and p-anisidine value. Fatty acids were measured as FAMES by GC-FID. The headspace oxygen, peroxide value and gravimetric measurements showed that induction time was considerably increased by the adsorption treatment, probably due to the reduction of residual ruthenium. The percent loss of CLA isomers was greater than that of linoleic acid isomers, probably because the initial concentration of linoleic acid was much greater. However, there was no change in fatty acid composition of CLARSO after adsorption. This treatment increased CLARSO oxidative stability, but the presence of ruthenium in the untreated oil was useful in conducting an accelerated oxidation study.

Structural and External Factors Affecting the Oxidation of Sterols. M. Lehtonen, A.M. Lampi, and V. Piironen, University of Helsinki, Helsinki, Finland.

Plant sterols and their conjugates are both naturally present in foods and they may be added into novel food products. Since the oxidation products of sterols may have harmful biological effects, their formation should be prevented during food processing and storage. This study investigated the effects of chemical (i.e., esterification, unsaturation degree of the acyl moiety and sterol structure) and external (i.e., temperature and medium) factors on the oxidation of sterols. The introduction of an acyl moiety to a sterol altered the physical state and polarity of the sterol and thus affected its oxidation. The increased unsaturation of the acyl moiety increased the oxidation rate of both the sterol and acyl moieties. No differences in the initial reactivities of these two moieties were observed, but they oxidised concomitantly. Both the increased temperature (100<140<180°C) and the increased unsaturation of the lipid medium intensified the oxidation of sterol esters and free sterol. The formed sterol ester and free sterol hydroperoxides decomposed into traditionally determined sterol secondary oxidation products and also underwent polymerisation as a rival reaction. In conclusion, by altering the chemical and physical properties of sterols, their deterioration reactions can be altered.

The Degree of Lipophilization Affects Antioxidative Efficacy of Ferulates in Omega-3 Enriched Milk. A.D.M. Sørensen¹, K.S. Lyneborg¹, P. Villeneuve², and C. Jacobsen¹, ¹National Food Institute, Technical University of Denmark, Kgs. Lyngby, Denmark, ²UMR IATE CIRAD, Montpellier, France.

Foods containing omega-3 PUFA are highly susceptible to oxidation. One strategy to limit lipid oxidation is addition of antioxidants. The efficacy of antioxidants can vary with the complexity of the food matrix. Lately, extensive work has been performed on phenolipids and their antioxidant efficacy in model emulsion systems. Results indicated a cut-off effect in relation to the alkyl chain length grafted to the phenolic compounds. The impact of emulsion composition on the antioxidant activity has previously been

demonstrated for caffeates in milk and mayonnaise. Different critical chain lengths (cut-off) were observed for the two food systems. 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 ferulic acid and its esters, ferulates, in fish-oil-enriched milk. Lipid oxidation was evaluated from 3 parameters measured over storage time: peroxide value, volatiles and tocopherol concentrations. The results demonstrated that the composition of food emulsions influenced the antioxidative effect of ferulates. Depending on the lipophilization degree, ferulates acted surprisingly either as antioxidants or prooxidants. These results were more complex than what was expected from the cut-off hypothesis.

Synthesis and Antiradical Properties of Novel Diacylglycerols Rosmarinate Conjugates. P.

Villeneuve, C. Bayrasy, E. Durand, and J. Lecomte, UMR IATE CIRAD, Montpellier, France.

In compartmentalized systems, it is generally considered advantageous for antioxidants to exhibit surface activity. Surface-activity, hence hydrophobicity, allows the antioxidant to fuse with lipid-water interfaces and membranes and to be efficiently taken up by living cells. Thus, hydrophobic antioxidants are supposedly more internalized within cells than their hydrophilic counterparts. As such, they are thought to more effectively deal with the many reactive oxygen species (ROS) released into the cytosol. One reliable strategy to design a surface-active antioxidant is to incorporate positioned lipophilic groups by lipophilization. To date, a multitude of lipophilized antioxidants have been synthesized to obtain multifunctional compounds called "phenolipids". To have a global picture of the role of the lipophilic moiety on antioxidant activity, we tested other lipophilic moieties consisting of diacylglycerols grafted onto rosmarinic acid. Accordingly, herein is described a chemo-enzymatic route to prepare these 1,2-diacylglycerol rosmarinate conjugates with various chain lengths. These phenolipids so prepared were then finally assessed for their antioxidant activity in a ROS-overexpressing cell line of human dermal fibroblasts.

LOQ 4b: Skin Lipids: Oxidation and Health

Chairs: K. Mahmood, Johnson & Johnson Consumer, USA; and A. Pappas, Johnson & Johnson, USA

Development of Volatile Compounds During Storage of Different Lipid Containing Skin Care Products at Various Conditions. A.F. Horn¹, B.R. Thomsen*¹, G. Hyldeg¹, R. Taylor², P. Blenkiron², R. Elliot³, and C. Jacobsen¹, ¹Technical University of Denmark, National Food Institute, Kgs Lyngby, Denmark, ²GlaxoSmithKline, Brentford, UK, ³GlaxoSmithKline, Raleigh, NC, USA.

Many skin care products contain various lipids to care and soften the skin. These lipids are either saturated or unsaturated. In the case of even small amounts of unsaturated lipids, these are at risk of oxidizing when exposed to heat, light or other conditions with a pro-oxidative effect. When stored in the homes of consumers skin care products may be exposed to relatively high temperatures and light. Hence, especially skin care products sold in countries with a warm climate can undergo lipid oxidation and develop volatile compounds with off-odours. This presentation will include results from a storage experiment on three cleansing milks stored between 14 and 84 days, under different conditions. The samples were exposed to heat (20°C, 40°C and 50°C), light (samples at 20°C) and iron (samples at 40°C). Samples were analysed for their development of volatile compounds by dynamic headspace gas chromatography-mass spectrometry and peroxide value, and compared to samples stored at 2°C in the dark. In addition, sensory analyses were carried out to assess the off-odours developed in the samples.

The Essential Role of Lipids in Skin Health and Physiology. A. Pappas, Johnson & Johnson, CPPW, Skillman, NJ, USA.

Skin lipids are mainly of sebaceous and keratinocyte origin. The subcutaneous layer is consisted of adipocytes. Human sebum is the predominant secreted mixture of skin lipids, mainly triglycerides, wax esters, squalene, and smaller amounts of free fatty acids, cholesterol and cholesterol esters. Elevated sebaceous lipid synthesis is a major factor involved in the pathogenesis of acne. The sebaceous gland has a unique lipid metabolism since it synthesizes lipid species that are not found in other cell types and tissues of the body. Complexity and uniqueness characterizes sebaceous lipids as $\Delta 6$ desaturation, wax ester synthesis and squalene accumulation are the unique manifestations of sebaceous lipid

metabolism. The importance of these unique sebaceous lipids for normal skin functions will be summarized. Impairment of sebaceous lipid pathways in animal models resulted in severe skin and also hair phenotypes. In addition essential fatty acids and their metabolites are fundamental for barrier function, healthy or diseased skin. New insights from clinical studies outline the importance of fatty acid metabolism for clear skin and normal skin barrier function. Understanding the roles of skin surface lipids is fundamental for decoding the basic skin physiology.

The Pivotal Role of Unsaturated Fatty Acids in Skin. J. Ntambi, University of Wisconsin, Madison, WI, USA.

Skin varies greatly in morphology, and contains a number of specialized structures that impart functional diversity to the organ. The diverse roles of the skin require the synthesis of large amounts of lipids, such as cholesterol, phospholipids, triglycerides, ceramides, cholesterol esters, wax esters and retinyl esters. Some of these lipids are used as cell membrane components, signaling molecules, and as a source of energy. An important class of lipid metabolism enzymes expressed in skin is the delta 9 desaturases, which catalyze mainly the synthesis of oleoyl- (18:1n9) and palmitoleoyl-CoA (16:1n7). These are the major monounsaturated fatty acids of skin lipids. Mice with a specific deletion of delta-9 desaturase-1 isoform (SCD1) in the skin (SKO) show deficiency in skin lipids, which additionally results in dry skin and hair loss. The SKO SCD1 animals also exhibit increased whole-body energy expenditure, protection against dietary-induced adiposity, hepatic steatosis and glucose intolerance. The increased energy expenditure in these mice does not result simply from heat loss through the skin. Rather, thermogenesis appears to be constitutively activated in these mice regardless of changes in the ambient temperature. These observations provide new insight into the role that skin unsaturated fatty acids plays in whole body energy metabolism.

Mediator Lipidomics Elucidates the Role of Oxygenated Lipids in Skin Inflammation. A. Nicolaou, University of Manchester, Manchester, UK.
The skin is the primary barrier from the outside

environment, protecting the body from injury, infections and water loss. It is characterized by active lipid metabolism and depends on systemic provision of polyunsaturated fatty acids (PUFA) that are important for the integrity of the epidermal barrier and cutaneous immune and inflammatory reactions. PUFA mediate biological processes through altering the cellular membrane composition, gene and protein expression, signalling events and production of lipid mediators. The targeted approach of mass spectrometry-based mediator lipidomics permits qualitative and quantitative analysis of cutaneous lipids including oxygenated PUFA derivatives formed via cyclooxygenase, lipoxygenase and cytochrome P450 reactions (e.g. eicosanoids, docosanoids, octadecanoids, lipoxins, resolvins, protectins and maresins). Using this technology we have shown that UVR-induced inflammation is supported by a multitude of eicosanoids produced in a temporal manner and explored how their profile is changing as inflammation resolves. We have also used this model of skin inflammation to explore the biochemical mechanisms mediating the beneficial effect of bioactives and nutrients (e.g. green tea catechins and n-3PUFA supplements), locally applied irritants, and identify potential lipid biomarkers of cutaneous disease.

Glycerol, Fatty Alcohols, Acids, and Ceramide Alternatives in Cosmetics. M. Anthonavage, Presperse, Somerset, NJ, USA.

The global cosmetic industry consumes billions of metric tons of fatty acids, fatty alcohols and glycerin each year as well as vast amount of synthetic alternatives to ceramides. The applications of these lipids span all product categories ranging from soaps and deodorants to hair and skin care. The importance of these lipid ingredients is fundamental to the performance and function of a formulation. These lipids provide both sensory and therapeutic benefits while modulating the penetration rate of other ingredients. Fatty acids are

referred to as emulsifiers while the fatty alcohols are referred to as emulsion stabilizers. Saturated fatty acids and fatty alcohols function mostly as emulsifiers, stabilizers and tactile sensory modifiers, while glycerin is primarily used as a humectant. Glycerin is a substance known for its exceptional physical versatility and stability. In addition, the array of newly developed synthetic ceramides and ceramide-like moieties are proving to be quite functional in the topical personal care arena as they are used for their penetration enhancement properties as well as their ability to modulate lamellar phase organization with other lipids within the skin. This presentation will review the use of fatty acids, fatty alcohols, glycerin and alternatives to ceramides for topical personal care applications.

Preparation and Analysis of Human Skin Surface Phytolipid Mimetics. J. Addy^{1,2}, R. Kleiman¹, and J. Brown², ¹Robert Kleiman Consultants, LLC, Sun Lakes, AZ, USA, ²Floritech, Chandler, AZ, USA.

A mimetic of human skin surface lipid (SSL) sourced from materials of botanical origin is described. Human SSL is composed of triacylglycerols, free fatty acids, wax-esters, squalene, sterol esters and sterols. The wax-esters and triacylglycerols found in the discussed mimetic are the result of interestification of jojoba oil (wax-esters) and macadamia oil (triacylglycerols). The palmitoleic acid present in macadamia oil is incorporated into the wax-esters forming a unique material simulating natural SSL. The sterol esters used in the mimetic are the result of esterification of plant sterols with the acyl-groups of macadamia oil. Phytosqualene, derived from olive, is used as a botanical source of squalene. Analysis of the mimetic is achieved with a combination of high performance liquid-chromatography, high temperature gas-chromatography, and mass spectrometry. The analyses by HPLC and GC/MS resolve and quantify the many different lipid classes found in the mimetic.

LOQ 5: Co-oxidation of Lipids and Proteins in Complex Foods

Chairs: S. Bis, Kemin Industries, USA; and U. Nienaber, Kraft Foods Inc., USA

Investigating the Primary Mechanism of Oxidative Deterioration in Muscle Foods. M.P. Richards and E.W. Grunwald, University of Wisconsin-Madison, Madison, WI, USA.

The challenge in understanding the primary pathway by which heme proteins promote oxidative degradation in muscle tissue is that heme protein autoxidation, ferryl radical formation, heme dissociation, heme destruction, and iron release can all occur in a very short time sequence so that the most relevant step related to lipid and protein oxidation is obscured. This presentation will describe the use of protein crystallography and site-directed mutagenesis techniques to improve our understanding of heme protein-mediated oxidative reactions in muscle foods. Protein crystallography has revealed the precise location of unique amino acids surrounding the heme pocket of fish hemoglobins (Hb) that facilitate rapid metHb formation and heme release compared to different amino acids at analogous sites in mammalian Hbs. This coincides with the greater ability of fish Hbs to promote oxidative degradation compared to mammalian Hbs. Site-directed mutagenesis studies demonstrate that increasing heme affinity in model heme proteins decreases lipid oxidation while decreasing heme affinity accelerates lipid oxidation. A feature of Hb is lower heme affinity compared to myoglobin. A heme capturing reagent is also described that can be utilized to differentiate between Hb-mediated oxidative degradation and that of other oxidants in muscle (e.g. myoglobin, iron, copper, and lipoxygenases).

Lipid Oxidation and Related Protein Modifications in Oil-in-water Emulsions. C.C. Berton-Carabin¹, M.H. Ropers², D. Guibert², V. Solé², and C. Genot², ¹Wageningen UR, Agrotechnology and Food Sciences, Wageningen, The Netherlands, ²INRA, Biopolymères Interactions Assemblages, Nantes, France.

Lipid oxidation is a major cause for the degradation of the sensory and nutritional quality of many food products. In such multicomponent systems, lipid oxidation often occurs simultaneously with co-oxidation phenomena, which affect other molecules such as proteins. Lipid and protein oxidation both involve the formation of free radicals and carbonyl reactive species. Both phenomena are

closely interrelated, notably because of the presence of interfaces and colloidal structures where proteins and lipids get into contact. However, the sequence of the involved reactions still remains unclear. We describe a coupled experimental approach to concomitantly assess lipid oxidation and protein modifications in protein-stabilized oil-in-water emulsions. Although both reactions were timely related, early protein modifications, monitored through measurements of tryptophan fluorescence, were detected prior to the development of the lipid oxidation markers. The nature of the involved protein modifications was then further investigated, for both interfacial and non-adsorbed proteins. Proteins located at the oil-water interface underwent extensive modifications, such as aggregation, carbonylation and loss in solubility. Conversely, non-adsorbed proteins in the aqueous phase of emulsions were hardly modified, and had a protective effect against lipid oxidation.

Differential Lipid Co-oxidation of Proteins in Tortilla Chips, Peanut Butter, and Wheat Flour. K.M. Schaich, Y. Dong, W. Wanibadullah, and G. Resch, Rutgers University, New Brunswick, NJ, USA.

Oxidizing lipids cause significant damage to proteins, including crosslinking and scission, browning, and surface modifications that alter solubility, structural organization, and intermolecular associations. Considerable variation occurs in co-oxidation patterns among food proteins. In tortilla chips, the dominant effect was massive disulfide and peptide crosslinking to form very large open protein aggregates; surface modifications that interfered with dye binding were also present. Crosslinking appeared to be mediated by lipid radicals or hydroperoxides rather than carbonyl-amine condensations. Proteins in peanut butter showed protein scissions and limited crosslinking; the major effect was extensive modification of surface residues that altered protein solubility, matrix structure, and interactions with lipids. Results were marked textural hardening, emulsion breaking, browning, and restructuring of lipids by lipid radicals and hydroperoxides and by formation of adducts with lipid carbonyls. In stored wheat flour, oxidation of sulfhydryl groups occurred, interfering with gluten associations. Thus, lipid concentration, amino acid composition, and nature of the food matrix all

appear to be important in directing specific molecular changes involved in lipid-protein co-oxidations.

Protein Oxidation in Foods. M. Lund, University of Copenhagen, Frederiksberg, Denmark.

Protein oxidation in food has through the last decades received increasing attention from the industry and academia and has been associated with a decrease in food quality such as reduced tenderness of meat. The most typical results of protein oxidation are amino acid side chain alterations, such as formation of protein carbonyls, loss of thiols, or generation of various methionine-derived oxidation products. The oxidative impairment may lead to protein cross-linking and changes in the physico-chemical properties of the proteins. However, which oxidation products are formed is highly dependent on food type as well as processing and storage conditions.

Antioxidant polyphenols from plant extracts may effectively protect against lipid oxidation, but the effect on protein oxidation is ambiguous. Covalent and non-covalent protein-phenol interactions influence protein functionality in food products. In fact, polyphenols in their oxidised form (i.e. quinones) may react with protein thiols and create thiol-quinone adducts, which may lead to increased protein cross-linking.

In living cells, small thiol-containing compounds work as antioxidants. This mechanism is currently explored in beer for improvement of flavour stability, and requires a regeneration of thiols by reducing compounds provided by the yeast during fermentation.

Co-oxidation of Lipid and Protein in a Pet Food Matrix. S. Cutler and B. Bowen, Kemin Industries, Des Moines, IA, USA.

This study was undertaken to determine the extent of oxidation of protein sources in pet food raw materials and their effect on diet stability in dry cat and dog food kibble. Protein oxidation was measured by carbonyl determination and oxidation of sulfhydryl groups with Ellman's reagent. Lipid oxidation measures were tracked with peroxide value (PV) formation by FOX-2 method. Kibbles were stored at 37°C for 12 weeks.

Chicken meals treated with an antioxidant product had lower carbonyl values and higher PV's than untreated chicken meals. These meals were then formulated into cat and dog food kibble (30% of diet) and extruded. Pet food kibbles made with

oxidized meal showed higher levels of carbonyls after extrusion when compared to those made with treated meal but similar PV. In kibbles coated with canola oil, PV's increased rapidly and carbonyls increased over time as well, indicating both lipid and protein oxidation occurring in the kibble. When coated with chicken fat, PV increased more slowly as did carbonyls in kibbles. When tested for palatability, cats preferred kibbles with lower carbonyl values even when PV were the same for the diets.

Quality Changes in Krill Products During Their Manufacturing Process. F.S.H. Lu¹, C. Jacobsen¹, and I. Bruheim², ¹Division of Industrial Food Research, National Food Institute, Technical University of Denmark, Kgs. Lyngby, Denmark, ²Olympic Seafood AS, Fosnavaag, Norway.

The quality of krill products is influenced by their manufacturing process and could be evaluated by their level of lipid oxidation and non-enzymatic browning products. Therefore, the objectives of this study were a) to investigate the effect of temperature towards the non-enzymatic browning reactions and lipid oxidation in krill products during the different steps in their manufacturing process; b) to investigate if the occurrence of non-enzymatic browning reactions in krill products is due to the presence lipid oxidation products. Characterisation of krill products sampled at different stages of the manufacturing process was made by determining their lipid composition, antioxidant content and profiles of volatile degradation products. In addition, a simple model system comprising amino acids was prepared with addition of lipid derived volatiles or non-enzymatic browning products. The development of non-enzymatic browning reactions in model system was investigated through the measurement of volatiles, pyrroles, free amino acid content and Yellowness Index. The use of thermal treatment was shown to result in development of non-enzymatic browning reactions in krill products during their manufacturing process. The occurrence of these reactions was ascribed to the presence of carbonyl compounds derived from lipid oxidation.

Interactions Between Oxidizing Lipids and Proteins. B.E.E.A. De Meulenaer, T. Cucu, B. Kerkaert, M. Obando Chavez, and A. Papastergiadis, Ghent University, nutriFOODchem Group, Ghent, Belgium.

Protein interactions with carbonyl compounds have been particularly studied in the framework of Maillard reaction systems. In such systems reducing

sugars and their degradation products react with proteins in order to produce so called advanced glycation end products. AGE's are considered to be important because of their impact on human health. Remarkably however, the interaction between oxidizing lipids, known to generate a complex mixture of carbonyl compounds as well, and proteins has been studied in considerable less detail. Only the reactions between individual amino acids and selected lipid oxidation products were studied more in detail in foods. This paper presents a selection of results obtained within our group on the interaction

between lipid oxidation products and proteins. Both auto-oxidation and photo-oxidation were considered while on the protein level, studies were conducted on dairy proteins, lysozyme, hazelnut and soy proteins. The paper will deal with the analytical complexity to study these interactions and the relevance of various molecular markers used to study them, the impact on the biological activity of selected proteins, the impact on protein digestibility and the behaviour of selected lipid oxidation compounds in the presence of proteins.

LOQ-P: Lipid Oxidation and Quality Poster Session

Chairs: H. Hwang, USDA, USA; A. Logan, CSIRO Animal, Food & Health Sciences, Australia; and B. Cooke, Dallas Group, USA

1. Effect of Refining Processes on Polyphenol and Tocopherol Content in Expeller-pressed Canola Oil and the Refining Byproducts. Y. Chen, A.

Appukuttan, and U. Thiyam, University of Manitoba, Winnipeg, MB, Canada.

Commercial canola oils undergo complex refining processes to achieve the desired quality. However, these processing steps also remove desirable minor components such as polyphenols and tocopherols. In the present work, the phenolic compounds and tocopherols eliminated from canola oil during four refining stages were characterized by HPLC, and their contents in four refining byproducts including spent bleaching clay (SBC), wash water (WW), soap stock (SS) and deodistillates (DDL) were also studied.

Highest amount of canolol was lost from oil during the bleaching step (84.9%). However, tocopherol degradation was observed to be most significant during the deodorization step (26.1%). Different individual polyphenols and tocopherols were observed in the refining byproducts. Sinapine was found as the major phenolic compound in SBC with concentration of 199 μ g/g. SS and WW contained desirable content of sinapic acid (344 μ g/g) and canolol (42.93 μ g/g), respectively. In addition, a new unidentified polar compound, probably polymerized derivative of canolol, and tocopherol was present in DDL with high amount (polar compound: 1.61mg/g; tocopherol: 3.75mg/g). The results indicated that high amount of polyphenols and tocopherols can be recovered from the expeller-pressed canola oil refining byproducts.

2. Recovery of Phenolics from Canola Oil Refining Byproducts to Improve Oxidative Stability of Canola Oil During Deep-frying. Y. Chen, A. Appukuttan, M.

Eskin, and U. Thiyam, University of Manitoba, Winnipeg, MB, Canada.

Desirable amount of phenolic compounds can be recovered from canola oil byproducts such as canola meals and deodistillate (DDL). The effectiveness of canolol (CAN) and phenolic extracts obtained from canola oil DDL were compared with BHT for stabilizing canola oil during deep-fat-frying. BHT, DDL and CAN were added to high oleic canola oils at 200 ppm level, followed by deep frying of

French fries at 185 \pm 5 $^{\circ}$ C for 5 days. Oil samples were taken for assessing oxidation by measuring peroxide value, p-Anisidine value, conjugated dienes /trienes, total oxidation (TOTOX) and color. CAN and DDL extracts both exhibited higher antioxidative effects than BHT or control oil during frying. Oils containing DDL and CAN extracts showed a considerable reduction in the hydroperoxides after the first day of frying, indicating their potential for reducing or inhibiting primary oxidation with the order of effectiveness being: CAN>DDL>BHT>Control. TOTOX values of oils with DDL and CAN were significantly lower than oil with BHT and control samples. Only a small but not significant reduction in the total antioxidant activity (TAA) was observed in oil containing CAN (from 93.64 to 90.37) after the first day of frying. These results suggest that both DDL and CAN can inhibit lipid oxidation during deep-fat-frying.

3. Antioxidant Activities of Annatto and Palm Tocotrienol-rich Fractions in Fish Oil and Structured Lipid-based Infant Formula Emulsion. L. Zou and C.

Akoh, University of Georgia, Athens, GA, USA.

Lipid oxidation in foods is a major concern with the increased use of polyunsaturated fatty acids. Addition of natural antioxidants may help prevent their oxidation. Although the antioxidant and biological properties of tocopherols have been investigated extensively, little is known about antioxidant activities of tocotrienols in foods. Commercially, palm and rice bran tocotrienol-rich fractions (TRFs) are mixtures of tocopherols and tocotrienols, whereas annatto TRF is virtually tocopherol-free.

The objectives of this study were to 1) determine and compare the antioxidant activities of commercial annatto and palm TRFs in fish oil and structured lipid-based infant formula emulsion, and 2) test the hypothesis that α -tocopherol can interfere with antioxidant activities of tocopherol-free annatto TRF in foods. The peroxide and anisidine values of oil and emulsion samples stored at 37 $^{\circ}$ C were measured over a 28-day period. The results showed that annatto TRF was a more effective antioxidant than palm TRF and α -tocopherol in both systems at 200 and 500 ppm. In addition, α -tocopherol did not attenuate antioxidant

activity of annatto TRF in these systems. Our findings may lead to the development of new natural antioxidants for food applications.

4. Alginate Oligosaccharides: Enzymatic Preparation and Antioxidant Properties Evaluation.

M. Falkeborg¹, L.Z. Cheong¹, C. Gianfico^{1,2}, K.M. Sztukiel¹, K. Kristensen³, M. Glasius³, X. Xuebing¹, and Z. Guo¹, ¹Dept. of Engineering, Aarhus University, Aarhus, Denmark, ²Dept. of Biology, Università di Roma, Rome, Italy, ³Dept. of Chemistry and iNANO, Aarhus University, Aarhus, Denmark.

Due to the growing trend in consumer preference for natural food ingredients, the interest for using antioxidants from natural sources is increasing. A promising source of natural antioxidants is marine oligosaccharides. This study evaluated the antioxidative properties of alginate oligosaccharides (AOs) prepared by enzymatic depolymerization of alginate. The time-course of depolymerization was analyzed to determine the extent of depolymerization necessary for preparation of AOs with the lowest degree of polymerization. Mass spectrometry and infrared spectrometry confirmed that the AOs were composed of dimers, trimers, and tetramers of mannuronate and guluronate. AOs showed radical scavenging activity (superoxide, hydroxyl and ABTS*) and at some concentrations, AOs inhibited lipid oxidation more than ascorbic acid. Comparatively, polymeric and monomeric alginates were weak radical scavengers, and the radical scavenging activity of AOs is hence suggested to be enhanced by the conjugated alkene acid structure, which formed during the enzymatic depolymerization. A mechanism based on resonance hybrid theory is proposed to explain the excellent antioxidant properties of AOs. This work demonstrated that AOs obtained from a facile enzymatic treatment of abundant alginate is an excellent natural antioxidant, which may find applications in the food industry.

5. Effect of Natural Antioxidants on the Oxidative Stability in Different Oil Systems. Y. Wang^{1,2}, X. Wang¹, Y. Zhang*², and H. Zhang², ¹Jiangnan University, Wuxi, Jiangsu, China, ²Wilmar (Shanghai) Biotechnology R&D Center Co. Ltd., Shanghai, China.

The interface property for oil and water emulsion system not only affects the lipid oxidation stability, but also related to the antioxidants efficiency. In this study, hydrophobic natural antioxidants, i.e. vitamin E (VE), ascorbyl palmitate

(AP), rosemary extracts (ROS), and hydrophilic ones, such as, epigallocatechin gallate (EGCG), ascorbic acid (AA), water-soluble rosemary extracts (W-ROS) were added in their effective concentrations which is under the national standard of margarine. Antioxidants were evaluated and compared in pure fat and emulsion system. The oil phase was palm-based bulk fat and samples were stored in an oven at 35±1°C for tests. The results showed that antioxidants have different polarities performed differently in the same system. The order of oxidation inhibitive effect in pure fat was VC > W-ROS > ROS > EGCG > AP. VE had no effect. In W/O systems, the anti-oxidative activities were as follows: EGCG > W-ROS > ROS > AP > VE, while VC showed pro-oxidation effect. For O/W emulsions, EGCG had significantly higher activity compared to others, and followed by AP, ROS and W-ROS. VC also acted as pro-oxidation. Overall, all the natural antioxidants had a strong synergism with VE. EGCG, ROS and W-ROS are recommended as the substitutes of BHA+BHT to maintain the quality of margarine.

6. Effects of Thiols on Hydrocarbon Oxidation and *cis/trans* Isomerization of Unsaturated Lipids. O.T. Kasaikina, D.A. Krugovov, and E.A. Mengele,

N.N.Semenov Institute of Chemical Physics RAS, Moscow, Russia.

Thiols are known as biological antioxidants which function by scavenging hydroxyl radicals, reducing hydroperoxides (LOOH) and H₂O₂, preventing protein oxidation. The effects of thiols (2-mercaptoethanol, RSH, cysteine, CSH, and glutathione, GSH) on hydrocarbon oxidation and *cis/trans* isomerization of unsaturated methyl linoleate, ML, were studied. The rate of *cis/trans* isomerization of unsaturated bonds of ML, catalyzed by thiyl radicals, which are formed in exchange radical reactions with thiols, was found to reduce in the presence of oxygen.

The oxidation rates of ML and hydrocarbon increase in the presence of thiols. Computer simulation of the co-oxidation of thiols with ML and hydrocarbons revealed a key role of minor free radical escape (<1%) in the interaction of thiols with hydroperoxides, the primary oxidation products, which determined the increase of common oxidation rate. The kinetics of free radical formation in reactions of RSH, CSH, and GSH with LOOH and H₂O₂ was studied by inhibitor's method using *b*-carotene as a free radical acceptor.

7. Stability of Different Variety Sesame Seeds During Oxidation in the Dark. E. Choe¹, K. Kang¹, M. Shin², K. Lee³, and J. Kim⁴, ¹Inha University, Incheon, Korea, ²Chonnam National University, Gwangju, Korea, ³Soonchunhyang University, Asan, Korea, ⁴Inje University, Busan, Korea.

Sesame seeds come in many colors depending on the cultivar harvested, with off-white colored sesame as the most traded variety. Other common colors are black and gold. Storage quality of sesame seeds depends mostly upon on the lipid oxidation which is significantly affected by minor compounds present. Lipid oxidation of different colored sesame seeds, white (WS), black (BS), and gold seeds (GS), were studied, along with monitoring of antioxidants and pigments under accelerated condition at 60°C in the dark. Fatty acid composition was not significantly different among WS, BS, and GS, with the highest content of oleic and linoleic acid, and antioxidant contents were not significantly different, either. BS and GS showed very similar lipid autoxidative stability to that of WS in spite of high content of pigments such as carotenoids and anthocyanins having antioxidant activity. Phosphatidylcholine present in WS at high amount could have contributed to comparable oxidative stability of WS to that of BS and GS. The results indicate that lipid autoxidation of sesame seeds during storage is hardly affected by the seed color, and thus compositional factors other than color should be a primary consideration for high storage quality.

8. Antioxidant Effects of Soybean Phospholipids in Oil Oxidation in Emulsion. J. Choe, B. Oh, and E. Choe*, Inha University, Incheon, Korea.

Phospholipid (PL) contains hydrophobic and hydrophilic moieties in the structure, and increase or decrease oil oxidation, depending upon environmental conditions. Composition of natural PL is affected by the sources, and their effects on the oil oxidation may be different. This study evaluated the effects of PL composite derived from soybeans and egg yolk, and individual phosphatidylcholine (PC), phosphatidylethanolamine (PE), and phosphatidylinositol (PI) from soybeans on the iron-catalyzed oxidation of oil in an emulsion consisting of canola oil and water (1:1, w/w). The oil oxidation was evaluated by headspace oxygen consumption and hydroperoxide formation, and PL was analyzed by HPLC. Soybean PL mainly consisted of PC, PE, and PI, while PC and PE constituted egg yolk PL. The oil oxidation in emulsion increased with time and soybean PL composite significantly decreased it.

Individual PC, PE, and PI also decreased the oil oxidation, with the lowest oxidation rate in the emulsion with PC. PL was degraded during oxidation of the emulsion, and the degradation was the slowest in PI, followed by PC and PE. The results suggest that the autoxidation of oil in emulsion can be controlled by soybean PL not by egg yolk PL, and PC contributed the most to decreased oil oxidation.

9. Effect of Freezing and Thawing Processes on Stability of Oil-in-water Emulsion Containing Flavor Components. Y. Watanabe, Y. Kono, and T. Hinohara, Kinki University, Higashi-Hiroshima, Hiroshima, Japan.

Limonene has been used as a flavor and fragrance ingredient in food and cosmetics, but its oxidation leads to off-flavor and deterioration of the products. An oil-in-water emulsion is useful as a utility form of limonene with strong lipophilicity. However the use of the emulsion through freezing and thawing it for the storage at low temperature to enhance the stability of the components in the emulsion has been a problem, as coalescence of the oil droplets tends to be promoted during the processes. The effects of the component coexisting with limonene in the oil phase and temperatures in freezing and thawing processes on stabilities of the emulsion and limonene were examined. Alkanes were used as the coexisting components. The changes in median diameter of the oil droplets in the emulsion with alkane after freezing and thawing at different temperatures were measured. The larger number of carbon atoms in alkane coexisting in the oil phase led to the larger change in the diameter of the droplets at each combination of freezing and thawing temperatures. Additionally the droplets size in the emulsion through freezing and thawing processes depended on the temperatures in both processes. The disappearance of limonene from the emulsion would be due to the destabilization of the emulsion by freezing and thawing it.

10. Effect of pH on the Physicochemical Stability of Chia Oil-in-water Emulsions. L.M. Julio¹, V.Y. Ixtaina^{1,2}, M. Fernández³, R. Torres³, J.R. Wagner^{*4}, S.M. Nolasco², and M.C. Tomás¹, ¹Centro de Investigación y Desarrollo en Criotecología de Alimentos (CIDCA) – (Facultad de Ciencias Exactas (FCE) UNLP – CONICET), La Plata, Argentina, ²Facultad de Ingeniería, Dto. de Ingeniería Química (TECSE), Universidad Nacional del Centro de la Provincia de Buenos Aires (UNCPBA), Olavarría, Buenos Aires, Argentina, ³Centro de Tecnología de

recursos Minerales y Cerámica (CETMIC), La Plata, Argentina, ⁴Dto. de Ciencia y Tecnología – Universidad Nacional de Quilmes (UNQ), Quilmes, Argentina.

Oil in water (O/W) emulsions with chia oil –with a high α -linolenic acid content- is an effective method to deliver omega-3 fatty acids into functional foods. The physicochemical properties of emulsions with sodium caseinate (NaCas) could be influenced by pH. Values of pH below the isoelectric point of proteins produce cationic droplets that influence lipid oxidation modifying iron-lipid interaction. O/W emulsions were prepared by homogenizing 10 wt% chia oil, 90% wt aqueous solution (2 wt% NaCas, with/without 10 wt% lactose, final pH 3 or 7) at 600 bar, stored ~1 month at 4.0±0.5°C. The influence of pH and the presence of lactose were determined by measuring Z-potential, particle size distribution, mean diameters, apparent viscosity, backscattering (BS) profiles, peroxide (PV) and *p*-anisidine (*p*-AV) values. The particle size distribution was monomodal for all the emulsions studied. De Brouker (D[4,3]) and de Sauter (D[3,2]) mean diameters were 0.38 and 0.29 μm , respectively without significant differences between samples. BS profiles did not exhibit important modifications during the storage. Z-potential increased from -54 mV at pH7 to positive +35 mV at pH 3. The apparent viscosity was low without differences between emulsions. Regarding oxidative stability, the different systems recorded low levels of PV and *p*-AV.

11. Fatty Acid Composition, Antioxidant Activity, and Oxidative Stability of Apricot Kernel Oil. S.

Uluata, Inonu University, Malatya, Turkey.

Turkey is one of the important apricot producer in the world. Malatya is the most important apricot growing region of Turkey. Apricot consumed both fresh and dried. Kernel of apricot consumed as snack and its oil uses many industries such as cosmetic, soap industry. Recently, apricot kernel oil is very popular due to chemical content. The aim of this study is to determine some chemical characteristics and oxidative stability. Apricot kernel oil was extracted by cold press system. Fatty acid compositions were determined by Gas Chromatography (GC-FID). Antioxidant capacity was measured by ABTS, DPPH assay. For oxidative stability, Peroxide value (PV), 2-thiobarbituric acid-reactive substance (TBARS) test used. According to results, Oleic acid was the main fatty acid 70.2%, followed by linoleic acid at 21.6%, respectively.

Initial (0.day) PV and TBARS value 0.07-2.75 meq/kg and 1.27-1.26 μg MA/g oil, respectively. ABTS value was 168.8 μg Trolox/g oil, DPPH value was 238.9 μg Trolox/g oil. During the thermal oxidative test, alteration PV and TBARS value of AKO were determined 84.4-151.1 meq/kg and 2.6-2.9 μg MA/g oil, respectively. Apricot kernel oil has high monounsaturated fatty acids and antioxidant capacity. The oil can be used as alternative oil.

12. Free Radical Pathway of Sphingolipid Destruction. A.

Lisovskaya, O. Shadyro, G. Semenkov, I. Edimecheva, and N. Amaegberi, Belarusian State University, Minsk, Belarus.

The possibility of the realization of the new pathway for sphingolipid destruction induced by γ - and UV-radiation, as well as HOCl, has been shown. This process results in the formation of 2-hexadecenal, which is characterized by a wide range of biological activity. The data obtained on radiation-chemical and photochemical transformation of sphingolipids and a number of α , β -amino- and amido-alcohols confirms the proposed free radical mechanism, which includes formation of N-centered free radicals and their further fragmentation. For the realization of such process, the presence of a free amino group in the sphingolipid molecule is necessary to ensure formation of N-centered radicals from the substrate on its interaction with reactive oxygen and chlorine species. The presence of an acyl group in the sphingolipid structure prevents these molecules from γ - and HOCl-induced destruction. At the same time it favors realization of the photodecomposition reactions resulting in the formation of 2-hexadecenal.

Therefore, the realization of non-enzymatic reactions leading to the formation of 2-hexadecenal in living organisms may influence cell functions. The results discussed above supposed to be taken into account in studies intended the development of novel medications for treatment of diseases associated with activation of free-radical reactions.

13. Oxidative Stability of Linseed Oil. I.

Edimecheva¹, A. Sosnovskaya¹, O. Shadyro^{2,1}, and A. Lisovskaya^{*2,1}, ¹Research Institute for Physical and Chemical Problems of the Belarusian State University, Minsk, Belarus, ²Belarusian State University, Minsk, Belarus.

The content of fatty acids, fat-soluble vitamins, and other minor biologically active substances in various samples of linseed oil of cold expression was determined. Kinetic relations have been obtained

reflecting accumulation of primary and secondary oxidation products and free fatty acids (FFA) in the linseed oil. Depletion in tocopherol and carotenoid contents during storage at room temperature in the absence and in the presence of atmospheric oxygen we established.

It is shown that during the storage of linseed oil the FFA composition changes significantly than the composition of fatty acid glycerides. Herewith the concentration of polyunsaturated fatty acid reduces, while the content of saturated and monounsaturated oleic acid increases.

The volatile organic compounds formed during the degradative oxidation of linseed oil have been identified using gas chromatography–mass spectrometry. The main volatile carbonyl products were 2,4-heptadienal and 3,5-octadiene-2-one. The linseed oil has been shown to be sufficiently resistant towards oxidative aging, provided that the recommended storage conditions are met, owing to a complex of antioxidants and their synergic agents present in the oil.

The effective stabilizing compositions that can significantly increase the shelf-life of linseed oil have been found.

14. Antioxidant Activity of Phenolic Compounds Added to a Functional Emulsion Containing Omega 3 Fatty Acids and Plant Sterols. R.R. Espinosa¹, M.T. Rodriguez-Estrada², S.M. Alencar³, and I.A. Castro*¹, ¹LADAF, Dept. of Food and Experimental Nutrition, Faculty of Pharmaceutical Sciences, University of São Paulo, São Paulo, Brazil, ²Dept. of Agricultural and Food Sciences, Alma Mater Studiorum-Università di Bologna, Bologna, Italy, ³College of Agriculture, Piracicaba, São Paulo, Brazil.

Omega 3 fatty acids (n-3 FA) and plant sterols esters (PSE) are bioactive compounds able to promote cardiovascular protection. However both are susceptible to oxidation, producing derivatives that annul their beneficial effects. Thus, the aim of this study was to compare the action of eleven natural phenolic compounds extracted from red propolis in the oxidative stability of an emulsion added of n-3 FA and PSE. Emulsions containing 1.63 g/100 mL of α -linolenic acid, 0.73 g/100 mL of stearoic acid and 0.65 g/100mL of PSE, without (CONT) or with phenolic compounds (vanillic acid, caffeic acid, trans-cinnamic acid, 2,4-dihydroxycinnamic acid, p-coumaric acid, quercetin, trans-ferulic acid, rutin hydrate, gallic acid, sinapic acid and trans,trans-farnesol) were heated at 90°C/10 min and stored at room temperature for 14

days. TBHQ and a mixture prepared with ascorbic acid/iron (ASCIR) were used as standards. Hydroperoxide (LOOH), malondialdehyde (TBARS), hexanal and 7-ketosterols were evaluated as oxidation markers. Sinapic acid, rutin hydrate and quercetin showed the highest antioxidant protection when LOOH and TBARS were taken as markers. Higher values of hexanal, malondialdehyde and 7-ketosterols were just found in the samples containing the pro-oxidant mixture (ASCIR). The antioxidant effect showed by sinapic acid and rutin hydrate was independent of their concentration (from 200 to 1000 ppm) and from the source of these natural molecules (extracted from red propolis or synthesized). Thus, sinapic acid, rutin hydrate and quercetin represent an alternative as natural antioxidant to replace TBHQ in functional food emulsions containing n-3 FA and PSE.

15. New Approach for Studying Oxidation Processes in Oils: An EPR Study. K. Rangelova, D. Barr, and A. Heiss, Bruker BioSpin Corp., Billerica, MA, USA.

Lipid oxidation is an undesirable series of free radical reactions involving oxygen that degrade the quality of the product. 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 radical formation in olive oil and other types of edible oils during forced oxidation at elevated temperatures and different storage conditions. 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. The assay was completely automated to monitor radical formation in up to twenty samples all in one assay period. The oxidation process was monitored for 1-2 hours as multi-point or end-point assays.

16. Vegetable and Natural Oils in Cosmetics. K. Mahmood, Johnson & Johnson Consumer and Personal Products, Skillman, NJ, USA.

The main purpose of this talk is to make researchers specially from adjacent disciplines aware of current choices of oils available in cosmetic industry with specific emphasis on oils already approved for use. Cosmetic industry in USA is self governed by an umbrella organization called Personal Care Products Council (PCPC). PCPC works

hand in hand with industry stakeholders and regulatory authorities to deliver a governance framework which serves all stakeholders and their respective interest also ensuring consistent approach to naming the cosmetic ingredients. Safe delivery and use of ingredients approved by PCPC remain responsibility of ingredient and product manufacturer.

Three main sources of oils and fats used in cosmetic industry, i.e. animal, botanical, and petroleum based will be discussed. Commercial suppliers and academic researchers can equally benefit from the information presented here. It is also expected that new ideas are generated to qualify innovative oils with additional benefits for cosmetics industry.

17. Generation of 3-MCPD Esters Under Deep-frying Conditions. K. Toho, R. Honma, and M. Shimizu, Kao Corporation, Global R&D - Health Care Food, Tokyo, Japan.

Fatty esters of 3-monochloropropane-1,2-diol (3-MCPD) are heat-induced process contaminants that are generated mainly through high temperatures during the deodorization process in edible oil production. Because these unintended contaminants have possible adverse effects on human health, a variety of efforts have been made to mitigate their impact. Some research has recently shown that these contaminants are generated not only during the refining process but also under a variety of cooking conditions. Some precautions have been suggested as counter measures for mitigation during the refining process, but these are difficult to apply to the cooking process.

In this study, we focused on deep-frying and demonstrated the influence that oil composition exerts on the generation of 3-MCPD during deep-frying temperatures. A simple deep-frying model was used for the study in order to reproduce variations in an actual cooking situation. Filter papers moistened with a sodium chloride solution were deep-fried in test oils. The relationship between the generation of 3-MCPD esters under deep-frying conditions and oil composition was investigated. An addition of alkali was effective in mitigating these contaminants.

18. Mana-cubiu (*Solanum sessiliflorum*) Extract Prevents Cholesterol from Oxidation in Model Systems. B. Barriuso², L.R.B. Mariutti*¹, A. Ansorena², I. Astiasarán², and N. Bragagnolo¹, ¹Dept. of Food Science, Faculty of Food Engineering,

University of Campinas, Campinas, São Paulo, Brazil, ²Dept. of Nutrition and Food Science, Physiology and Toxicology, Faculty of Pharmacy, University of Navarra, Pamplona, Navarra, Spain.

Heating procedures, storage conditions and presence of surrounding compounds are key factors behind the formation of Cholesterol Oxidation Products (COPs) in foods. Mana-cubiu (*Solanum sessiliflorum*), a native Amazonian fruit which has a high carotenoid and polyphenol content, has been previously reported to present good antioxidant properties. The aim of this study was i) to assess the protective effect of a mana-cubiu hydrophilic extract against cholesterol oxidation and formation of COPs in the presence or absence of docosahexaenoic acid (DHA), ii) to study the effect of storage under refrigeration. Four samples (cholesterol, cholesterol and mana-cubiu extract, cholesterol and DHA and cholesterol, DHA and mana-cubiu extract) were heated at 180°C for 7 min and stored 0 and 3 days at 4°C. Both cholesterol degradation and COPs formation were inhibited (54 and 90% inhibition, respectively) by mana-cubiu extract when cholesterol was heated alone. However, in samples containing DHA, no differences were found regardless the addition of antioxidant. Besides, storage under refrigeration did not quantitatively affect cholesterol oxidation in any sample.

19. Comparison of Lipid Oxidation Behavior in Surface Oil vs. Total Lipid in Low-moisture Foods. C.E. Gumus, L. Barden, and E.A. Decker, Dept. of Food Science, University of Massachusetts Amherst, Amherst, MA, USA.

There is a need to gain better understanding of lipid oxidation mechanism in low-moisture food systems in order to retard oxidation by new technologies. This study aimed to develop a method to extract the surface oil from a cracker model system, and to compare hydroperoxide and hexanal generation of the surface oil against total lipid oxidation. Although the period of lag-phase from the peroxide value tests were similar for both cases, the extent of oxidation was higher for the surface oil. This is likely due to the increased exposure of the cracker to oxygen. Therefore, analysis of oxidation products in total lipids could be an under estimation of rancidity. Furthermore, to compare the relative susceptibility of total and surface oils an oxidation sensitive fluorescent dye (Bodipy 665/676) was added to the cracker systems and intensities were measured by fluorescence. Bodipy, which partitioned at the same positions with lipophilic Nile

Red dye, was used to visualize the position of the oxidation under confocal microscope. While results showed that the dye did not oxidize at the same rate as the crackers, it shows promise as a visual aid.

20. Effect of Layer-by-layer Coatings and Localization of Antioxidant on Oxidative Stability of Encapsulated Bioactives in Oil-in-water Emulsions.

Y. Pan and N. Nitin, University of California Davis, Davis, CA, USA.

Oxidation of encapsulated bioactives in emulsions is one of the key challenges that limit shelf-life of many emulsion containing products. This study seeks to quantify the role of layer-by-layer coatings and localization of antioxidant molecules at emulsion interface in influencing oxidation of encapsulated bioactives. The oxidative barrier properties of the emulsions were simulated by measuring the rate of reaction of peroxy radicals with encapsulated radical sensitive dye in emulsions. Peroxyl radical permeation results demonstrated that gallic acid (model antioxidant) was more efficient when it was localized at the interface of emulsions compared to adding the same concentration of gallic acid to the aqueous phase. However, addition of one or two layers of short chain polymers (ε-polylysine and dextran sulfate) at the interface of emulsions was not capable of limiting peroxy radical permeation. Stability results of retinol (model bioactive) were in agreement with the results of peroxy radical permeation. Overall, the results of this study demonstrate the advantage of localization of antioxidant at the interface and the ineffectiveness of addition of short chain polymer coatings at the interface in limiting radical permeation and oxidation of encapsulated bioactives in oil-in-water emulsions.

21. Study Oxidation Parameters and Total Antioxidant Content in Some Dry Fruits During Their Storage at Room Temperature in Its Shelf Life.

I. Vieitez, B. Irigaray, N. Callejas, C. Rebellato, D. Estrade, and M. Grompone, Universidad de la República, Montevideo, Uruguay.

Antioxidant compounds in food play an important role as a health-protecting factor. Scientific evidence suggests that antioxidants reduce the risk for chronic diseases. Common nuts are important sources of natural antioxidants.

The aim of this work was to investigate the variation of peroxide value (PV), p-anisidine value, total content of tocopherols and polyphenols during storage (6 months at room temperature) of some

dry fruits: walnuts, Pecan nuts, hazelnuts, almonds, pistachios, peanuts and cashews.

PV and p-anisidine value were determined by AOCS Cd 8-53 and IUPAC 2.504 respectively. Phenolic compounds were extracted from the fruits at room temperature during 24 hours, under constant stirring, using 80% (v/v) of aqueous acetone, and tocopherols with hexane/isopropanol (3:2). These antioxidants were analyzed by HPLC with UV detector for polyphenols and with fluorescence detector for tocopherols.

Among all nuts, almonds and hazelnuts had the highest initial mean alpha-tocopherol content. Beta-gamma-tocopherols (initial) were prevalent in walnuts, Pecan nuts, pistachios, peanuts and cashews. Mean values oscillated between 78 ppm (cashews) and 236 ppm (walnuts).

PV was increased in all nuts during storage time. The largest increase took place in the Pecan nuts from 4.4 (initial) to 44.4 meq.O₂/Kg at 6 month.

22. A Multistage Approach to Evaluating Natural Antioxidant Mechanisms and Predicting Effectiveness in Foods.

K.C. Chang and K.M. Schaich, Rutgers University, New Brunswick, NJ, USA.

Replacement of synthetic antioxidant with natural antioxidant in foods has been limited by lack of ability to predict which compounds will effectively limit oxidation in complex matrices. To facilitate applications of natural antioxidants (AOX), a three-stage analytical approach is developed to provide basic radical scavenging mechanisms and predict effectiveness in food stabilization: 1) DPPH and ORAC assays to determine AOX mechanisms – single electron transfer (SET) vs hydrogen atom transfer (HAT); 2) lipid-based systems – bulk oils, fluid and lyophilized emulsions; 3) model foods, to determine molecular interactions and interferences with AOX. DPPH and ORAC assays show that oregano extract (water-soluble), mixed tocopherols (oil-soluble) and quercetin (partially oil- and water-soluble) are SET-dominant while chlorogenic acid (water-soluble) is HAT-dominant. These mechanisms are reflected in oxidized oils where SET-dominant phenols are most effective while HAT-dominant phenols are less active. Water enhances HAT reactions and slows oxidation inhibition. AOX solubility plays a role in partitioning in mixed phase systems, but dominant radical quenching mechanisms control reactions in each phase. Correlating these behaviors with AOX effectiveness in model foods will identify which assays most accurately predict natural AOX action in foods.

23. Effect of Various Frying Oils on Acrylamide and Advanced Glycation End-products (AGEs) Formation in Potato Chips. C. Jin, Y. Zhou, L. Gong, L. Cheng, and Y. Zhang, Zhejiang University, Hangzhou, Zhejiang, China.

To study the effect of various frying oils on acrylamide and AGEs (two Maillard reaction-derived hazards in potato chips) formation, which is not clear so far, 8 edible oils (rapeseed, olive, soybean, peanut, sunflower seed, palm, golden palm and lard) were heated to 180°C and started timing. At the points of 0, 0.5, 1, 2 and 4 h, batches of chips were fried for 3 min. Acrylamide and CML (a typical AGEs compound) contents of chips and carbonyl values and fatty acid compositions of oils were determined each batch.

Results showed that chips contained 541-2017 µg/kg acrylamide and 21-44 mg/kg CML, the latter was 10-46 times higher. Chips fried in palm oil, especially golden palm oil, contained the least acrylamide, probably due to its low levels of linoleic, linolenic acid and high levels of antioxidant components. Chips fried in lard were of the highest CML. Heated oil (180°C, 4 h) obviously promoted acrylamide formation (35%-139%), but showed no distinctive effect on CML. There were significant correlations between acrylamide and heating time ($r=0.9332-0.9965$), carbonyl value and heating time ($r=0.9824-0.9998$) and acrylamide and carbonyl value ($r=0.8438-0.9943$). Oxidation products of linoleic and linolenic acids might be important precursors of acrylamide during frying.

24. Formation of Toxic Aldehydes During Instrumented Dynamic *in vitro* Digestion of Marine Oil-enriched Milk. C. Genot¹, A. Meynier¹, P. Brestaz¹, M. Viau¹, L. Ribourg¹, B.R. Thomsen², and C. Jacobsen², ¹Biopolymères Interactions Assemblages, Nantes, France, ²Technical University of Denmark, Lyngby, Denmark.

The health benefits of n-3 long-chain PUFA (LC-PUFA) are well recognized and foods enriched in these PUFA, are now available for the consumers. However, n-3 LC-PUFA are prone to oxidation during food processing and storage but also during digestion including the intestinal step (Kenmogne-Domguia et al., Food Chem. 2013). The objective of this study was to quantify the formation of potentially toxic aldehydes: malondialdehyde (MDA), 4-hydroxy-2-hexenal (4-HHE), 4-HNE (4-hydroxy-2-nonenal) and volatile aldehydes during the *in vitro* digestion of n-3 oil enriched milk. Cow pasteurized milk (1% fat) was enriched with 0.5% (p/p) fish oil and submitted to successive gastric and upper intestine phases in an instrumented digester. Digested samples were taken at several time points both during the gastric and intestinal steps to quantify aldehydes, tocopherols and n-3 LC-PUFA. Volatile oxidation products were also analyzed at the end on the digestion. The data clearly show that both MDA and hydroxyalkenals were formed during the digestion of the enriched-milk emulsion. Tocopherols were also consumed. This occurred even without the addition of metmyoglobin, which has been used to initiate lipid oxidation during digestion in previous studies.

CJ, AM, and CG participate in Infogest COST action FA1005.