Annual Meeting Technical Paper Abstracts

Session A Thursday morning

Detergents & Surfactants I: Performance Evaluation and Formulation Technology

A1

Technical Steps to Liquid Autodish Detergent. James Kaeser, Colgate Palmolive Company, 909 River Road, Piscataway, NJ 08854.

The challenge of developing a liquid automatic dishwasher detergent was to meet consumer expectations of the liquid form while delivering the required cleaning performance in current automatic dishwashers. Technically, a slurry with good chemical and physical stability was only one element of a successful product. A significant step was fitting that slurry to the consumer's image of a liquid detergent. Many experiments were run to determine consumer acceptance of non-Newtonian fluid properties imparted by anisotropic clay particles. The end result was product quality specifications met by manufacturing.

A2

Rheology of Alumina Thickened Liquid Automatic Dishwasher Formulations. Steven L. Baxter, Vista Chemical Company, Box 500, Ponca City, OK 74602 and David A. Barclay, Vista Chemical Company.

Boehmite alumina has been studied as a rheology modifier in formulations comprised of surfactants, builders, and other components. Thickening the liquid automatic dishwasher formulation is a particular challenge because of high levels of suspended solids, complexity of the components (phosphates, silicates, surfactants, bleach, pH control agents, spotting control agents), and exact rheological requirements. The interaction of the alumina thickener with these formulation components is described in terms of formulation rheology. Also, a comparison with montmorillonite clays, another traditional thickener for these systems, is presented.

A3

Characterization of Foam Properties in Light Duty Liquid Dishwashing Products. Farrokh B. Malihi, Colgate Palmolive Co., 909 River Road, Piscataway, NJ 08854 and G.R. Riska, B. Hawrylak, C. Nguyen, Colgate Palmolive Co.

Good foaming properties is a key factor for selection of suitable surfactant systems for use in light duty dishwashing products. Although technically a direct relation does not exist between high foaming power and cleaning ability, the consumer considers the two closely related. Despite a number of test methods reported in the literature, a standardized universally accepted test method for characterization of foam performance of dishwashing products does not exist. For such methods to be predictive of consumer perception, one needs to consider consumer habits and practices which define experimental conditions in terms of product concentration, type and amount of food soil present, extent of mechanical energy and temperature. We have used a new soil titration technique to assess foam stability of a number of surfactant systems commonly used in formulation of manual dishwashing products. Results show good correlation with foam end point data obtained via labor intensive and time consuming manual dishwashing tests. This technique is described and illustrated by test results showing the effect of composition and concentration of the surfactant mixture, type of soil, temperature and water hardness. An attempt is made to relate the foam stability data to the surface chemical properties of the surfactant system.

A4

Characterization of Key Consumer Laundry Stains on Washed Fabrics. A.M. Wolff, Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 and R.S. Carpenter and M.G. Venegas, Procter & Gamble Company.

Identification and localization of key consumer stains remaining on washed fabrics was performed by various analytical methods. The analyses utilized histochemical reactions for broad categories of residual components, followed by immunocytochemical examinations at both the transmission and scanning electron microscopy level. The identification of predominant proteins, carbohydrates, and lipids, and their subsequent localizations resulted in the generation of a model for soil distribution and redeposition after various wash treatments.

A5

The Evaluation of Parameters Affecting the Precision of Launder-O-meter Test Methods. Walter N. Opdycke, Diversey Corporation, 1532 Biddle Avenue, Wyandotte, MI 48192.

The Launder-O-meter has been and continues to be an effective instrument for screening laundry detergent formulations. However, a major limitation to its effectiveness is its lack of precision. Often the standard deviations for triplicate measurements of soil removal are as high as ten percent of the average value. For some experiments, twenty percent can be expected. This lack of precision greatly confounds detergency evaluation. An obvious solution to this problem is to collect more data. Unfortunately, this would require much more time and labor or necessitate a reduction in the scope of the experiment. Another solution is to increase the reproducibility of the Launder-O-meter data. This paper describes the parameters which affect reproducibility. These factors include rinsing technique, liquor volume, washing order and mechanical action among others. In addition, methods will be described for increasing the precision of Launder-O-meter results.

A6

Enzyme Wash Performance Evaluation Using a Fluorescent Micro Method. Mark W. Empie, International

Bio-Synthetics, Inc., 8720 Red Oak Boulevard, Charlotte, NC 28217.

The efficacy of enzymes to remove food stains is typically determined using visible light reflectance measurements of washed soil cloths. Inherent in the methodology is the poor discrimination of performance when soil loads are very small. Alternatively, measurements of residual fluorescence of tagged stains offer the ability to determine removal on micro-scale with a high degree of quantitation. Wash performance tests will be compared demonstrating the efficacy of International Bio-Synthetics' Maxatase and Maxacal proteases in several typical detergent formulations for the removal of fluorescent tagged proteins from lightly soiled cloths.

A7

A Study of Detergent Builder Efficiency: Comparison Between Performance and Molecular Orbital Calculations. Dave McCall, Diversey Corporation, 1532 Biddle Avenue, Wyandotte, MI 48192.

In the continual search for new detergent builders, many molecules have been considered. A molecular orbital method is described here as a preliminary screening device to evaluate builder efficiency. The most important builder characteristic is the ability to sequester calcium and magnesium ions. Molecular orbital calculations are useful in calculating bond lengths and bond angles and, hence, are well-suited to predicting a molecule's chelating ability. In the last ten years, the ether polycarboxylates have been widely considered as detergent builders. A series of these ether polycarboxylates has been chosen to demonstrate the molecular orbital technique. The optimized geometries of these compounds have been computed and correlated to calcium binding stability constants and detergency performance.

Session B Thursday morning

Physical/Analytical Chemistry Techniques for Analysis/Characterization of Fats/Lipids I

B1

Physical Properties of Fully Hydrogenated Fats. L. deMan, deMan Food Technology Services, Inc., 58 Applewood Cres., Guelph, Ontario N1H 6B5, Canada, and J.M. deMan and B. Blackman, University of Guelph.

Fully hydrogenated soybean oil, beef fat, rapeseed oil, cottonseed oil, palm oil and a blend of rapeseed oil, palm oil and soybean oil were characterized by fatty acid composition, glyceride carbon number, and partial glyceride content, as well as melting and crystallization properties. The polymorphic behavior was established by x-ray diffraction analysis of the products in the flake or granular form and when freshly crystallized from the melt. The hard fats were dissolved in canola oil at levels of 20, 50 and 80%, and crystallized from the melt. Palm oil had the lowest crystallization temperature and the lowest melting temperature; rapeseed had the highest CT and soybean the highest MT. All of the hard fats crystallized initially in the alpha form. When diluted with canola oil only palm oil was able to maintain beta prime stability.

B2

Country of Origin Determination of Pistachio Nuts by Thermal Analysis and HPLC. Susan M. Dyszel, U.S. Customs Service, 1301 Constitution Ave., N.W., Room 7113, Washington, DC 20229, and Bruce C. Pettitt, U.S. Customs Service.

One major analytical problem frequently encountered in the labs of the U.S. Customs Service is that of determining the country of origin of an imported commodity. This is particularly challenging with natural products. This paper will describe the process for one such determination: pistachio nuts. Two approaches were taken, HPLC and DSC. It was found that the results of these two techniques were complimentary and confirmatory. In evaluating the resulting DSC data, an empirical approach was taken. It was assumed that the area under the thermal curve could be divided into three distinct thermal events: labeled A, B, and C. Of these, the ratio of area A to B was used as the indicator of the country of origin. The HPLC results paralleled the DSC curves as those samples having triglycerides of lower C-number and those with greater unsaturation displayed correspondingly lower melting temperatures, giving an increased area to segment A.

B3

A Solution Thermodynamic Study of Jojoba Oil-Solvent Systems by Inverse Gas Chromatography. Jerry W. King, USDA-ARS-NRRC, 1815 N. University St., Peoria, IL 61604, and Julie A. Woerner and G.R. List, USDA-ARS-NRRC.

A knowledge of the solution properties of concentrated jojoba oil-solvent mixtures is critical for the design of solvent extraction systems as well as end-use applications of the extracted oil. In this study, inverse gas chromatography has been applied for the determination of activity coefficients, Henry's Law coefficients, interaction parameters, and heats of solution at infinite dilution over a temperature range of 60-125°C. Negative deviations from Raoult's Law were found for most of the solute/solvent combinations studied except for the lower aliphatic alcohols. Calculated heat of mixing data for twenty diverse solute types suggest athermal solution behavior for many solute/jojoba oil combinations. A comparison of activity coefficient data (weight fraction basis) for jojoba versus soybean oil indicates larger activity coefficients in the latter solvent for alkane, aromatic, and specific chlorinated hydrocarbon solutes. Jojoba oil solubility parameters derived from solution interaction parameter measurements show a 14% reduction when compared to the soybean oil matrix. This result and end-use of the above data have implications in choosing extraction solvents, devolatization conditions, and extraction conditions for supercritical fluid solvents.

B4

Cloud Point Phenomena in Mixture of Anionic and Cationic Surfactants in Aqueous Solutions. Yasunari

Nakama, Shiseido Laboratories, 10150 Nippa-cho, Kohoku-ku, Yokohama-shi, 223 Japan, and Fuminori Harusawa and Isao Murotani, Shiseido Laboratories.

The phase diagram has been determined as a function of temperature for the water-stearyltrimethylammonium chloride-sodium-N-lauroyl-N-methyl-beta-alanine system. The existence of the lower consolute phase boundary, which can be identified with the cloud point was observed in the aqueous solution of the equimolar mixture of the cationic and anionic surfactants. The interaction between cationic and anionic surfactants was investigated by means of NMR and conductometric methods. The strong interaction between cationic and anionic surfactants was conformed in the ion parts by measurements of NMR. The maximum deviation from ideality was seen at the equimolar mixture in the measurements of conductance.

B5

Acid Value Determination of Carboxylic Acids via Laboratory Robotics. Patrick J. Slonecker, Quantum Chemical Corp., Emery Division, 4900 Este Avenue, Building 53, Cincinnati, OH 45232, and Timothy M. Mitchell, Quantum Chemical Corp., Emery Division.

The acid value of a carboxylic acid is an important parameter in the oleochemical industry. A typical quality control laboratory will often determine thousands of acid values in a year. We have developed a method for determining the acid value of selected fatty acid products via laboratory robotics. The throughput, precision and accuracy of the robotic method will be compared to existing manual methods.

B6

Determination of Free Fatty Acid (FFA) Using a Process Titrator. Barry J. Meneghelli, The Foxboro Company, Armstrong Road, Plymouth, MA 02360, and Charles Chaney and Ken Fletcher, The Foxboro Company, and Ron Rabczak, Colfax, Inc.

A new process titrator has been developed for the determination of free fatty acids (FFA). Using standard AOCS methodology, the Foxboro Field Programmable Analyzer (FPA) can routinely report fatty acid concentrations in the range of 0-1%. Initially, the titrator delivers a hot sample of known volume (8 or 20 cc, depending on the concentration level) to a heated teflon cell. Using neutralized alcohol as a reagent and alcoholic sodium hydroxide as a titrant, the analyzer can consistently determine the FFA content to better than 2%. The results obtained using the titrator are within 5% of the bench results on identical samples. Field trial results on samples with FFA values of 0-10%, whose melting points are 90-150° F and viscosities range from 100-200 centipoise will be discussed.

B7

Handling Uncontrolled Variation in Laboratory Terg-O-Tometer Tests. Alan H. Bohl, PQ Corporation, Research & Development Center, P.O. Box 258, Lafayette Hill, PA 19444.

Random variation, even under controlled laboratory conditions, often is higher than one might first expect. As a result, some subtle differences between formulations are difficult to discern. To remedy this, data from over 50 Terg-O-Tometer test runs were analyzed. Sources of uncontrolled variation were traced to such disparate sources as age of the light bulb used in the reflectometer, "age" of the unsoiled and soiled cloths, and the method of handling soiled cloths. This analysis allowed for the inclusion of these factors in the model and greatly improved its predictive accuracy.

Session C Thursday morning

Applications of Spectrometry for Characterization and Measurement

C1

Determination of Moisture, Protein and Oil in Whole Soybean Seed by Near-Infrared Transmittance. Charles R. Hurburgh, Jr., Iowa State University, Agricultural Engineering Dept., Ames, IA 50011, and R.A. Hartwig, Iowa State University.

Protein and oil content have been identified as important factors determining the economic value of soybeans. Protein and oil content are not currently used to price soybeans, but in 1989, the Federal Grain Inspection Service intends to offer protein and oil analysis as an optional service in Official inspections. While FGIS' analyses will be done with well-documented ground-grain near infrared reflectance technology, there is great need at the first point of sale for rapid whole-seed analysis. Two near-infrared transmittance instruments, the Tecator Infratec 1222, a scanning monochromator, and the Trebor 99, a diode-based fixed wavelength instrument, were calibrated against chemical methods. Soybean samples came from the 1985-1988 crop years. Standard errors of calibration and prediction were within 0.1-0.2 percentage points of ground-grain instruments on the same samples. An assessment of the future of whole grain analysis in the marketplace is presented.

C2

Carotenoid Composition and Vitamin A Values of Oils from Four Brazilian Palm Fruits. Jose A. Trujillo-Quijano, State University of Campinas, Faculty of Food Engineering, P.O. Box 6091, Campinas, SP 13.083, Brazil, and D. Rodriguez-Amaya, W. Esteves, and G.F. Plonis, State University of Campinas.

In oils extracted from fresh and sterilized fruits of oil palms (*Elaeis guineensis*, Jacq. tenera, dura dumpy and psifera and *E. oleifera*), phytofluene,13 *cis* alpha-carotene, alpha-carotene, 9 *cis* alpha-carotene, 13 *cis* beta-carotene, beta-carotene, 9 *cis* beta-carotene, ζ-carotene, xeaxanthin, beta-cryptoxanthin, polycislycopene, 13 *cis* lycopene and lycopene, were identified and quantified by normal phase open column chromatography (stepwise-elution), TLC, UV/VIS spectroscopy and specific chemical reactions. The sum of alpha and beta-carotene in all samples analyzed was higher than 80%, while the alpha:beta-carotene ratios were 1:1.9, 1:11.1, 1:2.2 and 1:2.6 for oils extracted from fresh

fruits of dura dumpy, psifera, tenera and *E. oleifera*, respectively. Total carotenoids contents (μg/g) and vitamin A values (R.E./100g) of these samples were 1,120.7 and 12,303 for dura dumpy, 283.2 and 2,612 for psifera, 660.5 and 7.614 for tenera and 1.576.8 and 21,691 for *E. oleifera*. The sterilization of fruits (127 C × 35 min.) produced an isomerization of pigments and losses of vitamin A values of approximately 40% and 25%, respectively.

C3

Reasons Underlying Differences in Wavelength Selection for the Estimation of Protein Content in Oilseeds by NIR Spectroscopy. Janet A. Panford, Canadian Grain Commission, Grain Research Lab, 1404-303 Main Street, Winnipeg, Manitoba R3C 3G8, Canada, and J.M. deMan, University of Guelph and P.C. Williams, Canadian Grain Commission.

Nine different types of oilseeds have been analyzed for their protein content using NIR spectroscopy. A computerized monochromator was used to scan and select the wavelength(s) that gave optimum results for each seed type. Absorption maxima were often in the same area of the spectrum but the number of wavelength points required and their order of selection differed among the seeds. Protein distribution appeared to influence absorption maxima, but amino acid composition did not appear to influence significantly the wavelengths used to the estimation of protein content in the oilseeds. Spectra of some protein fractions are presented. Statistical data indicated accuracy of NIR analysis comparable to standard chemical procedures.

C4

Applications of IR, NMR and PDMS for the Spectroscopic Characterization of Sucrose Polyesters. R.A. Sanders, Procter & Gamble, Winton Hill Technological Center, 6071 Center Hill Road, Cincinnati, OH 45224, and D.R. Gardner, J.D. Wendel, T.W. Keough, Procter & Gamble.

The characterization of sucrose polyesters using three different spectroscopic techniques will be presented. The techniques include infrared (IR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, and plasma desorption mass spectrometry (PDMS). Examples will be presented which show the unique information gained from each of the techniques. IR spectroscopy will demonstrate the presence of several key function groups and the ability to quickly distinguish sucrose polyesters from triglycerides. NMR spectroscopy provides a detailed picture of the sucrose backbone as well as fatty acid information. Finally, the ability of PDMS to provide molecular weight information and key fragmentation patterns will be presented.

C5

Plasma Desorption Mass Spectrometry of Sucrose Polyesters. T. Keough, Procter & Gamble Co., Winton Hill Technical Center, 6071 Center Hill Road, Cincinnati, OH 45224, and R. Sanders, M. Lacey, and D. Gardner, Procter & Gamble.

Molecular weight determination of large non-polar molecules is a continuing challenge of interest to lipid chemists. Techniques such as fast atom bombardment (FAB) and field desorption (FD) are most applicable to polar or ionic species. Non-polar lipids are ionized with low efficiency and substantial fragmentation so that very little molecular weight information is obtained. However, appropriate selection of matrix and use of cationization allow FAB applications to sucrose polyesters in the 1800-2500 dalton range. The ion currents obtained fluctuate dramatically depending on the sample solubility in the matrix, and molecular weight determinations on low μg levels isolated by HPLC are tedious or impossible. Still higher molecular weight lipid materials, such as sucrose polyester dimers, have been completely inaccessible by FAB in our hands. Plasma desorption (PD) mass spectrometry has greatly extended the range of molecular weights accessible to mass spectrometry. However, the primary application areas have involved relatively polar biomolecules such as proteins. This work presents PD mass spectra of sucrose polyester standards (sucrose octalinoleate, sucrose octadodecanoate) in the molecular weight 2000 range, and sucrose polyester dimer species in the MW 5000 range. Spectra are obtained on a few nmoles of sucrose polyester using NaI treated nitrocellulose as a substrate. The major benefits over FAB for sucrose polyester analysis are: ease of implementation, absence of matrix effects, improved sensitivity, and higher accessible molecular weight. Comparisons of FAB and PD spectra will be made, and relevant PD experimental details will be discussed.

C6

A Novel Spectrophotometric Assay for Lipase Activity Utilizing *cis*-Parinaric Acid. A.M. Rogel, Meharry Medical College, 1005 D.B. Todd Boulevard, Nashville, TN 37208 and W.L. Stone and F.O. Adebonojo, Meharry Medical College.

A new method for determining the activity of acylglycerol hydrolases (lipases) has been developed using a naturally-occurring fatty acid, *cis*-parinaric acid (PnA), that has unique spectroscopic properties. This method takes advantage of the reversible binding of fatty acids to bovine serum albumin (BSA). Unbound PnA has an ultraviolet absorption peak at 321.1 nm. When PnA binds to BSA the absorption peak shifts to 324.2 nm. For this assay, PnA and BSA are added to the reaction mixture in a 6:1 molar ratio allowing, initially, a maximum binding of PnA to BSA. Upon addition of lipase, PnA is displaced from BSA by oleic acid hydrolyzed from triolein. The spectral shift is monitored as a change in the ratio of absorbencies at 319.0 nm and 329.0 nm. This kinetic assay is simple, sensitive and inexpensive, and can be used to measure the activities of various calcium-independent lipases.

Session D Thursday morning

Plant Lipids I: Isopentenoid Metabolism in Plants & Fungi

D1

Cloning of Ergosterol Biosynthetic Genes in Fungi. Martin Bard, Purdue University, Dept. of Biology, 1125 E. 38th Street, P.O. Box 647, Indianapolis, IN 46223.

Sterols play a number of roles in fungi. In Saccharomyces, membrane sterols regulate membrane fluidity, permeability, the activity of membrane-bound enzymes and growth rates. This role of sterols has been called the "bulk" membrane function. Several investigators have suggested that sterols may have a hormonal or "sparking function" perhaps involving a sterol requirement in traversing the cell cycle. Recombinant DNA technology allows the cloning of ergosterol biosynthetic genes. Through gene disruption techniques, plasmids containing various ERG genes are disrupted and the disrupted alleles are allowed to replace wild type ERG genes such that Saccharomyces strains containing completely non functional ERG genes are obtained. This analysis permits an assessment as to which ERG biosynthetic genes are essential for yeast viability since Saccharomyces mutations unable to synthesize ergosterol are not only viable but do not require ergosterol for growth. Such strains may be genetically "leaky". Southern hybridization technology allows investigators to determine the "copy number" of important sterol genes using a cloned ERG gene as a probe to find non-allelic hybridizeable DNA. The cloning of three ergosterol genes will be discussed. Recombinant DNA techniques have become increasingly important in elucidating genetic requirements in sterol synthesis in fungi.

D2

Developmental Regulation of Membrane Lipids. D. James Morre, Purdue University, Dept. of Medical Chemistry, Life Sciences Research Bldg., West Lafayette, IN 47907, and Francis E. Wilkinson, Claude Penel, and Hubert Greppin, Purdue University.

The plasma membrane is a primary site of hormone and growth factor receptors and other types of informational and signalling systems that maintain or reflect a particular developmental state. Much effort has been directed toward the study of how membrane and receptor proteins are distributed within the membrane and are developmentally regulated. Less attention has been given to lipids. Interest in plasma membrane lipids has been stimulated by the discovery of a role for phosphoinositides in signal transduction and of the covalent attachment of lipids to proteins. Also potentially important to developmental regulation are the glycolipids, especially gangliosides. Gangliosides are altered during tumorigenesis. They increase upon early contact in nontransformed cell lines in culture but not with comparable transformed cell lines. An example of membrane differentiation involving phospholipids can be found in polarized epithelia where phosphatidylcholine is depleted in the apical domain of the plasma membrane compared to the basolateral domain. Other developmental alterations involving lipids concern sterols. In spinach, after a light period of 24 hours sufficient to induce flowering, plasma membrane sterols increase and the increase correlates with an alteration of membrane symmetry involving the external leaflet of the plasma membrane bilayer.

D3

Epiminoisopentenoids: Development and Application as Potential Fungicidal and Hypocholesterolemic Agents. Edward J. Parish, USDA-ARS, Russell Research Center, P.O. Box 5677, Athens, GA 30613, and George Popjak, UCLA School of Medicine and W. David Nes, USDA-ARS, Russell Research Center.

A series of new epiminoisopentenoids has been prepared by chemical synthesis at the Russell Research Center [*Synth. Commun. 18:* 221 (1988)]. These include 6,7-epiminogeraniol, 10,11-epiminofarnesol, 2,3;22,23-diepiminosqualene, 24,25-epiminolanosterol, and the known 2,3-epiminosqualene. As a result of continuing biochemical studies using N-fungal sterol biosynthesis inhibitors, we have recently reported on the fungicidal properties of 2,3-epiminosqualene [*Arch. Biochem. Biophys. 244:* 211 (1986)] and the metabolism of 2,3-epiminosqualene to 24,25-epiminolanosterol by *Gibberella fujikuroi* [*Lipids 23:* 375 (1988)]. In companion studies, incubation of 24,25-epiminolanosterol with *G. fujikuroi* resulted in an inhibition of C-24 alkylation and a mycelial accumulation of lanosterol and 24-desalkylsterols [*Biochem. Biophys. Res. Commun., 139:* 410 (1988)]. Additionally, we have found that incubations of 2,3-epiminosqualene and 24,25-epiminolanosterol with rat hepatoma cells interrupts the conversion of lanosterol to cholesterol and induces an accumulation of intermediates in this conversion [*Proc. R. Soc. Lond. B 232:* 273 (1987)] and a cessation of cellular growth (*J. Biol. Chem.*, in press). Due to lability of the aziridine function, it will be shown that these compounds can be converted to safe biodegradable end products which are nontoxic; as such, they promise to be effective with other commercial inhibitors of sterol biosynthesis as combination drugs/fungicides.

D4

Distribution and Biosynthesis of Sterols in *Kalanchoe daigremontiana*. Malgorzata Kalinowska, Warsaw University, Dept. of Biochemistry, AL. Zwirki i wig Ury 93, Warsaw, 02-089, Poland and W. David Nes, USDA-Russell Research Center and William R. Nes, Drexel University.

The sterol composition of photosynthetic plants has been examined throughout the phylogenetic hierarchy from the harmful cyanophytic bacteria which accumulate in sewage waste to vascular plants of agricultural importance, e.g., corn, wheat and rye. The sterol profiles of these plants are remarkably similar although detailed changes in the kind and amounts of specific sterols (and sterol classes e.g., free versus the esterified and glycosylated forms) are apparent as the plants progress through their respective life cycles. In this talk the relationship between sterol structure and occurrence during plant ontogeny will be discussed. Special attention will be given to the configuration and changes that result in the C-24 alkylated side chain.

D5

Wax Ester Production by Yeast. Bernard C. Sekula, CPC International, Division of Best Foods, 1120 Commerce Avenue, Union, NJ 07083.

Although not natural components of yeast lipids, wax esters are synthesized by yeasts when grown or fattened on fatty alcohols. No wax esters are produced when fatty acids or hydrocarbons are substituted for the fatty alcohols. The chain length and degree of unsaturation in the synthesized wax ester is influenced by the fatty alcohol substrate. The

synthesis of specific wax esters can be directed by supplementing the fatty alcohol with a fatty acid. In addition to normal wax esters, "keto" wax esters have been identified in oleyl alcohol-grown yeast lipids. These keto wax esters are esters of fatty alcohols and fatty acids in which the omega-1 carbon atom of the fatty acid has been oxidized to a ketone.

Session E Thursday morning

Analytical I: HPLC Applications

E1

High Performance Liquid Chromatographic Separation of Enantiomeric Alkyl Ether Glycerols. Kazuhito Maeda, USDA-ARS-ERRC, 600 E. Mermaid Lane, Philadelphia, PA 19118 and Thomas A. Foglia, USDA-ARS-ERRC

A series of 1-alkyl-3-trityl and 1-alkyl-2-benzyl-glycerols was synthesized to provide precursors for the preparation of platelet activating factor (PAF) homologues. The general intermediate employed in the synthesis of these classes of lipids was *racemic* 1,2-0-isopropylidene glycerol *1*. The latter compound after alkylation at the 1-0-position and subsequent removal of the isopropylidene protective group yielded a racemic 1-0-alkylglycerol *2*. Selective tritylation of compound *2* at the 3-position yields a 1-0-alkyl-3-0-trityl-glycerol derivative *3* which is then benzylated to give a 1-0-alkyl-2-0-benzyl-3-trityl-glycerol *4*. Selective removal of the trityl protective group gives the 1-0-alkyl-2-benzylglycerol *5* as the key intermediate in the synthesis of the mixed alkyl-acyl phospholipids. Since naturally occurring PAFs, i.e. 1-hexadecyl-2-acetyl-glycerophosphatidylcholine have the chiral *sn* configuration and our synthesis employed achiral intermediates, it was necessary to devise methods for their resolution into the required chiral precursors. The enantiomeric resolution of the racemic intermediate compounds *1-5* was investigated by high performance liquid chromatography (HPLC). The effects of substitutes, i.e. trityl, benzyl, hydroxy, or alkyl, on the optical resolution of compounds *1-5* were evaluated by the HPLC methods developed. Additionally, the utility of the analytical HPLC methods for the large scale resolution and isolation of enantiomeric isomers was investigated.

E2

A Comparison of Detection Methods for High Pressure Liquid Chromatography of Dimer Acids. J.A. Barnhorst, Quantum Chemical Corp., Emery Division, 4900 Este Avenue, Cincinnati, OH 45232, and K. Gates, and E.H. Fairchild, Quantum Chemical Corp., Emery Division.

Dimer acids find wide use in the preparation of polyamide resins, polyesters and other products, where the mono, di and tri-fatty component ratios must be critically regulated. It is essential to have methods that are rapid, reproducible and applicable to a wide range of feedstocks. The evaluation of dimer acids using HPLC has been hampered by difficulties in detection of the separated components. This paper will compare the various methods available to the chromatographer. Correlation of the various detection methods with gravimetric analysis will be shown.

E3

The Determination of Fatty Amides by HPLC. James Jasperse, Sherex Chemical Company, 5777 Frantz Road, Dublin, OH 43017.

A high pressure liquid chromatographic technique for separating fatty amides by chain length in the presence of fatty nitriles was developed. The separation used spherical silica with hexane/chloroform/glacial acetic acid (7:2:1, v/v/v) as the mobile phase. The HPLC method can be used to detect trace amounts of fatty amide in the presence of fatty nitrile with a recovery of 99%. Thin layer chromatography was used as a solvent scanning technique. The relationship between k values and Rf values was investigated.

E4

Establishing Adulteration of Olive Oil by Triglyceride Analysis. Richard V. Flor, U.S. Customs Service, 1301 Constitution Ave. N.W., Washington, DC 20229 and Brian David Martin, University of Maryland.

We report two approaches to establishing adulteration of olive oils with polyunsaturated vegetable oils. One hundred and two olive oils were analyzed by HPLC. The ratio of area % of LLL/LLO was plotted vs. area % LLO. In a scatter diagram all the samples which have LLL below 0.5% are clearly separated from those with LLL over 0.5%. We propose that 0.5% LLL is a naturally occurring cutoff: above this level adulteration with a vegetable oil is presumed. Additionally, olive-vegetable oil mixtures were analyzed. The mixture samples fall cleanly outside the region in Graph I where the presumed pure olive oils are found. GC analysis of the methyl esters of a subset of these olive oils affords the fatty acid distribution. Calculations of the predicted triglyceride (TG) distributions were made assuming random distribution. Nineteen TGs were plotted as area % found vs. area % (calcd/found). The range of values found for this ratio is reasonably tight usually much less than 0.4 for the 7 largest TGs. The range of ratio values broadens considerably for the 12 smaller TGs often a 2-fold variation in ratios. The random distribution model is strikingly poor for LLL: ca. 20-fold range for the calc/found ratios. The predictability for LLL also drops markedly as the amount of LLL increases. These observations are rationalized by assuming that the higher values for LLL, i.e. over 0.5%, are due to adulteration.

E5

Detection of Docosahexaenoic Acid Oxidation Products Using HPLC with Post Column Reactions. Martin P. Yurawecz, U.S. Food & Drug Admin. (HFF-413), Division of Food Chemistry & Technology, 200 "C" Street S.W., Washington, DC 20204, and Kim M. Morehouse, George D. Yang, Agnes N. Pho, Yuoh Ku, FDA.

The reaction of heme, luminol and lipid peroxides gives rise to chemiluminescent products. Lipid hydroperoxides formed from the air oxidation of docosahexaenoic acid (DHA) were monitored using chemiluminescence detection after a post-HPLC column reaction with heme and luminol. The derivation of the HPLC/chemiluminescence responses from peroxides was confirmed using post-HPLC column iodimetry. In an independent reaction of the oxidized DHA

to determine fatty acid content, the solution darkened upon heating with NaOH/methanol. In order to investigate which oxidized components were contributing to the color formation, the hot NaOH/methanol reaction was used as a post-HPLC column procedure. Using this system the formation of colored compounds was observed at the retention volumes of the DHA derived lipid peroxides which had been observed using HPLC/chemiluminescence and HPLC/iodimetry.

E6

Trace Analysis of Alkylphenol Ethoxylates. Edmund Kubeck, Texaco Chemical Co., P.O. Box 15730, Austin, TX 78761 and Carter G. Naylor, Texaco Chemical Co.

A method has been developed for quantitative determination of trace amounts of alkylphenol ethoxylates (APE) in environmental water. Levels below 1 μg/l can be detected and resolved into their complete oligomer distribution (1EO to 18EO). Integrity of the oligomer distribution is maintained. Isolation of the APE from water is achieved using a simple and rapid dual-column procedure. The first column removed interfering ionic materials, the second traps the APE on alkyl-bonded silica. Assay of the extract employs HPLC with a fluorescence detector.

E7

Liquid Chromatographic Determination of Olestra in Olestra-Containing Foods. Peter Y.T. Lin, Procter & Gamble Co., 6071 Center Hill Road, Cincinnati, OH 45224 and Patricia Hudson and Melissa A. Kling, Procter & Gamble.

A combined extraction and high performance liquid chromatographic (HPLC) procedure for determining the olestra content in foods has been developed. Depending on the type of food, different extraction procedures are used to extract the olestra-containing lipids from the food. The extracted lipids' olestra content is determined by a single chromatographic procedure using a reverse phase HPLC column. An external olestra calibration curve is used for the quantitation. A summary of the development and the applications of this method will be presented.

Session F Thursday morning

Mycotoxin Symposium I

F1

Aflatoxin in Cottonseed: An Overview of the Southern Regional Research Center's Multidisciplinary Approach to Problem Solution. L.S. Lee, USDA-ARS-SRRC, 1100 Robert E. Lee Blvd., P.O. Box 19687, New Orleans, LA 70199, and H.J. Zeringue, P.J. Cotty, M.A. Klich, J.E. Mellon, and W.R. Goynes, USDA-ARS-SRRC.

For the past seven years, scientists from SRRC have conducted field studies in Arizona as well as greenhouse and laboratory experiments at the Center in an effort to understand *Aspergillus flavus* infection of cotton and the subsequent toxin formation in developing seed. When and how does the fungus enter the boll? What ecological factors favor fungal entry? At what stage of development are bolls most vulnerable? Is there a varietal difference in susceptibility? What are some of the defense mechanisms employed by the cotton plant when challenged by the fungus? What factors in commercial fields favor infection of cottonseed by *A. flavus*? The problem has been approached by the combined technologies of microscopy, mycology, plant physiology, chemistry, and more recently plant pathology. An overview of the contributions made by scientists from these diverse disciplines will show the progress made at SRRC toward ultimate solution of the aflatoxin problem in cottonseed.

F2

Ochratoxin A: Methodology Incidence and Significance. Stanley Nesheim, Food and Drug Administration, 200 C Street S.W., Washington, DC, and Leonard Friedman and Albert E. Pohland, FDA

Ochratoxin A has been shown to be a potent renal carcinogen in studies with mice and rats. This metabolite of *Aspergillus* and *Penicillium* species has been found in grains, coffee, beans and animal tissues. In Europe it also has been found in human blood and in blood of domestic animals. A recent survey of blood from slaughter pigs in western Canada found 11.3% of the samples contaminated at concentrations greater than 10 ng/ml. Renal nephropathy in man and animals has been associated with ochratoxin A. Similar lesions were produced by controlled studies in experimental animals. While ochratoxin A contamination has been rarely reported in the U.S., increased surveillance activities are being initiated. Microbial species that can produce ochratoxin A are commonly found in many foodstuffs. To carry out monitoring programs, ELISA, HPLC and TLC procedures have been developed. These methods are sensitive to ochratoxin A levels of less than one ng/g. Mass spectrometry and chemical derivatization techniques have been used for confirmation of identity. Ochratoxin A is regulated in several European countries, with maximum allowed levels ranging from "detectable" to 50 ppb.

F3

SRRC's Progress on Alternate Solvent Research Emphasizing Aflatoxin Extraction from Cottonseed. R.J. Hron, Sr., USDA-ARS- SRRC, 1100 Robert E. Lee Blvd., New Orleans, LA 70126, and George Abraham and Myong S. Kuk, USDA-ARS-SRRC.

The presentation will discuss SRRC's recent progress in the development of a process using ethanol as an alternate solvent to hexane for the extraction of oil, gossypol and in particular aflatoxin from cottonseed. It will also include an up-to-date review of other solvents proposed for the extraction of aflatoxin.

F4

Perspectives on the Safety of the Ammoniation Procedure. Douglas L. Park, University of Arizona, Dept. of Nutrition & Food Science, Tucson, AZ 85721, and Louise S. Lee, USDA-ARS-SRRC and Albert E. Pohland, Food and Drug Administration.

Food safety decisions concerning hazards associated with aflatoxin contamination and decontamination through the use of ammonia must use data from toxicological tests and animal feeding studies viewed as a whole. Ammoniation of corn, peanuts, cottonseed, and meals to alter the toxic and carcinogenic effects of aflatoxin contamination has been the focus of intense research efforts for over 20 years. The studies involved chemical identification of aflatoxin-ammonia reactions in inert and meal matrices, effects of feeding treated versus non-treated aflatoxin-contaminated feeds to laboratory animals and domestic livestock, and the determination of toxicity profiles of isolated aflatoxin-ammonia reaction products in short-term tests. Workable systems for treating corn, peanut, and cottonseed products for animal feeds have been developed and put into operation in the United States as well as in European and African countries. The perspectives of the use, efficacy, and safety of ammoniation as a practical solution to aflatoxin detoxification in animal feeds are discussed.

F5

Comparison of Affinity Column and Solid Phase Sorbant Cleanup Techniques for the Determination of Aflatoxins in Raw Peanuts with Detection by Fluorometer and HPLC. Daniel Sweigart, Hershey Chocolate U.S.A., 19 East Chocolate Avenue, Hershey, PA 17033, and Sherri L. Farr, Hershey Chocolate U.S.A.

Within the past several years there has been a rapid emergence of new methodologies for the detection and measurement of aflatoxins in a wide range of foods. Comparison of the results between three of these methods will be presented. Naturally contaminated raw peanut meal samples and spiked raw peanut meal extracts were analyzed for aflatoxin by bromination/solution fluorometry (Aflatest™) and also by HPLC coupled with post column iodine derivatization and fluorometric detection. Sample extracts were cleaned up with a monoclonal antibody affinity column prior to direct fluorometric determination. For quantitation by HPLC, sample extracts were cleaned up with either a monoclonal antibody affinity column or a solid phase sorbant column prior to injection. A total of 20 naturally contaminated raw peanut samples were analyzed to determine correlation between methods. Sample preparation consisted of grinding and homogenizing 48 pound raw peanut samples in a vertical cutter mill followed by extraction of 100 gram sub-samples with 60:40 methanol: water using a 5:1 solvent:peanut ratio. Blank peanut extracts were spiked with aflatoxin at three different levels to determine accuracy. All three of the techniques showed excellent agreement as indicated by a mean correlation coefficient of 0.9987. The mean percent CV's were 6.4%, 5.5%, and 6.3% for the affinity column cleanup/fluorometer, affinity column cleanup/HPLC and solid phase sorbant cleanup/HPLC techniques respectively. Mean percent recoveries on spiked extracts were 98% for the three techniques with a minimum recovery of 96%. Detection limits were 0.5 ppb and 0.2 ppb for the fluorometer and HPLC methods respectively.

F6

ELISA Diagnostic Kits for Mycotoxins. Brinton Miller, Neogen Corporation, 620 Lesher Place, Lansing, MI 48912, and Catherine L. Dilley and Deborah Dixon-Holland, Neogen Corporation.

Neogen has developed the Agri-Screen line of diagnostic kits for Aflatoxin, Aflatoxin M_1, DON (Vomitoxin) T_2 and Zearalenone. The ELISA method (Agri-Screen^R) for analyzing Aflatoxin B_1 in cottonseed products and feeds has received AOAC Official First Action Approval and Interim First Action Approval for corn and peanut products. Agri-Screen utilizes the enzyme linked immunosorbent antibody (ELISA) technology which is quick, highly sensitive, and cost efficient. Immunobased assays depend upon the use of antibodies that recognize a particular toxin or chemical look-alikes. The Agri-Screen kit uses a direct competitive method: purified toxin conjugated to an enzyme, is mixed with a sample which contains native toxin. A control well with a known concentration is used for comparison. The more color in the well the less toxin is present. Agri-Screen can be used as a visual screen, a semi-quantitative test or a fully quantitative test utilizing a well reader. Agri-Screen can test many susceptible grains, nuts, milk, feed and processed foods. Feed manufacturers and poultry, swine and dairy producers use Agri-Screen to monitor feed quality. In addition, it can be used by nut shellers, flour, grain and rice millers, nut processors, snack food producers, confectioners, and ready-to-eat cereal producers. Because of its flexibility, Agri-Screen can be used in the field by nontechnical personnel, as well as in the laboratory. Agri-Screen has many advantages over current methods. It is fast, easy to run, inexpensive, and does not require the use of hazardous chemicals.

Session G Thursday morning

Canola in the United States

G1

Rapeseed Production in the Midwest. Walter H. Schmidt, Ohio State University, 952 Lima Avenue, Box C, Findlay, OH 45840.

Information will be presented from Illinois, Indiana, Michigan, Ohio and Kentucky regarding the status of canola production. Grain yields and preliminary research results will be given. This paper will include preliminary oil analysis from the 1988 production. Problems and successes associated with this crop will be presented. The future potential for canola as a cash crop will be examined.

G2

Rapeseed Production in the Mid-south 1986-1988. John F. Bradley, University of Tennessee, Milan Experiment Station, 205 Ellington Drive, Milan, TN 38358, and H.A. Fribourg, C.R. Graves, and G.N. Rhodes, Jr., University of Tennessee.

Winter rapeseed (*Brassica napus*) has been studied in field experiments at Milan in West Tennessee in the 1986-87 and 1987-88 growing seasons and currently. The purpose of this study was to determine whether the climatic and pedologic conditions of this area were suitable for winter rapeseed culture, and to determine the management required for obtaining acceptable yields. Focus was a high

erucic acid content in the oil. Mean yields were 2580 kg/ha ranging from 2190 kg/ha for 'Viking' to 3020 for 'Gorzanski'. There was no yield difference between 5.6 and 11.2 kg/ha seeding rates. September seeding yielded about 10% more than mid-October seedings; later had winter injury. There were no seeding date X seeding rate, seeding date X cultivar, or seeding rate X cultivar interactions. Three experiments were conducted with 0, 34, and 68 kg N/ha applied in the spring in all combinations, where rapeseed followed corn, fallow or grain sorghum. Yield response to N rates was similar regardless of preceding crop. Highest yields were obtained with 68 kg N/ha in fall plus 90 kg N/ha in spring. Atrizine used with a preceding corn crop at recommended rates did not affect subsequent rapeseed yield adversely. No yield response was obtained from fertilizer rates of 0 to 40 kg P/ha and 0 to 11 kg K/ha in all conditions. Yields obtained in these experiments with Gorzanski and Bridger (300 and 2800 kg/ha) were not very different from those obtained in Canada or Europe. Therefore, winter rapeseed grown in the Mid-South could be a viable winter crop.

G3

Breeding Canola for the United States. Matti Sovero, Calgene, Inc., 1920 Fifth Street, Davis, CA 95616.

Calgene's rapeseed breeding program aims to produce open pollinating populations, inbred lines, and hybrid varieties of canola for different growing areas in the U.S.A. The main emphasis is currently on fall planted *Brassica napus* targeted especially for the Southeast, Mid-south, Midwest and High Plains regions. Critical factors for adaptation in this area are winter hardiness, vernalization requirement, heat tolerance and earliness of maturity. Inadequate adaptation is typically expressed as low average yield, low average oil content and large variation in these and other important traits. Diseases and insect pests are not a major problem at the present, but their importance is expected to increase once rapeseed is more widely grown in the U.S. Anticipating these problems is essential for the future success of the breeding program. It has been noticed that cultivars available from Europe and other foreign sources generally have very narrow if any adaptation within this area.

G4

Canola in the United States - A Processor's Perspective. Joseph G. Endres, Central Soya Company, Inc., P.O. Box 1400, Ft. Wayne, IN 46801.

The physical task of converting a soy processing plant to handle canola and HEAR seeds will be discussed. Canola and HEAR are specialty seeds. The value of converting these seeds into oil and meal will be treated differently than the traditional soybean crushing margin concept. The new relationship between grower, processor and user will be explored.

G5

The Economic and Functional Acceptance of Canola Oil. James M. Stanton, Experience, Inc., 1200 2nd Avenue South, Suite 400, Minneapolis, MN.

Since 1982 imports of canola into the United States have grown at an annual rate of 75 percent. This rapid growth is due to the unique combination of economic and functional properties of canola. These same properties lead industry leaders to expect canola to become a major oilseed crop in the United States. This paper discusses the total economics of canola including return to growers, crushing margins, and economic considerations of food processors. The functional properties of canola will also be discussed, particularly how these properties affect its use in many food applications. The use of canola as a fatty acid source will also be covered.

G6

Acceptance of Canola Meal by the U.S. Feed Industry. Charles Dexheimer, Farmland Industries, 3315 N. Oak Trafficway, Dept. 191, Kansas City, MO 64116.

Canola meal produced from low erucic acid, low glucosinulate type rapeseed (canola seed) is nutritionally superior to meal produced from high glucosinolate type rapeseed. Canola meal can be included in rations for livestock and poultry at higher levels than rapeseed meal. Presently canola meal competes with soybean meal for inclusion into swine and poultry feeds and soybean meal, cottonseed meal, sunflower meal and other plant protein sources for inclusion into ruminant rations. Factors which limit the inclusion rate of canola meal into swine and poultry rations are: 1) lysine level and availability; 2) high fiber levels; 3) lower metabolizable energy than soybean meal; 4) sinapine content; 5) anti-palatability factors. Factors limiting its inclusion into ruminant rations are: 1) anti-palatability; 2) low level of undergraded protein. Presently the major factors that limit its inclusion are anti-palatability and lysine level for poultry and swine and cost per unit of protein for ruminant rations, particularly beef rations. Improving on any of the limiting factors will allow canola meal to be included at higher levels and add value to the product.

Session H Thursday afternoon

Surfactants & Detergents II: Recent Advances in Detergent Technologies

H1

New Builder Systems. Mark S. Greenberg, Procter & Gamble Co., Miami Valley Laboratories, 11810 E. Miami River Road, Cincinnati, OH 45217-8707.

The synthesis, physical-chemical properties and performance of a new, non-phosphorous builder will be discussed. This material, which is proprietary to the Procter & Gamble Company, is composed of a mixture of the sodium salts of tartrate monosuccinate and tartrate disuccinate. The performance of this builder in detergent compositions will be compared to phosphate and other non-phosphorous builders.

H2

Optimization of Alkoyloxybenzenesulfonate/Sodium Perborate Compositions for Laundry Bleaching Using an Automated Analysis Method. Allen D. Clauss, Procter & Gamble Company, Ivorydale Technical Center, 5299 Spring Grove Avenue, Cincinnati, OH 45217, and Kenneth A. Leslie and J. Keith Grime, Procter & Gamble.

Sodium perborate bleach activators of the type $RC(O)OC_6H_4SO_3Na$ (R=alkyl) were evaluated extensively for use in laundry detergents. In order to study the efficiency of the bleach system across a wide range of laundry washing conditions, an automated analysis system was developed which continuously monitors total available oxygen and peroxyacid bleach concentration in the wash solution as a function of time. The system was used to determine perhydrolysis profiles for the activator under actual laundry conditions in an automatic washing machine. The resultant perhydrolysis profiles were used to optimize the bleaching system with respect to peroxyacid generation across conditions.

H3

TAED and New Peroxycarbonic Acids as Highly Efficient Bleach Systems. G. Reinhardt, Hoechst AG, Marketing TH/ATA, Frankfurt am Main, D-6230 West Germany, and Hanspeter Gethoeffer, Hoechst AG.

In Europe the introduction of low temperature washing was possible only with the development of suitable bleaching systems based on perborate activators. Nowadays the most important activator is tetraacetylethylenediamine (TAED). In this presentation a survey is given of manufacture, efficacy and environmental properties of TAED. The efficacy of an activator system depends on the rate of perhydrolysis of the activator and the reactivity of the formed peroxyacid. A realistic model system was developed to determine the rate constants of these two reactions in washing liquor. Computer simulations based on these results give detailed insight into the bleach reaction. As highly efficient bleach systems the new class of imidoperoxycarbonic acids will be introduced. Their synthesis, efficacy and properties will be compared to known peroxycarbonic acids. The present results demonstrate the superiority of these new peracids, which might be interesting detergent additives in the future.

H4

Synthesis and Properties of Novel Triblock Oligomers with Soil Release Activity. Eugene P. Gosselink, Procter & Gamble Company, Miami Valley Laboratories, 11810 E. Miami River Road, Cincinnati, OH 45217, and Howard J. Krauss, Procter & Gamble Co.

A series of novel polyether-polyester-polyether triblock oligomers has been synthesized by the reaction of dimethyl terephthalate, monomethyl ethers of polyethylene glycols, and ethylene or propylene glycols. These low molecular weight oligomers, particularly those based on oligo(propylene terephthalate), have a better combination of solubility and soil release performance properties in a heavy duty liquid detergent context than previously commercially available materials. These advantages were obtained by capping to better control molecular weight and by reducing symmetry in the polyester "backbone" to decrease crystallinity. A minimum of four terephthalate moieties per oligomer is needed to provide good substantivity to a polyester fiber.

H5

Detergency Study: The Role of Soil Release Polymer. J.R. Hartman, Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217, and M.G. Venegas, S.L. Boyer, and E.B. Keller, Procter & Gamble Company, and S.K. Obendorf, Cornell University.

A detergency study on the role of soil release polymer on oily soil removal is presented. The effect of the addition of a soil release polymer to a built Heavy Duty Liquid Detergent as a function of fabric blend (cotton/polyester) and resin coating is explored. X-ray Microanalysis Techniques are used to visualize the location of oily soil within fabric yarn bundles and individual fibers. Comparisons are made on soil distribution and removal effects between laundry-added soil release polymers and commercial soil release fiber finishes.

H6

Detergency and Anti-Redeposition Performance of Polymer Blends for Laundry Powders and Liquids. Richard J. Holland, BASF Corporation, 1419 Biddle Avenue, Wyandotte, MI 48192.

Modern laundry detergent formulations are designed to provide a multitude of benefits to the consumer. Detergent/softener compositions clean and impart a pleasing "hand" to the fabric. High efficacy liquid detergents sometimes contain stain-inhibiting additives which release oily soil from synthetics. To provide these added benefits without inhibiting the soil removal process is a major problem for today's formulator. In "softergents" and liquids hydroxypropyl methylcellulose (HPMC) is often included to provide these oily soil redeposition and soil shield properties. But HPMC exhibits a negative synergism with particulate soils, significantly inhibiting the removal of clay from cotton, polyester and polyester/cotton fabrics. Blends of HPMC with other additives (i.e. carboxymethylcellulose) have been used to improve particulate anti-redeposition. But these additives do not enhance clay soil removal in the presence of HPMC. We have found that combinations of a modified nonionic polymer (Sokalan HP-22) with HPMC substantially restore clay detergency and anti-redeposition while providing excellent oily soil anti-redeposition and soil shield properties. Unlike traditional additives (CMC/HPMC) the combination of the modified nonionic polymer with HPMC performs extremely well on a broad spectrum of soils and fabric types consistent with modern laundry needs.

H7

Effect of Polyacrylate Molecular Weight on Laundry Detergent Performance. Michael B. Freeman, Rohm and Haas Company, 727 Norristown Road, Spring House, PA 19477.

The formulation of poly (acrylic acids) into laundry detergents as builder assists in soda ash and soda ash/

zeolite systems has been explored using a multi-faceted approach. Particular emphasis was placed on U.S. home laundry applications and the effect of polyacrylate molecular weight on the performance of these polymers in calcium sequestration, crystal growth inhibition, clay soil removal, and prevention of soil redeposition. Data will be presented to provide a basis for a fundamental understanding of the structure/property relationships of these polymers.

H8

Polymers to Enhance Performance in Liquid Detergent Formulations. Charles E. Jones, Rohm and Haas Company, 727 Norristown Road, Spring House, PA 19477.

This paper will introduce a class of patented water soluble polymers which are useful in detergents. The polymers are of particular value in liquid detergents (home laundry and light duty liquids) because of the compatibility of the polymers in effective amounts in liquid surfactant systems. In heavy duty liquid detergents the polymers provide a significant enhancement in the ability of the detergents to resist the redeposition of particulate soil, especially when cotton fabric is laundered. In addition, the removal of oily soil (such as sebum from perspiration) is enhanced. Data will be given to show that the polymers are effective lime soap dispersants, as well as effective dispersants for particulate material, making the polymers useful in light duty liquids for hand dishwashing. Further, when added in effective amounts the polymers do not adversely affect the activity of enzymes in liquid laundry detergents.

H9

Mechanism of Detergent Protease Action. M.S. Showell, Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217, and M.G. Venegas and W.C. Wertz, Procter & Gamble Company.

The role of the detergent matrix in solubilizing protein fragments produced by the action of Serine Proteases on proteinaceous soils is discussed. It was shown that the protease produces large insoluble fragments which are subsequently removed and suspended by the detergent. The ability of the detergent to solubilize these fragments determines the overall cleaning profile of enzyme containing laundry detergents. Additionally, the effects of pretreating stains with detergent alone and detergent plus protease are described. It was shown how protease activity, stability and the soil removal and suspension properties of the detergent matrix can be combined to optimize cleaning performance.

H10

Alkyl Polyglycosides: Processing Aids in Detergent Crutcher Slurries. A.D. Urfer, Henkel Corporation, 2200 East Eldorado Street, Decatur, IL 62525, and V.L. Lazarowitz and R.A. Aleksejczyk, Henkel Corporation.

Laboratory and commercial field tests demonstrate that alkyl polyglycosides can be used as viscosity reduction agents in detergent crutcher slurries. Laboratory studies show by adding 1-2% of alkyl polyglycoside the total solids of the crutcher slurry can be increased from 10% to over 20% without increasing the viscosity of the slurry in: Anionic/Carbonate Systems, Anionic/Nonionic/Carbonate Systems, Nonionic/Carbonate Systems, Anionic/Phosphate Systems.

The increased solids content translates into an increased production capacity for the manufacturer, since less water has to be removed per slurry mixture during the spray drying process. Commercial field tests with alkyl polyglycosides in anionic/nonionic/carbonate systems have confirmed laboratory studies. The crutcher solids were increased from 62% to 75% while maintaining the viscosity well within pumpable limits. Alkyl polyglycosides also help prevent nonionic surfactants from separating out of the slurry. This is a major problem for detergent manufacturers and the use of 1-2% alkyl polyglycoside surfactant completely eliminates this problem.

Session I Thursday afternoon

Value-Added Industrial Uses for Soybeans

I1

History of Industrial Utilization of Soybeans. William Shurtleff, Soyfoods Center, P.O. Box 234, Lafayette, CA 94549.

During the mid-1980s in the U.S. there has been a rebirth of interest in research on soybean utilization, and especially in industrial utilization. This paper will trace the background of that interest. As early as 980 A.D. the Chinese were using soy oil, mixed with tung oil, for caulking boats, and by the 1500s soybean cake began to be widely used in China as a fertilizer. The earliest known reference to industrial uses of soybeans in the West was in 1880, when Bryan, an American, noted that soy oil could be used as substitute for linseed oil in paints, or be burned in lamps. The heyday of interest in industrial utilization of soybeans took place in America during the 1930s and Great Depression, spurred largely by the work of Henry Ford, the Farm Chemurgic Council (founded in 1935), the Chemurgic movement, and the U.S. Regional Soybean Industrial Products Laboratory (founded in 1936 at the University of Illinois). The goal was to make industrial products from farm crops to help depressed farmers. The soybean was one of the great success stories of the Chemurgic movement. Starting in the mid-1980s foreign soybean competition, largely from Latin America, and huge surpluses of soy oil led to a rebirth of interest in research on soybean utilization, especially industrial utilization, that could lead to new value-added products for new markets. Promising applications included soy oil for printing inks, dust suppressants, diesel fuels, and the like.

I2

Use of Soy Protein in Paper Coating Applications. C.L. Garey, Consultant, 6310 Mesa Verde Drive, Lincoln, NE 68510.

Pigment coatings are applied to the surface of paper and paperboard in order to improve appearance and printing characteristics. The particles of the pigment are held on the surface by various binder materials, such as starches, latexes, soluble synthetics, casein, and proteins isolated from soybeans. Soy protein binders are products that have been chemically modified to provide a variety of coating properties. These include high surface strength, excellent opacity and brightness, high quality printing due to control of ink transfer and penetration, good water resistance, toughness for packaged goods, improved gluing characteristics, resistance to oily materials, etc. These binders are commonly found in coatings on food packaging including cereal boxes, soft drink and beer cartons, in posters needing water resistance, for specialty and high quality printing covers, playing cards, etc. They also have been used in printing inks, in paints, and with phenolics in abrasion binders. The paper industry is a growing market for the use of products derived from soybeans, an annually renewable resource.

I3

Soybean-based Wood Adhesives. Anthony H. Conner, Forest Products Laboratory, USDA, Forest Service, One Gifford Pinchot Drive, Madison, WI 53705-2398.

The use of soybeans (i.e., soybean flour) for adhesives is a recent development when compared to its history as a food source. From the development of soybean adhesives in the early 1920's, their use peaked in the 1940's at about 60 million pounds per year. Due to the introduction of highly-durable, exterior-grade synthetic adhesives after World War II, the demand for soybean adhesives declined to about 30 million pounds per year. However, the 1950's saw a reversal in this trend; demand peaked at 100 million pounds around 1956. From this point the demand for soybean adhesives, especially in the wood industry, has declined to negligible quantities at the present time. This presentation will review the use of soybean-based adhesives in the forest product industry. It will draw heavily on the use of soybean adhesive in the plywood industry which has been historically the major consumer. In addition, it will review recent research that might allow soybean-based adhesives to regain a foothold in this large market.

I4

Industrial Uses of Vegetable Oil. Ruxton H. Villet, USDA-ARS, National Program Staff, Room 232, Bldg. 005, BARC-West, Beltsville, MD 20705.

Chief industrial uses for vegetable oils will be reviewed. Fractional distillation can yield, for example, oleic acid (C_{18}-9-enoic) from soybean oil, linoleic acid (C_{18}-9,12-dienoic) from safflower oils, linolenic acid (C_{18}-9,12,15-trienoic) from linseed oil and ricinoleic acid (C_{18}-12-hydroxy-9-enoic) from castor oil. Chemical modification of these acids gives rise to a variety of useful compounds: for example hydrogenation of oleic acid produces stearic acid (C_{18}-anoic) while ozonolysis provides pelargonic (C_9-anoic) and azelaic (C_9-dioic) acids. Alkali cleavage of ricinoleic acid produces sebacic acid (C_{10}-dioic) and 2-octanol. Polyunsaturated acids (e.g. linoleic) can be converted to dimer acids. Within the USDA Agricultural Research Service post-harvest program on product utilization there is substantial focus on converting vegetable oils such as soybean oil to specialty chemical products. Biotechnological as well as chemical systems are being developed. A goal is to find substitutes for imported oils and to enhance the return on investment to the U.S. farmer and agribusiness.

I5

Vegetable Oils as Diesel Fuel Extenders. Marvin O. Bagby, USDA-ARS-NRRC, 1815 N. University St., Peoria, IL 61604.

Because of their favorable energy contents (about 90% of diesel fuel), vegetable oils from crops, such as soybean, peanut, sunflower, rape, and coconut have been evaluated in many parts of the world as fuels for compression ignition engines. Short-term tests were encouraging; however, longer-term endurance tests revealed problems generally attributable to inefficient combustion. These problems of incomplete combustion are more prevalent with direct-injection engines than with prechamber types. The high surface tensions and high viscosities of seed oils compared with diesel fuel contribute to the combustion problems by altering the injection event and fuel aerosol formation. Solutions to the viscosity problems have been approached in at least four ways: (1) transesterification, (2) dilution, (3) pyrolysis and (4) microemulsification. Extended tests with selected representative fuels have been encouraging. However, incomplete combustion persists. Gradual accumulation of the fuels, in particular intact triglycerides, on engine parts results in charred deposits. Buildup of fuel in the crankcase eventually leads to greatly altered viscosity of the lubricating oils. Current research emphasizes precombustion chemistry. Progress in these fundamental studies will be described.

I6

Use of Soybean Oil in News Ink Formulations. H. Wilson Cunningham, American Newspaper Publishers' Assoc., P.O. Box 17407 Dulles Airport, Washington, DC 20041.

During the 1980's, the American Newspaper Publishers Association, a trade association representing the newspapers of North America, conducted research to find alternative oils to replace the petroleum oil in the formulation of inks used to print newspapers. In 1986 ANPA licensed nonpetroleum newsink formulations using soybean oil, and commercial production commenced. Soybean oil has proven to be a good alternative oil because its solvency of resin binders has improved the dispersion of the color pigments within the ink. Color reproductions using soy oil color inks produced clearly superior prints when compared to petroleum based color inks. Soy oil based color inks have become a major market force in the 100 million pounds per year color newsink market. The use of soybean oil in the 350 million pounds per year black newsink market has been limited because of the cost differential between petroleum and soy oil and the lack of performance enhancements seen with color soy oil inks.

I7

Use of Vegetable Oils in Animal Feeds. Jerry C. Weigel, Archer Daniels Midland Company, P.O. Box 1470, Decatur, IL 62525.

All the various fats and oils commonly used in feed are predominantly composed of the same fatty acids, but in varying proportions. The gross energy value of all feed fats is around 9.4 calories per gram; therefore, the importance of a specific fat as a feedstuff depends on: 1) the utilizable or D.E. that can be derived from it, 2) the essential fatty acids it supplies to the diet. The vegetable oil that has promoted the most interest during the past year is soybean oil. The primary competitor of this product is corn and animal fat. The market potential is currently greatest for the swine industry, with poultry second. The application for soybean oil to the animal feeding industry is two-fold: 1) dust control/ health benefits, 2) nutritional.

I8

Vegetable Oil Use with Agrichemical Crop Protectants. George Kapusta, Southern Illinois University, Dept. of Plant and Soil Science, Carbondale, IL 62901.

The use of petroleum oil for various pest control applications has been recognized for many years, whereas the use of vegetable oils is relatively recent, dating mostly to the early 1970's. The American Soybean Association funded several researchers in the early 1980's to evaluate soybean oil as an additive or carrier for pesticides. Equal control of weeds was achieved when soybean oil was compared to petroleum oil as an additive with several postemergence herbicides. Soybean oil also was evaluated as the carrier, in lieu of water, for a wide range of soil-applied and postemergence herbicides. Herbicides applied in soybean oil volumes as low as 2.3 liters per hectare with rotary atomizer nozzles gave excellent control of weeds in most instances. Soybean oil as the carrier for foliar insecticides also has resulted in excellent control of several insect species.

Session J Thursday afternoon

Dietary, Omega-3, Essential and Other Fatty Acids

J1

Flax Consumption by Humans Increases Plasma and Red Cell Omega-3 Fatty Acids and Decreases Serum Cholesterol. Stephen C. Cunnane, University of Toronto, Dept. of Nutritional Sciences, Toronto, Ontario M5S 1A8, Canada, and David J.A. Jenkins, Sujata Ganguli, Julia K. Armstrong, and Thomas M.S. Wolever, University of Toronto.

Although the nutritional effects of flaxseed oil (linseed oil) have been studied extensively as the extracted oil, the effects of flax seed on omega-3 fatty acids and serum lipids have not been evaluated. We have studied the effects of milled flax (50g/day, 4 weeks, n=10) added directly to various meals in the daily diet of healthy volunteers. Blood samples were taken weekly before, during and after consuming the flax. Serum triglycerides (TG) and cholesterol (CH) were analyzed by automated colorimetric procedures. Plasma phospholipids (PL) and TG, and red cell phosphatidylcholine (PC) and phosphatidylethanolamine were separated by conventional TLC and the fatty acid methyl esters analyzed by capillary GLC. After 4 weeks on flax, serum CH decreased by 16 mg/dl (187 171 mg/dl, p,0.01) but serum TG and PL were unchanged (75±31 and 187±42 mg/dl, respectively). Alpha-linolenic acid (18:3n-3) and eicosapentaenoic acid (20:5n-3) did not change in serum PL or TG but increased 100% in red cell PC while the flax was being consumed (p,0.01). Therefore, flax added to the diet of apparently healthy individuals resulted in increased omega-3 fatty acids in plasma and red cells and decreased serum CH.

J2

Synthesis, Preparative HPLC Purification and Structure Confirmation of a New Fish Oil-Derived Omega-3 Polyunsaturate. J.G. Turcotte, University of Rhode Island, Dept. of Medicinal Chemistry, College of Pharmacy, Kingston, RI 02881-0809, and S.S. Shirali, and P.E. Pivarnik.

Abstract not available at press time.

J3

The Digestive Process and Therapy with Marine n-3 Fatty Acids in Acid, Ester or Triglyceride Form. R.G. Ackman, Canadian Institute of Fisheries Technology, Technical University of Nova Scotia, Box 1000, Halifax, NS B3J 2X4, Canada.

The use of marine n-3 fatty acids in clinical treatment of health problems in either acute or preventive roles is inevitable. A variety of products of triglyceride type are available. These are becoming non-standardized products and may differ not only in fatty acid total composition among products, but also in positional distribution of fatty acids. The consequences of these differences are examined in terms of the digestion and absorption of fats in man. It is proposed that triglycerides *per se* are unnecessary in most therapeutic roles and may be replaced by the ethyl ester or free fatty acid forms of marine n-3 fatty acids, permitting accurate dosage and minimizing excessive intake of other fatty acids.

J4

Effects of Safflower Oil, Evening Primrose Oil, Fish Oil and Liquid Paraffin on Human Plasma Essential Fatty Acid Levels. David F. Horrobin, Efamol Research Institute, POB 818, Kentville, Nova Scotia B4N 4H8, Canada, and Mehar S. Manku, Janet Shay, Kelly R.M. Ells, and Nancy Morse-Fisher, Efamol Research Institute.

Linoleic acid is metabolized to arachidonic acid via gamma-linolenic acid (GLA) and dihomogamma-linolenic acid (DGLA). It is commonly assumed that in humans linoleic acid is easily converted along this route. However, several reports indicate that very large increases in daily linoleate intake (10-40g/day) are unable to modify plasma levels of DGLA and arachidonic acid. We now report the effects of 14 days treatment with modest doses (4-6g/day) of

safflower oil (82% linoleic), Efamol evening primrose oil (72% linoleic, 9% GLA), fish oil (18% EPA, 12% DHA), Efamol Marine (80% Efamol + 20% fish oil) and an inert placebo, liquid paraffin. The only agent which had no significant effect on any essential fatty acid (EFA) in plasma phospholipids was the paraffin. This is therefore an appropriate inert placebo when modest doses of oil supplements are given. Efamol caused a significant rise in DGLA with no change in linoleic or arachidonic acids, consistent with previous reports of slow conversion of DGLA to arachidonic acid. Fish oil elevated EPA and DHA and reduced linoleic acid and DGLA while leaving arachidonic acid unchanged. Efamol Marine significantly raised both EPA and DGLA but had no effect on GLA or DGLA. This is consistent with recent in vitro observations suggesting that linoleic acid can be converted to arachidonic acid without mixing with GLA or DGLA pools (Voss and Sprecher, *Lipids 23:* 660-665, 1988). Safflower oil is therefore not an appropriate placebo for studies with GLA-rich oils. A truly inert placebo such as liquid paraffin should be compared with both GLA-containing oils and oils which contain linoleic acid as their only EFA.

J5

Essential Fatty Acids in Plasma Phospholipids from Normal Humans in Different Geographical Locations. Mehar S. Manku, Efamol Research Institute, POB 818, Kentville, Nova Scotia B4N 4H8, Canada, and Nancy Morse-Fisher, David F. Horrobin, Kelly R.M. Ells, and Janet Shay, Efamol Research Institute.

Although there are many reports in the literature of the normal levels of essential fatty acids (EFAs) in human plasma phospholipids, there appear to be no studies in which populations from widely different geographical locations have been investigated in the same laboratory using the same analytical techniques. We now report EFA plasma phospholipid levels in normal individuals from different locations in Canada, the USA, England, Scotland, Ireland, Japan and Zimbabwe. The most striking observation was the consistency of EFA levels irrespective of geographical location or diet. There were no significant differences between most populations in dihomogammalinolenic acid and only modest differences in linoleic, arachidonic and eicosapentaenoic acids. These observations suggest that plasma phospholipid EFA patterns are regulated according to the physiological needs of the organism and do not simply respond passively to dietary fatty acid intakes. The only exception to the general rule among the populations we studied was the Indian Community on Vancouver Island. This Indian group, whether on or off their traditional salmon-rich diet, had phospholipid EFA patterns quite different from any other group. Their EFA levels were consistent with slow or absent 6-desaturation.

J6

Effects of Dietary Fish Oil on Alkenylacyl Glycerophosphorylethanolamine Metabolsim in Platelets. Harold M. Aukema, University of Guelph, Dept. of Nutritional Sciences, Room 308, Animal Science/Nutrition Bldg., Guelph, Ontario N1G 2W1, Canada, and Bruce J. Holub, University of Guelph.

Healthy volunteers were given 20 capsules of a fish oil concentrate (MaxEPA) daily for 6 weeks, providing 3.6g eicosapentaenoic acid (EPA) plus 2.4g docosahexaenoic acid (DHA) per day, followed by a 6 week depletion period. It was estimated that of the total mass decrease in arachidonic acid (AA) in platelet phospholipid upon fish oil consumption, 37% was accounted for by the alkenylacyl glycerophosphorylethanolamine (GPE). Approximately 71% of the EPA increase was calculated to be represented by the alkenylacyl GPE plus diacyl glycerophosphorylcholine (GPC), with each contributing about equally. The fatty acid compositions were restored to initial values 6 weeks post-supplementation. In a second study with EPA-enriched human platelets, significant mass losses (nmols/2 $\times$ 10^9 platelets) of AA and EPA from GPC and phosphatidylinositol, but not diacyl GPE, alkenylacyl GPE, and phosphatidylserine, were detected upon collagen stimulation. The AA/EPA ration in the phosphatidic acid which accumulated upon agonist exposure indicated that it was derived predominantly from the inositol phospholipids. The marked enrichment of the alkenylacyl GPE in n-3 fatty acids at the expense of n-6 fatty acids may possibly contribute to the putative beneficial effects of fish oil on platelet reactivity and eicosanoid biosynthesis.

J7

Correlation of Isomeric Fatty Acids in Human Adipose Tissue with Clinical Risk Factors Associated with Heart Disease. E.A. Emken, USDA-ARS-NRRC, 1815 N. University St., Peoria, IL 61604, and L. Hudgins and J. Hirsch, Rockefeller University.

The percent of each individual *trans* and *cis* octadecenoic acid (18:1) positional isomer and each octadecadienoic acid (18:2) geometrical isomer in adipose tissue samples from 76 normalipidemic male subjects (age 47, range 23-78) was obtained by gas chromatographic analysis. The percentages for the isomeric fatty acids and other fatty acids present in adipose tissue were correlated with clinical risk factors for coronary heart disease. The mean values for total *trans* and total *cis* 18:1 isomers were 2.6 and 2.5%, respectively. The pattern for the *trans* and *cis* 18:1 positional isomers was similar to the pattern present in hydrogenated vegetable oil (HVO), except for the 11c-18:1 isomer which was two times larger. The percentages for the c,t- and t,c-18:2 isomers were low (mean = 0.25 and 0.09%). Less than 0.01% t,t-18:2 was present. An additional, unidentified 18:2 isomer (0.29%) and a conjugated 18:2 isomer (0.51%) were detected by mass spectroscopic analysis. The 11t-18:1 isomer correlated negatively with cholesterol and disease and total *trans*-18:1 isomers or individual 18:1 or 18:2 *trans* isomers which are mainly derived from HVO. Of the *cis*-18:1 isomers, 11c-18:1 correlated positively with serum cholesterol and low density lipoprotein-cholesterol (LDL-c) and the 13c-18:1 isomer was correlated with diastolic blood pressure ($p<0.05$). Of interest were significant, positive correlations between arachidonic acid (20:4w) and diastolic blood pressure, body mass index, triglyceride, cholesterol, LDL-c, and LDL-c/HDL-c. Stepwise, multiple regression analysis showed independent positive correlations between LDL-c and diastolic blood pressure. These relationships are possibly due to differences in the dietary intake and/or metabolism of 20:4s6.

Session K Thursday afternoon

Plant Lipids II: Fatty Acid and Lipid Synthesis in Plants

K1

Recent Progress with Plant Acyl Carrier Proteins. John B. Ohlrogge, Michigan State University, Dept. of Botany & Plant Pathology, East Lansing, MI 48824-1312, and James F. Battey, Alenka Hlousek-Radojcic, Katherine Schmid, and Martha A. Post-Beittenmiller, Michigan State University.

At least two roms of acyl carrier protein (ACP) occur in all higher plant species examined and these forms are expressed differently in different tissues. Recently our lab has isolated a genomic clone of ACP from *Arabidopsis* and found that it contains three introns; two in the transit peptide and one just downstream of the phosphopantetheine attachment site. We have also isolated a cDNA clone for ACP by immunological screening of a spinach root library. The derived amino acid sequence of this clone matches the N-terminal amino acid sequence of the minor form of ACP isolated from spinach leaf. This suggests that the same gene for ACP-II is expressed in both leaves and roots. In order to examine the consequences of overexpression of ACP *in vivo*, we have transformed tobacco plants with spinach ACP-I. A plasmid was constructed containing a fusion between the tobacco RuBisCo small subunit promoter and transit peptide and mature spinach ACP-I. The recombinant gene is under light regulation and is expected to produce the precursor ACP whose transit peptide would be cleaved as it is transported into the chloroplast. Western blot analyses of leaf homogenates from ACP-transgenic plants demonstrate that the spinach ACP accumulates to levels in excess of the endogenous tobacco ACPs and that the transit peptide is cleaved. Normally apoACP is not detected in plants. However, in the plants transformed with the spinach ACP approximately 50% of the spinach ACP is in the apo form.

K2

The Pathways of Fatty Acid Desaturation in Leaf Lipids. C.R. Somerville, Michigan State University, DOE Plant Research Laboratory, East Lansing, MI 48824, and J. Browse, Washington State University.

We have isolated a series of mutants of the small crucifer *Arabidopsis thaliana* with defects in various steps of leaf and seed lipid desaturation by screening mutagenized populations of plants by GLC. Analysis of the effects of the mutations on lipid composition suggests the existence of at least seven distinct enzymes which are involved in fatty acid desaturation in leaves. At least two of these are also involved in desaturation of seed lipids. Four classes of mutants have no significant effect on seed lipid composition. The effects of the mutations are summarized as follows:

fadA controls *trans*-Δ3 desaturation of 16:0 on plastid phosphatidylglycerol in leaves

fadB controls *cis*-Δ9 desaturation of 16:0 on sn-2 of monogalactosyldiglyceride in leaves

fadC controls *cis*-Δ12 desaturation of plastid lipids in leaves

fadD controls *cis*-Δ15 desaturation of extraplastid 18:1 in seeds and leaves

fadE controls *cis*-Δ12 desaturation of extraplastid 18:1 in seeds and leaves

fadF controls *cis*-Δ15 desaturation of extraplastid 18:2 in seeds and leaves

We are currently attempting to exploit the advantages of *Arabidopsis* as a model organism for molecular genetics to isolate the genes which complement these mutations.

K3

Reevaluation of the Initial Reactions of Fatty Acid Biosynthesis. Jan G. Jaworski, Miami University, Chemistry Department, Oxford, OH 45056, and Richard C. Clough and Susan R. Barnum, Miami University of Ohio.

A cerulenin insensitive 3-ketoacyl-acyl carrier protein synthase has been assayed in extracts of spinach leaf. The enzyme catalyzed the synthesis of acetoacetyl-acyl carrier protein at a rate 5 fold faster than acetyl-CoA:acyl carrier protein transacylase. Furthermore, the initial rates of acyl-acyl carrier protein synthesis were independent of the presence of cerulenin, an antibiotic known to inhibit 3-ketoacyl-acyl carrier protein synthase I from spinach. The major acyl-ACPs could be separated by polyacrylamide gel electrophoresis. In the presence of 100 μM cerulenin, the accumulation of butyryl- and hexanoyl-acyl carrier protein was observed, with no detectable long chain acyl-acyl carrier proteins or fatty acids being produced. In the absence of cerulenin, the long chain acyl-acyl carrier proteins also accumulated. These observations suggest the presence of a previously unreported 3-ketoacyl-ketoacyl-acyl carrier protein synthase which is specific for short chain acyl-CoAs and acyl-acyl carrier proteins and further suggest that this enzyme is involved in the initial reactions of fatty acid synthesis.

K4

Polypeptides Associated with Linolenate Levels in Soybean and Arabidopsis. David F. Hildebrand, University of Kentucky, N106 AGSCN, Dept. of Agronomy, Lexington, KY 40546, and T. Pfeiffer, J.A. Brockman, X. Wang, University of Kentucky and C.R. Somerville, Michigan State University and H.A. Norman, USDA-Beltsville.

Little information is available concerning the genes and gene products controlling α-linolenate biosynthesis because of the difficulty in working with the key enzyme(s) involved in the process. In order to gain information on polypeptides associated with linolenate synthesis, we have investigated mutant lines of soybeans and Arabidopsis with altered linolenate levels. A polypeptide has been found that is greatly reduced in C1640, a low linolenate soybean mutant described by Wilcox et al. Antibodies have been made against this polypeptide and the expression of this polypeptide in different tissues of soybean genotypes with varied fatty acid composition has been examined. A similar polypeptide has been found to be reduced in the low linolenate fadD mutant of Arabidopsis described by Browse and Somerville. The expression of this polypeptide relative to linolenate levels in Arabidopsis tissues grown under different temperature and light conditions has also been examined. The compound San 9785, which has been found to

reduce linolenate content of plant tissues, also reduces the level of this polypeptide in Arabidopsis and the similar polypeptide in soybeans. The significance of these findings relative to α-linolenate biosynthesis will be discussed.

K5

Growth Temperature and the Regulation of Fatty Acid Metabolism in Developing Soybean Seeds. Thomas M. Cheesbrough, USDA-ARS-NRRC, 1815 N. University Street, Peoria, IL 61604, and Sung Ho Cho, USDA-ARS-NRRC.

Change of environmental temperature is known to trigger changes in the lipid composition of metabolically active plant cells. These changes include shifts in the ratio of saturated to unsaturated fatty acids and modification of the lipid to protein ratio in the cell. We have investigated this phenomenon in developing soybean seeds to determine the mechanisms involved. Changes in fatty acid metabolism were induced by organ culture of developing pods, from greenhouse-grown plants, in liquid media for 20 hr at 20°, 25°, or 35°C. A time course analysis of the fatty acid composition in these seeds showed significant changes in the saturated:unsaturated ratio by 20 hr. When the enzymes for fatty acid metabolism were assayed in these seeds, four of the enzymes showed changes in both total and specific activity in 20° vs 35°Cultures. Further investigation indicated that 2 of these enzymes were present at limiting levels under all three conditions, while the other 2 enzymes were very high in 20 seeds and very low in 35° seeds. The two potentially rate-limiting enzymes were further analyzed to determine the cause of these changes in enzyme activity. CDP-choline:diacylglycerol phosphorylcholine transferases from 20- and 35-adapted cultures are kinetically identical, but the level of the enzyme changes 6-fold between the two conditions. These data indicate that the changes in enzyme activity may be due to changes in the amount of the enzyme and not to the induction of isozymes. Similar analysis is being conducted for stearoyl-ACP desaturase, the other rate-limiting enzyme.

K6

Cocoa Butter Biosynthesis: sn-Glycerol-3-Phosphate Acyltransferase Gene Studies. P. Fritz, Pennsylvania State University, and T. Heeyoung.

Cocoa butter is the major storage product of seeds of the cocoa plant, *Theobroma cacao*, comprising at least 50% of seed dry weight. It has unique properties that make it a valuable material in chocolate manufacturing. It is a mixture of triacylglycerols composed of 85% oleic acid in the 2-position, while the 1- and 3-positions are occupied by two kinds of saturated fatty acid, palmitic and stearic acids. Ninety six percent of cocoa butter is triacylglycerol. The fatty acid composition of cocoa butter is responsible for its unique melting point and contributes to the rich texture of chocolate products. The first step in the biosynthesis of triacylglycerols is catalyzed by glycerol-3-phosphate (G-3-P) acyltransferase. In cocoa, this enzyme brings a specific saturated fatty acid (palmitic or stearic) to the 1-position of the glycerol backbone. Our interest involves isolation of the gene for this enzyme, understanding its mode of regulation in the plant, and searching for possible ways to control the production of cocoa butter by manipulating the gene. The fatty acid composition of cocoa butter is thought to be primarily regulated by two factors: 1) enzyme specificity for fatty acids, and 2) fatty acid pools in cocoa cells. Until now, studies to determine the relative importance of these two factors were limited to *in vitro* experiments, but the ability to isolate the genes involved in these processes and to transfer the genes into plants now makes it possible to study these questions *in vivo*. Studying the acyltransferase function in transgenic plants —either cocoa or other oilseed plants—by using gene transfer techniques, will allow us to determine if it is possible to increase yields and control production of better and more uniform quality cocoa butter even in lower temperature geographical regions where poor quality butter is normally produced. At present, no plant G-3-P acyltransferase gene has been isolated though its value to the edible oil/fat industry could be enormous. Isolation of the gene for the same enzyme in other oilseed plants using the cocoa gene as a heterologous probe will help understand the regulation mechanism of fat/oil production in plants.

K7

Is Acetyl Transacylase the Condensing Enzyme? - Studies with the Purified Enzyme from Brassica Leaves. G. Thompson, Calgene, Inc., 1920 Fifth Street, Davis, CA 95616.

Abstract not available at press time.

Session L Thursday afternoon

Physical/Analytical Chemistry Techniques for Analysis/Characterization of Fats/Lipids II

L1

Textural Properties of Margarines. L. deMan, deMan Food Technology Services, Inc., 58 Applewood Cres., Guelph, Ontario N1H 6B5, Canada, and J.M. deMan and E. Postmus, University of Guelph.

Textural measurements were carried out on commercial margarines and butters, using a cone penetrometer (constant weight), the Instron Universal Testing Machine (IUTM) and the Ottawa Texture Measuring System (OTMS). The samples were conditioned for 24 hours at 10° and 21°C. With the IUTM and OTMS penetration and compression tests were done at a constant speed and from the recorded force-deformation curves the firmness (N/mm), peakforce (N) and total energy (J) were calculated. The hardness, measured with the cone penetrometer, correlated well with the textural measurements using the IUTM and OTMS. The measurements with the cone penetrometer were not less accurate than the other textural measurements. With one exception at 10°C all the samples showed a peak at the beginning of the force-deformation curve of compression, indicating brittleness. At 21°C two samples were brittle. Both samples were in the ß-crystalline form.

L2

Solidification Behavior of Margarine-base Vegetable Fats Blends. Ikukazu Tashima, Ajinomoto Co., Oils & Fats Research Labs, 7-41, Daikoku-cho, Tsurumi, Yokohama, Japan, and J. Kurashige, Ajinomoto Co. and Y. Nakanishi, Knorr Foods Co., and K. Sato and H. Ueyama, Hiroshima University.

Solidification behaviors of margarine-base vegetable fat blends are measured with a polarizing microscopic crystallizer system. This system comprises a growth cell (C.A.30 cm^3) surrounded by thermostated water circulated from two thermostats, a stirrer (120 rpm), a thermo-couple, and a CdS photo-sensor which enables detection of an appearance of crystals in supercooled melt through light passing two crossed-Nicols polarizers and the growth cell. An induction time of crystallization and the rate of crystallization are obtained with this system. The margarine-base fats and oils mixtures are made of soybean oil and six vegetable fats; hydrogenated soybean oils with IV=55 and IV=65, hydrogenated corn oil, hydrogenated rapeseed oil, hydrogenated palm olein, palm oil and esterified palm oil. The crystallization temperatures are 10° and 20°C. We confirmed that the induction time and the crystallization rate behave in a different manner depending on the fat blend. For instance, hydrogenated soybean fat blend reveal a short induction time and high crystallization rate. In contrast, the induction time is long, yet the crystallization rate is high in the hydrogenated corn fat blend. In three palm oil-base fat blends, both the induction time and crystallization rate revealed the slowest crystallization behavior. The crystallization properties are discussed in relation to viscous properties.

L3

Heats of Combustion of Fatty Esters and Triglycerides. Bernard Freedman, USDA-ARS-NRRC, 1815 N. University St., Peoria, IL 61604, and Marvin O. Bagby, USDA-ARS-NRRC.

Gross heats of combustion (Hg) have been measured for three classes of fatty esters and two classes of triglycerides (TG's). The esters include saturated methyl esters, Me 6:0-22:0, saturated ethyl esters, Et 8:0-22:0, and unsaturated methyl esters, Me 12:1-22J:1.. The TG's included the saturated TG's, C8:0-22:0, and unsaturated TG's, C11:1, C16:1, C18:1, 18:2, C20:1 and C22:1. Hg values were measured in a Parr adiabatic calorimeter according to modified ASTM D240 and D2015 procedures. Linear regression analysis (LINREG) related Hg to fatty acid chain length or carbon number (CN), number of valence electrons or electron number (EN), and molecular weight (MW). R^2 values for all equations were 0.99. The results obtained with LINREG for saturated methyl and ethyl esters were compared to results from another published method. LINREG was both more accurate and precise than was the literature method for these esters. Methods for correlating Hg of saturated or unsaturated TG's with molecular characteristics of these molecules have not been reported. With LINREG, we developed equations relating the Hg of these TG's to EN or MW with R^2 values of 0.99.

L4

Polymorphism of POS. N. Sagi, Fuji Oil Co., R & D Center, Izumisano, Osaka, Japan, and H. Hidaka and H. Mori, Fuji Oil Co. and K. Sato and T. Arishima, Hiroshima University.

Polymorphic behavior of POS (1,3-rac-palmitoyl-stearoyl-2-oleoylglycerol) using 99.9% purity sample was examined by x-ray diffraction (XRD), DSC, solubility measurement (tetradecane) and optical microscopy in comparison to SOS and POP. Both the melt-crystallized and solvent-crystallized samples were employed. The number of independent polymorphs was four, tentatively named alpha, gamma, pseudo-beta-prime and beta. Alpha is identical to that commonly observed in POP and SOS as the lowest-melting form. As for the highest-melting form, beta, the XRD short spacing pattern is identical to beta-1 of POP and SOS. This is consistent to the crystal habit; beta single crystals of POS showed the same shape as those of beta-1 forms of POP and SOS. However, the melting point of beta (POS), 35.9°C, is lower than those of beta-1 of POP, 36.7°C, and of beta-1 of SOS, 43.0°C. The solubility data showed that POS:beta is more stable than POP:beta-1 below about 13°C, yet the stability relation is reversed above this temperature. POS does not possess beta-2 which is the second stable form in POP and SOS. Concerning two intermediate forms, gamma and pseudo-beta-prime appear, the latter being more stable. The occurrence and transformation processes of these four polymorphs are discussed in relation to the molecular structures. The polymorphic behavior of the mixture systems of POP/POS/SOS also will be presented.

L5

Polymorphism of Asclepic Acid. Masao Suzuki, Nippon Oil and Fats Co., Research Laboratory, Ohama, Amagasaki, Japan, and N. Yoshimoto and K. Sato, Hiroshima University and M. Kobayashi, Osaka University.

Thermal and structural data of the polymorphs of asclepic acid (C_{18}:1,ω7) were measured with DSC and x-ray diffraction (XRD) using 99.9% sample, to relate them to the polymorphism of oleic acid (C_{18}:1,ω9) and petroselinic acid (C_{18}:1,ω12). The three mono *cis*-double bonded unsaturated acids singly differ in the aliphatic position of the double bond. A total of five independent polymorphs were obtained. Two forms, tentatively called 1 and 2, occur by a rapid melt solidification, revealing complicated DSC exothermic thermograms. Forms 1 and 2 are metastable, since they transform to more stable forms either by thermal annealing or by solution-mediated transformation. There are three stable polymorphs, 3, 4 and 5, all of which undergo successive reversible solid-state transformation. Form 3 transforms to Form 4 at -15.0°C with transition enthalpy (dH_t) of 7.8 kJ/mol. Form 4 converts to Form 5 at -1.4°C (dH_t=0.7 kJ/mol), and Form 5 melts at 13.8°C with dH_m=39.8 kJ/mol. To compare with oleic acid, dH_m of Form 5 is quite the same as that of alpha. However, in oleic acid, there is no transformation like the 4-5 transition, and dH_t(3-4) is smaller than dH_t(gamma→alpha) of oleic acid of 8.8 kJ/mol. Interestingly, the value of dH_t(3-4) is quite similar to dH_t(gamma→alpha) of palmitoleic acid (C_{16}:1,ω7). Since the gamma→alpha transition of palmitoleic and oleic acids shows an order-disorder molecular conformational change, it appears that the transitions from Forms 3 and 4 to Form 5 of asclepic acid involve the similar conformational changes. The XRD data support this interpretation. To compare with petroselinic acid, no common nature is revealed. Hence, two

conclusions are deduced with respect to the positional effects of the double bond; (a)ω7 and ω9 positioned acids reveal the order-disorder transition, but ω12 positioned acid does not, (b) a total polymorphic behavior remarkably differs from each other.

L6

Particle Size Analysis of Fat Crystals. J.M. deMan, Dept. of Food Science, University of Guelph, Guelph, Ontario N1G 2W1, Canada, and P. Chawla, University of Guelph and L. deMan, deMan Food Technology Services, Inc.

Fat crystals can be visualized by polarized light microscopy and electron microscopy. Determination of crystal size distribution has only been possible recently using image analysis, laser light scattering, or sedimentation methods. For the last two methods fats have to be diluted because the concentration of crystal particles is too high. This requires a diluent which is miscible with the oil phase but will not affect the crystals. Certain aliphatic alcohols satisfy this requirement. Isobutanol was found satisfactory for most fats. Fats were dispersed in isobutanol and the diluted dispersions measured with a Spectrex laser particle size analyzer. Results will be presented for margarine and shortening fats giving crystal particle size distributions and polarized light micrographs. The validity of the procedure was established by analysis of the fatty acid composition of the crystals isolated from the isobutanol dispersions and the liquid oil separated from the fats.

L7

Seeding Effects on Solidification and Physical Behavior of Dark Chocolate. Iwao Hachiya, Meiji Seika Co., Food R&D Laboratories, 5-3-1, Chiyoda, Sakado, Saitama, Japan, and T. Koyano, Meiji Seika Co. and N. Sagi, Fuji Oil Co. and K. Sato, Hiroshima University.

The seeding effects of various fat crystals on the rate of crystallization, demolding property and fat blooming of dark chocolate were examined. The crystallization rate was measured with a rotational viscometer at the crystallization temperature of 30°C. The demolding property was evaluated at 15°C. The fat bloom stability was tested through temperature-cycles of 32°C/20°C and 38°C/20°C. The fat seed crystals of a mean dimension of 45 μm were pulverized with a cryo-mill below -60°C; the materials employed are CB (cocoa butter), SOS (1,3-distearoyl-2-oleoylglycerol), BOB (1,3-dibehenoyl-2-oleoylglycerol) and SSS (1,2,3-tristearoylglycerol). The effect of polymorphism was also examined. The results are summarized in the following. (a) All seed crystals accelerated the solidification rate in the following order; beta-1 (SOS) > Form VI (CB) Form V (CB) > mixture of pseudo-beta-prime and beta-2 (SOS) > beta-2 (BOB) > pseudo-beta prime (BOB) >> beta (SSS). (b) The seeds of Form VI of CB, beta-1 of SOS and beta-2 of BOB preferably crystallized Form V of cocoa butter in dark chocolate and, accordingly, revealed better demolding property. The seed of beta of SSS caused both worse demolding property and the fat bloom. (c) As for the anti-bloom stability, the seeding of Form VI of CB and beta-1 of SOS at 0.05-1.00 wt% seed concentration was effective in case of 32°C/20°C temperature cycle, but ineffective in case of 38°C/20°C cycle. However, beta-2 of BOB showed remarkable anti-bloom stability for the two temperature cycles. The 5 wt% addition of beta-2 of BOB completely prevented the fat blooming even by the 38°C/20°C cycle.

Session M Thursday afternoon

Mycotoxin Symposium II

M1

Aflatoxin in Cottonseed: Effect of Inoculum Strength on Toxin Levels in Individual Cottonseed. L.S. Lee, USDA-ARS-SRRC, 1100 Robert E. Lee Blvd., P.O. Box 19687, New Orleans, LA 70179.

Reports in the literature indicate an increase in aflatoxin associated with a decrease in inoculum size following inoculation of *Aspergillus flavus* onto autoclaved laboratory media. Similar results were obtained with living cotton bolls. Bolls on cotton grown on the grounds of SRRC were inoculated 30 days from flower with spores from serial dilutions of a water suspension of *A. flavus*. Inoculation was through wound sites that simulated exit holes made by pink bollworms. Five bolls were inoculated with the initial spore suspension and with the 3rd, 5th, 7th, and 9th dilutions. Bolls were harvested after an additional 30 days. Seeds in the inoculated locks were hand-ginned and assayed for aflatoxin. Results varied from lock to lock but toxin levels were consistently higher for locks receiving inoculum of less than 50 spores (9th dilution) than were detected in seeds from locks inoculated with the undiluted spore suspension that contained approximately 5×10^8 spores. Higher levels of toxins in seeds from bolls receiving the smallest inoculum may explain the extremely high levels of contamination of a few seeds from bolls naturally contaminated with *A. flavus*.

M2

Immunochemical Methods for Monitoring Aflatoxin Contamination in Animal Feeds. Douglas L. Park, University of Arizona, Dept. of Nutrition & Food Science, Tucson, AZ 85721, Sam M. Rua, Jr., Henry Njapau, and Karen Jorgensen, University of Arizona.

Four commercially available aflatoxin test kits based on immunochemical technology were used to monitor aflatoxin contamination on-site in whole cottonseed and mixed feed. Sample collection points included cotton gins, cottonseed oil pressing plants, ammoniation plants and dairy farms. The kits utilizing monoclonal antibodies to measure aflatoxin levels can be divided into two categories: enzyme-linked immunosorbent assay (ELISA) and affinity chromatography: Aflatoxin concentrations were determined on-site and in the laboratory using the test kits. The A.O.A.C. referee TLC method was used to confirm aflatoxin concentrations and identity. Alternative sampling and sample preparation devices and procedures were evaluated. There was 80% agreement, i.e., < or > 20 ng aflatoxins/g, between all test kit results as well as TLC values. The use of a reader, either on-site or in the laboratory, increased the number of correct responses, 77% versus 84%.

M3

Comparison of A.O.A.C. 'CB' TLC Method and Aflatest™ Method of Analysis of Aflatoxin Spiked Samples. Kevin F. Donahue, Vicam Corporation, 29 Mystic Avenue, Boston, MA 02145, and Mary Trucksess and Kathryn Young, FDA.

Until recently analytical methods for aflatoxin detection and measurement were based on time consuming classical chemical thin layer chromatographic methods. These methods involved the use of extraction and the partitioning of aflatoxin with hazardous organic solvents such as chloroform and benzene. The end result is obtained by subjective visual interpretation of TLC plates. Recent developments in antibody technologies have provided new and powerful tools for the analysis of grains, nuts, milk and other foodstuffs. These tools take advantage of the highly selective immuno-chemical properties of monoclonal antibodies developed to specifically recognize aflatoxin and its derivatives. The affinity chromatographic approach makes possible a rapid (5-10 minutes) one-step clean up procedure of sample extracts. Measurement of the separated aflatoxins can then be made by direct fluorometry or by HPLC analysis. The affinity column approach also allows the use of safer and more economical extraction using only methanol and water. In this study the monoclonal antibody affinity column methods were compared to an established and generally accepted thin layer chromatographic method. Identically prepared sets of 50.0 gram aflatoxin spiked and naturally contaminated corn, peanut meal and peanut butter samples were distributed to two laboratories. The spiked samples were spiked with a mixture of aflatoxins B1, B2 and G1 dissolved in a small volume of chloroform. All the samples were in the range of 0 to 50 ppb total aflatoxins. The FDA laboratory analyzed the samples by the A.O.A.C. approved 'CB' TLC method. In the Vicam laboratory the samples were prepared by the Aflatest™ monoclonal affinity column method and aflatoxin concentration was determined by both direct fluorometric measurement and by reverse phase HPLC. The analyses proved the affinity column methods to be comparable with the 'CB' TLC method. The correlation coefficients between the TLC method compared to the affinity column method with direct fluorometric measurements and HPLC analysis were both 0.997 for the peanut butter samples. The correlation coefficient of the Aflatest™ direct fluorometric results vs. the Aflatest™ HPLC analysis was 0.987. The correlation of the aflatoxin spiked into the peanut butter samples and the amount detected by the Aflatest™ fluorometric method was 0.995. The correlation coefficients ranged between 0.97-0.999 for comparison between the two laboratories for the corn and peanut meal samples. The performance of the faster, more economical Aflatest™ methods demonstrates that they are a viable alternative to the accepted 'CB' TLC method.

M4

Aflatoxin Decontamination in Peanuts Using Water Flotation: A Process Study. James C. Henderson, Procter & Gamble, 6071 Center Hill Road, Cincinnati, OH 45224, and William Hagen, Procter & Gamble.

A patented process to separate aflatoxin-contaminated peanuts from uncontaminated peanuts will be demonstrated by video tape. Contaminated peanut lots taken through the process, from incoming raw peanuts to peanut butter in the jar, will be analytically profiled. Data from three analytical procedures will be presented: 1) Aflatest™ affinity column chromatography, 2) thin-layer chromatography (TLC), and 3) high performance liquid chromatography (HPLC) with post-column iodine derivatization.

Session N Thursday afternoon

Pharmacological Effects of Lipids and Proteins

N1

Fatty Acyl-CoA Reactions Involved in Sex Pheromone Biosynthesis in the Housefly. A.H. Vaz, University of Nevada, Dept. of Biochemistry, Reno, NV 89557, and G.J. Blomquist and R.C. Reitz, University of Nevada.

(Z)-9-Tricosene (23:1 hydrocarbon [Hy]) is the major sex pheromone component of the matured female housefly. The biosynthesis of this sex pheromone occurs by the elongation of oleoyl-CoA (18:1-CoA) to 24:1-CoA which is then converted to 23:1 Hy. The chain length specificities of the elongation reactions were examined, and it was shown that microsomal preparations from males and previtellogenic females elongate 18:1-CoA, 22:1-CoA and 24:1-CoA to all even numbered fatty acids (FA) to 30:1 FA, whereas microsomes from matured females do not elongate efficiently beyond 24:1 FA. We next examined the effect of 20-hydroxyecdysone (20-HE) on the chain length specificity of the elongation reactions. The ratio of the 24:1 to 26:1 FA formed from the elongation of 18:1-CoA was about 3 fold greater in the 20-HE treated males compared to the non-treated males. Lastly we examined the conversion of 24:1-CoA to 23:1 Hy. Only matured females formed 23:1 Hy. Thus, these data suggest that in the housefly the hormone 20-HE regulates the chain length specificity of the fatty acyl-CoA elongation reactions and the conversion of 24:1 FA to 23:1 Hy.

N2

Differences in Polyisoprenoid Metabolism in 1- and 24-month Old Mouse Kidney and Liver. Dean C. Crick, University of Western Ontario, Dept. of Biochemistry, London, Ontario N6A 5C1, Canada.

Dolichol has been shown to accumulate with senescence in a variety of organisms and tissues. This phenomenon was investigated using tritiated water to label mouse dolichol and its phosphorylated form (Dol-P) *in vivo*. An improved procedure for extraction of Dol-P was developed, involving saponification of the tissue to convert dolichol acyl esters and complex phosphorylated forms to free dolichol and Dol-P. Total cholesterol and dolichol were extracted from a 45% KOH saponification mixture which was then diluted to 15% KOH thus facilitating the extraction of Dol-P. Results show that there are age-associated changes in the pool sizes of cholesterol, dolichol and Dol-P in mouse tissues as well as changes in dolichol and Dol-P metabolism. The cholesterol content of kidneys (per g of tissue) was 4-fold lower in older animals while the amount of cholesterol/g liver remained constant. The dolichol content of both

tissues increased 2-fold. The amount of Dol-P in kidneys increased 7-fold over 23 mo., while the concentration in liver decreased from 4.5 μg/g to undetectable levels. Metabolic labelling experiments using tritiated water demonstrated that the rate of synthesis of total dolichol (dolichol + Dol-P) in the kidneys did not change as a function of age. However, the kidneys of young mice incorporated 3 times more radioactivity into dolichol than Dol-P, whereas old mice incorporated more radioactivity into Dol-P. In liver, the rate of dolichol synthesis decreased 2-fold over 23 mo. The rates of synthesis of Dol-P in livers of young and old mice were not compared as Dol-P was undetectable in livers from older animals, even though the [1-^{14}C]Dol-P tracer was recovered in good yield. The data indicate that the metabolism of dolichol and Dol-P is independently regulated in different tissues and that the major age-associated change in dolichol metabolism may be an alteration of the balance between dolichol kinase and dolichyl phosphate phosphatase activities. The extent to which these age-associated changes affect the enzymes associated with N-linked protein glycosylation is currently under investigation.

N3

Dietary Fat and the Phospholipid Molecular Species of Rat Photoreceptor Membranes. Rex D. Wiegand, Cullen Eye Institute, Baylor College of Medicine, One Baylor Plaza, Houston, TX 77030, and Ann Stinson, Cynthia A. Koutz, and Robert E. Anderson, Cullen Eye Institute, Baylor College of Medicine.

We have examined the relationship between dietary fatty acids and their transport and incorporation into rod outer segment (ROS) phospholipids (PL) of rat retina. Female weanling rats were fed diets containing either 10% (wt/wt) hydrogenated coconut oil (HCO), safflower oil (SO), or linseed oil (LO) for four months. Phosphatidylcholine, phosphatidylethanolamine, and phosphatidylserine were isolated from ROS and the fatty acids and molecular species (MS) determined. Plasma lipid profiles were also examined. We found: 1) ROS PL MS from the SO group showed a selective replacement of 22:6(n-3) with 22:5)(n-6) compared with the HCO and LO group. 2) ROS PL MS from the HCO and LO groups were similar, even though the HCO diet contained no polyunsaturated fatty acids (PUFA), indicating the retina conserves PUFA, especially 22:6(n-3). 3) Plasma lipid classes from the HCO, SO and LO groups were enriched in 20:3(n-9), 20:4(n-6), and 20:5(n-3), respectively. These PUFA were apparently not taken up and incorporated in ROS PL MS since the levels of these 20-carbon PUFA were not elevated in ROS. Our data suggests that the retina has mechanisms to selectively remove 22-carbon PUFA from circulation for ROS PL synthesis.

N4

Conversion of *trans* Octadecadienoic Acid Isomers to Isomers to *trans* Arachidonic Acid in Mice. E.C. Beyers, Illinois State University, (temporary address) USDA-ARS-NRRC, 1815 N. University St., Peoria, IL 61604, and E.A. Emken, USDA-ARS-NRRC.

Groups of mice were fed fat-free, semi-purified diets supplemented with 2% by weight of dideuterated *cis*-9, *cis*-12-octadecadienoic acid (c,c-18:2-d_2), *cis*-9, *trans*-12-octadecadienoic acid (c,t-18:2), and tetradeuterated *trans*-9, *cis*-12-octadecadienoic acid (t,c-18:2-d_4). Mice from each diet were sacrificed on days 2, 3 and 4. Total lipids from liver, heart, plasma, and brain were analyzed by gas chromatography and gas chromatography-mass spectroscopy. Liver data indicated that the overall conversion rate for c,t-18:2 to a "c,t"-20:4 isomer was nearly the same as the rate of conversion of c,c-18:2-d_2 to 20:4-d_2. The conversion rate for 9t,12c-18:2 isomer to "t,c"-20:4 was about 10 times lower. Data for the metabolic intermediates indicated that compared to c,c-18:2-d_2, c,t-18:2 was preferentially desaturated and t,c-18:2-d_4 was preferentially elongated. In fact, elongation of 6c,9c,12t-18:3ω6 to 8c,11c,14t-20:3ω6 was identified as the rate-limiting step involved in the formation of "c,t"-20:4 rather than the delta-6 desaturase step. The t,c-18:2-d_4 isomer was a poor substrate for delta-6 desaturase, and the main metabolic product formed was the "dead end" elongation product, 11t,14c-20:2-d_4. The amount of the "c,t"-20:4 isomer incorporated into heart lipids was 2-3 times higher than for 20:4-d_2. The amount of t,c-18:2-d_4 in brain lipid was 3-5 times greater than for c,t- or c,c-18:2-d_2, but incorporation of 20:4-d_2 was ca. 3 times higher than for "c,t"-20:4 and ca. 15 times higher than for "t,c"-20:4. These results indicate that the double-bond configuration of 18:2 has a major effect on desaturase, elongase and acyltransferase rates. The facile conversion of c,t-18:2 to "c,t"-20:4 suggests c,t-18:2 may have biological importance because its "c,t"-20:4 metabolite may influence prostaglandin metabolism or be converted to a biologically active prostaglandin or leukotriene isomer.

N5

Membrane Cholesterol in Novikoff Hepatoma Cells and its Effect on Gap Junction Formation. Barbara Malewicz, Hormel Institute, University of Minnesota, 801 16th Avenue, N.E., Austin, MN 55912, and Rita A. Meyer, Ross G. Johnson, and Wolfgang J. Baumann, University of Minnesota.

Gap junctions (GJ) are important regulators of cellular function. Gap junctions control the transmission of stimuli and the transfer of metabolites between cells, and they have been implicated in numerous cellular processes including the regulation of cell growth and cell differentiation as well as carcinogenesis. Although gap junctions assemble and function in the lipid milieu of the plasma membrane, there is a paucity of information on GJ lipids and on the role of lipids in GJ assembly and function. We now have gathered evidence that gap junction assembly and function is influenced by cholesterol. Novikoff hepatoma cells were enriched with cholesterol in their plasma membrane and GJ assembly and function were followed by freeze-fracture electron microscopy and dye injection, respectively. A 4-fold increase in cell cholesterol did not alter cell growth or phospholipid synthesis. However, up to a 50% increase in plasma membrane cholesterol increased the number of GJ aggregated particles up to 6-fold, whereas GJ plaque size doubled. Higher cholesterol levels inhibited the formation of functional junctions. Our data supports the concept that a modest increase in cell membrane cholesterol induces junction formation, whereas excessive cholesterol levels impede the assembly of gap junctions.

N6

Disproportionations Among the Fatty Acids of Plasma Lipids in Human Disease. Ralph T. Holman, University of Minnesota, The Hormel Institute, 801 16th Avenue, N.E., Austin, MN 55912.

The patterns of polyunsaturated fatty acids (PUFA) in plasma lipids of patients suffering from a variety of diseases have indicated that in many diseases there are deficiencies of individual PUFA or groups of them. In these instances, the PUFA appear to be replaced by increased saturated and monounsaturated fatty acids. Closer examination of the patterns of individual saturated and monounsaturated fatty acids reveals that disproportionations among short- to long-saturated fatty acids also occur in some diseases and in some lipid classes of plasma. These phenomena will be shown and discussed.

N7

Pilot Study of HDL Compositional Differences in USSR and U.S. Men. Frank T. Lindgren, University of California, 315 Donner Lab, Berkeley, CA 94720, and Alex V. Nichols, Ronald M. Krauss, and G. Adamson, University of California, Peter D. Wood, Stanford University, and John J. Albers, Anatoly Klimov, and R. Oganov, University of Washington.

A collaboration involving Leningrad and Moscow (USSR) middle-aged males (each n=21) and two Stanford exercise and weight control entrant male groups (n=21) matched on high density lipoprotein cholesterol (HDL-C) was studied for major lipid and lipoprotein parameters. This was to resolve reported discrepancies regarding a negative relationship (U.S.) and no relationship (USSR) between HDL-C and coronary heart disease mortality. Mean HDL-C for the Leningrad group was 62 and for the Stanford group 60 mg/dl. The Leningrad mean total cholesterol values were 226 and for Stanford 223 mg/dl; triglyceride values were 107 for Leningrad and 102 mg/dl for Stanford. Analytic ultracentrifugation (AnUC) revealed significantly higher concentrations ($p<0.05$) in HDL_2, and more significantly lower concentrations ($p<0.01$) of the smaller HDL_3 for Leningrad. HDL_3 values for Leningrad and Stanford matched controls were 215 and 260 mg/dl, respectively, whereas HDL_2 values were 100 and 72 mg/dl, respectively. These findings were confirmed by gradient gel electrophoresis A similar study was made of the Moscow males (n=21). Mean HDL-C for both Moscow and Stanford was 56 mg/dl; triglyceride levels were 80 and 87 mg/dl, and total cholesterol was 222 and 213 mg/dl, respectively. Both mean body mass index and ages were essentially identical in Leningrad, Moscow and the matching Stanford populations, 25.1-25.6 kg-height^{-2} and 48.6-49.7 years. Also, the Moscow males had significantly lower HDL_3 type ($p<0.001$); however, the HDL_2 concentrations, although higher, did not reach significance. HDL_3 values for Moscow and Stanford controls were 221 and 268 mg/dl, respectively, whereas HDL2 values were 91 and 81 mg/dl, respectively. The mean wt% composition of cholesterol to total AnUC-determined mass was 17.7% for Leningrad, 17.9% for Moscow, but less for Stanford, namely 16.3% for the Leningrad match and 16.0% for the Moscow match. These data are consistent with a lower content of HDL3 in Russians compared to the Stanford matched groups. These findings suggest HDL size, apolipoprotein, and possible compositional differences in USSR males compared with matched U.S. males.

Session O Friday morning

Surfactants & Detergents III: Cosmetics & Toiletries

O1

Soap Production Via Fatty Acid Methylesters. Giovanni Franco Moretti, Ballestra S.p.A., Via Fantoli, 21/17, Milano 20138, Italy, I. Adami and C. Mazzanti, Ballestra, S.p.A.

The production of soap via fatty acid methylesters is described by discussing some topics concerned with processing as well as with product characteristics and performances. Besides the saponification step, the production of methylesters from triglycerides by ester-inter-change reaction and the glycerine recovery and refining are illustrated, to give a wide outlook on the whole production route. More in detail, for each of the above mentioned section of the process, the following points are emphasized: 1. process description and scheme; 2. operating conditions; 3. raw materials and utilities consumptions; 4. product characteristics; 5. overall advantages; 6. technical and economical comparison with corresponding traditional processes.

O2

The Use of Mild Surfactants in Soap Bars. John A. Hockey, Lever Bros. Research & Development Ctr., 45 River Road, Edgewater, NJ 07020, and Joan Barrows, William Becker, Richard Murahata, Paul Shark, and Alan P. Greene, Lever Research, and Darcee Duke Strube, Consultant.

Traditionally, soap has been the surfactant of choice for use in the formulation of washing bars. Synthetic surfactants, or "syndets", have seen limited use in specialized products, particularly as a means by which to deliver skin care benefits. It is expected that the demand for such products will grow, in conjunction with the aging of the population, and the heightened awareness of skin problems, such as irritation and dryness, resulting from the use of the traditional soap bars. Although the irritation potential of soap can be somewhat alleviated by the incorporation of additives, the delivery of a significant and perceivable skin care benefit can best be provided by the formulation of bars with synthetic surfactants, or with blends of soap and synthetic surfactants. In this paper the formulation of soap bars which incorporate synthetic detergents, and which deliver measurable skin benefits to the consumer, will be discussed. The use of laboratory screening methods to achieve the desired biophysical properties will be reviewed, and the results of the screening procedures compared to larger scale clinical methods of analysis. Finally, the results of paired comparisons of traditional "soap" products and products formulated with "syndets" using both objective and subjective methods of analysis, will be presented.

O3

New Acylamino Acid Compound for Cosmetic Formulations. Kazutami Sakamoto, Ajinomoto U.S.A., Inc., Glenpoint Centre West, 500 Frank W. Burr Blvd., Teaneck, NJ 07666-6894, and Jon Packer, Centerchem, Inc.

A wide range of N-Acylamino Acids have been synthesized and their properties evaluated, exploring potential commercial applications. This work has led to identifying N-epsilon-Lauroyl Lysine as an excellent candidate for cosmetic applications. This compound was prepared by selective acylation of the epsilon-Amino group in L-Lysine. The resulting material has been studied and previously reported by Sagawa et al (1) IFSCC (1986) Barcelona, Spain. where its properties in terms of spreadability (coefficient of friction), adhesive power, water repelency, pH buffer capacity and antioxidative activity were elucidated. The safety of this material was also presented and shown to be well suited for cosmetic use. The insolubility in both polar and non-polar solvents was stated to suggest its possible use as a cosmetic powder ingredient. Application work since that time strongly supports the value of N-epsilon-Lauroyl-Lysine in cosmetic formulation. The unique crystal structure and surface properties result in a highly esthetic material with excellent compaction characteristics. Pressed powder formulations have been prepared with exceptionally creamy textures, superior application and blending characteristics and enhanced wear properties. Additional work also suggests its use in liquid make-ups, under make-up foundations, facial and body moisturizing products and loose powder compositions. This paper will highlight relevant characteristics and discuss application and formulation strategies for this exciting, new cosmetic raw material.

O4

A New Series of Improved Polyglycerol Esters. Victor Landeryou, Lonza, Inc., Res. & Dev., 3500 Trenton Avenue, Williamsport, PA 17701-0187, and Larry Hall and Joel Rogelberg, Lonza, Inc.

A series of polyglycerol esters with generally higher HLB values has been prepared. These materials show exceptionally good color, odor and taste. The properties and physical characteristics of these improved polyglycerol esters will be discussed. Some compatibility data will be presented. More importantly, the discussion will focus attention on cosmetic use benefits such as emulsification, thickening, foaming and foam alteration.

O5

Triglycerides as Primary Emollients in Commercial Skin Care Products. Branko Sajic, Stepan Company, 22 West Frontage Road, Northfield, IL 60093.

In our continuing effort to study new raw materials and their possible applications, triglycerides have emerged as primary emollients in commercial skin products. This presentation will discuss specific points of interest such as preparation, manufacturing, applications, physical and chemical properties. Some excellent performance benefits in skin care applications have been found. What makes this chemical class of compounds attractive to the formulating chemist will be discussed including safety, stability, availability, formulating ease, biodegradability and comedogenicity.

O6

Alkyl Polyglycosides: A Natural for the Personal Care Industry. J.R. Varvil, Henkel Corporation, 2200 E. Eldorado Street, Decatur, IL 62525, and R.A. Aleksejczyk, Henkel Corporation.

Alkyl polyglycosides are mild, biodegradable, yet effective surfactants. These qualities make alkyl polyglycosides a natural for the personal care industry. As a nonionic, the glycoside molecule functions with common anionics in shampos and hand soaps to clean and condition. Lathering tests show alkyl polyglycosides perform as well as other common surfactants used for conditioning and mildness. Alkyl polyglycoside surfactants, in shampoo formulations, compliment salt viscosity building effects even without alkanol-amides, in some cases. Alkyl polyglycosides exhibit flexibility and compatibility with common conditioning ingredients, including cationics. In addition, alkyl polyglycosides are derived from natural renewable resources. The personal care industry can now realize the advantages offered by the alkyl polyglycosides molecule.

O7

Hydantoin Based Preservative/Surfactants. Daniel W. Lemke, Lonza, Inc., 3500 Trenton Avenue, Williamsport, PA 17701, and Larry K. Hall, Lonza, Inc.

A new and unique family of dual-performance (preservative/surfactant) compounds has been prepared. Their physical data, surfactancy properties (i.e., cmc, G_{cmc}, and preparation of various emulsions and dispersions), and biological activity against yeast, mold, and three types of bacteria have been determined. The performances of these compounds are compared to other structurally similar preservatives and surfactants.

O8

Multi-Functional Role for Lauricidin. Jon J. Kabara, Lauricidin, Inc., 414 Green Street, Galena, IL 61036.

Originally discovered as an antibacterial and antiviral lipid, Lauricidin, glyceryl monolaurate, has been shown to have unique multi-functional properties. This highly purified monolaurin can function as an emulsifier, emollient, thickening agent, deodorant, transdermal agent, as well as a preservative/germicide. All of these functional activities are achieved with a chemical which has no toxicity. The FDA considers monoglycerides of edible fatty acids as Generally Regarded As Safe (GRAS). As an emulsifier, Lauricidin is superior to other glyceryl monolaurates commercially available. Data will be presented which shows that Lauricidin forms O/W emulsions which have smaller and more uniform particle size. Emulsions therefore are more stable and easier to preserve. The presence of a chelator in the formula often yields a product where no other preservative is necessary. In addition to the above effects Lauricidin as a penetrating enhancer in transdermal applications will be discussed.

Session P Friday morning

Nutrition as a Basis for Value-Added Products from Oilseed Proteins

P1

Identification of the Chemical Form of Selenium in Soybeans. April C. Mason, Purdue University, Dept. of Foods & Nutrition, West Lafayette, IN 47907, and Rosemary Rodibaugh, Purdue University.

Soybeans provide a high quality economical source of vegetable protein that is being used in many new food formulations. When using soybean as the protein source in diet formulas, it is important to evaluate its nutrient content. Selenium is a trace mineral essential in human and animal nutrition. Selenium functions in the antioxidant glutathione peroxidase enzyme system. The selenium content of soybeans is variable, dependent on selenium levels in the soil where crops are produced. The majority of selenium in soybeans is associated with protein. In hydroponically grown, ^{75}Se-selenium intrinsically labeled soybeans, over 80% of the radiolabel was associated with protein. The 11s and 7s storage proteins contain the greatest amount of selenium of the extractable soybean proteins. Purified 11s and 7s proteins have been carboxymethylated to protect the sulfur and selenium containing amino acids, acid hydrolyzed and subjected to amino acid analysis. Results indicate that selenomethionine is the predominant form of ^{75}Selenium labeled amino acid. These results show that the major storage proteins of soybeans could be a good source of selenium and have potential as a source of selenium for human food purposes.

P2

Effect of Phytate on Mineral Bioavailability. Connie M. Weaver, Purdue University, Dept. of Foods & Nutrition, West Lafayette, IN 47907.

Phytic acid, the storage form of phosphorus in plants, has long been associated with mineral binding. Addition of phytic acid to human and animal diets reduces zinc absorption in humans and animals who lack phytase. To study the effect of phytase on mineral absorption from soybeans, plants were grown hydroponically in nutrient culture with different levels of phosphorous to produce seeds with a range in phytic acid concentration. Seeds were also labeled with radioisotopes of calcium, iron, or selenium, the level of phytic acid in soybean seeds produced little effect on absorption of these three minerals in rats. Thus, the adverse effect of phytic acid on zinc bioavailability does not appear to hold true for other minerals.

P3

The Positive Effects of Phytic Acid on Fe and Cu Bioavailability: An Interaction Story. Dennis T. Gordon, University of Missouri-Columbia, Dept. of Food Science & Nutrition, 122 Eckles Hall, Columbia, MO 65211.

Phytic acid, myo-inositol hexakisphosphate, the phosphorous storage compound in cereals and oilseeds has been implicated as impairing Zn bioavailability in animals and humans. However, from an overall perspective, the ingestion of phytic acid in foods should not be considered antinutritional. More recent research has shown that phytic acid will enhance the bioavailability of both Fe and Cu. The action of phytic acid on the bioavailabilities of Fe, Zn and Cu represents a classic example of nutrient interactions as affected by a dietary component. The major reason phytic acid can affect Fe, Zn and Cu bioavailabilities is because of the similar chemical properties of these elements. The mechanisms in the intact animal and at the cellular level to explain these interactions will be presented. Based on more up-to-date nutrient interaction studies, phytic acid should be viewed positively as a dietary component regulating not impairing nutrient bioavailability.

P4

A Comparison of the Effects of Dietary Casein and Cottonseed Isolate on the Serum Lipids of Normal and Tumor-bearing Rats. John D. Radcliffe, Texas Woman's University, 1130 M.D. Anderson Blvd., Houston, TX 77030.

In comparison to dietary casein, cottonseed isolate, when fed at an isonitrogenous level, is hypolipidemic in normal Fischer 344 fats, with animals fed the cottonseed isolate having lower serum levels of cholesterol, triacylglycerol and total lipids than those fed casein. When Fischer 344 rats are implanted with a transplantable methylcholanthrene-induced sarcoma known to induce severe hyperlipidemia, the lipid-lowering effect of dietary cottonseed, vis-a-vis casein, is abolished; moreover, serum lipids are higher in tumor-bearing rats fed the cottonseed isolate than in those fed casein. Thus, the influence of dietary protein quality on serum lipids is altered by the presence of neoplastic disease.

P5

Effects of Dietary Animal and Plant Proteins on Plasma Amino Acid Concentrations, Insulin and Glucagon Concentrations in Non-Diabetic and Streptozotocin-Diabetic Rats. Mija Lee, Texas Woman's University, P.O. Box 24134, TWU Station, Dept. Nutrition & Food Science, Denton, TX 76204, and Nancy DiMarco, Texas Woman's University and Balachandra Kudchodkar, University of North Texas.

Dietary source of protein was found to affect the levels of glucose in diabetic rats. Hepatic uptake of plasma amino acids plays a major role in gluconeogenesis, which in turn is modulated by hormones. This study examined the effect of dietary protein [Casein (CAS) vs soybean protein (SOY)] on plasma amino acids and hormone levels in diabetic and non-diabetic (ND) rats. Diabetes increased plasma glucose levels in both groups but the levels were considerably higher in [SOY] fed animals (SOY: 242+29 mg/dL vs CAS: 180+30 mg/dL). In diabetic rats fed casein, total amino acid levels were increased 20%, but were slightly decreased in those fed soybean. The changes were mostly due to changes in glucogenic and ketogenic amino acids. Diabetes did not significantly affect the fasting plasma insulin levels in both dietary protein groups. Fasting plasma glucagon levels on the other hand were significantly increased in (DIAB) rats fed [SOY]. [ND: 166+13 pg/mL vs DIAB: 347+43 pg/mL].

Dietary casein had no significant effects on the plasma glucagon levels in diabetic rats. These data suggest that in diabetic rats, dietary soybean protein has a marked effect on the secretion of glucagon which in turn may stimulate the uptake of gluconeogenic and ketogenic amino acids by liver which may result in increased levels of glucose.

P6

Effects of Dietary Protein on Metabolism of LDL APO B in Rabbits. Samir Samman, University of Western Ontario, Dept. of Biochemistry, London, Ontario N6A 5C1, Canada, and Pramod Khosla and Kenneth K. Carroll, University of Western Ontario.

Rabbits fed semipurified diets containing casein have elevated plasma cholesterol levels compared to those fed soy protein. As part of ongoing studies on the mechanism of casein-induced hyper-cholesterolemia, 2 groups of 6 rabbits were fed these diets for 14 to 16 weeks. Low density lipoproteins (LDL) of animals fed the casein diet were foiund to have significantly higher cholesterol, triacylglycerol, phospholipid and apolipoprotein B (apo B) concentrations compared to the particles isolated from soy protein-fed animals. Kinetic studies showed that the fractional catabolic rate of LDL-apo B was significantly lower in animals fed casein compared to those fed soy protein (0.023 vs. 0.079 pools/hr; $P<0.05$) regardless of whether the tracer LDL was obtained from donors fed casein or soy protein. The production rate of LDL-apo B tended to be higher in casein-fed animals. These results show that the efficiency of removal of LDL is reduced in animals fed casein compared to those fed soy protein and that the source of LDL has no effect on the efficiency of its subsequent removal. The accumulation of LDL in casein-fed aninals is consistent with the down-regulation of the LDL receptor.

P7

Protein and Co-products Invited Lecture. David Kritchevsky, Wistar Institute, 36th and Spruce Street, Philadelphia, PA 19104.

Abstract not available at press time.

Session Q Friday morning

Oilseed Processing: State-of-the-Art

Q1

Drying of Soybeans and Making Use of the Effect for the Dehulling. W. Fetzer, Buhler Brothers Ltd., Dept. DM-4, Uzwil CH-9240, Switzerland.

In the conventional front dehulling of soybeans, seed dryers are required to reduce the moisture content to 9% to 10.5% depending on the seed properties. The mechanics of seed drying is discussed and shown, that a modified drying process makes it possible to dehull soybeans at a higher moisture level. Instead of the conventional seed dryer this system features a conditioning column combined with fluidbed technology. Instead of drying the whole soybean, the surface is dried only. If conditions require the system is designed to have a drying to a requested level mode. The conditioned soybeans are subjected to hot air in a fluid bed. Since the soybeans are already conditioned at the inlet of the fluid bed only one minute retention time in the fluidbed is required. The short heat treatment in the fluidbed does hardly reduce the water solubility index of the protein which is of great importance for the production of white flakes.

Q2

Microscopic View of Why the Expander Improves Extractability. Leslie Watkins, Texas A&M University, Food Protein Res. Center, F.M. Box 183, College Station, TX 77843.

The addition of an expander step to the soybean extraction process improves extractibility and reduces the overall energy requirements. Microscopic photos illustrate accomplishment not normally visible and explain reasons for lower residual oil and residual hexane in meal. Effects of expanders on oil quality and energy as well as capacity will be examined.

Q3

Automated Computer Moisture Control of Commercial Dryers. Peter L. Douglas, University of Waterloo, Dept. of Chemical Engineering, Waterloo, Ontario N2L 3G1, Canada, and Gerry Sullivan, University of Waterloo and Mike Whaley, Dantec Electronics Ltd.

The control of outlet moisture in many drying operations is essential to the satisfactory operation of the dryer to produce a quality product. The control of moisture is often performed using experienced operators to adjust throughput, temperature and other operating conditions to achieve a desired result. The continuous sensing of moisture coupled with computer control of a dryer can have a dramatic impact on throughput, quality and energy consumption. This paper outlines the key issues surrounding continuous moisture measurement and automatic dryer control for commercial drying units. A novel and commercially successful dryer control system will be discussed. Results of manual and computer controlled dryers will be presented to illustrate the economic benefits of computer controlled dryers.

Q4

Theory and Practice in Designing of Flakers. W. Fetzer, Buhler Brothers Ltd., Dept. DM-4, Uzwil CH-9240, Switzerland.

As long as the modern oil milling industry is existing, flakers are used for the seed preparation. The design of these flakers are based on experience made in the actual field of application. This paper discusses the theoretical aspects of the engineering of flakers and compares the various solutions today applied in the practice. But also the influence of the seed preparation and the installation of the flakers are shown. Based on these facts conditions are listed that a modern flaker should comply with in order to reduce maintenance costs and to minimize the danger of roll damages. A new design of flakes is introduced which features new ideas to forestall the most common problems of flakes.

Q5

The Vegoil Expander - How it is Used to Improve Extractability of Oilseeds Material. Maurice Williams, Anderson International, 6200 Harvard Avenue, Cleveland, OH 44105.

The use of expanders as a means of improving the extractability of oilseed materials is becoming more and more popular in the vegetable oil industry. In existing solvent extraction plants the addition of expanders can, for a modest capital investment, significantly increase plant capacity, or increase plant efficiency at the same capacity, or correct for persistent processing problems, such as poor quality flakes or crumbly pre-press cake. Usually a combination of all three is achieved. For a new solvent extraction plant, the use of expanders can allow for the selection of a smaller sized, and less expensive, extractor system. This paper describes the Expander: How it works on several different kinds of oilseed materials describing preparation, expansion, and post-expansion treatment of the oilseeds and describing the kinds of benefits and improved efficiencies attainable by expansion.

Q6

Factors Influencing the Pyrophorisity of Spent Bleaching Clay. Dennis B. Jenkins, Engelhard Corporation, P.O. Box 877, 6177 Sunol Blvd., Pleasanton, CA 94566, and Dennis R. Taylor, Engelhard Corporation.

Pyrophorisity of spent bleaching clay is a multi-stepped process involving a first-stage low-temperature spontaneous heating, a second-stage high-temperature spontaneous combustion and, in some cases, flaming combustion. In the interest of reducing the risk of pyrophorisity, a study was undertaken to determine the effects of filter cake variables on pyrophorisity. Since the first-stage spontaneous heating initiates pyrophorisity, the study focused on variables which promote or inhibit this first-stage reaction. The variables investigated were oil type, clay type, oil retention, moisture content, carbon content, cake age, and antioxidant content. Two types of test were used to measure spontaneous heating: 1) Differential Scanning Calorimetry was used to measure fundamental thermal responses (heat of reaction, onset temperature and peak temperature) and, 2) A constant-temperature fixed-interval spontaneous heating (CaTFISH) test was used to measure an empirical response (minimum reaction temperature). Using a factorial experimental design, fundamental and empirical screening studies were performed to eliminate insignificant variables. The screening studies reveal that clay type, oil retention, moisture, carbon, and antioxidant content significantly affect spontaneous heating. Based on this information, significant variables were tested in more detail using the empirical CaTFISH test. Results show that an increase in antioxidant content reduces the risk of pyrophorisity. The response surface of moisture and oil retention shows that an increase in filter cake moisture consistently reduces the pyrophorisity risk. The response surface also displays a pyrophorisity-risk maximum for oil retention in the intermediate range.

Q7

Alternative Preparation Methods Utilizing the Extruder. Robert Pavlik, French Oil Mill Machinery Co., P.O. Box 920, Piqua, OH 45356, and Tim Kemper, French Oil Mill Machinery Co.

Several methods have been developed by manufacturers to replace the traditional soybean preparation process. Until recently these did not include the extruder. However, the extruder is gaining acceptance in soybean preparation. This paper examines the use and benefits of the extruder as an addition to the preparation process and its use in completely new process methods. By looking at the overall preparation process for ways to simplify and improve it, a new preparation method has been researched and a patent applied for. Operating data and results will be presented.

Q8

Extraction of Soybean Oil from Fine Soy Flour. Cinping Nieh, University of Arkansas, Dept. of Food Science, Fayetteville, AR.

Soybean oil was extracted from fine full fat soy flour in a countercurrent extraction system using several stages with centrifugal separation. Oil in fine flour was very easily dissolved by hexane with only a couple of minutes required to reach the equilibrium. However, due to the hold-up volume (about 100% of the defatted meal), the separation of miscella from the meal required several stages to finish. The actual extraction amounts were close to what we expected by calculation. Five stages of extraction were required to reach a 25% final miscella with the initial flour containing 22.35% oil and less than 1% residual oil left in the defatted meal. Because of the hold-up volume and to reduce the number of stages, a second solvent was applied after the initial hexane extraction. The second solvent was 50% aqueous ethanol (v/v) which has a higher density than the hexane miscella. Using a second solvent, we found that not all the hexane miscella had been displaced. There was considerable residual oil left in the meal. To determine where the residual oil was, a dye, beta-carotene, was mixed into the hexane used to extract the flour. After washing with the second solvent, a reddish yellow defatted meal indicated that the residual hexane miscella was trapped inside the flour particles and could not be displaced by the second solvent. Using the second solvent it was still possible to add hexane after centrifugal separation and to do a second stage hexane extraction in the presence of the water ethanol mixture. In the presence of the second solvent only two hexane extractions were needed to decrease residual oil to 1%.

Session R Friday morning

Value-Added Feed Products from Protein and Co-Products: Changing Resources and Needs

R1

Co-Products from Wet Corn Milling as Animal Feeds. Jerry C. Weigel, Archer Daniels Midland Co., P.O. Box 1470, Decatur, IL 62525.

Feed ingredients derived from corn wet milling vary widely in composition and properties. The four feed prod-

ucts derived from the wet milling process are: 1) corn gluten feed, 2) corn gluten meal, 3) corn germ meal, 4) corn steep liquor. These feed products have specific properties that allow their use in all phases of animal production. Product usage and specifications have changed dramatically over the past year as more knowledge has been gained about the properties and performance of each of these ingredients in diets for different species and classes of livestock. Recent data demonstrated unique properties of each of these ingredients when compared to conventional feeding regimes (cereal grains, silages, soybean meal, animal proteins, etc.). Research is continuing to find more uses for the co-products from the corn wet milling industry.

R2

Rice Bran as a New Feedstuff. Wallace W. Migura, Uncle Ben's, Inc., P.O. Box 1752, Houston, TX 77251-1752.

Rice bran, the by-product of the husked rice kernel consisting of the outer bran layers and the germ, has been used primarily as an animal feed ingredient for the duration of the rice industry in the U.S. because of the fat instability of non-parboiled rice bran, the high ash content of parboiled rice and the relatively low commodity volume. Its unsuitability as a food item has made rice bran suitable as a feed ingredient because of its quality protein and high fat content. Rice germ is normally sold domestically under a 12-12-12 guarantee, minimum 12 percent each protein and fat and maximum 12 percent fiber. Non-parboiled bran is normally 12-13 percent protein, 15-17 fat and minimum 10 percent free fatty acid (FFA). Parboiled rice bran is 16-17 percent protein, 22-24 percent fat and 2-4 percent FFA. Bran is normally sold "as is" or mixed with high-roughage rice hulls in approximately a 2/3:1/3 hulls:bran mix, which is called rice mill feed. Recent developments in rice bran stabilization allow inactivation of rice bran lipase and subsequently lower FFA values, resulting in a higher quality non-parboiled rice bran. Defatting of rice bran introduces a new feed ingredient. Defatted parboiled rice bran contains approximately 22 percent protein, with a P.E.R. of 0.9-2.1 and a fat content of 1.0-1.5 percent, resulting in an alternative high quality protein feed ingredient, especially for the fish and mariculture industries, for poultry, pets and swine. Rice oil is a monounsaturated vegetable oil (45 percent oleic acid) and can be used in rations to modify carcass lipid composition.

R3

Detoxification and Deallergenation of Feed Meals. Khee Choon Rhee, Texas A&M University, Food Protein R&D Center, College Station, TX 77843, and Byongki Kim and Edmund W. Lusas, Texas A&M University.

Meals from many oilseeds often contain undesirable toxic and/or allergic compounds which severely reduce their value and limit their uses in feeds. To remedy these problems, a series of extruder-based processes have been developed to chemically destroy toxins and allergens in meals so that the resulting products can safely be used in compounded feeds for poultry, swine and cattle feeding. Thus far, these new techniques have successfully been applied to meals from peanuts for aflatoxins, cottonseeds for gossypol and aflatoxins, and castor seeds for CB-1A allergen.

R4

Value Added Meat By-Product, Feather Meal, and Animal Fats. Russell E. John, National Renderers Association, 2250 E. Devon Avenue, Des Plaines, IL 60018.

The use of feather meal as a by-pass protein source in ruminant diets has resulted in sufficient demand for feather meal to allow it to be used for its protein value instead of pulling down the value of other ingredients as a disposal problem. Improved processing of blood meal, its probable by-pass characteristics, and a blending of dry fat into the formula opens many research doors for better utilization of these valuable by-products. Blends of feather meal, blood meal, meat-and-bone meal, and dry fat would appear to balance nutrient deficiencies that occur in the single ingredient. Modern processing procedures for "ready to cook" and "ready to eat" have resulted in a different raw material going to the renderer. In order to produce a consistent end product, the renderer must either adjust raw material input or blend the rendered material to a standard specification. The development of a fat-like product with no calories and no cholesterol is proceeding through regulatory channels. This product will probably appear in fast food oils that are now rendered and used in animal feed as an energy source. The reduced value as a result of the energy dilution may alter the recycling path of these oils from a valuable by-product to a disposal problem.

R5

Recent Advances in Upgrading Industrial Fish to Value Added Products. Anthony P. Bimbo, Zapata Haynie Corp., P.O. Box 175, Reedville, VA 22539.

Over 90 million metric tons (MMT) of fish are landed worldwide. Of this around 30% are processed into fish meal and oil. Economic and social pressures, opportunities for special markets away from the traditional markets and new product areas utilizing the unique properties of fish proteins and lipids have given the fish meal and oil industry new life. Fish meal processing is in a state of change. Raw material freshness, new low temperature cooking and drying techniques are producing products with excellent nutritional value. These new special meals are finding uses in aquaculture, early weaned pigs, mink, ruminant and pet diets. Fish lipids whether present in the meal or as fish oil are rich in omega-3 fatty acids. When fed to food animals, these omega-3 fatty acids deposit in the meat and depot fat. Concepts for "super chickens" with an equivalent amount of omega-3 fatty acids to lean fish are being developed. Low cholesterol eggs with omega-3 fatty acids and a lower cholesterol content are also under study. Food products, such as margarine type spreads, salad dressing and meat products that can deliver 2 grams per day of omega-3 fatty acids in a tasty, stable product, are not far away. Edible fish protein in the form of minces and surimi made from industrial fish species are also being developed. These products offer excellent functionality, omega-3 fatty acids and good nutritional composition. They can be formulated into a variety of meat type products thus bringing us to the Age of Engineered Foods.

R6

Alkaline Peroxide Treated Crop Residues as Ruminant Feeds. J. Michael Gould, USDA-ARS-NRRC, 1815 N. University Street, Peoria, IL 61604.

Crop residues such as wheat straw, cornstalks, and soybean stover are of limited value as ruminant feed because the carbohydrate portion of these materials is intimately associated with lignin, which prevents its hydrolysis by cellulolytic enzymes. In nature, lignin is degraded by certain fungi using an enzyme that requires hydrogen peroxide as an oxidant. In the absence of lignin-degrading enzymes, crop residue can be partially delignified by treatment with a dilute, alkaline solution of hydrogen peroxide (pH 11.5). Alkaline hydrogen peroxide (AHP)-treated crop residues exhibited dramatic increases in their digestibility by ruminant animals. AHP-treatment increased the digestibilities of a wide range of lignocellulosic crop residues, although the largest improvements appeared to be associated with residues from monocotyledonous plants. In feeding trials, beef cattle, dairy cattle, and sheep fed diets containing alkaline hydrogen peroxide-treated wheat straw (AHP-WS) exhibited feed efficiencies and performance characteristics similar to animals fed corn-based diets. AHP treatment also removed the feed intake restriction normally associated with lignocellulose-based diets, so that feed intakes with AHP-WS based diets were similar to those observed for corn-based diets. AHP technology is expected to become commercially available in the near future.

R7

Low-Cost Dry Extrusion of Feeds. Leroy J. Hanson, Triple "F", Inc., 10104 Douglas Avenue, P.O. Box 3600-Urbandale Branch, Des Moines, IA 50322.

The concept of low-cost dry extrusion was based on the need for reducing the capital investment by eliminating pre-processing and post-processing of the product. A rugged machine was developed which could be operated under a wide variety of conditions with inexperienced personnel. The concept of dry extrusion is basically one of converting an energy source to heat through the use of friction and utilizing natural ingredients such as water, oil, or something that melts as a lubricant. By being able to adjust the machine for a wide variety of ingredients, it is possible to cook, sterilize, expand and dehydrate a wide variety of feed ingredients. The principle of dry extrusion has been used to destroy inhibitors, rupture oil cells, gelatinize starch, and produce unique shapes. A wide variety of naturally occurring proteins, carbohydrates, and fats can be utilized in the extrusion process, producing ingredients and finished products which are more digestible, more palatable, and unique. The Dry Extrusion Process can be used for both animal and human foods, and has particular application in the less-sophisticated markets or where economics favor high value with low-cost processing. This process is being used in a wide variety of by-products from the processing business. The future for extrusion is extremely good because of the added value that can be realized through its application.

R8

Extrusion of High-Energy Feedstuffs. Galen J. Rokey, Wenger Mfg, Inc., 714 Main, Sabetha, KS 66534.

Feeds have typically been processed to varying degrees depending upon the economics involved and the performances required in the animal. However, requirements to formulate high-energy diets include addition of very high levels of fat which have also complicated processing. The extrusion cooking process has been modified to accommodate these changes by attention to the following four areas: 1) raw material formulation, 2) system configuration, 3) processing conditions, and 4) final product specifications.

R9

Significance, Measurement and Processing of Proteins Resistant to Ruminal Degradation. Marshall D. Stern, University of Minnesota, Dept. of Animal Science, 130 Haecker Hall, St. Paul, MN 55108.

Ruminants derive their intestinal protein supply from dietary protein which escapes ruminal degradation and microbial protein which is synthesized in the rumen. Recently proposed systems for calculating the protein requirements of ruminants require a measure of the proportion of dietary protein that is degraded in the rumen. Because in vivo estimates are labor intensive, time consuming and subject to considerable error, alternative in vitro procedures have been developed such as ammonia release in incubated rumen fluid, diazotization, nitrogen solubility and incubation with proteolytic enzymes. The use of low degradable or protected proteins in diets fed to ruminants with high protein requirements improves the amino acid supply to the animal and concurrently decreases excessive ammonia production, thereby reducing stress on liver metabolism. Because soybean meal is a high-quality protein which is extensively degraded in the rumen, various processing methods and treatments have been used to increase its resistance to microbial degradation in the rumen. Treatments include physical or chemical processes such as heat, aldehydes, sodium bentonite, tannins, sodium hydroxide, propionic acid, blood, alcohol, xylose and calcium lignosulfonate. Animal responses to these treatments have been inconsistent and may be due to either underprotection or overprotection.

Session S Friday morning

Fats and Oils Processing I

S1

Quality and Processing Distinctions for Canadian Canola. James Dyck, CSP Foods Ltd., Box 190, Saskatoon, Saskatchewan S7K 3K7, Canada, and Mark Pickard, CSP Foods Ltd.

This paper will review the unique features of processing Canadian canola with reference to both crushing and refining. New technology and its effects on processing and product quality will be emphasized. Efforts of research and industry have combined to provide continual improvements in the quality and processability of this crop and its oil products.

S2

Bleaching - Why We Do What We Do. Dennis Otten, Cargill, Inc., 1660 18th Street, P.O. Box 357, Sioux City, IA 51102.

From a processing point of view why we bleach as we do. My talk includes clay dosages and types of material which are dictated by the quality desired.

S3

Filtration of Vegetable Oil. Edward H. King, Jr., Industrial Filter & Pump Mfg. Co., 5900 West Ogden Avenue, Cicero, IL 60650.

A review of various types and designs of pressure filters utilized in all process stages in extraction and refining of vegetable oils. This begins with filter presses that are manually operated, then to the latest types of pressure filters featuring semi and fully automatic operation. The filters are engineered and designed to include features required for each specific process requirement. The functions can be for primary, polish, or heel filtration. Filter presses and pressure leaf, tubular, horizontal plate, and sock filters will be illustrated and discussed.

S4

Hydrogenation - A User's View. David A. Allen, Acatos & Hutcheson, P.O. Box 27, Dunnings Bridge Road, Bootle Merseysid, L30 6XR, England.

Many refineries, especially in Europe, handle multiple feedstocks through their hydrogenation plants. Oils as diverse as fish oils, vegetable oils and lauric fats are often handled in identical autoclaves within the same plant. This situation imposes particular demands for catalyst performance and autoclave design and operation. These demands will be identified and discussed with a view to defining the performance for an ideal catalyst and autoclave combination. Pointers for future developments, especially for autoclaves will also be discussed.

S5

Considerations for Selecting Deodorization Facilities. Calvin T. Zehnder, Consultant, 5502 Hidden Road, Jan-Apr:Box 2505-Bonita Sprgs,FL 33959, Louisville, KY 40291.

This paper will review the steps and/or parameters which should be considered by a refiner in planning for upgrading or installing new deodorization facilities. Refiner's marketing position, variety of stocks processed, operating conditions preferred, energy and environmental impacts will be included for the deodorizer and ancillary equipment.

Session T Friday morning

Flavor Quality & Stability: Effect of Minor Oil Constituents

T1

The Antioxidant Effects of Tocopherols and ß-Carotene in Vegetable Oils. E.N. Frankel, USDA-ARS-NRRC, 1815 N. University St., Peoria, IL 61604.

Tocopherols and carotenoid pigments are important minor constituencies in vegetable oils known to influence their oxidative and flavor stability. Tocopherols have a dual function: scavenging free radicals to interrupt lipid autoxidation, and quenching singlet oxygen to inhibit photosensitized oxidation. In soybean esters, we found a-tocopherol to inhibit the effects of singlet oxygen during photoxidation sensitized with chlorophyll. After processing, about 60 to 70% of the tocopherols remain in soybean oil. However, the tocopherol content in refined, bleached and deodorized soybean oil, ranging between 700 and 1000 ppm, is above the optimum range between 400 to 600 ppm for antioxidant activity. Tocopherol contents reported in other refined oils (300-600 ppm in rapeseed, 300-500 ppm in sunflower, 700-800 ppm in corn oil, and 400-700 ppm in cottonseed oil) are generally regarded as adequate for protection against oxidation. ß-carotene is another multiple-action inhibitor of lipid oxidation. As a natural quencher of singlet oxygen, ß-carotene protects lipids by interfering with photosensitized oxidation. It may also behave as an effective reducing agent by trapping radicals. We recently found that ß-carotene protects soybean oil against light oxidation when used at concentrations below 20 ppm. At these low concentrations, ß-carotene is effectively protected against free radical oxidation by an excess of naturally occurring tocopherols. In methyl esters of soybean oil free of tocopherols, 1000 ppm of ß-carotene was needed to achieve protection against light oxidation. In soybean oil, however, ß-carotene at high concentrations produced off-flavors and promoted oxidation. Since ß-carotene is almost completely removed during processing of vegetable oils, for antioxidant uses at low concentrations, it would have to be added on the cooling side of the deodorization step.

T2

Effects of Chlorophylls and Other Minor Components on the Oxidative and Flavor Stability of Vegetable Oils. Yasushi Endo, Tohoku University, 1-1 Tsutsumidori-Amamiyamachi, Sendai 981, Japan, and Kenshiro Fujimoto, Tohoku University, Riichiro Usuki, Shokei Women's Junior College, and Takashi Kaneda, Koriyama Women's College.

Various minor components such as chlorophyll-related compounds in soybean and other vegetable oils were examined for their effects on the oxidative and flavor stability. Pheophytins, the major chlorophyll-related compounds in refined vegetable oils, together with chlorophylls accelerated the photooxidation of rapeseed and soybean oils, while in the dark, they acted, on the contrary, as antioxidants. Although the effect of chlorophyll-related compounds on the oxidative stability was important, they scarcely affected the flavor stability of vegetable oils. Soybean oil was found to be the most susceptible for flavor reversion induced by light irradiation. As the purified soybean oil triglyceride was much more stable against flavor reversion than original soybean oil in spite of its much less oxidative stability, the involvement of minor components, which were eluted with n-hexane/diethyl ether (1:1) on silicic acid column chromatography, was suggested in flavor reversion.

T3

Mixed Tocopherols: Effective Antioxidants for Animal Fats. C.J. Megremis, Henkel Corporation, 5325 S. 9th

Avenue, LaGrange, IL 60525, and W.F. Froula and J.P. Clark, Henkel Corporation.

Animal fats are much more susceptible to oxidative rancidity than vegetable oils. Although vegetable oils are more unsaturated than animal fats, the tocopherols naturally present in the vegetable oils protect them from autoxidation. Tocopherols are not synthesized by animals, only plants. Consequently, animal fats do not normally contain sufficient tocopherols to protect them from oxidation. We examined the antioxidant effectiveness of tocopherols in lard, chicken fat, milk fat, and menhaden oil (a highly unsaturated marine oil). Addition of tocopherols produced a large increase in the stability of the animal fats as measured by the AOM test. The marine oil was too reactive to be evaluated by the AOM test, so a weight gain method was developed to measure its stability. Tocopherols were surprisingly effective in stabilizing this oil. Tocopherols worked well even at low levels, and no pro-oxidation was observed even at tocopherol concentrations greater than 1000 ppm.

T4

Stability of Low Linolenic Acid Canola Oil to Accelerated Storage at 60°C. N.A. Michael Eskin, University of Manitoba, Dept. of Foods & Nutrition, Winnipeg, Manitoba R3T 2N2, Canada, and L. Malcolmson, S. Durance-Tod, and R. Przybylski, University of Manitoba, and R.A. Carr and J. Mickle, POS Pilot Plant Corporation.

A low linolenic acid (3.1%) canola oil was subjected to the Schaal oven test at 60 C over 12 days and compared to a high linolenic acid (11.5%) canola oil (Westar). Chemical indices of rancidity included peroxide value (PV), hydroperoxide value (HV), TBA and volatile analyses. Based on these measurements the low linolenic oil exhibited remarkable stability in contrast to the normal progress of rancidity associated with high linolenic acid oils. This was confirmed by sensory evaluation of the same oils by ten experienced panelists using both odor intensity and pleasantness. No significant differences in either odor intensity or pleasantness were perceived by the trained sensory panel for the stored low linolenic acid canola oil compared to significant for the high linolenic acid (West) canola oil. This study demonstrates the enhanced stability of the low linolenic acid oil to accelerated storage conditions.

T5

Tocopherol Composition of Vegetable Oils Affects Flavor Quality and Stability. K. Warner, USDA-ARS-NRRC, 1815 N. University St., Peoria, IL, 61604, and T.L. Mounts, USDA-ARS-NRRC.

Samples of soybean, sunflower, and low erucic acid rapeseed/canola (LEAR) oils were analyzed for the four tocopherol isomers by high performance liquid chromatography (HPLC) with an evaporative light-scattering mass detector. The HPLC analyses showed that the oils had levels of tocopherols in the order of highest to lowest as follows: sunflower, alpha > beta > gamma > delta; LEAR oil, gamma > alpha > delta > beta; and soybean oil, gamma > delta > alpha > beta. Sensory analyses of oxidized oils for flavor and gas chromatographic volatiles analyses for hexanal contents showed that soybean oil had the best flavor and oxidative stability, followed by LEAR oil, and sunflower oil. Results of the HPLC analyses were statistically correlated with flavor scores and hexanal contents of oxidized samples of the same oils. The correlation coefficient was 0.97 ($P<0.01$) between flavor scores and levels of gamma tocopherol, indicating that the oils with the higher levels of gamma tocopherols were the most stable. On the other hand, an inverse relationship was shown between flavor scores and alpha tocopherol contents with a coefficient of -0.95 ($P < 0.01$), indicating that oils with higher amounts of alpha tocopherol were the least stable. The correlation coefficients calculated between hexanal contents and tocopherol contents were -0.90 ($P < 0.05$) for gamma and 0.88 ($P < 0.05$) for alpha tocopherol.

T6

The Effect of Linalyl Acetate on Oxidized Cholesterol Derivative Formation in Heated Lard. Pearlly S. Yan, Iowa State University, 106 MacKay Hall, Ames, IA 50011, and Pamela J. White, Iowa State University.

Lard, with the addition of ten times the amount of cholesterol originally present, was heated to 180°C (frying temperature) for 28 days. Formation of oxidized cholesterol derivatives (OCDs) was followed by using gas chromatography. Also, lard treatments with added cholesterol (ten times) were heated with the addition of 0.02 land 0.04% linalyl acetate, and 0.3 ppm polydimethyl siloxane, a known high-temperature antioxidant. The high-temperature antioxidant activity of linalyl acetate has been demonstrated previously in soybean oil heated to 180°C to 10 days. A comparison of OCD formation was shown among lard treatments with and without the additives.

T7

Quenching Effects of Diamagnetic and Paramagnetic Coordinating Nickel(II) Chelates on Singlet Oxygen Oxidation of Soybean Oil. S.H. Lee, Ohio State University, Dept. of Food Science & Nutrition, 2121 Fyffe Road, 122 V.H., Columbus, OH 43210-1097, and D.B. Min, Ohio State University.

The quenching effects of 0, 30, 60 or 90 ppm of diamagnetic coordinating bis-(di-n-butyldithiocarbamato) nickel(II), and 0, 500, 1,000 or 1,500 ppm of paramagnetic coordinating [2,2'-thiobis-4-(1,1,3,3-tetramethylbutyl)-phenalto](n-butylamine) nickel (II) on singlet oxygen oxidation of soybean oil containing 4 ppm chlorophyll were studied by determining the peroxide values and headspace oxygen contents by gas chromatography during light storage. As bis-(di-n-butyldithiocarbamato) nickel(II) concentration increased from 0 to 30, 60 and 90 ppm, peroxide values of soybean oil decreased from 7.67 to 6.47, 5.11 and 3.66, and headspace oxygen contents increased from 6.71 to 7.34, 7.65 and 7.96, respectively, after 24 hour storage under light. As [2,2'-thiobis-4-(1,1,3,3-tetramethylbutyl)-phenalto](n-butylamine) nickel (II) minimized the singlet oxygen oxidation of soybean oil. The results showed that diamagnetic coordinating bis-(di-n-butyldithiocarbamato) nickel(II) is at least 15 times more efficient than paramagnetic coordinating [2,2'-thiobis-4-(1,1,3,3-tetramethylbutyl)-phenalto](n-butylamine) nickel (II) in minimizing the singlet oxygen oxidation of soybean oil. The quenching mechanisms and kinetics of these two nickel(II) chelates will also be discussed.

T8

Oxidative Stability of Meadowfoam Oil/Minor Constituents. Robert R. Lowry, Oregon State University, Dept. of Agricultural Chemistry, Corvallis, OR 97331-6502, and Ian J. Tinsley, Oregon State University.

Meadowfoam is a promising new oilseed crop that yields a stable oil suitable for industrial applications. The oil is stable for prolonged periods not only at room temperature in most applications but also for up to 200 hours in the AOM test. It essentially retains its original viscosity at the end of the test period. Samples of crude and refined oil were used for the tests (conducted at 98°C with air bubbling through the oil continuously) with peroxide values being run periodically. Analyses of the minor constituents, tocopherols and sterols, were carried out on samples removed during the test periods. Normal and reverse phase HPLC, respectively, were used for these analyses. The unusual stability of the oil will be discussed in relation to both the minor constituents and the basic fatty acid structure.

Session U Friday morning

Plant Biotechnology I

U1

Plant Biotechnology and the Fats and Oils Industry. J.B.M. Rattray, University of Guelph, Dept. of Chem. & Biochem., Guelph, Ontario N1G 2W1, Canada.

The fats and oils industry stands to benefit considerably from applications of the various techniques of biotechnology. Design improvements both in yield and composition will be required to meet the projected marked increases in the world demand for vegetable oils. Better agronomic practices and post-harvest technologies must be considered. Plant breeding programs will be assisted by greater knowledge of the genetic diversity of available germplasms for the development of strains possessing such desirable qualities as local adaptability, resistance to pest infestation and herbicide action, and modified fatty acid composition of the seed oil. Use of general cell culturing procedures, genetic transformation, somatic hybridization and embryogenesis will complement conventional breeding practices and shorten the development time for the introduction of desirable varieties. Gene transfer may be performed using various vector systems including liposomes. Regulation and manipulation of enzyme activities involved in the determination of fatty acid chain length and degree of unsaturation will be sought through mutagenesis and somaclonal variations. Industrial requirements for particular fatty compounds such as (C_8, C_{10}) acid, erucic acid, eicosa-5-enoic acid and liquid waxes await further development of cuphea, crambe, meadowfoam, jojoba and novel plants as commercial crops. High cost specialty products such as γ-linolenic acid and EPA may be produced by culturing isolated plant cells or microalgae but applications may be limited by the overall economics.

U2

New Oilseed Opportunities from Biotechnology. W.R. Scowcroft, Biotechnica Canada, Inc., Suite 170, 8th Street, N.E., Calgary, Alberta T2E 7B7, Canada.

Worldwide, vegetable oils have a value in excess of $US35 billion of which 80% is used for human consumption. While soy oil dominates the market, major changes are occurring in the supply/demand of oils from other crops. Most notable is the rapid increase in demand for and supply of rapeseed (canola) which currently has a growth rate of 9% per annum. The rapid rise to prominence of rapeseed is due to the worldwide acceptance of the "canola" quality standard namely, low erucic acid in the oil and low glucosinolate content in the meal. The development of this crop was pioneered by Canada. Though commodity oils will dominate the world market for some time to come, genetic modification of oil composition will provide new market opportunities. These opportunities derive from niche market specialization by food manufacturers and increasing consumer preference for nutritionally better oils. Among the oilseed crops, rapeseed is scientifically most amenable to modification of oil composition. The natural variation that exists in fatty acid composition enables direct selection in conventional breeding programs for altered fatty acid composition. The tools of biotechnology have been more successfully developed in rapeseed than in any other oilseed crop. Thus there is now substantial focus on the modification of oil composition by genetic engineering. Flax, primarily considered as a source of industrial oil, has been genetically modified to yield an oil with a fatty acid composition suitable for human consumption. The oil of zero linolenic acid flax is directly comparable with that of sunflower and corn oil.

U3

Genetic Diversity of Lipids in Germplasm. R. Kleiman, USDA-ARS-NRRC, 1815 N. University St., Peoria, IL 61604.

Plants generally produce lipids as glycerol molecules esterified with normal unsaturated fatty acids. However, a significant number of plants, collected in the wild, depart from this mold and produce unusual acyl groups or use unique ways of assembling them. For example, there are plants that produce glycerides with more than three fatty acids per glycerol molecule, seed oils without detectable amounts of glycerides, and oils with cyanolipids as backbones. Sources and structures of unusual fatty acids will be reviewed, including those with unusual positions of unsaturation (both olefinic and acetylenic), with combinations of oxygenated functional groups, and with cyclic structures. In some cases, an attempt will be made to use composition for chemotaxonomic purposes.

U4

Introduction and Expression of Foreign Genes in Canola and Other Crop Species. D. Shah, Monsanto, St. Louis, MO.

Abstract not available at press time.

U5

Cell Culture Techniques and Canola Improvement. K.P. Pauls, University of Guelph, Crop Science Dept., Guelph, Ontario N1G 2W1, Canada.

Microspore culture and protoplast fusion have been

used to make marked changes in the characteristics of canola (*Brassica napus*), the principal oilseed of Northern latitudes. The culture of immature pollen cells (called microspores) results in the production of haploid plants. Microspore cultures have been used with *in vitro* selection techniques to obtain herbicide resistant plants. The procedure has also been used in conjunction with colchicine doubling, to rapidly fix traits in a homozygous state, thus saving several years of variety development time. Furthermore, the simplified genetic ratios that are found in doubled haploid populations make haploidy an attractive system to apply to the examination of the inheritance of agronomic traits like oil content and oil composition. In the cell fusion procedure the complete genomes, both nuclear and cytoplasmic, of the two parents are brought together in a heterokaryon. Nuclear fusion and organelle sorting processes can result in a large variety of plants with different mixtures of nuclear and cytoplasmic traits. Protoplast fusion has been used to resynthesize amphiploid *B. napus* from its progenitor species (*B. oleracea* and *B. campestris*) and to introgress novel traits into rapeseed. Also haploid protoplasts from atrazine resistant *B. napus* lines were fused with haploid protoplasts from cytoplasmic male sterile (CMS) lines of *B. napus* to combine these cytoplasmic traits in one plant. This circumvented the natural barrier that exists to the production of cytoplasmic hybrids because of the maternal inheritance of cytoplasmic traits.

Session V Friday afternoon

Surfactants & Detergents IV: Surface Chemistry of Surfactants.

V1

Status of Surfactant Phase Science. Robert G. Laughlin, Procter & Gamble Company, Miami Valley Laboratories, Box 398707, Cincinnati, OH 45239.

Heterogeneous equilibria in aqueous surfactant systems is complex, relative to non-surfactant systems, because of the existence of liquid crystal phases as well as liquids and crystals. This area is both academically interesting and technically important, but it has during the past few years become clouded by uncertainty. Previously unrecognized phases have been found to exist in historically well-studied soap-, sodium dodecyl sulfate-, and monoglyceride-water systems. The structure and composition range of various liquid crystals has also been a matter of dispute. These problems may be attributed in part to limitations of the methods which investigators have used. A particularly important problem has been the lack of applicable isothermal methods; this has forced most investigators to rely mostly on isoplethal techniques, which for many aspects of phase studies are inherently flawed. This situation has changed recently, with the advent of new techniques which are based on composition variation by diffusive transport. The status of this area, both as to phase information and methodology, will be considered during this talk.

V2

Solubilization of Organics in Micelles and Mixed Micelles. Sherril D. Christian, University of Oklahoma, Dept. of Chemical Engineering, Institute for Applied Surfactant Research, Norman, OK 73019, and Edwin E. Tucker and John F. Scamehorn, University of Oklahoma.

Accurate information about the solubilization of organic solutes, either in molecular or ionic form, by surfactant micelles and mixed micelles is needed in applying several colloid-enhanced separation methods for purifying aqueous streams. In micellar-enhanced ultrafiltration (MEUF), organic solutes are removed from aqueous solutions by adding a surfactant at concentrations well above the critical micelle concentration (cmc) and passing part of the solution (the permeate) through an ultrafilter having pore sizes small enough to prevent passage of the micelles and bound organic. The permeate stream contains the organic solute at a small concentration, nearly equal to that of the unsolubilized organic in the retentate solution, and surfactant at a concentration approximating the cmc. Organic ions are strongly attracted to ionic surfactant micelles having a charge opposite that of the organic anion or cation is expelled from the permeate solution by the presence of a surfactant having micelles with the same charge as the organic ion. This is an example of a Donnan exclusion effect, capable in many cases of concentrating the organic ion in the permeate by a factor of 10 to 100 or more, compared to the retentate.

V3

Effects of Chemical Structure and Molecular Environment on the Dynamic Surface Tension of Aqueous Solutions of Surfactants. X.Y. Hua, Brooklyn College-CUNY, Surfactant Research Institute, Brooklyn, NY 11210, and M.J. Rosen, Brooklyn College-CUNY.

The dynamic surface tensions of aqueous surfactant solutions for a number of highly purified compounds, such as n-dodecyl ethers of polyoxyethylenated alcohols, sodium salts of sulfated n-dodecyl ethers of polyoxyethylenated alcohols, N-dodecyl-N-benzyl-N-methyl glycine, and sodium di (2-ethylhexyl) sulfosuccinate, were measured. We have generalized the following factors determining dynamic surface tension values: (a) the effect of surfactant concentration; (b) the effect of temperature; (c) the effect of salt (NaCl) addition; (d) the effect of organic additives; (e) the effect of number of oxyethylene units in the surfactant hydrophilic head; (f) the effect of chain length in the hydrophobic tail; (g) the effect of branching in the hydrophobic tail.

V4

Fundamental Surface Active Properties of Branched Alkyl Sulfate and Ethoxysulfate Surfactants I. Ramesh Varadaraj, Exxon Research & Engineering Co., Clinton Township, Route 22 East, Annandale, NJ 08801, and P. Valint, J. Bock, and S. Zushma, Exxon, and X.Y. Yuan, Z.H. Zhu, D.S. Murphy, and Milton Rosen, Brooklyn College-CUNY.

Guerbet surfactants are a unique class of amphiphiles where the carbon atom beta to the head group carries an alkyl substituent. Guerbet sulfates and ethoxysulfates surfactants were synthesized and their interfacial properties determined at the air-water and decane-water interface in an attempt to understand how hydrocarbon chain

branching, chain length and oxyethylene bridge length influence their interfacial and aggregation properties. Comparison of the interfacial properties of the Guerbet surfactants with the linear counterparts reveals that hydrocarbon chain branching introduces significant differences in the properties. Introduction of oxyethylene groups between the hydrophobe and head group sulfate increases surfactant solubility in water but decreases the magnitude of the differences in properties between the Guerbet and linear systems. Reduction in the Guerbet hydrophobe from C16 to C12 influences interfacial and aggregation properties in a manner similar to chain length reduction in linear systems. The dependency of these properties on the relationship of hydrophile and lipophile structure will be discussed.

V5

Fundamental Surface Properties of Branched Alkyl Sulfates and Ethoxysulfates II - Properties of Two Highly Purified Isomeric Compounds. D.S. Murphy, Brooklyn College-CUNY, Surfactant Research Institute, Brooklyn, NY 11210, and Z.H. Zhu, X.Y. Yuan, and M.J. Rosen, Brooklyn College-CUNY, and J. Bock, S. Zushma, P.L. Valint, and R. Varadaraj, Exxon Research.

Various interfacial properties of two isomeric compounds, $C_{16}H_{33}(OC_2H_4)_5SO_4Na$, sodium salts of sulfated polyethenoxylated Guerbet-type alcohols, were measured and compared. In both compounds, the hydrophobic group had C_6 and C_8 alkyl groups attached to the ß-carbon, but in one the groups were both straight-chain and in the other they were both branched. Properties measured were surface tension, interfacial tension against hexadecane, contact angles on Teflon and Parafilm, Draves wetting, and Ross-Miles foaming, for solutions of the compounds in aqueous 0.1M NaCl at 25°C. Properties of the two compounds were compared to elucidate the effect of the branching in the alkyl groups. The compound with branched alkyl groups showed more effective surface and interfacial tension reduction, and better wetting and foaming, while the compound with straight-chain alkyl groups gave more efficient surface and interfacial tension reduction, micelle formation, and contact angle reduction.

V6

Properties of Pseudo-Nonionic Complexes of Anionic and Cationic Surfactants. Ammanuel Mehreteab, Colgate Palmolive Co., 909 River Road, Piscataway, NJ 08854, and Frank J. Loprest, Colgate Palmolive Co.

Pseudo-nonionic complexes of anionic and cationic surfactants have characteristics that are different than either of their surfactant components. In contrast to ionic surfactants, they exhibit cloud point phenomena similar to nonionic surfactants. Size measurements, using quasi-elastic laser light scattering method, show that the complexes form vesicles or micelles that are larger than those of the individual surfactants. Surface tension measurements indicate that they are more efficient and effective than either of their components. The above results and the effect of electrolyte and variations of hydrophobic and hydrophilic portions of the surfactant components on the cloud point temperature and surface tension of the pseudo-nonionic complexes will be presented.

V7

Microemulsions, A New Alternative for the Washing Process? Fred Schambil, Henkel KGaA, Henkelstr. 67, Postfach 1100, Dusseldorf-Holthausen, D-4000, West Germany, and Milan-J. Schwuger and Peter Kurzendorfer, Henkel KGaA.

The correlation between the phase behavior of aqueous solutions of surfactants and the removal of fat and oil from fabrics has been the subject of numerous publications. The principal mechanisms for the removal of fatty soil in detergency are the so-called rolling up, the spontaneous emulsification, the solubilization, and the formation of mixed phases, e.g. liquid crystals, between fatty soil and surfactants. Recently, increased attention has been paid to microemulsions because of their unusual properties. Water and oil can be made completely miscible by adding a sufficient amount of a surfactant. Ternary mixtures of water, oil, and surfactant may also separate into three liquid phases with a minimum of interfacial tension between the aqueous and the oil-rich phase which facilitates the basic mechanisms of soil removal. In case of long-chain ionic surfactants, the addition of co-surfactants like medium-chain alcohols is necessary. In this paper a review of the definitions, the properties, and the applications of microemulsions in detergency is given. Whereas most of the published literature is concerned with nonionic surfactants of the alkylpolyglycol ether type and pure straight-chain hydrocarbons, first results with ionic surfactants (alkyl sulfates) in combination with pentanol and hexanol and practical oils (mineral oil, olive oil or sebum) are presented here. The detergency performance tests are compared with the results obtained with liquid detergents and laundry aids. The results lead to the conclusion that the application of microemulsion systems may be especially useful in cases where high amounts of surfactants or solvents shall be substitutes, such as in the field of prewash soil and stain removers.

V8

The Effect of Polar Soil Components on the PIT and Optimum Detergency Conditions. Kirk H. Raney, Shell Development Company, 3333 Highway 6 South, Houston, TX 77082, and Herbert L. Benson, Shell Development Company.

Previously reported results have shown that the optimum removal of a hydrocarbon soil from polyester/cotton fabric occurs above the cloud point at the phase inversion temperature (PIT) of the nonionic detergent-water-soil system. Through comparison of phase behavior measurements to radiotracer detergency studies using model sebum soils, i.e., cetane/oleyl alcohol and cetane/oleic acid blends, the relevance of the PIT to removal of nonpolar/polar soil mixtures has now also been demonstrated. For these soils, the PIT is typically *below* the cloud point temperature and the highest level of soil removal is found between the PIT and cloud point rather than only at the PIT. This relatively temperature-insensitive soil removal can be attributed to the preferential solubilization of the polar soil components which continually changes the composition of the residual soil during the washing cycle. These findings may explain the long-observed result that 4- to 5-EO alcohol ethoxylates are preferred for the removal of nonpolar soils while 6- to 9-EO ethoxylates are the more effective detergents for sebum soils.

V9

Surfactant Precipitation Kinetics. Lori A. Hole, University of Oklahoma, Institute for Applied Surfactant Research, 100 E. Boyd, Room F-339, Norman, OK 73019, and John F. Scamehorn and Jeffrey H. Harwell, University of Oklahoma.

Substantial progress has been made in the last five years in understanding and modeling the thermodynamics of surfactant precipitation in processes such as calcium precipitating anionic surfactants and anionic/cationic surfactant mixture precipitation. However, in practical applications, the actual system may be far from equilibrium. For example, substantial supersaturation can occur in a ten minute wash cycle. In this study, the rate at which precipitation occurs has been measured for the aforementioned specific systems, as well as others. Calorimetry has been found useful for this purpose, but other methods are also employed to quantify the phenomena. The effect of both system type and composition (e.g., surfactant concentration), and temperature is discussed.

Session W Friday afternoon

Dietary Fiber: Potential for Use in Value-Added Co-Products

W1

Dietary Fiber: Overview and Update. Frederick R. Dintzis, USDA-ARS-NRRC, 1815 N. University St., Peoria, IL 61604.

The historical evolution of the present concept of dietary fiber, from the folklore idea of "roughage" through the 150 year old analytical use of "crude fiber", is reviewed. Some highlights of analytical methodology and nutritional aspects of dietary fiber will be discussed. There is present general agreement to the definition that dietary fiber consists of those plant cell components, mainly the nonstarch polysaccharides, cellulose, hemicellulose and pectic substances, that are resistant to hydrolysis by human digestive enzymes. Procedures from the two major approaches to dietary fiber analysis, the enzymatic-gravimetric and the enzymatic-chemical methods, are still being refined with full agreement on acceptable methodology not yet achieved. Research in the past 10 years has provided evidence of some beneficial physiological effects associated with fiber-containing diets.

W2

Incorporation of Total Dietary Fibers into Foods. Dennis T. Gordon, University of Missouri-Columbia, Dept. of Food Science & Nutrition, 122 Eckles Hall, Columbia, MO 65211.

Dietary fiber is added to food for one or more of the following reasons: functionality, caloric reduction or nutrition-health benefits. Since total dietary fiber (TDF) can be divided into insoluble and soluble fractions, and each fraction contributes to these objectives differently, the distribution of fractions must be considered. Additional decisions that must be made are: 1) should the TDF be visible or invisible and; 2) what amount is or can be incorporated into the final product? These criteria represent 12 combinations that contribute to a final product and there are more! The common sources of TDF to use in foods are: 1) NATURAL: wheat, corn, soy, oats and modified products thereof; 2) EXTRACTED: cellulose, guar, carboxymethylcellulose, psyllium and; 3) SYNTHETIC: polydextrose. The key to the entire issue of incorporating TDF into foods is in knowing their physio-chemical properties. The purpose of this review is to integrate the physio-chemical properties of various sources of TDF in meeting a food product's need for qualitative identity, caloric reduction and health/nutrition benefits.

W3

A Review: The Commercialization of Fiber in the Baking Industry. Bernard L. Bruinsma, Roman Meal Co., P.O. Box 11125, 2101 S. Tacoma Way, Tacoma, WA 98409.

A description of various fibers that are being used to produce Light[R] products today will be provided. Characteristics that make Light[R] products unique and how these can be met in production of various baked products will be reviewed. The baking industry has one of the largest categories of calorie reduced/high fiber products and this paper will examine how they have progressed from the first product 12 years ago into the multitude of products today, and the technology that has been necessary to meet this expanding calorie reduction/high fiber need. The physiological effects of various fibers in baked products will be discussed briefly.

W4

Health Benefits of Dietary Soy Fiber. Rose Ann Shorey Kutschke, University of Texas at Austin, GEA 115, Graduate Nutrition Div., Austin, TX 78712.

In the early 1970's, Burkitt and Trowell enunciated and expanded on the hypothesis that many diseases of western civilization were linked to the consumption of refined foods with diminished fiber content. This hypothesis has generated thousands of research studies probing for methods of analysis, physiochemical functions, and health benefits of various fiber constituents. The major commercially available fiber source from oilseeds is Fibrim[R] soy fiber which is comprised of cell wall material of soybean cotyledons. It is derived from dehulled, defatted soybean flakes. Fibrim[R] supplements of approximately 25 g/day for four to nine weeks have been shown in a variety of clinical trials to exert beneficial effects on plasma cholesterol levels, glucose tolerance and insulin release, and regular laxation. These benefits were accrued with no apparent negative effect on mineral absorption and excretion. Fibrim[R], consumed three times a day with meals by free-living subjects, or twice a day at 0800 and 2000 by patients with documented hypercholesterolemia, produced significant decrements in plasma total cholesterol. The average decrease in free-living subjects was 8% and in Type II or IV patients on NIH diets was 5%. Hyperlipidemic patients with impaired glucose tolerance exhibited reduced fasting glucose levels and reduced glucose areas when given Fibrim[R] for 9 weeks. Obese diabetics had improved glucose tolerance and significantly reduced postprandial triglyceridemia when treated

with the fiber. Supplements of 25 to 60 g Fibrim^R per day to healthy men increased fecal weight and moisture and decreased transit time from mouth to cecum. In addition to its potential health benefits, Fibrim^R soy fiber is bland and odorless and is an extremely versatile and palatable food ingredient.

W5

Potential Value of Isoprenoid Co-Products in Health Maintenance. Charles E. Elson, University of Wisconsin-Madison, Dept. of Nutritional Sciences, 1415 Linden Drive, Madison, WI 53706.

The diverse branches of plant isoprenoid pathways yield end-products of commercial significance serving as raw materials for chemical, rubber and plastics industries and as ingredients for pharmaceutical, cosmetic, food and beverage industries. Isoprenoid products of plant metabolism may also play physiologically relevant roles. We have linked the cholesterol-lowering actions of barley and palm oil to a lipid-soluble constituent, alpha-tocotrienol. This vitamin E analogue exerts a dose-dependent suppression on hepatic mevalonate synthesis whereas the saturated analogue, alpha-tocopherol, is not effective in lowering serum cholesterol levels. Other isoprenoid products reported to suppress mevalonate synthesis include ubiquinone, menaquinone and a number of the monoterpenes. Although its role remains to be delineated, there is a requirement for a mevalonate-derived product in the transverse of the cell cycle. Geraniol, d-limonene and tocotrienol, all of which have a mevalonate-suppressive and concomitant cholesterol-lowering action, are potent anticarcinogens. Plant products associated with lower risks for cancer and cardiovascular disease typically are rich sources of the diverse isoprenoid end-products.

W6

History and Current Policy on Fiber Labeling of Foods. John Vanderveen, Food and Drug Administration, 200 C Street, S.W., Washington, DC 20204.

The first regulatory policy on labeling of fiber in foods was formulated from a 1940 hearing record on dietary properties of food purporting to be or represented for special dietary uses. Regulations promulgated in 1941 limited claims for fiber to the lowering of the calorie content of foods. For many years, the FDA has not objected to label statements that such foods as bran and prunes promoted normal laxation. A 1975 FDA Monograph on laxation products included fiber containing foods. In the 1970's, the FDA also encouraged labeling to contain implicit information about the health promoting qualities of foods by including nutrition information and adjective title labeling. A regulation proposed in 1984 and finalized in 1987 designated an AOAC gravimetric procedure for fiber to be used for estimating fiber in conjunction with calorie calculations. Until 1984, regulations prohibiting claims for the usefulness of foods and/or food constituents in prevention or treatment of diseases were successfully enforced through new drug regulations. Food claims for the usefulness of dietary fiber for the lowering of cancer risk marked a turning point in FDA policy. The FDA reconsidered its policy in the interest of providing consumers with important health-related information and in 1987 published a proposal to permit health claims which were not fraudulent or misleading. A final regulation designed to meet these objectives is currently being implemented.

Session X Friday afternoon

Fats and Oils Processing II:

X1

Formulating Refined Vegetable Oils. John Hasman, Sigma Quality Foods, 92 Central Avenue, Farmingdale, NY 11735.

Refined vegetable oils provide the formulator with an array of attributes and choices which are often not apparent from a first-glance analysis of routine chemical data. The technical literature amply confirms what many AOCS members have also experienced through project work—the only substitute for cocoa butter is cocoa butter. Cost, however, is one titratable piece of data lacking in the data and in the formulator's desired list of finished product attributes. A fixed cost specification defines a narrow field of selectable oils and limits the formulator to a manageable number of processing techniques. Characteristics of refined and further processed oils are discussed as they relate positively or negatively to attributes important to the different categories of fat containing food products. Processing effects on attributes are also discussed. In addition, a hypothetical model for minimizing cost while maximizing expected performance is proposed.

X2

Interesterification with Emphasis on Canola Oil. Robert Delaney, C&T Refinery, 4910 South Boulevard, Charlotte, NC 28217.

Modernization for the process of interesterification has evolved by the demand for new and unique products. The process has changed very little but the introduction of unique source oils with unique physical and chemical properties continues to open new avenues for investigation. Canola oil with naturally low amount of saturated fatty acids and high monosaturated content has been suggested to be nutritionally favored. Applications for rearranged products benefitting from these attributes are those fats with special plastic or crystallinity requirements.

X3

Formulation & Packaging of Margarines, Fine Fats & All-Purpose Shortenings. Klaus Kyritz, Prairie Margarine, Inc., 14711 128th Avenue, P.O. Box 429, Edmonton, Alberta T5L 3H3, Canada.

The paper will deal with the formulation and packaging processes involved in the manufacture of packaged margarines and shortenings from deodorized base oil stocks. Main emphasis will be on the use and function of additives, supercooling, formation of desired crystal structure and processing conditions to achieve the desired end product.

Changing consumer awareness in packaging, ingredients and labelling will also be briefly discussed.

X4

Demanding Quality in Oil Processing. Werner Zschau, Süd-Chemie AG, P.O. Box 20 22 40, 8000 Munich 2, West Germany.

The production of fats and oils is a very complex sequence of many steps starting with growing of the right organisms and ending with the consumption of the produced products. Each of these many steps needs a lot of knowledge and the will to perform it so well that the final product is not just well accepted but also healthy. One fault in the whole sequence can cause detrimental consequences which not only reduce the yield but also the quality of the desired product.

Session Y Friday afternoon

Fatty Acids & Fatty Chemicals—Hydrogenation

Y1

A Catalyst Evaluation Procedure for Production of Alkyl Amines. F. Friedli, Sherex Chemical Company, and R.M. Gilbert, Sherex Chemical Company.

A procedure was developed that examines the effectiveness of nickel catalysts for hydrogenation of fatty nitriles to amines. Rate of reaction, selectivity, and iodine value elimination were key parameters studied. Both sponge and supported nickel catalysts were tested using tallow nitrile as the feedstock. The proposed procedure can be used for new catalyst screening and is ideally suited for quality assurance testing of production catalysts. The procedure will be presented in detail describing conditions, raw material handling and procedure variations.

Y2

Soybean Oil Hydrogenation with Advanced Gas Reactor. Mark K. Weise, Linde Division-Union Carbide, Old Saw Mill River Road, Tarrytown, NY 10591, and S. Sefa Koseoglu, Texas A&M University.

The Linde Division of Union Carbide developed the Advanced Gas Reactor (AGR) to increase the mass transfer rates of stirred tank reactors. Pilot tests have demonstrated the AGR's ability to reduce the batch time and catalyst concentration for hydrogenation of various feedstocks. Texas A&M's Food Protein R&D Center has performed a series of pilot tests comparing the AGR with conventional agitators in soybean oil hydrogenation. The paper presents the effect on reaction rate and catalyst concentration, along with the product specifications, such as iodine value, percent *trans* isomer, fatty acid composition, and solid fat index.

Y3

Computer Automated Hydrogenation Catalyst Evaluation System. David J. Vavrek, Akzo Chemicals, Inc., 8401 West 47th Street, McCook, IL 60525.

As a modernization effort, a fixed-bed continuous catalytic hydrogenation reactor was modified to provide for computer-automated operation. The development of the software, along with assembly and physical interfacing of the hardware were all completed in-house. The reactor column was primarily designed to convert long chain fatty nitriles to primary amines. Computer monitoring/control not only evaluates catalysts more effectively, but assures close control of the column over a wide range of potential operating conditions. Other major benefits include improved safety, data quality, and test unit productivity. Hardware and software aspects, general principles involved in the interfacing, advantages/disadvantages and the factors behind the decision to interface will be covered as well as problems encountered.

Y4

Application of Laser Light Detector in HPLC Separations of Fatty Acid Derivatives. Gerald Szajer, Akzo Chemicals Inc., 8401 West 47th Street, McCook, IL 60525, and Linda Yodual, Akzo Chemicals Inc.

Derivatives of fats and oils have been analyzed using HPLC with a variety of detectors. Refractive index has been used extensively but it has a serious drawback in the area of solvent gradients. Many derivatives, especially fatty amines, require solvent programming due to varying polarities of functional groups. We have successfully employed the Laser Light Scattering Detector (LLSD) for HPLC separations of triglycerides and fatty amines. These separations were done using various columns and solvent mixes. Examples of separations of mono, di, and trialkyl amines in non-aqueous solvents will be presented. Various chromatographics and detector variables which must be controlled for optimum results will be discussed.

Y5

Applications of Wiped-Wall Stills in Fish Oil and Ester Purification. R.G. Ackman, Canadian Institute of Fisheries Technology, Technical University of Nova Scotia, Box 1000, Halifax, Nova Scotia B3J 2X4, Canada, and W.M.N. Ratnayake, Health and Welfare Canada and D. Matthews, Technical University of Nova Scotia.

The Pope wiped-wall still is a versatile apparatus for research and small-scale production operations involving fish oils or concentrates of the omega-3 fatty acids available in quantity from fish oils. The mechanically induced and agitated thin oil film overcomes the viscosity problem of oils in vacuum stripping of PCBs. As a still it can readily be operated to purify the heat-sensitive omega-3 fatty acids of fish oils, especially eicosapentaenoic and docosahexaenoic, by distillation of either acids or esters below the critical temperature of 240°C.

Y6

Biological Consequences of the Hydrogenation Process. J.L. Zevenbergen, Unilever Research Laboratory, P.O. Box 114, AC Vlaardingen, 3130, The Netherlands.

The safety of the hydrogenation process has been the subject of many investigations. Since 1945 many multi-

generation studies with various animal species fed (partially) hydrogenated vegetable oils have been reported. Trans fatty acids, products of the hydrogenation process, have been suggested to play a role in a number of diseases, like atherosclerosis and cancer. Therefore, from time to time concern was expressed about the general safety of these isomeric fatty acids in the diet. But neither animal experiments nor epidemiological data have provided any indication for specific effects of *trans* fatty acids. On the contrary, during the last few years it has generally been recognized that *trans* fatty acids do not exert any undesirable effects provided sufficient linoleic acid is present in the diet. Recently, at the Unilever Research Laboratory in Vlaardingen, we performed two rat studies to define this minimal level of linoleic acid. We therefore compared the effects of diets with high doses of *trans* fatty acids (20% of total energy) with those of diets rich in either saturated or *cis*-monounsaturated fatty acids on a number of parameters selected to assess the safety of food components, on eicosanoid synthesis, on membrane functioning, on platelet aggregation and on fatty acid oxidation. We did not find any effect of 20 en% *trans* fatty acids with 2 en% linoleic acid in the diet. Based on our work and the work described in the literature we conclude that provided 2 en% linoleic acid is present in the diet, *trans* fatty acids, as present in partially hydrogenated vegetable oils, do not have specific effects. In view of the average level of linoleic acid in our diet (normally more than 2 en%) and the present and expected levels of consumption of *trans* fatty acids (about 8 g/day), there is no reason for concern with respect to the safety of the hydrogenation process.

Y7

Hydrogenation of Oxidized Oil. Jesse E. Covey, Consultant, 1404 Avenue R, Plano, TX 75074, and Peter J. Wan, Kraft, Inc. and Robert R. Allen, Consultant.

Portions of refined and bleached soybean oil were stored at various temperatures for various lengths of time, then hydrogenated to 70 iodine value to find the effect of peroxides on the rate of hydrogenation and on characteristics of hydrogenated product. Samples were treated up to 3 weeks at up to 65°C and provided samples with up to peroxide values of 358. All samples were analyzed, hydrogenated, and reanalyzed. Peroxide value affected the fatty acid composition as determined by gas chromatography, the calculated iodine value based on fatty acid composition, and rate of hydrogenation. Peroxide value also affected the selectivity of hydrogenation and slope of the solids curve in hydrogenated product.

Y8

Hydrogenation Catalyst Poisons Present in Industrial Fats and Oils, Fatty Acids and Methyl Esters. Charles R. Milburn, Sherex Chemical Company, Inc., P.O. Box 646, Dublin, OH 43017, and C. Joseph Toney, Sherex Chemical Company, Inc.

Phosphorous, sulfur and chlorine are the most notable hydrogenation catalyst poisons present in industrial triglycerides. Multiple samples of B.F. tallow, crude coconut oil, palm kernel oil, denatured canola, and rapeseed oil have been analyzed for these poisons at various stages in the normal processing sequence to produce fatty acids and methyl esters. This data is needed for the analysis of options to minimize the total processing cost for producing hydrogenated fatty acids or methyl esters. It will point out the potential impact of including catalyst poisons in a raw material quality control program for industrial fats and oils.

Y9

Effect of Hydrogenation on the Properties of Palm Oil and Palm Olein. Peck Hong Yap, University of Guelph, Dept. of Food Science, Guelph, Ontario N1G 2W1, Canada, and J.M. deMan, University of Guelph and L. deMan, deMan Food Technology Services, Inc.

Palm oil and palm olein were hydrogenated with a commercial nickel catalyst at 175 C and 103 kPa hydrogen pressure. The hydrogenation rate was higher for palm olein than for palm oil. With the palm oil hydrogenation the maximum level of *trans* isomers reached was 19% at I.V. of 27. With palm olein maximum *trans* level was 24% at I.V. of 31. For both products, the 18:2 content was reduced to zero at I.V. of about 40-42. There was a slight increase in 18:1 level up to this I.V. in the palm oil but not in the palm olein. The solid fat content of the hydrogenated products was investigated by pNMR. The melting behavior of the hydrogenated products was studied by DSC.

Session Z Friday afternoon

Analytical II: Magnetic Resonance Spectroscopy-High Resolution and Pulsed Applications

Z1

Separation and Identification of Sucrose Monolinoleate Positional Isomers by Reversed-Phase HPLC and NMR Spectroscopy. Fouad S. Ezra, Procter & Gamble Company, Miami Valley Laboratories, P.O. Box 398707, Cincinnati, OH 45239-8707, and Jack D. Wendel, Anne F. Russell, Matthew J. Doyle, and William H. Schmitz, Procter & Gamble Company.

Long-chain fatty acid esters of sucrose have found wide use as food emulsifiers, cosmetic adjuvants and excipients in pharmaceutical formulations. A number of factors including fatty acid chain length, the extent of esterification and isomeric distribution of these surfactants can significantly impact product performance. Reversed-phase HPLC methods have traditionally suffered from an inability to adequately separate positional isomers of fatty acid esters, making their quantification difficult. We have developed a gradient reversed-phase HPLC method, using a mixture of acetonitrile and water, which resolves all eight positional isomers of sucrose monolinoleate. Isomer-enriched fractions were isolated by preparative HPLC and examined by high-resolution ^{13}C and ^{H}NMR spectroscopy. The sites of esterification for one minor and two major HPLC fractions were uniquely identified to be the hydroxymethyl carbons F-1, G-6 and F-6. These assignments are based on a downfield

shift of the hydroxymethyl carbon and a corresponding upfield shift of the neighboring carbon resonances. The structures of the remaining isomers are currently being characterized by a combination of one-dimensional and homonuclear two-dimensional (COSY) ^{H}NMR spectroscopy at 500 MHz.

Z2

Nondestructive Determination of Oil Composition in Seeds Using Magic Angle Sample Spinning NMR. V. Rutar, Iowa State University, Department of Chemistry, Ames, IA 50011.

Nuclear magnetic resonance is used to study liquid-like components in various seeds and other biological systems. Adoption of magic angle sample spinning reduces line broadening arising from differences in magnetic susceptibility and spectra show superior resolution. Signals of abundant ^{1}H spins which are detected within one minute appear very suitable for routine measurements of oil composition. They can be utilized in large-scale breeding programs designed to improve oil quality, because NMR analysis does not destroy the seed. Subsequent planting preserves the full genetic potential of individual specimens and better varieties can be developed. ^{13}C spectroscopy generally requires longer measuring times, but it also has some important advantages. Large dispersion of chemical shifts facilitates precise assignments of resonances as illustrated by a detailed identification of liquid components in single fir seeds. Results also reveal that *cis*-5, *cis*-9, *cis*-12-octadecatrienoic and *cis*-5, *cis*-9-octadecadienoic fatty acid are selectively esterified to the CH_2-O- group in the glycerol backbone. Nondestructive versions of NMR provide additional insight into metabolic processes during germination. Hydrolysis of carbohydrates, proteins and other initially solid substances gives rise to characteristic resonances which become an important source of information about the single seed.

Z3

Nitrogen-14 NMR Spectroscopy of Quaternary Ammonium Ion Cationic Surfactants. T. Michael Rothgeb, Procter & Gamble Company, Ivorydale Technical Center, 5299 Spring Grove Avenue, Cincinnati, OH 45217, and Elizabeth Jacobs, Procter & Gamble Company.

Nitrogen-14 nuclear magnetic resonance spectroscopy (^{14}N-NMR) is shown to be a powerful qualitative and quantitative tool for the rapid, non-destructive analysis of quaternary ammonium ion cationic surfactants. Analysis using ^{14}N-NMR is useful for the identification and quantitation of quaternary nitrogen compounds in complex mixtures. The ^{14}N-NMR analysis method described is selective for quaternary nitrogen compounds and does not suffer interferences from other non-quaternary nitrogen compounds. Analysis time is less than one hour for samples containing 1 to 5% of a typical quaternary nitrogen cationic surfactant. Accuracy and precision for quantitation are quite good, comparable to other spectroscopic and wet chemical and analytical methods. Finally, information on the cationic surfactant type and the type of nitrogen substitution can be obtained from the ^{14}N chemical shift.

Z4

Olestra - Measurement of Solid Fat Content by Pulsed Magnetic Resonance Spectroscopy. B.L. Madison, Procter & Gamble, 6071 Center Hill Road, Cincinnati, OH 45224, and Tim Guffey (speaker), Procter & Gamble and Don Boatman, Procter & Gamble.

The measurement of Solid Fat Content (SFC) by pulsed magnetic resonance (PMR) as applied to olestra will be discussed. Comparisons between dilatometric measurements and PMR will be shown, as well as solids measurement using different PMR instruments. The applicability of PMR measurement to a wide range of solid-containing mixtures will be discussed.

Z5

The Protective Effect of Water on the Decomposition of Methyl Linoleate Hydroperoxide. H. Chen, Washington State University, Dept. of Food Science, Pullman, WA 99164-6330, and E.G. Schanus (speaker), Provesta Corporation and D.J. Lee, Washington State University.

A proton nuclear magnetic resonance (NMR) spectrometer was used to study the methyl linoleate hydroperoxide (MLHP) decomposition catalyzed with Co^{+2} in a model system. The decomposition of MLHP was monitored quantitatively by determining changes in the area of the peak associated with the -OOH moiety of the molecule. The apparent rate constant at five levels of Co^{+2} was determined by the plot of natural logarithm of concentration of MLHP vs. time. The rate law of the decomposition of MLHP was proposed. A modification of the Schenk and Schulte-Elte method was employed to prepare MLHP using methyl linoleate as a substrate. Column chromatography and thin layer chromatography (TLC) were used for the MLHP purification.

Z6

The Use of Small Nuclear Magnetic Resonance Spectrometers in the Food Processing Industry. Robert M. Pearson, Tri-Valley Research, 3590 Churchill Court, Pleasanton, CA 94566, and John Q. Adams, Adams Systems.

This NMR symposium is ample evidence of the growing awareness of the use of NMR in the agricultural/food industries. The use of high resolution NMR to study chemical structures in both liquid and solid samples is becoming well known in these industries. These studies are most often done in central NMR facilities using large, sophisticated and therefore expensive NMR spectrometers. Small NMR spectrometers are routinely used to measure the properties of edible oils, but have had only limited use in on-line process control applications. In this paper we shall describe some of the techniques and methods we have developed for on-line applications of modified IBM/Bruker Minispec spectrometers. These include the development of new software and hardware process control measurements. Methods will be described which allow quantitative measurements of the various types of hydrogen found without weighing the sample. These methods greatly simplify the use of NMR in on-line applications.

Z7

Synthesis of Deuterated Methyl Arachidonate. R.O. Adlof, USDA-ARS-NRRC, 1815 N. University St., Peoria, IL 61604.

Deuterated methyl arachidonate (methyl *cis*-5-, *cis*-8-, *cis*-11- and *cis*-14-eicosatetraenoate-17,17,18,18-d_4) was prepared for use in both in vitro and in vivo metabolism studies. The deuterium atoms were incorporated into the tetrahydropyranyl (THP) ether of 5-hexyn-1-ol by using Wilkinson's catalyst; the product was hydrolysed to the alcohol and was then converted to the iodide by H_3PO_4/KI. The hexynyl iodide was coupled with 2-propyn-1-ol via a Grignard reaction, and the resultant acetylenic alcohol (2-octyn-1-ol-d_4) was converted to the bromide by Ph_3PBr_2. The bromide was again coupled with 2-propyn-1-ol by a Grignard reaction. The di-acetylenic alcohol produced (3,6-undecadiyn-1-ol-d_4) was next converted to the bromide (Ph_3PBr_2) and then to the iodide (KI/Acetone). To synthesize the other half of the molecule, 5-hexyn-1-ol was oxidized to 5-hexynoic acid, and the acid was coupled by a Grignard reaction with 1-bromo-2-propyne to yield 5,8-nonadiynoic acid. The acid was coupled by a Grignard reaction with the previously prepared iodide to yield the tetraacetylenic precursor of arachidonic acid, 5,8,1,14-eicosatetraynoic acid-17, 17, 18, 18-d_4. The tetraacetylenic acid was reduced to the tetraolefinic acid with hydrogen gas and Lindlar catalyst, and the methyl ester was prepared by diazomethane. Over- and under-reduced material was removed by use of reverse-phase chromatography, and *trans* isomers were removed by silver resin chromatography. Methyl arachidonate-d_4 (98% pure) was prepared in an overall yield of ca. 7% and with an isotopic purity of > 90% d_4.

Z8

The Protective Effect of Water on the Decomposition of Methyl Linoleate Hydroperoxide Catalyzed with Cobalt (II). H. Chen, Washington State University, Department of Food Science, Pullman, WA 99164-6330, D.J. Lee and G.O. Caviness, Washington State University, and E.G. Schanus, Provesta Corporation.

Various amounts of water were added to a model system containing MLHP and Co^{+2} and the decomposition of MLHP was studied using a proton nuclear magnetic resonance (NMR) spectrometer. As the concentration of water increased, the rate of decomposition decreased. At 1.5% level of water, the rate reached a minimum value. The apparent rate constants between the systems with and without Co^{+2} at same water level were compared. The NMR spectrum indicated that there was a metal-water complex formed in the model system during the reaction. The interaction between water and metal ion could also contribute to the decrease in the rate of MLHP decomposition. Possible mechanisms to explain the protective effect of water in the model system were discussed.

Z9

Determination of the Degree of Fatty Acid Esterification of Olestra by HPLC and SFC. P.Y.T. Lin, Procter & Gamble Company, 6071 Center Hill Road, Cincinnati, OH 45224, and J.K. Howie, Procter & Gamble Company.

Capillary supercritical fluid chromatography (SFC) is used to monitor the progress of the manufacture of olestra by allowing separation of each of the partially esterified sucrose species from each other and from sucrose octaester. The average degree of esterification is then calculated. It is also possible to quantitate unreacted methyl esters and sucrose in the same analysis. The high performance liquid chromatography (HPLC) is also used to separate the partial esters from the octaesters of olestra. This procedure has much shorter analysis time and uses simpler equipment which provides better uptime. However, the HPLC method cannot simultaneously provide information on residual methyl esters and sucrose. A summary on the development of these chromatographic determinations on the degree of esterification of olestra will be presented. A comparison of the two procedures will also be provided.

Session AA Friday afternoon

Value-Added Feed Products from Protein and Co-Products: Value-Addition by Processing

AA1

Utilization of Full-fat Oilseeds and Oilseed Meals in Dairy Feeding. Larry D. Satter, USDA-ARS, U.S. Dairy Forage Research Ctr., 1925 Linden Drive West, Madison, WI 53706, and Marty Faldet, USDA-ARS, U.S. Dairy Forage Research Center.

The high energy content of oilseeds is an attractive dietary feature for cows in early lactation that are in negative energy balance and need larger amounts of protein to balance the calories being mobilized from body tissue. Use of heat-processed whole seeds to increase the amount of protein escaping microbial destruction in the ruminant forestomach has increased and can be profitable for the dairy farm. Current methods of heat processing oilseeds, extrusion or roasting, often do not achieve optimum protection of protein from microbial destruction in the rumen. Soybeans, held at temperatures of 295°F for at least 30 min. can supply 50% or more lysine to the small intestine than unheated soybeans, as estimate by an in vitro method for determining protein degradation by rumen microbes and DNFB measurements of lysine availability. Heated oilseeds may be more useful as protein supplements in dairy diets utilizing alfalfa or grass as a forage rather than corn silage. Feeding of oilseeds can reduce the protein content of milk, and this is a potential problem, especially where milk is used for cheese production.

AA2

Calcium Soaps as a Fat Supplement for Ruminants. D.L. Palmquist, Ohio State University, Ohio Agric. Research & Development Ctr., Dept. of Dairy Science, Wooster, OH 44691.

Dietary fat is increasingly important as an energy supplement for high-producing ruminants. Feeding of free fats and oils is limited by inhibitory effects of long-chain fatty acids on rumen microbes. We have shown that calcium

soaps are inert in the rumen with respect to microbial activity and yet they are digested efficiently (>80%) due at least in part to the high acidity of the ruminant duodenum. A commercial calcium soap, developed as an energy supplement for ruminants, is now marketed successfully in over 20 countries worldwide.

AA3

Soybean Proteins in the Diets of Preruminant Calves. W.G. Schmutz, Central Soya, 1200 N. Second Street, Decatur, IN 46733.

Substitute proteins have been used for several decades to replace milk proteins in calf milk replacers. Economics and supply have generated the interest in substitute proteins. In the past few months, interest has become even greater as the world supply of suitable milk proteins has become almost nonexistent. The soybean proteins have to be used to the greatest extent to replace milk proteins. However, performance is reduced when compared to all milk protein milk replacers. While the nutrient requirements of the calf are known, study of the digestive system of the pre-ruminant calf suggests a system designed to digest milk proteins. Soybean proteins fail to form an abomasal casein clot, increase the rate of passage, reduce proteolytic enzyme secretion, thereby reducing protein digestibility, nitrogen retention, and calf performance. This has limited the use of soybean proteins in milk replacers. The disturbances in digestive function and absorption may be the result of an allergic reaction in the intestinal tract. The purpose of this paper is to review various soybean protein products which are being developed by various physical and chemical procedures in an attempt to develop products which will be able to promote performance similar to milk proteins.

AA4

Utilization of Full-Fat Soybeans by Swine. Gary L. Cromwell, University of Kentucky, Animal Sciences Dept., Lexington, KY 40546-0215.

Soybeans are high in protein (37%) and oil (19%) and provide a good source of amino acids and energy for pigs. However, soybeans must be heated in order to destroy the protease (trypsin) inhibitors; otherwise growth rate and efficiency of feed utilization are depressed if raw soybeans are fed to growing pigs. Extruders, infra-red heaters and gas-fired heaters have been used to heat-process soybeans. When properly heated, a corn-whole soybean diet is equal to a corn-soybean meal diet supplemented with 4-5% fat, and produces more efficient gains (i.e., lower feed:gain ratio) than a conventional corn-soybean meal diet. Breeding swine seem to better tolerate the inhibitors in uncooked soybeans. In research studies, pregnant sows fed raw soybeans as the only source of supplemental protein had normal reproductive performance. A similar diet fed during lactation caused greater sow weight loss and reduced weaning weights in pigs. A genetically-modified soybean low in the Kunitz trypsin inhibitor has been developed. Initial studies with this mutant suggest that it is better utilized than normal soybeans, but the inhibitors are still sufficiently high to reduce performance when unheated beans are fed to growing pigs.

AA5

Advances and Challenges in Poultry Feeding. Park W. Waldroup, University of Arkansas, Dept. of Animal & Poultry Science, Fayetteville, AR 72701.

Solvent-extracted soybean meal is the dominant protein source used in poultry feeds, providing approximately two-thirds of the supplemental protein in poultry feeds. With the exception of the amino acid methionine, it provides a good balance of the essential amino acids needed for poultry. Even with this dominant position in the poultry industry, soybean meal is not without problems. The carbohydrate content of soybeans includes a nitrogen-free extract (NFE) content of about 30% and a fiber content of about 6%. Much of this is accounted for in the oligosaccharides, polysaccharides, hemicellulose, and cellulose. The carbohydrates are not easily hydrolyzed by digestive enzymes of mammalian species. Pierson et al. (Poultry Sci. 59:845) found the digestibility of soybean NFE to be only 4 percent. Parsons et al. (Poultry Sci. 60:2687) reported that the chicken digested only about 46% of the dry matter content of dehulled soybean meal. This low rate of digestion of the carbohydrate fraction represents a considerable loss of potential dietary energy. Since about 75% of the average cost of a poultry feed goes toward providing the energy needs, the economic value of soybean meal would be considerably improved by either improving the digestibility of the carbohydrate fraction or by removing it during processing.

AA6

Use of Oilseeds and Meals in Feeding Catfish. R.T. Lovell, Auburn University, Fisheries Department, Auburn, AL 36849.

Channel catfish are the largest volume aquaculture product in the United States. Production in 1988 was approximately 270,000 tons. This required 480,000 to 500,000 tons of feed containing 32% crude protein. Most feeds contain 48 to 50% solvent extracted, dehulled soybean meal. Soybean meal is not deficient in any of the 10 essential amino acids for channel catfish; lysine and methionine + cystine are first limiting. Including 5 to 10% fish meal or meat and bone meal in a basal soybean meal-corn diet increases weight gain by channel catfish; this improvement in fish response cannot be completely explained on a dietary essential amino acid basis. Roasted, full-fat soybean meal is not suitable for use in catfish feeds because of the high oil content which increases fattiness in the fish.

AA7

Use of Soybeans, Cottonseed, Meat and Bone Meal, and Dried Blood in Shrimp Feeds. A.L. Lawrence, Texas A&M University System, Port Arkansas, TX 78373, and F. Castille, Texas A&M University.

Substitutions of various feedstuffs for fish and shrimphead meals in practical feeds were tested in growth trials conducted in tanks to evaluate the feedstuffs as alternative sources of protein in feeds for penaeid shrimp. The results indicated that soybean meal can replace large amounts of fish and shrimphead meals as protein sources

without adversely affecting either survival or growth of shrimp. Cost comparisons suggest that the use of soybean meal has the potential to reduce the cost of commercial shrimp feeds in areas where high quality animal meals are expensive or unavailable. Factors which affected the ability of penaeid shrimp to utilize soybean meal in feeds were the species of shrimp, the size of the shrimp, and the protein level of the feed. Effects of substituting soybean meal for high quality animal meals can also be influenced by the presence of natural foods. Cottonseed meal can also be substituted for shrimphead and fish meals without reducing growth, but at lower levels than soybean meal. Inexpensive animal meals such as meat and bone meal or dried blood adversely affected growth at lower levels than those of soybean and cottonseed meals.

AA8

Advances in Dog, Cat and Zoo Animal Feeding. Jim Corbin, University of Illinois, Dept. of Animal Sciences, 1207 W. Gregory Drive, Urbana, IL 61801.

U.S. dog and cat foods are a $6.4 billion industry with an annual production of 5.6 million tons. The nutritional requirements of cats and dogs have been studied extensively during the past fifteen years. Ratios between dietary amino acids have indicated both symbiotic and antagonistic results. Hirakawa has demonstrated the antagonism of excess dietary cystine resulting in severe skin aberrations in puppies. Cat nutrition, including the role of taurine in the production of feline dilated cardiomyopathy and central retinal pathology, is becoming more fully understood. Scientists are becoming more aware of metabolic abnormalities, such as lethal hepatic copper retention in some dog breeds. These developments plus trends in pet food production will be discussed. More is known about the nutritional requirements of dogs and cats than is known about the nutritional requirements of mankind. America's dogs and cats receive a better balanced diet than is consumed by America's children.

AA9

Biotechnology in By-Product Feeds Processing and Utilization. T. Pearse Lyons, Alltech Biotechnology Center, 3031 Catnip Hill Pike, Nicholasville, KY 40356.

Modern feed manufacturers are expected to improve feed efficiency and animal health utilizing cheaper and cheaper raw materials. The almost historical reliance on items such as growth hormones, steroids, and antibiotics will soon be forbidden as nutritionists and veterinarians response to the demand of the public for animals reared on all-natural feedingstuffs. By reevaluating the role of biotechnology, tomorrow's animal nutritionists will be able to not only respond to these demands, but also do so with greater feed efficiency and in a natural way. The often overlooked and always misunderstood biological tools of enzymes and microencapsulated lactic bacteria, selected strains of yeast culture and buffer paks will be discussed. By using these four natural allies, feed efficiency and liveweight gain can be improved, and the paper will discuss applications and a mode of action of these various techniques.

Session BB Friday afternoon

Plant Biotechnology II

BB1

Somatic Embryogenesis in the Biotechnology of Grasses and Cereal Crops. Indra K. Vasil, University of Florida, 511 Carr Hall, Gainesville, FL 32611, and Vimla Vasil, University of Florida.

Regeneration of plants from cultured cells and tissues is an important and integral part of plant biotechnology. Methods for the efficient recovery of plants from tissue cultures of grasses and cereal crops have been developed only recently by the use of immature embryos or explants from young leaf bases and floral tissues. Such tissues contain uncommitted and undifferentiated cells which divide in culture to form tissues that regenerate plants by the process of somatic embryogenesis. In the absence of a natural vector system such as *Agrobacterium tumefaciens* which is widely used for the transformation of dicotyledonous species, direct DNA delivery systems which often require regeneration from protoplasts are required for monocot transformation. The importance of embryogenic cultures in addition to many other reasons lies in the fact that in spite of extensive efforts transgenic plants of this important group of food plants have been obtained only when protoplasts isolated from embryogenic ell cultures were used for genetic transformation. This paper will describe the establishment of the embryogenic regeneration systems for grasses and cereal crops and their successful use in genetic transformation studies.

BB2

Detection of Glucosinolates by Polyclonal Antibodies to Sinigrin. Raymond S.C. Wong, Allelix, Inc., 6850 Goreway Drive, Mississauga, Ontario, L4V 1P1, Canada

The total utilization and acceptance of canola meal as feed has been limited by the presence of glucosinolates. Numerous analytical procedures are available for use in grain monitoring, breeding selection, quality control and research activity. Not a single available procedure was found to have all the desirable features of speed, simplicity, sensitivity, precision and accuracy. The use of antibodies to assay the presence of glucosinolate could be developed into such procedures with most of the desirable features. The first step of the development of an enzyme linked immunosorbent assay (ELISA) was the preparation of antibodies to one of the simple forms of glucosinolates-sinigrin. The molecular size of sinigrin is too small to be effective in eliciting antigenic response when injected into host animal. Several attempts were made to raise antibodies from rabbits by complexing or conjugating with carrier molecule or particle. A chemical conjugation procedure published by F. Hassa et al [*J. Agric. Food Chem. 36*:398(1988)] was used and successful results were obtained. Antibodies to sinigrin were detected from antisera of two rabbits immunized with sinigrin-bovine serum albumin conjugate. Assay (ELISA) was set up with sinigrin-ovalbumin conjugate as the plate coating antigen and conjugate of anti-rabbit IgG urease as the enzyme linked conjugate. Results of competitive inhibition with free sinigrin and cross reactivity with canola

crude seed extract were also demonstrated. Potential use of this procedure for glucosinolate determination will be discussed.

BB3

Progress in Biotechnological Approaches in the Improvement of Soybean Seed Quality. David F. Hildebrand, University of Kentucky, N-106 AGSCN, Lexington, KY 40546, and E.G. Williams, G.B. Collins, and T.R. Kemp, University of Kentucky.

Recently, several groups have been able to regenerate transformed soybean plants. Paul Christou and co-workers at Agracetus have used a particle acceleration DNA delivery technique. Maud Hinchee and the Monsanto group have used a cotyledonary node regeneration system coupled with Agrobacterium mediated gene transfer. We have used a somatic embryogenesis regeneration system also coupled to Agrobacterium. We are currently comparing these three and other approaches in terms of their efficiency in producing transformed soybean plants. A focus of our program is the improvement of seed quality. Work is in progress on improving the feed value of soybean meal by introducing genes that would increase the methionine content of the protein. Studies on gene products involved in lipid peroxidation have lead to new strategies for the genetic engineering of soybeans for improved value of protein and lipid products. some of these genes have been cloned, vectors constructed and transgenic plant tissues produced. We have also identified gene products associated with polyunsaturated fatty acid biosynthesis. Additionally, work is in progress on the transformation of soybeans with genes which could improve the fatty acid composition.

BB4

Molecular Biological Approaches to Enzyme Modifications in Oilseeds. Ross Eccleshall, Sungene Technologies Corporation, 2050 Concourse Drive, San Jose, CA 95131 and Candace Poutre, Charu Agrawal, Carol Uyeda, Menq-Yun Wang, and David Zaitlin, Sungene Technologies Corporation.

Seeds contain as major components, triacylglycerols and polysaccharides. The alteration of specific enzymes involved in the synthesis or modification of these components will allow the production of specialty products or byproducts with enhanced value. By introducing seed-specific genes into oilseed crop species, the expression of new enzymatic functions or the attenuation of pre-existing enzyme activities will permit, for example, the synthesis of triacylglycerols of essentially a specific molecular species. The sources of these new genes include other plant species and microorganisms. Microorganisms are particularly attractive gene sources because it is possible, by techniques of microbial molecular genetics, to modify existing enzymes to have a desired substrate specificity and then to isolate the relevant genes for introduction into plants. The application of these ideas to properties of oils from specific oilseeds will be discussed.

BB5

***Arabidopsis* Plants with Altered Seed Storage Lipids Obtained by Chemical Mutagenesis - Isolation of Genes Via Transposon Tagging.** Douglas W. James, Jr., Advanced Genetic Sciences, Inc., 6701 San Pablo Ave., Oakland, CA 94608 and Hugo K. Dooner, Advanced Genetic Sciences, Inc.

With a view towards ultimately customizing the fatty acid composition of rapeseed oil (*Brassica napus*), we are studying *Arabidopsis*, a diploid cruciferous plant with a small genome that is easily transformed and regenerated. To isolate the genes that effect desired changes in FA composition, we are using an approach called "transposon tagging." After subjecting seeds to mutagenesis, mutants are identified that are deficient in one or more FA's (i.e., a gene has been tagged by its loss of function). The chemically-induced mutants are then crossed to transposon-bearing plants. Progeny are screened for phenotypes resembling the chemically-induced mutant parents, indicating that these individuals would be carrying the transposon at the same locus. Transposon-specific probes can then be used to identify and isolate the gene. We have run FA analyses on about 2000 pedigreed M3 seed collections from EMS mutagenesis and have found over 60 phenotypes in which the composition differed from wild type in at least one FA by greater than 4 standard deviations. After re-screening siblings of the phenotypes first identified, three important heritable mutants were chosen for transposon tagging: G30, lacking 18:3; 4A5, deficient in 18:2 and 18:3; and 9A1, lacking all FA's greater than C 18. Characteristics of these mutants and progress in obtaining plants carrying transposons will be discussed.

BB6

Purification and Characterization of Diacylglycerol Acyltransferase from Soybean. Prachuab Kwanyuen, USDA-ARS-NRRC, 1815 N. University St., Peoria, IL 61604 and Richard F. Wilson, North Carolina State University, Box 7631, Raleigh NC 27695.

Diacylglycerol acyltransferase (EC 2.3.1.20) is the enzyme responsible for catalysis of triacylglycerol synthesis in oilseed crops. This highly hydrophobic membrane-bound protein has been purified from soybean seed. Techniques required for that original work and biophysical properties associated with the protein, including amino acid composition and sequence data, will be presented. This work not only provides a basis for molecular genetic regulation of triacylglycerol content in oilseeds, but also allows the determination of the role that this enzyme may have in affecting altered fatty acid composition in storage lipids. It is believed that diacylglycerol acyltransferase confers significant influence on the composition of triacylglycerol molecular species. This belief will be supported by data from kinetic analyses of the substrate specificities exhibited by purified enzyme from genotypes with genetically altered fatty acid composition.

Session CC Saturday morning

Surfactants & Detergents V: New Directions in Surfactants & Higher Alcohols

CC1

The Effect of Sodium Citrate in a Liquid Laundry Detergent at Various Wash Temperatures. Karen L. Pratt, Miles, Inc., 1127 Myrtle Street, Elkhart, IN 46514.

Data will be presented that show sodium citrate built liquid laundry detergents out-perform the same detergents without a builder added over a wide range of temperatures from cold water (15°C) to hot water (90°C). Terg-o-tometer testing was done using an anionic surfactant with 5%, 10% and 15% sodium citrate added. Two types of stain were tested on two types of cloth: ground-in clay on cotton and on cotton/polyester; dust-sebum on cotton and on cotton/polyester. The wash temperatures of the test were 15°, 20°, 40°, 50°, 60°, 70°, 80°, and 90°C.

CC2

Effect of Anionic and Nonionic Structure on the Detergency of Anionic/Nonionic Mixtures. R. Kok, Shell Research B.V., Koninklijke/Shell Laboratorium, Badhuisweg 3, Amsterdam, 1031 CM, The Netherlands and T.A.B.M. Bolsman, Koninklijke/Shell Laboratorium.

Mixtures of anionic and nonionic surfactants are known for their synergistic effects on physico-chemical properties and application characteristics. For this reason, we have investigated the relation between oily soil removal and the phase characteristics of anionic/nonionic mixtures as a function of anionic and nonionic structure. The anionics selected were alkylarene sulphonates with different alkylchain lengths, phenyl positioning and aromatic substitution patterns. The nonionics chosen were alcohol ethoxylates with different ethylene oxide contents. A fast method based on a titration procedure, has been developed for the selection of the optimal ratio. It is shown that anionic and nonionic structural parameters, as well as their ratio, have a pronounced effect on the kinetics and ultimate detergency performance. In addition, the nature of the soil plays an important role.

CC3

Effect of Hydrophobe Structure on Ethoxylate Distribution in Nonionic Surfactants. C.A. Smith, Union Carbide Corporation, P.O. Box 8361 (740-2405), So. Charleston, WV 25303, and R.M. Weinheimer and J.H. McCain, Union Carbide Corporation.

The ethoxylate distribution for any nonionic surfactant depends mainly upon two factors: (1) the catalyst used in the ethoxylation reaction, and (2) the structure of the starting alcohol. In recent years, much effort has been devoted to developing catalysts which will produce surfactants with "narrow" ethoxylate distributions. These successful efforts have led to new commercial products, such as the TERGITOL^{R} Narrow Molecular Weight Surfactant series. This paper describes the effect of alcohol structure, particularly alkyl substituents in the 2-position on the distribution of ethoxylates produced using narrow molecular weight catalyst technology. These effects are compared and contrasted with the analogous effects observed with conventional base catalysts. Experimentally determined rates are presented for several alcohols and their corresponding ethoxylates. Models for predicting ethoxylate distribution as a function of alcohol structure are discussed.

CC4

Determination of Relative Rate Constants in the Ethoxylation of Alcohols. Paul R. Geissler, Exxon Chemicals, P.O. Box 241, Baton Rouge, LA 70821, and Adrian E. Johnson, Jr., Louisiana State University and Larry D. Talley, Exxon Research & Engineering.

Earlier work in our laboratory developed a Supercritical Fluid Chromatographic method of analysis that accurately and easily determined ethylene oxide distributions in ethoxylated alcohols. This work was presented at the 79th National Meeting and has been submitted for publication in the *JAOCS*. A flexible computer program has recently been written that calculates, from these SFC data, ethoxylation rate constants for all of the sequential ethoxylation steps relative to that of the initial ethoxylation of the feed alcohol. A second program calculates ethylene oxide distributions in ethoxylated alcohols from these ratios of rate constants, often called distribution coefficients. Distribution coefficients were determined for base-catalyzed ethoxylations of normal octanol in both the pure state and in mixtures. They are not substantially affected by the presence of either another alcohol, such as 2-ethylhexanol, or a highly ethoxylated alcohol, such as 2-ethylhexanol ethoxylate with an average ethylene oxide/alcohol ratio of nine. Slightly contrary to past published results, they were found to increase with increasing ethylene oxide content of the reactant ethoxylate up ethylene oxide/alcohol ratios of at least six. Their values, however, change as the average ethylene oxide content of the ethoxylated alcohol reaction medium increases. Using distribution coefficients averaged over an ethylene oxide/alcohol molar ratio range of two to ten, model predictions closely match experimentally determined ethylene oxide oligomer distributions.

CC5

Structure/Performance (Detergency) of Nonionic Surfactants for Various Soil Types. Michael J. Gula, Exxon Chemical Company, P.O. Box 241, Baton Rouge, LA 70821.

Four nonionic surfactants were compared for their inherent detergency with various soil types. The surfactants studied were ethoxylates of four commercially available synthetic alcohols; alkylphenol, Ziegler linear alcohols, oxo-linear alcohols, and oxo-branched alcohols. Soil removal and redeposition were determined in standard Terg-O-Tometer tests under a variety of test conditions, using several soil and fabric types. The results indicate that different products do exhibit selectivity for certain soil types.

CC6

Effects of Hydrophobe Structure on the Performance Properties of Nonionic Surfactants. Albert F. Joseph, Union Carbide Corporation, Bldg. 740, Room 2409, P.O. Box 8361, South Charleston, WV 25314, and Kevin W. Dillan, Union Carbide Corporation.

The technical considerations which must be addressed when selecting a nonionic surfactant include physical, chemical, performance, and environmental properties which are dependent on the structure of the surfactant molecule. The current investigation considers the effect of nonionic surfactant hydrophobe structure on key physical and performance properties. Surfactants of interest include linear primary alcohol ethoxylates, secondary alcohol ethoxylates, and nonylphenol ethoxylates with degrees of ethoxylation ranging from 3 to 30 moles of ethylene oxide. Physical

properties studied include density, viscosity, aqueous gel range, pour point, water solubility (cloud point), solvent solubility, and aqueous surface tension (critical micelle concentration). The performance evaluation includes Ross-Miles foam, Draves wetting, detergency, paper de-inking, hard-surface cleaning, and emulsification. Trends within and among the surfactant families are discussed.

CC7

Comparative Biodegradability of Linear and Branched Alcohol Ethoxylates. A.I. Hughes, Exxon Biomedical Sciences, Inc., Mettlers Road, CN 2350, E. Millstone, NJ 08875, and D.R. Peterson and R.K. Markarian, Exxon Biomedical Sciences, Inc.

Detergent formulations and other cleaning products are often developed using linear alcohol ethoxylates or nonylphenol ethoxylates. Branched alcohol ethoxylates have not been evaluated as widely for detergent application due to the perception that branched biodegrade slowly. Test results from standard screening tests performed on linear and branched alcohol ethoxylates will be presented. The results suggest that branched alcohol ethoxylates perform nearly as well as linear alcohol ethoxylates in standard laboratory biodegradation screening tests. These experimental findings will be discussed in terms of the current and historical beliefs regarding the biodegradation potential of branched versus linear materials.

CC8

L.A.S. Fate Cycle in the Environment. J.L. Berna, Petresa, Orense 68, Madrid, Spain 28020, and A. Moreno and J. Ferrer, Petresa, and F. Ruiz-Bevia, University of Alicante.

An extensive and thorough L.A.S. monitoring exercise has been conducted using specific H.P.L.C. analytical determinations in all cases. The study has been carried out in nine different sewage treatment plants covering three different design systems, as well as during sludge preparation and soil-amending operations. L.A.S. removal was in all cases very high, between 98-99%. The removal mechanism of L.A.S. in sewage treatment plants depends on the system used, the anaerobic or aerobic digestion of sludges, and the water hardness. This parameter is most influencing on the amount of L.A.S. removed during the primary settling, therefore, not being exposed to the biological treatment. L.A.S. leaving the plants adsorbed onto the sludges continues the biodegradation process during the soil amendment operation and no accumulation effect was detected in any case considered in the study, neither during the sewage treatment, nor on the sludge amended soils.

Session DD Saturday morning

New Functionalities for Value-Added Proteins

DD1

Factors Affecting the Functionality of Pea (*Pisum sativum*) Protein Isolates. Jeff D. Culbertson, Central Michigan University, Dept. of Human Ecology, Mt. Pleasant, MI 48859.

The functionalities of plant proteins dictate their acceptance and use in modern food systems. The functionality of protein isolates from peas (*Pisum sativum*) is influenced by method of extraction, protein composition, lipid content, and conditions of storage. Oxidation of coextracted lipids decreases protein solubility and foaming ability. Controlling the moisture content of isolates during storage may minimize deleterious oxidation effects. The use of limited heat treatments may improve the functionality of pea isolates.

DD2

Potential for Substituting Bovine Plasma for Egg Proteins in Bakery Products. Suzanne Lee, Iowa State University, Ctr. for Crops Utilization Research, 102 Dairy Industry Building, Ames, IA 50011, and Lawrence Johnson and Jane Love, Iowa State University.

Eggs, especially egg white, play a critical functional role in baked products due to their unique solubility, foaming, emulsifying and heat coagulation properties. Bovine plasma, a by-product of the livestock slaughtering industry, is the only alternative protein known to possess similar properties. Spray dried bovine plasma is now commercially available and being used as meat binders in comminuted meats and surimi. This paper will discuss the potential of plasma to partially or completely replace egg ingredients in cakes. White layer cakes made with plasma replacing all egg white at an equivalent protein level have about 92% of the volume of those made with egg white. Enzymatically hydrolyzed plasma performs even better. Nearly equivalent performance can be achieved by replacing 1.1 part of plasma protein for 1.0 part of egg white protein. Plasma cakes have less crowning profile, darker crust and slightly darker crumb. Sensory evaluations indicate that more than 60% of untrained panelists prefer cakes made with plasma to those made with egg white. Panelists indicate cakes made with plasma are moister, softer, more tender and sweeter. Plasma can be treated with glucose oxidase to extend stabilities of flavor and functional properties without affecting cake baking potential.

DD3

Manipulating Muscle Protein Functionality in Processed Meat Products. Denise Smith, Michigan State University, Dept. of Food Science & Human Nutrition, East Lansing, MI 48824-1224.

Proteins are the principal functional and structural components of processed meats. An understanding of the physicochemical properties of proteins is required to control the waterholding, fatholding and textural attributes of finished meat products. Extrinsic and intrinsic factors can be manipulated to produce the desired protein functionality in traditional and novel meat products. Extrinsic factors which influence functionality include pH, salt concentration, heating history, processing method and storage conditions. Intrinsic properties are determined by the structure and composition of proteins in the meat system. The relative proportions of water-soluble, salt-soluble and insoluble

proteins within a muscle type (e.g. striated vs. smooth) have a large influence on product functionality.

DD4

A New Molecular Basis for the Salt-Induced Solubility Profiles of Food Proteins. Thomas F. Kumosinksy, USDA-ARS-ERRC, 600 E. Mermaid Lane, Philadelphia, PA 19118.

Biotechnology holds the promise for the food industry to produce proteins with tailor-made functional properties. Without a fundamental knowledge of the molecular bases of these properties, implementation of this concept will be strictly empirical and product preparations will be costly. One such functional property is the phenomenon of salt-induced precipitation of proteins (salting-out) and their resolubilization (salting-in) which, until now, has only been discussed in a qualitative manner. Now, a new molecular basis which uses Wyman's theory of Thermodynamic Linkage and non-linear regression analysis, has been developed for quantitating these salt-induced solubility profiles. Here, the solubility of a protein species can be thermodynamically linked to the binding of salt to that species. Salting-out can be described by a salt binding constant, K_1, and N, the number of moles of salt bound to a protein; salting-in can be described by the corresponding terms k_2 and m. This methodology was successfully tested on salt-induced solubility profiles of native and heat-denatured soybean isolates using the lyotropic series of salts as well as the calcium induced solubility profile of various casein components of Bovine milk under a variety of environmental conditions. The variation of the derived parameters will be discussed in terms of modern theories of protein structure and interactions. These results clearly demonstrate that salt-binding to charged groups on a protein surface can have large influences on the protein solubility.

DD5

Thermodynamics of Flavor-Ligand Binding to Purified Soy. Sean O'Keefe, Iowa State University, Dept. of Food Technology, 147 Food Technology Lab, Ames, IA 50011, and Patricia A. Murphy, Iowa State University.

The off-flavors associated with soybean proteins still are the major problem in acceptance of soy products for human foods. The interactions of these flavor compounds with soy protein are complex and not well understood. Removal of these flavors will be a complex task. The binding kinetics of butanal, pentanal, hexanal, octanal, 2-hexanone, 3-hexanone, 2-nonanone, 5-nonanone, hexanol and hexane were studied using highly purified glycinin and ß-conglycinin ± reducing agent, high ionic strength, NaN_3. Glycinin had significantly more binding sites than ß-conglycinin. Positive cooperativity was observed. Surface hydrophobicity was greater for ß-conglycinin than glycinin and higher for both proteins at 5°C than 20°C. Reducing agent, NaN_3 and ionic strength affected binding kinetics. TS values were greater than H, suggesting that entropy was driving the reactions, but free energy increased as aldehyde chain length increased. The flavor-binding model will have to include hydrophobic and hydrogen bonding.

DD6

Effects of Extrusion on the Protein Quality of Cornmeal-Cottonseed Snacks. Mary Ellen Camire, Texas Woman's University, Dept. of Nutrition & Food Sciences, P.O. Box 24134, Denton, TX 76204, and C. Clay King, Texas Woman's University.

Glandless cottonseed flour (GCF) is an excellent source of both dietary protein and fiber. A Baker Perkins MPF 50 twin screw extruder was used to produce expanded cornmeal-based snacks containing 12.5 and 25% by weight partially defatted GCF. Response surface analysis of four factors (%GCF: 0-25, Barrel temperature: 150-200 C, screw speed: 350-450 rpm, and % water in the mix: 18-21.5) was used to optimize the extrusion conditions necessary for nutritional and functional qualities. In general, the addition of GCF increased expansion and decreased lightness and yellow color compared to similarly processed 100% cornmeal controls. Other evaluations included water-holding capacity, *in vitro* protein digestibility, available lysine, and protein solubility in SDS and mercaptoethanol. A sensory panel evaluated the dried collets for intensity and preference of color, flavor, hardness, and toughness.

Session EE Saturday morning

Fat Substitutes I

EE1

Fat Substitutes—One Option to Low-Calorie Foods. Norman O.V. Sonntag, Consultant, 306 Shadowood Trail, Ovilla, TX 75154.

The advantages and disadvantages of fat substitutes for use in low-calorie foods will be contrasted with the alternate option of the use of low-fat formulations. Methods for preliminary evaluation of fat substitutes, including enzyme hydrolysis *in vitro*, and estimation and determination of calorific value will be outlined, and wherever possible, limitations indicated. The problem of *anal leakage* observed with some candidates in test animal feeding studies with high dose levels will be reviewed and possible solutions outlined. Estimates will be given for the cost of leading fat substitutes based on known raw material costs and estimated processing costs for the required steps in the synthesis.

EE2

New Aspects of Sucrose Polyesters Since Mattson and Volpenhein. J.A. Wei, FII, P.O. Box 72, Colonia, NJ 07067.

Few inventions in the food business have had the impact of a P & G patent of 1971 assigned to Mattson and Volpenhein. P & G has itself continued research and development, culminating in a FDA application in May 1987, an imaginative patent application in February 1986 based on physical properties and an issued U.S. Patent of December 1988 on uses. Work in Germany has indicated a new process. This is also the case of a Japanese work and an American one by a third party. Laboratory efforts of the author of Washington State University plus its follow-up

will be stressed from the technical and economic viewpoints of sucrose polyesters.

EE3

Worldwide Potential of Fat Substitutes Through the Year 2000. James M. Stanton, Experience, Inc., 1200 2nd Avenue South, Suite 400, Minneapolis, MN 55403, and Raymond H. Dull, Experience, Inc.

The high percentage of calories derived from fats in the U.S. diet has become an increasing health concern. Recent interest in the U.S. has focused on fat substitutes as one way to lower caloric fat as a percentage of total caloric intake. This paper reviews the current fat substitute situation in the U.S. and predicts the effect that fat substitutes will have on per capita fat consumption in the major world markets.

EE4

Olestra and the Evolution of Fats and Oil Technology. Carolyn Bergholz, Procter & Gamble Co., Winton Hill Technical Center, 6071 Center Hill Road, Cincinnati, OH 45224.

Olestra is a noncaloric fat replacement made from vegetable oil and sugar. Its physical properties are comparable to those of conventional edible fats and oil, and it can be used interchangeably with full calorie fats in a wide variety of foods, including those that are cooked, baked, or fried. It is the latest technology in the evolution toward products with lower saturated fat, from all vegetable shortening, to vegetable oils, to olestra, a nonabsorbable fat. A Food Additive Petition seeking approval to use olestra to replace up to 35% of the fat in shortening and oils used in the home and up to 75% of the fat used for deep fat frying in restaurants and commercial production of snack foods like potato chips was filed. Foods made with a shortening or oil containing olestra have the same taste and organoleptic properties as those made with conventional oils. The chemical, physical, and biological properties of olestra will be reviewed, and examples of the fat and calorie reduction possible with olestra will be provided.

EE5

Esterified Propoxylated Glycerols - A New Non-Caloric Oil and Fat Substitute. Charles F. Cooper, ARCO Chemical Company, 3801 West Chester Pike, Newtown Square, PA 19073.

Esterified propoxylated glycerols are being investigated as possible non-caloric fat and oil substitutes. They are similar to natural fats and oils except that oxypropylene units have been incorporated into the structure. In general, standard techniques can be used to analyze and characterize EPG's. However, certain modifications are required due to properties which are not typical of natural oils and fats. These will be discussed along with the general nature of the compounds themselves.

EE6

Prolestra - A New Sucrose Polyester and Protein Composition. Robert S. Aries, Reach Associates, Inc., South Orange, NJ 07079.

The use of 30% or less of sucrose polyesters permits the avoidance of anal leakage and depletion of oil soluble vitamins particularly E. Proteins from a wide variety of vegetable and animal sources are added for a maximum of 76% triglyceride oil substitution. Particulation process engineering can be used. The composition is usable for ice cream, salad oil, mayonnaise, spreads, sauces, salted snacks and baked goods, some formulations are indicated.

EE7

Malonate Esters: New Synthetic Fat Substitutes for Food Use. Marshall E. Spearman, Frito-Lay, Inc., Research & Development, 900 North Loop 12, Irving, TX 75061 and John G. Fulcher, Frito-Lay, Inc.

Fatty alcohol esters of malonic and alkylmalonic acids are being developed as fat substitutes suitable for high-temperature applications. These liquid or semi-solid materials can be synthesized from diethyl malonate or malonyl dichloride. Chemical identity was established by MS and carbon NMR. A mixture of 85:15 oleyl:stearyl alcohol was used to prepare dialkyl dihexadecylmalonate (DDM): mp 96°F with a SFI of 11% at 100 F. Fried potato and tortilla chip products prepared with DDM have been analytically characterized. Sensory panel analyses have also been completed. A lipase assay was used to estimate digestibility *in vitro*. Relative to triolein (100% digestion), low digestibility was found for dialkyl malonate (4.7%), dialkyl hexadecylmalonate (3.3%), and DDM (2.5%). Absorption of DDM was assessed by *in vivo* feeding studies in rats. From recovery of oil in the feces (4-week study) and radiocarbon-labelled tissue distribution/balance studies, it can be concluded that less than 0.1% of the ingested DDM is absorbed. The toxicology of DDM was evaluated in a subchronic feeding study. At low concentrations, no toxic effects were found. Higher exposure rates produced milk gastrointestinal effects (such as anal leakage of oil). In addition, LD50 studies have been conducted and indicate that DDM is nontoxic at tested doses. In conclusion, DDM is a new synthetic fat substitute that is minimally digested and absorbed, thermally stable, and that may be useful for preparing food products.

Session FF Saturday morning

Fats and Oils Processing III

FF1

Chlorophyll Removal in Canola Oil: A New Concept. S.K. Brophy, Oil-Dri Corporation of America, 22149 N. Pet Lane, Prairie View, IL 60069, and D.D. Brooks, A. Brophy, and G.R. Goss, Oil-Dri Corporation of America.

Canola is emerging as a major oil processed in North America. Research was conducted into the effective bleaching of canola oil with a non-acid activated bleaching clay (NABC), the NABC enhanced with acids, and an acid activated bleaching clay. The acid enhanced NABC (with 4 percent citric or phosphoric acid, w/w clay) demonstrated a most effective color and chlorophyll removal. Super degummed canola oils were obtained from commercial refinery and subsequently were bleached under vacuum conditions

(50 mm Hg) at 120°C for 30 minutes in the laboratory. Clay dosages used were 1, 2 and 4 percent (w/w oil).

FF2

Effect of Nitrogen Purity Upon Storage Stability of Corn, Soy, and Canola Oils. Roger D. Sinram, A.E. Staley Mfg. Co., 2200 E. Eldorado Street, Decatur, IL 62525, and Elizabeth E. Smith, Air Products and Chemicals, Inc.

Twenty-liter portions of non-hydrogenated corn, soy, and canola oils were deodorized in the lab, and 600-ml alliquots of each oil were placed into 1000-ml stoppered Erlenmeyer flasks. Each oil was equally sparged continuously from a manifold connected to a nitrogen gas supply for a 7-day period. Oil samples were periodically analyzed for degradation products, including changes in color, free fatty acid, peroxide value, flavor and flavor volatiles. The experiment was repeated at several nitrogen purities (ranging from 97.0 to 99.999% with oxygen ranging from 3.0 to 0.001%) at temperatures of 37, 65, and 93°C and at two moisture levels. Excellent correlations were observed between several of the breakdown changes. The data were plotted and statistically compared to establish optimum nitrogen purity required for storage of each oil type. As expected, oxidative stability for all three oil types varied but was directly proportional to nitrogen purity. Temperature extremes appeared to have more effect on oil stability than the presence of moisture. Some of the proposed chemistry that occurred in the study will be discussed. It is thought that the optimum nitrogen purity levels generated from this experiment may be extrapolated to real-world oil storage systems.

FF3

Nitrogen Supply Optimization: Purity, Cost and Operation. Ken Brown, Union Carbide Corporation, Linde Div., Old Saw Mill River Road, Tarrytown, NY 10591.

The most cost effective means of supplying nitrogen to facilities is being investigated. On-site systems such as membrane and pressure swing adsorption (PSA) units are now readily available and are being evaluated against merchant liquid nitrogen and exothermic gas generating systems. Purity requirements and utilization are major factors. Safety and product quality will determine the minimum purity requirements. Flow profile and use pattern will further define the appropriate supply method. Factors and procedures for choosing the most optimum nitrogen supply system will be discussed. A specific case history with a major fats and oils producer will be discussed.

FF4

Interim and Emergency Hydrogen Supply Options. Kathleen A. Kuberka, Union Carbide Corporation, Linde Div., Old Saw Mill River Road, Tarrytown, NY 10591.

Hydrogenation is a very important process in the manufacture of oleochemicals. A continuous reliable supply of hydrogen is necessary for process operation. Generally, oleochemical manufacturers operate and maintain their own on-site sources of hydrogen. Planned and unplanned outages occur with these on-site systems. Special merchant supply systems have been constructed and are available to supply a continuous flow of hydrogen during these outage situations and will be discussed.

FF5

Modified Bleaching. J.M. Bogdanor, W.R. Grace & Co., Davison Chemical Division, 7379 Route 32, Columbia, MD 21044.

A novel method of bleaching is discussed. The method employs the use of two adsorbents, silica gel to remove soaps and phospholipids and an adsorbent to remove chlorophyll. Adsorbent use is optimized by adding the silica adsorbent continuously to the oil prior to the vacuum bleacher and precoating the filter press with the chlorophyll reagent. In this way soaps and phospholipids, known to poison the chlorophyll capacity of bleaching earths, are removed before the oil contacts the chlorophyll reagent. Modified bleaching can be used with caustic and physical refining. The ultimate extension of this unique form of bleaching is Modified Caustic Refining; elimination of the water wash centrifuge combined with modified bleaching. Modified bleaching results in better process control, quality and economics compared to traditional bleaching. Theory and results from lab and commercial tests will be discussed.

FF6

The Role of Fat and Emulsifiers in the Viscosity of Food Emulsions. Andre J. Eydt, Food Consultant, 66 West 94th Street, #11 E, New York, NY 10025.

The physical chemistry aspects of how to create viscosity in the processing of food emulsions and how to find the optimum operating conditions by judiciously using the effects of mechanical, physical and chemical parameters will be presented. The mechanical constraints of a process are given by the configuration of the equipment as to geometry and power capabilities. It is within the art of the engineer to exploit these limitations by fully understanding the physical chemistry underlying the process. It will be shown that one physical way of adjusting emulsion viscosity is to take advantage of the characteristics of the solid fat index (SFI) curve of a particular fat or to change it by manipulating the fat composition to get the system to work within the desired temperature range to overcome particular short-term processing constraints and provide long-term finished product shelf-stability as well. The chemical influence on emulsion viscosity is determined by the emulsifiers used and a knowledge of their molecular configuration is paramount to optimizing the process. As the interactions of these mechanical, physical and chemical parameters are often not obvious, a mathematical analysis of carefully designed sets of experiments was used and became a powerful and cost effective research tool.

FF7

Integrated Oils and Fats Processing. David W. Foster, KBC Process Automation, Chilworth Research Centre, Southampton, Hampshire, United Kingdom, S01 7NP.

Modern oils and fats refineries demand the application of state-of-the-art computer control systems to optimize the

use of sophisticated processing equipment. This paper describes a formal approach to their specification and design enabling islands of automation to be avoided. Applications of systems to both batch and continuous refining are described. The paper describes how by application of formal top down business analysis techniques, information technology strategies can be developed leading to full integration of the refinery processes. Optimal processing conditions can then be determined by analysis of the data obtained from the systems, enabling the benefits of integration to be realized and profit margins improved.

FF8

Tallow Simulating Product from Castor Oil. R.K. Trivedi, Harcourt Butler Technological Inst., Nawabganj, Kanpur, 208 002, India, and A.K. Vasishtha, Harcourt Butler Technological Institute.

Tallow simulating product from castor oil was prepared by three different routes, viz. (i) hydrogenation of castor oil at 130°C, 2.0 kg/cm^2 hydrogen pressure and 0.5% Ni catalyst for 6 h resulting in a product having iodine value 4.2, hydroxyl value 154.0 and slip point 84.0°C, which on subsequent dehydration at 230°C with 0.5% $KHSO_4$ under 40 mm Hg gave a tallow like product, (ii) pre-dehydration of castor oil to obtain a product having iodine value 126.0 and hydroxyl value 28.0 followed by hydrogenation at 190°C, 2.0 kg/cm^2 hydrogen pressure, and 0.2% Ni catalyst (75% recycled) for 3 h yielded a product having hydroxyl value 19.2, iodine value 47.0, and slip point 49.0°C, (iii) simultaneous dehydration of castor oil in presence of 2.0% activated earth, 0.5% activated carbon and hydrogenation at 200°C, 1.5 kg/cm^2 hydrogen pressure and 0.2% nickel catalyst for 8 h yielded a product having iodine value 50.4, hydroxyl value 14.0, and slip point 47-48°C. Out of the above three routes, simultaneous dehydration and hydrogenation process was found to be the most convenient and efficient.

Session GG Saturday morning

Analytical III: General Analytical Measurements

GG1

Isolation and Identification of Flavor Compounds in Beef Tallow. Elizabeth K. Parle, University of Illinois, 1208 W. Pennsylvania Ave., Urbana, IL 61801, and E.G. Perkins and Barbara Klein, University of Illinois.

Beef tallow has long been considered a preferred deep-fat frying medium at fast food establishments. This is primarily due to an apparent desirable flavor imparted to foods fried in beef tallow. However, many fast food chains have been switching from beef tallow to vegetable oil/tallow blends or 100% vegetable oil in response to growing consumer concern regarding animal fats. Sensory evaluation was performed in which beef tallow, vegetable shortening, and deodorized beef tallow were compared using the oils themselves as well as french fries fried in the fats. Although differences were seen when comparing the actual fats, no differences were noted upon frying of french fries in the various fats. High-vacuum cold-finger distillation was employed to collect high molecular-weight volatiles of possible flavor significance in beef tallow. The distillate was then fractionated into polar and non-polar fractions and analyzed by Gas Chromatography. Volatile analysis using the External Closed Inlet Device developed by the USDA coupled to Gas Chromatography/Mass Spectrometry enabled the identification of volatiles in the fats themselves in addition to french fries fried in the fats. Over 90 compounds were found in beef tallow.

GG2

Vaccenic Acid as a Major Component of the Triacylglycerols in Residual Oils of Canola Meals. J.K. Daun, Canadian Grain Commission, Grain Research Laboratory, 1404-303 Main Street, Winnipeg, Manitoba R3C 3G8, Canada.

Canola oil has been observed to contain about 3% vaccenic [(n-7) C18:1] acid. Analysis of the hexane-extracted lipids from canola meals showed as much as 18% vaccenic acid in a total of 54% C18:1 fatty acids. The vaccenic acid was found in the triacylglycerol fraction of the extract. A similar increased level of vaccenic acid was found in the triacylglycerol portion of the second and third extracts from sequential extraction and regrinding of canola seeds using hexane as the extraction solvent. These findings suggest that vaccenic acid may be an important constituent in structural triacylglycerols.

GG3

Separation FAME Hydroperoxide by Capillary SFC. Robert M. Sauer, Jr., University of Illinois, Dept. of Food Science, 382D AESB, 1304 W. Pennsylvania Ave., Urbana, IL 61801.

The purpose of the current investigation is to examine the efficacy of supercritical fluid chromatography (SFC) for the separation of complex mixtures of fatty acid methyl ester hydroperoxide isomers. SFC has demonstrated the ability to directly separate the four positional isomers (–9, –12, –13, and –16) of methyl linolenate hydroperoxides. The 9 and 13 hydroperoxides of methyl linoleate have also been separated. Work has also begun on the separation of methyl oleate hydroperoxides with this procedure. Due to the relatively low separation temperatures afforded by SFC, it is possible to directly separate these peroxides without hydrogenation or reduction to related hydroxy derivatives. Thus, the direct separation of the positional isomers of methyl ester peroxides is possible. The ultimate goal of this work is to develop a method of directly analyzing the changes that occur to lipids as a result of processing and storage of foods by coupling supercritical fluid extraction with supercritical fluid chromatography (SFE/SFC).

GG4

Capillary Gas Chromatographic Analysis of Multiple Long Chain Nitrogen Derivatives. Chu-nan Wang, Akzo Chemicals, Inc., 8401 West 47th Street, McCook, IL 60525, and Lincoln D. Metcalfe, Akzo Chemicals, Inc.

Multiple long chain fatty nitrogen derivatives are widely used in many industrial and consumer applications. The

composition of the alkyl chain distribution as well as the other information provided by gas chromatography is of great interest to the manufacturers and the formulators. However, the high molecular weight range (500 to 1000) and the high boiling points of these compounds create a difficult task for routine gas chromatographic analysis. Many problems have been observed when attempting to use packed columns to analyze these chemicals. The development of the bonded phase capillary column has proved to be a useful solution to this problem. We have found not only improved resolution but also faster analysis time. Using a three-meter DB-1 bonded capillary column with 0.25 um film thickness, we separated monalkyl homologues, dialkyl, tri-alkyl and other components of interest. The optimum instrument conditions have been developed and the many multiple long chain compounds in fatty amines, amides and quaternary ammonium compounds have been identified.

GG5

Separation of Lipids by High Temperature GC. Zelda Penton, Varian Instrument Group, 2700 Mitchell Drive, Walnut Creek, CA 94598

Traditionally, lipids have been hydrolyzed and the resulting fatty acids methylated prior to GC determination. Some separation of the intact lipids has been effected in the past with short packed columns. With the advent of fused silica capillary columns and on-column injection a few years ago, further progress was made in the determination of these compounds. Recently, additional progress has occurred in this important application with the development of capillary columns with higher temperature limits and gas chromatograph ovens that can be heated to over 400°C. In this paper, the separation of lipids is described on the Varian 3410 high temperature gas chromatograph. This instrument is equipped with a temperature-programmable injector that is simpler to use than an on-column injector. Triglycerides were separated on a fused silica column heated to 415 and 345. The retention time of tribehenin (C_{69}) under high temperature conditions was only 15 minutes as compared to 31.5 minutes at 345. The last few peaks in the high temperature run were sharper and more easily handled by the data system. It has been reported in the literature that triglycerides may degrade in the column. Conditions for optimal recovery of saturated and unsaturated triglycerides will be discussed.

GG6

Isomerization of 18:3Δ9c, 12c, 15c, 18:3Δ6c, 9c, 12c and 18:3Δ5c, 9c, 12c During Heat Treatment. J.L. Sebedio, INRA, Station de Recherches sur la Qualite des Aliments de l'Homme, 17, rue Sully, Dijon, BV, 1540 21034, France, and A. Grandgirard, Ch. Septier, J. Prevost, INRA.

Three types of oils: linseed, borage, and pine seed oil, containing respectively 18:3Δ9c, 12c, 15c; 18:3Δ6c, 9c, 12c; and 18:3Δ5c, 9c, 12c were heated at 240°C for 10 hours under nitrogen. The heated oils contained a mixture of polar components, polymers, cyclic fatty acid monomers and C1S unsaturated fatty acid geometrical isomers. The heated oils were saponified, esterified and then submitted to column chromatography to isolate the non polar fractions. The no polar fractions which contained the cyclic fatty acid monomers and the 18:3 geometrical isomers were fractionated by HPLC using MeOH as solvent. The 18:3 fraction was further fractionated by $AgNO_3$-TLC and the resulting bands were submitted to a hydrazine reduction. The resulting monoenes were isolated by HPLC and further separated in *cis* and *trans* isomers by $AgNO_3$-TLC. The position of the ethylenic bond on the monoenes was determined using ozondysis in BF3-MeOH. The structures of the ozonolysis products were elucidated by GC-MS. From these results, it was then possible to determine the structures of the trienes. The quantities of all the geometrical isomers formed were determined by GLC using CP Sil 88 and DB-Wax columns. The results will be discussed as a function of the position of the ethylenic bond on the carbon chain.

GG7

Volatile Decomposition Products from Autoxidized Triglycerides Containing Linoleate and Linolenate. E.N. Frankel, USDA-ARS-NRRC, 1815 N. University St., Peoria, IL 61604, and S. Selke, USDA-ARS-NRRC and K. Miyashita, Tohoku University.

Four unsaturated triglycerides found in vegetable oils were synthesized to determine the effect of fatty acid glyceride position on their relative oxidative stabilities. Capillary gas chromatography provided a sensitive method to follow the volatile oxidation products of mixtures of trilinolein and trilinolenin and of synthetic triglycerides containing linoleate and linolenate in different known positions. We measured the relative amount of linoleate oxidation by analyzing for hexanal, 2-heptenal and 2,4-decadienal; and the relative amount of linolenate oxidation by analyzing for 2,4-heptadienal and 2,4,7-decatrienal. Significant differences in the distribution of volatile products were observed according to the triglyceride precursors. On autoxidation at 40°C, the synthetic triglycerides LLnL and LLLn (L=linoleic, Ln=linolenic acid) formed initially about the same amounts of volatiles and ratios of linolenate-to-linoleate products. A 2:1 mixture of trilinolein/trilinolenin produced initially more total volatiles and higher ratios of linolenate-to-linoleate products than the corresponding synthetic triglycerides. On the other hand, LnLLn formed less volatiles and a lower ratio of linolenate-to-linoleate products than LnLnL. A 1:2 mixture of trilinolein/trilinolenin produced less total volatiles and higher ratios of linolenate-to-linoleate products than the corresponding synthetic triglycerides. This new information may permit us to better understand the influence of triglyceride structure on the relative stability of vegetable oils.

Session HH Saturday morning

Nutrition and Biology

HH1

Modulating Effects of Dietary Omega-3 Fatty Acids on Membrane Phospholipids and Kidney Function in Health and Disease. Bruce J. Holub, University of Guelph, Dept. of Nutritional Science, Room 308, Animal Science/Nutrition Bldg., Guelph, Ontario N1G 2W1, Canada.

The ingestion of fish oil containing eicosapentaenoic acid (EPA) plus docosahexaenoic acid (DHA) has been observed to offer potential clinical benefit in lupus nephritis, IgA nephropathy, cyclosporine-induced nephrotoxicity, and in the altered plasma lipid/lipoprotein profiles found in hemodialysis and nephrotic syndrome patients. The plasma triglyceride-lowering effect of fish oil in patients with nephrotic syndrome may offer benefit in lessening the progression of glomerular damage and risk of cardiovascular disease. The consumption of fish oil significantly alters the levels and fatty acid profiles (particularly the n-6 and n-3 series) of renal lipids including the compositions of the ether-containing phospholipids. The substitution of n-3 fatty acids for arachidonic acid (AA) in blood platelets and neutrophils results in a reduced formation of thromboxane A_2 and leukotriene B_4, respectively. The potential benefits of dietary fish oil in certain renal disorders may be mediated via an altered synthesis of the various eicosanoids (prostaglandins, thromboxanes, and leukotrienes) and platelet-activating factor (PAF).

HH2

Changes of Tissue Phospholipid (PL) Fatty Acid Profiles in the Spontaneously Hypertensive (SHR) and Normotensive (WKY) Rats During Fat Depletion. Y.S. Huang, Efamol Research Institute, P.O. Box 818, Kentville, Nova Scotia B4N 4H8, Canada, and D.E. Mills and R.P. Ward, University of Waterloo, and D.F. Horrobin and V.A. Simmons, Efamol Research Institute.

The development of atherosclerosis and hypertension in SHR has been associated with abnormal lipid metabolism. This is supported by the fact that the pathological progress is exacerbated by essential fatty acid (EFA) deficiency. Our preliminary study showed earlier development of EFA deficiency symptoms in SHR compared to WKY during EFA depletion. This suggests that either the availability of EFA is reduced or the catabolism of EFA is enhanced in SHR. The present study examined changes in tissue PL fatty acid profiles of SHR compared to WKY, and whether such changes might be responsible for the earlier development of EFA deficiency in SHR. Forty weanling SHR and WKY rats were maintained on a fat-free (FF) semisynthetic diet for 12 weeks. Four rats from each group were killed at various intervals. Liver, heart, red blood cells (RBC), plasma, and kidney PL fatty acids and skin total fatty acids were analyzed by GLC. After 4-wk on the FF diet, the SHR grew significantly more slowly and the EFA deficiency symptoms appearing thereafter were more severe in SHR than WKY. The levels of 18:2n-6 and 20:4n-6 decreased rapidly during the first two weeks but slowed thereafter. The levels of 20:3n-9 rose rapidly during the first 5 weeks and then leveled off. No significant difference in the triene/tetraene ratio a biochemical marker of EFA deficiency, in plasma, RBC and liver PL was observed. The changes in fatty acid pattern of the skin lipids were not significantly different between the two strains. However, the levels of 20:3n-9 in heart and kidney PL tended to be lower, whereas 18:2n-6 in heart PL and 20:4n-6 in kidney PL tended to be higher in SHR than WKY. This result of a low triene/tetraene ratio in heart and kidney PL in SHR suggests that the biochemical index for EFA deficiency in tissue PL is not correspondent to the early development of morphological EFA deficiency symptoms in SHR.

HH3

Differential Incorporation of Dietary n-6 and n-3 Fatty Acids by EFA-Deficient Genetically Hypertensive (SHR and BHR) and Normotensive (WKY) Rats. David E. Mills, University of Waterloo, Waterloo, Ontario N2L, Canada, and Y.S. Huang, Efamol Research Institute, and R.P. Ward, University of Waterloo.

The present study examined the incorporation into tissues of dietary n-6 and n-3 fatty acids in genetically hypertensive (SHR), borderline hypertensive (BHR, SHR, WKY), and normotensive (WKY) EFA-deficient rats, in order to determine whether differences in the accumulation of eicosanoid precursors exist in the various strains. Weanling (21 day) male SHR, BHR, and WKY rats (n=28/strain) were placed on a Teklad fat-free diet until 10 weeks of age. At that time 4 animals/strain were killed for tissue fatty acid analysis. Remaining animals then received supplements (3 wt %) of either safflower (SAF), evening primrose (EPO), or fish oil (F) for 7 days, after which they were killed for fatty acid analysis of liver, heart, kidney, erythrocyte, and plasma phospholipids. In all tissues sampled, severity of EFA-deficiency was in the order SHR > BHR > WKY. In addition, EPO was more effective than SAF in reducing the 20:3n-9/20:4 ratio. While all animals appeared to incorporate dietary n-6 fatty acids in a similar fashion, SHR demonstrated a reduced ability to incorporate n-3 fatty acids in a similar fashion, SHR demonstrated a reduced ability to incorporate n-3 fatty acids into all tissues examined, and demonstrated markedly reduced levels of 20:5 and 22:6 in tissues examined in comparison to WKY and BHR. These differences in accumulation of eicosanoid precursors between genetically hypertensive and normotensive rats could result in qualitatively different patterns of eicosanoid production and altered blood pressure regulation.

HH4

The Distribution of Alpha-Linolenic Acid in the Body Tissues of Rabbits Fed Semi-Synthetic, High Fat Diets. Gary J. Nelson, USDA-ARS, Western Human Nutrition Research Center, P.O. Box 9997, Pres. of San Francisco, CA 94129, and Darshan S. Kelley, Perla C. Schmidt, and Claire M. Serrato USDA-ARS-WRRC.

Alpha-linolenic acid (ALA), the precursor of the n-3 family of polyunsaturated fatty acids, is normally a minor component of most diets as well as body tissues. Feeding studies with elevated levels of twenty-carbon, n-3 polyunsaturated fatty acids, such as eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA), have demonstrated that these compounds accumulate in selected tissues, displacing linoleic and oleic acids. This study was designed to determine the extent to which ALA, the metabolic precursor of EPA and DHA, accumulates in body tissues when fed at high levels for extended periods. New Zealand white rabbits were fed 110g/day of semi-synthetic, high fat (24% of total calories) diets containing either: 1) hydrogenated soybean oil (HSBO) (78% 18:0); 2) safflower oil (SO) [72% 18:2(n-3)]; 3) linseed oil (LO) (48% ALA); or 4) menhaden oil (MO) (9% EPA and 4% DHA). After six months, tissues were taken for analyses of their fatty acid composition. In the animals fed LO diet, the percentage of ALA in the tissues examined [plasma (21.0), red cells (9.3), platelets (15.4), and liver (13.5)] was lower than that in the diet. The ratio (0.28) of the

percentage of liver ALA to diet ALA was lower than the comparable ratios for other major dietary fatty acids in animals fed the other three diets. These ratios were 0.58 for 18:2(n-3) liver/diet for the SO diet, 0.69 for 18:0 liver/diet for the HSBO diet, and 1.69 for EPA+22:5(n-3)+DHA liver/diet for the MO diet. The data indicate that, while dietary ALA is readily absorbed into the circulation (it was not excreted in the feces), it is not accumulated in the tissue stores to the same extent as the other fatty acids fed in this study. The inclusion of a double bond in the 3-position from the methylene end of the carbon chain in eighteen carbon polyunsaturated fatty acid appears to significantly alter the manner in which the compound is utilized.

HH5

Lipid Metabolic Effects of n-3, and n-6 PUFA, Monounsaturated and Saturated Dietary Fatty Acids in the Rabbit. John E. Bauer, University of Florida, J-144, JHMHC, Gainesville, FL 32610, and Patricia A. Schenck, University of Florida.

We have previously reported hypercholesterolemia in rabbits fed casein-menhaden oil containing diets associated with elevated intestinal mucosal cell microsomal ACAT activities. This work has presently been extended to include saturated and mono-unsaturated dietary fat sources to further elucidate the role of dietary polyunsaturated to saturated fat ratios (P/S) in this response. Casein/wheat starch diets were used which contained 14% (w/w) of either menhaden (MHO, P/S =1/0), safflower (SAF, P/S = 6.0), cocoa butter (P/S = 0.1) or olive (OLV, P/S = 0.4) oils. While SAF diet feeding protected the animals from casein-induced hypercholesterolemia, a marked response was seen when the MHO diet was fed with intermediate responses observed when COB or OLV diets were consumed. Marked elevations of lipoprotein cholesterol were found in all the MHO group low density fractions, while animals fed the OLV diet had more lipoprotein cholesterol in the very low density fraction. Liver microsomal ACAT activities were unchanged and HMG-CoA reductase activities were deceased when MHO and SAF diets were fed. Intestinal microsomal ACAT activities were increased in MHO diet fed rabbits while HMG-CoA reductase activities were similar in all groups. Serum arylesterase activities were elevated only in the SAF diet fed groups. Lipid analysis of hepatic and intestinal esterified cholesterol concentration of MHO diet fed rabbits. Fatty acid compositional analysis of microsomes demonstrated an enrichment of n-3 polyunsaturated fatty acids (PUFA) in the MHO group, and n-6 fatty acid patterns in spite of dietary fat source, most likely the result of desaturase and elongase activities. Bile analysis revealed increased free cholesterol concentrations with MHO diet feeding. The changes seen with fish oil feeding suggest a possible exacerbation of casein-induced enterohepatic recirculation of biliary cholesterol. This possibility is supported by increased intestinal ACAT activities and potential assembly of cholesterol-rich postprandial lipoproteins with their presentation to the liver. The hypercholesterolemic effect does not appear directly related to dietary P/S ratio.

HH6

Effects of Dietary Protein on Cholesterol and Lipoprotein Metabolism. K.K. Carroll, University of Western Ontario, Dept. of Biochemistry, Room M316 Health Sciences Centre, London, Ontario N6A 5C1, Canada, and S. Samman and E.M. Kurowska, University of Western Ontario.

Rabbits fed semipurified, cholesterol-free diets develop hypercholesterolemia when the diets are formulated with casein or other animal proteins but not when soy protein or other plant proteins are used. The hypercholesterolemia in casein-fed animals is associated with decreased excretion of fecal neutral sterols and bile acids, enhanced intestinal absorption of cholesterol, increased pool size of low density lipoprotein (LDL) in plasma, increased production rate and decreased fractional catabolic rate of plasma LDL, and down-regulation of LDL receptors, compared to these parameters in rabbits fed soy protein. It has been suggested that dietary proteins affect plasma cholesterol and lipoprotein levels by altering the enterohepatic circulation of cholesterol and/or bile acids, but the primary events in the mechanism have not been identified. The hypercholesterolemic effect of dietary casein is dose-dependent and increases as the level of casein in the diet is increased. A mixture of amino acids in the proportions found in casein produces a similar hypercholesterolemia, suggesting that the effect may be due to an amino acid or combination of amino acids rather than non-protein components present in preparations of casein.

HH7

Canola Oil in Atlantic Salmon Nutrition. R.G. Ackman, Canadian Institute of Fisheries Technology, Technical University of Nova Scotia, Box 1000, Halifax, Nova Scotia B3J 2X4, Canada, and S.M. Polvi, Technical University of Nova Scotia, and R.L. Saunders and S.P. Lali, Fisheries & Oceans Canada.

Atlantic salmon (*Salmo salar*) can be readily raised on diets rich in a number of fats, although a role for a certain proportion of preformed n-3 C_{20} and C_{22} fatty acids has long been recognized. Canola oil as the main energy source for post-smolt fish has been compared to herring oil with satisfactory growth. Details of linoleic and linolenic fatty acid metabolism in these fish have been established by comparisons with alternative sources of long-chain n-6 and n-3 fatty acids.

Session II Saturday morning

Plant Biotechnology III

II1

Cell Culture of Plant Seed Tissue—Effect of Some Growth Conditions on Fatty Acid Composition. Glenn Fuller, USDA-ARS-WRRC, 800 Buchanan St., Albany, CA 94710, and Allan E. Stafford and Charles Hague, USDA-ARS-WRRC.

The desaturase enzyme systems which convert monoenoic C_{18} fatty acids to dienoic and trienoic acids are not well characterized. In order to elucidate the biochemistry of these systems in oilseeds a source of plant tissue with desaturases of known and constant activity was sought. Callus cultures were prepared from cotyledon tissue of

sunflower and flax seeds, the former having an active 18:1→18:2 desaturase and the latter having both 18:1→18:2→18:3 desaturases. Cultures were grown on modified Murashige-Skoog media in the light and in the dark at 30°C, then analyzed quantitatively by gas chromatography and GC-MS for fatty acid composition and qualitatively by thin-layer chromatography for specific lipids. Lipid composition was compared to that of vegetative tissues of *Lemna minor* also grown in dark and light. Activities of enzyme systems were determined by radio labelling using ^{14}C-acetate and oleate. Tissues grown in the dark maintained a composition characteristic of seed tissue which the fatty acid pattern changed in the light to approximate that of vegetative tissue. Differences will be discussed in terms of known mechanisms of fatty and biosynthesis.

II2

Production of Seed Lipids via Culture of Somatic Embryos. Jules Janick, Purdue University, Dept. of Horticulture, W. Lafayette, IN 47907.

Embryogenesis, the transformation of a single cell (typically the zygote) to a miniature organism (the mature embryo), involves an array of developmental episodes that represents a microcosm for one of the great themes in biology: morphogenesis. Experimental embryology moved into the forefront of science with two sensational but unexpected discoveries: embryogenesis from phloem cells of carrot reported independently in 1958 by Steward, Mapes, and Mears; and Reinert; and embryogenesis from datura microspores by Guha and Maheshwari in 1964. The agricultural exploitation of somatic embryogenesis (embryogenics) may come about through exploitation of (1) rapid regenerative potential of somatic embryos, (2) *in vitro* production of cotyledonary metabolites, (3) production of homozygous lines via andiogenesis, and (4) exploitation of somaclonal variation. The possibility of *in vitro* production of cotyledonary lipids of cacao (cocoa butter), jojoba (liquid wax esters), and borage (gamma linolenic acid) will be reviewed.

II3

Specialty Oils from Microalgae. D.J. Kyle, Martek Corporation, 6480 Dobbin Road, Columbia, MD 21045.

The oceanic microalgae represent a major repository of storage lipids which may some day be commercially exploited. In their dilute concentration in the sea, they cannot be harvested efficiently, but when cultivated in photobioreactors the biomass density can easily exceed 10g dry wt/l. Depending on the value of the oil, this approach could be commercialized. For example, many diatoms produce large amounts of the long chain omega-3 polyunsaturated fatty acids eicosapentaenoic and docosahexaenoic acids (EPA and DHA). In fact, the fish from which omega-3-rich oil is presently extracted, are likely bioaccumulators of these compounds which originate from the primary producing phytoplankton. We have several microalgal strains in culture which produce greater than 40% of their dry weight in storage oil which is enriched in EPA as the sole omega-3 fatty acid. These strains demonstrate considerable plasticity in terms of the amount and type of fats produced and offer a tremendous potential for genetic improvement. Other specialty oils that are amenable to production by microalgae include those labelled with deuterium or carbon-13 for use as NMR tracers internal standards, or diagnostic reagents. Using sealed photobioreactors designed with gas loop closure, isotopically labelled CO_2 can be fed to the cells for batch photosynthetic biotransformation into fats and oils. Similarly, cells can be grown in heavy water for deuterium labelling. The utilization of microalgae as a source of labelled compounds is not a new concept, but the commercial application of this technology requires highly efficient systems which exhibit high ratios of mass conversion.

II4

The Development of Canola with Novel Fatty Acid Profile. Raymond S.C. Wong, Allelix Crop Technologies, 6850 Goreway Drive, Mississauga, Ontario L4V 1P1, Canada, and J. Patel, E. Swanson, and J. Grant, Allelix, Inc.

In the classical development of canola, the successful elimination of erucic acid from rapeseed has stimulated a lot of research interest in genetic manipulation of further modifying the fatty acid composition in canola. Recently, canola oil has gained substantial recognition and acceptance in the U.S. market as "health" oil of good nutritional quality. The nutritional quality aspect of the crop is being defined by chemical composition. A review of the development of canola oil with modified fatty acid profile will be presented.

II5

A Systems Approach to Development and Commercialization of Crops with High Erucic Acid for Industrial Oils. Melvin G. Blase, University of Missouri, Columbia, MO, and Donald L. Van Dyne, University of Missouri.

High erucic acid oil from agricultural crops such as rapeseed and crambe have excellent characteristics for use in many different types of industrial applications. The primary problem in developing such uses is coordinating crop production, processing, marketing, and developing end product uses. Any of these activities can be done individually; however, all must be done concurrently for a new self-sustaining industry to develop in an efficient manner. Commercialization of new crops will be most successful if final product demand is market driven. This provides a derived demand for products all the way back to production agriculture. Another necessary ingredient is profit. It must: 1) exist at each step before private industry will become involved; and 2) is absolutely necessary to sustain an economically viable industry over time. The process of commercializing new crops is neither simple nor easy. It requires the input and interaction of scientists from many different disciplines. Moreover, it requires the full cooperation of business, industry, academia, and government. Such an integrated system has been developed in an attempt to commercialize industrial rapeseed and crambe. This paper describes the successes and limitations of the systems approach being used.

II6

Somaclonal Variation and Somatic Embryogenesis in Oilseed Crops. Raghav Ram, Sungene Technologies

Corp., 2050 Concourse Drive, San Jose, CA 95131 and John Hemphill, Eric Eikenberry, Andrea Graves, Chuong Van Phan, Mary Ishizaki, Terry Andreasen, Juan Romero, Meng-Yun Wang, David Catlin, Huang Hsiuluan Chen, and Sally Thorson, Sungene Technologies Corp.

Plant regeneration from tissue cultures can be accomplished via organogenesis or embryogenesis. Organogenesis is generally considered to occur from a group of cells, whereas somatic embryos originate from single cells. Somatic embryos can originate directly from an explant, or indirectly through a callus phase preceding embryogenesis. Today, tissue culture technologies are widely used from crop improvement. In addition to playing an important role in the transfer of foreign genes tissue culture systems are also used in generating useful variants (somaclonal variants) with agronomic potential. The importance of somatic embryogenesis in the production of somaclonal variation in sunflower, sesame, soybean and rapeseed will be discussed.

Session JJ Saturday afternoon

General Open Session on Flavor Stability and Oxidation

JJ1

Quantitative and Qualitative Effects of Carotenoids and Tocopherols on the Singlet Oxygen Lipid Oxidation. Mun-Yhung Jung, Ohio State University, Dept. of Food Science & Nutrition, 2121 Fyffe Road, Vivian Hall 122, Columbus, OH 43210 and David B. Min, Ohio State University.

The effects of 0, 1×10^{-5}, 2.5×10^{-5} or 5×10^{-5}M canthaxanthin, beta-carotene and beta-apo-8'-carotenal, which has 13, 11 and 9 conjugated double bonds respectively, on the singlet oxygen oxidation of soybean oil in methylene chloride containing 3 ppm chlorophyll were studied by measuring the contents of peroxides and conjugated dienes during light storage. Canthaxanthin showed the greatest antioxidant activity, followed by beta-carotene and then beta-apo-8'-carotenal. That is, as the double bonds in the carotenoids increased, the antioxidant activity increased. The rate constant of singlet oxygen oxidation of soybean oil was $1.3 \times 10^5 M^{-1}sec^{-1}$. The rate constant of singlet oxygen quenching by beta-carotene in soybean oil in methylene chloride was $0.5 \times 10^{10} M^{-1}sec^{-1}$. Beta-carotene quenches singlet oxygen and does not quench triplet state chlorophyll. The effects of 0, 1×10^{-3}, 2×10^{-3} or 4×10^{-3}M alpha, gamma and delta-tocopherols on the singlet oxygen oxidation of soybean oil were studied by measuring the headspace oxygen disappearance and peroxide formation. The results showed that delta-tocopherol has the least antioxidant activity among 3 tocopherols. The results also showed that alpha-tocopherol has higher antioxidant activity than gamma-tocopherol at 1×10^{-3}M concentration, at 2×10^{-3}M, alpha and gamma-tocopherols have similar antioxidant activity, but at 4×10^{-3}M, alpha-tocopherol has less antioxidant activity than gamma-tocopherol.

JJ2

Studies on Oil Quality and Stability. Melinda Guzman-Harty, Ross Laboratories, 625 Cleveland Avenue, Columbus, OH 43216, and Normanella DeWille, Ross Laboratories.

Oil manufacturers generally use Peroxide Value (P.V.) and Sensory Scores to establish the quality of their oils prior to shipment. Although these tests provide some evidence of the oxidation status of the oil, they do not measure progressive and/or persistent deterioration of the oil. An additional test for oil oxidation, the Thiobarbituric Acid (TBA) Number measures the levels of the more stable secondary oxidation products, the aldehydes, which are formed in damaged oils. The nonvolatile aldehydes can account in part for the oxidized or rancid tastes. Comprehensive studies using P.V., TBA Number, Sensory Scores, and Fatty Acid Composition were conducted to estimate the stability of different oils with increasing time and temperature. Correlation of these values to characterize the oils will be discussed.

JJ3

Comparative Study of Soybean Oil Oxidation Methodology. G.R. Goss, Oil-Dri Corporation of America, 22149 N. Pet Lane, Prairie View, IL 60069, and D.D. Brooks, S.K. Brophy, and B. Hayden, Oil-Dri Corporation of America.

Currently, the vegetable oil industry utilizes four oxidative stability tests: active oxygen method (AOM), rancimat conductivity test, Schaal oven test and room temperature storage test (RTST). This study compares the oxidative stability of six bleached soybean oils and six deodorized soybean oils under laboratory conditions by these four methods. The degree of oxidation was monitored by peroxide value, p-anisidine value, and conjugated dienes. The bleaching procedure included a commercially available non-acid activated bleaching clay (NABC), the NABC further enhanced with citric acid and a commercially available acid activated clay, all at concentrations of 0.5 and 1.5 w/w percent. Bleaching conditions were 30 minutes at 120°C and 50 mmHg. Deodorization conditions were 60 minutes at 260°C and 0.5 to 1.5 mmHg. Incongruities appear between the RTST and the three other accelerated oxidative stability tests. Furthermore, oxidative stability as predicted by initial totox values did not correlate with actual observed stability by the four methods. Within the parameters of each individual stability test, oils processed with the citric enhanced NABC were consistently the most stable.

JJ4

Flavor and Stability of Potato Chips Fried in Soybean, Cottonseed and Palm Olein Oils. Myung-Joo Han, University of Tennessee, Food Technology & Science, P.O. Box 1071, Knoxville, TN 37901, and Sharon L. Melton, University of Tennessee.

Potato chips were fried in cottonseed oil (CSO), partially hydrogenated soybean oil (PHSO) or palm olein (PO) and stored for 0-, 2- and 4-weeks in light or dark at 23°C. Chip samples were analyzed for moisture (MC) and oil (OC) contents, color and peroxide value (PV). Chips from each oil stored for 0- and 4-weeks in light or dark were analyzed for flavor volatiles by GCMS and for flavor by 48 panelists. Chips contained an average of 1.65% MC and 41.0% OC. PV of PHSO chips was lower than PV of CSO or PO chips. PV of chips stored in light increased linearly across storage

with the slope dependent on the oil. The PV of PHSO and PO chips stored in dark did not change across storage, but PV of CSO chips increased linearly. Panelists liked the flavor of CSO chips (3.4) better than the flavor of PHSO (4.3) or PO chips (4.0). They liked the flavor of 0-week chips (3.6) the same as that of chips stored in dark (3.7), but less than that of chips stored in light (4.5). The concentrations of 13 chip volatiles, mainly pyrazines and carbonyls, were different among the oils. Storing chips in dark decreased the concentrations of 14 volatiles and storing chips in light decreased levels of 11 volatiles and increased levels of 2. Levels of 2-ethyl-5,6-dimethyl pyrazine and t,t-2,4 decadienal, considered desirable in chip flavor, were decreased by storage in light.

JJ5

The Stability of Potato Lipids During the Production of Potato Granules. M. Lilja, SIK-The Swedish Institute for Food Research, P.O. Box 5401, Goteborg S-402 29, Sweden, and H. Lingnert, SIK-The Swedish Institute for Food Research.

The lipid content of potato tuber is only 0.5% on a dry weight basis. Still, the oxidation of these lipids limits the storage time of potato granules. Probably, the lipid oxidation starts already during the process from raw potato to potato granules. We have studied the lipid changes during an add-back process of potato granules. The fatty acid amount and composition of the lipid classes of potato and potato granules were analyzed and the changes in free fatty acid (FFA) content during process were studied. The free fatty acids were separated from the neutral lipids on a HPLC and quantified by use of gas chromatography. The amount of FFA increased in the first stages of the process and decreased during the further processing. The activity of the lipolytic enzymes was studied, as well, in the first stages of this process. This enzyme activity could explain the liberation of free fatty acids from the lipids. The importance of these FFA was evaluated in a storage test. The lipid oxidation was followed by head-space measurements of hexanal.

JJ6

Fatty Acid Composition of *Candida utilis*. Parvin Zandi, Biochemical and Bioenvironmental Research Center, Sharif University of Technology, P.O. Box 11365/6891, Tehran, Iran.

A sample of biomass (*C. utilis*) produced under the following conditions: in a 100-lit fermenter (batch), at t = 30°C, pH = 4.5, O_2 = 6ppm, medium: sugar-beet molasses plus Ammonium sulphate and minerals, process: centrifuged, suspended in water and spray dried at 200°C. Lipids of the dried cells were extracted with chloroform-methanol (1:1). Free fatty acids were separated by saponification of lipids (with KOH in aq. methanol) followed by acidifying with 5N H_2SO_4. Fatty acid methyl esters (FAME) were prepared using BF_3-CH_3OH reagent (14%). Analysis of FAME by gas liquid chromatography (GLC) revealed: C_{16}:O (11.8%), C_{16}:1 (51.6%), C_{18}:O (4.3%), C_{18}:1 (32.3%), with traces of C_{12} and C_{14} fatty acids.

Session KK Saturday afternoon
Seeds and Oils: A General Discussion

KK1

Evaluation of Enzymatic Processes for Extraction of Oil and Protein From Soybeans. S.S. Koseoglu, Food Protein R&D Center, Texas A&M University, F.M. Box 183, College Station, TX 77843-2476, and T.W. Kwon, Korea Food Research Institute and E.W. Lusas, Texas A&M University.

The applicability of cell wall degrading enzymes to improve oilseed extraction and soymilk production was studied. The combined effects of flour particle size and enzymatic extractions enable production of soymilk products which contain about 94-98% of the original oil and protein. This is a significant improvement over traditional processes in which recovery is approximately 73% of the original protein. The increased recovery of oil and protein from soymilk residues or solids should significantly improve the economics of the process and the principles might be applicable to increase oil recovery from the aqueous extraction process.

KK2

Volatiles from Microwave-Treated Stored Soybeans. J.M. Snyder, USDA-ARS-NRRC, 1815 N. University St., Peoria, IL 61604, and T.L. Mounts and R. Holloway, USDA-ARS-NRRC.

Soybeans were microwaved to prevent deterioration during storage. Microwave time was varied from 4, 6, 8 and 10 min., in 2 min. increments, and the treated and control soybeans were stored for 8 weeks at 40°C. Damage was monitored by analysis of peroxide value and free fatty acid content of the extracted oil and by volatile analysis of the full fat meal and extracted oil. Volatiles were measured by multiple headspace extraction, and the formation of hexanal was monitored in both the oil and meal. During storage of the control beans, peroxide values increased from 0.41 to 1.20 meq/kg, hexanal concentration changed from 29 to 94 ppb and free fatty acid content increased from 0.4 to 1.7%. Soybeans that were microwaved for 4 or 6 min. had peroxide values of about 1 meq/kg and hexanal concentrations of 39-44 ppb after storage, indicating partial inactivation of lipoxygenase enzymes. However, soybeans that were microwaved for 8 min. or more tended to oxidize during storage to a greater extent than the control soybeans, showing higher peroxide values and greater formation of hexanal in the samples. This suggests that soybeans microwave-treated in excess of 8 min. are heat damaged and susceptible to deterioration during storage. Free fatty acid content of the oils from all of the microwave-treated soybeans was about 0.4% initially and did not increase with storage, indicating inactivation of hydrolytic enzymes.

KK3

Effect of Moisture, Microwave Heating, and Live Steam on Phospholipase D Activity in Soybeans and Soy Flakes. G.R. List, USDA-ARS-NRRC, 1815 N. Univer-

sity St., Peoria, IL 61604, and T.L. Mounts and A.C. Lanser, USDA-ARS-NRRC.

A radiochemical method was used to assay phospholipase-D activity in whole and flaked soybeans subjected to a variety of storage and enzyme inactivating conditions. The crude enzyme was isolated and incubated with a mixture of choline-C^{14}-labeled phosphatidylcholine. The amount of liberated radioactive choline was used as a measure of enzyme activity. Whole soybeans, ranging from 10-18 percent moisture, were stored at 40°C and sampled weekly for up to 4 weeks. Although the enzyme was active in all samples, the optimum moisture for enzyme activity was about 14 percent. Beans held for 1 week at 14% moisture showed that phospholipase-D remained active at temperatures up to at least 60°C. Whole soybeans ranging from 12-18 percent moisture were exposed to microwave heating conditions. During the early stages of heating, the enzyme was activated, and then was gradually destroyed by the time the temperature of the beans reached 115°-120°C. Approximately 8-10 minutes of microwave heating was required to completely destroy enzymatic activity. Under microwave heating conditions, high correlations (r = .93-.98) were found between enzyme activity and temperature. The destruction of phospholipase-D in soyflakes treated with live steam was also investigated. As observed with microwave heating, the enzyme is activated during the initial stages, but is rapidly destroyed at temperatures of about 110°C.

KK4

Determination of Oil and Oil Quality (Linolenic Acid) in Industrial and Edible Oil Flax. R.S. Bhatty, Crop Development Centre, University of Saskatchewan, Saskatoon, Saskatchewan S7N 0W0, Canada, and G.G. Rowland, University of Saskatchewan.

The rapid determination of oil on whole flaxseed using the near-infrared spectroscopy (NIRS) will be described. The procedure eliminates the tedious and time-consuming sample grinding to obtain a uniform particle size and allows rapid screening of flaxseed for oil. The NIR spectra of whole and ground flaxseed, best wavelength combinations obtained and statistical parameters of oil determined on whole and ground seed will be presented. A related study was conducted to determine the suitability of the colorimetric procedure (thiobarbituric acid reaction) for rapid determination of linolenic acid in flax oil. The protocol of the procedure and its relationship to linolenic acid determined on a half-seed by gas-liquid chromatography will be presented.

KK5

Oxo Fatty Acid Composition of the Seed Oil of the Family Cucurbitaceae. Daniel P. Schwartz, USDA-ARS-ERRC, 600 E. Mermaid Lane, Philadelphia, PA 19118.

When chicken lipids are irradiated in air with low doses of gamma irradiation, small amounts of oxo fatty acids (OFA) containing one or more double bonds conjugated with the oxo group are generated. In order to better study the characteristics of this lipid class, a number of seed oils were analyzed to determine whether this class occurs naturally, thus furnishing a potential source of model compounds. The seed oil of members of the Cucurbitaceae family, which includes cucumbers, melons, gourds, pumpkins and squash, contain relatively high concentrations of OFP with at least two conjugated double bonds that are also conjugated with the oxo group. The OFA are readily isolated by transmethylating the extracted oil, reacting the methyl esters with 2,4-dinitrophenylhydrazine in the presence of monochloroacetic acid, and fractionating the hydrazones on alumina. The derivatives are examined spectrophotometrically, and an approximate concentration is calculated based on the absorption maximum and molar absorptivity. The OFA content of some of the members of Cucurbitaceae increases as the seeds age. Structural identification of the major OFA in some varieties is anticipated.

KK6

A Survey of Investigations on Chemistry and Utilization of Chinese Tallow Tree (*Sapium sebiferum* [L.] Roxb.). Xu Bu Qing, Shanghai Cereal Science Research Institute, 441 Guang Fu Xi Lu, Shanghai, People's Republic of China.

This paper reviews the following developments of Chinese Tallow Tree (*Sapium sebiferum*) in the last decades, concerning chemical and physical investigations of the glyceride composition, structure and polymorphism for Chinese vegetable tallow, and the glyceride composition and structure for Stillingia oil from the fruits of *Sapium sebiferum*, the separations and identifications of some new natural organic compounds, the isolations of phorbol ester and its derivatives related to the fresh leaves, roots and barks of *Sapium sebiferum*. In recent years there have been patents used to manufacture confectionery Chinese vegetable tallow in food industry, and the possible utilizations of Chinese vegetable tallow, Stillingia oil and some of new natural organic compounds in industry, agriculture, and pharmaceutical industry.

Session LL Saturday afternoon
Fat Substitutes II

LL1

Dietary Fat and Cancer Risk. Michael Pariza, University of Wisconsin, Food Research Institute, Dept. of Food Microbiology & Toxicology, Madison, WI 53706.

It has been widely publicized that dietary fat increases the risk of some types of cancer, but the scientific data are far from clear. Epidemiologic studies are complicated by the fact that fat and calorie intake are closely correlated, and it is well documented in animal studies that calorie intake is directly related to cancer risk. Experimental data indicate that the only fatty acid that has the potential to increase cancer risk is linoleic acid, an essential fatty acid. Dietary linoleic acid is required for the optimal development of carcinogen-induced mammary, colon, and pancreatic neoplasia in rodents. Moreover, the amount of linoleic acid needed for maximal tumor development exceeds by about 5-fold the amount required by a young rat for optimal growth. However, we have established that a modest degree of calorie restriction (20% less than the ad libitum level) has

a great inhibiting effect on mammary tumor development in rats and 'overrides' the enhancing effect of linoleic acid. The effect of calorie restriction is dependent in part on rat strain. Hence, Fischer rats are more sensitive than Sprague-Dawley rats, indicating the importance of genetic influence. We have also established that CLA, a mixture of isomers each containing a conjugated double bond system, derived from linoleic acid, has the capacity to inhibit carcinogenesis in mice. The relationship between fat versus calorie intake, and linoleic acid versus CLA, will be discussed.

LL2

TATCA: Results of a Two-Week Dietary Exposure Study in Rats. Mark Bieber, Best Foods, a Div. of CPC International, 1120 Commerce Avenue, Union, NJ 07083.

TATCA (trialkoxytricarballylate), also known as a "retrofat", is a non-hydrolyzable, edible oil-like compound which can be used as a zero calorie oil substitute. TATCA was fed at 0.15, 0.75, 1.5, 3.0, 6.0, 9.0% of an ad lib chow diet to male weanling rats for two weeks. The compound was mixed with a corn oil vehicle so that all animals received the same amount of total lipid (10% added fat). At the end of the experimental period, half the animals in each group were necropsied, while the other half ate the same chow diet with 10% added corn oil for an additional week. All animals grew well; blood chemistries were unchanged between control and experimental groups; food intake was increased in the two highest dose groups; and no physical abnormalities were noted except for slight anal leakage in some of the animals eating the 6% level and most of the animals eating the 9% level. Within one day of compound withdrawal, anal leakage ceased. Stool total weight and lipid weight increased proportionally with increasing TATCA in the diet. Recover of TATCA in the four highest dose groups as assessed by excess fecal lipid weight was 97 ± 14%. The HPLC fingerprint of the compound recovered from the fecal lipid extract was identical to that fed. This research demonstrates that TATCA functions as a non-absorbable oil substitute.

LL3

Metabolism and Disposition of Esterified Propoxylated Glycerol (EPG). Lawrence W. Masten, ARCO Chemical Company, 3801 West Chester Pike, Newtown Square, PA 19073.

Results will be presented of metabolism/disposition studies utilizing ^{14}C-esterified propoxylated glycerol (EPG) in the rat. These studies are primarily designed to examine whether EPG versions can be absorbed from the GI tract. Additionally, they will examine whether EPG can be hydrolyzed and the resulting metabolites are absorbed. Should this occur, the studies will be able to diferentiate which portion of the EPG molecule is involved. An effort will be made to identify the target organs for accumulation and the primary routes for metabolism and excretion.

LL4

Nutritional/Medical Role of Special Lipids. Vigen K. Babayan, Harvard Medical School, New England Deaconess Hospital, 194 Pilgrim Road, Boston, MA 02215, and Edward A. Mascioli, Bruce R. Bistrian, and George L. Blackburn, New England Deaconess Hospital.

The critical role of fats and oils in our diet has become the subject of much attention and debate. It is timely to present and discuss a class of specialty fats which can play a very positive role in the health and nutrition of not only the hospitalized patient, but the public as well. Structured lipids based on medium chain length fatty acids and desired ratios of unsaturated and polyunsaturated long chain fatty acids are proposed and described as an alternative approach to our conventional fats and oils. A more specific lipid classification is suggested since our present-day knowledge imposes the use of subgroups in the identification and classification of fats, oils, and the fatty acids involved.

LL5

Polysiloxanes: Potential Noncaloric Fat Substitutes. Sami A. Hashim, St. Luke's-Roosevelt Hospital Center, Amsterdam Ave. & 114th Street, New York, NY 10025, and E. Filippo Bracco, St. Luke's-Roosevelt Hospital Center.

The fat-like attributes of liquid polysiloxanes have suggested studies of their use as fat substitutes in the diet of rats. These "oils" are organic derivatives of silica with linear olymeric structure: (RRR)Si-O-(Si(RR)-O)n-Si(RRR), in which R can be an organic radical such as all methyl or partly methyl and partly phenyl groups. These compounds are inert, nontoxic and nonabsorbable; are resistent to oxidation, hydrolysis or degradation; and are similar in solubility to edible oils and fats. Two compounds have been incorporated into the diet of two types of rats: Polyphenylmethylsiloxane (PPMS) with a viscosity of 75 centistokes (cs), and polydimethylsiloxane (PDMS) with a viscosity of 350 cs. Obese Zucker rats fed for 5 weeks a diet containing 22% (w/w) PPMS lost significant weight, whereas controls fed the same diet without PPMS gained weight. Thus, obese Zucker rats did not compensate for caloric dilution. In another study Sprague Dawley rats were rendered obese by high fat diet (35% of calories), then were given the same diet diluted 10%(w/w) with PDMS. The animals were able to compensate for caloric dilution when compared with controls fed the undiluted diet.

LL6

The Effect of Powdered Cellulose on Oil/Fat Uptake During the Frying of Battered Food Products. Jit F. Ang, James River Corporation, Cellulose Division, 650 Main Street, Berlin NH 03570.

Powdered cellulose, which is a natural polymer of beta-1,4-glucan, has been used as a food ingredient for many years. Since it is an insoluble fiber with an average total dietary fiber content of not less than 99% (dwb), powdered cellulose is also considered non-caloric. Depending on its physical structure, this ingredient can retain approximately 4 to 10 times its weight in water or about 2.5 to 8.5 times its weight in oil. Due to its preference for hydrophilic groups, the effects of powdered cellulose on oil/fat uptake during frying was investigated. Results indicated that batter formulations containing 3% (dwb) powdered cellulose (120-micron in fiber length) exhibited significantly reduced oil/fat content after frying. This reduction in oil/fat uptake

ranged from about 10 to 40%. The reduction was also dependent on the type of food investigated as well as the frying medium used. As a result of strong hydrogen bonding between water molecules in the batter with the cellulose fibers, displacement of water by oil/fat during the frying process was restricted. In addition, taste panels indicated a preference for the cellulose batter due to its better appearance and less oily mouthfeel.

LL7

Nutrifat - A Natural Products Fat Replacer. Melvin Wolkstein, Reach Associates, Inc., South Orange, NJ 07079.

A dextrin amalgam with an allowed soluble fiber, called NutriFat C is usable immediately for replacing 50% of the fat or oil content of a food. Combined with a vegetable and natural protein, it can replace up to 81% fat or oil and is called NutriFat PC. About three times its weight of water is used for organoleptic results, calorie value of less than 3 cal/gm and costs equal to those of 100% triglycerides. Instant NutriFat has been pregelatinized and also replaces up to 81% of the edible oils but requires no heating for water absorption. NutriFat can be utilized with U.S. Patent 4,626,441 which covers the use of aspartame and acesulfame K synergists for frozen desserts and fruit yogurt.

Session MM Saturday afternoon

Fats and Oils Processing IV

MM1

Winterizing of Vegetable Oil in Conjunction with Alkali Refining. K.W. Klein, Centrico, Inc., 100 Fairway Ct., Northvale, NJ 07647, K.P. Eickhoff, Westfalia Separator AG.

Since wet winterizing of vegetable oils was looked at with skepticism by the vegetable oil industry over the past 10 years, it has proven to be a successful method to remove waxes. Wet winterizing is a process employed to remove waxes from vegetable oil using centrifuges within the refining process immediately after refining but before the washing stage. The process, including the advantages and limitations of dewaxing sunflower and corn oil, will be described. The possibilities of dewaxing oils with a high wax content, such as rice bran and grapeseed oil, will be mentioned.

MM2

Plant Construction & Operating Economics. Joe Anglin, Process Systems, Inc., 1790 Kirby Parkway, Suite 300, Memphis, TN 38138.

This paper will explore the subject of plant construction and operating economics. Beginning with the evaluation of construction methods and costs and how they relate to safety, quality, and reliability. The real cost of designing the plant for the worst case operation, and pitfalls of making the budget fit the project. How to standardize and save money. Design objectives and the cost factors that affect production. Try something new, invest in technology.

MM3

Degumming of Vegetable Oil. Chris L.G. Dayton, Central Soya Co., Inc., P.O. Box 1400, Ft. Wayne, IN 46801.

The use of degumming in the refining of vegetable oils is a generally accepted and practiced process in industry today. The process of degumming provides the raw material, gums, that can be further processed to make vegetable "Lecithin"; and a source of crude degummed oil for caustic or physical refining. When the use of degummed oil is employed in caustic refining the by-product, soapstock, may be simply and traditionally acidulated reducing the liability on the waste water treatment. In physical refining the processing loss will be minimized in subsequent steps. This presentation reviews selected methods and patents in the overall "degumming" of soybean and canola oil to yield an oil of high quality and stability. Methods and patents which may be discussed describe water, acid, special, and super degumming.

MM4

Winterization or Dry Fractionation: A Fast Growing Technology. Alain F. Tirtiaux, S.A. Fractionnement Tirtiaux, 8 Rue de Fleurjoux, 6220 Fleurus, Belgium, and Etienne Deffense, S.A. Fractionnement Tirtiaux.

Originally regarded as inaccurate or inconsistent, dry fractionation technology say its development boosted by that of palm oil. Since then, it hasn't stopped improving, and it is now considered as an important step in edible oil and fat refineries, margarine plants and even in dairies. This paper will update the state of the technology developed by Tirtiaux, including both crystallization and separation sections. The theory of crystallization will also be reviewed with examples taken from palm oil and butter oil processing. Finally, a survey will be made as well on hardened fats (soy, rape and fish oil), on animal fats and on cottonseed oil.

MM5

Degumming. Anthony Athanassiadis, DeSmet.

Abstract not available at press time.

MM6

Plant Economics. Norman J. Smallwood, Core Team, P.O. Box 248, Ankeny, IA 50021.

Abstract not available at press time.

MM7

Chemical Refining. Reginald Bacchus, POS Pilot Plant Corporation, 118 Veterinary Road, Saskatoon, Saskatchewan S7N 2R4, Canada.

Abstract not available at press time.

MM8

Pre-refining of Vegetable Oil. Ken Carlson, Johnson-Loft Engineers, Inc., 3100 Kerner Blvd., Suite C, San Rafael, CA 94901.

Physical refining of soybean, rapeseed, sunflower oil, etc. is today an interesting alternative to alkali-refining. A good result requires an efficient pre-refining that reduces the phosphatide content down to 5-16 ppm phosphorous. This is followed by a bleaching step, which removes the remaining phosphatides and oxidation products as well as coloring substances. Vegetable oils contain hydratable phosphatides which can be removed by treatment with water. Most oils, especially seed oils contain in addition nonhydratable phosphatides, NHP. It has been shown that citric acid and phosphoric acid solutions are good degumming agents. They are powerful complexing agents and form complexes with the NHP. The complexes are hydratable and pass into water which is added after the treatment with acid. These properties are utilized in, e.g. the Unilever "Super degumming" and the Alfa-Laval "Special degumming."

Session NN Saturday afternoon

HPLC of Triglycerides and Lipids—A Worldwide Perspective

NN1

Analysis of Bovine Milk Fat Triacylglycerols by Reversed Phase High Pressure Liquid Chromatography and Mass Spectrometry (LC/MS). A. Kuksis, University of Toronto, Banting & Best Dept. Med. Res., 112 College St., Toronto, Ontario M5G 1L6, Canada, and L. Marai and J.J. Myher, University of Toronto.

The short chain triacylglycerols of the fourth most volatile 2.5% molecular distillate of butteroil and the total triacylglycerols of whole bovine milk fat, and of a rearranged sample of butterfat, were resolved by high pressure liquid chromatography on a conventional reversed phase column and the component triacylglycerol species were identified by chemical ionization mass spectrometry. The identification of components was confirmed by LC/MS analysis of various fractions of the distillate segregated on the basis of chain length, degree of unsaturation and the geometric configuration of the monoanoic double bond by $AgNO_3$-thin-layer chromatography. The order of reversed phase HPLC elution was determined for more than 100 major and minor species making up the bulk of the distillate and the bovine milk fat triacylglycerols. It is concluded that the complex triacylglycerol mixtures of bovine milk fat cannot be reliably identified on the basis of relative retention times and equivalent chain length observed on reversed phase columns. due to great variation in ion yields with the triacylglycerol type and diacylglycerol fragments selected, exact quantitation of molecular species was not possible without calibration of the analytical system with appropriate triacylglycerol standards.

NN2

HPLC Assay of Lipid Peroxidation in Biological Systems. Harold H.O. Schmid, Hormel Institute, University of Minnesota, 801 16th Avenue, N.E., Austin, MN 55912.

Lipid peroxidation induced by oxygen free radicals is considered to be associated with a number of pathological membrane alterations, including myocardial ischemia-reperfusion injury. Reperfusion with oxygen-rich medium after periods of ischemia can actually exacerbate cellular injury, presumably through the generation of oxygen free radicals leading to lipid peroxidation. Membrane lipid peroxidation is a complex process which is most commonly assayed by the quantification of its end products such as malondialdehyde and short-chain hydrocarbons or by other, relatively nonspecific, techniques such as determinations of carbonyls, lipoperoxides, conjugated dienes, fluorescent pigments or chemiluminescence. Recent developments in high-performance liquid chromatography (HPLC) have made it possible not only to fractionate phospholipids into classes and molecular species, but also to separate oxidized species from their parent compounds. In addition, HPLC can be used to separate malondialdehyde from other thiobarbituric acid-reactive substances. We have applied this technique to the assay of lipid peroxidation induced in rat heart mitochondria and other subcellular preparations by various treatments known to generate oxygen free radicals. The results of these experiments are reported and compared to those obtained with complementary methodology.

NN3

HPLC Analysis of Fats Modified by Oxygenated Fatty Acids. Friedrich Spener, University of Munster, Dept. of Biochemistry, Münster D-4400, West Germany, and L. Haalck, University of Münster.

Castor oil is an excellent source for oxygenated fatty acids that can be incorporated directly into other fats and oils by lipase-catalyzed interesterification. Such reactions, e.g. modification of beef tallow with ricinoleic acid, are carried out with good yields in solvent-free stirred tank reactors. However, product control is difficult as the mixtures of new and old triglycerides as well as hydrolysis products are barely resolved by HPLC and standards for identification are not available. We thus prepared oxygenated triglycerides by interesterification of standard lipids with define oxygenated fatty acids and obtained best separations with two 12 cm reversed-phase columns (S3 ODS 2) operated in tandem with an isocratic eluent system. Based on equivalent carbon numbers (ECN) we developed an equation that allows to predict retention times for oxygenated triglycerides and to identify critical pairs in complex mixtures.

NN4

Separations of Acyl- and Alkyl Glycerol Enantiomers by HPLC on a Chiral Phase and their Applications. Toru Takagi, Hokkaido University, Dept. of Chemistry, Faculty of Fisheries, Hakodate 041, Japan.

Complete HPLC separations of racemic monoacyl-, monoalkyl-, diacyl-, dialkyl-, and monoalkylmonoacylglycerol in a pure form to enantiomers were carried out as 3,4-dinitrophenylurethanes on two chiral phases, N-(S)-2-(4-chloro-phenyl)isovaleroyl-D-phenylglycine and N-(R)-1-(1-naphthyl)-ethylaminocarbonyl-(S)-valine chemically bonded to amino-propyl silanized silica, respectively. The formations of hydrogen bonding and charge transfer complex between the derivative and the chiral phase will contribute the enantiomer resolution by the steric interaction between

the long chain of the sample and the bulky group near the chiral center on the stationary phase. The chiral phases also separated the derivatives as a normal phase on the basis of numbers of carbon and olefinic bond. The optimum conditions for analyses of the enantiomer mixture having various acyl groups were investigated. The extension of the column length and decreasing of the solvent polarity made retention times longer and improved the peak resolution significantly. The examination of the stereospecificity of lipases in the hydrolysis and synthesis of acylglycerols was done by the HPLC on the chiral column. The HPLC analyses of the monoacylglycerols (MG) and diacylglycerols from hydrolysis of a simple triacylglycerol (TG) or esterification of glycerol with a fatty acid gave the ratio of the stereospecific isomers, and the stereospecificity of the lipase was calculated from the ratio. Analyses of stereospecific distribution of acyl groups in TG without enzymes were done by the HPLC on the chiral column. A TG was degradated with EtMgBr, sn-1(3) and sn-2 MG fractions were separated from the products by boric acid-impregnated silica TLC, and then sn-1(3) MG was fractionated based on the unsaturated degree by silver nitrate and boric acid-impregnated silica-TLC. Analysis of the MG fraction by the HPLC on the chiral phase columns gave the stereospecific distribution of acyl groups in TG.

NN5

Applications of High Performance Size Exclusion Chromatography (HPSEC) to the Analysis of Used Fats. Edward G. Perkins, Dept. of Food Science, University of Illinois, 1208 W. Pennsylvania Ave., Urbana, IL 61801 and Chun Hua Qian, University of Illinois and J. Caldwell and R. A. Yates, Dallas Group of America.

The high molecular weight compounds formed in edible oils during deep frying are related to oil quality changes and food product quality. They are also related to the foaming characteristics and discard point of the oil. HPSEC was applied to the determination of high molecular weight degradation products formed in fats and oils during deep frying in both laboratory and restaurant settings. High efficiency polystyrene gel columns and porous silica columns were employed with tetrahydrofuran or toluene as the mobile phase at a flow rate of 1.0 ml/min to effect separation. Analyses were usually completed within 15 minutes. Detectors employed were both refractometry and infrared spectroscopy, which exhibited different quantitative parameters. Preliminary data indicated a relationship between the amount of polar and polymeric materials present in the used oils and taste panel result.

NN6

Analysis of Marine Oils by HPLC. Bengt Herslof, Karlshamns AB, Lipidteknik Div., P.O. Box 15200, Stockholm 65 S-104, Sweden.

There is a growing interest in marine oils, especially the fish oils, from the scientific as well as from the consumers point of view. The interest in non-hydrogenated oils is due mainly to the physiological potential of the 20:5 and 22:6 fatty acid residues. The composition of fish oils has hitherto been expressed in terms of the fatty acid composition, performed by gas chromatography of the methyl esters. In accordance with the fast progress of triglyceride separation in vegetable oils by HPLC there is a need for a similar development on the fish oils. However, the number of fatty acids present in a fish oil is generally larger than in most vegetable oils, thus giving a much more complex triglyceride composition which may be difficult to resolve in the same way as simpler mixtures. In this work different fish oil products are investigated by a combination of chromatographic techniques. The focus is on the possibility to separate and identify triglyceride species and to be able to differentiate and characterize fish oils by means of HPLC.

NN7

Application of High Performance Size Exclusion Chromatography (HPSEC) for the Evaluation of Health Food Oils. Vijai K.S. Shukla, Aarhus Oliefabrik A/S, Aarhus C. DK-8100, Denmark.

There is ample body of evidence indicating (n-3) and (n-6) essential fatty acids (EFA) role in modulating human metabolism. Dietary therapy has been extensively used in the treatment of several metabolic disorders such as diabetes, eczema, multiple sclerosis, etc. In all these studies either evening primrose oil or fish oil capsules have been used as dietary supplements. Several of these clinical studies generated extremely conflicting results. As EFA's are very susceptible to oxidation, their oxidative stability is an important characteristic for the quality assessment of these health food oils. This paper presents the successful application of high performance size exclusion chromatography for the evaluation of these oils and attempts are made to correlate these results to the rancidity values as measured chemically.

Session OO Saturday afternoon

Enzymes and Novel Applications to Some New and Old Lipid Systems

OO1

Synthesis of Triglycerides at High Substrate Concentrations with Lipase. Francoise Ergan, Biotechnology Research Institute, 6100 Royalmount Avenue, Montreal, Quebec H4P 2R2, Canada, and Michael Trani and Gerald Andre, Biotechnology Research Institute.

Mucor meihei lipase immobilized on different supports is used to catalyze synthesis reactions between glycerol and oleic acid. No organic solvent is necessary to solubilize the substrates, which allows for the use of a reaction medium composed solely of the necessary substrates. Water produced in the reaction evaporates due to the high temperature used for the process. A conversion of 80% of oleic acid into triolein is obtained in about 100 hours at 60°C when using the substrates in stoichiometric amounts. Varying the ratio of glycerol over oleic acid allows for the preferential synthesis of either mono-, di- or triolein. For a ratio between 0.23 and 0.70, the only product of the reaction is triolein in amounts equivalent to the use of the total available glycerol. A ratio of 1 is the optimal ratio for the highest production of triolein, however, this triolein is contaminated with 20% diolein. A ratio above 1 shows a continuous

decrease in the triolein yeild accompanied by an increase in diolein and monoolein. A ratio of 2 yields to a complete conversion of the oleic acid into 60% triolein, 35% diolein and 5% monolein. The best diolein synthesis (50%) is obtained with an initial ratio of 3, yielding 22% of each mono- and triolein with 5% of the oleic acid left. At an initial ratio of 4, although glycerol is in excess compared to oleic acid, 20% of the oleic acid is not incorporated in glycerides. The triolein yield is low (5%), monoolein is increasing (25%) while diolein remains constant at 50%. We have shown that preventing the free evaporation of water inhibits the reaction. The effect of temperature has been studied between 34°C and 80°C. Experiments are being carried out to push the conversion even further towards glycerides.

OO2

Selectivity of Lipase Catalyzed Interesterification over Hydrolysis in Triglycerides. George Abraham, USDA-ARS-SRRC, P.O. Box 19687, New Orleans, LA 70179, and Min Kun Chang, USDA-ARS-SRRC and Vijay John, Tulane University.

This study examines lipase action on a substrate consisting of long chain triglycerides such as are found in vegetable oils. Our objectives were to understand and characterize factors that affect product yields and the selectivity to interesterification over hydrolysis. We have examined the role of water content and the effects of organic solvents in the maintenance of lipase activity and in improving interesterification product yields. The use of reversed micelles as an alternate mode of substrate enzyme contact with minimum water content was also examined. The high temperature GC technique used for the analyses in this study will also be presented.

OO3

Chemistry of Thiol Esters that are Useful for Lipase Assays. Philip E. Sonnet, USDA-ARS-ERRC, 600 E. Mermaid Lane, Philadelphia, PA 19118, and Mary Welch Baillargeon and Gordon G. Moore, USDA-ARS-ERRC.

Thiol esters of 2-mercaptoethanol and 3-mercapto-1,2-propanediol are useful substrates for a continuous spectrophotometric assay of lipase activity. An efficient synthesis of such esters from the thiols that avoids O-acylation, and a discussion of the tendency for transacylation are provided. Specific sequential esterification of 2-mercaptoethanol allows the preparation of unsymmetrical diesters. The utility of such materials in evaluating lipase fatty acid selectivity will be discussed.

OO4

Synthesis of Lipid Experimental Anti-AIDS Drugs. J.G. Turcotte, University of Rhode Island, Dept. of Medicinal Chemistry, College of Pharmarcy, Kingston, RI 02881-0809, and H.K. Singh, N.N. Bhongle, and N.C. Motola, University of Rhode Island.

Abstract not available at press time.

OO5

Polyunsaturated Algal Fatty Acid in Larval Oyster Nutrition. R.G. Ackman, Canadian Institute of Fisheries Technology, Technical University of Nova Scotia, Box 1000, Halifax, Nova Scotia B3J 2X4, Canada, and G.S. Napolitano, Dalhousie University.

The larval oyster is initially dependent on stored triglyceride in its early life but later the energy store is primarily glycogen. There may be a practical role for arachidonic acid as a precursor of prostaglandins in the larval oyster. The available sources of this fatty acid in phytoplankters will be reviewed and compared with results for analyses of larval oyster lipid classes. Mixed phytoplankton cultures as feed generally give superior results and among the possible factors is the generally unrecognized 3,6,9,12,15-octadecapentaenoic. The chromatographic properties of this acid will be discussed.

OO6

Enzymatic Production of Monoglycerides. Aleksey Zaks, Enzytech, Inc., 763 D Concord Avenue, Cambridge, MA 02138.

Monoglycerides represent an important class of surfactants which are widely used in the food, pharmaceutical and plastic industries. Currently, they are produced commercially by glycerolysis of fats. The major drawbacks of the chemical process are the low product yield and the high cost of purification. Described is a process for the preparation of monoglycerides via lipase-catalyzed transesterification of triglycerides in an alcohol medium. In the process, a selected lipase is added to the emulsion of triglyceride in alcohol (e.g., ethanol) containing a certain amount of water (3-5%). The formed suspension is agitated until the reaction is complete, after which enzyme is removed, and the monoglyceride product is separated from the reaction mixture. As opposed to the chemical method (which affords the production of a-acylated monoglycerides), the present process results in the production of monoglycerides acylated in a ß-position. The yield of isolated ß-monoglycerides is 85-90%. The advantages of the present process over the traditional chemical method include high yield, low by-product formation, easy product separation, and formation of valuable fatty acid esters as a second major product of the reaction.

OO7

Eicosapentaenoic and Docosahexaenoic Acid Contents of Components Produced by Pancreatic Lipolysis of a Marine Oil. Valerie J. Bush, University of Connecticut, Dept. of Nutritional Sciences, Storrs, CT 06268, and Robert G. Jensen, University of Connecticut.

The compounds produced by pancreatic lipolysis (5 min) of a fish oil preparation, presumably enriched in eicosapentaenoic (EPA) and docosahexaenoic acids (DHA), were isolated and the fatty acid identified. The quantities (wt%) were: original oil; EPA 2.3 and DHA, 11.4; residual oil, 0.1 and 2.2; free fatty acids (FFA), ND and 3.1; diacyl glycerols (DG), 2.5 and 15.8; and monoacylglycerols (MG); 3.1 and 14.7. Some enrichment of DHA occurred in the DG and MG. Some of this acid was apparently located in the *sn*-2 position and pancreatic lipolysis of both acids appears to be hindered confirming previous reports. Although the amounts of DHA in the residual oil were much lower than in the original oil, the quantity in the FFA was relatively low.

OO8

The Use of Oats as a Natural Lipase Bioreactor. Inmok Lee, Iowa State University, Food Technology Dept., Ames, IA 50011, and Earl G. Hammond, Iowa State University.

The caryopses of oats that are obtained by dehulling the grain contain a very active lipase on their surface. If the caryopses are moistened and immersed in oil they constitute a natural lipase bioreactor. The starch inside the caryopses absorbs the water necessary to activate the enzyme and for the hydrolysis of triglycerides. The system segregates the oil and water phases which minimizes the problems of pH control and separation of reaction products. Hydrolysis was monitored by titration of the free fatty acids in the oil phase and by thin layer chromatography. The optimum amount of water was about 20% of the weight of the caryopses. The optimum temperature was about 40°C. The reaction may be accelerated by gentle agitation or by reducing the viscosity of the oil phase by the addition of nonpolar solvents. All attempts to adjust the pH of the caryopses by adding alkalies and buffers resulted in reduced reaction rates. The reaction is inhibited by the accumulation of glycerol in the interior of the caryopses and free fatty acids in the oil phase. The lipase hydrolyzes all three positions of glycerol and there is little accumulation of mon- or di-glyceride in the lipid phase. Oat varieties vary significantly in the amount of lipase they contain. The reaction rate can be accelerated by adding additional lipase either from oats or other sources. The time to obtain hydrolysis that is 90% complete can vary from a few days to several weeks. The faster systems require changing the oats during the reaction because of glycerol inhibition. The glycerol released can be recovered by extracting the caryopses with water. The oats can be recycled. Even with long reaction times there was no evidence of microbiological deterioration of the wet oats when immersed in oil. The moist oat bioreactor also is capable of esterifying fatty acids with alcohols and catalyzing interesterification reactions.

POSTERS

Toxicity Assessment of Oils During Heating and Frying. Lung-Bin Hau, National Taiwan University, Graduate Institute of Food Science & Technology, Taipei, Taiwan, Republic of China, and Hui-Jane Lee, National Taiwan University.

When fats and oils are used for food preparation, complex chemical reactions take place producing volatile and nonvolatile products. Among the nonvolatile products, polar compounds, cyclic monomers and non-urea adduct fractions are the major concern of oil toxicity. In this study, the potential toxic substances were fractionated from the abused oils, and the significance of each fraction in terms of its toxicity was evaluated by a feeding study. Soybean oil and sunflower oil were collected after heating and frying process. Total polar materials, non-urea adduct fractions, and cyclic monomers were determined quantitatively. Feeding studies were carried with diets containing different fractions of the fried oils. Male Long-Evans rats were fed for six weeks. Growth rate, feed efficiency, liver enlargement and microsomal enzyme activities were evaluated. The results indicated that consumption of abused fried oil and its non-urea adduct fraction showed growth depression, liver enlargement, decreased feed efficiency and increased microsomal enzyme activities. The toxicity of the total polar materials was much less significant.

The Use of Proton Nuclear Magnetic Resonance Spectroscopy to Study the Decomposition of Methyl Linoleate Hydroperoxide. H. Chen, Washington State University, Dept. of Food Science, Pullman, WA 99164-6330, and D.J. Lee and G.O. Caviness, Washington State University and E.G. Schanus, Provesta Corporation.

A proton nuclear magnetic resonance (NMR) spectrometer was used to study the methyl linoleate hydroperoxide (MLHP) decomposition catalyzed with Co^{+2} in a model system. The decomposition of MLHP was monitored quantitatively by determining changes in the area of the peak associated with the -OOH moiety of the molecule. The apparent rate constant at five levels of Co^{+2} was determined by the plot of natural logarithm of concentration of MLHP vs. time. The rate law of the decomposition of MLHP was proposed. A modification of the Schenk and Schulte-Elte method was employed to prepare MLHP using methyl linoleate as a substrate. Column chromatography and thin layer chromatography (TLC) were used for the MLHP purification.

Characterization of Chlorophylls Present in Edible Oils. Edward A. Pfannkoch, W.R. Grace & Company, 7379 Route 32, Columbia, MD 21044, and James M. Bogdanor, W.R. Grace & Company.

Chlorophylls and their derivatives are common contaminants in many crude vegetable oils. Trace levels of these pigments impart an objectionable green color to oil as well as reduce the oxidative stability of the oil in the presence of visible light. Removal of these trace pigments is usually accomplished by adsorption to solids during the bleaching step in the oil refining process. When assessing the effectiveness of these adsorbents total chlorophyll is usually estimated colorimetrically without regard for the particular pigment species remaining in the oil. We have developed solid-phase extraction conditions based on Sep-Pak™ cartridges to allow subsequent analysis of the pigment species present in vegetable oils. High performance liquid chromatography (HPLC) with photodiode array detection and HPLC/thermospray mass spectrometry has been used to characterize the chlorophyll derivatives present in vegetable oil before and after bleaching. These results can be used to improve the design and selectivity of adsorbents for chlorophyll removal from vegetable oils.

Epoxidation of *Lesquerella* and *Limnanthes* Oils. Kenneth D. Carlson, USDA-ARS-NRRC, 1815 N. University Street, Peoria, IL 61604, and Marvin O. Bagby and Robert Kleiman, USDA-ARS-NRRC.

Lesquerella gordonii and *Limnanthes alba* Benth. are potential new crops. Their triglyceride oils containing 55-60% of the unusual fatty acids, 14-hydroxy-*cis*-11-eicosenoic and *cis*-5-eicosenoic acids, respectively. Both oils are predominantly unsaturated (3% saturated acids), and have similar iodine values (90-91), from which oxirane values of 5.7% are possible for the fully epoxidized oils. Each oil was epoxidized with m-chloro-perbenzoic acid and oxirane values were found to be 5.0% (Lesquerella) and 5.2% (Limnan-

thes). The epoxy acid composition of each product was examined by GC and GC/MS of the methyl esters, and data showed that epoxidized Lesquerella oil contained 55% 11,12-epoxy-14-hydroxy-eicosanoic acid and epoxidized Limnanthes oil contained 63% 5,6-epoxy-eicosanoic acid. Synthesis and characterization of these interesting epoxy oils will be discussed.

Synthesis of Trierucin and Production of Very High-Erucic Acid Oils. Kenneth D. Carlson, USDA-ARS-NRRC, 1815 N. University Street, Peoria, IL 61604, and Marvin O. Bagby, USDA-ARS-NRRC.

The need for substantial quantities of triglyceride oils with very high erucic acid contents prompted us to study their synthesis through incorporation of high levels of trierucin (glyceryl trierucate). Both base- and acid-catalyzed reactions were explored, and direct synthesis and interesterification approaches were used. Products with up to 75% trierucin were routinely obtained, but these usually contained diglycerides and erucic acid as coproducts. By refining these products, oils with up to 90% erucic acid could be obtained. Rapeseed and crambe oils, which contain 70-80% erucic acid, with perhaps 40% trierucin form. The course of the syntheses, characterization of the reaction products, and formulation of oils with 60-90% erucic acid will be disclosed.

Dissociation of Calcium Soaps of Long-Chain Fatty Acids in Rumen Fluid. P.S. Sukhija, Ohio Agricultural Res & Dev Center, Ohio State University, Dept. of Dairy Science, Wooster, OH 44691, and D.L. Palmquist, Ohio State University.

Dissociation of 5% solutions of calcium soaps of soya, tallow, stearic acid, and palm fatty acid distillate buffered to pH values of 5.0, 5.5, 6.0, and 6.5 was measured in terms of release of free calcium. Dissociation was dependent on pH of the medium and total unsaturation of fatty acids in the soaps. Dissociation was maximum at pH 5.0 and minimum at pH 6.5. When dissociation was very small, unsaturated fatty acids were released preferentially. Dissociation of 5% solutions also was studied by titration with 1N HCl. Release of calcium ions was directly correlated with decrease in pH value. The estimated pH values were 5.0, 4.5, 4.6, and 4.5 for calcium soaps of soya, tallow, palm fatty acid distillates, and stearic acid, respectively, and were near the interception point of the two curves representing Ca^{++} released and pH changes over the graph. Complete dissociation of the soaps occurred at pH values 4.7, 3.5, 2.5, and 1.8 in calcium soaps of soya, palm fatty acid distillates, tallow, and stearic acid, respectively, which was, in general, directly related to unsaturation of the soaps.

Metabolic Labelling of Polyisoprenoids in Isolated Rye Embryos. Robert T. Rymerson, University of Western Ontario, Dept. of Biochemistry, London, Ontario N6A 5C1, Canada, and Kenneth K. Carroll, University of Western Ontario.

Polyisoprenoid alcohols, homologous series of a-saturated dolichol or a-unsaturated polyprenol, and their phosphorylated and acyl ester derivatives seem to be ubiquitous among higher plant and animal tissues. Dolichyl phosphate (Dol-P) is an obligatory intermediate in the dolichol cycle by which N-linked glycoproteins are synthesized. Dicotyledonous seeds contain only dolichol whereas monocotyledonous seeds, such as *Secale cereale* (rye), contain approximately equal amounts of dolichol and polyprenol, thus providing a useful system for studying the final steps of biosynthesis in which polyprenyl pyrophosphate (Pol-PP) is formed and ultimately converted to dolichol. Both dolichol and polyprenol have been successfully labelled with tritium by germinating isolated rye embryos in tritiated water for 20 h; a significant amount of tritium was incorporated into both types of compounds. The phosphorylated forms have also been labelled using both tritiated water and [^{32}P] phosphoric acid under similar conditions. Only small amounts of tritium were incorporated while the labelling by ^{32}P was very efficient. In terms of mass, the major homologues of rye dolichol and polyprenol contain 15 and 16 isoprene units, whereas the predominant homologues of the phosphorylated forms contain 16 and 17 isoprene units. The incorporation of ^{32}P and ^{3}H into the phosphorylated and alcohol forms, respectively, showed homologue distributions that were similar to the mass distributions.

Effect of Peanut and Peanut Flour Addition on the Yield and Quality of Tofu. Bon Tong Lim, Dept. of Food Science, University of Guelph, Guelph, Ontario N1G 2W1, Canada, and J.M. deMan, University of Guelph and L. deMan, deMan Food Technology Services, Inc.

Tofu made with 10 and 20% of soybeans replaced by raw Ontario grown peanut kernels had significantly lower yield, moisture and protein contents ($p<0.05$) compared to tofu made with 100% soybeans. There was a significant increase ($p<0.05$) in hardness of tofu at 10% peanut kernel substitution. The firmness of tofu decreased significantly ($p<0.05$) at both 10 and 20% peanut kernel substitution. Tofu made by blending of soybeans with 10, 20 and 30% of partially defatted peanut flour had lower yield, less moisture and lower protein ($p<0.05$) compared to tofu made with 100% soybeans. Tofu made with 10 and 20% of soybeans replaced by peanut flour were significantly harder ($p<0.05$) compared to tofu made with 100% soybeans. However, the firmness of tofu decreased significantly ($p<0.05$) as more peanut flour was added. SEM-images of tofu showed a regular honeycomb-like protein network structure. Replacement of soybeans with both raw peanut kernels and peanut flour resulted in more compact, coarse and irregular honeycomb-like network structure.

The Vitamin E Content of Selected Foods: Data for USDA's Nutrient Data Bank. John L. Weihrauch, USDA-HNIS-NDRB, 6505 Belcrest Road, Hyattsville, MD 20782, and Johanna Lehmann, Lipid Nutrition Laboratory (retired).

The response of the public to recommendations to increase the proportion of unsaturated fat in their diet has led to the need to monitor the vitamin E levels in the American diet and food supply and has created the need for reliable, up-to-date compilations of data on the vitamin E content of foods. To meet the need, the U.S. Department of Agriculture is maintaining the Nutrient Data Bank and releases timely representative data in Agriculture Handbook No. 8 and in provisional tables. The purpose of this report is to present

data on the alpha, gamma, and delta tocopherols in 100 foods. The data are given in terms of milligrams of tocopherol per 100 grams of food and as the vitamin E activity expressed in alpha tocopherol equivalents. The use of internal and external standards for method validation and differences in the analytical procedures employed by the two laboratories and the possible effect on the data are discussed. The possible effect on the data by storage, processing, and food preparation is examined. Additional data are needed on vitamin E by collaboratively tested, rapid, and reliable methods.

Automation of the Assay for Tocopherols by HPLC Using Laboratory Robotics. Charles Marks, Distillation Products Ind., Eastman Kodak Co., P.O. Box 1910, Rochester, NY 14603, and Fred Bean, Distillation Prod. Ind., Eastman Kodak Co.

Our current assay method for tocopherols using HPLC utilizes automation equipment such as autosampler and an electronic integrator giving the system the capability to run up to 24 hr/day. However, someone has to prepare the samples and introduce into the samples to the autosampler along with the pertinent sample information into the integration system. The purpose of this work is to interface a robot with the HPLC to prepare samples and provide for total automation of the assay for tocopherols.

Heated Fats, Dietary Nutrient Levels and Hepatic Oxidative Stress. J.C. Alexander, University of Guelph, Dept. of Nutritional Sciences, Guelph, Ontario N1G 2W1, Canada, and P.G. Harris and T.S. Kok, University of Guelph.

Canola oil was heated in the laboratory for 72 hours at 180°C with three periods of eight-hour aeration. The thermally oxidized oil was fed at a level of 15% in a semipurified diet to weanling male rats for a period of four weeks. The effects of varying dietary levels of the vitamin mix (0.5, 1.0 and 2.0%) on growth-related parameters, and on several hepatic enzymes and biomolecules associated with the glutathione redox cycle were investigated. At all vitamin levels rats fed heated oil had as good growth responses as those given fresh fat. The oxidized oil caused consistent liver and kidney enlargement, and the relative weight of the kidneys was greatest at the lowest vitamin level. The activities of glutathione reductase and G-6-P dehydrogenase were not affected by the oxidized fat nor the level of vitamins in the diet. Heated fat suppressed the glutathione peroxidase activity at all dietary vitamin levels, but the suppression was most with the 2.0% vitamin mix and related to a high value for the fresh fat. On the other hand, catalase values were enhanced substantially by the oxidized oil regardless of the level of vitamins fed. Therefore, the catalase enzyme may be more important in controlling peroxide levels than the glutathione peroxidase system.

Silica Refining of Oils With Little or No Chlorophyll. J.M. Bogdanor, W.R. Grace & Co., Davison Chemical Division, 7379 Route 32, Columbia, MD 21044, and G.J. Toeneboehn, W.R. Grace & Co., Davison Chemical Div.

For oils containing little or no chlorophyll the bleaching step is used to remove soaps and phospholipids. Red and yellow colors in "heat bleachable" oils can be effectively reduced in the deodorizer. Data will be shown for refining of corn oil and palm oil with commercial silicas, such as TriSyl™ and TriSyl 300. Emphasis will be placed on finished oil quality (i.e., color, phosphorus and trace metals content and stability). Results will be compared to refining with commercially available bleaching earths.

Effect of Canola Oil on Plasma Phospholipid Fatty Acid Composition of Healthy Young Men. Bruce E. McDonald, University of Manitoba, Dept. of Foods & Nutrition, Winnipeg, Manitoba R3T 2N2, Canada, and E.J. Corner and V.M. Bruce, University of Manitoba.

Changes in the fatty acid composition of plasma phosphatidyl choline (PC), ethanolamine (PE) and alkenylacyl ethanolamine (PPE) in response to dietary canola oil (CAN) or sunflower oil (SUN) were studied in 8 normolipidemic men. The study was divided into 3 periods: 6-day experimental and two 18-day experimental. The CAN and SUN diets were fed in a cross-over design. Approximately 28% of the total energy (75% of the fat) was from a mixture of fats during the pre-experimental period and either CAN or SUN during the experimental periods. Dietary fat source had a significant ($p<0.05$) effect on plasma phospholipid (PL) fatty acids: 18:1n-9, 18:3n-3 and 20:5n-3 were higher and 18:2n-6 lower in the PC fraction, 18:1 was higher and 20:4n-6 lower in the PE fraction, and 18:1 and 20:5 were higher and 20:4 and 22:5n-6 lower in the PPE fraction on the CAN diet. In general, the content of n-3 fatty acids was higher and n-6 fatty acids lower on the CAN diet than on the SUN diet; fatty acid patterns and levels in the plasma PL were similar to those reported in platelet PL.

Specificity of Lipases from *Pseudomonas cepacia* and *Humicola lanuginosa*. Donna R. Galluzzo, University of Connecticut, Dept. of Nutritional Sciences, Storrs, CT 06269-4017, and Robert G. Jensen, University of Connecticut and Birgitte Huge-Jensen, Novo Industri A/S.

Partially purified lipase preparations from the microorganisms, *Ps. cepacia* and *H. lanuginosa* were obtained from Novo Industri A/S. The fatty acids released from 18:1-16:0-18:1 were about 4/1 18:1/16:0 and from 16:0-18:1-16:0, 4/1 16:0/18:1 after 3 and 5 minutes of digestion. When equimolar mixtures of saturated triacylglycerols (TG, 4:0-16:0) and 18:1-18:1-18:1 were hydrolyzed, *H. lanuginosa* lipase digested 12:0, 14:0, and 16:0 TGs more rapidly than 4:0-10:0. The lipase from *Ps. cepacia* hydrolyzed greater quantities of 6:0 TG after 5 and 10 minutes. When equimolar mixtures of tri-18:1, 18:2, alpha-18:3, and gamma-18:3 were hydrolyzed, the *Humicola* lipase digested alpha-18:3-18:3-18:3 two times more rapidly than gamma-18:3-18:3-18:3, while the *Pseudomonas* lipase showed the opposite selectivity. The lipases were not stereospecific, were selective for primary esters of TGs, and showed selectivity for certain fatty acids. Supported in part by a grant from Novo Industri A/S.

Production of Cocoa Butter-Like Fat from Interesterification of Vegetable Oil. Min-Kun Chang, USDA-ARS-SRRC, P.O. Box 19687, 1100 Robert E. Lee Blvd., New Orleans, LA 70179, and George Abraham, USDA-ARS-SRRC.

Preparation of a cocoa butter-like fat from hydrogenated cottonseed oil and olive oil by enzymatic interesterifi-

cation was studied. Equal amounts of hydrogenated cottonseed oil and olive oil were mixed at 70°C. An immobilized lipase (Lipozyme, Novo, Inc.), weighing one-tenth of total oil weight, was added to initiate the reaction. The optimum reaction time to produce the major components of cocoa butter, 1(3)-palmitoyl-3(1)-stearoyl-2-monooleine (POS) and 1, 3-distearoyl-2-monoolein (SOS), was four hours. The reaction was terminated by removing the lipase using suction filtration. The cocoa butter-like fat product was isolated from the reaction mixture by two filtration steps. The first filtration was performed at room temperature to remove the saturated triglycerides. The cocoa butter-like fat product was precipitated from the first filtrate by cooling to 4°C. This precipitate was collected by a second filtration at 4°C. The overall yield of our cocoa butter-like fat product was 19.1%. Chromatographic analysis of the product by reverse phase HPLC has shown it contains similar triglyceride components as cocoa butter with slightly increased amounts of diglyceride components. The melting point of this product as measured by differential scanning calorimeter was 39°C. This value compares well to the 36°C melting point of natural cocoa butter.

Choline Phospholipid Aggregation and Non-Aggregation Monitored by Multinuclei Magnetic Resonance Techniques. V.V. Kumar, The Hormel Institute, University of Minnesota, 801 16th Avenue, N.E., Austin, MN 55912, and R. Murari, Rorer Central Research and Wolfgang J. Baumann, University of Minnesota.

Earlier work from our laboratory had shown that nitrogen-14 spin-lattice relaxation times ($^{14}N\ T_1$) and quadrupolar ^{13}C-^{14}N couplings (J_{CN}) of choline phospholipids are most sensitive to changes in the nitrogen environment [*J. Am. Chem. Soc. 103*: 1238, (1981)] We now found that measuring of $^{14}N\ T_1$ and J_{CN} of lysophosphatidylcholine (lysoPC) can be useful to monitor changes in phospholipid head group association and in the state of lysophospholipid aggregation. We determined $^{14}N\ T_1$ and J_{CN} values of lysophosphatidylcholines of different chain length in aqueous dispersion (110 mM). We found that the ^{13}C NMR spectra (20 MHz) of lysoPC with a carbon chain of up to C_{10} show a well resolved triplet for the choline methyls ($J_{CN} = 3.3 \pm 0.5$ Hz); however, the methyl triplet collapses to a singlet for lysoPC with 12 or more carbons in the aliphatic chain. The $^{14}N\ T_1$ values (5.74 MHz) decline from 0.172 s for C6 lysoPC to 0.093 s for C_{12} lysoPC, but little change occurs for lysoPC with a chain length of C_{14} and longer (0.06 s). The data are consistent with our calculations which predict that triplet broadening occurs at $^{14}N\ T_1$ values shorter than 0.086 s with eventual collapse of the splittings. The effect of lysoPC concentration on the spectral parameters was also investigated.

High-Performance Liquid Chromatographic Analysis of Gossypol-Aminopropanol Complex. Robert J. Hron, Sr., USDA-ARS-SRRC, P.O. Box 19687, New Orleans, LA, 70179, and Myong S. Kuk and George Abraham, USDA-ARS-SRRC.

Existing HPLC methods determine pure gossypol only whereas the present official AOCS method determines both gossypol and other physiologically active gossypol-like compounds which react with 3-amino-1-propanol and aniline. The feed industry uses the official AOCS method which is complex and produces results which do not correlate well between laboratories. The poster presents a new HPLC procedure, based upon Walter Pon's AOCS wet chemistry method using 3-amino-1-propanol as a complexing agent, for the quantitative determination of free and total gossypol to less than 1 PPM in cottonseed oil, meal and ethanolic miscellas. The new HPLC method is simpler to use, much more sensitive, produces results that should correlate well between laboratories and does not use toxic aniline.

Altered Compositions and Synthesis of Phospholipid and Triglyceride in Liver of Rats Consuming a Fish Oil Concentrate. Young K. Yeo, Kyungpook National University, University of Guelph (mailing address), Room 308 Animal Science/Nutrition Bldg., Guelph, Ontario N1G 2W1, Canada, and Diana J. Philbrick and Bruce J. Holub, University of Guelph.

Male Sprague-Dawley rats were fed diets containing 10% by weight sunflowerseed oil (SO) or a fish oil concentrate enriched in omega-3 fatty acids containing supplementary linoleic acid (FO group). The FO group exhibited lower (by 40%) levels (nmols/g tissue) of triglyceride relative to the controls (SO) as well as moderately higher levels of selected phospholipids and altered fatty acid profiles (including n-6 and n-3 series). Studies with [^{3}H]glycerol *in vivo* also revealed an increased *de novo* synthesis of phospholipid relative to triglyceride in the FO group as compared to the control group. For example, the ratio of newly-synthesized [^{3}H]glycerol: [^{3}H]phosphatidylcholine was only 1.9:1.0 in the FO group as compared to 3.3:1.0 in the control (SO) group. The possible biochemical mechanisms underlying these effects of dietary FO will be presented.

Alternative Solvents for Peroxide Value Determination. D.D. Brooks, Oil-Dri Corporation of America, 22149 N. Pet Lane, Prairie View, IL 60069, and S.K. Brophy, B. Hayden, and G.R. Goss, Oil-Dri Corporation of America.

Iso-octane and methylene dichloride were used as a replacement solvent for chloroform in the Official AOCS Method Cd 8-53 for the determination of Peroxide Values. The iso-octane solvent required an increased reaction time of three minutes to achieve the same results as the chloroform solvent. The methylene dichloride solvent required no alterations to the official procedure to achieve the same results as the chloroform solvent.

Fractionation of Polyenoic Acids from Marine Lipids with Lipase. Toru Takagi, Hokkaido University, Dept. of Chemistry, Faculty of Fisheries, Minato-cho, Hakodate, 041, Japan.

Polyenoic fatty acid concentrates (20:5(n-3) 30-40$ and 22:6(n-3) 25-30%) obtained from Japanese sardine oils by the urea adduct method were esterified with methanol in various organic solvent media using some commercial microbial lipases. One microbial lipase showed the selective esterification of 20:5(n-3) in the presence of 22:6(n-3). In the best condition, the polyenoic acid mixtures gave the EPA concentrates (20:5(n-3) contents higher than 50% in the yields of about 60%) as the methyl ester fraction and the DHA concentrates (22:6(n-3) contents about 50% in the yields of about 40%) as the unesterified fatty acid fraction by one esterification process. These results showed that the selective esterification by the microbial lipase is a useful

method for the effective fractionation of 20:5(n-3) and 22:6(n-3). Since the procedures are carried out without heating under nitrogen, the polyenoic acid concentrates obtained by this method do contain little amounts of autoxidized and polymerized products.

Properties and Substrate Specificity of Lipase Activity from Oat (*Avena sativa*) Seeds. George J. Piazza, USDA-ARS-ERRC, 600 E. Mermaid Lane, Philadelphia, PA 19118, and Alexander Bilyk, USDA-ARS-ERRC.

We have re-examined the properties of the lipase from ungerminated oat seeds. The lipase can be liberated from dry seeds by homogenization in buffered water, followed by filtration and low speed centrifugation. The supernatant lipase activity remains unchanged for at least 24 hours under refrigeration. The lipase activity can be pelleted by centrifugation at 8,000*g* for 45 minutes, demonstrating that the lipase is bound to a particulate fraction. Lipase activity dependent on calcium ion. In reactions with triglyceride the lipase hydrolyzes all three positions and is therefore positionally nonspecific. However, the lipase is selective toward fatty acids with one double bond. This selectivity is evident with highly pure glycerides containing a single type of fatty acid and is also observed with synthetic mixed glycerides and those from natural fats.

Carbon-13 FT-NMR Examination of Positional Isomerism in Fats and Oils. J.D. Wendel, Procter & Gamble Company, Winton Hill Technical Center, 6071 Center Hill Road, Cincinnati, OH 55224, and D.R. Gardner, Procter & Gamble Company.

The metabolism of triglycerides involves enzymatic cleavage of position specific sites on the glycerol backbone. Because of this, it is becoming increasingly important to the nutritionist to know the position, nature and relative amounts of fatty chains present in edible fats and oils. Following the lead of Ng and co-workers, high-resolution Carbon-13 NMR has been used successfully in our laboratory to answer these questions. An examination of the carbonyl and olefinic resonances of triglycerides contained in several commercially available fats and oils will demonstrate the ability to distinguish between specific unsaturated and saturated fatty acids. An investigation of several fully saturated triglyceride systems will also be presented. This work will demonstrate how high-field Carbon-13 NMR can differentiate these materials based on both chain length and backbone position.

The Total Degumming Process. Albert J. Dijkstra, N.V. Vandemoortele Coordination Center, Prins Albertlaan 12, P.O. Box 40, Izegem, B-8700, Belgium.

A novel degumming process, applicable to both undegummed and water-degummed oils, is described. Such "totally degummed oils" have residual iron contents below 0.2 ppm Fe and residual phosphorus contents that are on average below 5 ppm P. They can therefore be physically refined to yield a stable refined oil while using the same amount of bleaching earth as commonly used for alkali refined oils prior to deodorization. They can also be alkali refined with reduced oil loss to yield a soap stock that only requires slight acidification for fatty acid recovery and avoids the strongly polluting soap splitting process. The total degumming process involves dispersing a non-toxic acid such as phosphoric acid or citric acid very finely into the oil, allowing a contact time and then mixing a base such as caustic soda or sodium silicate into the acid-in-oil emulsion, whereby the degree of neutralization is so low as to avoid forming soaps, because the latter would lead to increased oil loss. Subsequently, the oil is passed to a centrifugal separator where most of the gums are removed from the oil stream as a gum phase with minimal oil content. The oil stream is then passed to a second centrifugal separator to removal all remaining gums as a dilute gum phase which is recycled. Washing and drying or in-line alkali neutralization complete the process. An overall yield improvement of 0.5% has been observed after adoption of the total degumming process.

Synthesis and Enzymatic Activity of 1-0-Alkyl-2-Acetyl-sn-Glycero-3-Thiophosphocholine. Robert T. Swindell, Tennessee Technical University, Dept. of Chemistry, Box 5055, Cookeville, TN 38505, and David J. Crouse, Tennessee Technical University.

Synthesis of 1-0-alkyl-2-acetyl-sn-glycero-3-thiophosphocholine (I) is described. Chimyl alcohol is treated with trityl chloride/pyridine to form the 3-0-trityloxy compound (II). Compound II is acetylated, the protective trityloxy group removed and the thiophosphocholine moiety introduced using choline tosylate and thiophosphoryl chloride. Reaction of (I) with phospholipase A_2 was used to determine stereochemical purity. Synthetic procedures and problems and potential biological roles of (I) will be discussed.

Quantitation of Phospholipids in Animal Tissues by Iatroscan TLC/FID. Remi de Schrijver, Catholic University of Leuven, Laboratory of Nutrition, Kard. Mercierlaan 92, Leuven, 3030, Belgium, and Daniel Vermeulen, Catholic University of Leuven.

The Iatroscan TH-10 system allows the separation of lipids by means of chromatography on Chromarods and the subsequent detection of the lipid components by flame ionization. Although this combined system has proven to be useful in lipid analysis, certain phospholipids are not resolved. A technique has been developed to separate and quantitate the phospholipids present in animal tissues: lysophosphatidylcholine, sphingomyelin, phosphatidylcholine, phosphatidylserine, phosphatidylinositol, phosphatidylethanolamine and diphosphatidylglycerol. The method involves the use of oxalic acid impregnated chromarods SII, the addition of an internal phospholipid standard to the extracted lipids, a two-step development and scanning procedure employing an acidic and a basic solvent system and the determination of a calibration curve for each phospholipid. The precision and accuracy of the Iatroscan method has been shown to be generally similar to the established TLC-phosphorus technique.

Lipase Catalyzed Formation of Fatty Amides. Raymond G. Bistline, Jr., USDA-ARS-ERRC, 600 E. Mermaid Lane, Philadelphia, PA 19118, and Alexander Bilyk, USDA-ARS-ERRC

Certain lipases in hexane facilitate the preparation of fatty amides at 20°C. The lipases investigated were from

the fungi *Candida rugosa*, *Mucor miehei* and porcine pancreas. Reactants were various primary alkylamines and several derivatives of fatty acids; namely 4-hydroxymethyl-2,2-dimethyl-1, 3-dioxolane, octanoic ester (HDDO), triglycerides and the methyl esters of C6-C_{16} fatty acids. Optimum yields of fatty amides were obtained using *M. miehei* lipase as catalyst. The lipase from this source effectively catalyzed the formation of fatty amides from primary amines and the fatty substrates. No reaction was observed in similar experiments using one secondary amine.

Analysis of *trans* Fatty Acid Methyl Esters from Commercial Vegetable Oils by Silver-Loaded High Performance Liquid Chromatography & Capillary Gas Chromatography. G.S. Saupe, Procter & Gamble Company, 6071 Center Hill Road, Cincinnati, OH 45224, and R.A. DePalma, Procter & Gamble Company.

A collaborative study completed in April, 1988, demonstrated the precision of measurement of *trans* levels in fatty acid methyl esters (FAME) from commercial vegetable oils with a single gas chromatographic analysis. This analysis uses highly polar cyanopropyl silicone stationary phase to separate the *cis* and *trans* FAME. Levels of *trans* from less than 1% to 25% are quantitated with this method with good precision. Additional analyses of the samples by the traditional infrared method for *trans* show an offset of 2-4% *trans* between the two methods, with the gas chromatographic method reporting lower results than the infrared method. To resolve this discrepancy, a two-step separation procedure was used. A silver-loaded high performance liquid chromatographic separation [Christie, W.W., *J. High Res. Chrom. Chrom. Commun. 10:* 148 (1987)] is used to separate the FAME by degree of unsaturation and double bonds geometry. The fractionated FAMEs are then collected and analyzed by the gas chromatography (GC) with a cyanopropyl silicone stationary phase. This procedure should show that coelution of the *trans* monoenes with the cis monoenes is responsible for the low results with the GC method. An estimate of the GC resolution required for a more accurate *trans* measurement can be made from these experiments.

Chiral Column Reassessment of the Stereospecificity of Monoacylglycerol Acyltransferase (MGAT) from Rat Intestine. R. Lehner, University of Toronto, Charles H. Best Institute, 112 College Street, Toronto, Ontario M5G 1L6, Canada, and Y. Itabashi and A. Kuksis, University of Toronto.

The stereospecificity of crude and partially purified MGAT was determined using a chiral column for the separation of the diradylglycerols resulting from the acylation of 2-monooleoyl-, sn-1-monopalmitoyl- and sn-3-monopalmitoyl-[2-^{3}H]-glycerol and 2-monooleylglycerol with [1-^{14}C]oleoyl CoA. The 3,5-dinitrophenylurethane derivatives of sn-1,2- and sn-2,3-enantiomers were resolved by HPLC using N-(R)-1-(alpha-naphthyl)ethylaminocarbonyl-(S)-valine as the chiral liquid phase and hexane-ethylene dichloride-ethanol 150:20:1 as the mobile phase (Takagi & Itabashi, Lipids *22*, 596-600. 1987). With 2-monooleoylglycerol, the overall yield of higher acylglycerols was 70%: 60% diacyl- and 40% triacylglycerols. Of the diacylglycerols, 90% was sn-1,1- and 10% sn-2,3-dioleoylglycerols. With 2-monooleylglycerol, the overall yield of acylation products was 56%: 96% diradyl- and 4% triradylglycerols. Of the diradylglycerols, 90% was sn-1-oleoyl-2-oleyl- and 10% sn-2-oleyl-3-oleoylglycerols. There were no X-1,3-isomers formed. The sn-1- and sn-3-monopalmitoylglycerols yielded only the corresponding X-1,3-palmitoyl-oleoylglycerols in 60% yield. It is concluded that the crude as well as the purified MGAT of rat intestinal mucosa are clearly capable of acylating the sn-1- and sn-3-, but not the sn-2-positions of monoacylglycerols. Since the sn-2,3-diradylglycerols do not accumulate, both sn-1,2- and sn-2,3-enantiomers appear to be acylated to triacylglycerols.

Olestrin—An Amalgam of Sucrose Polyesters and Dextrins. M. Knezevich, Reach Associates, Inc., South Orange, NJ 07079.

Organoleptic qualities are good for a dextrin composition of 0.5-4 DE which also confers excellent texture properties to a synergistic mixture of 30% or less of sucrose polyesters and at least 24% of triglyceride oil, thus avoiding anal leakage and depletion of fat soluble vitamins. Usable for aspartame fruit yogurt and frozen desserts in conjunction with U.S. Patent 4,626,441, salad oils, muffins, cakes, mayonnaise, and others and to achieve calorie values of about 1 cal/gm (raw) and 3 cal/gm for the fat replacing composition.

Identification of Molecular Species of Enantiomeric Diacylglycerols by Chiral Phase LC/CIMS of the 3,5-Dinitrophenylurethanes. Y. Itabashi, University of Toronto, Charles H. Best Institute, 112 College Street, Toronto, Ontario M5G 1L6, Canada, and L. Marai and A. Kuksis, University of Toronto.

The chiral HPLC column provides a complete resolution of enantiomeric diacylglycerols containing identical fatty acids, while resolution of enantiomers containing different fatty acids results in overlap or interdigitation of many chromatographic peaks, and identification of individual sn-1,2- and sn-2,3-species becomes difficult or impossible. We have observed that the 3,5-dinitrophenylurethane (DNPU) derivatives of diacylglycerols used in the analysis yield characteristic [M-DNPU]+ and [RCO+74]+ ions on chemical ionization mass spectrometry, which allows determination of the molecular weight and fatty acid pairing for each species. For combined LC/CIMS analysis we have modified the original solvent system to contain hexane-dichloroethane-acetonitrile 85:10:5 (v/v/v). The analyses were performed on a liquid chromatograph equipped with a column (25 cm x 4.6 mm ID) containing D-naphthylethylamine polymer as the chiral liquid phase and interfaced via direct liquid inlet probe with a quadrupole mass spectrometer. The method was standardized with synthetic sn-1,2- and sn-2,3-dipalmitoyl and dioleoylglycerols and was applied to the identification of molecular species of enantiomeric diacylglycerols generated by Grignard degradation from cocoa butter, corn oil and other natural fats.

Influence of *cis* and *trans* Unsaturation on the Structural and Thermal Properties of Monoacid Triglycerides: SSS, OOO and EEE. Veronique Gibon, Facultes Universitaires Notre Dame de la Paix, 61, rue de Bruxelles, Namur, 5000 Belgium, and A. Desmedt, F. Durant, and Cl. Deroanne.

The thermal properties of natural fats, polymorphism and intersolubility, are essentially due to triglycerides which are the principal constituents of such matters. The complexity of the thermal behavior of fats is due to the great variety of triglycerides which may differ by the length of the hydrocarbon chains, by their unsaturation degree and by their position on the glycerol residue. In crude fats, only *cis* type unsaturated fatty acids (oleic, linoleic, linolenic...) are found; *trans* double bonds do not exist in nature but are generated by the main industrial processes such as hydrogenation. The presence of *trans* fatty acids in the refined fractions modify their technological properties: polymorphism, kinetic of polymorphism and intersolubility. From a nutritional point of view, the *trans* isomers may induce modifications of the biochemical processes. In order to precise the importance of *cis* or *trans* unsaturations on a technological point of view, we have undertaken the study of the structural and thermal properties of stearic, oleic and elaidic triglycerides; powder x-ray diffraction, NMR spectroscopy and differential scanning calorimetry are useful tools in order to elucidate the physico-chemical properties of such compounds. In a first part, polymorphism, kinetic of polymorphism and intersolubility of monoacid triglycerides: SSS, OOO and EEE have been investigated. From a structural point of view, we have shown that, according to the polymorphic form, the conformational properties of EEE are similar to that of the corresponding saturated molecule SSS or to that of the corresponding *cis* unsaturated triglyceride OOO. The study of the intersolubility of these three compounds has shown a different affinity of *cis* and *trans* unsaturated compounds versus completely saturated hydrocarbon chains. The co-crystallization possibility of *trans* unsaturated and saturated chains and from *trans* unsaturated and *cis* unsaturated ones shows the possibility of EEE to adapt with the two types of lattice. The study of the kinetic of polymorphism has shown that OOO and EEE accelerate the ß'→ß transition of SSS, while the origin of the two phenomena is quite different. The relation between the polymorphic form and the possibility of reorganization of EEE near the *trans* double bond shown in the structural analysis also appears in the kinetic study, after adjunction of some percents of OOO in EEE. All those results allow to confirm that, from structural and thermal points of view, EEE has an intermediate behavior between SSS and OOO.

Composition and Nutrition of Soybean Foods. A.M. Almazan, International Institute of Tropical Agriculture (IITA), P.M.B. 5320, Ibadan, Nigeria, and K.E. Weingartner, University of Illinois, International Agriculture (INTSOY).

Cassava-soy chips were prepared using mixtures of cassava, low-fat (5%) and full fat (15%) soybean flour. They were packed in plastic bags and stored at 35°, 25°, and 10°C for 1, 3, 4, 6, 10 and 17 weeks. A taste panel ranked 5 kinds of chips for color and flavor at 0, 1, 3 and 4 weeks. During storage, two-tailed simple paired comparison tests were conducted on chips: (a) made with and without soy flour; (b) chips containing 5% and 15% soy; and (c) newly fried and stored. Oil, fatty acid, total cyanide, and dry matter content were monitored during storage. At each storage temperature, there was: no change in FFA content in the chips; a decrease in dry matter content, chip crispness and cyanide content over time. There was no significant different in flavor preference for chips made with or without soybean flour. So, the inclusion of soy flour in fried cassava chips is consumer acceptable. Fired cassava-soy chips can be adequately stored in sealed plastic bags for 4 weeks. This will enable small cottage industries to produce and sell cassava-soy chips at a low price.

Custom Encapsulation Processes. William W. Harlowe, Jr., Southwest Research Institute, 6220 Culebra Road, San Antonio, TX 78284, and C.W. Lew, H.W. Schlameus, D.J. Mangold, and R.E. Lyle, Southwest Research Institute.

Capsule size requirement is one of the most critical factors in selecting an encapsulation process as the several different physical and chemical processes from which to choose are limited to specific size ranges. Several processes, such as the centrifugal and submerged extrusion nozzle, disk/spray dryer, air suspension, interfacial polymerization, coacervation and solvent evaporation, are reviewed. Active materials such as flavors, essential oils, enzymes, perfumes, vitamins and drugs can be effectively encapsulated to enhance performance of products. Examples of water-soluble shells such as gelatin, poly(vinyl alcohol), algin and methylcellulose, and a similar group of water-insoluble shells such as paraffin waxes, hydrocarbon resins, polyethylene and shellacs, along with the preferred release mechanism of each class, are described. The physical property relationship of shell wall thickness vs payload (active ingredient) for various size capsules is presented.

Characteristics of a Solubilized *Brassica napus* Lipase. R.J. Weselake, Plant Biotechnology Institute, National Research Council of Canada, Saskatoon, Saskatchewan S7N 0W9, Canada, and L.W. Thompson, D. Tenaschuk, and S.L. MacKenzie, Plant Biotechnology Institute.

Lipase (triacylglycerol acylhydrolase EC 3.1.1.3) was extracted from the microsomal fraction (10,000 to 150,000g) of dark grown seedlings of *Brassica napus* L. cv Westar using 1% (v/v) Triton X-100. Lipase was partially purified by Sephacryl S-300 gel filtration and DEAE-BioGel ion-exchange chromatographies. The resulting enzyme preparation was stable when stored at -20°C in 50% (v/v) glycerol. The lipase had an apparent M of 250,000 based on gel filtration chromatography in the presence of detergent. Lipase activity was optimal near neutral pH and the reaction approached maximum velocity at a concentration of 0.5 to 1mM emulsified triolein. The initial velocity of the enzyme reaction increased between 10°C and about 50°C with a discontinuity in the slope of the Arrhenius plot at 32°C. However, the enzyme preparation lost about 20% and 80% activity when pre-incubated at 40°C and 60°C, respectively, for 1 hour. Concentrations of detergents required for 50% inhibition of lipase activity were 100 fM Triton X-100, 1 mM CHAPS, 270 fM sodium dodecyl sulphate and 35 fM cetyltrimethylammonium bromide. The inhibitory effect of Triton X-100 was reversible. N-Octyl ß-D-glucopyranoside stimulated lipase activity by 2-fold at a concentration of 4 mM but was 50% inhibitory at 15 mM.

Recent Nutritional Studies on Palm Oil and its Fractions. Daniel T.S. Tan, PORIM, P.O. Box 10620, Kuala Lumpur, 50720, Malaysia, and Khor Hun Teik, University Malaya.

Palm oil has been consumed by peoples in the tropics since many decades ago without any apparent adverse effect on health. Recent scientific studies in our laboratories and in others in other parts of the world have indicated that palm oil lowers plasma cholesterol and has antithrombotic properties in experimental animals. Palm oil is extremely rich in tocopherols and tocotrienols. Tocotrienols isolated from barley has been shown to inhibit cholesterol synthesis in broiler. In this study, a vitamin E concentrate, palm vitee, isolated from palm oil has been tested for its effect on plasma cholesterol and lipoprotein cholesterol levels in several human volunteers. Before taking the palm oil vitamin E concentrate, the fasting plasma cholesterol and lipoprotein cholesterol levels were determined and after one month on the palm oil vitamin E concentrate, the plasma cholesterol and lipoprotein cholesterol levels were again determined. Our results show that the plasma cholesterol and lipoprotein cholesterol levels were all depressed as compared to the initial values before treatment. The reduction in cholesterol levels vary from 5% to 36% of its initial values. But more profound reduction was seen in volunteers with hypercholesterolemia. Hence the effect of palm oil feeding and palm vitamin E supplementation on induced hypercholesterolemia in rats and hamsters was also investigated and the results will be discussed in relation to the human findings.

The Solubilization and Differentiation of CDP-choline:1,2-diacylglycerol choline-phosphotransferase and CDP-ethanolamine:1,2-diacylglycerol ethanolaminephosphotransferase in Hamster Liver.
Patrick C. Choy, University of Manitoba, Dept. of Biochemistry, 770 Bannatyne Avenue, Winnipeg, Manitoba R3E 0W3 Canada and Karmin O (speaker), University of Manitoba.

Phosphatidylcholine and phosphatidylethanolamine are the major phospholipids in eucaryotic cells. CPT and EPT are the enzymes that catalyze the final steps of the *de novo* biosynthesis of phosphatidylcholine and phosphatidylethanolamine, respectively. The two enzyme activities are bound to the microsomal membranes. It was not clear whether these two activities were catalyzed by the same or separate enzymes. Attempts to solubilize them for further purification were met with very limited success. In this study, we examined the effect of neutral, anionic and cationic detergents on both enzyme activities. In the present of Triton X-100 and octyl glucoside, EPT activity was more stable and more readily soluble than CPT. Both enzyme activities were solubilized from the hamster liver microsomes with Triton QS-15. The solubilized microsomal preparation was applied to a DEAE-Sepharose column and enzyme activities were eluted by a KCl gradient. The EPT activity was resolved into a major and a minor peak but one CPT activity peak was detected. Although the CPT peak appears to elute slightly ahead of the major EPT peak, there was a general overlap between these two activity peaks. Both enzyme activities were substantially enhanced after DEAE- Sepharose chromatography which suggests the presence of an inhibitor in the microsomal preparation. Our work indicates that treatment with Triton QS-15 is a facile approach for the solubilization of both CPT and EPT activities in the microsomes, and our results provide additional evidence to the postulation that CPT and EPT are two separate enzymes.