Abstracts

Unless indicated by *, first name given is speaker.

1

LIPID METHODOLOGY—CHROMATOGRAPHY AND BEYOND. A. Kuksis, Banting and Best Department of Medical Research, University of Toronto, 112 College St., Toronto, Ontario M5G 1L6, Canada.

The recent successful separation of molecular species of polar glycerophospholipids by high pressure liquid chromatography (HPLC) essentially completes the chromatographic resolution of lipids, which started with the determination of fatty acid methyl esters and continued with the analysis of intact, natural triacylglycerols. This great analytical achievement, however, is of limited interest to lipid biochemistry and metabolism, unless a distinction can also be made between old and new molecules within a species, and among molecular species of various ages. The separation of natural and isotope-labeled species needed for metabolic studies is clearly beyond conventional chromatographic resolution. In the past, specific radioactivity has been determined as a means of distinguishing the relative turnover rates of different molecular species, or among different parts of the same molecular species, and many successful combinations of various chromatographic techniques with radioactivity monitoring have been described. While these techniques are satisfactory for the comparison of the relative rates of incorporation of certain singly labeled markers into the lipid molecule, they are unsuitable in studies where more than one radioisotope atom can occur in a single molecule, and radioisotopes cannot generally be used for identifying new and old molecules. An experimental approach is provided by the combination of stable isotope-labeling and gas liquid chromatography (GLC) with mass spectrometry (MS). In this instance, the mass spectrometer provides a degradation of the resolved molecular species, permitting determination of the distribution of the stable isotope label within the molecules as well as the total labeling of each molecule. Modern mass spectrometers allow the simultaneous monitoring of a series of masses, which can be selected to represent various types of combinations of old and new components, and the relative proportions of each new and old species can be calculated by computerized data processing. Both electron impact and chemical ionization MS can be combined with GLC and the desired information can be obtained following appropriate calibration. Either ^{13}C- or ^{2}H-labeling is satisfactory for this purpose. This technique has been extensively used in monitoring the composition of the natural and stable isotope-labeled glycerolipid molecules in various preparations of animal tissues and cell cultures. More recently, a combination of HPLC and MS has been developed. It has the potential advantage of assessing the stable isotope distribution and content of the polar glycerophospholipid molecules, which cannot be directly resolved by GLC. The direct combination of liquid-liquid chromatography and MS is limited to chemical ionization MS, which yields fewer fragments than electron impact MS. This system may be potentially used in monitoring the relative stable isotope labeling of natural phospholipids from various sources. In addition to the stable isotope content of the fatty acid and the glycerol moieties, that method may also yield the stable isotope content of the nitrogenous bases and of the carbohydrate moiety, when present. As a result, it may be experimentally feasible to obtain chromatographic lipid profiles of metabolically active systems which include both chemical composition and the relative chronological age of each molecule. This provides an indication of the relative specific activity of the molecules and of their turnover rates, thus further extending the usefulness of chromatography in biochemistry and physiology.

2

BIOCHEMISTRY OF UNSATURATED FATTY ACID ISOMERS. E.A. Emken, USDA Northern Regional Research Center, 1815 N. University St., Peoria, IL 61604.

Recognition that catalytic hydrogenation changes the configuration and position of the double bond and alters the physical properties of unsaturated fats prompted numerous early investigations to determine the biochemical effects of "*trans* isomers." More recent research has provided data on positional isomer metabolism. Some aspects of fatty acid isomer metabolism are now reasonably well settled, but other issues are not resolved. Recent human and animal data have provided good evidence that isomers in hydrogenated oils are well adsorbed and incorporated into all organs or tissues. Analyses of human tissues also indicate that hydrogenated oils are the major source of fatty acid isomers in the U.S. diet. Tissue composition data combined with isolated enzyme studies and isotope tracer experiments with whole organisms show unquestionably that structural differences between various fatty acid isomers influence specific biochemical transformations. Examples are differences in the reaction rates and/or specificities of acyl transferase, lipase, desaturase and cholesteryl esterase/hydrolase for various positional fatty acid isomers. Isolated microsomes and mitochondria also have been used to identify differences in acyl CoA activation, oxidation and elongation of positional isomers. In addition, isotope tracer experiments show that preferential metabolism of individual positional isomers occurs in vivo. In vivo studies with diets containing adequate levels of linoleic acid show that hydrogenated vegetable oils produce no obvious physiological changes. Experiments with specific polyunsaturated isomers are reported to produce changes in blood cell properties, pulmonary weight, linoleic acid requirements and tissue lipid composition. These changes may be related to a number of factors such as membrane fluidity and permeability, cell function, synthesis of arachidonic acid, homo-γ-linoleic acid or prostaglandins. Still to be resolved are whether differences in the biochemistry of fatty acid isomers are desirable or undesirable and whether these differences contribute to long-term or subtle changes important to the etiology of atherosclerosis and cancer.

3

MEMBRANOUS SYSTEMS AND THEIR ACTIVITY—AN OVERVIEW. D.F.H. Wallach, Tufts University School of Medicine, Boston, MA.

The internal space of eukaryotic cells is circumscribed and subdivided by membranes. Compartmentalization is most pronounced in cells that are biosynthetically active. There is continuous interchange of membrane components, even whole membrane segments. All membranes are permeability barriers, but their specific functions are far more complex. Biomembranes consist of 2, in instances dissimilar, 2.5 nm polar lamellae, each bordering on an aqueous compartment, as well as on a central apolar layer. Proteins generally make up 2/3 of the membrane mass. The plasma membrane (PM) is 8-9 nm thick, about 70% protein by mass and contains a high proportion of cholesterol. It is specialized for exchanges between the extra- and intracellular spaces. It bears the equipment to pump ions into and out of the cell and to generate membrane potentials that drive the uptake of some nutrients and the export of waste products by facilitated processes. The PM has the capacity to internalize itself in the form of vesicles, making soluble materials within these vesicles and components attached to or inserted into the vesicle membrane available to the cell interior. The PM bears receptors for extracellular messengers and contains part of the machinery to convert extra- into intracellular information. The PM bears the molecules that identify "self" and contains the apparatus for communication with other cells. Some cells' PM carry the machinery to react against "nonself." In most cells, the inner aspect of the PM is normally linked to microtubules and microfilaments. The nucleus is bounded by a double membrane system, the nuclear envelope. Each membrane of the envelope is 6-9 nm thick. Their protein/phospholipid mass ratio lies near 3. There is little cholesterol. The outer nuclear membrane (ONM) is continuous with the endoplasmic reticulum (ER) and is studded on its cytoplasmic surfaces with membrane-associated polysomes that are active in protein synthesis. The space between the inner nuclear membrane (INM) and the ONM is continuous with the spaces of the ER. The ONM contains enzymes characteristic of ER and is linked to cytoskeletal elements. The INM is more rigid and appears to be intermittently associated with DNA. Some nuclear DNA may be initiated in association with the INM. Some DNA repair enzymes are associated with the nuclear membrane. At intervals, the INM and ONM join to form nuclear pore complexes, highly complex structures specialized for the transfer of macromolecules. The ER consists of flattened membrane tubes and vesicles of which the internal spaces, the cisternae, form channels extending throughout the cytoplasmic space. The molar ratio of protein to phospholipid is near 3. Cholesterol content is low. The ER bears the machinery for many steps in lipid, steroid and protein biosynthesis. During the synthesis of membrane proteins and proteins destined for export, polysomes attach to the cytoplasmic aspect of the ER to give rough ER. The ER is in dynamic communication with the Golgi membranes and PM by "membrane flow." Golgi membranes (GM) occur as stacks of flattened membrane vesicles. The Golgi space is extracytoplasmic. Vesicles budding off the ER fuse with GM. This allows glycosylation of material brought from the ER. The addition of sugar groups may begin in ER cisternae and continue in the Golgi spaces, or begin in the Golgi spaces. After glycosylation of a protein residue or ceramide with D-galactose, D-glucose or D-xylose, other monosaccharides are added by glycosyl transferases with the mediation of membrane-associated dolichols, long-chain, unsaturated isoprenoid alcohols. When a protein or lipid is ready for export, this occurs by budding of clathrin-coated Golgi vesicles which then fuse with the PM. Lysosomes (LY) are membrane-bounded vesicles that are 0.25-0.5 μm in diameter and contain hydrolytic enzymes. Some of these enzymes are exported via the Golgi apparatus, having been

glycosylated with sugars that act as ligands for receptors on the PM of the cell producing the enzymes. Subsequent receptor-mediated internalization of the enzyme-bearing PM domains forms primary LY. These degrade macromolecules which are delivered in vesicles that have budded in from the PM and fuse with the primary LY to form secondary LY. The mitochondria are double-membrane structures with elongate or globular shapes. The outer membrane is smooth. The inner membrane has folds or invaginations, cristae, which increase surface area. Within the inner membrane is a gel, the matrix, containing enzymes, mitochondrial DNA, ribosomes and associated machinery. The outer mitochondrial membrane (OMM) is relatively permeable, has a protein/phospholipid mass ratio of about unity and bears a number of enzymes. The space between the OMM and the inner membrane contains several enzymes. The inner mitochondrial membrane (IMM) consists of 80% protein and 20% phospholipid, including the unusual acidic lipid diphosphatidylglycerol. There is no cholesterol. More than 60 membrane proteins are associated with the inner membrane. These include the enzymes and proteins for electron transfer and oxidative phosphorylation, as well as numerous transport proteins.

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Abstract 4 appears on the last page.

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ENERGY CONSERVATION AND THE FATS AND OILS INDUSTRY. Billy F. Brooks, Energy Division, Anderson Clayton Foods, 3333 N. Central Expressway, Richardson, TX 75080.

The supply and use of energy has become a serious consideration for our society not because of its shortage, but because of its nontraditional location and source of supply relative to traditional uses. This supply vs use imbalance has already led to national and international economic and political crises that have involved governmental, financial, industrial and all other world communities. The supply side of the dilemma will not go away. It is not solved and it will not be solved by the government bureaucrats who have spent so much time and tax payers' money trying to solve it. The solution will come from the world's technical community. Through ingenuity and invention underway, nontraditional forms of energy can now be converted to traditional forms so that the world's finite supply of nonrenewable energy can fill the gap until next century when the use of renewable forms of energy can provide infinite supply. The use consideration is not so technical. There is no secret to proper and efficient use of energy—engineers have known how to do it for years. The challenge is to practice what we know and to use energy more productively the first time, then reuse it again and again. The opportunity exists for the scientist and engineer to apply basic classroom skills with real entrepreneurship to stretch the BTU and maximize production. At one of the sessions in this conference, you will hear practical, proven techniques that can make you a hero in your company if you go back and convince your boss that you knew all along how to save BTUs and bucks. At other sessions, you will hear comments that should stimulate your "How to make a better mousetrap without really trying" thinking so that next year you can come back to this conference and tell us how you salvaged and saved BTUs and bucks.

6

BIOTECHNOLOGY OF FATS AND OILS. A.T.James, Unilever Research Laboratory, Colworth House, Sharnbrook, Bedford, U.K.

A review will be given of the existing biotechnological processes and their advantages and disadvantages, together with identification of some of the gaps in knowledge required for further exploitation. A description of cloning techniques yielding perennial crops, e.g., the oil palm, will be given with an indication of the future roles of recombinant DNA transformation for all types of improved oil crops.

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VEGETABLE OIL—PRODUCTION AND PROCESSING INNOVATION—CURRENT AND FUTURE. R.R. Regutti and A.R. Baldwin, Cargill Inc., PO Box 9300, Minneapolis, MN 55440.

Energy costs, need for increased productivity, environmental concerns and new technologies are having important effects on vegetable oil production and processing. Some of these changes are discussed and a projection of the current trends in processing is provided into the next decade or so. Emphasis is on adjusted treatments during the major processing steps involved.

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EDIBLE OILS OF THE FUTURE. L.H. Wiedermann, American Soybean Association, Singapore.

The best way to look at the future is to understand our historical developments and current practices. For food, the world depends on comparatively few fat and oil sources and that basically is not likely to change. We can, however, expect to see significant shifts within these sources as the world strives to meet its basic dietary needs. Protein demands, for both direct and indirect consumption, will continue as the most immediate controlling factor. This is impacted by political and socioeconomic influences such as tariffs and changes in eating habits where functional performance requirements are superimposed on basic caloric needs. Technological advances, both via conventional and genetic engineering, will be significant in tailoring these traditional oil sources, and the role for biotechnology rests with small-volume, high-technical-content products. What we will have from these new technologies in the more distant future will still depend on what we want and what we will allow to happen.

9

DETERMINATION OF LIPASE SPECIFICITIES. Robert G. Jensen* and Felice A. Dejong, Department of Nutritional Sciences, University of Connecticut, Storrs, CT 06268.

When acylglycerols are hydrolyzed by lipases, the following types of specificity have been observed: (a) positional; preference for primary esters, (b) fatty acid; short-chain vs long-chain, (c) stereospecific; lipolysis of one primary *sn* ester more rapidly than the other, and (d) influence of substrate structure. Specifications have been determined by using acylglycerols of known structure as substrates followed by analysis of the digestion products. All of the types of specificity have been found with synthetic acylglycerols. Detection of stereospecificity requires enantiomeric acylglycerols which are difficult to synthesize, so other methods have been developed. These involve the generation of *sn*-1,2-(2,3)diacylglycerols (DG) and identification of the individual molecular species. Trioleoylglycerol can be the substrate. If the lipase is stereospecific then either *sn* 1,2 or 2,3 will predominate. The DG species can be identified by (a) conversion to phosphatidylphenols (PPh) and treatment with phospholipase A-2 which hydrolyzes the *sn*-2 acid and from the *sn*-3 PPh. The unreacted *sn*-1 can be separated by thin layer or high performance liquid chromatography, (b) conversion to phosphatidylcholine (PC) and digestion with phospholipase C. The enzyme digests *sn*-3 in 2 min and *sn*-1-PC in 180 min, (c) resolution of the DG with NMR and (d) measurement of optical rotation. Enantiomeric DG have a specific rotation of + or -2.8 which can be increased by derivitization. Applications of these procedures will be discussed and data on various lipases presented.

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ENZYMATIC FAT SPLITTING WITH LIPASE FROM *CANDIDA CYLINDRACEA*. Warner Linfield, U.S. Department of Agriculture, Agricultural Research Center, 600 East Mermaid Lane, Philadelphia, PA 19118.

Commercially available purified dry lipase from *Candida cylindracea* was used to achieve essentially quantitative hydrolysis of olive oil and tallow. The effects of time, temperature, pH, buffer system and the concentration of enzyme and water on lipolysis were studied. A minimal concentration of 0.07% of lipase, based on the weight of triglyceride, was required to hydrolyze olive oil completely. Tallow required a higher concentration of 0.35%. Olive oil lipolysis was done at room temperature (22-26 C) whereas tallow required a higher temperature around 40 C in order to keep the reaction mixture fluid. Complete hydrolysis typically required 12-16 hr. A low water level was found to be advantageous because the enzyme concentration in the aqueous phase was kept high, and accordingly, the concentration of the resulting glycerol was also high. A pH range of 5.2-5.6 and pH 7.0 afforded optimal rates of lipolysis. The choice of buffering system is important. Mixed phosphate, phosphate-citrate and citrate-citric acid gave comparable results. These were more effective than an acetate/acetic acid buffer which reduced the rate of hydrolysis by 10%. The use of an unbuffered system reduced the rate of hydrolysis of either oil or tallow by 10-15%. Addition of calcium or sodium ions did not affect the hydrolysis of an unbuffered system. The addition of bovine serum albumin, nonionic surfactants or taurocholate reduced the hydrolysis rate.

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POSITION SPECIFICITY AND CONTROL OF LIPOLYSIS IN THE CASTOR BEAN. Robert L. Ory* and Allen J. St. Angelo, Biochemistry Research, Oilseed and Food Laboratory, USDA-ARS, SRRC, PO Box 19687, New Orleans, LA 70179.

Earlier studies of lipases in peanuts, cottonseed and castor beans showed highest activity in castor beans. The acid lipase appeared to be specific for the C-1 and C-2 positions of triglycerides. However, it has been proposed that transfer of the C-2 fatty acid to the outer positions occurred, not by direct isomerization, but by cleavage of the C-2 fatty acid and reacylation of the C-1 and C-3 positions. Such a mechanism would require the presence of an acyl transferase. This

paper reports evidence for acyl transferase activity in the soluble infranatant fraction from castor beans. The enzyme requires coenzyme A, ATP, and Mg^{++} for optimal activity. It uses free fatty acids as substrate much more easily than it uses triglycerides. Lipase activity in germinating seeds is apparently controlled by activation of acid proteinase and phosphatase associated with the lipase in spherosomes. As storage oil in the seed decreases upon germination, lipase activity also decreases. Additional substrate does not increase activity of the lipase, indicating a decrease in the amount of enzyme. A mechanism for the loss of lipase activity due to action of phosphatase and proteinase on the lipase is proposed.

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CONTROL OF FATTY ACID CHAIN LENGTH IN THE PEA APHID *A. PISUM*. Robert O. Ryan*, Mertxe de Renobales and Gary J. Blomquist, Biochemistry Department, University of Nevada, Reno, NV 89557.

Approximately 70% of the fatty acid in the pea aphid *A. pisum* is myristate. *In vivo* studies with [1-^{14}C]2:0 show this insect is capable of synthesizing myristic acid de novo. Examination of the products of partially purified fatty acid synthetase (FAS) indicate this enzyme possesses a chain length specificity similar to that found in other organisms (i.e., C_{16} and C_{18} fatty acids). However, when partially purified FAS is incubated with a separate protein fraction, the chain length specificity is altered and myristate is produced. This fraction was inactivated by boiling, did not catalyze the biosynthesis of fatty acids from acetyl-CoA, malonyl-CoA and NADPH, but did possess thioesterase activity. Phenylmethanesulfonylfluoride (PMSF) treatment of FAS resulted in inhibition of FAS activity. Addition of the thioesterase protein fraction overcomes this inhibition of FAS and results in the production of fatty acids. This ability to relieve the inhibition of FAS by PMSF was directly proportional to the concentration of thioesterase. The thioesterase enzyme was found have to a specificity for 14, 16 and 18 carbon acyl-CoA and was much less active on a C_{12}-CoA. Therefore, the control of fatty acid chain length can be attributed to the presence of a soluble acyl thioesterase in this insect which interacts with and modifies the products of FAS.

HONORED STUDENT PRESENTATION

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STEAROYL-CoA DESATURASE AND FATTY ACID SYNTHETASE ACTIVITIES IN MORRIS HEPATOMA 7288C. Raphael A. Zoeller* and Randall Wood, Department of Biochemistry, Texas A&M University, College Station, TX 77843.

Low levels of $\Delta 9$ desaturase activity in host-grown hepatoma 7288CTC prompted us to examine the desaturase system in cultured hepatoma 7288C cells were exogenous lipids and endocrine affects could be more closely controlled. The Morris minimal deviation hepatoma cells were grown in roller cultures to near confluency, harvested, and separated into subcellular fractions after rupture by nitrogen cavitation. The cytosolic and microsomal fractions were used to assay fatty acid synthetase (FAS) and stearoyl-CoA desaturase activities, respectively. The cultured cells show FAS activity comparable to normal liver, but stearoyl-CoA desaturase activity of this system was well below that of normal liver (84 pmol min^{-1} mg^{-1}). Examination of the individual components in the electron transport system of stearoyl-CoA desaturase showed cytochrome b_5 reductase to be quite active and cytochrome c reductase, while lower in activity than normal liver (275 nmol min^{-1} mg^{-1}), was still active enough so as to not be limiting. The microsomal cytochrome b_5 content, however, was extremely low (>10 pmol mg^{-1}). The data suggest that the low activity of stearoyl-CoA desaturase in these cultured hepatoma cells is due either to a deficiency in cytochrome b_5 content, low terminal desaturase enzyme levels, or both. Reconstitution studies must first be performed to determine which are responsible. (This work was supported by United States Public Health Service Grant CA 20136 from the National Cancer Institutes.)

HONORED STUDENT PRESENTATION

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EFFECT OF DIETARY SUCROSE AND GLUCOSE ON FATTY ACID ACYL DESATURASE ACTIVITIES IN RAT LIVER. Remi De Schrijver*, University of Ghent, Heidestraat, 19, 9220 Merelbeke, Belgium, and Orville S. Privett, The Hormel Institute, University of Minnesota, 801 16th Ave. NE, Austin, MN 55912.

In nutritional experiments, it has been demonstrated that substitution of dietary sucrose for glucose may raise serum triglyceride and cholesterol levels and accelerate fat accumulation in the liver, showing different effects of these carbohydrates on lipid metabolism. The objective of our study was to investigate the effect of dietary sucrose vs glucose on the 6- and 9-acyl desaturase activities in the liver of rats fed fat-free or fat-supplemented diets. For a period of 9 weeks, male weanling Sprague-Dawley rats received one of the following isocaloric semisynthetic diets: (a) 45% sucrose (SU) + 10% hydrogenated coconut oil (HCO), (b) 45% glucose (GL) + 10% HCO, (c) 45% SU + 10% safflower oil (SAF), (d) 45% GL + 10% SAF, (e) 67% SU, fat-free, (f) 67% GL, fat-free. The fat-free diets, as well as the diets containing HCO, were essential fatty acid (EFA)-deficient. Animals of all groups were killed by exsanguination and the liver microsomal fraction was isolated by ultracentrifugation for fatty acid analysis and determination of the 6- and 9- acyl desaturase activities, using [1-^{14}C]linoleic acid and [1-^{14}C]stearic acid as substrates. The rats kept on the EFA-deficient diets showed higher liver weights and elevated fat accumulation in the liver, mainly due to higher triglyceride levels. These effects were significantly more pronounced in the rats fed sucrose. However, dietary sucrose, as compared to glucose, did not exert significantly different effects on the fatty acid composition of the liver microsomes, nor on the 6- and 9-acyl desaturase activities, showing no alterations in these systems by the dietary carbohydrate source.

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N-ACYLATION OF ETHANOLAMINE PHOSPHOLIPIDS IN NORMAL AND INFARCTED CANINE MYOCARDIUM: A NEW PATHWAY OF MAMMALIAN PHOSPHOLIPID METABOLISM. P.V. Reddy, V. Natarajan, P.C. Schmid and H.H.O. Schmid*, The Hormel Institute, University of Minnesota, Austin, MN 55912.

N-Acylethanolamine phospholipids, which are found in infarcted but not in normal canine myocardium, were produced by preparations of normal myocardial tissue incubated in the presence of millimolar concentrations of Ca^{2+}. Biosynthetic activity with endogenous substrates was associated with both microsomal and mitochondrial fractions, exhibited an alkaline pH optimum and yielded *N*-acyl derivatives of both diacyl and alkenylacyl glycerophosphoethanolamines. The time course of *N*-acylethanolamine phospholipid synthesis and degradation was followed after pulse labeling of myocardial ethanolamine phospholipids with [1,2-^{14}C]ethanolamine. Enzymic *N*-acylation of both phosphatidylethanolamine and lysophosphatidylethanolamine was demonstrated by incubating these substrates with homogenates of myocardial tissue. Neither free fatty acids nor acyl CoA derivatives served as acyl donors but some of the constituent fatty acids of exogenous phosphatidylethanolamine were recovered among the amide-linked fatty acids of the *N*-acylethanolamine phospholipids. *N*-Acylation may thus occur by the transfer of *O*-acyl groups catalyzed by a Ca^{2+}-dependent phospholipase. Incubation of both glycerol-labeled and amide labeled *N*-acylphosphatidylethanolamine with myocardial cell-free preparations in the presence of NaF yielded phosphatidic acid and *N*-acylethanolamine, indicating phospholipase D activity. This enzyme was associated primarily with the microsomal fraction, did not require Ca^{2+} and had an acidic pH optimum. *N*-Acylethanolamines are biologically active compounds which accumulate in infarcted canine myocardium. Thus, *N*-acylation of ethanolamine phospholipids may constitute an important injury-induced metabolic event aimed at the protection of ischemic myocardial tissue.

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GAS LIQUID CHROMATOGRAPHY AS A REGULATORY TOOL IN THE LIPID AREA. A.J. Sheppard, T.S. Rudolf and C-S.J. Shen*, Division of Nutrition, Bureau of Foods, Food and Drug Administration, 200 C St. SW, Washington, DC 20204.

Gas liquid chromatography (GLC) is currently used as a regulatory tool in the lipid area: (a) to determine adherence to label claims for saturated fatty acids and cholesterol as part of nutrition labeling of foods; (b) to detect and determine the amount of adulteration of ice creams and other dairy products using vegetable oils as a substitute for cream; and (c) to determine the authenticity of vegetable oils. GLC methods which provide accurately quantitative determination of saturated, monounsaturated and polyunsaturated fatty acids and cholesterol content of foods are being used for regulatory analysis of samples subject to nutrition labeling requirement of foods. Under 1975 nutrition labeling regulations, a product is required to be labeled as to lipid composition when a claim is made, or it can be labeled voluntarily by the manufacturer. Adulteration of dairy products continues to be a problem in today's market place. Quantitative determinations of selected individual fatty acids, such as butyric and palmitic acids, and individual sterols, such as cholesterol and sitosterol, by GLC methods provide results not only for the detection of nonmilk fat but also for the determination of the degree of adulteration of samples of ice cream and other dairy products. GLC methods are far superior to other chemical methods for both qualitative and quantitative identification of adulteration of lipids. Another regulatory concern in the lipid area has been the labeling of the source of vegetable oils in the ingredients statement. Using GLC methods, the authenticity of a given oil can also be determined by comparing the fatty acid and sterol profiles of the sample to those of the authentic oil samples. The

development of these GLC methods and case histories of their applications will be presented and discussed.

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USE OF GAS LIQUID CHROMATOGRAPHY FOR MONITORING THE FATTY ACID COMPOSITION OF CANADIAN RAPESEED. J.K. Daun* and P.B. Mazur, Grain Research Laboratory Division, 1404–303 Main St., Winnipeg, Manitoba, Canada R3C 3G8.

In order to monitor the conversion of Canadian rapeseed from high-erucic types to low-erucic-acid types, the Canadian Grain Commission instituted a program to monitor the fatty acid composition of rapeseed at the farm level, in railway carlot shipments and in export cargo shipments. Initially, in order to process up to 20,000 samples/year, a procedure involving combined extraction and methylation was developed. Methyl esters were analyzed within 5 min by manual injection on a nonpolar column with special attention given to the total C22 fatty acids. As the conversion to low-erucic-acid rapeseed types was accomplished, fewer samples were required for monitoring and more attention was given to fatty acid compositional details. In the system used at present, fatty acid composition of rapeseed samples is determined on a mixed-phase column which gives good resolution of the major fatty acids in rapeseed. Through the use of an autosampler and a minicomputer, up to 50 samples/day are analyzed and individual reports are generated giving fatty acid compositional details, as well as estimates of iodine value and saponification value.

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RAPID FOOD ANALYSIS WITH CAPILLARY COLUMNS. Hal T. Slover* and Raymond H. Thompson, Jr., USDA, Nutrient Composition Laboratory, Bldg. 264, BARC-East, Beltsville, MD 20705.

Capillary gas chromatographic columns provide high-efficiency GLC separations, but the time required is sometimes considered excessive. The variables that can be manipulated to speed the analysis are column temperature, column length, phase loading, nature of the carrier gas, and carrier gas linear velocity. Column temperature may be varied within wide limits defined by the stationary phase and sample type: for fatty acid analyses, practical temperatures are in the range 130-200 C. Column length is determined by the required efficiency; for some analyses, 2-m columns may suffice. Thin coatings of stationary phase give shorter retention times than thick coating, the principal limitation being the need to cover active sites on the column wall. Hydrogen may be used as the carrier gas to achieve faster analyses; higher carrier gas linear velocities also shorten retention times. Some of the practical effects of these variables as they affect food fatty acid analyses will be discussed with examples.

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FATTY ACIDS OF ENDANGERED MARINE TURTLES: A PROBLEM IN SPECIATION. Jeanne D. Joseph* and Gloria T. Seaborn, National Marine Fisheries Service, PO Box 12607, Charleston, SC 29412-0607.

Despite U.S. federal regulations prohibiting the importation and use of endangered marine turtle products, cosmetic preparations purporting to contain turtle oils of unspecified origin are commercially available. Consequently, law enforcement personnel of the U.S. National Marine Fisheries Service, U.S. Customs, and U.S. Fish and Wildlife Service need methods for identification of marine turtle oils in cosmetics. The limited amount of published information on turtle oils suggests that speciation of turtle oils by fatty acid analysis might lead to development of the required methods. Employing flexible, fused silica WCOT (Carbowax 20M) column GLC, we have analyzed fatty acid methyl esters (FAME) of (a) depot fats of 3 loggerhead turtles; (b) rendered oils of 4 different marine species and one commercial turtle oil of unknown biological origin; (c) depot fats of 2 aquarium-held turtles, a Kemp's Ridley and an albino green turtle; and (d) muscle lipid and depot fat of a single loggerhead. At this time, our data suggest that while fatty acid composition is somewhat variable among individuals of the same species, much larger differences may be found among species. The compositions of the 4 marine turtle oils were, unquestionably, marine in character, whereas that of the fifth turtle oil was high in 18:2ω6 and 18:3ω3, typical fatty acids of terrestrial plants. Comparison of the aquarium-held albino green turtle FAME with those of rendered green turtle oil demonstrated the effect of dietary fatty acids on the composition of turtle depot fats. As expected, significant differences were noted in muscle lipid and depot fat FAME of the single loggerhead examined.

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GAS CHROMATOGRAPHY OF HALOGENATED LIPIDS. H.B.S. Conacher*, J.F. Lawrence and R.K. Chadha, Food Research Division, Health Protection Branch, New Research Centre, Health & Welfare Canada, Tunney's Pasture, Ottawa, Ontario, Canada K1A 0L2.

Over the past decade, an active program to study halogenated lipids has been maintained in our laboratories. This program, which has included studies on brominated lipids, chlorinated lipids, and, more recently, the halohydrin lipid derivatives, has resulted in several important advances in the gas chromatographic identification and determination of long-chain, halogenated fatty acids in both foods and animal tissues. An overview of the problems and ensuing advances, which include derivative formation, the use of better chromatographic conditions to permit direct gas chromatography of the halogenated acid esters, and the use of selective halogen detectors, will be presented.

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THE GAS CHROMATOGRAPHY OF COMMERCIAL FATTY ACID DERIVATIVES: STATE OF THE ART–1982. L.D. Metcalfe, A.A. Schmitz* and C.N. Wang, Armak, Co., 8401 W. 47th St., McCook, IL 60525.

Many derivatives of fatty acids are important commercial chemicals. Long-chain amines, nitriles, amides, quaternary ammonium compounds, alcohols, and their ethylene oxide adducts are among the most important of these. This paper describes the present use of gas chromatography (GC) in their analysis. GC has played an important role in the analysis of fatty acid derivatives for over 20 years. New developments in this area of analysis are still being made. Base-treated, packed columns continue to be useful for separating many amines. Derivatization makes it possible to separate unsaturated amines on the basis of double bonds using polar columns. *Cis* and *trans* separation can be accomplished with cyanopropylsilicone columns. Amides can be chromatographed on the cyano columns. Recently, good separations of all types of fatty chemicals have been made using glass capillary columns. GC-mass spectrometry combined with computer technology have been used to identify unknown peaks and also to characterize fatty chemicals. TC has been used with great success in solving environmental problems. It has been used to determine traces of contaminating chemicals such as nitrosamines and also raw material residues such as methyl chloride, ethylene oxide and acrylonitrile.

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Withdrawn.

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X-RAY DIFFRACTION AND CALORIMETRIC STUDIES OF LIPIDS AND MEMBRANES. G. Graham Shipley, Biophysics Institute, Departments of Medicine and Biochemistry, Boston University School of Medicine, Boston, MA 02118.

X-Ray diffraction studies of model and native membranes have provided structural information relevant to lipid conformation, lipid-lipid and lipid-protein interactions, and protein organization in membranes. Starting with information from simple crystal studies of membrane phospholipids (phosphatidylethanolamine and phosphatidylcholine) and glycolipids, important features of lipid conformation and molecular packing will be discussed. This precise structural information will provide the rationale for interpreting X-ray diffraction and calorimetric data of hydrated membrane lipid systems. Specific systems to be discussed include phosphatidylcholine, phosphatidylserine in the presence and absence of monovalent and divalent cations, and galactocerebrosides. The relevance of these studies to lipid organization in native membranes will be discussed.

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LIPID POLYMORPHISM AND MEMBRANE FUNCTION. P.R. Cullis, Biochemistry Dept., University of British Columbia, Vancouver, B.C. V6T 1W5, Canada.

Biological membranes commonly contain a vast variety of lipid molecules, differing in both fatty acid composition and type of polar headgroup. The reasons for such diversity constitute a fascinating problem for the membrane biochemist. In particular, it is commonly assumed that the major functional role of lipids is to provide an inert, semipermeable, bilayer matrix with which functional proteins may be associated. However, a single phospholipid species such as phosphatidylcholine could satisfy such a structural role, implicitly posing the question as to why the many other lipid species are present. An important physical property of lipids which has not received detailed attention until recently concerns the ability of certain individual species and mixtures of lipids to adopt nonbilayer structures (particularly the hexagonal H_{II} phase). This may occur either naturally or in response to variation of pH, or in the presence of divalent cations, among other factors. It is our strong contention that the availability of nonbilayer structures per se, or the properties of lipid molecules which allow them to adopt various structures, can play important roles in membrane function. In particular, evidence will be presented to support the possibility

that nonbilayer, "inverted micellar" lipid structure plays intermediary roles in membrane fusion processes. Alternatively, it will be pointed out that the preference for a particular phase indicates that the lipids exhibit a certain molecular shape, and that the availability of lipids with a variety of shapes may play important roles in providing optimal sealing and packing of the lipid-protein interface.

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THE EFFECT OF BILAYER CURVATURE ON SYSTEM PROPERTIES. T.E. Thompson, Department of Biochemistry, University of Virginia, Charlottesville, VA 22908.

Small unilamellar vesicles about 200 Å in diameter formed from binary mixtures of phospholipids display transbilayer compositional asymmetries. Vesicles of this type also have unusual stability characteristics and exhibit unusual gel-liquid crystalline phase-transition behavior. It has been suggested that these characteristics are the result of molecular packing constraints which reflect the large difference between the small radii of curvature of the inner and outer bilayer faces. This interpretation is supported by examination of unilamellar phospholipid vesicles ranging in diameter from 200 to 800 Å. In marked contrast to small vesicles, no transbilayer compositional asymmetry is found in 800-Å unilamellar vesicles composed of phosphatidylcholine (PC) and phosphatidylethanolamine (PE). Correlation analysis of size distributions and calorimetric phase-transition profiles obtained from unilamellar dipalmitoyl PC vesicle dispersions shows the unusual phase-transition behavior to be a property of vesicles less than 800 Å in diameter. Also, gel phase fusion of unilamellar vesicles occurs only in dispersions of vesicles of less than this diameter. These observations and others suggest the curvature-induced packing constraints are not appreciable in bilayer vesicles larger than 800 Å in diameter. (This work supported by USPHS NIH grants GM-14628 and GM-235-73.)

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MODELS OF BILAYER PHASE TRANSITIONS IN RELATION TO THERMODYNAMIC AND STRUCTURAL MEASUREMENTS. V. Adrian Parsegian*, National Institutes of Health, and R.P. Rand, Department of Biological Sciences, Brock University, St. Catharines, Ontario, Canada.

With few exceptions, models of the famous order-disorder hydrocarbon chain transition in bilayers concentrate primarily on chain statistics and treat polar group interactions as secondary. This is done even though melting temperatures are wildly sensitive to polar group type and despite major changes in multilayer water content when hydrocarbon chains freeze. In this talk, various models of bilayer transitions will be reviewed and a method for examining polar group contributions will be described. In phase transitions, lateral interactions between polar groups on the same face are more important than those between bilayers. Indeed, the bilayer transition may be better considered to be 2 order-disorder transitions: one by the hydrocarbon chains, and the other by the polar groups. The intermediate "ripple" phase may occur when the chain and the polar group transitions cannot manage to happen together.

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THE RELATIONSHIP BETWEEN MEMBRANE LIPID FLUIDITY AND PHASE STATE AND ATPase ACTIVITY IN *ACHOLEPLASMA LAIDLAWII* B. J.R. Silvius and R.N. McElhaney*, Department of Biochemistry, University of Alberta, Edmonton, Alberta T6G 2H7, Canada.

A careful analysis of the temperature dependence of the Na^+,Mg^{2+}-ATPase activity in *A. laidlawii* B membranes has been done. Temperature-dependent changes in the "fluidity" and phase state of the lipids of these membranes have also been monitored by ^{19}F nuclear magnetic resonance spectroscopy and differential scanning calorimetry. At temperatures above the midpoint of the gel to liquid-crystalline membrane lipid phase transition, Arrhenius plots of ATPase activity are nonlinear, with their slopes increasing in a gradual and progressive manner with decreasing temperature. The temperature dependence of ATPase activity is not influenced by membrane lipid composition in this temperature range. The absolute activity of the ATPase, however may vary significantly with fatty acid composition, but there is no clear relationship between enzyme activity and lipid "fluidity" (hydrocarbon chain orientational order and motional rates). Near the lipid phase-transition midpoint temperature, Arrhenius plots of ATPase activity begin to curve downward much more steeply. However, appreciable ATPase activity remains at temperatures near the lipid phase-transition lower boundary, and some enzyme activity persists until temperatures 10-20 C below the phase-transition lower boundary are reached. Thus, although the position and cooperativity of the bulk membrane lipid phase transition clearly influences the position and cooperativity of the ATPase "activity transition," these processes are not identical. We suggest that this enzyme is inactivated when its boundary lipids undergo a fluid-to-ordered phase-transition that is driven by the bulk lipid phase-transition, but which is less cooperative and which takes place at a lower temperature than the latter.

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THERMOTROPIC PHASE TRANSITIONS OBSERVED IN NORMAL HUMAN MYELIN BY MICROCALORIMETRY. M.A. Moscarello, Dept. Biochemistry, The Hospital for Sick Children, 555 University Ave., Toronto M5G 1X8, Ontario.

Myelin was isolated from normal human white matter and stored in lyophilized state at -20 C. For calorimetry, 50 mg was suspended in 1 mL of 10 mM HEPES buffer, pH 7.4, containing 10 mM NaCl, and homogenized gently to make a uniform suspension. The entire 1 mL was added to the sample cell and 1 mL of buffer was added to the reference cell of the calorimeter. The samples were heated routinely from 10-90 C at different heating rates varying from 30-120 C/hr, depending on the experiment. Three well-defined endothermic phase transitions were observed at 32-35 C, 60-65 C, 70-75 C. The transitions were observed in lyophilized myelin and freshly isolated myelin which had not been frozen. Storage at -20 C for 2-3 yr did not alter the transitions. The transitions could not be attributed to lipid, because a whole lipid extract of myelin gave a broad transition over the whole temperature range. Purified lipids, cerebroside and cerebroside sulfate gave sharp transitions but not at the temperatures of the transitions in myelin already mentioned. The purified proteins, basic protein and lipophilin (a purified proteolipid) showed no cooperative phase transitions. Extraction of basic protein by dilute acid from myelin did not affect the low temperature transition at 75-80 C. We concluded that the thermotropic transitions in myelin were due to protein-lipid complexes. (Supported by a grant from the MRC, Canada.)

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OBJECTIVE INSTRUMENTAL ANALYSES OF FLAVOR STABILITY OF OIL. David B. Min, Department of Food Science and Nutrition, The Ohio State University, 2121 Fyffe Road, Columbus, OH 43210.

The flavor qualities of soybean oil, hydrogenated soybean oil and corn oil which were exposed to 700-ft fluorescent candle light for various periods of time were analyzed by a gas chromatographic method and sensory evaluation method. The linear regression analyses were developed for predicting sensory scores using the contents of 2,4-decadienals of oil. The correlation coefficients (r) between predicted sensory scores and the amounts of 2,4-decadienals for soybean oil, hydrogenated soybean oil and corn oil were 0.99, 0.98 and 0.95, respectively. The disappearance of dissolved free oxygen in oils during storage was measured by a newly developed oxygen analyzer. The correlation (r) between dissolved free oxygen disappearance and flavor compound formation in oil was 0.94. The applications of gas chromatographic flavor compound measurement and dissolved free oxygen measurement in oil will be reported as the objective instrumental methods to evaluate the flavor stability of oil.

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VOLATILE LIPID OXIDATION PRODUCTS. E.N. Frankel, USDA Northern Regional Research Center, 1815 N. University St., Peoria, IL 61604.

Much attention has been given to the volatile decomposition products in oxidized fats, and studies on the source of these products are still controversial and difficult to interpret. This review discusses the precursors of volatile oxidation products, the mechanism of their decomposition, and consequences on flavor and odors of lipids. New knowledge in these areas would be expected to lead to improved methods of controlling flavor deterioration of fat-containing foods. Much attention has been given recently to the analyses of hydrocarbons in the breath of experimental animals as an index of in vivo lipid oxidation. A better understanding of the origin of these volatile oxidation products may also elucidate the mechanism of biological lipid oxidation.

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MECHANISM FOR THE DEVELOPMENT OF REVERSION FLAVOR IN SOYBEAN OIL. Stephen S. Chang* and Chi-Tang Ho, Dept. of Food Science, Rutgers, The State University, PO Box 231, New Brunswick, NJ 08903.

A classical problem in using soybean oil is the development of a characteristic beany and grassy flavor, known as reversion flavor, when the peroxide number of the oil is still quite low. It has been reported that 2-pentylfuran, an autoxidative decomposition product of linoleate, is predominantly responsible for the beany flavor of reverted soybean oil. However, there are other vegetable oils, such as cottonseed and corn oil, which contain linoleate but do not

develop reversion flavor. Because soybean oil is different from the other oils in that it contains 7% of linolenate, the possible formation of *cis* and *trans* 2-(1-pentenyl)furan and *cis* and *trans* 2-(2-pentenyl) furan in reverted soybean oil through the autoxidation of linolenate is suspected. These 4 compounds were synthesized. Their sensory evaluation in oil indicated that they could contribute to the beany and grassy flavor. This hypothesis is finally confirmed by their identification in the volatile flavor constituents from a sample of reverted soybean oil.

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LIPID DECOMPOSITION AND FLAVOR STABILITY OF IRRADIATED AND HEATED FOODS. Arbsook Witchwoot* and W.W. Nawar, Department of Food Science and Nutrition, University of Massachusetts, Amherst, MA 01003.

Since prehistoric times, man has been heating his food to modify its flavor and texture and to improve its keeping quality. A significant amount of research has been done to study the volatile compounds produced in foods by heat and to correlate such compounds with flavors typical of various heated foods. In general, the lipid fraction of most foods appears to be the major contributor to the volatile pattern. Radiation-preservation is becoming more and more attractive as an additional method available to the industry for the improvement of shelf-life in many foods. As with heat, decomposition of the fat is, without question, the major contributor to the radiolytic volatile pattern of most irradiated foods. Although many of the volatiles produced by both treatments are similar, there are certain unique components strictly typical of each. Furthermore, the flavor of irradiated fat is, indeed, different from that of heated fat. In this paper, a comparison of the volatile pattern of both heated and irradiated samples of beef and pork, as well as those of model systems of ethyl and propyl esters and triglycerides will be given. The relationship of such analysis to flavor and off-flavor will be discussed.

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COMPARATIVE ANALYSIS OF COMMERCIAL SOY ISOLATES' VOLATILE FLAVOR COMPOSITIONS. Sherman S. Lin, Anderson Clayton Foods, W.L. Clayton Research Center, 3333 N. Central Expressway, Richardson, TX 75080.

Commercial soy isolates with different flavor qualities were analyzed for their volatile flavor compositions using the adsorption/desorption technique and GC/MS. An internal standard was used to standardize each GC peak for comparison among samples. A total of 31 compounds was identified in the sample containing most volatiles. Great differences were observed in qualitative and quantitative composition of volatiles among the samples analyzed. From the difference of volatile composition and flavor characteristics, the contributing factors for various flavor notes in commercial soy isolates are postulated as: fishy—trimethylamine; green beany, stale—pentanal, hexanal and 2-pentyl furan; roasted, nutty—pyrazines, 2,5-dimethyl-, 2-ethyl-6-methyl-, trimethyl- and 2,5 dimethyl-3-ethyl-; earthy—1-octen-3-ol and 3-octen-2-one; cooked, sweet, cereal—benzaldehyde. Enzyme-hydrolyzed soy isolate contains drastically more pyrazines, both in variety and quantity. Membrane process yields an isolate with a much cleaner flavor and much fewer volatiles. The technique of analysis and the interpretation of data will be discussed.

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OLIVE OIL FLAVOR AND TECHNOLOGY. Enzo Fedeli, Stazione Sperimentale Oli e Grassi, via Giuseppe Colombo, 79- 20133 Milano, Italy.

Olive oil is one of the rare fats which is consumed without being refined because the consumer appreciates both the smell and taste. Extraction technology has a strong impact on organoleptic properties; in effect, most of the flavor is due to chemical components naturally present in the aqueous phase of the olive fruits, the so-called "vegetation water." We have elucidated the structures of the majority of vegetation-water chemical components by extracting them through several procedures and analyzing the extracts or their fractions by GLC-MS. Looking at the structures, it is easy to recognize that most of the components are soluble both in water and in oil, and that their concentration in the aqueous phase is largely dominated by the amount of water present in the extraction stage and by the time of contact between the aqueous and oil phases. The traditional extraction technology, based on the use of cagepresses, imposes high contact times of extremely emulsified water/oil mixtures, followed by a partial separation with centrifuges and then by decantation. The amount of aqueous phase present in the whole process is that derived from vegetation water. In those conditions, a full separation of the oil and water phases is extremely slow and an equilibrium is attained for the flavoring compound concentration in the 2 phases. Modern technology is based on the separation by horizontal centrifuges of the components of a water/olive pulp mixture created by adding water to the milled olives in 3 fractions, solid, oil and water. Oil and aqueous phases are then submitted to centrifugation for complete separation. The amount of water and contact time are such as to cause a decreased concentration of flavoring substances in the oil, which also means a decrease in the keeping quality of the product because most of the vegetation-water chemical components are strong antioxidants.

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THE CULTIVATION OF CELLS—A MOST CRUCIAL PROCEDURE IN BIOTECHNOLOGY. P.S.S. Dawson, Prairie Regional Laboratory, National Research Council of Canada, Saskatoon, Saskatchewan, Canada S7N 0W9.

A basic understanding of the cell is required if biotechnology is to flourish as a scientific endeavor and thus avoid becoming an empirical art in the manner of much contemporary fermentation practice. The acquire this knowledge, a rational study of the cell has to be made, inevitably, by the study of the cell population. Traditionally this has been accomplished by cultivating cells in batch culture, a technique that is now known to be of limited use largely because of developments arising from the newer methods of continuous and synchronous culture. An outline of these developments in methods for cultivating cells is given, and of the changing perspectives involved there relating to cell growth and performance. More absolute methods are available now to replace outdated empirical ones for examining, investigating and utilizing cells, and hence establish a better foundation on which to build and develop the new technology. While these developments are largely restricted to microbial cells, at present, the wider applications to tissue cells (plant and animal) are considered, too, besides multidisciplinary and interdisciplinary aspects of these matters, necessarily inherent to biotechnology.

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GENETICS AND BIOTECHNOLOGY. Scott T. Kellogg, Genetics Division, Bethesda Research Laboratories, PO Box 6009, Gaithersburg, MD 20877.

The exceptionally rapid growth of genetics and biotechnology in both realized and potential applications requires that these areas be delineated clearly due to possible impacts on several diverse disciplines. A discussion of molecular biology history is required in order to contrast classical genetic systems with recent rapid advances in genetics. Basically, there are 3 phases of growth in genetic engineering and its applications: genetic studies of single gene/single gene product systems, genetic analysis and control of multiple gene systems within a metabolic pathway, and genetic research of multiple gene/multiple gene product systems in organisms other than *Escherichia coli*. It is these last 2 phases that are currently underway. Finally, several genetic engineering/biotechnology applications are outlined, e.g., in the area of gene product overproduction, or in the area of hydrocarbon conversions.

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IMMOBILIZED CELLS: A PROCESS IN BIOTECHNOLOGY. Ivan A. Veliky, National Research Council, Division of Biological Sciences, Ottawa, Ontario K1A 0R6, Canada.

A viable cell with its potential of biocatalytic activity is a nucleus of the present biotechnological era. By understanding the cell biochemistry and physiology, we can define, modify nad optimize the environmental conditions for the cell to grow and produce a biomass or a useful metabolite. By concentrating an active cell biomass in a bioreactor, it is possible to increase the efficiency of a desired fermentation or bioconversion process significantly. One of the techniques for this is immobilization of active cells in a matrix of low toxicity to the cells and physically resistant to the substrate and components of the nutrient medium used. The technique of immobilization of cells and the design of a bioreactor is illustrated by immobilized *Saccharomyces cerevisiae* and *Zymomonas mobilis*, both of which are known to produce ethanol, and by immobilized *Trichoderma reesei*, a strain with high cellobiase activity. The immobilization technique, including its advantages and drawbacks, will be discussed.

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RECENT ADVANCES IN DESIGNS OF BIOLOGICAL REACTORS. Henry R. Bungay, Department of Chemical and Environmental Eng., Rensselaer Polytechnic Institute, Troy, NY 12181.

Several years ago, the air-lift fermenter was shown to be more economical than a stirred tank fermenter for many systems with high demand for oxygen. At present, attention is focused on reactors with special features such as removal of a volatile product by operation at reduced pressure or using a heavily flocculated culture that is easy to retain in the reactor. There are also schemes for using immobilized enzymes in separate reactors or in conjunction

with fermentation vessels. This paper reviews new types of microbiological and enzymatic reactors and elaborates on 2 projects from the author's laboratory: lamellar sedimentation for cell recycle and very high rate continuous fermentation. Yeast cells have been collected efficiently in a lamellar settler that would be inexpensive to construct and has essentially no operating cost. Very high rate continuous culture can be valuable for treating toxic wastes because excellent cultures are selected automatically or there may be new fermentations for biochemicals associated with cells dividing rapidly. New equipment designs are essential to exploit fully the advances in genetic engineering and to broaden the applications for fermentation technology by lowering costs.

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THE DEVELOPMENT OF COMPUTERIZED PROCESS CONTROL FOR INDUSTRIAL SOLVENTS BIOSYNTHESIS FROM RENEWABLE RESOURCES. R.J. Neufeld*, B. Volesky, A. Mulchandani, D. St.-Onge, L.J. Vroomen, Sr., and L. Vroomen, Jr., McGill University, Department of Chemical Engineering, 3480 University St., Montreal, PQ H3A 2A7, Canada.

Recent developments in fermentation technology are partially due to the renewed interest demonstrated for the bioproduction of liquid fuels and industrial solvents from renewable resources. One such process, the acetone-butanol-ethanol fermentation, is being evaluated at present from the perspectives of reactor design, computer control, modeling and simulation, microbial strain development, and optimization of the continuous process. These developments will be discussed as they relate to the overall economics of the process.

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POSSIBLE INDUSTRIAL APPLICATIONS OF BIOTECHNOLOGY. N. Kosaric, Faculty of Engineering Science, The University of Western Ontario, London, Ontario, Canada N6A 5B9.

Biotechnology is an emerging technology applicable in various industries and industrial operations. Some industries in which biotechnology may be particularly applicable are the food processing, energy-related, oil recovery, mining and waste management industries. In food processing operations, various products obtained by microbial synthesis could be utilized to replace the currently used synthetic ingredients. These products could be food stabilizing agents, emulsifiers, vitamins, amino acids, single-cell proteins, food enzymes, low-molecular-weight and fatty acids, water binding agents, flavors, foaming agents, e.g. Some of these are currently being used and some could be developed. Due to the present energy crisis, new avenues for the production of fuels are being investigated. Of particular interest is utilizing abundant natural renewable resources as substrates for the production of fuel ethanol, acetone, butanol, methane, hydrogen and various organic solvents. Of the raw materials, "energy crops" (e.g., Jerusalem artichokes, fodder beets), cellulosic materials and agricultural and industrial wastes could be efficiently upgraded and converted to usable fuels. Due to increased demands for oil, enhanced oil recovery methods are being developed for either a more complete recovery of the oil deposits or for recovery of heavy oils and tar sands. Microbial action in situ can help in increasing the recovery yield by various methods under investigation (e.g., water and steam flooding, fire flooding). Also, microbes and microbial products can help in breaking the generated W/O and O/W emulsions, which in turn ensures a higher oil recovery and control of tailing waters. Microbial products could also be helpful as surface-active agents used in mining and flotation operations. Specific microbial leaching, geobiochemical processes and concentration of specific minerals (e.g., scheelite) are of interest. New and improved processes for microbial wastewater treatment are also being investigated. This technology is of particular interest for specific industrial wastewaters and for treatment, recovery and utilization of industrial sludges. This paper will review these possibilities and also present some data from the author's laboratory regarding the approaches just described.

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PHILOSOPHY AND CONCEPT OF DESIGN OF OIL MILLS FROM AN OPERATING PERSPECTIVE. D.S. Hopkins, CSP Foods LTD, Box 190, Saskatoon, Saskatchewan S7K 3K7, Canada.

This paper will briefly review the approach to oil mill operations design covering labor, safety and process quality control. The application of distributed control systems (microprocessors) to operations design has the basis for improved operation and management information. Improved labor flexibility and utilization requiring higher levels of training for operating and maintenance personnel; product quality assurance and control; and improved energy management will be among items examined.

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THE PREPRESSING OF RAPESEED AND SUNFLOWER IN THE SIMON-ROSEDOWNS 'G' TYPE PRESS. Jim Davie, Simon-Rosedowns Ltd., Cannon St., Hull, England HU2 OAD.

The prepressing of rapeseed and sunflower seed in the Simon-Rosedowns 'G' type press is discussed. Actual operating data obtained over the last few years from plants in North America are presented and advice offered on how to obtain optimal performance on various seeds. Maintenance requirements are highlighted and specific recommendations are made.

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THE EFFECT OF RAPESEED FINES ON THE PROCESSING OF CANOLA OIL. M.D. Pickard, CSP Foods Ltd., PO Box 190, Saskatoon, Saskatchewan S7K 3K7, Canada.

The rapeseed/canola obtained from combine harvesting is contaminated by parts of the pod, straw, pebbles and sand. Also included are seed fragments and small, low quality seeds. In various stages of seed cleaning, light-weight impurities such as seed fragments, dust and light, low-quality seeds are removed from the main stream of high-quality seeds. These so-called fines do contain significant amounts of oil (17-20% by weight) and are valuable to the processor even though they do contain higher amounts of chlorophyll and free fatty acids than higher quality seed. Pilot plant primary processing and bench-scale refining and deodorization of seed samples containing 0, 2, 5 and 10% fines, as cleaned through commercial equipment, yielded oils which were subjected to chemical and sensory analysis. Although the results were incomplete at the time this abstract was written, the results will help to determine the effect of rapeseed/canola fines on resulting crude and refined oil quality.

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VPEX—A NEW OIL EXTRACTION PROCESS. Wolfgang Stein, Fried, Krupp GmbH, Krupp Industrie -und Stahlbau Werk Horburg, Seevestrasse/Bohnhofsinsel, D2100 Hamburg 90, Federal Republic of Germany.

The basic aspects of whole seed cold processing will be described. Extractability of the presscake, the overall energy balance as well as operational and investment cost will be considered in the evaluation of this new process.

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SUPERCRITICAL EXTRACTION OF VEGETABLE OIL SEEDS. N.R. Bulley*, Dept. of Bio-Resource Eng., M. Fattori, Dept. of Bio-Resource Eng., and A. Meisen, Dept. of Chemical Eng., The University of British Columbia, 2357 Main Mall University Campus, Vancouver, B.C. V6T 1W5, Canada.

Research on the extraction of oil from canola with supercritical CO_2 is in progress. The experimental apparatus and procedures are described. Equilibrium and rate data for the oil/canola/supercritical CO_2 system were obtained as a function of temperature, pressure, CO_2 flow rate and seed pretreatment. The data are used for the conceptual design and preliminary economic analysis of an industrial-size facility extracting oil from canola with supercritical CO_2. Some practical aspects of designing and operating such a plant are discussed.

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MEAL DESOLVENTIZING AND FINISHING. Andre Lebrun and Michel Knott, De Smet Engineering, and Guy L. Posschelle*, De Smet U.S.A. Corp., 2625 Cumberland Parkway/Suite 200, Atlanta, GA 30339.

Soybean is the most widespread oilseed processed around the world, but the technology used in its processing is often erroneously extrapolated for the processing of other material. This paper will examine the traditional process consisting of stacked DT, horizontal rotary steam dryers and air coolers, and an analysis is made for its convenience in the processing of soft seeds such as rapeseed and sunflower. Factors affecting the sizing of the desolventizers are considered. An analysis also is made of alternate techniques such as: combined DTDC, DTC and DC systems; vertical rotary air dryers; vertical fixed and rotary air coolers or combined air dryers and coolers; vacuum dryers and coolers; and fluidized bed coolers and pneumatic cooling and conveying. Comparisons of energy, airflow and steam consumption are outlined.

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AUTOMATED SOLID FAT CONTENT MEASUREMENT. Mark Matlock, Archer Daniels Midland Co., PO Box 1470, Decatur, IL 62525.

Pulsed nuclear magnetic resonance (PNMR) has been used often for the measurement of solid fat content. One disadvantage of this method, however, is the number of computations required to convert PNMR signal values to a solid fat percentage. This was corrected by interfacing a computer directly to the instrument.

The computer reads signal values from the PNMR, performs the necessary calculations and prints a report documenting the analysis. This paper details the hardware and software used in the interfacing project.

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FLOW MEASUREMENT AND METERING IN THE FATS AND OILS INDUSTRY. Michael R. Conran, Conran & Co., 5 Cottonwood, Bloomington, IL 61701.

The presentation will deal primarily with flow measurement and metering in the vegetable oil industry. The material will encompass 2 sections. The first will discuss pertinent industry terms; the second will be devoted to typical applications in vegetable oil extraction and refining. Both will be supported by slides. In covering industry terms, a basis will be given for understanding the applications presented in the second section. Rate, capacity, range and accuracy will be discussed. The mode terms of rate and totalization also will be reviewed. Applications will be from extraction and refining and will be presented in general process sequence. The measured fluids will include hexane, miscella, vegetable oil from crude to refined, water, steam and nitrogen. In each typical application, sizes will be discussed along with acquisition cost of the equipment. The justification for the use of the particular device in the example will be outlined.

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HYDROGEN PLANT INSTRUMENTATION. Richard G. Daniel, Technical Services Hydrogen, Inc., 2514 MacLaren Circle, Doraville, GA 30360.

In the early 1930s when the first hydrogen plant was engineered and built in this country for the vegetable oil industry, very little was thought of the utilities consumed or the manpower needed to operate the plant. Power, or energy and manpower were very economical and the finished product of hydrogen was the consideration. As in all industry, this changed slowly for awhile, but for the past 5 years, very rapid changes have occurred. With the cost of energy and manpower ever increasing, it was evident that great changes would be made rapidly by the leaders of the companies engineering and building hydrogen plants. There was first great improvement in plant efficiency by going to pneumatic instrumentation. Then came the early analog, and then the digital devices which enabled industry to use microprocessor control systems. By using the latest instrumentation, industry has been able to produce larger quantities of hydrogen with less energy, less labor and at a lower cost.

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BOILER INSTRUMENTATION AND CONTROL TODAY MUST SAFE FUEL. Herbert Buntzel, Jr.*, and James Pridmore, The Syconex Corp., 1203 Roy Ave., Houston, TX 77007.

Criteria for the selection and the type of combustion controls today are much different than in the past. High fuel costs have placed emphasis on efficient operation. The boiler and control system must be capable of low excess air firing. Developments in reliable flue gas analysis to measure and be used as a controlled variable are vital parts of efficient control. Systems must be capable of being expanded into higher levels of energy management and, therefore, must lend themselves to expansion into distributive systems for better operations management. Existing combustion systems are studied to determine their condition, the value of improvements that can be made, and their individual savings. A cash flow and ROI analysis will allow a determination of a staged investment program to decrease fuel usage and improve profits.

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INSTRUMENTATION IN VEGETABLE OIL PROCESSING. Walter E. Farr, Anderson Clayton & Co., PO Box 2538, Houston, TX 77001.

The importance of instrumentation to properly control all processes in the manufacture of vegetable oils is now well accepted. A properly automated system can be brought on-line with consistent quality product employing new operators and supervisors, but only if the proper choices of instrumentation have been made and only if the instrumentation is properly installed. The best instrumentation system for a particular operation is one that uses or considers the latest in technologies, consistent with the total process involved the level of sophistication required, and one that considers both the mechanical process and the chemistry of the process. Instrumentation in oil processing can reduce manpower requirements, improve yields, improve quality, reduce energy usage, reduce regrade or rework, and allow reduction in inventories. A reduction in manual tasks allows the operator more time to monitor the total process and to become better trained in true process control. A properly instrumented system (data acquisition and display) gives line supervisors and managers the tools needed for quick and effective evaluations of production rates, yields and adherence to specifications. This paper describes how a complete instrumentation system can be designed, using the continuous vacuum bleaching operation as an example. Control of flow, pressure, temperature, level and process monitoring is described. Automatic ratio control of filter-aid and bleaching clay-to-oil flow is handled by the use of a digitally controlled volumetric dry feeder. In addition, proper sizing of automatic caustic-to-oil ratio systems, including the use of digital blending for caustic control, is discussed. Review of refinery loss monitoring systems is given. The advantages of automation of filtration systems by the use of automatic sequence control of filter cycle and cleaning cycle is explained. A unique, automatic filtration efficiency-monitoring system is described. The importance of instrumentation maintenance in the success of automated systems is stressed.

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PROCESS MANAGEMENT AND CONTROL TRENDS IN THE VEGETABLE OIL INDUSTRY. John E. Blanchard, The Foxboro Co., Mechanic St.–Cocasset Bldg., Foxboro, MA 02035.

There have been 2 major incentives influencing recent trends to improve process control systems and instrumentation in production facilities. The first is the increased costs of energy, raw materials and labor, as well as inflation and the credit market. Second, process management and control systems and instrumentation have been approved substantially over the past decade. This paper will survey the trends in process control from early analog and digital devices to the present microprocessor-based, interactive, distributed control systems. The basic functional elements traditionally found in a control system will be identified to better understand the capabilities of a distributed control system.

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RAPESEED OIL EXTRACTION BY WET MILLING. L.L. Diosady*, L.J. Rubin, N. Ting and O. Trass, Department of Chemical Engineering and Applied Chemistry, University of Toronto, Toronto, Ontario M5S 1A4, Canada.

The Szego mill is a patented slurry mill developed by one of the authors (O. Trass) and his coworkers, primarily for producing coal-oil mixtures. This mill was applied to the simultaneous size reduction and solvent extraction of rapeseed. In these laboratory tests, the effects of solvent-to-seed ratio, contact time, rate of rotation and the percentage hold-up on the oil extraction efficiency were investigated. The particle size distribution, the residual oil content of the extracted meal and the oil content of the solvent phase were determined. The results show that the Szego mill is very efficient in contacting the seed with the solvent. Solvent-to-seed ratio is equal to or lower than that of conventional percolating bed extractors, yet the equipment is very compact, and is suitable for handling rapeseed or other materials that cannot form freely percolating flake beds. The Szego mill promises to be a viable alternative for conventional oilseed extraction equipment.

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NEW LOOK AT ISOPROPYL ALCOHOL AS AN OILSEED EXTRACTION SOLVENT. Don A. Sullivan*, Shell Development Co., Westhollow Research Center, PO Box 1380, Houston, TX 77001, Leslie R. Watkins, Anderson Clayton & Co., Houston, TX, and Larry A. Johnson, Food Protein R&D Ctr., Texas A&M University, College Station, TX.

Bench and pilot-plant-scale countercurrent extraction tests have extended the work of previous investigators in using isopropyl alcohol as a solvent to extract oilseeds. The IPA process has several advantages compared to the current hexane extraction process. High quality, semirefined soybean oil, containing only small amounts of phosphatides and free fatty acids, is produced. Untoasted soybean meal from the IPA process has good protein solubility, low urease activity and low trypsin inhibitor level. Energy consumption is comparable to, or less than, that of the hexane process. IPA is a less hazardous solvent because of its relatively higher flash point and water miscibility. The process may be retrofitted to current hexane extraction equipment with minor equipment modifications and additions.

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DEVELOPMENT OF A PILOT-PLANT PROCESS FOR THE EXTRACTION OF SOY FLAKES WITH AQUEOUS ISOPROPYL ALCOHOL. E.C. Baker, Northern Regional Research Center, USDA-ARS, 1815 N. University St., Peoria, IL 61604.

Soy flakes were extracted with aqueous isopropyl alcohol (IPA) at 170 F in a Kennedy countercurrent continuous extractor at a retention time of 71 min. Concentration of IPA was varied from 85.0 to 90.5% w/w and included the 87.7% IPA-water azeotrope. Solvent-to-meal ratios were varied from 1.5 to 3.0. The oil-IPA miscella leaving the extractor was chilled and then passed through

a coalescer to yield an oil phase and an IPA phase. The IPA phase was reheated to 170 F and recycled to the extractor, accounting for ca. 75% of the solvent requirement—the balance comes from desolventized meal distillate, oil stripper distillate and a small amount of make-up IPA. The crude oils had about one-tenth the phospholipid content as that of crude oil extracted with hexane, providing a possibility that the degumming step in crude oil refining may be eliminated.

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VIBRATION IN THE FLAKING MILLS. Joachim Bauermeister, Hermann Bauermeister GmbH, Hamburg, West Germany.

Vibrations occurring in flaking mills are very often the cause of horizontal ridges and broken ends on the rolls. Both problems, in turn, reduce the quality and extractibility of the flakers. The horizontal ridges are primarily caused by dynamic flexing of the machine at the roll gap. The amplitude of the vibration is in direct proportion to the through-put of the product; therefore, the dynamic load effect on the deformation of the mill frame has a decisive influence on the efficiency of the machine and the service life of the rolls. By computer model-analysis of a flaking mill of the conventional design and vibration analysis made on a machine in operation, typical design weak points with regard to the dynamic load deformation have been determined. The following measures will improve the dynamic behavior of flaking mills: (a) structural profiles welded between the main side frames of the machine give strength and stiffness against torsion. The welding of these connections is important to avoid the flexing of a bolted connection. The increase in the stiffness of the machine frame significantly improves the dynamic behavior; (b) the differential and main drive is altered to eliminate all sheaves which produce bending loads on the roll shafts and barrels caused by an asymmetrical mass distribution along the working face of the rolls. The rolls are driven and differential speeds are produced by a special gear box which directly drives both rolls; (c) the hollow profiles welded to the frame for stiffening can be filled with a material, such as steel shot, to act as a reaction mass (passive absorption) against the forces produced during flaking. These measures will decisively improve the dynamic behavior of flaking mills, and thus increase the efficiency and prolong the service life of the rolls.

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PHYSICAL REFINING OF EDIBLE OIL. David C. Tandy* and William J. McPherson, EMI Corporation, 3166 Des Plaines Ave., Des Plaines, IL 60018.

Physical refining of edible oils has received renewed interest since the early 1970s when the process was reintroduced on a large scale to refine palm oil in Malaysia. Subsequent laboratory and field tests have clearly shown that physical refining is superior to caustic refining, not only for high FFA oils such as palm, but also on low FFA oils. In either case, the physical refining system reduces oil loss compared to caustic refining and also eliminates the pollution associated with soapstock acidulation. In physical refining, however, the oil pretreatment and efficiency of the distillation are 2 of the most important factors that must be considered to guarantee continuous production of high-quality oils. This paper will review the physical refining system as it is designed today and how it is adapted for use on different edible oils. Also, a short review of all the advantages of physical refining over caustic refining will be presented.

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AN UPDATE ON FOOD FATS FROM PALM OIL. Peter Kalustian, Peter Kalustian Associates, Inc., 239 Reserve St., Boonton, NJ 07005.

The significant increase in palm oil production will continue, particularly in Malaysia, where the production is expected to more than double within 10 years. A significant quantity of this palm oil goes into the export world trade. Palm oil production is now second to soybean oil. It has a significantly higher yield per acre than any other oil-bearing material and harvesting is on a year-round basis. The plantation, mill and refining operations are reviewed. The major processing is by use of the efficient physical refining process. Markets have developed extensively by the large-scale, efficiently processed and economically priced palm olein. The mid-fraction of solvent-fractionated palm oil is used as the principal component of cocoa butter extenders, or CBE. It has already been demonstrated that oil content of palm fruit can be increased from 20 to 28% more. Commercial testing is underway. Production of a higher unsaturated oil of 70 iodine value has been done experimentally and its further testing is underway, also.

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FRACTIONATION OF PALM OIL BY DENSITY GRADIENTS. Augustine S.H. Ong*, Palm Oil Research Institute of Malaysia, 18th Floor, Angkasa Raya, Jalan Ampang, Kuala Lumpur 04-06 Malaysia, and P.L. Boey, C.C. Chuah and C.M. Ng, Universiti Sains Malaysia.

This paper describes a method of fractionation of vegetable, animal and fish oils, and particularly palm oil. The method involves adding a medium made up of 2 common solvents to the oils. Upon centrifugation, the olein and stearin are separated by the medium in the middle. Thirteen media which are made up of a combination of 2 from 9 common solvents, viz., water, propylene glycol, glycerine, acetone, methanol, ethanol, *n*-propanol, isopropanol and butanone, are found to be effective in olein-stearin separation. However, the water-isopropanol system was studied in greater detail. The fractionation process can be done at any suitable temperature and is independent of the method of crystallization of the oil. The used medium can be reused up to 7 times. The olein fractions obtained have good properties. Compared with the relevant crude palm oil, there is a definite increase in tocopherols (ca. 20%), and in linoleic acid composition (ca. 10%). Fractionation of the Special Prime Bleached (SPB) crude palm oil at 16 C yielded an olein fraction with a cloud point of 4.8 C. Fractionation of hydrogenated palm kernel oil yielded a stearin fraction similar in melting point (36 C) to that of cocoa butter. This fractionation process could also be extended with suitable modification to include degumming and neutralization. The olein fractions obtained after fractionation were found to be free from phosphatides and the free fatty acid content was reduced to as low as 0.02%. The development of this fractionation into a continuous process has been demonstrated using the Alfa-Laval LAPX 202 separator. Fractionation of crude palm oil using density gradients yielded 6 stearin fractions of different characteristics: iodine values of 52.8 to 37.5 and fatty acid composition (unsaturation 47.3-32.5%). Triglyceride analysis according to carbon number showed great differences, especially in C48 and C52 (C48 from 5.5 to 29.3%, and C52 from 40.9 to 23.9%).

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FACTORS INFLUENCING THE INTERESTERIFICATION AND FRACTIONATION OF PALM OIL. Y. Kakuda* and J. Huertas, Department of Food Science, University of Guelph, Guelph, Ontario N1G 2W1, Canada.

The influence of ethyl oleate levels and reaction times on the interesterification of palm oil was studied in the presence of 2 catalyst preparations. The catalyst, sodium methoxide, was prepared in a methanol/xylene mixture or in dimethylsulfoxide. The resulting interesterified product was separated by solvent fractionation to produce a liquid and solid fraction. The effectiveness of each procedure was monitored by measuring iodine value, dropping point, fatty acid composition, triglyceride composition and yields of each fraction. The results indicated a significant effect due to ethyl oleate levels but no effect due to reaction time. The melting point of the interesterified material decreased from 38 to 30 C, the iodine value increased from 52 to 66, whereas the oleic acid content increased from 39 to 57% and the palmitic acid decreased from 44 to 25%. The final olein fractions had a melting point of 17-24 C with an iodine value of 66-67.

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PLANT STEROLS IN FATS AND OILS PROCESSED IN THE UNITED STATES. S.L. Melton* and T. Plerksophon, Department of Food Technology and Science, University of Tennessee, PO Box 1071, Knoxville, TN 37901.

Campesterol, stigmasterol and β-sitosterol were analyzed (mg/100-g sample) in corn, cottonseed, soybean, coconut and palm oils at different stages of processing in corn oil margarines and in shortenings. Analyses were performed by gas chromatography on sterol acetate derivatives prepared from the unsaponifiable material in each sample without prior clean-up. The iodine values (IV) and *trans* isomer content of each sample also were determined. Recoveries of each sterol from palm oil were 96% for campesterol, 82% for stigmasterol and 92% for β-sitosterol. Soybean oil samples ranging in IV of 63-133 and *trans* isomer content (TI) of 0-54% had, per 100-g sample: 18-41 mg campesterol, 10-39 mg stigmasterol and 70-143 mg β-sitosterol. Shortening (IV, 85-95 and TI 16-27%) which contained partially hydrogenated soybean oil and partially hydrogenated palm or cottonseed oil had, per 100 g: 11-24 mg campesterol, 12-27 mg stigmasterol and 52-105 mg β-sitosterol. Corn oil margarines (IV 95-115 and TI of 15-29%) had, per 100 g: 27-90 mg campesterol, 14-30 mg stigmasterol and 120-436 mg β-sitosterol. Campesterol, stigmasterol and β-sitosterol contents per 100 g of the following oils were, respectively: for cottonseed oil (IV 107-113) 12-20 mg, 1-5 mg and 153-347 mg; for palm oil (IV 54-68), 2-7 mg, 2-7 mg and 8-24 mg; and for coconut oil (IV 9-11), 3-4 mg, 6-7 mg and 39-58 mg. Small amounts of brassicasterol and Δ^5-avenasterol also were found in most of the fat and oil samples but were not quantitated.

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REPULSIVE VAN DER WAALS INTERACTIONS AND THEIR POSSIBLE APPLICATION IN TECHNOLOGICAL PROCESSES. A.W. Neumann* and D.R. Absolom, University of Toronto, C.J. van Oss, S.U.N.Y.A.B., S.N. Omenyi and W. Zingg, University of Toronto.

In his paper in 1937 on the London-van der Waals attraction between particles, Hamaker mentioned the hypothetical possibility that the resultant action between 2 particles embedded in a liquid might be a repulsion, rather than an attraction, if the London-van der Waals force between particles and liquid is greater than between the particles themselves. It has been demonstrated that this situation prevails when the surface tension of the liquid medium is intermediate between the surface tensions of the 2 materials. The following illustrations and potential applications will be discussed: (a) small particles, embedded in the melt of a suitable matrix material, will be either engulfed or swept along by the solidification front, depending on whether the van der Waals forces between the solid matrix and the particles are attractive or repulsive. (b) Small particles adhering to a solid-liquid interface can be made to detach by adjusting the surface tension of the suspending liquid so that repulsion occurs. This possibility is of relevance in detergency. Examples from the biological area will be discussed: detachment of white cells and proteins from polymeric substrates. (c) The question of attachment to solid substrates, rather than detachment as just discussed, will be considered from the same viewpoint. Strategies to maximize and minimize particle adhesion and macromolecule adsorption will be considered. (d) Particle-particle interaction can be considered from the same viewpoint. Three different phenomena will be considered: (a) phase separation of pairs of polymer species dissolved in the same solvent, (b) dissociation of macromolecular complexes, and (c) stability of particle suspensions.

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DIFFUSION OF AMPHIPHILES IN ORGANIC SOLIDS: I. THEORY FOR MEASURING DIFFUSION CONSTANT OF SURFACTANTS IN ORGANIC HOUSEHOLD SOILS. J.A. Wingrave, Technical Service Laboratory, Conoco, Inc., PO Box 1267, Ponca City, OK 74601.

A gravimetric technique is developed to measure mass uptake of surfactants from aqueous solutions by solid organic phases. The mathematics of the diffusion process are evaluated so that the diffusion constant can be calculated. To examine the mathematics, the diffusion constant for a number of surfactants in a synthetic sebum is calculated from experimental diffusion data. The effects of surfactant molecular structure on the diffusion constant and rate of diffusion are discussed. Direct application of this work to such subjects as cold-water detergency and laundry pretreatment is explored.

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FACTORS AFFECTING THE INTERFACIAL TENSION OF MIXED SURFACTANT SYSTEMS. K.W. Dillan* and G.C. Johnson, Union Carbide Corp., Silicones Building, Tarrytown Technical Center, Tarrytown, NY 10591.

Previously reported results dealt almost exclusively with parameters governing the interfacial tension between nonionic surfactant solutions and oils commonly encountered in detergency processes. In the current investigation, these efforts are expanded to include multicomponent, mixed surfactant solutions. Statistical design methods and standard regression techniques are used to delineate the behavioral differences of alcohol ethoxylates, alcohol ethoxysulfates, linear alkylbenzene sulfonates and blends thereof, under a given set of solution conditions. Changes in pH, temperature, electrolyte concentration and/or valency and surfactant concentration are found to markedly alter the apparent surface activity of mixed surfactant systems and thereby illustrate an inherent difficulty in formulating an all-purpose detergent. Expectedly, significant differences are usually noted between nonionic and anionic surfactants, but performance variations are also observed within each surfactant class as the solution conditions are changed. Cationic fabric softeners have a marked influence on interfacial tension with most surfactant systems and thus significantly alter the detergency properties of the solution. The practical implications of these results are addressed and the correlation with "real life" performance is considered.

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SYNERGISM IN BINARY MIXTURES OF SURFACTANTS. Milton J. Rosen and Xi Yuan Hua[1], Department of Chemistry, Brooklyn College, City University of New York, Brooklyn, NY 11210.

The conditions derived previously for 3 types of synergism in aqueous binary mixtures of surfactants, i.e., mixed micelle formation, surface tension reduction efficiency and surface tension reduction effectiveness, are reviewed and verified by use of experimental data from the chemical literature. They involve the experimentally determined parameters, β and β^M, related to the interaction between the 2 surfactants in the mixed monolayer at the aqueous solution/air interface and in the mixed micelle, respectively. The experimental data needed to determine whether a binary surfactant system is capable of synergism in these respects are: (a) the surface tension-log concentration curves of the individual surfactants in the vicinity of their critical micelle concentrations (cmc), (b) the cmc of at least one mixture of the 2 surfactants, and (c) the solution phase concentration of at least one mixture of the 2 surfactants needed to produce a surface tension attainable by both individual surfactants. From the available data, some tentative generalizations regarding the effect of chemical structure and the molecular environment on the values of β and β^M have been made.

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APPROACH TO A FUNDAMENTAL MEASUREMENT OF FOAM STABILITY OF DETERGENT SOLUTIONS. Gary M. Nishioka, Owens/Corning Fiberglas, Granville, OH 43023, and Sydney Ross, Rensselaer Polytechnic Institute, Troy, NY 12181.

A model from which to compute the decay in surface area of foam caused by interbubble gas diffusion was recently proposed by Lemlich (*Ind. Eng. Chem.* Fundamentals 17:89 [1978]) and Ranadive and Lemlich (*J. Colloid Interface Sci.* 70:392 [1979]). The law employed for the growth of larger bubbles at the expense of smaller bubbles by means of gas diffusion is mathematically identical to the growth law for Ostwald ripening of precipitates with convection allowed. Modifications of the model that bring it closer to experimental conditions are introduced. These consist of incorporating a head space boundary condition and film thinning by capillary and gravitational drainage. Computed decay curves are compared with decay curves measured experimentally by the method of headspace pressure measurements (Nishioka and Ross, *J. Colloid Interface Sci.* 81:1 [1981]). Improvements of the experimental measurement of foam decay and additional modifications of the computational method are also discussed.

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WITHDRAWN

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THERMODYNAMICS OF SURFACTANT SOLUTIONS. Sydney Ross, Rensselaer Polytechnic Institute, Troy, NY, and Ian D. Morrison, Xerox Corporation, Webster, NY.

Surface activity is defined as the lowering of surface tension or of interfacial tension of a solvent by a solute in dilute solution. It is measured quantitatively by how much a solute may be diluted to achieve a lowering of the tension by a given fraction at a given temperature. The more dilute the solution that produces the effect sought, the more surface active is the solute. The equation of state of the system is obtained by an application of thermodynamics of solution; it relates bulk concentration, surface concentration and surface tension. From such an equation, one can derive 3 equivalent formulations, from each of which has been eliminated one of the 3 variables. The surface-tension isotherm relates the lowering of the surface tension to the bulk concentration; the adsorption isotherm relates the surface concentration to the bulk concentration; and the surface equation of state relates the spreading pressure, π, where $\pi = \sigma^\circ - \sigma$, to the area per mole ($A = 1/\Gamma$).

General formulations for the 3 congeneric equations are derived, and some attempts to apply them to binary systems of aqueous surfactant solutions are outlined. All such attempts must provide reasonable models or approximations to evaluate the various activity coefficients, both in bulk and surface solutions, of the 2 components.

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DEPENDENCE OF SUSPENSION STABILITY ON PARTICLE INTERACTION FORCES. D.R. Absolom*, University of Toronto, Canada, S.N. Omenyi and R.S. Snyder, NASA, Huntsville, AL, C.J. van Oss, S.U.N.Y.A.B., Buffalo, NY and A.W. Neumann, University of Toronto, Canada.

This contribution deals with the stability of suspensions of small particles in various liquids. Red cells from various species have a range of shapes and sizes, but are all below 10 μm in diameter. As they also have different surface charges and effective Hamaker coefficients (van der Waals interactions), they are suitable model particles for the study of suspension stability. The experiments presented here are droplet sedimentation tests, conducted with the view that the electrostatic interactions are repulsive and the van der Waals interactions are attractive or zero. In the presence of dilute concentrations of $La(NO_3)_3$, the zeta-potentials of various particles as determined by microelectrophoresis are reduced. By lowering the surface tension of the suspending liquid (γ_{LV}) through the admixture of varying concentrations of dimethyl sulfoxide (DMS), the van der Waals attraction between the particles is reduced, and at a certain surface tension of the liquid, becomes negligible. At this DMSO concentration and at large negative surface potentials, maximal stability of the suspension is achieved. Reduction in the electrostatic repulsion with maintenance of a low van der Waals attraction significantly reduces suspension layer stability. It is concluded that maximal stability of particle suspension can be attained in the absence of cross-linking ions, at high zeta-potential and low van der Waals attraction. The latter condition is attained by means of lowering the surface tension of the suspending liquid to a value which is equal to the surface tension of the particles themselves.

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THE TESTING OF SURFACE TENSION THEORIES. J.K. Spelt*, D.R. Absolom, M.R. Soulard and A.W. Neumann, Department of Mechanical Engineering, University of Toronto, 5 King's College Rd., Toronto, Ontario M5S 1A4, Canada.

In the field of surface science today, a number of competing theories exists regarding the nature and magnitude of molecular interactions at solid/liquid interfaces. The different schemes which have been devised to predict interfacial tensions often provide widely conflicting results. It has thus become necessary to devise convincing strategies to facilitate the testing of these various theories and methods. One such test involves the observation of particle rejection or engulfment at advancing solidification fronts. Theoretical predictions of the free energy of engulfment, $\Delta F^{eng} = \gamma_{PS} - \gamma_{PL}$ (where γ_{PS} and γ_{PL} are, respectively, the particle-solid and particle-liquid interfacial tension) are checked by direct microscopic observation. A second test which is currently being studied is aimed at providing a more clear understanding of the mechanisms which underlie solid/liquid interactions. According to the theory of F.M. Fowkes, the surface tension at a solid/liquid interface may be expressed as the algebraic sum of surface tension components due to the various intermolecular forces acting across the interface. One consequence of this theory is that 2 liquids, one polar and other nonpolar, with the same overall surface tension should have different contact angles on a given solid surface. This prediction provides the basis for a direct test of the Fowkes model. The procedures and results of both the engulfing and the contact angle tests are described.

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SYNTHESIS AND ANALYSIS OF GEOMETRICAL AND POSITIONAL OCTADECENOATE ISOMERS. Randall Wood*, Moghis Ahmad, Theresa Lee and Roberto deAntueno, Department of Biochemistry & Biophysics, Texas A&M University, College Station, TX 77843.

The *cis* and *trans* octadecenoates with the double bond located between the $\Delta 2$ and $\Delta 14$ positions have been synthesized by selective partial reduction of the corresponding alkynoic acid intermediates. Positional octadecynoates were synthesized using a variety of one-step and multistep procedures. Acetylenic fatty acids with the triple bond near the center of the molecule can be synthesized in high yields in a one-step reaction, whereas the synthesis of ynoic acids with the triple bond at either end of the hydrocarbon chain is considered more difficult. Generally, the location of the double bond in the desired fatty acid, the commercial availability of starting materials, and the quantities of desired fatty acid dictate the route of synthesis. Octadecynoates and *cis* and *trans* octadecenoates were examined by thin layer chromatography (TLC) and capillary gas liquid chromatography (GLC) using polar (SP 2340) and nonpolar (SP 2100) liquid phases. Some isomers exhibited unexpected TLC behavior. Although pairs of geometrical isomers were easily resolved by GLC, complex mixtures of the geometrical isomers overlapped, making the separation of *cis* and *trans* isomers by argentation TLC necessary prior to GLC analysis. The best separation of positional isomers was achieved on the polar capillary column: except for the $\Delta 6$, $\Delta 7$ and $\Delta 8$, all the *cis* octadecenoate isomers were separated. A hypothesis is advanced to explain the unusual chemical and chromatographic properties of some of the octadecenoate isomers.

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SYNTHESIS AND CHARACTERIZATION OF ALL THE GEOMETRICALLY ISOMERIC, METHYL 9,12- AND 12,15-OCTADECADIENOATES AND 9,12,15-OCTADECATRIENOATES. Henry Rakoff* and Edward A. Emken, Northern Regional Research Center, ARS, USDA, 1815 N. University St., Peoria, IL 61604.

The 4 geometrically isomeric methyl 12,15-octadecadienoates-9,10-d_2 were prepared by the Wittig reaction between *cis*- or *trans*-3-hexenyltriphenyl-phosphonium bromide and methyl 12-oxo-dodecanoate-9,10-d_2 with butyl lithium in ethyl ether. The Wittig reaction between hexyl-3,3,4,4-d_4-triphenylphosphonium bromide and methyl 12-oxo-*cis*- or *trans*-9-dodecenoate was used to prepare the 4 geometric isomers of methyl 9,12-octadecadienoate-15,15,16,16-d_4, whereas the same reaction between *cis*- or *trans*-3-hexenyltriphenylphosphonium bromide and methyl 12-oxo-*cis*- or *trans*-9-dodecenoate afforded the 8 geometrically isomeric methyl 9,12,15-octadecatrienoates. In each case, the stereochemistry of the double bond formed in the Wittig reaction was controlled by choice of reaction conditions. At room temperature, the Wittig reaction gave a product mixture with 80-85% *cis* geometry in the double bond formed. When the reaction was run at -40 C followed by protonation with methanol and slow warm-up to room temperature, the product mixture had 60-65% *trans* geometry in the double bond generated. Pairs of isomers formed during each synthesis were separated by partial silver resin chromatography. Physical constants presented include ^{13}C nuclear magnetic resonance chemical shifts, melting points, equivalent chain lengths and percentage *trans* by IR.

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THE ORGANIC SYNTHESIS OF RADIOACTIVE FATTY ACIDS AND THEIR CONVERSION TO PROSTAGLANDINS. Howard Sprecher, The Ohio State University, Department of Physiological Chemistry, 5170 Graves Hall, 333 W. 10th Ave. Columbus, OH 43210.

[1-^{14}C]-Labeled fatty acids are made by coupling the diGrignard complex of an ω-acetylenic alcohol, i.e., $HC \equiv C\text{-}(CH_2)_y\text{-}OH$ with a substituted propargyl bromide, i.e., $R\text{-}(C \equiv C\text{-}CH_2)_x\text{-}Br$ to give a polyacetylenic alcohol of the type $R\text{-}(C \equiv C\text{-}CH_2)_x\text{-}C \equiv C\text{-}(CH_2)_y\text{-}OH$. Following reduction with Lindlars catalyst, the ethylenic alcohol is purified by TLC. *Trans* contaminants and over-reduced alcohols are removed by argentation TLC after converting the alcohol to the acetate. After saponification, the alcohol is converted to the mesylate which is then reacted with $Na^{14}CN$ in dimethylsulfoxide. The nitrile is hydrolyzed to the methyl ester with 25% anhydrous HCl in methanol. The methyl ester is then sequentially purified by TLC and argentation TLC. After saponification, the purity of the [1-^{14}C]-labeled acid is determined by thin layer chromatography and reverse-phase high performance liquid chromatography. When [1-^{14}C]-7,10,13,16-docosatetraenoic acid was incubated with rabbit kidney medullary microsomes, a homologous series of prostaglandins was produced which is similar to those derived from arachidonate. The methods used for fractionating and characterizing these compounds will be discussed.

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OPPORTUNITIES IN FATTY ACID CHEMISTRY THROUGH DOUBLE AND TRIPLE BOND MIGRATIONS. Leonard S. Silbert, Eastern Regional Research Center, USDA/ARS, 600 E. Mermaid Lane, Philadelphia, PA 19118.

Long-chain fatty acids and their derivatives, especially when functionalized at predetermined positions along the chain, are important intermediates in chemical synthesis. However, with the exception of the α-methylene carbon, direct substitution of any selected carbon position is unsolved and continues to be a challenging research problem. Unsaturated fatty acids may serve as surrogates of saturated members for the introduction of substituents along the chain because of the double bond mobility in isomerization and migration reactions. In this context, the triple bond of acetylenic acids may similarly participate. However, most acetylenic acids are prepared from the parent olefinic acids. In this paper, an

overview will be presented of various methods used for the positional modification of unsaturated fatty acids. This discussion will center on methods for the specific isomerization and migration of double and triple bonds to the terminal ends of the fatty acid chain. Other reactions which will be discussed include isomerization of α,β- and β,γ-olefinic acids, isopropenyl and vinyl ester isomerizations, protection-deprotection reactions, and the olefin metathesis reaction. Included in presentation of the migration reactions is the author's recent successful development of the triple bond migration of 9-octadecynoic (stearolic) acid to the terminal acetylenic 17-octadecynoic acid.

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ACID-CATALYZED DECOMPOSITION OF LINOLEIC ACID HYDROPEROXIDE. H.W. Gardner* and E.C. Nelson, Northern Regional Research Center, Agricultural Research Service, USDA, 1815 N. University St., Peoria, IL 61604.

A number of strong mineral acids or organic acids catalyzed the conversion of linoleic acid hydroperoxide to a mixture of products. As assessed by chromatography, the products obtained were qualitatively independent of the acid used; however, the rate of hydroperoxide decomposition was much greater with strong mineral acids than with more weakly acidic organic acids. When HCl was tested as a catalyst, it was found that a plot of log k (k=rate constant) of hydroperoxide degradation against the Hammett acidity function (H_0) was a linear relationship with a slope of 1.28. Examination of the reaction products gave insight into the possible mechanism of reaction. When 13-L(S)-hydroperoxy-*cis*-9,*trans*-11-octadecadienoic acid was reacted in the presence of 0.1 M H_2SO_4 for 1 hr in 90% methanol (by vol) and then esterified with diazomethane, the main products were (-)-methyl *trans*-12,13-epoxy-*threo*-11-methoxy-*cis*-9-octadecenoate and a mixture of isomeric methyl hydroxydimethoxyoctadecenoates. Presumably, the methoxy ethers arose from participation of the methanol solvent. A small amount of (-)-methyl *trans*-12,13-epoxy-*threo*-11-hydroxy-*cis*-9-octadecenoate in the product mixture was indicative of the participation of the small amount of water in the solvent (<10% by vol). Based on the product structures and the retention of optical activity by the epoxides, a heterolytic mechanism is proposed to explain the results. Because epoxides also are products of homolytic decomposition of linoleic acid hydroperoxide via oxy radicals, it was not wholly anticipated that a heterolytic process would yield a similar result. The possible relevance of this acid catalysis to biochemical problems will be discussed.

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OXIDATIVE DEGRADATION OF (Z,Z)-3,13-OCTADECADIEN-1-YL ACETATE IN FIELD AND LABORATORY AGING EXPERIMENTS. M.A. Golub* and N. Alves, Albany International-Controlled Release Division, 110 A St., Needham Heights, MA 02194, C.E. Yonce, USDA/SE Fruit and Nut Tree Lab, and J. Weatherston, Albany International.

The use of biorational control methods has gained wide acceptance in insect pest management strategies during the past decade. In one such strategy, controlled release formulations of insect mating attractants, sex pheromones, have been used to disrupt the mating process of the target insects. Such formulations are effective only when the integrity of the pheromone components is maintained over a long period of time under field conditions. Many of the pheromones used in these formulations are long-chain, 12- to 18-carbon, unsaturated aldehydes, alcohols or esters and, as such, are related to lipids. Thus, it is not surprising to find that these compounds undergo photosensitized oxidation when subjected to field conditions. This paper reports studies on the degradation of (Z,Z)-3,13-octadecadien-1-yl acetate (ODDA). The stability and release rates of several formulations of ODDA were studied under a variety of conditions. It was found that laboratory-aged samples of formulations without antioxidants maintained their chemical integrity as determined by infrared spectroscopy and gas chromatography throughout a 16-wk aging period whereas changes were observed in field-aged samples of the same formulation after 28 days. Under different field conditions, it was observed that field-aged samples containing antioxidant remained unchanged for 200 days whereas changes could be detected in the same formulation without antioxidant after 42 days. The rate of disappearance of ODDA from the formulation without antioxidant was 1.5 times the rate from the formulations with antioxidant. The presence of hydroperoxides in the unprotected formulations has been hypothesized. Attempts to determine the identity of the degradation products will be discussed.

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^{1}H-NMR OF MEMBRANES. Alex MacKay, Department of Physics, University of British Columbia, Vancouver, B.C. V6T 1W5, Canada.

Due to the high NMR sensitivity and natural abundance of protons, the proton magnetic resonance of membranes is relatively easy to perform, but the interpretation is difficult due to the lack of specificity of proton sites and the complexity of the spectra. The broad, featureless ^{1}H-NMR spectra from large-diameter phospholipid membranes have no resolved splittings or chemical shifts and, in general, their linewidth does not relate directly to molecular order. The spectral lineshapes are dominated by residual dipolar interactions which reflect the anisotropy of motion of membrane components. A number of methods have been applied to study membrane structure and motion using proton magnetic resonance, including spectral simulation and the measurement of spectral moments and of relaxation behavior. In membrane systems, the mean square orientational order parameter for all intramethylene proton-proton vectors in a fatty acyl chain can be measured and, if the fatty acyl chain is partially deuterated, the orientational order parameter for a single methylene group can be obtained. In favorable circumstances, it has been possible to distinguish between the proton NMR signals from phospholipid molecules and those from membrane-bound particles (e.g., proteins). ^{1}H-NMR studies of a rhodopsin/dimyristol phosphatidylcholine reconstituted membrane have indicated the onset of motions of the rhodopsin molecules when the molar ratio of lipid to protein is increased.

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DEUTERIUM NMR IN MEMBRANE RESEARCH. Ian C.P. Smith, Division of Biological Sciences, National Research Council, Ottawa, Ontario K1A 0R6, Canada.

Deuterium NMR of labeled fatty acyl chains provides the least equivocal probe of membrane structure; it involves no perturbation of the lipid system and the degree of molecular ordering may be calculated directly from the spectrum. Rates of motion may be obtained from relaxation data, but the values obtained are dependent on the motional model employed, as with all other methods to date. The latter is at least simplified by a priori knowledge of the order parameter. The method will be illustrated by means of applications to the microorganism *Acholeplasma laidlawii* containing labeled 14:0, 16:0, 18:1 and cyclopropane-bearing fatty acids. This includes the properties of both liquid-crystalline and gel-state lipid. The use of the moments of the ^{2}H-NMR spectra to quantitate fractions of different lipid states, the onset of molecular motions, and the degree of homogeneity of the lipid state will be described. Manifestations of lipid-protein interactions will also be outlined.

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^{13}C NMR OF MEMBRANES AND COMPLEX LIFE. J.H. Prestegard, Yale University, Department of Chemistry, PO Box 6666, 225 Prospect St., New Haven, CT 06511.

Carbon-13 nuclear magnetic resonance (^{13}C-NMR) offers several advantages for the investigation of motional and structural properties of biological membranes and membrane components. Natural abundance carbon spectra of vesicular membranes and micellar structures offer sufficient resolution that numerous resonances from discrete molecular sites can be resolved and assigned. Because ^{13}C natural abundance is low for carbon, specific sites can be enriched to make resonances from minor membrane components dominate otherwise complex spectra. Carbon spectra offer not only chemical shift but also spin relaxation parameters that are easily interpreted in terms of motional properties of lipids that may be perturbed upon interaction of membrane components. These advantages will be illustrated using examples that include spectra of glycolipids that act as receptors for membrane-active agents such as choleratoxin, and spectra of phospholipids that display preferential interactions with membrane proteins such as glycophorin A. A recently developed analysis of dipolar relaxation mechanisms for ^{13}C-labeled phospholipids will be presented and applied to systems such as those cited here.

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CHARACTERIZATION OF MEMBRANE ORGANIZATION BY ^{31}P-NMR. H.C. Jarrell*, R.A. Byrd, R. Deslauriers and I.C.P. Smith, Division of Biological Sciences, National Research Council of Canada, Ottawa K1A 0R6, Ontario, Canada.

^{31}P-NMR has been used extensively to investigate the organization of both model and biological membranes. A brief overview of the interpretation of ^{31}P-NMR lineshapes with respect to lipid polymorphism of phospholipid membranes, as well as a discussion of methodology, will be given. The extension of the concepts used for interpreting phospholipid ^{31}P-NMR spectra to phospholipid systems, in particular the lipids of the ciliated protozoan *Tetrahymena pyriformis*, will be discussed.

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MORPHOLOGY OF NONLAMELLAR PHOSPHOLIPID STRUCTURES AND IMPLICATIONS FOR BIOLOGICAL MEMBRANE FUNCTION. Philip L. Yeagle*, Arlene Albert and Karen Ferguson,

Department of Biochemistry, 102 Cary Hall, SUNY/Buffalo School of Medicine Buffalo, NY 14214, and S.W. Hui and Tom Stewart, Roswell Park Memorial Institute.

The structural phases in mixtures of soybean phosphatidylethanolamine (PE) and egg phosphatidylcholine (PC) were studied with X-ray diffraction, freeze fracture electron microscopy, and ^{31}P-NMR. An intermediate state between bilayer and hexagonal structures was found, consisting of arrays of lipidic intramembranous particles. The arrays gave rise to an anisotropic ^{31}P-NMR spectrum commonly accredited to a hexagonal structure. A phase diagram of this mixed system is proposed. Fusion between bilayers of this system can be induced by freezing and thawing. Contact points between bilayers were observed by freeze fracture electron microscopy and isotropic motional averaging was detected by ^{31}P-NMR. A molecular model of point defect structure is proposed as an intermediate stage of fusion. This knowledge and the above techniques were applied to a study of the major lipids of the plasma membrane of *Tetrahymena*. PE from this membrane formed hexagonal phases above 10 C. The aminoethylphosphonate formed a lamellar phase up to 20 C, but converted to a hexagonal phase structure of 40 C. Small amounts of PC stabilized the lamellar structure. ^{31}P-NMR spectra of the intact ciliary membranes were consistent with phospholipid bilayer at 30 C, suggesting that PC in the membrane stabilized the lamellar form, even though most of the lipid of that membrane prefers a hexagonal phase in pure form at 30 C.

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LIPID-PROTEIN INTERACTIONS IN RECONSTITUTED MODEL LIPOPROTEINS. D.J. Vaughan*, General Foods, Research Dept., 520 William St., Cobourg, Ontario K9A 4L4, Canada, W.C. Breckenridge, Biochemistry, Dalhousie University, and N.Z. Stanacev, Clin. Biochemistry, Univ. of Toronto.

Apolipoproteins A-I, A-II, C-I and C-III$_2$ prepared from human plasma were reconstituted with sonicated vesicles of *sn*-3-dimyristoyl lecithin and *sn*-3-dimyristoyl lecithin:cholesterol (10:1). The lipid-protein interactions were monitored by electron spin resonance spectroscopy using isomeric 5'-, 12'- and 16'-(N-oxyl-4'',4''-dimethyloxazolidine) stearoyl spin-labeled lecithin probes. The temperature-induced phospholipid phase transition for reconstituted vesicles containing apolipoprotein A-I or A-II as monitored by 5'- and 12'-(N-oxyl-4'',4''-dimethyloxazolidine) stearoyl spin-labeled lecithins was broader than those detected by 16'-(N-oxyl-4'',4''-dimethyloxazolidine) stearoyl spin-labeled lecithin. Furthermore, the phospholipid phase transition for vesicles containing apolipoproteins C-I or C-III$_2$ as observed by 5'-(N-oxyl-4'',4''-dimethyloxazolidine) stearoyl spin-labeled lecithin was broader than those reported by 12'- and 16'-(N-oxyl-4'',4''-dimethyloxazolidine) stearoyl spin-labeled lecithin probes. These results indicate that apolipoproteins A-I and A-II in these model lipoprotein recombinants are partially embedded within the hydrocarbon region of the lipid bilayer but do not span the entire lipid bilayer. Apolipoproteins C-I and C-III$_2$, however, appear to be localized nearer the surface of the bilayer closer to the lipid-water interfacial region.

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INTERACTIONS BETWEEN PHOSPHATIDYLCHOLINE VESICLES AND BASIC POLYPEPTIDES OR PROTEINS. Ian M. Campbell* and Asha B. Pawagi, Division of Life Sciences and Department of Zoology, Scarborough College, 1265 Military Trail, West Hill, Ontario, Canada.

Because the net charge on phosphatidylcholine (PC) molecules is zero at biological pH, it is frequently assumed that, in membranes, this major phospholipid cannot interact with charged particles. Our studies, in which basic polypeptides or proteins were associated with preformed PC vesicles, show that with the membranes below phase transition, a small but measurable surface interaction occurs and, with the membranes above phase transition, the polycations alter the hydrophobic region of the membranes. When saturated (DPPC) vesicles were transformed to the liquid-crystalline phase, the polycations caused an increase in the optical, molecular and electron density of the membranes without any measurable alteration in the size of the vesicles. This effect rapidly reversed when the gel phase was restored. When, however, the DPPC membranes contained as little as 5% unsaturated PC (DOPC or DLPC), reversal of the effect by restoring the gel phase was partially or completely impaired. When vesicles were prepared from pure DOPC, DLPC or natural lecithin, association with polycations caused major alterations in ultraviolet absorption by the olefinic bonds in the acyl chains. Subsequent studies on phosphatidylserine (PS) vesicles showed only a strong surface interaction with the polycations unless the surface charge had been diminished by prior addition of divalent cations (Ca^{2+} or Mg^{2+}). With reduced surface charge on these vesicles, surface interaction by the polycations was greatly reduced and, as with PC vesicles, the polycations induced major alterations in ultraviolet absorption by the olefinic bonds. Thus it seems that if the surface charge on a membrane is low, basic polypeptides or proteins can alter the environment within the interior of the membrane.

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THYROIDAL INFLUENCE ON HEPATIC OUTPUT AND SERUM LEVELS OF RAT APOLIPOPROTEINS A$_I$ (APO A$_I$) AND E (APO E). R.A. Frank*, H.G. Wilcox and M. Heimberg, Department of Pharmacology, Crowe Bldg. #300, Univ. of Tennessee Center for Health Science, 874 Union Ave., Memphis, TN 38163.

Administration of triiodothyronine (T_3) enhances activity of cytochrome-linked α-glycerophosphate dehydrogénase (α-GPD), depresses hepatic output of triglyceride, and lowers serum cholesterol. Preliminary experiments indicated a positive correlation between thyroidal status and hepatic output or serum levels of apo A$_I$. To examine the effect of hormonally altered hepatic output on serum levels of apo A$_I$, 250-g rats were thyroidectomized (TX); T_3 was infused at rates of 9.6 μg/day (hyperthyroid) or 1 μg/day (replacement) by Alzet minipumps. Vehicle alone was infused to TX (hypothyroid) and sham-operated (euthyroid) rats. Livers were removed after 3, 5, 9 or 14 days' treatment for 4 hr perfusion in vitro. Thyroidal status was evaluated by serum T_3 levels and activity of α-GPD in hepatic mitochondria. Apo A$_I$ was measured in serum and perfusate by radioimmunoassay. In the hyperthyroid, a 2-3-fold increase in hepatic output of apo A$_I$ coincided with a doubling of serum apo A$_I$ levels. In the hypothyroid, the output of apo A$_I$ was depressed to .25 normal, but coincided with transient or negligible drops in serum apo A$_I$ concentrations. In addition, apo E was severely depressed in plasma high density lipoprotein from hyperthyroid rats, as estimated by SDS-polyacrylamide gel electrophoresis. In altered thyroidal states, hepatic output clearly contributes to changes in serum concentrations of apo A$_I$; however, these effects may be modulated by peripheral metabolism of lipoproteins. (Supported by grants from the NIH and PMAF.)

HONORED STUDENT PRESENTATION

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INTERACTION OF LIPIDS WITH *E. COLI* MEMBRANES AND INTESTINAL BRUSH BORDER MEMBRANES. P. Proulx, University of Ottawa, Department of Biochemistry, Faculty of Health Sciences, 275 Nicholas St., Ottawa, Ontario K1N 9A9, Canada.

E. coli cells were exposed to sonicated suspensions of labeled lipids under different conditions. Wild-type *E. coli* B cells incorporated readily only lysophosphoglycerides whereas *E. coli* D21F2, a heptose-lacking mutant, incorporated diacyl phosphoglycerides cholesterol and other neutral lipids quite effectively. The incorporation of [^{32}P]lysophosphoglycerides into *E. coli* B was accompanied by breakdown to water-soluble products and by some conversion to diacyl analogs. Divalent cations other than Mg^{++} enhanced the incorporation of exogenous lipids in both strains but inhibited acylation of lyso derivatives. In *E. coli* B, Ca^{++} caused the conversion of lysophosphatidylethanolamine to a more acidic type of lipid yet to be characterized. Brush border cell membranes isolated from rabbit small intestine were also found to incorporate phosphoglycerides cholesterol and neutral lipids quite readily in the presence of added Ca^{++}. The effect of lipid uptake on membrane properties was investigated briefly and it was found that incorporation of 1-palmitoyl glycerophosphorylethanolamine of up to 30-40 nmol/mg protein in the *E. coli* B strain led to a significant decrease in the fluidity of the NADH oxidase environment as could be assessed for Arrhenius plots of the oxidation activity.

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LOCAL ANESTHETIC EFFECTS ON CELL MEMBRANE. R.C. Aloia, Dept. of Anesthesiology, Loma Linda Univ. Med. Ctr. and Veterans Admin. Hosp., Loma Linda, CA, W. Mlekusch, Dept. of Medical Chemistry, Univ. of Graz, Graz, Austria, and D.D. Gallo, Dept. of Anesthesiology, Loma Linda Univ. Med. Ctr.

To assess the interaction of anesthetics with membrane lipids at the molecular level, the accessibility of phosphatidylethanolamine (PE) and phosphatidylserine (PS) to fluorodinitrobenzene (FDNB) in the rat erythrocyte membrane was investigated under different dietary conditions. Erythrocytes were obtained from rats fed a stock diet (CHOW), a partially hydrogenated coconut oil diet (PHCO) or a soybean oil diet (SOY) and were exposed to FDNB in the absence or presence of lidocaine, tetracaine or bupivacaine. Cell lipids were fractionated by thin layer chromatography and the dinitrophenyl derivatives of PE and PS were isolated and assayed colorimetrically. The local anesthetics reduced the number of PS and PE molecules exposed to the outer surface of the inner monolayer in the rat erythrocyte, as determined by accessibility to FDNB. For tetracaine, maximal reduction occurred with cells from rats fed the soy diet and minimal reduction was with the PHCO group. Lidocaine exhibited less masking of PS with cells from the

rats fed PHCO than with those fed the other 2 diets; the effects of lidocaine and bupivacaine were essentially independent of diet. The data are consistent with local anesthetics promoting redistribution of membrane phospholipids. Enhancement of association of phospholipids with proteins or formation of inverted micelles or hexagonal H_{II} phases are 2 possible mechanisms for removal of membrane phospholipids from exposure to the outer surface of the inner monolayer.

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OXIDATIVE DECOMPOSITION PRODUCTS OF ERYTHROCYTE MEMBRANE LIPIDS. F.J. Bunick* and W.W. Nawar, Department of Food Science & Nutrition, University of Massachusetts, Amherst, MA 01003.

Lipid breakdown in biological systems occurs via a complex mixture of enzyme-catalyzed and spontaneous oxidations, resulting in damage to cell membrane integrity and the production of physiologically active compounds. A detailed study of the oxidation of lipids in a natural membrane system, concentrating on mechanism and end-product formation, would greatly aid in understanding how these oxidations affect a tissue or organism as a whole. A natural membrane which lends itself to these initial studies is the erythrocyte ghost. Hemoglobin-free ghosts (HFG) prepared according to Dodge et al. are used as the initial substrate for this investigation. HFG are freeze-dried to yield quantities of a lipid bilayer system or are solvent-extracted and dried to yield a bulk lipid system. Oxidation of these systems in a pure oxygen environment at 80 C was done for a number of days before analysis of both volatile and nonvolatile oxidation products. Volatiles are collected using vacuum distillation with liquid nitrogen cold finger traps and subsequently are analyzed by gas chromatography and mass spectrometry. Nonvolatiles are being studied using thin layer and column chromatographic techniques. Exact identification of oxidation products is still in progress, but preliminary results show that, although the bulk lipid system produces a number of volatiles due to oxidation, the lipid bilayer system does not. Presumably, the oxidation products expected, such as hydroperoxides and epoxides, do not decompose rapidly under the temperature conditions of this study and nonvolatile products are formed.

HONORED STUDENT PRESENTATION

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THE ENHANCED INCORPORATION OF EXOGENOUS ARACHIDONIC ACID INTO PHOSPHATIDYLINOSITOL AND PHOSPHATIDYLCHOLINE OF GERBIL PLATELETS STIMULATED WITH THROMBIN. David E. Agwu*, Bruce J. Holub, Ian B. Johnstone and Stewart Crane, Department of Nutrition, University of Guelph, Guelph, Ontario N1G 2W1, Canada.

The degradation of platelet phospholipids via phospholipase activity is known to occur during thrombin-induced platelet aggregation. Both phosphatidylinositol (PI) and phosphatidylcholine (PC) are considered to be sources of the released arachidonic acid which becomes a substrate for prostaglandin and thromboxane A_2 formation. In this work, the effect of thrombin on the incorporation of exogenous arachidonic acid into platelet membrane phospholipids was studied. Suspensions of gerbil platelets were incubated in aggregometer cuvettes with [^{14}C] arachidonic acid in the absence and presence of thrombin, and product formation was monitored by thin layer chromatography and scintillation counting. Within 30 sec, the entry of arachidonic acid into PI was increased by 150% in thrombin-stimulated platelets relative to controls. Under identical conditions, the incorporation into PC was increased by only 35%. These results suggest that the incorporation of exogenous arachidonic acid via lyso-PI and lyso-PC acyltransferase activities may be intimately associated with thrombin-induced platelet aggregation. (Supported by the NSERC of Canada.)

HONORED STUDENT PRESENTATION

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ETHER-LINKED HOMOSERINE LIPID AS A CONSTITUENT OF THE PHOTOSYNTHETIC MEMBRANE IN THE GREEN PLANT CELL. David R. Janero, Department of Physiological Chemistry, Johns Hopkins University School of Medicine, Baltimore, MD 21205.

Polar glycerolipid containing an ether linkage to diacylglycerol has been identified in the photosynthetic (thylakoid) membrane in the green alga *Chlamydomonas reinhardtii* 137$^+$ (wild-type). Ether lipid constitutes ∿10% of the membrane's polar lipid mass, and the proportion of ether lipid in the photosynthetic membrane is ∿40% of the total found in the cell. Chemical analyses and high-resolution Fourier-transform proton nuclear magnetic resonance spectroscopy (NMR) have been used to define the molecular structure of the ether lipid and various derivatives prepared therefrom. The ether lipid consists of a single compound, the zwitterionic lipid 1(3),2-diacylglyceryl-(3)-*O*-4′-(*N*,*N*,*N*-trimethyl)homoserine (DGTS). Quantitation of the esterified fatty acids as their methyl ester derivatives by gas liquid chromatography (GLC) demonstrates that 16-carbon and 18-carbon acids predominate in thylakoid DGTS, with an unsaturated-to-saturated ratio of ∿1.8. No *trans* unsaturated acids were detectable by argentation chromatography of the fatty acid esters. The fatty acid complement of thylakoid DGTS is distinct from the cellular DGTS acyl profile, indicating that thylakoid DGTS forms a distinct subpopulation in situ at the molecular level. These results provide the first demonstration that DGTS is a bonafide membrane lipid and, specifically, that an ether-linked glycerolipid is a component of the thylakoid membrane of a green plant cell.

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POSSIBLE ROLE OF NEUTRAL LIPIDS IN COLD HARDENING OF CITRUS TREES. Harold E. Nordby*, U.S. Citrus & Subtropical Products Laboratory, 600 Ave. S, NW (PO Box 1909), Winter Haven, FL 33880, and George Yelenosky, U.S. Horticultural Res. Station.

In recent studies on changes in fatty acid profiles in citrus leaves upon being cold-hardened, triacylglycerides, and to a less extent, other neutral lipids, were observed to increase quantitatively as well as in degree of unsaturation. These observations suggest the neutral lipids may have a role in protecting biomembranes against cold damage. To help understand the possible role of neutral lipids in the cold-hardening process, the structures of neutral lipids present in leaves of cold-hardened citrus seedlings were compared with those of nonhardened seedlings. Triacylglyceride structures were determined by argentation TLC-GLC and by HPLC. The fatty acid compositions of mono-, diacylglycerides and other neutral lipids were determined by GLC. Possible biosynthetic relationships between these neutral lipids and phospholipids will be discussed.

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LIPOGENESIS AND MEMBRANE BIOGENESIS IN THE EUKARYOTIC CELL CYCLE. David R. Janero, Department of Physiological Chemistry, Johns Hopkins University School of Medicine, Baltimore, MD 21205.

Polar glycerolipid synthesis attendant to the biogenesis of cellular membrane has been studied using highly synchronous, axenic cultures of the green alga *Chlamydomonas reinhardtii* 137$^+$ (wild-type). A protocol involving pulse exposures of synchronous algae to radioactive acetate and to ^3H_2O was devised to measure lipogenesis throughout the 12-hr light/12-hr dark cell cycle. Application of the protocol revealed significant cyclic variations in the synthesis of polar glycerolipid by synchronous *Chlamydomonas*. Highest lipogenic rates are confined to the photoperiod (mid-to-late G_1), whereas a comparatively negligible level of lipid production characterizes the dark period (S, M and early-to-mid G_1). Subcellularly, the kinetics with which glycerolipid is assembled into the photosynthetic (thylakoid) membrane matrix parallel the cellular kinetics of glycerolipid synthesis through the synchronous cycle. Such coordination between lipogenesis and thylakoid lipid assembly indicates that diminution in the assembly of thylakoid lipid results from the lack of availability of the requisite polar glycerolipid during periods of decreased lipogenesis. These data suggest that lipogenesis in actively cycling cells not only provides lipid for membrane production, but also serves as the critical rate-determining, if not rate-limiting, step to the lipid assembly supporting membrane biogenesis.

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SYNTHESIS AND PHYSICAL PROPERTIES OF CEREBROSIDE SULFATE CONTAINING α-HYDROXY-PALMITIC ACID AND PALMITIC ACID. Kavalelil M. Koshy* and Joan M. Boggs, Biochemistry Dept., Hospital for Sick Children, 555 University Ave., Toronto, Ontario M5G 1X8, Canada.

The physical properties and phase behavior of cerebroside sulfate, an important lipid in myelin, are not well understood, primarily due to the lack of synthetic species of well-defined composition. This lipid occurs in myelin in both the α-hydroxy and nonhydroxy fatty acid forms. Free hydroxyls on the fatty acids, the sphingosine base and the carbohydrate, as well as the amide moiety of sphingolipids may participate in intermolecular hydrogen bonding between neighboring lipid molecules in the bilayer. In order to investigate the hydrogen bonding properties of cerebroside sulfate, we have developed a method to synthesize palmitic and hydroxy palmitic acids by hydrolyzing bovine brain cerebroside sulfate with methanolic potassium hydroxide and reacylating the 1-0-(β-D-galactosyl-3-sulfate)-sphingosine with palmitoyl chloride or 2-D,L-acetoxy-palmitoyl chloride. The acetoxy protecting group was then hydrolyzed with methanolic potassium hydroxide. The products were purified and the D and L isomers of the α-hydroxy form were

separated by column chromatography. The contribution of the acyl chain α-hydroxy group to intermolecular hydrogen bonding was investigated by studying the phase transition by differential scanning calorimetry. The hydroxy fatty acid form melted 10-15 C higher and with a lower enthalpy and entropy than the nonhydroxy form, indicating that the acyl hydroxyl group contributes a stabilizing and ordering effect to the lipid, probably due to an increase in intermolecular hydrogen bonding.

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CHANGING PRACTICES AND CHANGING RESIDUES IN ANIMAL FATS AND PLANT OILS. Richard Frank, Provincial Pesticide Residue Testing Laboratory, Ont. Ministry of Agriculture and Food, University of Guelph, Guelph, Ontario N1G 2W1, Canada.

The development of synthetic organic pesticides following World War II was a boon to increased food production and the reduction of insect-borne human diseases. Chemicals were found to control many pests in the production of a multitude of crops and animals. (a) The first concerns occurred in the early 1950s over residues in food supplies and acute hazards to the occupationally employed. Legislative action at both the Federal and Provincial levels dealt with these concerns. (b) During the 1960s, a second set of concerns arose over the environmental impact from widespread use of pesticides. This resulted in further legislative actions to protect the environment again at both levels of government. (c) During the 1970s, yet another series of concerns arose, this time over the long-term effects of pesticides on human health. Cracks appeared in the integrity of the chemical industry to satisfactorily conduct toxicological studies. Another period of legislative action appears to be on the way to correct this situation. Running concurrently over these 3 decades has been an increasing incidence in the appearance of natural resistance among pests to synthetic chemicals; this is beginning to alarm agrologists. Integrated pest management programs are hurriedly being tested as replacements for the protective programs that have been in existence. Success is not ensured.

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DETERMINATION OF ORGANOHALOGEN PESTICIDES IN VEGETABLE OIL BY-PRODUCTS. S.J. Young, M. Clower, Jr., J.A.G. Roach and D. Firestone*, Bureau of Foods, Food and Drug Administration, Washington, DC 20204.

A method is presented for determination of organohalogen pesticides and metabolites in vegetable oil by-products. The method uses gel permeation and Florisil column chromatographic separations for sample clean-up. Organohalogen pesticide residues are detected with a ^{63}Ni electron capture gas chromatographic system used in conjunction with 3 different gas chromatographic columns. Residue identities are confirmed by gas chromatography/mass spectrometry. Results of analysis of vegetable oil deodorizer distillates are presented, as well as recovery data for a number of organohalogen pesticides.

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LIPOPHILIC CONTAMINANTS IN THE GREAT LAKES ECOSYSTEM. Richard L. Thomas, Canada Centre for Inland Waters, Great Lakes Biolimnology Laboratory, PO Box 5050, Burlington, Ontario L7R 4A6, Canada.

Studies conducted during the past decade have revealed the extent of contamination of the Great Lakes ecosystem. Public concern at the levels observed associated with fishery closures have placed the Great Lakes at the vanguard of the effort to control environmental contamination. Studies have been directed toward observations of levels and time trend analysis at all trophic levels; analysis of sedimentary systems to determine mass balances, sources and dispersal within the lake bodies; the role of atmospheric precipitation and on research to determine transfer of materials between environmental compartments. An overview of such studies is presented with specific reference to DDT, PCB and Mirex. Current information and concerns with TCDD also are presented to illustrate difficulties encountered in the emerging concerns with ultra trace levels of highly toxic compounds.

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THE "PBB" EPISODE IN MICHIGAN. Mary E. Zabik, Michigan State University, Dept. of Food Science and Human Nutrition, 139 Food Science Building, East Lansing, MI 48824.

Accidental incorporation of the polybrominated biphenyl (PBB) compound Firemaster® Ff-1 in place of magnesium oxide into high-protein dairy pellets in May 1973 initiated the PBB incident. PBB were manufactured to be incorporated into flame-retardant polymers because of their thermal stability; thus, they were not meant to be used in food or feed or in any product coming into contact with food or feed. Dramatic reduction in milk production of a 300-animal herd instituted the search for a toxic component which was identified in April 1974 as PBB. Cross-contamination of other feeds led to destruction of thousands of cattle, swine, sheep and poultry, as well as products from these animals. Although foods containing levels of PBB which exceeded the FDA's tolerances were off the market by late 1974, concern exists for the possible public health effects related to PBB ingestion. Of special concern were the effects of PBB exposure for persons on quarantined farms. Several different public health studies have failed to produce any conclusive evidence of impaired health, but continued health surveillance of persons exposed to PBB is underway. The PBB incident also initiated numerous research studies into animal and enzyme toxicity studies, environmental degradation and stability during processing and cooking.

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DYNAMICS OF DIOXINS AS IT PERTAINS TO INDICATORS OF POLLUTION. J.R. Roberts* and M.J. Boddington, Environmental Secretariat, National Research Council Canada, 100 Sussex Dr., Ottawa, Ontario K1A 0R6.

The bioaccumulation potential of various pesticides in fish has been experimentally correlated to the water:octanol partition coefficient of the chemical. It is possible to develop new equations relating to different organisms such as birds and mammals based on the theoretical relationships of the organisms' differing metabolic requirements and the different exposure vectors (e.g., water, air, food). The predictors can be used in a limited manner to make judgments about the types of indicator organism most useful for environmental monitoring, as well as the meaning of any detected residues. These points are illustrated with reference to 2,3,7,8-tetrachlorodibenzo-*p*-dioxin data in fish and bird eggs from Lake Ontario. Although the hypotheses presented are experimentally untested, they could offer a useful predictive tool for those interested in the collection and interpretation of xenobiotic residues from field sampling programs.

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GLOBAL OVERVIEW OF LEGISLATION AIMED AT CONTROL OF CONTAMINANTS AND PESTICIDE RESIDUES IN FATS AND OILS. B.L. Smith, Food Regulatory Affairs Division, Health and Welfare Canada, Room 200, Health Protection Branch Building, Tunney's Pasture, Ottawa, Ontario K1A 0L2, Canada.

Control of contaminants and residues of agricultural chemicals is an increasing problem in an industrialized society. New programs and legislation to control environmental concerns clearly impact on relatively mature and stable legislation and programs directed at the production and sale of safe, unadulterated foodstuffs. The role of international agencies in developing regulatory guidelines is outlined together with a discussion of regulatory principles involved in control of contaminants and pesticide residues in both the environment and in foods. Canadian food and environmental control legislation is reviewed to illustrate the complexity of modern regulatory control in this area.

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ENERGY SAVING TECHNIQUES IN CONTINUOUS DEGUMMING AND REFINING. E.G. Latondress, Davy McKee Corporation, 10 S. Riverside Plaza, Chicago, IL 60606.

The energy requirements for the individual operations in the continuous caustic soda process are discussed. The electrical power requirements for the process are basically determined by the throughput rate which fixes centrifuge motor sizes. The electrical power requirements are not subject to significant reduction without a basic change in the process. However, steam usage may be reduced by as much as 75% by proper heat recovery methods. The selection of process streams for most effective heat recovery is discussed.

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CURRENT PRACTICES IN CONTINUOUS COTTONSEED MISCELLA REFINING. Blake Hendrix, Sullivan Systems Inc., 900 Larkspur Landing Circle, Suite 100, Larkspur, CA 94939.

Miscella refining of crude cottonseed oil has become a generally accepted commercial process for the past 20 years. The simple and efficient continuous process for removal of undesirable impurities is described, having changed little in its basic form since discovery 40 years ago. The individual unit processes, control systems, process flow chart, chemical reactions and oil-to-hexane ratios used in miscella refining are described. The several advantages to miscella refining vs conventional oil refining are noted.

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FIELD EVALUATION OF EXTRACTION PERFORMANCE. Edward D. Milligan and David C. Tandy*, EMI Corp., 3166 Des Plaines Ave., Des Plaines, IL 60018.

Two factors affect the efficiency of extraction for a percolation-type oilseed solvent extractor. The first is extractability of the oilseed, which is a measure of the ability of the solvent to permeate

the structure of the seed, extract the oil from the matrix and the move to the surface of the seed. The second is washability, which is a measure of the ability of the bed to permit removal of surface oil from the seed by contact with washes of successively fresher solvent. This relates to the physical bed conditions which allow for optimal flow of solvent through the bed and maximal drainage rate from the bed. Several practical methods of determining these factors in the field are presented and discussed and the effects of seed properties such as moisture, flake thickness, fines and the bed density achieved in the extractor are examined.

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USE OF Y-ZEOLITE/CLAY BLENDS IN THE BLEACHING OF VEGETABLE OILS. Dennis R. Taylor*, Charles B. Ungermann and Zenon Demidowicz, Filtrol Corp., 3250 E. Washington Blvd., Los Angeles, CA 90023.

New data are presented on Y-zeolite/clay blends for simultaneous color and fatty acid reduction during bleaching of vegetable oils. In particular, the importance of the zeolite exchangeable cation utilized (Li, Na, K, NH_4, Mg, Ca, Ba, Mn, Fe, Co, Ni, Zn) with regard to its effect on bleaching and fatty acid removal, is described. Also, the relative instability of aged Y-zeolite/clay blends for bleaching is discussed; evidence is presented to explain Y-zeolite/clay blend instability in terms of clay ⇔ zeolite cation exchange in the solid state.

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CANOLA OIL DEGUMMING. L.L. Diosady*, Department of Chemical Engineering and Applied Chemistry, University of Toronto, Toronto, Ontario M5S 1A4, Canada, P. Sleggs and T. Kaji, The Cambrian Group.

The chemical degumming of crude oil produced from low-glucosinolate canola varieties of rapeseed was investigated. Commercially produced samples of Tower and Candle oils were used. Phosphoric, nitric and citric acids in aqueous solutions and maleic anhydride were used. The process was optimized in terms of the treatment chemicals, the concentration of reagents, rate of mixing, reaction time and temperature. Degummed oil quality was evaluated by measuring phosphorus, iron, calcium and free fatty acid levels, and Lovibond colors. The best degummed oils were refined, bleached and deodorized. Some samples were also hydrogenated. Phosphorus levels in the degummed oil were reduced to below 50 mg/kg. Upon refining, the usual phosphoric acid pretreatment step may be eliminated without affecting the final quality of the oil. Based on these results, chemical degumming of canola oil offers significant advantages over conventional aqueous degumming.

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PRACTICAL PROCEDURES FOR AUDITING INDUSTRIAL BOILER PLANTS. K. Allison, Corporate Energy Department, Nabisco, Inc., East Hanover, NJ 07936.

The industrial boiler plant is an area of opportunity in virtually every industry to save energy and reduce costs by using relatively simple, inexpensive auditing procedures. An energy audit consists of inspection, measurement, analysis and the preparation of recommendations. A complete boiler plant program will consider each individual boiler, boiler room auxiliary equipment, steam distribution and return systems and stream end-use equipment. This paper summarizes the practical procedrues, techniques and instrumentation which Nabisco uses in its boiler plant energy conservation program.

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MAKING YOUR STEAM SYSTEM MORE EFFICIENT. John A. Kremers, Application Engineers, Armstrong Machine Works, Three Rivers, MI 49093.

In times of rising fuel costs, it is necessary to understand your steam and condensate systems better to insure that they are operating efficiently. This paper discusses steam distribution, steam traps and condensate return. Steam trap types and their operations are explained, along with typical uses and expected service life for each type. Good and bad characteristics for each trap are provided. The testing of installed steam traps is outlined generally for each type of trap, along with methods of correcting bad traps. Reference is made to costs which could be expected in a plant with little or no maintenance of steam traps.

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IN-USE ENERGY EFFICIENT MOTOR OPERATION. Giles W. Willis, Jr.*, and Bruce K. Colburn, Entek Associates, Inc., PO Box 285, College Station, TX 77841.

Most of the energy used in industrial facilities today is for steam or electrical conversion through alternating current motors. Nowhere is this more evident than in processing industries in which motors are used to move products by driving screw, or to run belt conveyors, elevators, blowers, and machines which clean, grind, or mill the product. It would not be uncommon in a typical food processing mill for the cost of operating motors to exceed one-third of a million dollars per year. Present alternating-current induction motors typically operate, under less than 50% load, at less than maximal efficiency. Motor drives are often improperly sized to the load and may never operate even near their full capacity. This usually results in inefficient operation which costs the user. Energy surveys in industrial plants necessitate measurement of watts and vars, or their equivalents. To ascertain the accuracy and viability of noninvasive and fast tests, a measurement technique for on-site load determination was investigated. This was determined from a motor test study with 3 purposes: (a) to compare the new, so-called "energy efficient" motors with typical drives, (b) to determine power vs speed characteristics under varying load voltage conditions to ascertain the feasibility of using speed and voltage for load determination for a given motor class, and (c) to determine performance characteristics above and below name-plate voltage (a common problem in oil mills). Results show that (a) standard textbook machine models are poor descriptors of partially loaded motors, (b) "energy-efficient" motors can be more inefficient than standard motors, and (c) plant voltage regulation can be important for energy efficient operation and improvement in power factor. The experimental results are presented along with engineering criteria to implement practical cost and energy savings measures for motor-drive operations.

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ADJUSTABLE SPEED DRIVES AS APPLIED TO CENTRIFUGAL PUMPS. John C. Conzett, John D. Robechek and Robert L. Mervis*, Reliance Electric Company, 24703 Euclid Ave., Cleveland, OH 44117.

Centrifugal equipment–pumps and fans–consume 30% as much energy as all of the passenger cars in the U.S. Combined with the large increase in both demand charges and usage charges for electric power, any easy method to reduce power consumption of centrifugal pumps or fans without reducing system performance is welcome news to today's plant engineer. Adjustable speed drives provide that advantage. Pump systems most often operate at full flow or are varied by throttling valves to reduce flow rates. These valves may automatically regulate the system via electronic or pneumatic devices. Reducing flow rates by partially closing a valve wastes large amounts of energy. Varying the speed of the pump to control flow rates can save a significant amount of energy because the pump does not have the pressure restriction of a partially closed valve in the system. By examining the performance curves of the pump, a typical system curve of a hydraulic system and efficiencies of various flow control systems, we will show the energy savings using adjustable speed drives. Payback periods of less than 3 years are not unusual for adjustable speed drives when compared to unregulated or valve-controlled systems. In addition to energy savings, the wear on pump seals, inpellers, cavitation damage to pipes, elbows, valves, and other equipment can be greatly reduced with adjustable speed drives. Finally, a method for calculating energy savings and investment payback periods for the purchase of adjustable speed drives will be presented. It will demonstrate how to evaluate your own application to establish your priorities on conversions and new installations, and realize the savings that may be available to you.

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COOLING TOWERS AND ENERGY CONSERVATION–PRACTICAL APPLICATIONS. Robert Burger, Burger Associates, Inc., PO Box 344566, Dallas, TX 75234.

There are 2 major areas of energy savings: (a) generation of cold water in the cooling tower; and (b) utilization of the cold water in the chemical process and/or refrigeration plant. This paper will investigate the various operating elements of the cooling tower, their functions and how to upgrade them to produce colder water by more efficiently using modern, state-of-the-art engineering. Case histories will be discussed illustrating savings and return of investment (ROI) due to planned maintenance and modern rebuilding. Crossflow vs counterflow, selection, bid evaluation and certified testing will provide a broad-based "hands-on" discussion. Presentation will be augmented with actual field-condition slides.

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A NEW DEODORIZER CONCEPT OPTIMIZING ENERGY RECOVERY AND FLEXIBILITY. W.R. Raes, Extraction De Smet NV, Antwerp Belgium.

An extremely flexible, single-shell deodorizer has been developed composed of several batches automatically programmed. This concept allows up to 3 feed-stock change-overs per hr while the intermixing between the successive oils or fats is avoided. Heat ex-

change between the cold, incoming oil and the deodorized product occurs in a drop-tank cooler by means of a secondary circuit. This concept allows recovery of a maximum of thermal energy from deodorized oil. This new type of deodorizer already has been in operation for several months in oil refineries, treating blends for specialty fats. It is particularly indicated for fats and oils in the margarine industry.

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CONSISTENCY OF FATS. J.M. deMan, Department of Food Science, University of Guelph, Guelph, Ontario, Canada N1G 2W1.

The consistency of fats can be measured with the cone penetrometer (AOCS method Cc 16-60). Several suggestions have been made to convert readings of penetration depth into parameters such as yield value, hardness or hardness index. This may extend the usefulness of the method. Motor driven penetrating devices yield results in terms of force/area or stress. More basic information about the rheological properties of fats can be obtained with creep measurements. This includes the viscous flow component as well as instantaneous and retarded elastic components. Such methods are more suitable for research purposes than for quality control. Characteristics and application of various methods will be examined.

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RHEOLOGY AND MICROSTRUCTURE OF MAYONNAISE. M.A. Christman, J.H. Guth, D.N. Holcomb*, W.M. Loris and F.J. Sasevich, Kraft Inc., R&D, Basic Food Science Laboratory, 801 Waukegan Road, Glenview, IL 60025.

Two leading retail mayonnaises were examined by rheological methods (including dynamic testing), particle sizing techniques and microscopy. Samples were prepared for scanning electron microscopy and examined by existing techniques and acceptable results were obtained. Dynamic testing data (storage and loss moduli, loss tangents) were obtained as functions of temperature and sweep frequency. Changes in microstructure and rheological parameters due to sample abuse were measured and compared for the 2 brands.

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MELTING POINT DETERMINATION OF FATS. J.M. deMan* and L. deMan, Department of Food Science, University of Guelph, Guelph, Ontario, Canada N1G 2W1.

A variety of methods exist for the determination of the melting point (mp) of fats. These include the Wiley mp (AOCS method Cc 2-38), open capillary slip point, softening point and Mettler dropping point. The conditions under which the tests are performed influence the values obtained. Several of these methods were compared using a variety of fats, including margarine and soft margarine oils, lard, butter and hydrogenated Canola oils. The Mettler dropping point values were found to coincide with the extrapolated solid fat curves obtained using wide-line NMR for all fats except butterfat. The reproducibility of the Mettler dropping point and softening point were excellent; that of the slip point was poor.

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ASSESSMENT OF SELECTED TEXTURAL CHARACTERISTICS OF TABLE SPREADS. B. Vane* and M. Vaisey-Genser, University of Manitoba, Faculty of Human Ecology, Dept. of Foods and Nutrition, Winnipeg, Manitoba R3T 2N2, Canada.

Textural parameters were defined for both brick and tub market forms of brand-name margarines produced from canola, corn, soy or sunflower oil and butter. The margarines were characterized by fatty acid composition, including levels of *trans* fatty acids, using gas liquid chromatography. Textural properties of firmness (TUf) and work to soften were measured using the General Foods texturometer and 7-10-member trained sensory panels using magnitude estimation. Sensory assessments were also made of spreadability (Sp) and rate of mouth-melting (Sm, sec). Texture measurements were performed at 4 C and 21 C. Levels of total *trans* plus saturates correlated well with texturometer firmness at 4 C (r^2 = 0.94). There was excellent agreement between the texturometer and panel firmness measures and between panel assessments of spreadability and texturometer firmness (r^2 = 0.93). Addition of work to soften measurements, made by either instrument, did not significantly improve the latter relationship. However, combining rate of mouth-melting with firmness increased the coefficient of determination (r^2) to 0.96 yielding the prediction equation: Sp = TUf + Sm. General comparisons showed that, at 4 C, brick products were significantly firmer, more resistant to work softening and slower to melt than the tub market form. Bricks at 21 C were similar in all textural parameters to the tubs at 4 C.

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TEXTURIZATION AND OPTIMIZATION OF SOY CHEESE. A.H. Chen*, Anderson Clayton Foods, Richardson, TX, J.W. Larkins, Michigan State University, and Y.C. Jao, Miles Laboratory.

The influence in soy cheese texturization due to levels of soy concentrate, particle size, activation pH, NaCl and NaMH PO_4 were investigated according to a Central Rotating Composite Experimental design. Textural parameters of hardness, toughness, cohesiveness and chewiness were used to specify the profile of cheese texture. Colby and Velveeta textures were successfully obtained through multi-response optimization. These 2 textural profiles were verified by a trained panel to be valid.

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SUNFLOWER PERFORMANCE—AGRONOMIC ASPECTS. Alvin J. Jarvi, Cargill, Inc., Fargo, ND 58102.

Sunflower performance is influenced by the cultivar, the environment, and the interaction of cultivar and environment. The environment is only partially controlled by the farmer and involves the interaction of many factors which vary greatly from day to day and from season to season. Good agronomic practices, which at least in part modify the environment, lead to the establishment of optimal use of the growing season. Plant populations used in the major production area range from 35,000/ha to 60,000/ha with planting depth ranging from 3 cm to 10 cm, depending on soil moisture. Nitrogen is the most common limiting soil nutrient and, generally, as yields increase in response to nitrogen fertilizer, there is a corresponding decrease in oil content. Adequate weed control is very important during the first 3 weeks after emergence and is accomplished mechanically and/or chemically. Sunflower is frost-tolerant during both the seedling stage and the postflowering period, and is most susceptible during the period of rapid growth and flowering. Sunflower is not a highly drought-resistant crop, but is effective in utilizing soil moisture to depths of over 2 m.

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SUNFLOWER DISEASES—CONTINUING CHALLENGE. W.E. Sackston, Department of Plant Science, Macdonald Campus of McGill University, Ste. Anne de Bellevue, Que. H9X 1CO, Canada.

Sunflower, the second most important oilseed crop in the world, was developed as a crop in eastern Europe, but is a native of North America. The pathogens causing many of its major diseases are also native to North America. Although it is a profitable crop, sunflower has fairly low value per hectare. Disease control must therefore be inexpensive, by resistant varieties, seed treatment or cultural practices, rather than by repeated field application of chemicals. Rust, a limiting factor in many countries, has been successfully controlled everywhere by resistance from wild sunflowers discovered in Canada about 1950. New races are posing problems in Argentina and Australia, but new resistance may be available. Verticillium wilt has been destructive in some areas, but resistance is available from wild sunflowers and Russian high-oil varieties. Downy mildew, which is highly destructive in many countries, has been effectively controlled by 2 genes from the original rust-resistant material. A new race attacking this resistance was discovered in 1980; resistance to it appears to be available. Sclerotinia stalk rot and head rot, caused by a pathogen with wide host range, is much harder to control by breeding. Leaf spot diseases have long been a limiting factor in some European countries and elsewhere, but were considered minor in North America until recently. Broom rape, a root parasite which almost destroyed the crop in the USSR and elsewhere in eastern Europe, does not attack in North America. It is controlled by resistant varieties.

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GENETICS AND BREEDING OF SUNFLOWER. G.N. Fick, SIGCO Research Inc., Breckenridge, MN 56520.

Development of high-yielding, disease-resistant sunflower hybrids was an important factor in the rapid expansion of sunflower production during the last decade. A great deal of genetic diversity is present in breeding populations and among the wild species of *Helianthus* for further improvement of sunflower. Progress is being made in developing new lines and hybrids with improved seed yield, agronomic type, oil percentage, disease and insect tolerance and self-compatibility—a trait that lessens the dependency on bees for pollination. Sunflower oil is composed primarily of palmitic, stearic, oleic and linoleic acids, with linoleic accounting for about 70% of the total of northern grown production. Of special interest is the recent identification of genotypes with oleic acid percentages as high as 80%. It appears feasible to incorporate the high-oleic characteristic into agronomically suitable hybrids.

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INSECT PROBLEMS OF SUNFLOWERS. A.P. Arthur, Agriculture Canada Research Station, 107 Science Crescent, Saskatoon, Sask. S7N 0X2, Canada.

Many insect pests belonging to several different groups attack cultivated sunflowers in North America. Sunflowers are native to

this continent and weeds belonging to the same or closely related species are abundant throughout areas where cultivated sunflowers are grown. Thus, most sunflower insects are native and have been multiplying rapidly during the recent expansion in sunflower production. Discussion of the insect pests of sunflowers is facilitated by grouping them according to the part of the sunflower plant attacked. I will discuss the species as (a) leaf feeders, (b) steam and root feeders, and (c) head feeders. The leaf feeders are usually the easiest group to control. They are exposed to view, they and their damage easily evaluated, and effective insecticidal controls applied where necessary. The stem and root feeders such as the carrot beetle in the South and cutworms further north can cause severe damage before control measures are applied. However, many other species of stem feeders can be present in large numbers without causing economic damage. The head feeders include the sunflower moth, the banded sunflower moths, the sunflower seed maggot, the seed midge and the seed weevil. These pests are potentially very damaging and are difficult to control with insecticides once they have entered the head. Traps baited with a synthetic pheromone are now available to monitor the abundance of sunflower moths. Further research on early warning systems to detect the abundance and distribution of other pests in this group is especially important. These will enable growers to apply controls before the pests are protected within the heads and will reduce the application of insecticides when they are not required.

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SUNFLOWER MEAL AND HULLS UTILIZATION. E.W. Lusas, Food Protein Research and Development Center, FM Box 183, College Station, TX 77843.

Unlike soybeans, which are grown as a feed protein meal source, sunflowers are grown primarily for their oil content. Nevertheless, sunflower meal is the world's fourth largest feed protein pool. Interest in sunflower oil mill by-products typically develops only after they become available locally; studies in the USSR and western Europe precede research in the US. The high fiber content of meal from undehulled seed limits its use in high-energy feeds for nonruminants. However, expense and difficulties of dehulling have resulted in considerable amounts of US sunflower meal being produced at levels below 41% protein, which would compete for traditional soybean or cottonseed meal markets. This paper reviews the composition and use of sunflower meal and separated hulls.

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THE NUTRITIONAL, FUNCTIONAL AND ORGANOLEPTIC PROPERTIES OF SUNFLOWER PROTEINS. Frank W. Sosulski, Department of Crop Science, University of Saskatchewan, Saskatoon, Sask. S7N 0W0, Canada.

Several investigators have demonstrated that sunflower hulls must be removed before oil extraction to avoid the transfer of dark pigments into the flour. Therefore, confectionery sunflower seeds would be preferred over hybrid oilseed cultivars which are difficult to dehull. The desolventized flours have an attractive white color which darkens on contact with moisture due to the presence of chlorogenic acid and other pigments. The removal of color-forming compounds with acidic butanol results in protein emulsification properties. Succinylated sunflower proteins show improved oil retention and foaming properties, but water absorption was not improved. Enzyme hydrolysis of the sunflower protein isolate will alter functional properties, depending on the degree of hydrolysis and method of enzyme inactivation. HVP products have excellent flavor profiles. Organoleptic properties can be improved substantially by extrusion-cooking and excellent fibers have been prepared by spinning techniques.

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EFFECTS OF CARBON-CHAIN AND PHENYL ISOMER DISTRIBUTION ON THE USE PROPERTIES OF LINEAR ALKYLBENZENE SULFONATE–A COMPARISON STUDY OF "HIGH" AND "LOW" 2-PHENYL LAS HOMOLOGS. K. Lee Matheson and Ted P. Matson, Technical Service Laboratory, Chemicals Research Division, Conoco Inc., PO Box 1267, Ponca City, OK 74603.

Use properties of the individual carbon-chain homologs of linear alkylbenzene sulfonate ranging from C_{10} through C_{14} of both the high 2-phenyl ($AlCl_3$ type) and low 2-phenyl (HF type) processes are examined. Foam stability tests are run on typical dishwashing liquids, and optimal carbon chain lengths are reported at a variety of water hardnesses. Comparisons are also made between phenyl isomer distributions. Blended homologs are tested to simulate typical commercial products. Comparisons of interfacial tensions show correlation with dishwashing tests. Detergency tests of individual homologs and blends thereof at high and low 2-phenyl isomer distributions are run on typical laundry product formulations at different water hardnesses.

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AN INTELLIGENT WASHING MACHINE FOR THE EVALUATION OF LAUNDRY DETERGENTS. James R. Trowbridge, Colgate-Palmolive Co., 909 River Road, Piscataway, NJ 08854.

A computer-controlled washer can be programmed to automatically evaluate a large number of washing compositions for soil removal. Variable amounts of as many as 6 different detergent components are added with metering pumps. A continuous roll of soiled cloth passes through a washer and past a reflectance meter onto a take-up reel. Washing action is provided by a vertical reciprocating shaft attached to a plate which rubs on the fabric while tension is maintained by a spring-loaded roller. The length of the wash, number of rinses and addition of components is controlled by the computer program. Upon completion of the wash and rinse cycle, the fabric is advanced about 10 cm. Washed areas appear as lighter colored bands on the fabric. In one mode of operation, a large factorial experiment is programmed in advance. After an initial calibration of metering pumps, the apparatus runs unattended. In another mode, the computer receives feedback from the reflectance meter and a simplex procedure is used to determine the direction of maximal cleaning. Following the execution of a small number of initially programmed washes, the computer selects the succeeding wash compositions.

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RELATIONSHIP OF NONPOLAR SOIL DETERGENCY WITH CLOUD POINTS AND SOLUBILIZATION RATES FOR ALCOHOL ETHOXYLATE SURFACTANTS. Herbert L. Benson, Shell Development Co., Westhollow Research Center, PO Box 1380, Houston, TX 77001.

Relationships between detergency at cool washing temperatures and alcohol ethoxylate properties such as ethylene oxide contents, cloud points, micelle or aggregate sizes and relative solubilization rates have been studied. Using blends of pure, homogeneous ethoxylates, optimal detergencies for nonpolar soils at 25 C have been observed at 4 mol ethylene oxide/mol alcohol, or ca. 10 HLB, over a C_{10} to C_{14} hydrophobe range. For each of these unbuilt systems, this optimum occurred at a cloud point near the ice temperature. Relative rates and capacities for paraffin solubilization, as measured via a dipping probe turbidimeter, have been found to increase greatly as cloud points of the systems decrease and approach the solution temperature. Such increases in solubilization rates appear to be related qualitatively to the above detergency results for the low cmc ethoxylate blends. Cloud point depression by addition of sodium sulfate also has been found to enhance detergency, particularly at low temperatures.

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HEAVY-DUTY LIQUID DETERGENTS. Jadwiga Palicka, Nordtend AB, Box 320 25, S-126 11 Stockholm, Sweden.

New European concentrated heavy-duty liquid detergents for household washing will be reviewed. The presentation covers ingredients and their functions, performance evaluation of detergency, ash content, graying and brightening effects. The main advantages over the current powder detergents for washing at 30, 40 and 60 C will be discussed particularly: stain removal, no necessity of prewashing, energy and time savings.

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IMPROVED PRODUCTIVITY OF A RADIOTRACER DETERGENCY METHOD BY INCREASED AUTOMATION. W.T. Shebs*, J.G. Rankin, C.F. Incaprera and K.H. Herndon, Shell Development Co., PO Box 481, Houston, TX 77001.

Productivity of a radiotracer detergency test method which generates several thousand samples per year has been substantially improved by automating record-keeping, data acquisition and report generation. A group of programs has been written to acquire large amounts of data from liquid scintillation counters, a γ counter and pH meters. The programs also maintain detailed records of each swatch, provide current status of all swatches entered into the system, and make all calculations necessary to generate final test results. A Burcon microcomputer operating in a time-sharing environment allows multiple users to perform laboratory operations simultaneously. The programs (written in PL/I) are all interactive and the terminal screen displays a list of possible responses at each step. These menus, combined with careful design of the screen displays, minimize the amount of operator training necessary and allow the occasional user to complete processing successfully. The amount of time required to complete data processing has been reduced by ca. 35% and the automating of record keeping and other tasks has further improved productivity and reduced turnaround time. A brief description of the component programs is included.

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CORRELATION BETWEEN THE COLORIMETRIC TRISTIMULUS METHOD (LAB) AND A METHOD USING RADIOTRACERS TO DETERMINE DETERGENCY. Héctor J. Sepúlveda* and Ricardo Castanedo, Fábrica de Jabón La Corona, S.A., Plan de Guadalupe #65, Casa 43, Santa María Ticomán, México 14, DF.

Soil was extracted from clothes belonging to workmen from fat-splitting and fatty acid distillation plants. The fat soil composition was determined by gas liquid chromatography. Using fatty acids of known components, a mixture was prepared at average percentages of the analyzed soil. To paste the soil, lanolin was used to obtain the standard soil which was divided into 2 parts: (a) one sample to which carbon black was added; (b) another to which labeled fatty acids were added with carbon-14 in the carboxyl group. Four labeled soils were tested with the following fatty acids: one with palmitic acid, one with oleic acid, one with linoleic acid and a mixture of all 3. Several woolen fabrics (2.5 g each) were soiled simultaneously under the same conditions as these with carbon black as well as for those containing radiotracers. The washing trials were done in a Terg-O-Meter under the following conditions: two 10-minute washes each, room temperature (20 C), 125 rpm, detergent solution concentration 0.3%, washing water hardness 150 ppm and bath relation 1:40 by wt. The removed, redeposited soil was evaluated in the first and second washes. Clothes containing carbon black were evaluated by reflectance technique using a Hunterlab Colorimeter. Meanwhile, the clothes treated with labeled soils were evaluated with a liquid scintillation counter using the channel-ratio method. The results were treated statistically, first supposing a dependency between the fat soil removal and the black carbon, after treating the 2 variables as if they were aleatories, thus calculating the correlation coefficients.

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WITHDRAWN

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BLEACHING AT COLD TEMPERATURES WITH SODIUM HYPOCHLORITE: INTERACTIONS OF CONCENTRATION, TIME, pH, AND TEMPERATURE WITH STAIN REMOVAL AND FABRIC STRENGTH. LoErna Palmer*, University of Kentucky at Lexington, and Charles Riggs, Texas Woman's University.

In response to recent concern for energy conservation regarding laundering of clothing and linens at lowered temperatures while maintaining adequate whiteness, this study investigated stain removal and fabric degradation actions of sodium hypochlorite bleach on wine- and tea-stained 100% cotton fabric. Cold temperatures of 5 and 25 C were studied in relationship to other temperatures and selected levels of concentration, bleach soak times and pH values. Optimal bleaching conditions giving acceptable levels of stain removal and retention of fabric strength were also determined. Blue and green reflectance readings were used to calculate whiteness values and percentage of stain removal values, whereas tensile strength measurements were used to determine fabric degradation. An "acceptable bleach treatment" category was established, having a minimum of 75% whiteness and 90% of original breaking strength. Thirty-nine percent of the 456 stained, bleached specimens occurred within this range. Various pH levels were not significant. However, a low concentration of 200 ppm available chlorine (recommended laundry wash level) was more satisfactory than a high concentration of 1,600 ppm (recommended stain removal level). An 8-fold savings in cost of bleach product would also be possible if low concentration was selected. Acceptable bleaching action occurred at all 4 temperatures. However, cold and warm temperatures each occurred twice as frequently as low-cold or hot temperatures. Acceptable bleaching at cold temperatures was therefore possible. Selecting cold temperatures would provide energy savings for the consumer, textile mill, or commercial laundry. Even though all bleach soak times proved acceptable under certain conditions, the 1-hr treatment was most effective. If bleaching must be done during the normal 8-15 min home laundry cycle, then a warm temperature of 45 C should be chosen. An extended or overnight (1-16 hr) bleach soak treatment was not damaging if a cold temperature of 25 C was selected.

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PERFORMANCE AND SKIN IRRITATION DUE TO SURFACTANTS CONTAINING ANIONICS IN COMBINATION WITH CATIONICS OR NONIONICS. Teruhisa Satsuki*, Seiichi Ohta, Osamu Okumura and Daini Saika, Lion Corp., No. 13-12,7-chome, Hirai, Edogawa-ku, Tokyo, Japan.

The detergency, foaming ability and skin irritation of anionic surfactants in combination with cationic, nonionic or amphoteric surfactants were estimated. Investigations were made on detergency and adsorption of binary surfactant systems containing anionic compounds by triglycerides. It was observed that, in cationic or amine oxide systems, LAS produced no synergistic effect, but AOS and AES produced high synergy. This detergency is correlated to the adsorption of the surfactant by triglycerides. We believe the soil adsorption of surfactants lowers the interfacial tension between soil and aqueous solution of surfactants, thus weakening the adhesive energy between soil and glass, thereby improving the detergency of the systems. Foaming ability, another important performance, is produced best by AOS and amine oxide systems. After studies on skin reactions, it was found that skin irritation or roughness correlates to the protein denaturation caused by anionic surfactants. This can be prevented by addition of cationic surfactants or amine oxides. These facts point to a new dishwashing detergent formulation which has high detergency and low skin irritation.

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STUDIES ON THE ADSORPTION OF DIALKYL DIMETHYL AMMONIUM CHLORIDE. Koichi Yamada, Kenji Yokoi, Osamu Okumura* and Daini Saika, Lion Corp., No. 13-12,7-chome, Hirai, Edogawa-ku, Tokyo, Japan.

Dialkyl dimethyl ammonium cloride (DADMAC) is widely used as fabric softener. We studied the adsorption state of DADMAC and effective factors of the adsorption on fabric. By X-ray and differential scanning calorimeter (DSC) analyses, the molecule of DADMAC was supposed to be adsorbed on the fabric as bimolecular layer or multimolecular layer when fabric was treated in aqueous dispersion of DADMAC. It has been well known that the effective factors of the adsorption of DADMAC on fabric are the temperature of the liquid, the liquid pH, the concentration of DADMAC, the hardness of water, the liquor ratio, kind of fabrics and mechanical power. In addition to these factors, it became clear from our study that the dispersed particle size of DADMAC was also a very effective factor. The finer the particle size, the higher was the adsorbing velocity on fabric. Fine-particle-size DADMAC aqueous dispersion, prepared by adding the suitable nonionic surface-active agent and hydrotrope under a certain shearing force, gave excellent softening and antistatic properties as well as good storage stability under a wide range of temperatures.

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THE CHEMISTRY OF LIPID HYDROPEROXIDES: DOES THE CHEMICAL DECOMPOSITION OF LIPID HYDROPEROXIDES ACT AS A MODEL FOR BIOCHEMICAL DEGRADATION? H.W. Gardner, USDA Northern Regional Research Center, Agricultural Research Service, 1815 N. University St., Peoria, IL 61604.

Lipid hydroperoxides are reactive compounds that decompose by a number of pathways. Usually, these reactions lead to a mixture of secondary products. The familiar free radical reactions of lipid hydroperoxides are initiated by the formation of either an oxy or a peroxy radical from homolysis of the hydroperoxide group. Rearrangement of oxy and peroxy radicals plays one of the most important roles in the formation of end-products. Such rearrangements result in formation of epoxides, cyclic peroxides and prostaglandin-like fatty acids. The mechanisms and pathways of radical rearrangement studied by use of chemical models will be reviewed. These studies will be correlated with the conversion of lipid hydroperoxides to similar fatty products in biological systems. Heterolytic reactions also can be involved in pathways to products. For example, secondary products derived from lipid hydroperoxides, such as epoxides, will solvolyze. Lipid hydroperoxides themselves will decompose by heterolytic processes. When linoleic acid hydroperoxide was treated by acids, among the products were epoxides with structural similarity to certain of the epoxides derived from oxy radical rearrangement (a detailed report of this work will be presented in another session). The possibility will be discussed that some of the epoxides obtained as products in biological systems

may arise from heterolysis of lipid hydroperoxides, rather than from homolysis.

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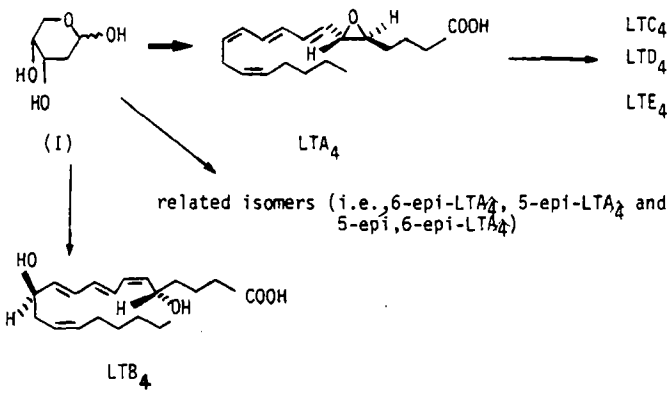
RECENT DEVELOPMENTS IN THE SYNTHETIC APPROACHES TO LEUKOTRIENES. Yvan Guindon*, Joshua Rokach, Robert Zamboni and C.K. Lau, Merck Frosst Laboratories, PO Box 1005, Pointe-Claire/Dorval, Quebec H9R 4P8, Canada.

Leukotrienes are recently identified natural products derived from arachidonic acid. These chemical "mediators" are implicated in allergic and inflammatory states. A stereospecific, comprehensive and chirally economical synthesis of LTA_4 (as LTD_4, LTC_4, LTE_4 and related isomers), as well as LTB_4 using the same commercially available chiral precursor, 2-deoxy-D-ribos (I), will be presented. Related isomers (i.e., 6-epi-LTA_4, 5-epi-LTA_4 and 5-epi,6-epi-LTA_4)



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BIOCHEMISTRY OF THE LEUKOTRIENE PATHWAY OF ARACHIDONIC ACID. Pierre Borgeat* and Bernard Fruteau De Laclos, Molecular Endocrinology Lab, Le Centre Hospitalier de l'Université Laval, 2705 Laurier Blvd., Quebec, Canada G1V 4G2.

Recent studies on the metabolism of arachidonic acid in leukocytes have led to the discovery of a novel family of bioactive compounds, the leukotrienes, named after their origin (leukocytes) and because of their structural characteristic, the conjugated triene. Arachidonic acid is initially transformed into the 5S-hydroperoxyicosatetraenoic acid (5-HPETE) in a lipoxygenase-type reaction. The 5-HPETE is then either reduced to the corresponding 5-hydroxy acid, or transformed into a labile allylic epoxy acid, the 5S,6S-oxido-7,9,11,14-icosatetraenoic acid (leukotriene A_4, LTA_4). LTA_4 is further metabolized to LTB_4, a 5S,12R-dihydroxy-6,8,10,14-icosatetraenoic acid, and to LTC_4, a product of the reaction glutathione with LTA_4, the 5S-hydroxy-6R-S-glutathionyl-7,9,11,14-icosatetraenoic acid. LTC_4 is sequentially transformed to LTD_4 and LTE_4 by enzymatic cleavage of the γ-glutamyl and glycyl residues. LTB_4 has potent proinflammatory and myotropic activities; LTC_4, D_4 and E_4, which are also very potent myotropic substances, were identified as the bioactive components of the Slow Reacting Substance of Anaphylaxis (SRS-A), and are considered important mediators of immediate hypersensitivity reactions. Various aspects of the biochemistry of the leukotriene pathway and the structure elucidation of SRS-A will be reviewed briefly.

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ACETYLENIC ACIDS AS INHIBITORS OF VARIOUS PATHWAYS OF ARACHIDONIC ACID METABOLISM. Barbara A. Jakschik, Philip Needleman and Howard Sprecher[a], Department of Pharmacology, Washington University Medical School, St. Louis, MO 63110, and [a]Department of Physiological Chemistry, Ohio State University, Columbus, OH 43210.

A series of acetylenic acids varying in chain lengths, as well as in number and position of triple bonds, was tested for their effect on arachidonic acid metabolism via the cyclooxygenase and 12-lipoxygenase in platelets and via the cyclooxygenase and 5-lipoxygenase in homogenates of rat basophilic (RBL-1) leukemia cells. With platelets, we found analogs that preferentially: (a) inhibited cyclooxygenase only; (b) inhibited the 12-lipoxygenase only; (c) inhibited both the cyclooxygenase and lipoxygenases; and (d) analogs which inhibited neither enzyme. There was a direct correlation between the rank order of potency of the acetylenic analogs to inhibit platelet cyclooxygenase and to suppress aggregation. On the other hand, analogs that inhibited the platelet 12-lipoxygenase only were very weak inhibitors of platelet aggregation. With RBL-1 cells, a number of trends which differentiate the 5-lipoxygenase from the cyclooxygenase were observed: (a) in general, the potency of the acetylenic acids to inhibit the 5-lipoxygenase increased with the carbon chain length up to 20 carbons; (b) a minimum of 3 triple bonds is necessary for the inhibitory action; (c) with the 20-carbon Δ8 and Δ6 acetylenic acids, activity decreased when the number of triple bonds increased from 3 to 4. These structure-activity relationships were not observed with the cyclooxygenase. The Δ4 acetylenic acids proved to be an interesting group of compounds. They did not inhibit the cyclooxygenase or 5-lipoxygenase, but were good inhibitors of SRS synthesis. These inhibitors provide potentially powerful tools for dissociating the functional significance of the different arachidonate metabolic pathways.

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PHARMACOLOGICAL ACTIONS OF LEUKOTRIENES. Pierre Sirois, Unité de Recherche pulmonaire, Faculté de Médecine, Université de Sherbrooke, Sherbrooke, P.Q., J1H 5N4, Canada.

Developments in the biochemistry of arachidonic acid have led to the discovery of a new series of metabolites called leukotrienes (LT) produced by the action of a C-5-lipoxygenase. Some of these lipids were shown to be the active components of SRS-A. Synthetic material made possible the systematic investigations of their pharmacological properties. LTA_4, LTB_4, LTC_4, LTD_4 and LTE_4 were shown to be stronger constrictors of guinea pig and human lung parenchymal strips than histamine. LT also contracted the human bronchus, the guinea pig trachea and ileum, and their effects were inhibited by FPL-55712. LTA_4 and LTB_4 did not induce a contraction of the guinea pig ileum. Whether LTA_4 and C_4 act on the LTD_4 receptor or need to be converted to LTD_4 requires further investigations. Rat and rabbit lung tissues were many times less sensitive to LT than guinea pig and human lungs. On the guinea pig parenchyma, the action of LTB_4 appeared to be mediated by the formation of TxA_2 and to interact with a specific receptor. Administration of LT in vivo caused bronchoconstriction and changes in blood pressure in guinea pigs. They were also shown to be vasoconstrictors and to increase vascular permeability in guinea pig skin. Apart from its strong myotropic activity, LTB_4 also appeared to possess definite properties for attracting, aggregating and degranulating leukocytes.

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LIPOXYGENASE, LIPID PEROXIDATION AND CELL PROLIFERATION. David G. Cornwell*, Nobuhiro Morisaki and Rao V. Panganamala, The Ohio State University, College of Medicine, 370 West 9th Ave., Columbus, OH 43210.

Polyunsaturated fatty acids inhibit cell proliferation with a number of cell lines in tissue culture. These cell lines include guinea pig medial cells, human fibroblasts, human fetal neural cells and a human glioma cell clone. The inhibition of cell proliferation is not correlated with prostaglandin biosynthesis. The fatty acids undergo lipid peroxidation in a time-dependent manner when they are incubated with the cells in culture. A variety of antioxidants inhibit either the biosynthesis of lipid peroxides or the breakdown of lipid peroxides to radicals. These antioxidants restore clonal growth and decrease the population doubling times for cells treated with polyunsaturated fatty acids. These studies support the classic definition of vitamin E as a cell proliferation factor. (Supported in part by research grant HL 11897 from the National Institutes of Health.)

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THE USE OF WIDE-LINE NMR IN BREEDING HIGH-OIL CORN. D.E. Alexander, University of Illinois, Department of Agronomy, S-110 Turner Hall, 1102 S. Goodwin Ave., Urbana, IL 61801.

Four samples of corn grain ranging from 4.6-14% oil were scanned by a Schlumberger 104 wide-line NMR in early October 1960 in the Moffett Laboratory of Corn Products Co. by T.F. Conway and S.A. Watson. The correlation between NMR values and percentage oil was 0.95+. Eight months later, they reported that oil in single maize kernels could be accurately measured. Wide-line NMR has been used since then in breeding programs at the University of Illinois. Approximately one million samples have been analyzed on the original PA-7, and an equal number on 2 PAT-20 units. Breeding research has been of 2 kinds: the development of high-oil populations by single-kernel phenotypic recurrent selection and the monitoring of oil content of new inbreds and their hybrids. A synthetic variety (Alexho) at the 21st cycle of selection possessed ca. 15% oil. Several other pools have undergone selection as well (Syn. D.O., Reid Yellow Dent, Iowa BS10). Three high-oil inbreds have been released to the seed trade (R802A [7%], R805 [9%], R806 [9%]). A hybrid with 6.5-7.0% oil is now being marketed. Recurrent selection for grain yield is now in its second cycle in Alexho Elite, a synthetic possessing both high oil (9%) and good combining ability for grain yield.

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PRACTICAL APPLICATION OF NMR SPECTROSCOPY IN THE DEVELOPMENT OF HIGH-OIL HYBRIDS OF SUNFLOW-

ER, *HELIANTHUS* SPP. W.S. Harada, Dahlgren & Co., 1220 Sunflower St., Crookston, MN 56716.

The identification of high-oil inbred lines of sunflower, *Helianthus annuus*, is greatly facilitated by use of the wide-line nuclear magnetic resonance (NMR) analyzer. The nondestruction of seed and the rapidity of the analysis have proven to be of greatest significance in a breeding program. The testing of breeder's seed uses as little as 6.5 mL of seed which is air-dried to ca. 10% moisture content. The experimental hybrids are tested using 130 mL of seed which is oven-dried at 150 C for 1 hr. The results of using NMR in the development of high-oil sunflower hybrids have been positive. Data indicate that an increase in oil content of 6% was attained in one cycle of selection for high-oil individuals of a population.

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DETERMINATION OF PERCENTAGE FAT IN CHOCOLATE AND CONFECTIONERY PRODUCTS BY WIDE-LINE NUCLEAR MAGNETIC RESONANCE. Denise Turato, Hershey Chocolate Co., 19 E. Chocolate Ave., Hershey, PA 17033.

The rapid determination of percentage fat by wide-line nuclear magnetic resonance (NMR) measuring the proton resonance of hydrogen atoms in a liquid phase is described. The method is applicable to a variety of chocolate and confectionery products whose matrices contain different types of fats and oils. Using various instrumental conditions, optimal operational parameters were established, providing a more exact separation of narrow liquid resonance from broad solid resonance. Compensation for the broad solid resonance of metallic iron was achieved by gate-width adjustment. Calibration of the NMR was performed using an aliquot of the same fat or oil contained in the sample. Samples were analyzed by signal integration. The positive bias associated with sample moisture levels >3% was adjusted by use of a correction factor in the calculation. The precision studies indicated relative standard deviations ranging from 0.1-0.8% absolute fat percentage. Accuracy studies comparing the NMR to 4 other fat methodologies demonstrated standard deviations ranging from ±.22-.37%. The measurement of percentage fat by wide-line NMR offers a rapid means of data generation for process control and the elimination of hazardous chemicals and problems associated with chemical disposal.

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THE DETERMINATION OF OIL IN A DRY FOOD MIX BY WIDE-LINE NMR. H. Fred Lewis* and Elpidio de la Teja, Thomas J. Lipton, Inc., Englewood Cliffs, NJ.

A method has been developed for quickly and accurately measuring the oil content of a dry food mix using wide-line NMR. This was accomplished by setting the NMR to respond to the oil proton decay signal rather than the water signal through an adjustment of the electronic gate width. The instrument was then calibrated using a dry food matrix containing known amounts of added oil from 0 to 20%. The calibration samples were sealed in high density polyethylene vials. This calibration curve, along with the NMR, were then used to determine the oil level in samples produced in a pilot plant blender and excellent correlation with the actual oil content was obtained.

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PRAXIS PULSED NMR: A SOUND OPTION FOR FULLY INTEGRATED SOLID FAT CONTENT MEASUREMENT. Jack H. Mellema*, Kraft, Inc. R&D, 801 Waukegan Rd., Glenview, IL 60025, Bryan L. Madison, The Procter & Gamble Co., Robert Manning, Glidden Durkee Foods, and John Whit, The Praxis Corp.

A method has been developed through an industry collaborative study for the determination of the solid fat content of vegetable oils and fats using the Praxis SFC 900 spectrometer. A calibration procedure was established for the instrument through the use of a series of tristearin in olive oil standards. The observed values for solids content were plotted against the known values for these standards. Corrected SFC values for each instrument were obtained using a fifth-order polynomial multiple linear regression equation. Repeated SFC analyses on 4 different sample types of fats were performed among laboratories to give standard deviations ranging from 0.4 to 1.1 over the 5 temperatures investigated. Correlation equations were developed to compare SFI by dilation and SFC by P-NMR. A correlation coefficient of 0.99 was observed.

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LIPIDS OF ARCHAEBACTERIA: EXTREME HALOPHILES, METHANOGENS AND THERMOACIDOPHILES. T.A. Langworthy, Department of Microbiology, School of Medicine, University of South Dakota, Vermillion, SD 57069.

The membrane lipids of archaebacteria differ from those of eukaryotic and prokaryotic cells by the presence of isopranyl glycerol ether lipids and the absence of fatty acid ester derived glyceride residues. The glycerol ethers are of 2 types, either diphytanylglycerol diethers or dibiphytanyldiglycerol tetraethers. The latter tetraether is the structural equivalent of 2 molecules of diphytanylglycerol ether which have been condensed head-to-head through the geminal ends of the phytanyl chains. Either or both glycerol ether structures may be present, depending on genera. The thermoacidophilic archaebacteria are more specialized in that the biphytanyl chains may contain 1-4 cyclopentyl rings which appears to be a response to the high temperatures for growth. Some archaebacteria, as a consequence of the tetraethers which span the membrane, appear to possess a membrane structure which exists as a lipid "monolayer" rather than the universally acknowledged lipid bilayer. Several of the diether-containing polar lipid structures have been well established. Knowledge of the variety of tetraether polar lipid structures, however, is still largely unknown, but both symmetrical and asymmetrical substitution of polar head groups has been established in some instances. Among neutral lipids, squalenes and hydrocarbons appear to be universal, although alkylbenzenes have also been detected in thermoacidophilic archaebacteria. The structure, function and biogeochemical implications of archaebacterial lipids will be considered.

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ETHER LIPIDS OF ANAEROBIC BACTERIA. Howard Goldfine, University of Pennsylvania, Microbiology, School of Medicine, 209 Johnson Pavilion, Philadelphia, PA 19104.

Because anaerobic bacteria are diverse phylogenetically, no single description of their lipids is possible. Many species of clostridia contain 1-O-alk-1'-enyl 2-acyl phosphoglycerides (plasmalogens). These ether lipids have also been found in anaerobic spirochetes, gram-negative rods and cocci. In species containing plasmalogens, these lipids are reported to represent from 15 to nearly 100% of the total phospholipid. The polar head groups and other features of their structures vary considerably. Studies on the phase behavior of ether lipids in anaerobes has been aided by the ability of certain clostridia to utilize exogenous fatty acids when endogenous synthesis is inhibited. Highly elaidate-enriched plasmenylethanolamine and an unusual glycerol acetal of this plasmalogen, enriched in elaidate or oleate, have been studied by differential scanning calorimetry and with fluorescent probes. The results of these studies will be reviewed. The adaptation of microorganisms that contain ether lipids to variations in growth temperature may involve changes in: (a) the degree of unsaturation and chain length of the acyl and/or alkenyl chains, (b) the polar head group composition, and (c) the content of plasmalogens. Our studies with several anaerobes have revealed different patterns of acclimatization, which will be described. Although the biosynthesis of plasmalogens in higher organisms is well known, it is clear that strictly anaerobic bacteria cannot use the oxygen-dependent animal pathway, which proceeds through dihydroxyacetone phosphate and saturated ether lipid intermediates. Studies with *Clostridium butyricum* suggest that the synthesis of plasmalogens is kinetically closely linked to the synthesis of the corresponding diacylphospholipids in vivo. Work in progress on the anaerobic pathway will be described.

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MEMBRANE LIPIDS OF YEASTS AND FUNGI. James B.M. Rattray, Department of Chemistry, University of Guelph, Guelph, Ontario N1G 2W1, Canada.

The general classes of lipids occurring in the membranes of yeast and fungi are typical of those present in other eukaryotic cells. Thus, the several membranous systems provide the major location for the polar lipids and sterols which occur in association with varying quantities of protein. The protein:lipid ratio can range from 0.66 to 2.1 and varies with the particular membrane and conditions of growth of the microorganism. Phosphatidylcholine, phosphatidylethanolamine, phosphatidylserine, phosphatidylinositol (PI) and diphosphatidylglycerol generally account for the bulk of the membrane phospholipids, although under certain circumstances, other phospholipids may predominate. Both sterol and steryl esters occur as membrane components resulting in molar ratios of sterol:phospholipid ranging from 0.4 to 0.8. Depending on growth conditions, the sterol component may be partially replaced by squalene. A variety of sterols have been found in yeast with ergosterol being the major sterol of most species. The fatty acid component of the different membrane lipids generally has a major composition of C_{16} and C_{18} saturated and unsaturated acids; the degree of unsaturation is governed by species and growth conditions. Proliferation of specific membranous systems can be obtained under a variety of conditions. Studies, in particular, have been made on yeast grown under semi-anaerobic conditions, or exposed to trace quantities of potentially carcinogenic hydrocarbons, or using methanol as the sole source of carbon. Analyses have revealed the presence of a variety of membraneous systems showing a wide range of compositional differences, including the major occurrence of PI in methanol-assimilating *Hansenula polymorpha* and alterations in the phospholipid, sterol and squalene components of *Saccharomyces cerevisiae*

exposed to benzo(α)pyrene. Such systems can provide an additional approach to the study of membranes and allow deductions to be made on the interrelationships existing among lipid composition, membrane structure and biological activity.

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ARSENOLIPIDS OF ALGAE. A.A. Benson* and R.V. Cooney, Scripps Institution of Oceanography A-002, LaJolla, CA 92093.

All aquatic plants detoxicate arsenate. This capability is essential in low-phosphate environments where natural arsenate levels are comparable. Detoxication proceeds via successive reductions and methylations to trimethylarsine from which trimethylarsoniumlactate is produced. It is phosphatidylated to yield phosphatidyltrimethylarsoniumlactate. This phospholipid and its lyso derivative are rapidly degraded in the membrane-associated depuration process. Glycerophosphoryltrimethylarsoniumlactate occurs in all algae, occasionally as a major water-soluble constituent. In most algae, however, another related water-soluble arsenical accumulates in greater concentration. It is anionic and appears to contain sulfoquinovose in glycosidic linkage to trimethylarsoniumlactate. *Dunaliella* species possess 2 arsenolipids and are unique in producing the highest percentages of lipid from radioarsenate. The second arsenolipid appears to not be a phospholipid. Its molecular weight is high and it contains polyisoprenoid components. The arsenic content of aquatic algae is low, even in waters where phosphate:arsenate ratios are unity. Their rapid metabolism of radioarsenate and production of membrane lipid suggests function of a mechanism for arsenic depuration by extramural removal of trimethylarsonium groups from the membrane lipid bilayer. Antimony is similarly transformed to membrane lipid.

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LIPIDS OF DIATOMS. M. Kates, Department of Biochemistry, University of Ottawa, Ottawa, Ontario K1N 9B4, Canada.

The lipids of both marine and freshwater diatoms are unusual in that they contain high proportions of sulfur-containing polar lipids which can be detected by labeling with ^{35}S. Apart from the ubiquitous plant sulfolipid, sulfoquinovosyldiglyceride, 3 novel sulfolipids have been identified: (a) phosphatidylsulfocholine, a sulfonium analog of lecithin that is the major polar lipid component and completely replaces lecithin in some diatoms; (b) 1-deoxyceramide sulfonic acid in which the fatty acid group is mostly *trans*-3-hexadecenoic acid; and (c) a sterol sulfate ester, 24-methylene cholesterol sulfate. The novel sulfolipids have been found to occur in all membrane fractions examined (chloroplasts, plasma membrane or endoplasmic reticulum). Evidence will be presented showing that the sulfocholine moiety of sulfonium analog of lecithin is derived from methionine and that the deoxyceramide sulfonic acid is biosynthesized from cysteine. The virtual absence of nitrogenous base containing polar lipids and their replacement by sulfolipids in diatoms may perhaps be explained by their utilizing methionine and cysteine, rather than serine, for biosynthesis of their membrane polar lipids.

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MEMBRANE LIPIDS OF PROTOZOA. Guy A. Thompson, Jr., Department of Botany, University of Texas, Austin, TX 78712.

Protozoa offer the lipid chemist a number of interesting prospects. These range from the utilization of phytoflagellates such as *Dunaliella* for the commercial production or carotenoids and glycerides to the application of ciliates as experimental model systems for basic metabolic research. They have been widely exploited for research, because the structure and lipid metabolism of protozoan cells are generally quite similar to cells of higher plants and animals, including man. Protozoa quickly respond to massive dietary lipid supplements or the imposition of extreme temperatures or salinities in a manner that can be conveniently studied and then interpreted to explain the reactions of more complex organisms to a similar stress. This is exemplified by studies of acclimation to low temperature by the ciliate *Tetrahymena pyriformis*. The immediate effect of chilling temperatures is to stimulate increased fatty acid desaturase activity. The resulting changes in lipid composition can be detected within 15 min in *Tetrahymena* microsomal membranes. However, movement of the modified lipids to certain other parts of the cell is quite slow. As the altered lipids arrive at various intracellular membrane destinations, they have a marked fluidizing effect on the membrane involved. Indeed, membrane fluidity increases too much and too rapidly in some cases to be explained simply by the initial modest increase in phospholipid fatty acid unsaturation. A detailed study by combined gas chromatography-mass spectrometry of diglyceride tert-butyldimethylsilyl ethers derived from individual membrane phospholipids revealed an unexpectedly high degree of low-temperature-induced retailoring of phospholipid molecular species to produce new combinations of preexisting fatty acids. Subtle compositional changes of this type, which escape detection by routine fatty acid analysis, can be of great physiological importance.This example illusatrates the new insights which can be gained through the use of simple organisms as model systems.

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TOXICOLOGICAL ACTIVITIES OF MYCOTOXINS. Timothy D. Phillips, Department of Veterinary Public Health, Texas A&M University, College Station, TX 77843.

Biochemical mechanisms involved in the toxic actions of mycotoxins are important. The best understood of these toxic agents are the aflatoxins, a closely related group of coumarin metabolites which are biosynthesized by species of *Aspergillus* fungi. The aflatoxins have invoked much concern about fungal toxins because of their potential as carcinogenic agents and because of their occurrence in foodstuffs designed for human consumption as well as their occurrence in human tissues. It is important to realize, however, that other mycotoxins, such as rubratoxin B, ochratoxin A, citrinin, patulin and penicillic acid, also are of toxicological importance. The simultaneous occurrence of 2 or more mycotoxins in foods and feeds is receiving increasing interest because of their potential for toxic interaction in combination. Moreover, mycotoxins may be one of the environmentally important multicausal factors involved in a variety of human and animal diseases. Biological and toxicological activities of mycotoxins are numerous and vary markedly according to target specificity. Data are reported which indicate that several lactone-containing mycotoxins exert a cellular action through disruption or alteration of membrane transport processes by reaction at accessible membrane sulfhydryl receptors regulating phosphorylation of the transport enzyme.

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HALOGENATED HYDROCARBONS IN HUMAN TISSUE—BIOLOGIC AND TOXIC EFFECTS. S. Safe*, L. Safe and L. Robertson, Department of Veterinary Physiology and Pharmacology, College of Veterinary Medicine, Texas A&M University, College Station, TX 77843, and A. Parkinson, J. Gyorkos, M.A. Campbell and S. Bandiera, University of Guelph, Guelph, Ontario N1G 2W1, Canada.

Halogenated hydrocarbons and aryl hydrocarbons are widely used in industry and agriculture as flame retardants, hydraulic fluids, dielectric fluids and pest control agents. Most of these compounds are highly lipophilic and resistant to chemical and ecological breakdown and have been identified in all environmental matrices including fish, wildlife, human blood, adipose tissue and breast milk. The halogenated hydrocarbons most frequently identified in human tissues include DDT and its metabolites, the isomeric hexachlorocyclohexanes, dieldin, heptachlor epoxide, nonachlor, oxychlordane, hexachlorobenzene and numerous polychlorinated biphenyl (PCB) isomers and congeners. Although the toxicology of the individual pollutants has been reported, very little data are available on the effects of the halogenated hydrocarbon mixtures identified in human tissues. We have recently reported the synthesis of the major PCB congeners identified in human tissue and will discuss the biochemical toxicology of "reconstituted breast milk PCB." (Sponsored by Health and Welfare Canada, The National Institutes of Health [1 RO1 ESO 2798-01], The Texas Agricultural Experiment Station and the Natural Sciences and Engineering Research Council of Canada.)

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EFFECTS OF STRUCTURE ON THE ACTIVITY OF POLYBROMINATED BIPHENYLS (PBB) AS MICROSOMAL ENZYME INDUCERS. L.W. Robertson*, Department of Veterinary Physiology and Pharmacology, College of Veterinary Medicine, Texas A&M University, College Station, TX 77843, A. Parkinson, Hoffmann-La Roche, Inc. and S. Safe, Texas A&M University.

FireMaster BP-6, a mixture of polybrominated biphenyl (PBB) isomers and congeners, is a widespread environmental contaminant in the state of Michigan. The industrial PBB mixture is highly lipophilic and is routinely quantitated in human adipose tissue and breast milk. In order to evaluate this complex mixture, the effects of structure on the activity of synthetic PBB as microsomal enzyme inducers was studied in the immature male Wistar rat. Using enzymic assays and ligand-binding measurements, PBB congeners were classified as phenobarbitone (PB)- or 3-methylcholanthrene (MC)-type inducers of cytochrome P-440-dependent monooxygenases. Important qualitative differences in the modes of induction exist between PBB and their chloro analogs. Where analogy exists, PBB are, in general, the more potent inducers. The structure-activity rules for PBB as PB-type inducers are as yet unresolved. PBB with at least 1 *meta* and 2 *para* bromines are MC-type inducers of cytochrome P-448, whereas PCB require at least 2 *meta* and 2 *para* chlorines for this activity. PBB which are mono or di *ortho* derivatives of the MC-type inducers may be mixed (PB + MC)-type inducers. (Sponsored in part by the Natural Sciences and Engineering Research Council of Canada.)

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POTENTIATION OF HALOALKANE-INDUCED HEPATOTOXICITY BY KETONES AND KETOGENIC CHEMICALS. Gabriel L. Plaa, Département de pharmacologie, Faculté de médecine, Université de Montréal, C.P. 6128, "A", Montréal, Québec, Canada H3C 3J7.

Chloroform and carbon tetrachloride are potent hepatotoxicants. The injury is induced by reactive metabolites generated by the mixed-function oxygenase system. In recent years, it has been shown that the liver injury can be potentiated in animals previously exposed to certain ketones (acetone, methyl ethyl ketone, methyl *n*-butyl ketone, 2,5-hexanedione, chlordecone) or ketogenic chemicals (isopropanol, 1,3-butanediol, *n*-hexane, alloxan). The potentiation is dose- and time-dependent. Such a toxic interaction has been documented in humans exposed to isopropanol and carbon tetrachloride in an industrial setting. In animals, the potentiation results in a lateral shift of the haloalkane dose-response curve and a lowering of the no-effect threshold level. The severity of the liver injury is also augmented. Regarding the biological mechanisms involved in these interactions, enhanced formation of reactive metabolites seems to play a major role. However, there are indications that the hepatocellular organelles may also be rendered more susceptible to attack by the reactive metabolites.

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COMPARATIVE TOXICITY AND PHARMACOKINETIC BEHAVIOR OF THREE TETRACHLOROBENZENE ISOMERS IN THE RAT. D.C. Villeneuve* and I. Chu, Environ. Contaminants Section, Environmental Health Centre, V.E. Valli, Dept. Pathology, Univ. of Guelph, and V.E. Secours and G.C. Becking, Environmental Health Centre, Room 319, Tunney's Pasture, Ottawa, Ontario K1A 0L2, Canada.

Tetrachlorobenzenes (TCB) are chemicals that have had a variety of industrial applications and are demonstrated environmental contaminants. This study was initiated because of the paucity of toxicity data on these chemicals and concern over their potential health effects. Groups of male and female Sprague-Dawley rats were fed 1,2,3,4-, 1,2,4,5- or 1,2,3,5-TCB in their diets at levels of 0, 0.5, 5.0, 50 or 500 ppm for 90 days. Growth rate and food consumption were not affected by any of the 3 isomers. No treatment-related deaths were observed. A number of toxic changes were demonstrated in rats fed 1,2,4,5-TCB at the 2 highest dose levels. These included hepatomegaly, nephromegaly, increased serum cholesterol and hepatic microsomal aniline hydroxylase and aminopyrine demethylase activities. In contrast, none of these changes was found in rats treated with 1,2,3,4- and 1,2,3,5-TCB. Dose-dependent increases in severity and prevalence of histological changes were observed in the thyroid, kidney and liver of the treated animals. Changes which were produced by 1,2,4,5-TCB were more severe than those of the other 2 isomers. There was also a difference in toxic response between the 2 sexes with the males being more susceptible than the females. In a separate pharmacokinetic study, male rats were given, by gavage, single doses of each of the three ^{14}C-labeled TCB at 1 mg/kg or 10 mg/kg in corn oil and monitored for 7 days. 1,2,4,5-TCB was eliminated at a much slower rate and accumulated in tissues to a higher extent than the other 2 isomers. These data suggest that the difference in the toxicity of the 3 TCB isomers could be explained, in part, by their pharmacokinetic behavior.

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THE *Ah* RECEPTOR: AN INTRACELLULAR SITE MEDIATING THE BIOLOGICAL EFFECTS OF SMALL LIPOPHILIC XENOBIOTICS. Allan B. Okey, Division of Clinical Pharmacology, The Hospital for Sick Children, 555 University Ave., Toronto, Ontario M5G 1X8, Canada.

The risks associated with exposure to environmental chemicals ("xenobiotics") are more easily assessed when one knows the specific mechanisms by which foreign chemicals interact with biological systems. Recently we have identified and characterized a cellular protein, the *Ah* receptor, which specifically binds a number of highly toxic and carcinogenic lipophilic xenobiotics. Initially, the *Ah* receptor is located in the cytoplasmic compartment of the cell. After xenobiotic ligands bind to the receptor, the ligand receptor complex migrates into the cell nucleus. The principal function of the *Ah* receptor is to induce the synthesis of cellular enzymes (mostly cytochrome-P-450) which metabolize a wide variety of lipophilic substances. Induction of cytochrome-P-450 is especially high in the liver of mammals. The induced cytochromes generally function to "detoxify" foreign lipophilic chemicals, but in the process of metabolism, P-450 can generate chemically reactive (electrophilic) intermediates which may cause cell death, mutations or cancers. Substances metabolized by the induced cytochrome-P-450 include polycyclic aromatic hydrocarbons (e.g., benzo(*a*)pyrene; benz(*a*)anthracene), polychlorinated and polybrominated biphenyls, nitrosamines, N-acetylarylamines, terpenes and most lipophilic drugs. Many of these compounds are toxic only after "metabolic activation" by cytochrome-P-450. Chemicals which bind to the *Ah* receptor with highest affinity (and hence are potent inducers of cytochrome-P-450) include polychlorinated dibenzo-dioxins (e.g., 2,3,7,8-tetrachlorodibenzo-*p*-dioxin, "TCDD") and dibenzofurans, polycyclic aromatic hydrocarbons, PCB and PBB. As yet, no "normal" physiologic substance from within the animal is known to bind to the *Ah* receptor. Virtually all chemicals which bind to the receptor with high affinity are highly toxic and/or carcinogenic. Binding of xenobiotics to the *Ah* receptor appears to be an important part of the mechanism by which xenobiotics cause toxicity, but the exact nature of the toxicity response is not yet known.

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THE LONG-RUN PRICE OUTLOOK FOR FATS AND OILS. Ed Fryar, U.S. Department of Agriculture, Room 212, GHI Building, 500 12th St., SW, Washington, DC 20250.

Current and anticipated market conditions between now and 1985 indicate that the price of most fats and oils will generally remain below the levels of the 1970s. This outlook is based on the assumption that supply will continue to grow at about the current rate and that there will be a slight slowdown in the growth of demand. The major factors affecting supply will be the number of animals slaughtered in developed countries, the relative profitability of soybeans and corn in the U.S., and the number of palm and coconut trees in Southeast Asia. On the demand side, major influences will likely be the growth in per capita income in developed countries, worldwide growth in population, and the number of animals fed in North America and Western Europe.

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SYNTHETIC FATTY CHEMICALS IN THE 1980s: THE OUTLOOK FOR OLEFIN FEEDSTOCKS. Thomas Gibson, SRI International, 333 Ravenswood Ave., Menlo Park, CA 94025.

Production of synthetic fatty chemicals will remain highly dependent on the supply of ethylene, for which U.S. demand will increase at an average 3.5-5% annual rate during 1980-90. Approximately 5% of the 1980 ethylene consumption of 12.2 million metric tons (27 billion pounds) was converted to alcohols, acids, olefins and derivatives that compete with comparable products from natural sources. Future choice between natural or synthetic products will depend on the relative escalating cost of ethylene produced from steam cracking of natural gas liquids or petroleum-derived naptha and gas oil. Even with the rapid growth in ethylene from ethane in Canada, the Middle East and Southeast Asia, additional domestic capacity will likely be required to meet 1990 demand. Demand for linear detergent alcohols will increase 2.5-3% annually during 1980-85, and additional synthetic production will be concentrated in companies with highly integrated positions from olefins to alcohols and their derivatives. Production of linear plasticizer range alcohols from α-olefins will likely decline in the face of competition from alcohols derived from less expensive propylene and butylenes. Synthetic fatty acids, especially the C_5-C_{11} range, provide a brighter outlook and can be produced intentionally without concern for marketing of by-products. Synthetic fatty chemicals will remain a small factor within olefins markets but will continue to compete economically with chemicals from fats and oils.

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FATTY ALCOHOLS: NATURAL OR PETROCHEMICAL FEEDSTOCK IN THE 1980s? E.C. Leonard, Humko Chemical, PO Box 125, Memphis, TN 38101.

Fatty alcohols may be produced from tallow- and coconut-oil-based fatty acids and fatty methyl esters ("natural" feedstocks), or from ethylene. Fatty alcohols have progressed through 3 precursor category generations since World War II—natural, petrochemical (ethylene) and, most recently, natural once again. The projected 1980s fatty alcohol feedstock situation is discussed based on macroeconomic factors that are expected to prevail throughout the decade.

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CRAMBE—POTENTIAL SOURCE OF INDUSTRIAL CHEMICALS. James L. Fowler* and Koert J. Lessman, Box 30, Department of Agronomy, New Mexico State University, Las Cruces, NM 88003.

Crambe (*Crambe abissinica* Hochst), a promising new oilseed crop, is one of the richest known sources of erucic acid which makes up 55-60% of the seed oil glycerides. Traditionally, rapeseed oil has been the source of erucic acid and oil containing erucic acid for American companies. The current trend in those countries producing rapeseed, however, is the development of rapeseed varieties low in erucic acid with improved nutritional qualities of the oil as a food. This has increased the importance of crambe as a domestic

source of oil high in erucic acid for industrial purposes. Crambe is also a substitute for petrochemical raw materials for the organic chemical industry. For example, in the lubricant product area, oxidative cleavage of crambe oil hydrocarbon chains gives pelargonic acid and dibasic (azelaic and brassylic) acids. From these cleavage products, liquid esters of the types used as synthetic lubricants and functional fluids can be made. Intact crambe oil has proved quite useful as a mold lubricant in the continuous casting of steel and, if its price were competitive, could likely replace mineral oil in a variety of other lubricant applications, e.g., in cold-rolling steel and manufacture of textiles. A straightforward chemical transformation converts fatty acids from hydrolysis of crambe oil into liquid wax esters that may be useful in making high-pressure lubricant additives. Two nylons (13 and 1313), which contain repeating units that have longer uninterrupted polymethylene chains than other nylons, can be made from crambe oil. Thermosetting resins have been made from azelaic and brassylic acids which, as indicated, can be produced from crambe oil. A variety of plasticizers and an excellent slip and antiblocking agent for plastic films are among the plastic additives that can be made from crambe oil. Simple hydrogenation converts crambe oil into a relatively hard wax that may be suitable for commercial applications ranging from cosmetics to polishes and waxes.

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HIGH-MOLECULAR-WEIGHT AMINES: NATURALLY OR PETROCHEMICALLY DERIVED. R.A. Reck, Armak Company, 300 S. Wacker Dr., Chicago, IL 60606.

A very large variety of high-molecular-weight amines can be produced from natural feedstocks such as fats and oils or from petroleum feedstocks such as synthetic acids, alcohols, olefins or ethylene derivatives. When crude oil was low in price, the routes from this feedstock were more financially attractive. At the $34/barrel price, this situation is different. Various routes to amines from petroleum sources and natural fats and oils will be described and raw material parameters will be given. Raw material costs, along with ancillary feedstocks, will be given with the objective of evaluating the economic advantages of each feedstock.

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Not available at press time.

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PROVIDING LUBRICITY IN FOOD-FAT SYSTEMS. Terry R. Bessler* and Frank T. Orthoefer, A.E. Staley Manufacturing Co., Building #63–2200 E. Eldorado, Decatur, IL 62525.

Lubricity, in particular mouth feel, is an important factor in production of vegetable oil bases for product formulations. Certain functional characteristics are necessary for good texture at various temperatures. These characteristics are dependent on degree of unsaturation, fatty acid distribution, and degree of geometrical isomerization during processing. Proper selectivity and activity of hydrogen catalysts used in hardening of the oils are essential. Sufficient solid fat content must be balanced by necessary oxidative stability. Products discussed include salad oils, frying oils, pourable and spoonable dressings, filled dairy products, margarines and bakery shortenings. Past, present and future industry technology will be evaluated for each type of food-fat product. Customer needs have greatly affected the course of research in this area.

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FAT AND OIL SYSTEMS PROVIDING LUBRICITY AND STRUCTURE. Frank R. Kincs, Bunge Edible Oil Corp., PO Box 192, Kankakee, IL 60901.

This paper discusses food systems using fats and oils to achieve the dual functions of lubricity and structure. Specific applications in bread and rolls, pie crust, puff pastry and danish, as well as peanut butter stabilization, are discussed. Functionality in each application is related to solid fat index, consistency and, ultimately, composition.

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FAT AND OIL SYSTEMS PROVIDING LUBICITY AND AERATION. Edward J. Campbell, ADM Refined Oils, PO Box 1470, Decatur, IL 62526.

Specific product application of industrial shortenings and margarines for the production of cakes, cake mixes, cookies and biscuits require fat and oil systems with functional characteristics of lubricity and aeration. To provide this functionality, we will look at product formulation and processing treatment. Crystal structure and emulsifiers perform a major role in finished product performance. Type of source oil, hydrogenated stocks, esterification and blends of base stocks, both soft and hard fractions, necessary for suitable crystal structure and plastic range are given. Plasticizing conditions and tempering requirements and their effects on product quality and performance are reviewed. The types and quantities of suitable emulsifers, both single and multiple systems, and their effect in finished, baked foods is shown. Mixing and creaming properties and aeration of all-purpose plastic cake shortenings and margarines, as well as fluid, pumpable liquid shortenings, are a necessary functional characteristic. Retail shortening and margarine development and formulation as related to lubricity are presented.

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FAT AND OIL SYSTEMS PROVIDING LUBRICITY, STRUCTURE AND AERATION. Alexander E. Thomas III, Durkee Foods Division–SCM Corp., Dwight P. Joyce Research Center, PO Box 8827, Strongsville, OH 44136.

Fats, oils and fatty derivatives are important constituents of most foods. The functional role of these lipids is determined by physicochemical properties intrinsic to specific molecular compositions. The relationships among composition, properties and functional characteristics are discussed for products for which the functional characteristics are dependent on lubricity, structure and aeration. Such products typically include ice cream, mellorine, whipped cream, whipped topping, icings and fillings. The evolutionary development of fats, oils and fatty derivatives for these formulated foods is described and the driving forces to these evolutionary changes are discussed relative to technology and consumer need. An attempt is made to predict possible future advances in technology applicable to formulations which provide lubricity, structure and aeration.

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FAT AND OIL SYSTEMS PROVIDING LUBRICITY, STRUCTURE AND MOISTURE BARRIER. Fred R. Paulicka, Durkee Foods Division–SCM Corp., Dwight P. Joyce Research Center, PO Box 8827, Strongsville, OH 44136.

Fats, oils and certain fatty derivatives comprise an important class of food ingredients. The functional characteristics provided or imparted to end-use food products by these ingredients depend on their physical and chemical properties. Lubricity, structure and moisture barrier properties are typical of important functional characteristics imparted to food products by these ingredients. The relationships between the composition and physical properties of ingredients and their functional characteristics are discussed. Emphasis will be placed on ingredients such as hard butters, emulsifiers and speciality oils and their application to provide lubricity, structure and moisture barriers in finished confectionery, frozen food and coated fresh or dried fruit. The historical development of fatty ingredient technology as it relates to market or customer needs is presented. Potential future developments in ingredient technology to provide lubricity, structure and moisture barriers are also discussed.

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SUNFLOWER DEVELOPMENT IN FRANCE. E. Chone and G. de la Taille, CETIOM, 174, ave. Victor-Hugo, 75116 Paris, France.

Sunflower cultivating areas have increased by 4-fold since 1977–from 37,000 ha to 155,000 ha. The high increase in sunflower plantings went along with production improvement, which led to increased production during the last crop year–6 times higher than in 1977 (385,000 tons vs 67,000 tons). Sunflower crops are clustered essentially in a crescent-shaped area from the center of France (Berry) to the southwest, through Aquitaine, where 85% of the sunflower crop is located. There were both technical and economic reasons for developing sunflower as a crop. Dry conditions during fall 1978 had forced Western producers to cultivate sunflower in their best lands instead of winter rape, which was unable to reach the emergence stage. Thus, many producers from these areas experimented with this crop. In view of the promising results obtained and a better understanding of cultural techniques developed by the CETIOM, greater areas were taken, especially from corn, and put into sunflower production. This opportunity was only possible thanks to the considerable amount of research done for many years. We shall emphasize again, in particular, that thanks to the simultaneous use of the male cytoplasmic sterility discovered by Leclercq (INRA) and mildew-resistant sources from the U.S., breeders could provide producers with hybrids, which were homogeneous, mildew-resistant and better performers. Without these mildew-resistant hybrids, sunflower growing would not be possible in France. Furthermore, the development of adequate techniques, especially for weed control and second ploughing of the crop, required several years of experiments by CETIOM. Sunflower has a very strong demand on the market because of the qualities of its oil which is highly appreciated all over Europe–a market which has been greatly fostered by the EEC policy. As a matter of fact, a Community regulation warrants that producers will receive a minimal selling price. Now, for several years, parity rates of sunflower reference prices in

comparison with those of cereals have always been more favorable to sunflower. More and more attractive prices combined to yields are increasingly considered as satisfying have led to interesting margins for producers. That is all the more so that direct costs linked to sunflower cropping are relatively slightly modified by the general cost increase and remain low (little nitrogenous fertilizer, few treatments and reduced drying costs).

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APPLICATIONS OF SUNFLOWER OIL. Richard H. Purdy, Richard H. Purdy, Inc., Novato, CA 94947.

Sunflower oil has had successful application in the manufacture of salad oils, dressings and margarines. The advantages and problems associated with its use in the edible oil industry will be considered. Further potential application may include use as a valuable substitute for nondairy fats in the food industry.

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THE INCREASING CONSUMPTION OF SUNFLOWER EDIBLE OILS AND MARGARINE IN FRANCE: ECONOMICAL, INDUSTRIAL AND NUTRITIONAL REASONS. Jean Paul Helme, Lesieur Cotelle & Associes, 122, ave. du Gl Leclerc, 92103 Boulogne-Billancourt, France.

We shall discuss consumer trends in France for these last 10 years for edible oils, as well as for spreadable margarines. We shall introduce studies concerning the physical refining as applied to sunflower oil, as well as the comparison of the different winterization processes, regarding yields. The physicochemical standards of the neutralized-bleached-deodorized (NBD) oils thus obtained will be explained. We will emphasize the fatty acid composition variations. Finally, we will note the well known nutritional advantage in preventing cardiovascular diseases (CVD). We will present studies dealing with the use of polyunsaturated edible oils in deep-fat frying.

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EVALUATION OF EXTRACTIVE CONTACT UNITS FOR OIL EXTRACTION FROM DEHULLED SUNFLOWER SEEDS. L. Tranchino and F. Melle*, Assoreni-Anfa, 00015 Monterotondo, Rome, Italy.

The efficiency of an extractive system generally depends on factors such as kinetic, thermodynamic and technological parameters. Each of these factors separately affects the extractive effectiveness, although the over-all result depends on their interaction. In this work, various simple models of solid-liquid contact apparatus are derived to clarify this interaction. This analysis is applied to the extraction of lipids with hexane from dehulled sunflower seeds. Experimental results obtained with this system, using different extractors, are also presented. The comparison of experimental and predicted data provides preliminary indications for the optimization of the extraction system. These results were obtained on a pilot plant built and operated by Assoreni.

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ALMOST COMPLETE DEHULLING OF HIGH-OIL SUNFLOWER SEEDS. L. Tranchino*, F. Melle and G. Sodini, Assoreni-Anfa, 00015 Monterotondo, Rome, Italy.

An almost complete dehulling (hull residue < 3%) of sunflower seeds, before oil extraction reduces to a minimum both the transfer of pigments from the hull to the flour and the content of fiber in the finished product intended for human consumption. The results of previous investigations on high-oil sunflower seed dehulling have put forward the existence of many technical problems and generally low yields. In this paper, the results of our work on the dehulling of high-oil seeds with an air jet impact huller are presented. The effectiveness of dehulling has been measured as a function of the characteristics of the seed (e.g., variety, moisture) and of the operative parameters (e.g., impact velocity). The optical analysis of the impact of the seeds on the target was also done using high-speed cinematography (about 8,000 frames/sec) to have a better view of the phenomenon and to measure the parameters of energy involved. It appears that the use of proper seed momentum, which is function of the characteristics of the seed, can allow the selective hull breaking without kernel breakage. On the basis of these findings, the optimal conditions for higher oil sunflower seed dehulling were identifed. However, in order to obtain almost complete hull-free kernels, it is necessary to separate the unhulled seeds, the hulls and the kernels obtained from the dehuller. The unhulled seeds may then be recycled to the same or to a different dehuller. Following these guidelines, an integrated dehuller-separator system which produces nearly complete hull-free kernels from high-oil sunflower seed has been set up.

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WINTERIZATION OF SUNFLOWER OIL. Z. Leibovitz and C. Ruckenstein, H.L.S. Ltd., PO Box 193, Petah Tikva 49-101, Israel.

Theoretical considerations are given regarding the wax and triglyceride contents in sunflower oil. The influence of the crude oil quality on the winterization process is discussed. Separation of waxes and triglycerides by centrifuges or filters, oil quality after winterization, and descriptions of different systems of sunflower oil winterization with or without filter aid are detailed, as well.

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CONSIDERATIONS REGARDING STORAGE AND DECORTICATION OF SUNFLOWER SEED: PRACTICAL METHODS EXECUTED IN A MODERN SUNFLOWER FACTORY. Z. Leibovitz and C. Ruckenstein, H.L.S. Ltd., PO Box 193, Petah Tikva 49-101, Israel.

Principal factors which influence storage of sunflower seed, such as moisture, oil content, temperature, enzymatic reactions and respiration, are discussed along with a definition of critical moisture. Storage of 33,000 tons of sunflower seed is possible at a new factory in North Dakota, which will be described. Advantages are given for decortication regarding energy saving, protein content of meal and oil quality. Methods or decortication are enumerated, including conditions for minimizing the losses. A description is given of a decorticating plant with a capacity of 1,500 tons/24 hr. Use of husks for burning or pelleting is suggested.

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THE NEW FACILITIES AND EQUIPMENT OF THE ITERG-CETIOM PILOT PLANTS: FIRST RESULTS IN THE EXPERIMENTS ON OILSEEDS PROCESSING AND VEGETABLE OIL TREATMENTS. A. Uzzan, ITERG, 10/A, rue de la Paix, 75002 Paris, France.

ITERG (French Fats and Oils Research Institute) and CETIOM (French Oilseeds Research Center) together have created a joint institution named GERDOC (Groupe d'Etude de Recherche et Developpement sur les Oleagineux et Corps Gras) which operates several pilot plants devoted to the study of oilseeds and their products. The GERDOC facilities are integrated in a larger Center (including Research Laboratories, and an education and training school for specialists in the fats and oils production) located in Pessac in the neighborhood of Bordeaux, near the Faculty of Sciences of Talence. These facilities include: (a) a technological plant for seed treatment (storage, handling, cleaning and dehulling); (b) a crushing plant capable of crushing 1 ton/day of any kind of oilseed, with grinding, rolling, cooking and pressing equipment; (c) a solvent extraction plant capable of extracting, using any kind of solvent, seeds and beans as well as fatty meals, from 100 to 500 kg by batch process. This equipment permits the study of desolventization and toasting of the meal and their influence on the meal quality and safety; (d) an oil processing plant for refining, hydrogenation, fractionation and other treatment on the oils and fats. These integrated plants have 2 main aims: to produce oil and meals from new varieties of seeds (before putting them into agricultural production on a large scale) in order to check their chemical sensorial and nutritional properties; and to elaborate and control progress in the processing itself. The program of studies may include research at the collective level, as well as on a private level (on contract). The paper will describe the equipment of each plant and the first results of the main research in progress at the collective level, e.g., improvement of the productivity, product quality and safety.

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SIMULATION FOR PROCESS PLANNING AND CONTROL. Steven Duket and A. Alan B. Pritsker, Pritsker & Associates, PO Box 2413, West Lafayette, IN 47906.

The use of simulation methodology as support for process planning and control will be presented. The general concept of simulation modeling and how it can be used to assist process engineers in designing and operating systems will be discussed. Several actual simulation applications will then be described. For these applications, emphasis will be placed on problem formulation, model verification, and the analysis of results. Inferences to edible oil processes will be made where appropriate. The presentation will stress how existing simulation languages and other support software can be (and have been) used to simplify the process of performing simulation analyses. In this regard, SLAM II, a simulation language that facilitates the modeling of a variety of system configurations, will be described. The use of a simulation data language, SDL, for storing inputs to models, and maintaining outputs will also be presented. The use of statistical analysis routines and general purpose plotting programs will be illustrated by example.

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BETTER PROCESS OPERATION AND INFORMATION WITH A PROCESS CONTROL COMPUTER. William R. Biles, 7207 Regency Square, Suite 250, Houston, TX 77036.

Process control computers are widely used in chemical plants and petroleum refineries. The methods developed in these industries have reduced the cost and difficulty of computer control. Control computers are now practical and useful in the food oil refinery, especially in hydrogenation.

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APPLICATION OF COMPUTER CONTROL TO A PILOT PLANT. S.T. Schlager*, A.J. Schwartz, S.G. Bendzunas and J.J. Furjanic, Miles Laboratories, Inc., PO Box 70, Elkhart, IN 46515.

Computerized data analysis and control was applied to 4 pilot plant reactors operating in batch mode. The pilot plant responsibilities include: (a) providing necessary engineering data and process control strategies to scale-up new processes from laboratory to production; (b) conducting process development studies on current plant processes; and (c) supplying quantities of product for further studies. The objectives of the computerization were: (a) to speed the flow of the work through the pilot plant by providing more and better information to the research scientist and more reproducible results; (b) to provide a significantly improved information base for process control and analysis; and (c) to develop technology and methods for adoption of computer process control in production equipment. These objectives led to the design and implementation of a distributed, hierarchical computer system vertically integrating microcomputers, a minicomputer and a large mainframe computer for process control, batch handling and analysis, and data archival. The structure and application of the system will be described.

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LINOLENIC ACID AS AN ESSENTIAL FATTY ACID AND ITS INTERACTION WITH LINOLEIC ACID. Ralph T. Holman, Hormel Institute, University of Minnesota, 801-16th Ave. NE, Austin, MN 55912.

A case of linolenic acid deficiency involving neuropathy has been studied. The deficiency was induced by total parenteral nutrition using a safflower oil emulsion and symptoms appeared after several weeks. Analysis of serum lipids for polyunsaturated fatty acids revealed a marginal linoleic acid deficiency and a very significant deficiency of $\omega 3$ fatty acids. Changing to TPN with a soybean oil emulsion containing 6.9% of the fatty acid linolenic acid eliminated symptoms of neuropathy and restored the $\omega 3$ to positive balance, despite a continuing linoleic acid deficiency. The quantitative aspects of requirements of linoleic and linolenic acids and the interaction of these acids with each other will be discussed.

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THE POSSIBLE INVOLVEMENT OF DIETARY LINOLEIC ACID IN THE DEVELOPMENT OF MYOCARDIAL NECROSIS IN RATS. J.K.G. Kramer*, E.R. Farnworth, B.K. Thompson and A.H. Corner, Animal Research Centre, Agriculture Canada, Ottawa, Ontario K1A 0C6, Canada.

Myocardial necrosis has been observed in male albino rats fed for at least 4 months on diets containing vegetable oils. A positive correlation has been found between dietary linolenic acid and the incidence of myocardial lesions in rats. Partial isomerization of linolenic acid, as might occur during processing of the oil containing linolenic acid, does not affect the incidence of heart lesions. Adding dietary saturated fatty acids to the diet, however, reduces the incidence of heart lesions significantly. But adding triolein did not alter the lesion incidence. Other test animals, such as pigs, monkeys and female albino rats, do not show this peculiar response observed in male rats. Linolenic acid is nearly quantitatively absorbed by the rat. In the heart, linolenic acid is converted to C22 polyunsaturated fatty acids (PUFA) which are incorporated into the cardiac phospholipids. When the concentration of linolenic acid is 5-15% of the dietary fatty acids, nearly all the C22 PUFA are from the linolenic acid family; very little of the C22 PUFA from the linoleic acid family are found. The level of arachidonic acid, however, does not appear to be affected at these concentrations of linolenic acid. These results indicate that the conversion of arachidonic acid was not affected, but only the subsequent conversion of arachidonic acid to the C22 PUFA. The changes in the C22 PUFA profile, however, may not be the only explanation of myocardial necrosis in male rats. The addition of dietary saturates did not alter the relative concentration of the C22 PUFA but still reduced the incidence of heart lesions in male albino rats. Changes in the other fatty acids, as well as the growth of the animal, may contribute to the development of heart lesions. Nevertheless, the changes in PUFA of cardiac phospholipids appear to predispose the rat heart to myocardial degeneration changes. The lower concentration of C22 PUFA in pig and monkey heart lipids as compared to rats' supports this hypothesis.

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POLYUNSATURATED FATTY ACIDS AND THE DEVELOPING BRAIN. Brian L. Walker*, Maxwell S. Lamptey and Marilla A. Samulski, Department of Nutrition, University of Guelph, Guelph, Ontario N1G 2W1, Canada.

Lack of dietary linoleic and linolenic acids during the final week of gestation resulted in impaired learning behavior in adult rat progeny. Lack of dietary linolenate during that period also resulted in slight impairment of maze learning. In pups born to dams fed an essential fatty acid (EFA)-deficient diet, brain lipids at birth contained fewer polyunsaturated fatty acids and more saturated and monoenoic fatty acids than did those from dams fed a corn-oil-containing diet. At weaning, these differences were not evident, indicating that the EFA stores were mobilized during lactation, even if the diet lacked these acids. Lack of dietary linolenate during gestation resulted in low levels of 22:6(n-3) and high levels of 22:5-(n-6) in the brains of the progeny at birth, especially in the ethanolamine glycerophosphatides. Analyses of fetal brain lipids showed that there is a marked increase in C22-polyunsaturated fatty acids during the final week of gestation, particularly in the 3 days immediately before birth, and it is during this period that the long-chain polyunsaturated fatty acids exhibit a marked response to maternal dietary fat, with 22:5(n-6) increasing rapidly in the absence of dietary n-3 acids. Brain oxidative metabolism and enzymes involved in neurotransmitter metabolism were not substantially altered by these dietary manipulations. Although deposition of long-chain fatty acids was associated with normal brain development, the biochemical basis for this association remains to be elucidated.

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RETENTION OF POLYUNSATURATED FATTY ACIDS IN BRAIN AND RETINA LIPIDS FROM LINOLENIC-ACID-DEFICIENT OR CONTROL RATS TRANSFERRED TO A FAT-FREE DIET FOR ONE YEAR. J. Tinoco*, B. Medwadowski, P. Miljanich, I. Hincenbergs and M.A. Williams, Department of Nutritional Sciences, University of California, Berkeley, CA 94720.

Rats were raised for 2 generations on control or linolenic-acid-deficient diets. Rats of the second generation were transferred to fat-free diets at ages 9-11 weeks, and first-generation rats were kept on the original diets. All rats were killed 54 weeks later, and acyl groups in total lipids of retina and ethanolamine-, serine-, choline- and inositol phosphoglycerides (EPG, SPG, CPG and IPG) of brain, muscle and liver were analyzed. In rats fed fat-free diets, 20:3(n-9) increased in all lipids analyzed. In retinas of rats started on the control diet and transferred to the fat-free diet, the proportion of 22:5-(n-6) increased whereas the proportions of all other n-3 and n-6 fatty acids decreased. An increase in 22:5(n-6) was also seen in brain IPG, EPG, SPG and CPG, liver IPG, EPG, SPG and CPG, and in muscle IPG, SPG and EPG of these rats. Retention of n-6 and n-3 fatty acids was usually higher in retina and brain lipids than in liver or muscle lipids. Docosapentaenoic acid was isolated from brain lipids of second-generation rats that had been started on the control diet and transferred to the fat-free diet. The terminal double bond was located in the n-6 position, as shown by partial oxidation of the molecule and identification of caproic acid (C_6) as the main monocarboxylic oxidation product.

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POLYUNSATURATED FATTY ACIDS, PROSTAGLANDINS, AND THE IMMUNE RESPONSE. Patricia V. Johnston*, G.A. Boissonneault, Linda J. Magrum and Lisa A. Marshall, Burnsides Research Laboratory, University of Illinois, 1208 W. Pennsylvania, Urbana, IL 61801.

A brief description of some immunological terms will be followed by a review of the possible roles of the essential fatty acids (EFA) and their metabolites in the immune response. The influence of dietary fatty acids on prostaglandin (PG) synthesis and the function of PG in the immune response will be discussed. Recent studies in this laboratory on the effects of dietary fatty acids on immunity will be described. One study shows that EFA deficiency leads to depressed PG synthesis by splenocytes from rats challenged with antigen. Other studies examine the possibility that the macrophage is the main PG-producing cell which modulates the activity of T- and B-cells. The effects of dietary α-linolenic acid on the PG synthesizing capacity of immunocompetent cells will be described. It will be shown that increasing the level of α-linolenic relative to linoleic acid in the diet leads to marked changes in the fatty acid composition of cells of the immune system. Higher levels of dietary α-linolenic acid lead to depressed deposition of elongated, desaturated fatty acids of the $\omega 6$ series and increased deposition of the $\omega 3$ series with a consequent depression in the PG-synthesizing capacity of splenocytes, thymocytes, macrophages and peripheral lymphocytes. The effects of these changes on some cell functions will be discussed.

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A QUESTION OF FATTY ACID ESSENTIALITY. M.A. Crawford,

Nuffield Laboratory, London NW1, P. Budowski, Rehovolt University, Israel, W. Hare and A.G. Hassam, Department of Biochemistry and Nutrition, Nuffield Laboratories of Comparative Medicine, Zoological Society of London, Regent's Park, London NW1, U.K.

Linoleic and α-linolenic acids. Evidence in primates (skin and hair), rats (retina and learning) and chickens (cerebellum) suggest that α-linolenic acid has essential functions which are different than those of linoleic acid. Alteration of the n-3 fatty acid intakes changes prostanoid synthesis and suggests that n-3 fatty acids may be required for the control of prostaglandin synthesis as well as for cellular structures. *The long chain derivatives of 18:2,n-6 and 18:3,n-3.* The rate of conversion of linoleate to arachidonate is strikingly limited by the 5 and 6 desaturases. Isotope and metabolic studies suggest that for evaluation of foods, it is necessary to consider the individual acids in each family as different EFA. *Oleic acid requirements.* Oleic acid is quantitatively the most important fatty acid in human milk. Is oleic acid nutritionally important? Studies on humans and on experimental animals indicate that a dietary source of oleic acid is needed to maintain pace with utilization during early development. *A requirement for fat?* In undernutrition of lactating mothers on low-fat diets, the rate of synthesis of C16 and C18 fatty acids for milk secretion does not appear to be adequate. While the requirement for protein may have been overestimated, a need for fat may have been underestimated if optimal function, rather than growth, is used as a target. *Essentiality.* We wish to present a new view on the essentiality of fatty acids. Basically, the essentiality of fats is not analogous to that of amino acids or vitamins. While there are clearly identifiable requirements for certain fatty acids, once these requirements are met, the need is for a balance of different fatty acids to enable optimal conditions to be achieved for cell membranes and prostanoid biosynthesis. That balance can be affected by the amounts of saturated fats, carbohydrates, type of carbohydrate as well as the quantities of linoleic, α-linolenic acids and their long chain derivatives.

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LINOLENIC ACID IN LOW-FAT FOODS. J.L. Beare-Rogers, R. Hollywood and E. O'Grady, Bureau of Nutritional Sciences, Health Protection Branch, Department of National Health and Welfare, Ottawa, Ont., Canada K1A 0L2.

Because (n-3) fatty acids appear to be essential nutrients in the diet of man, an examination of their content in vegetables was undertaken. Common green vegetables contain less than 1% fat, but can be a significant source of α-linolenic acid. Beans, broccoli, Brussel sprouts, cabbage, lettuce, spinach, onions and parsley contain more linolenic acid than linoleic acid, but peas, celery and iceberg lettuce contain more linoleic than linolenic acid. On the basis of 100 g raw vegetable, linolenic acid in broccoli was 160 mg; in Brussel sprouts, 150 mg; and in peas and beans about 50 mg. If a recommended intake of linolenic acid is 300-500 mg/1,000 calories, green vegetables can contribute a large portion of this nutrient.

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POS CANOLA CHECK SERIES. Myles Marianchuk and John Blake*, POS Pilot Plant.

POS has instituted 4 separate Canola check series for Canola seed, Canola meal, crude and crude degummed oil and refined, bleached and deodorized Canola oil. These series, begun in July 1980, are devised to help laboratories involved or interested in Canola analysis to calibrate their analysis procedures. This paper will describe the organization of the program, describe special features of Canola analysis, indicate and discuss less-than-reliable analyses and describe the active participation of the program organizers to improve the reliability of some of the analyses.

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ROLE OF THE AOCS SMALLEY PROGRAM IN QUALITY ANALYSES. J.W. McEwan, Central Soya Co. Inc., Decatur, IN.

This program is named for Frank N. Smalley, a charter member of the AOCS. In 1909, he was chief chemist for the Southern Cotton Oil Co., the same year in which the AOCS was formed. Smalley checked the proficiency of his firm's laboratories by distributing weekly meal samples that had been prepared in his Savannah laboratory. Other analytical chemists saw the value of such a program and asked to participate. In 1915, the Uniform Methods Committee, under Dr. Smalley, adopted this program. In 1955, the name was formally shortened to the Smalley Committee. It continues to function largely with the aid of volunteer help. The AOCS is greatly indebted to the people and industries who give their time and talents. In 1981, an ad-hoc committee reviewed the Smalley Committee and each of the series involved and declared the program was functioning well and carrying out its intended purpose. You are encouraged to become acquainted with the wide range of series and to participate in those several where you may benefit.

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EFFECT OF METHODOLOGY ON THE RESULTS OF FATTY ACID METHYL ESTER CHECK SAMPLE RESULTS. Carl W. Fritsch, General Mills, Inc., 9000 Plymouth Ave. N., Minneapolis, MN 55427.

The determination of the fatty acid composition of fats and oils by the gas chromatographic analysis of the fatty acid methyl esters is one of the check samples series offered by the AOCS. About 100 collaborators participate each year. No restrictions are placed on the procedures the participants may use; however, each year the collaborators are asked to fill out a procedure questionnaire. The response obtained from the 1980-81 participants were tabulated and are presented. The participants were grouped into 2 or 3 categories each, depending on the procedure used for the ester preparation, the peak area correction, the type of column packing, the column length, and the column temperature. Then the fatty acid composition of the oils was recalculated for each of these subgroups. No significant differences were found between the results of these subgroups and those for all collaborators.

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OILSEEDS GRADING–QUALITY CONTROL IN OILSEEDS MARKETING. J.K. Daun* and L.D. Davidson, Canadian Grain Commission, Grain Research Laboratory, Room 1404–303 Main St., Winnipeg, Manitoba, Canada R3C 3G8.

Grading systems are used in many countries to aid in separating grains into marketable groups according to quality. Systems used in Canada, Sweden and Australia for grading oilseeds, especially rapeseed, are compared to proposed ISO standards. The relationship between grade, degrading factor and end-use quality is shown for the Canadian Grain Grading system which relies on a visual assessment of quality only. The future use of NIR technology and other rapid, nonvisual techniques for quality assessment in grading oilseeds will be considered.

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QUALITY CONTROL IN AN OILSEED CRUSHING PLANT. Stewart J. Campbell, United Oilseed Products Ltd., PO Box 1620, Lloydminster, Alberta S9V 1K5, Canada.

A strong emphasis on quality control provides the technical foundation on which the reputation of the oil and meal products from a crushing plant are established. Through a continuing program of sampling, analysis and research, a crusher is able to provide superior quality products with minimal variation in product quality. Quality control departments also provide analytical services to technical management and operators involved in optimizing the manufacturing process on a least-cost basis. Analytical methods involving NIR spectroscopy and GLC are described for characterizing process meal materials. Official AOCS methods are favored for assessing oil quality, as these methods are widely used for trading purposes. However, several instrumental methods are being considered to supplement the existing methods.

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QUALITY CONTROL IN EDIBLE OIL PRODUCTION FROM CRUDE DEGUMMED OIL TO FINISHED PRODUCTS. Allan Roden*, CSP Foods Ltd., PO Box 8060, Dundas, Ontario, Canada L9H 5E7, and Gordon Ullyot, CSP Foods Ltd., Nipawin.

This paper will deal with the testing procedures used in the production of edible oil products from crude degummed oil. Included will be the tests done at various stages in the production, test methods used and what is considered acceptable results. Processes covered will include receiving oil, alkali refining, bleaching, hydrogenation, deodorization, bulk shipping and packaged finished product.

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Not available at press time.

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TOPOGRAPHY OF LIPID SYNTHETIC AND DEGRADATIVE ENZYMES. Rosalind A. Coleman, Dept. Pediatric Metabolism, Box 3028, Duke Univ. Medical Center, Durham, NC 27710.

The location of the enzymes of phosphatidylcholine (PC), phosphatidylethanolamine (PE) and triacylglycerol biosynthesis within the transverse plane of the hepatic endoplasmic reticulum has important implications regarding the early events of lipid topogenesis: the access of substrates to active sites during the synthesis of complex lipids, the integration of lipids into membranes, the formation of membrane bilayers, and the biosynthesis and secretion of lipoproteins and bile. Evidence was derived from studies using proteases and other impermeant inhibitors, from investigations of latency and substrate permeation, and from localization of products. These studies strongly suggest that glycerolipids are synthesized asym-

metrically on the cytoplasmic surface of the endoplasmic reticulum. Membrane bilayers would grow by insertion of phospholipids on the cytoplasmic side of the endoplasmic reticulum. Rapid transmembrane movement of PC, PE and triacylglycerol to the lumenal surface must occur during membrane and lipoprotein biogenesis. Similar studies of the microsomal triacylglycerol lipase and cholesterol esterase activities suggest that these degradative enzymes may also face the cytosolic side whereas data derived from other investigators strongly indicate that phospholipase II faces the lumenal side of the endoplasmic reticulum. Knowledge about the sites of degradation of membrane components will prove crucial to understanding events of lipid topogenesis that involve membrane recycling, the provision of specific fatty acids for phospholipid remodeling, and the recovery from pathological states involving hepatic steatosis.

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RAPID TURNOVER OF INTRACELLULAR MEMBRANES IN SECRETORY CELLS. Alvah H. Phillips, The University of Connecticut, The Biochemistry & Biophysics Section U-125, Storrs, CT 06268.

The protein and phospholipid components of microsomal membranes have been found to undergo a rapid and apparently concerted turnover in myeloma and hepatic cells. The rate of turnover of these components is similar to the rate of transit of secretory product through these cells. These observations have lead to the hypothesis that unidirectional membrane flow, accompanied by rapid synthesis of membrane at the origin of flow and its rapid degradation at or near the terminus of flow, may be the mechanism for intracellular transport of secretory product. In attempts to further test this hypothesis, we have examined the distribution of rapidly turning over membrane components in subfractions of MOPC 41 myeloma cells and have obtained evidence suggesting that these components are assembled at a relatively specific intracellular site and then rapidly transferred (or transformed) to other membranes before they are degraded. This finding is consistent with the concept of rapid flow of newly synthesized membrane. Recent evidence bearing on the possible relationship between rapid membrane turnover and secretion of immunoglobulin light chain by these cells will be presented.

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ORGANIZATIONAL CHANGES IN RAT LIVER MICROSOMES INDUCED BY LYSOPHOSPHATIDYLCHOLINE. S. Parthasarathy*, R. Murari and W.J. Baumann, The Hormel Institute, University of Minnesota, 801 16th Ave., NE, Austin, MN 55912.

Membrane changes in rat liver microsomes resulting from interaction with exogenous lysophosphatidylcholine (lysoPC) were studied by enzymatic and nuclear magnetic resonance (NMR) techniques. For this purpose, isolated microsomes were incubated with lysoPC at various concentrations, and the solubilized material was separated from the pellet by ultracentrifugation. Analyses showed that lysoPC was readily incorporated into the microsomes, releasing both protein and lipid into the supernatant. With increasing concentrations of lysoPC, there was a proportionate increase of β-glucuronidase and esterase in the medium, whereas several lipid biosynthetic enzymes, such as choline and ethanolamine phosphotransferases, as well as diacylglycerol, lysoPC and ethanol acyltransferases, remained mostly associated with the pellet. Mannose 6-phosphatase was susceptible to proteolytic attack only after lysoPC treatment. Similarly, mannose 6-phosphatase latency was totally lost in the pellet; however, the latency was restored by enzymatic reacylation of the lysoPC on the membrane via lysoPC acyltransferase utilizing fatty acyl coenzyme A. ^{13}C and ^{31}P NMR demonstrated that lysoPC treatment of the microsomes resulted in dynamic and structural membrane alterations. The implications of these results on the current understanding of the topography of the microsomal membrane will be discussed.

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THE RELATIONSHIP BETWEEN Ca^{2+} FLUX AND PERMEABILITY MODULATION IN THE INNER MITOCHONDRIAL MEMBRANE. Douglas R. Pfeiffer, The Hormel Institute, University of Minnesota, 801 16th Ave. NE, Austin, MN 55912.

The accumulation and release of Ca^{2+} from mitochondria are critical in the control of cytoplasmic Ca^{2+} levels and thus in the regulation of cell function. Evidence is accumulating which indicates that the direction of Ca^{2+} flux across the inner mitochondrial membrane is controlled by modulation of permeability. Permeability control is produced by altering steady-state levels of lysophospholipid and free fatty acid arising from or converted to membrane phospholipids. When energy-dependent Ca^{2+} accumulation occurs, an intramitochondrial phospholipase A_2 is activated. If the media contains a second type of agent (Ca^{2+} releasing agent), the accumulated cation is not retained. Release of Ca^{2+} is accompanied by collapse of the membrane potential, proton uptake, accelerated respiration, loss of endogenous cations, pyridine nucleotide oxidation, and large amplitude swelling. These findings indicate that an inner membrane permeability increase is responsible for loss of Ca^{2+}. The products of phospholipid degradation (1-acyl lysophospholipids and polyunsaturated fatty acids) accumulate along the same time course as the change in permeability. Several lines of evidence indicate that lysophosphatidylethanolamine, at levels of ca. 0.5 mol % of lipid P, is primarily responsible for increased permeability. Ca^{2+} releasing agents are proposed to act by inhibiting reacylation by direct or indirect mechanisms. Ultrastructural studies indicate that mitochondria are heterogeneous with respect to their sensitivity to Ca^{2+} and releasing agents. Upon passing from the impermeable to the permeable state, the organelles are first transformed from the aggregate to the orthodox form and then to swollen and disrupted forms. Evidence is presented that both steps are phospholipase A_2-dependent and that the first step is reversible. It is proposed that the first transformation can account for ruthenium-red-induced Ca^{2+} release and apparent disequilibrium between transmembrane Ca^{2+} gradients and membrane potential without proposing the existence of an endogenous Ca^{2+} release carrier. Mitocondria which have been treated with Ca^{2+} and a Ca^{2+} releasing agent have properties similar to those derived from ischemic tissue. Ischemic heart synthesizes *N*-acylethanolamine from endogenous phosphatidylethanolamine by *N*-acylation followed by phosphodiesterase action. The product inhibits phospholipase A_2-dependent permeability changes, electron transport and the development of membrane potential. These findings suggest that the production of *N-acylethanolamine* is a natural protection mechanism which minimizes mitochondrial damage in injured cells.

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OXIDANT-INDUCED ALTERATIONS IN ERYTHROCYTE MEMBRANES. Paul Hochstein, Institute for Toxicology, 1985 Zonal Ave., University of Southern California, Los Angeles, CA 90033.

A diverse group of chemical agents is known to cause anemia. These agents react with oxygen to form a variety of cytotoxic metabolites, e.g., H_2O_2, O_2^-, $^1O_2$ and •OH. These substances have the capacity to react with membrane components to initiate the peroxidation of phospholipids and the aggregation of proteins. As a consequence, the microviscosity of the erythrocyte membrane is decreased and the affected cells become less deformable. The inability of erythrocytes to deform in the microcirculation of the spleen may result in their sequestration and removal, and the development of anemia. The extent of oxidant and free-radical damage to erythrocyte membranes may be influenced by a number of plasma factors. Among these are the thyroid hormones and uric acid. The thyroid hormones act to potentiate membrane damage whereas uric acid may protect cells through its capacity to scavenge $^1O_2$ and •OH.

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PHOTODAMAGE TO MITOCHONDRIAL MEMBRANES. Rolf J. Mehlhorn, Membrane Bioenergetics Group, Life Sciences Bldg., Room 2544, University of California, Lawrence Berkeley Laboratory, Berkeley, CA 94720.

Nitroxides have been used to characterize destructive oxidative reactions initiated by visible light in mitochondrial membranes. Preincubation of membranes at 37 C releases free flavins and other products from the membranes which have considerable destructive potential under illumination. After such preincubation, photodamage to respiratory enzymes is associated with bound flavin whereas lipid peroxidation is photosensitized by free flavins. The combination of ethylene diamine tetraacetic acid and flavin mononucleotide, a prolific source of superoxide radicals under illumination, inhibits lipid peroxidation, showing that superoxide can protect against oxidative attack under appropriate conditions. Photodamage is correlated with nitroxide destruction, yet no protection against photoperoxidation is conferred by treating membrane suspensions with water-soluble nitroxides. The spin trap 5,5 dimethyl-1-pyrroline-N-oxide (DMPO) gives rise to an ESR-detectable species in a nonradical process; thus spin trapping results can be misleading. Evidence implicating free radicals in photodamage will be reviewed.

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INFLUENCE OF PHOSPHOLIPASES ON MEMBRANE LIPID PEROXIDATION. Alex Sevanian* and Samar Muakkassah-Kelly, University of Southern California, Institute for Toxicology, 1985 Zonal Ave., Los Angeles, CA 90033.

Membrane-associated phospholipases are proposed to contribute to the maintenance of membrane integrity and, in this regard, could protect against lipid peroxidative damage. Phospholipase action is made evident by the elimination of oxidized fatty acyl groups from phospholipids which could otherwise be disruptive to the membrane. Although excessive phospholipase activity would in itself be deleterious to the membrane, coordinated action within the

functional constraints of the membrane would serve to modify its composition or eliminate damaged or undesirable phospholipids. The elimination of peroxides would minimize the potential for propagation and decomposition reactions within the membrane. Supporting this concept is evidence that phospholipases A and C display markedly increased activity toward phospholipid epoxides in model membranes and with in vitro microsomal preparations. Measurement of malondialdehyde and peroxide products following iron-ascorbate-induced lipid peroxidation in liver microsomes revealed increased amounts of these products in the incubation medium (free) compared to control samples exhibiting minimal peroxidation. This effect is readily observed when microsomes are subjected to mild peroxidizing conditions. The ratio of free vs membrane-associated peroxides or malondialdehyde is also reduced if membranes are treated with specific phospholipase inhibitors. Physicochemical and structural factors appear to govern much of the phospholipase activity displayed against oxidized membrane phospholipids. A discontinuity in the otherwise hydrophobic interior of the membrane would occur following peroxidation, permitting phospholipase action. This activity would complement the action of other protective enzyme systems such as epoxide hydrolase and glutathione peroxidase.

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PROTEIN CONFORMATIONS AND THEIR STABILITY. C. Nick Pace, Department of Biochemistry and Biophysics, Texas A&M University, College Station, TX 77843.

Our understanding of the denaturation of globular proteins has increased substantially in recent years. The reaction of interest is: native (N) $\rightleftharpoons$ denatured (D), where N is the globular, native state of the protein which is now well defined as a result of numerous structural determinations by X-ray diffraction studies, and D represents unfolded, denatured states of the protein whose structure depends on the denaturant used to promote unfolding. Through experimental studies, much is known about the kinetics, thermodynamics and mechanism of this reaction. For example, it is known that the free energy change for this reaction under physiological conditions, ΔG_D, is between 5 and 15 kcal/mol for a fairly wide range of globular proteins. Thus, the globular conformation which is absolutely essential for the biological function is only marginally stable. In addition, these ΔG_D values are remarkably sensitive to small changes in the structure of the protein. It has been shown that single amino acid substitutions can dramatically increase or decrease ΔG_D values and some substitutions surely lead to unfolding of the polypeptide chain. Most chemical alterations in the structure of a protein, e.g., cleavage of a peptide bond, or modification of an amino acid side chain, lead to decreases, often sizable, in the conformational stability. The remarkably low conformational stability of globular protein is important, in part, because many important properties of the protein, e.g., solubility and proteolytic digestibility, change substantially when the protein unfolds. Developments in the area of protein denaturation of most interest to protein chemists and food technologists will be illustrated and discussed. (Supported by NIH Grant AM 19 112 and Welch Foundation Grant A-798.)

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SEED PROTEIN STRUCTURE, BIOSYNTHESIS AND PROSPECTS FOR GENETIC ENGINEERING. Timothy C. Hall, Agrigenetics Corp., Agrigenetics Research Park, 5649 E. Buckeye Road, Madison, WI 53716.

Civilization depends on continual increases in the efficiency of production of seed oils and proteins. Premium prices for seed crops designed to be more economical in processing for specific purposes can be envisaged as technological advances resulting from the powerful new methods available for studying seed proteins and for enhancing their quality and quantity. Most seed proteins accumulate as concentrated reserves, often in water-insoluble forms which reduce problems associated with high osmotic pressures. The structure of bean, corn and wheat storage proteins is now well defined, and features related to the proteins' transport across membranes have been characterized. The number of genes coding for these foodstuffs is being established and insight to the reasons for differential efficiencies in expression is being gained. Recombinant DNA technology has permitted detailed studies on the transcription and translation of individual seed protein genes. Further developments through chemical modification of protein characters in respect to the nutritional balance of amino acids and digestibility are underway, and progress toward interspecies transfer of beneficial genes is evident.

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GLYCOPROTEINS: SWEET, SLIPPERY AND SEXY! Derek T.A. Lamport, MSU-DOE Plant Research Lab, Michigan State University, E. Lansing, MI 48824.

As the title implies, we can view glycoproteins from several different perspectives and at various intellectual levels. Therefore, this talk is a discussion of what glycoproteins signify to: biochemists, chemists, food chemists, evolutionary biologists . . . and even beer drinkers! First, we shall define terms, e.g., glycoproteins and the closely related proteoglycans share glycopeptide linkages. Of the many topics which could be explored and questions raised, the following few merit special attention. (a) Handling glycoproteins: a brief perusal of purification and analytical methodologies including deglycosylation via anhydrous fluoride; (b) glycopeptide linkages: which amino acids, sugars and amino sugars exist in glycopeptide substituents? What is the size of the oligosaccharide substituents? (c) The role of glycoprotein glycosylation: what does the "oligosaccharide information" mean? Is glycosylation necessary for secretion? Does glycosylation protect? For example, how does glycosylation affect physical properties such as thermal stability, and resistance to denaturation and proteolysis? Why don't plants contain sialic acid? Glycoproteins and sex?! Cheap attention getting mechanisms: sex inducers, glycohormones, cell-cell recognition including fertilization and lubrication; (d) origin of glycoproteins: speculation about origins makes an interesting connection for oil chemists. Archaebacterial methanogens almost certainly generated the methane pockets often associated with the giant fossil "compost heaps" (more often referred to as oil-bearing strata). Archaebacteria also "invented" cell surface glycoproteins, presumably as a defense mechanism, and Archaebacteria (rather than true bacteria) probably gave rise to the primitive eukaryote cell which evolved toward multicellularity and morphogenesis because an extracellular matrix based on glycoproteins made this extraordinary diversification, and us, possible! (This work is supported by the Department of Energy Contract EY-76-C-02-1338.)

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AGGLUTINATING FACTORS IN GRAIN SORGHUM (*SORGHUM BICOLOR* [L.] MOENCH). J.N. Neucere, Southern Regional Research Center, USDA, ARS, PO Box 19687, New Orleans, LA 70179.

Macromolecules in plant, animal and microbial tissues that interact with cell surfaces are well documented. Many of these molecules are glycoproteins (phytoagglutinins in plants) having a wide range of carbohydrate composition. Studies on different varieties of grain sorghum showed the presence of such factors that agglutinate human red blood cells. Among the varieties, some variation in titers for agglutination was observed. At least 2 simple sugars were shown to inhibit agglutination. After screening the ABO blood group for agglutination, no specificity was observed. Heat stabilities and possible inhibition of metabolic enzymes by the factors will also be discussed.

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SOY PROTEIN HYDROLYSIS IN MEMBRANE REACTORS. Munir Cheryan* and W. David Deeslie, Department of Food Science, Dairy Manufacturers Building, University of Illinois, 1302 W. Pennsylvania Ave., Urbana, IL 61801.

An ultrafiltration (UF)-based enzyme reactor system for continuous hydrolysis of proteins was developed to overcome limitations of the traditional batch process. A continuous stirred tank reactor (STR) was coupled to a hollow fiber module in a semi-closed loop configuration. Effect of operating variables (enzyme concentration, substrate concentration, flow rate and reactor volume) on substrate conversion and mass flux of product was studied. A model combining Michaelis-Menten kinetics and mass balance for ideal CSTR fit the data well between 55 and 94% conversion levels. Capacity of the reactor, defined as quantity of product produced/time/unit weight of enzyme, was a sensitive function of enzyme level. A 10-fold decrease in enzyme level lowered conversion from 70 to 50%, but increased capacity 900%. Increasing flow rate also improved capacity, but substrate level and reactor volume had small effects on capacity. Reactor decay was a function of operating temperature, dilution rate, calcium ion level and enzyme leakage. Productivity of the reactor system, defined as weight of hydrolyzate/unit weight of enzyme, was at least 10-20 times greater than a batch reactor operating under otherwise identical conditions. The UF reactor output is more consistent and uniform, requires fewer subsequent operations and has interesting functional properties.

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PRODUCTION OF LOW-PHYTATE AND LIGHT-COLORED PROTEIN ISOLATES FROM DEFATTED SUNFLOWER FLOUR. Y.R. Choi, K.C. Rhee* and E.W. Lusas, Food Protein Research and Development Center, F.M. Box 183, Texas A&M University, College Station, TX 77843.

Defatted sunflower flour contains about 2.8% phytate and 3.2% chlorogenic acid. Approximately 80% of the phytate was present in water-soluble form at pH 4-5, at which ca. 15% of the total sunflower flour protein was solubilized. More phytate became bound to protein with increasing pH. The sunflower flour exhibited unique

pH-dependent solubility profiles of protein, phytate and chlorogenic acid in solutions of water/isopropanol mixtures. These unique solubility characteristics enabled separation of phytate and chlorogenic acid from protein by washing the flour with mixtures of water/isopropanol at pH 4.5. Loss of protein by the washing was about 18%. Low-phytate and low-chlorogenic acid protein isolate was then produced from the washed flour by extracting the protein with an alkaline solution containing a 0.001% reducing agent, and precipitating at pH 4.5.

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CHARACTERISTICS AND UTILIZATION OF DRY-ROASTED NAVY BEAN PROTEIN FRACTION. Mary E. Zabik*, Mark A. Uebersax and Jen P. Lee, Department of Food Science & Human Nutrition, 139 Food Science Building, East Lansing, MI 48824.

Navy beans (*Phaseolus vulgaris*) were dry-roasted in a solid-solid heat exchanger, dehulled by air aspiration, pin-milled and air-classified to yield a high-protein fraction. Proximate analyses, nitrogen solubility indices and oligosaccharide contents of this high-protein fraction were determined as influenced by processing parameters which affected final product temperature. Farinograms of wheat/bean protein fraction composite flours were run. A high-protein bean flour fraction was selected from these dry roasting treatments and used in product development. Quality characteristics and consumer acceptability of high-protein prototype products were evaluated. This high-protein navy bean fraction performed well at moderate levels of substitution in wheat-based, baked products.

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MICROBIAL OILS AND FATS: AN OVERVIEW. C. Ratledge, Department of Biochemistry, University of Hull, Hull HU6 7RX, U.K.

Although the concept of using microorganisms to produce oils and fats is far from new, we are now seeing such an unparalleled upsurge of interest in biotechnology that it is becoming imperative for the oil industry to reexamine the capabilities of microorganisms in this area. Microorganisms: bacteria, algae, yeasts and fungi, can all accumulate lipid. With some organisms, this can be up to 70% of their biomass. The lipid composition may vary among the various classes, but in the yeasts, especially, the principal lipid component is triacylglycerol which accounts for 90% of the total lipid. Moreover, the fatty acid distribution on the glycerol moiety in these yeasts follows that found in plants and with the fatty acids being the same (e.g., oleic, palmitic, linoleic and stearic acids), a case can be made for considering yeast oils as direct substitutes for plant oils. In some examples, a high content of hydrocarbon has been recognized in the microbial oil, making the material of potential use as a fuel. In other cases, unusual lipids have been found or else high yields of such lipids as phospholipids, sterols and even poly-β-hydroxybutyrate have been achieved which has then attracted commercial attention. In still further examples, hydrocarbons have been used both to tailor-make specific lipids and to encourage overproduction of waxes and sugar-lipid esters both in bacteria and yeasts. Possibilities for future development hinge very much on the availability of suitable feedstocks on which to grow these oleaginous microorganisms. However, with extensive total resource utilization programs now being developed, shortage of substrate may not be a serious long-term impediment to the successful development of single cell oil.

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BACTERIAL PRODUCTION OF FATS AND OILS. Morris Wayman* and Agnes C. Kormendy, Department of Chemical Engineering and Applied Chemistry, University of Toronto, Toronto, Ontario M5S 1A4, Canada.

In their classic paper "Microorganisms as a Potential Source of Oils and Fats" (*Process Biochemistry*, November 1974) Whitworth and Ratledge describe the formation and composition of oils and fats in yeasts and fungi. We shall review the corresponding situation with respect to bacteria. We have studied in particular *Arthrobacter AK19* (ATCC 27779) which, under proper growth conditions, produces very high concentrations of fats and oils, above 75%. Conditions for oil production will be described. The composition was found to be dependent on the sugar substrate: when glucose was the carbon source, triglycerides formed 91% of lipids, whereas with xylose, 77% of the lipids were triglycerides. In both cases, the remainder was largely phospholipids. On a glucose substrate, 42% of the triglycerides were 16:0, 5% 16:1, 15% 18:0, 24% 18:1; with minor quantities of 14, 15 and 17. On a xylose substrate, the corresponding figures were 36, 11, 6 and 30%. Thus, the xylose-grown bacteria oil was rather more unsaturated. It is probable that oil composition is dependent also on life cycle and other growth parameters. This offers the opportunity to grow oils to specification for various uses.

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POTENTIAL FOR OIL PRODUCTS FROM ALGAE. Neil S. Shifrin, JBF Scientific Corp., 2 Jewel Dr., Wilmington, MA 01887.

The exceptionally large photosynthetic productivity of microalgae has received much attention over the years and many attempts have been made to exploit this potential resource for various applications. Oil production from microalgae is a relatively new application and it offers some unique opportunities for the vegetable oil industry, which traditionally has been concerned with conventional agricultural crops. An overview of this application including its advantages and limitations is presented. Compared to areal yields from soybeans, microalgae could produce up to 30 times more oil. Moreover, algal crops offer many possibilities for further enhancing oil production because cell generation times are short and, thus, physiological manipulation can be substantial. This notion is especially important considering the current interest and advances in biotechnology. Nitrogen starvation is one physiological manipulation which has been shown to double and triple the oil content of many algae with the added benefit of reduced fertilizer requirements. Increased culturing temperatures have also resulted in increased oil yields. Also, significant variations in the content and quality of oil among different species and even among different strains of a given species suggests several possibilities for genetic optimization of oil-producing species adapted to minimally controllable outdoor culturing conditions. This will lead to high product yields of specific fatty substances from easy-to-operate mass culture microalgae farming. Oils from microalgae are not likely to replace conventional vegetable oils, but will someday be available to enhance the nation's production and range of fats and oils for energy and other commercial uses. The potential is enormous, but research is needed to better understand the limitations and to refine the technologies that will lead to commercial algal mass cultures. However, this research and the benefits derived therefrom can only be realized when the concept is generally accepted for using biotechnologies to develop unconventional crops as a source of renewable oils to replace dwindling or limited conventional supplies.

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PRODUCTION OF FATS AND OILS BY MICROORGANISMS. Earl G. Hammond* and Bonita A. Glatz, Dept. of Food Technology, Iowa State University, Ames, IA 50011.

The production of fats and oils by microorganisms has been frequently suggested but never reduced to a practial process. A possible way in which such processes could become commercially feasible is in the utilization of carbohydrate-rich food processing byproducts such as cheese whey and the permeate from whey ultrafiltration. The low intrinsic value of these materials and the rising cost of traditional disposal methods stimulates interest in new technology. Lactose in permeate can be fermented to an oil by the yeast *Candida curvata* in a process economically comparable to the frequently advocated ethanol fermentation. *C. curvata*, in common with other Candida species, produces an oil whose glyceride structure closely resembles that of cocoa butter. More work is needed to optimize the process: nutrient requirements and their effect on oil production need to be defined; mathematical models that will allow optimization of the fermentation need to be developed. An advantage of oil production with microorganisms that should be exploited is the ease with which mutants can be produced and selected to improve the efficiency of the process and later the characteristics of the product. *C. curvata* is characterized by the wide range of substrates it can use, so many by-products other than whey might be used profitably. Another possibility that deserves exploration is that of modifying fats by fermentation. Some organisms that deposit fat also digest it very well. This may be exploited to upgrade low-quality fats and oils.

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STEROLS OF YEAST: A MODEL FOR BIOTECHNOLOGY IN THE PRODUCTION OF FATS AND OILS. L.W. Parks*, R.J. Rodriguez and M.T. McCammon, Department of Microbiology, Oregon State University, Corvallis, OR 97331-3804.

The ease of culture, reproducibility and genetic manipulation of microorganisms makes them ideally suited for the commercial production of fats and oils. Many yeasts and fungi produce lipids in high purity and in abundance. Ergosterol production in the yeast *Saccharomyces cerevisiae* can serve as an important model system for using the biotechnology of microorganisms in the production of fats and oils. Ergosterol is an alcohol that is extremely insoluble in water but is easily dissolved in organic solvents. This makes sterol separation by saponification and extraction relatively uncomplicated. Ergosterol is a cheap, readily available source of precursor for vitamin D. Structurally modified sterols are also obtained from mutated cells. These unusual sterols are valuable precursors for chemical modifications to hormones, growth mutators, drugs and potent fungicides. Yeast mutants can be isolated following muta-

genesis by using enrichment procedures with echinocandin and nystatin. Organisms forming high yields of modified sterols are obtained. In addition, newer procedures of genetic manipulation allow the introduction of non-yeast genes into this organism. The potential is great for developing specific organisms programmed to produce specific lipid structures.

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MICROBIAL LIPASES AS CATALYSTS FOR THE INTERESTERIFICATION OF OILS AND FATS. A.R. Macrae, Unilever Research, Colworth Laboratory, Sharnbrook, Bedford MK44 1LQ, U.K.

Extracellular microbial lipases catalyze to hydrolysis of triglycerides. The reaction is reversible, and as a result of concurrent breakdown and resynthesis of the triglycerides, exchange of fatty acyl residues between triglyceride molecules occurs when lipases are incubated with oils and fats. This interesterification reaction becomes the dominant reaction under conditions in which hydrolysis is restricted by limiting the availability of water to the reaction system. Therefore, it is possible to use microbial lipases as catalysts for interesterification of mixtures of triglycerides or triglycerides plus free fatty acid. Use of specific lipases which catalyze reaction only at the 1- and 3-positions of triglycerides gives products which are unobtainable by chemical interesterification methods. Some of these products have properties of value to the oils and fats industry. The catalysts for enzymatic interesterification are prepared by solvent precipitation of a microbial lipase in the presence of an inorganic support material. The resulting lipase-coated catalyst particles are collected by filtration and dried. For batch interesterification reactions, the dried catalyst particles are activated by addition of a small amount of water and then stirred with a feedstock mixture of either triglycerides or triglycerides plus free fatty acid dissolved in hexane. At the end of the reaction period, the catalyst particles are removed by filtration, and the interesterified triglycerides are isolated from the reaction products by conventional fat fractionation techniques. The lipase catalyst can be reused in subsequent batch reactions. As an alternative to the batch reaction system, a continuous interesterification process can be operated by pumping water-saturated feedstock through a packed bed of activated catalyst particles.

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THE APPLICATION OF HYDROCARBON-OXIDIZING MICROORGANISMS TO LIPID PRODUCTION. W.R. Finnerty, Department of Microbiology, University of Georgia, Athens, GA 30602.

The ability of microorganisms to oxidize various hydrocarbons or hydrocarbon derivatives to characteristic and specific lipids is unique. Such biotransformations are oxygen-dependent, ambient temperature reactions characterized by efficient substrate utilization and high product yields. Many paraffinic hydrocarbons ranging from methane to kerosene are oxidized to acids, alcohols, ketones, dibasic acids, aldehydes, wax esters and glycerides. Aromatic hydrocarbons are oxidized to 1,2-diols, dibasic acids, phenol acids, alcohols, aldehydes and hydroxy acids. A series of novel biotransformations has been reported in which symmetrical ethers ranging in chain length from C14 to C20 are converted to alkoxyacetic acids and dibasic acids. The selective cooxidation of refractory hydrocarbons by microorganisms has been shown to be possible through mixed substrate reactions in which carrier substrate represents a readily and easily oxidized hydrocarbon. A comprehensive overview of microbial activities toward hydrocarbons will be presented in the context of unique and specific production of lipids.

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CRITICAL REVIEW OF STATE OF ART OF PARTIAL HYDROGENATION. Lyle F. Albright*, Purdue University, West Lafayette, IN, and A.H. Chen, Anderson Clayton Foods, Richardson, TX.

Considerable progress has been made in the last 30 years in obtaining a better understanding of the mechanism of partial hydrogenation of triglyceride oils. It should be emphasized that isomerization reactions also occur during hydrogenation and the resulting isomers have major effects on the properties of the final oil. Although important modifications have been made in the last few years in reactor design, and in the catalysts used for partial hydrogenation, better application of the knowledge obtained in the laboratory and the pilot plant could lead to processes that will result in improved or unique properties of the final product, lower operating costs, decreased consumption of energy and hydrogen, and fewer labor requirements. This paper reviews the current state of the art of processing, of hydrogenation (and isomerization) fundamentals, and suggested process modifications for the future.

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RATE FACTORS IN LIQUID PHASE HYDROGENATION. B. Andersson, Chalmers Univ. of Technology, Sweden, T. Berglin, EKA-Kemi AB, Sweden, and V. Hatziantoniou, R. de Vos and N.-H. Schoon*, Dept. of Chem. Reaction Eng., Chalmers Univ. of Technology, Sweden.

The study of the reaction conditions on the surface of the catalyst is complicated by the fact that the specific catalytic properties of the surface is screened in various ways owing to the presence of transport resistances that give rise to important gradients of concentration close to the outer surface and within the pores of the catalyst. Direct electrometric methods have been studied to measure the hydrogen concentration in bulk solution and the hydrogen activity on the surface of the catalyst. Alternative catalyst geometries have also been studied to eliminate the transport resistances in liquid-phase hydrogenation.

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SELECTIVITY OF NICKEL CATALYST FOR THE HYDROGENATION OF HIGHLY UNSATURATED MARINE OILS. J-L. Sebedio*, G. Finke and R.G. Ackman, Fisheries Research & Technology Laboratory, Technical University of Nova Scotia, PO Box 1000, Halifax, N.S. B3J 2X4, Canada.

A refined menhaden oil (IV-189) was hydrogenated using different experimental conditions of temperature (140-250 C), agitation (600-1,200 rpm), hydrogen pressure (20-60 psig), and amount of nickel catalyst (0.2-0.6%). Samples were collected as the hydrogenation proceeded from an iodine value of 189 to an iodine value of 90. The fatty acid compositions of selected partially hydrogenated samples were determined using class fractionation through methoxy-bromomercuri-adducts. The selectivity of the nickel catalyst was determined for the C_{20} isomers using a computer method based on considering the hydrogenation process as a system of consecutive first-order reactions. The differences in the selectivities obtained by computer simulation were verified by the monoethylenic isomer distributions which were obtained by a combination of preparative gas liquid chromatography, mercuric adduct and silver nitrate fractionations, and ozonolysis in BF_3-MeOH.

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EFFECT OF THE PRESENCE OF SULFUR DURING THE HYDROGENATION OF CANOLA OIL. J.M. deMan* and E. Pogorzelska, Department of Food Science, University of Guelph, Guelph, Ontario, Canada N1G 2W1, and L. deMan, Food Specialties Co. Ltd., Ajax, Ontario, Canada.

Sulfur was added to refined and bleached canola oil before hydrogenation in the form of allyl isothiocyanate and the effects on hydrogenation rate and fatty acid composition were determined. The effect was more pronounced under selective conditions (200 C and 7 psi) than under nonselective conditions (160 C and 44 psi). Sulfur added at the level of 3 mg/kg under selective conditions stopped the hydrogenation at IV 81, with 5 mg/kg at IV 88. Under nonselective conditions, there was a decrease in reaction rate, but even with 10 mg/kg added S, the reaction could be made to reach IV 70. The amount of S bound to the catalyst was determined and in all cases was less than the amount that was bound to Raney nickel. Relatively more sulfur was bound at lower temperature (longer time) and higher pressure. Addition of 3 mg/kg of S or more resulted in considerably higher formation of *trans*-isomers.

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VAPOR-PHASE HYDROGENATION OF METHYL ESTERS OF FATTY ACIDS, A POSSIBLE WAY TO STUDY FUNDAMENTAL REACTION PROPERTIES OF FAT HYDROGENATION. J.-O. Lidefelt, Karlshamns Oljefabriker AB, J. Magnusson and N.-H. Schöön*, Dept. of Chem. Reaction Eng., Chalmers Univ. of Technology, Sweden.

A new technique was developed to study the reaction conditions at the surface of the catalyst during hydrogenation of methyl esters of fatty acids. The hydrogenation was performed in vapor-phase instead of liquid-phase in a so-called gradient-free reactor. Adsorption equilibrium studies of different methyl esters were performed according to the Kubin-Kucera dynamic method. The adsorption study showed that methyl linoleate and methyl oleate are adsorbed equally strongly on the surface of the catalyst. These esters are more strongly adsorbed on a copper-on-alumina catalyst than on a nickel-on-alumina catalyst. The adsorption rate constant of hydrogen on this copper catalyst was, moreover, found to be only 3% of the corresponding constant for the adsorption on the nickel catalyst. Methyl linoleate was found to react with hydrogen molecules instead of with adsorbed hydrogen atoms in the presence of the copper catalyst. The hydrogenation of methyl oleate in the presence of the nickel catalyst was a reaction of high order with respect to the hydrogen concentration. Different reaction mechanisms will be discussed. The selectivity properties of the vapor-phase hydrogenation were the same as those found in the liquid-phase process.

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PLATINUM GROUP METAL CATALYSTS IN THE HYDROGEN-

ATION OF NATURAL OILS. Paul N. Rylander, Engelhard Industries, 429 Delancy St., Newark, NJ 07105.

All metals in this group make hydrogenation catalysts. Many investigators over the last several decades have examined these catalysts in the hydrogenation of natural oils. Some of this work is reviewed with the results interpreted in terms of reaction conditions, metal, catalyst preparation, support and metal location. Useful generalities are sought.

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THE SPECIFIC ASPECTS OF FATTY ACID HYDROGENATION WITH Ni CATALYSTS. Helmut Klimmek, UNICHEMA International, Steintor 9, PO Box 1280, 4240 Emmerich, West Germany.

Specific theoretical and practical aspects of fatty acid hydrogenation with Ni catalysts are outlined. The influence of the catalyst quality, as well as the quality of fatty acids to be hydrogenated, on the overall fatty acid hydrogenation process is described. The discussion will include a short survey of items such as commercial availability of various types of Ni catalysts, how catalysts are produced, how they work and how to test these catalysts. An understanding of the details will support the proper selection of commercially available Ni catalysts for specific applications in fatty acid hydrogenation.

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DISCUSSION OF PROBLEMS ENCOUNTERED IN STARTING UP LABORATORY-SCALE HYDROGENATION. F.V. Lee-Poy, L.L. Diosady and P.W. Sleggs, The Cambrian Engineering Group Limited, 2465 Cawthra Road, Mississauga, Ontario L5A 3P2, Canada.

In light of public and official concern over the health aspects of the *trans*-isomers produced during the hydrogenation of fats and oils, a number of laboratories may be interested in setting up their own laboratory-scale hydrogenation programs in order to develop hydrogenation processes that will suppress *trans*-isomerization. However, before experiments to evaluate selectivity can be started, proper performance of the hydrogenator must be ensured. For example, reproducible results must be achieved so that comparisons can be made and conclusions drawn. Also, the reaction environment must promote the preservation of catalytic activity. These and other drawbacks, together with their solutions, will be discussed for the benefit of those who may be embarking on a laboratory-scale hydrogenation program.

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METHODS AND EQUIPMENT FOR ON-FARM RECOVERY AND PROCESSING OF SUNFLOWER OIL FOR USE IN DIESEL ENGINES. L.F. Backer*, L. Jacobson and J.C. Olson, North Dakota State University, Agricultural Engineering Department, Fargo, ND 58105.

A small Japanese screw expeller and filter press have been used to recover oil from sunflower seed. This expeller and filter are of a size suitable for on-farm use. Feeding rate and percentage oil recovery are examined. The expeller housing was instrumented with strain gauges in an attempt to correlate pressure-to-feed rate and oil recovery. A standardized filtration procedure was used to determine filtration rates of 4 commercial sunflower oils at various temperatures and pressures.

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ECONOMIC ANALYSES OF SUN OIL FUEL. Delmer L. Helgeson* and LeRoy W. Schaffner, Agricultural Economics Department, North Dakota State University, Fargo, ND 58105-5636.

Vegetable oil as an extender or substitute for diesel fuel is receiving increased attention from farmers and other agencies concerned with energy. If research confirms that sun oil can be used in diesel engines without harmful effects, there will be increased interest in how farm operators can procure vegetable oil and at what cost. Many farmers are interested in providing their own supply of sun oil on the farm, whereas others may be interested in procuring their supply from commercial sources. This paper provides information for on-farm processing of whole sunflower seed. Investment and operating costs for 3 sizes of screw-type presses were estimated—0.35 ton, 1.67 tons and 5.0 tons/8-hr day. Costs were estimated for processing 4,800 gal of sunflower oil (sun oil) annually and for operating each of the presses 2,400 hr (300 days)/year. The 4,800 gal was estimated to be the volume of diesel fuel an average North Dakota farm would consume each year. The cost/gal to process 4,800 gal of sun oil was estimated by charging current market rates for all resources. Costs were also estimated for operating the presses 300 days/year using current market prices for all resources, and under another scenario that excluded fixed building costs. On-farm sun oil processing costs were compared with commercial processing plant costs that covered a wide range in processing plant sizes ranging from 500 to 2,000 tons/day. This permits evaluating the per unit cost of supplying a crude sun oil product as an alternative diesel fuel under different organizational structures.

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ENDURANCE TEST OF SUNFLOWER OIL AS A DIESEL FUEL. Mariusz Ziejewski and Kenton Kaufman*, Agricultural Engineering Department, North Dakota University, Fargo, ND 58105.

Two endurance tests were completed on a diesel engine in the Allis-Chalmers Engine Division at Harvey, Illinois. The 2 tests included a 500-hr baseline test with #2 diesel fuel and a 600-hr test with a 50/50 blend of alkali-refined sunflower oil with #2 diesel fuel. A continuous test cycle of 3 min at high idle and 10 min at peak torque was used. During the baseline test, there were no significant problems with engine operation. However, problems were experienced during operation on the blended fuel. While using the blended fuel, (a) there was abnormal carbon build-up on the injection nozzle tip, (b) the nozzle opening pressure dropped 10-15%, (c) the injection nozzle needles stuck, (d) there was excessive carbon build-up on the intake ports, (e) operation problems of the turbocharger were observed, and (f) piston ring sticking problems were experienced.

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INVESTIGATION OF PLANT OIL (SOYBEAN) AS A DIESEL FUEL EXTENDER. Joseph F. Peters*, B.J. Schroer, Myrton Rand, Curtis Adams and M. Carl Ziemke, Johnson Environmental & Energy Center, University of Alabama in Huntsville, Huntsville, AL 35899.

The Johnson Environmental and Energy Center (JEEC) has recently completed an investigation of plant oil, specifically, degummed soybean oil, as a diesel fuel extender. Fuel blends of one-third degummed soybean oil and two-thirds no. 2 diesel (2:1 blend) and one-half degummed soybean oil and one-half no. 2 diesel (1:1 blend) were used in a 6-cylinder, 404-in.^{3}, turbocharged direct injection engine. A total of 800 hr was logged in 3 phases; 200 hr with the 2:1 blend, 200 hr with the 1:1 blend, and 400 hr with the 2:1 blend. The Engine Manufacturers' Association (EMA) recommended test cycle was used. The first two 200-hr tests were used to investigate crankcase oil contamination by unburned soybean oil. Relative crankcase oil viscosity was determined at 50-hr intervals. The variation of viscosity was small when the 2:1 fuel blend was used. After 100 hr with the 1:1 blend, the crankcase oil viscosity was 3.5 times at 150 hr and 5 times at 200 hr. Using the 2:1 fuel blend during the first 200 hr, the corrected maximal horsepower (CMH) remained practically constant, ranging from 133 to 132 CMH. During the 200-hr test using the 1:1 fuel blend, the CMH dropped to 113 CMH. After investigating crankcase oil contamination and finding no adverse effect with the 2:1 fuel blend, a 400-hr test using the 2:1 fuel blend was initiated, changing crankcase oil at 100-hr intervals. The initial CMH was 123.6 but dropped to 106.2 at the end of 129 running hr. It remained relatively constant for the balance of the 400-hr run, varying from a high of 110.1 to a low of 105.2. The obtained data suggest that the major portion of this damage occurred when using the 1:1 fuel blend. The CMH decreased during the 200-hr test of the 1:1 fuel blend and in the initial 100 hr of the 400-hr run using the 2:1 fuel blend. The CMH remained virtually constant during the initial 200-hr test with the 2:2 fuel blend and during the last 300 hr of the 400-hr test. Indications are that a 2:1 fuel blend is acceptable.

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EXTRACTION AND UTILIZATION OF WINTER RAPE OIL AS A DIESEL FUEL EXTENDER. C.L. Peterson*, G.L. Wagner, J.C. Thompson, D.L. Auld and R.A. Korus, Department of Agricultural Engineering, BEL, Rm. 318, University of Idaho, Moscow, ID 83843.

Most of the winer rape production in the U.S. is grown in the Palouse area of eastern Washington and northern Idaho. Even though the total acreage of the crop is small at present, the adaptability of the crop, yield of oil per acre and low iodine number make it an attractive source of emergency fuel to guarantee the continued agricultural production of the area in case of a petroleum shortage. The varieties of winter rape currently grown are high in erucic acid and glucosinolates, and the oil produced has a viscosity about 17 times that of diesel fuel. These factors present problems requiring special consideration if winter rape is to be economically and reliably used as a fuel. The University of Idaho program on this oil is interdisciplinary, involving plant scientists, chemical and agricultural engineers, animal scientists and agricultural economists seeking solutions to production, extraction and utilization of both oil and meal. An automatically controlled, on-farm processing system of 45 kg/hr capacity is in use for extracting the winter rape oil used in engine tests. Filtration of the oil involves a 48- to 72-hr settling period and a 3-stage forced filtration system. Flow rates, extraction percentages, percentage foreign matter and energy

requirements for varying input seed temperatures will be reported. Fuel formulas have been developed through laboratory viscosity and oxidation tests. Formulas developed thus far include vegetable oil/diesel fuel mixtures with commercial detergent, dispersant and antioxidant additives. Fuel temperature at the injector nozzle of the engine has been measured to aid in comparing the formula viscosity to diesel at injection temperature. Formulas developed have been used in short- and long-term engine screening tests. Characteristic performance data from 3 types of engines and engine wear data from long-term engine screening tests of 800-hr duration will be presented. Crankcase oil analysis data will also be included. Although vegetable oil utilization in the engine still cannot be recommended for general use, engine piston ring gumming, wear and power loss have been reduced and engine life has been greatly extended compared to earlier tests with pure safflower oil.

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SUMMARY OF WORK WITH VEGETABLE OIL AS A SUBSTITUTE FOR DIESEL FUEL AT THE UNIVERSITY OF SASKATCHEWAN. R.C. Strayer, Department of Agricultural Engineering, University of Saskatchewan, Saskatoon, Canada.

Early in 1980, a project funded by a research grant from Agriculture Canada to investigate the feasibility of using canola (rapeseed) oil as a fuel for diesel engines was instigated at the University of Saskatchewan. Three organizations are jointly conducting the overall project, each examining certain portions of it. A Saskatchewan Research Council economic study indicated that there is a favorable energy output-input ratio from the production and oil extraction of canola, in the range of 4-6:1. At present, the cost of canola oil is slightly more than twice that of diesel fuel, and the economic feasibility will depend on the rate of increase of canola oil compared to other energy costs. Engine tests involved a 2-cylinder Petter diesel and a 6-cylinder John Deere turbocharged diesel. Results were similar for both engines, and indicated that: (a) maximal power was essentially the same when burning canola oil as when burning diesel fuel; (b) specific fuel consumption was about 6% higher when burning canola oil, but because it has a heating value 14% less than diesel fuel, the thermal efficiency is somewhat higher when operating on canola oil; (c) there were no starting problems down to 10 C; (d) there were fewer particulates in the exhaust when burning canola oil; and (e) there was generally less combustion noise when burning canola oil. The high viscosity of canola oil—about 35 times that of diesel fuel at 20 C—will pose a major problem in using it at low temperature. Blending with diesel fuel and the creation of a methyl ester from the canola oil both proved effective in reducing viscosity, but neither lowered the pour point appreciably. Efforts on reduction of pour points and further work on blends and on heating the fuel will be described.

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EFFECTS OF PROCESSING AND CHEMICAL CHARACTERISTICS OF PLANT AND ANIMAL OILS ON DIESEL ENGINE PERFORMANCE. C.R. Engler*, L.A. Johnson, W.A. LePori and C.M. Yarbrough, Food Protein Research and Development Center, F.M. Box 183, Texas A&M University, College Station, TX 77843.

Performance characteristics of different plant and animal oil fuels in a single-cylinder diesel engine are compared. Fuels were prepared by taking sunflower oil, cottonseed oil and beef tallow through various stages of refining. These fuels were then tested in a water-cooled, single-cylinder diesel engine having a precombustion chamber fuel injection system. Short-term tests indicate that crude plant oils are not satisfactory fuels by themselves, but may give satisfactory performance when blended with diesel fuel. Degummed oils generally gave acceptable performance, indicating that further processing is unnecessary for short-term operation. Performance characteristics of different oils processed to the same degree also are compared. Longer term testing is required before any plant or animal oil can be recommended as a substitute for diesel fuel.

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FLUOROCARBON-HYDROCARBON INTERACTIONS IN INTERFACIAL AND MICELLAR SYSTEMS. Pasupati Mukerjee, School of Pharmacy, University of Wisconsin, Madison, WI 53706.

The interactions of fluorocarbons and hydrocarbons have been demonstrated to be extremely nonideal in several interfacial and micellar systems. Results from several different studies will be presented including (a) surface tensions of nonideal mixtures of liquid fluorocarbons and hydrocarbons and their interfacial tensions against water; (b) adsorptions of fluorocarbon and hydrocarbon surfactants to air/water, hexane/water and perfluorohexane/water interfaces, and a comparison of relative affinities; (c) formation of mixed micelles of fluorocarbon and hydrocarbon surfactants and evidence of partial miscibility of micelles; (d) comparison of adsorption of fluorocarbon and hydrocarbon surfactants to graphon; and (e) comparison of wetting powers of fluorocarbon and hydrocarbon surfactants.

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DETERMINATION OF SURFACE TENSIONS AND CONTACT ANGLES FROM THE SHAPE OF AXISYMMETRIC INTERFACES. Y. Rotenberg*, L. Boruvka and A.W. Neumann, Department of Mechanical Engineering, University of Toronto, 5 King's College Rd., Toronto, Ontario M5S 1A4, Canada.

A numerical algorithm is developed which calculates the surface tensions of axisymmetric fluid interfaces. In addition, the value of a contact angle at the contact of the fluid interface with a restricting wall can be determined. The method of solution optimizes a Laplacian curve which will have a best fit for a measured curve which represents the fluid interface. From measured coordinate points on the curve, the algorithm develops a suitable initial value for starting the optimization procedure. The optimized values are the coordinates of the origin (apex) of the Laplacian curve, the value of the curvature at the origin and the shape parameter, which is a characteristic of the capillary system. The computational method is not limited to any particular shape or specific properties of the capillary system: both configurations of a sessile drop or of a pendant drop are treated alike. Values of interfacial tensions as low as 10^{-2} ergs/cm^2 have been determined. It is anticipated that very much smaller interfacial tensions can be determined, also. The application of the technique consists of 2 steps: (a) acquisition of an image of a pendant or sessile drop; (b) determination of a number of coordinate points on the drop profile. In addition to the data in b, the only other input information required is the densities of the 2 fluid phases.

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THE EFFECT OF PARTICLE SHAPE ON PARTICLE ENGULFMENT BY SOLIDIFICATION FRONTS. R.P. Smith*, D.W. Francis, S.K. Li, Z. Policova, D.R. Absolom and A.W. Neumann, Department of Mechanical Engineering, University of Toronto, 5 King's College Rd., Toronto, Ontario M5S 1A4, Canada.

A particle embedded in the liquid phase of a solidifying matrix material will, upon encountering the solidification front, be either engulfed by the solid phase or pushed along by the advancing front. For low solidification rates, this phenomenon is governed solely by the change in free energy of adhesion of the particle to the solid-liquid interface, ΔF^{adh}. If ΔF^{adh} is negative, the particle is engulfed, and if ΔF^{adh} is positive, the particle is pushed. ΔF^{adh} thus provides the thermodynamic driving force for particle pushing. At higher rates of solidification, the effects of viscous drag on the particle become important. Ultimately, as the solidification rate is increased, a critical solidification front velocity, V_c, will be reached at which the viscous drag equals the thermodynamic driving force. If the solidification rate is increased further, the particle will be engulfed. The possibility thus exists for determining ΔF^{adh} from the measurement of V_c, the front velocity at which the particle just becomes engulfed. This provides a unique technique for determining the surface tension of small particles, γ_{PV}, because ΔF^{adh} is a function of γ_{PV}. The practice of determining γ_{PV} from V_c measurements is now well established in our laboratory and has been applied to several practical systems, i.e., coal powders, oil sands and suspensions of biological cells. The dependence of V_c on particle shape was not considered in establishing this relationship. Theoretically, the particle shape will affect both the viscous drag on the particle and the repulsive force between the particle and the solid-liquid interface. It was, indeed, observed that particles of certain shapes are engulfed at freezing front velocities significantly different from the expected V_c. Because in most systems of practical interest the particles are irregularly shaped, it is important to understand the effects of particle shape on engulfing. Thus, theoretical, as well as experimental, aspects of shape effects will be discussed.

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SURFACE TENSION OF BITUMEN EXTRACTED FROM OIL SANDS. Z.M. Potoczny*, E.I. Vargha-Butler and A.W. Neumann, Department of Mechanical Engineering, University of Toronto, 5 King's College Rd., Toronto, Ontario M5S 1A4, Canada.

The surface tension of bitumen obtained from different extractions of tar sand was determined by direct measurements and by means of contact angle measurements with water and/or other liquids or films of bitumen. The modified Wilhelmy technique was used at elevated temperatures in the temperature range from 40 to 100 C. The upper temperature boundary was determined by vapor pressure and thermal stability of bitumen, whereas the lower boundary was determined by the viscosity of bitumen. It was observed that the value of surface tension, γ_{LV}, is dependent on the solvent used in each extraction. At low temperature, the high viscosity of the bitumen does not allow conventional surface tension measurements, e.g., by the Wilhelmy technique. Therefore, films of bitumen were prepared by film casting from solution. It involves placing a few drops of the solution on a glass slide and spinning the slide on the rotor of a centrifuge at a relatively low speed until all the sol-

vent has evaporated, leaving a thin film of bitumen on the glass. Contact angles of water and/or other liquids were measured directly on each "solid" film surface by the sessile drop technique. The surface tension of bitumen were then calculated by means of an equation of state relation. Surface tensions of "solid" bitumen films obtained in this way also depend on the solvent used in the extraction and the temperature at which the extraction was performed. The surface tension values from the direct determination were extrapolated to room temperature, and then compared with surface tension values obtained from the contact angle measurements. The agreement is satisfactory and it was concluded that the surface properties of bitumen can be characterized at low temperatures by means of contact angle measurements.

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THE USE OF IMAGE ANALYSIS FOR THE QUANTIFICATION OF THE SIZE DISTRIBUTION OF DISPERSE SYSTEMS. D.R. Absolom*, Hospital for Sick Children, D.G. Wicks, General Foods Research, C.D. Myers, General Foods Research, and A.W. Neumann, University of Toronto.

Image analysis is a system specifically designed for extracting quantitative geometric information from images. The video-based image analyzer uses a television camera coupled to a suitable imaging device (e.g., a microscope) to produce an electronic video image of the particles of interest. The detected features may be counted, measured or classified according to a wide range of geometric, densitometric and textural criteria. We have investigated the possibility of using this technique for evaluating the size distribution of emulsions. Several oil/water disperse systems, prepared by sonication of commercial, food-grade oils, were examined. Image analysis appears to offer several advantages over conventional Coulter Counter® analysis. These include: (a) the direct microscopic evaluation of the particles following calibration of the system against precisely known reference standards, and (b) suspension of the particles in any liquid of any ionic strength without extensive dilution of the disperse system being required. Histograms on the basis of particle volume, assuming a spherical shape, were developed for both the image and Coulter Counter® analyses. A comparison of the results obtained will be presented.

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PURITY ASPECTS OF HIGHER α-OLEFINS. A.H. Turner, Shell International Chemical Co., Ltd., CIMK/52, Shell Centre, London SE1 7PG, U.K.

The various processes which are used commercially to manufacture detergent-range α-olefins are compared in terms of the quality of the products obtained. Thermal cracking of N-paraffins gives the least pure olefins. Processes based on ethylene oligomerization are superior and, of these, the Shell Shop process gives α-olefins which are somewhat better in quality than processes based on aluminum alkyl chemistry. The practical consequences of the presence of internal and vinylidene olefins, dienes and paraffins in α-olefins are considered for the manufacture of α-olefin sulfonates, linear alkylbenzene, epoxides, alkyl bromides, mercaptans and copolymers with ethylene (linear low-density polyethylene). Low levels of impurities are desirable in most cases to minimize formation of unwanted by-products, or to reduce the costs of bleeding of inert components, or to ensure that the quality of the final product meets the requirements of the marketplace.

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FATS AND OILS FOR LEATHER FIBER LUBRICATION—CURRENT PRACTICES. Frank Scholnick, U.S. Department of Agriculture, Agricultural Research Service, Northeastern Region, Eastern Regional Research Center, 600 East Mermaid Lane, Philadelphia, PA 19118.

Emulsified fats and oils are used in leather processing to lubricate the fibers of hides and skins while imparting flexibility to the leather and increasing its strength. The process is called fat liquoring. Oil-in-water emulsions are applied to leather at elevated temperatures and result in coating the fibers, preventing fiber cohesion during drying and enabling fibers to slide past each other in service. The emulsions may be anionic, nonionic or cationic or blends. Anionic fat liquors are often prepared by sulfation or sulfonation of natural oils, whereas cationic fat liquors principally contain alkylated long-chain amines. Nonionic fat liquors may contain oxyethylated glycols, polyols, or phenols. More recently, sperm oil analogs have been synthesized and used in fat liquoring. The application of jojoba oil is currently under investigation.

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SELECTIVE AMIDATION OF FATTY METHYL ESTERS WITH N-(2-AMINOETHYL)-ETHANOLAMINE UNDER BASE CATALYSIS. R. Gabriel, Stepan Chemical Co., Edens & Winnetka, Northfield, IL 60093.

The reaction of N-(2-aminoethyl)-ethanolamine (AEEA) with saturated fatty methyl esters derived from coconut oil occurs under noncatalyzed conditions to yield principally N-(2-hydroxyethylamino)-ethyl fatty amide (I), derived from the condensation of the primary amine moiety of AEEA with the methyl ester. In the presence of 0.25 wt % sodium methoxide at low reaction temperatures (<90 C), 2 carboxamides are formed, the secondary monoamide I and also the tertiary monoamide, N-(2-aminoethyl)-N-(2-hydroxyethyl) fatty amide (II). As this mixture of 2° and 3° monoamides is heated to higher reaction temperatures (>120 C), the concentration of 2° monoamide (I) increases with concomitant decrease in 3° monoamide (II). As the reaction time is increased at the elevated temperature, the 3° monoamide continues to disappear. Increasing the base concentration to 2.5 wt % sodium methoxide promotes selective formation of amide II at low temperature. The results constitute evidence that at least 2 mechanisms are operating in fatty methyl ester amidations with AEEA and provide a classic example of thermodynamic vs kinetic control. Because amides I and II are intermediates to imidazoline amphoteric surfactants (e.g., powerful detergents, wetting agents, emulsifiers), knowledge of the reaction mechanisms in operation during the condensation of fatty methyl esters with AEEA will permit better understanding of the resultant products and the related processing conditions.

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C_{19} DIACID-BASED POLYAMIDES. Nelson E. Lawson* and T.T. Cheng, Union Camp Corp., PO Box 412, Princeton, NJ.

Polyamides and copolyamides were prepared from C_{19} diacid derived from the Koch reaction of oleic acid. The effect of changing polymerization conditions and catalysts, codiacids, diamines, monobasic and tribasic acids on the reaction rate and polymer properties was determined. A formulation consisting of C_{19} diacid, adipic acid (2:1 molar ratio) hexamethylene diamine and 1.5% trimer acid to control hot creep reacted at 275 C for 5 hr in the presence of a phosphoric acid catalyst appeared to give an optimal hot-melt adhesive for adhering leather.

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METHOD OF ANALYSIS FOR DEOXYNIVALENOL PRODUCTION BY *FUSARIUM ROSEUM* ON CORN, WHEAT, RICE AND BARLEY. G.A. Bennett*, S.E. Megalla and O.L. Shotwell, Northern Regional Research Center, 1815 N. University St., Peoria, IL 61604.

A method was developed to determine the production of deoxynivalenol by several isolates of *Fusarium roseum* on corn, wheat, rice and barley. Deoxynivalenol was extracted with methanol/water (50:50, v/v) 2X and partially purified by partitioning with ethyl acetate and acetonitrile/petroleum ether. Toxin is isolated by silica gel column chromatography (CB column). Interfering materials are removed from the column with washes of benzene, benzene/acetone (95:5, v/v), and chloroform/methanol (98:2, v/v). Deoxynivalenol is eluted with chloroform/methanol (95:5, v/v) and quantitated by gas chromatography of the trimethylsilyl derivative. This procedure is sensitive to 0.200 μg/g toxin, and recoveries of 75% (from spiked corn) were obtained at levels of 2 and 10 μg/g. Zearalenone production can also be monitored with this procedure.

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MODIFIED GOSSYPOL ASSAY PROCEDURES FOR ACID HYDROLYZED GLANDED COTTONSEED KERNELS. K.C. Rhee, Y.R. Choi and E.W. Lusas*, Food Protein Research and Development Center, F.M. Box 183, Texas A&M University, College Station, TX 77843, and R.W. Glass, Frito-Lay Co.

Wide variations in assay results were experienced when analyzing total and free gossypol contents in acid hydrolyzates of glanded cottonseed kernels. Basic chemistry studies showed that, although the majority of gossypol is, indeed, destroyed during the selected acid hydrolysis process, other compounds, which interfere with the official gossypol assay, are also produced. As a result, the current extraction method for assaying gossypol in cottonseed meal is not applicable for acid hydrolyzates. Therefore, a modified extraction procedure was developed specifically to assay for gossypol in cottonseed hydrolyzates and their products.

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VARIATIONS IN CYCLOPROPENOID FATTY ACIDS COMPOSITION IN COTTONSEEDS. Gordon S. Fisher* and John P. Cherry, ARS, USDA, Southern Regional Research Center, PO Box 19687, New Orleans, LA 70179.

The cyclopropenoid fatty acids (CPA) malvalic and sterculic acids in cottonseed oil can cause adverse physiological effects in animals when ingested in sufficient quantities. Hence, it is desirable to keep CPA quantities in cottonseeds and their products as low as possible. Large samples are required for the classical techniques used to quantitate CPA, thus limiting studies on the variability of these constituents among cotton varieties to average values for large

numbers of seeds. Development of a gas chromatographic method for quantitating the individual CPA malvalic and sterculic acids in less than 1 mg of lipid (*JAOCS* 58:945, 1981) permitted studying among seeds and within seed variations of these fatty acids. Among seeds variation of CPA composition in lipids was small; coefficient of variation ranged from 10% for individual seeds of the same boll to 20% for individual seeds compared among 14 varieties. Within seed variations were large. Percentages of CPA in lipids gradually decreased from 30% in the root tip to about 2% at the upper end of the axis, and 0.1% in the portion of the cotyledon nearest to the hull. The axial portion of the cottonseed is only about 5% of the kernel, yet it contained over one-half of the CPA in cottonseeds. CPA composition in different portions of immature seeds and in seeds germinated for several days in the dark was similar to those at the mature stage. Dihydrosterculic acid was also concentrated in the axis. There was no evidence of CPA in the phospholipid fraction of the oil. The high concentration of CPA in the root tip suggests that they may play some type of physiological role in cottonseeds.

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THIN LAYER CHROMATOGRAPHIC AND SPECTRAL ANALYSES OF POSSIBLE AFLATOXINS WITHIN GRAIN DUSTS. W.V. Dashek*, T. Eadie, G.C. Llewellyn, S.A. Olenchock and G.H. Wirtz, Depts. of Biology, Pharmacology, Medical Biochemistry and Microbiology, West Virginia University, Virginia Commonwealth University, Department of General Services, Mycotoxin Laboratory, Richmond, Virginia, and Division of Respiratory Disease Studies, NIOSH, Morgantown, West Virginia.

The National Institute for Occupational Safety and Health is interested in assessing the hazards to grain workers associated with respirable grain dusts of all types. One of these hazards could involve the occurrence of mycotoxin-producing fungi within grains. Aflatoxins, a class of mycotoxins, are hepatocarcinogens, mutagens, teratogens and toxins. Here, we report an attempt to determine whether airborne dusts from barley, spring wheat, Durum wheat, flax and oats, as well as settled dusts, contained aflatoxins. These dusts were collected at port grain terminals in the Superior-Duluth region of the U.S. One hundred mg fr wt lots of each dust were mixed with 6 mL chloroform for 1 hr and then filtered. The chloroform was evaporated to dryness and the residue was reconstituted in 100 μL chloroform and spotted onto 20 × 20 cm, 250 μm thick Adsorbosil-1 thin layer plates. Then 10 μg each of AFB_1, AFB_2, AFG_1 and AFG_2 were spotted onto the plates as markers. The plates were developed in unlined chambers containing 100 mL absolute chloroform/3 mL 95% methanol and then viewed with a UV source. Four fluorescent bands were observed for each dust except corn. The compound(s) comprising bands 1 (lowest R_f), 2, 3 and 4 (highest R_f) exhibited red, blue, blue-green and red fluorescences, respectively. The compound(s) which comprise band 2 of all but possibly flax dust possessed the same or nearly the same (0.47 ± 0.07 to 0.51 ± 0.05) R_f values as AFB_1 (0.46 ± 0.06). Thin layer chromatographic (involving multiple solvent systems) as well as ultraviolet and infrared spectroscopic attempts to verify the possible occurrence of AFB_1 within the dusts will be reported. In addition, quantification of purported AFB_1 by high pressure liquid chromatography, fluorodensitometry and a visual dilution technique will be detailed. This work was supported by WVU Medical Corporation and NIH Biomedical Research Grant no. 5507-RR05433-18, and the National Institute for Occupational Safety and Health.

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ALTERED LIPID METABOLISM IN HEXAFLUOROACETONE (HFA)-INDUCED TESTICULAR ATROPHY. Peter J. Gillies* and Ki-Poong Lee, E.I. du Pont de Nemours and Company, Inc., Haskell Laboratory for Toxicology and Industrial Medicine, PO Box 50, Elkton Road, Newark, DE 19711.

Many chemicals induce testicular atrophy (TA), characterized by inhibition of spermatogenesis and degeneration of germinal cells. HFA was used in this study as a model compound with which to investigate possible mechanisms of chemically induced TA. Because gonadotoxins often affect carbohydrate and lipid metabolism, lipogenesis from [^{14}C] glucose was investigated in testes from control and treated rats. Treated rats (HFA rats) were dosed, dermally, with 130 mg/kg/day HFA·sesquihydrate for 14 days; pair-fed control rats (PFC rats) were dosed with an equal volume of water. HFA rats developed TA, characterized by impairment of the maturation of spermatocytes and spermatids; similar changes were not observed in testes of PFC rats. Compared to PFC rats, the incorporation of [^{14}C] glucose (dpm/mg lipid-free dry weight) into total phospholipids, triacylglycerols and sterols + diacylglycerols was increased 3-fold ($p<0.05$), and the sp act of total testicular lipid (dpm/mg lipid) was increased 2-fold ($p<0.05$) in testes from HFA rats. In contrast to other lipid fractions, the incorporation of [^{14}C]-glucose into cholesteryl esters + hydrocarbons was decreased 3-fold ($p<0.05$) in testes from HFA vs PFC rats. Because squalene is the major lipid labeled in this fraction, sterologenesis may also be inhibited in the testes of HFA rats. Lipid metabolism thus is significantly altered in HFA-induced testicular atrophy.

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RESIDUAL TOXIC EFFECTS OF HEATED FAT AFTER FEEDING FRESH CORN OIL. H.G. Gabriel*, J.C. Alexander and V.E. Valli, Departments of Nutrition and Pathology, University of Guelph, Guelph, Ontario N1G 2W1, Canada.

The feeding of thermally oxidized fats (TOF) to animals results in a variety of toxic symptoms. The extent of recovery from TOF toxicity was studied in rats. Corn oil (CO) and olive oil (OO) were thermally oxidized at 180 C for 72 hr with aeration. The product was distilled under reduced pressure and the distillate esterified with ethanol. A purified 15% TOF diet was fed to male weanling rats for 30 days, after which the TOF was replaced with fresh CO. The new diet was fed to all experimental groups for either 30 or 60 days. TOF diet consumption and feed efficiency were similar to the control diet. Lower final body weights were observed for the TOF animals after 60 days with fresh CO. No such residual effect was noted on organ weights upon substituting fresh CO for TOF. Changes in levels of organ lipids resulting from feeding TOF persisted throughout the experiment. Substituting fresh CO for 60 days caused the plasma 18:1 concentrations to drop well below levels found after the 30 days with TOF. Cardiac and renal glycogen levels were depressed by TOF, and rose dramatically upon feeding the fresh CO diet. Tissue proteins increased significantly in the hearts of the TOF animals. The change to fresh CO resulted in a return to control levels after 60 days. Numerous tissue fatty acid changes, involving primarily 18:1, 18:2 and 20:4 resulted from feeding the TOF diets, most occurring in the free fatty acid and triacylglyceride fractions. After 60 days of feeding fresh CO, only minor differences persisted in the original TOF groups compared to the controls. Histopathological examination of various organs revealed extensive damage, especially to the lung, liver and testes. Some reversal of the histopathological injury was obtained from feeding the fresh CO diet for 60 days.

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DIETARY METHIONINE AND CHOLINE AND THEIR EFFECTS ON MYOCARDIAL LESIONS IN MALE RATS. E.R. Farnworth*, J.K.G. Kramer, A.H. Corner and B.K. Thompson, Animal Research Centre, Agriculture Canada, Research Branch, Ottawa, Ontario, Canada K1A 0C6.

Diets containing 20% casein and 20% vegetable oil have been used for some time in rat feeding trials done to establish the cardiopathogenicity of vegetable oils. Recently, the methionine status of this diet has been questioned. An experiment was therefore undertaken to determine if the 20-20 diet is methionine-deficient and what effect it has on the incidence of heart lesions in rats. Six diets containing 20% soybean oil and 20% casein with or without supplementation with choline (0, 500, 1000 mg/kg) and/or methionine (1.5 g/kg) were fed to weanling, male Sprague-Dawley rats (25/diet). A control diet low in methionine (20% soy protein) and containing 10% soybean oil was also fed to 25 animals. Urine urea and formimino-glutamic acid (FIGLU) were measured after 3, 6 and 12 wk to determine the degree of methionine deficiency. Methionine and choline supplementation to the basal diet containing casein had little effect on urea or FIGLU levels. Animals which received diets supplemented with methionine grew significantly better than rats which received no supplment. Choline supplementation had no effect on growth performance. Liver sections stained with oil red-O stain showed a response to choline supplementation and to a lesser extent to methionine. The incidence of myocardial lesions in the rats after 16 wk on the diets was not influenced by the methionine or choline status of the diet.

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QUALITY CONTROL IN PROCESSING DRYING OILS. Bob Pierce, Honeymead Products Co., 25—44th Ave. NE, Minneapolis, MN 55421.

A brief history of linseed oil, its production trends, uses and prospects for the future are discussed. Methods of processing, effects of process variables on oil quality, how quality is measured and how it is maintained are the main topics of this paper. While linseed oil production declined steadily for many years after World War II, it has stabilized in recent years and shortages of petroleum products could cause a return to linseed oil in the form of water emulsions. Brief references to other drying oils will be included. Quality control begins with seed quality and covers storage, cleaning, processing and degumming. Refined oils described include alkali-refined, blown, heat bodied and chemically modified oils. Present quality control methods are described. Petroleum methods such as the "Foots" test for degummed oils are described. Recent developments used on occasion include liquid chromatography,

TLC, UV and IR spectroscopy, but the real workhorse has been gas chromatography. Recent developments in capillary GC and fused silica columns have improved separations and reduced analysis times. Near infrared reflectance shows some promise for future quality control work.

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QUALITY CONTROL IN PROCESSING INDUSTRIAL OILS AND FATTY ACIDS. David J. Kriege, Emery Industries, Inc., 4900 Este Ave., Cincinnati, OH 45232-1491.

Cost-effective, timely and precise quality control in a high technology specialty fatty chemical company challenges the imagination. Creative use of modern, rapidly developing analytical instrumentation and electronic equipment is essential. An overview of the newest instrumentation and how it is used in our laboratories will be presented. Also discussed will be examples of time and precision studies on tests run according to standard or modified AOCS methods using such equipment compared to historical techniques. Examples of problems (opportunities) encountered in our laboratories as a result of analytical methods, new equipment, sampling, exposure and disposal of toxic materials will be presented for discussion.

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QUALITY OF COMMERCIAL OIL AND OILSEED PRODUCTS. W.B. Sizer, General Testing Laboratories, Division of SGS Supervision Services Inc., 1001 E. Pender St., Vancouver, B.C. V6A 1W2, Canada.

In Canada, as in the U.S., quality of commercial oil exports is determined by independent laboratories, whereas quality of oilseed exports is controlled by government agencies. An independent laboratory has no direct control of oil exported. The oil is sampled and analyzed at time of shipment to determine whether certain contract specifications are met. Because a particular oil may be shipped to any of a number of countries with different end-uses, analysis requirements are not necessarily the same. Besides analysis, other precautions are taken to ensure that quality is maintained. These include inspection of ships' tanks for cleanliness and suitability. In respect to oilseeds in Canada, quality is controlled at various stages by district adherence to grading standards regarding such items as dockage, seed maturity and moisture. All of this sampling and control work is done by the Canadian Grain Commission, a government agency. Grading standards make no reference to oil content, and as most exports of oilseed are sold on a certain minimal oil content, an analysis for oil content is performed by an independent laboratory on samples taken by the Canadian Grain Commission at the time of shipment.

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QUALITY CONTROL IN THE USE OF DEEP FRYING OILS. S.G. Stevenson*, M. Vaisey-Genser and N.A.M. Eskin, Dept. Foods and Nutrition, H508 Duff Roblin Building, 190 Dysart Road, Winnipeg, Manitoba R3T 2N2, Canada.

The chemical and physical changes that occur in frying fats during use and their significance to fat life and to finished product quality are reviewed. The more commonly used quality control tests to monitor these changes are examined as is their applicability to food service institutions and food processors. The advantages and disadvantages of these tests and possible modifications to improve their ease for on-the-spot testing are discussed. Chemical tests such as free fatty acids (FFA), hydroperoxide value (HV) and peroxide value (PV) are available to those operations having laboratory facilities whereas sensory and physical tests including foam height, color, smoking, viscosity, odor and product flavor are generally used by most food service facilities for on-the-spot assessment. The reliability of these tests, however, depends on the source and type of frying fat, the food being fried and, in sensory and physical tests, on the skill and experience of the operator. Studies completed recently in our laboratory found a high correlation between polar compounds or FFA and length of frying time which suggests that either could predict oil abuse accurately. Recent adaptations which could facilitate on-the-spot testing by semiskilled personnel including a spot test for FFA and an instrument capable of monitoring the change in dielectric properties of an oil during frying will be examined. Regardless of the quality control test used, the question of specifying reliable cut-off levels which can be related to the health and sensory constraints remains. This will also be discussed.

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THE ROLE OF THE RESEARCH LABORATORY IN THE DEVELOPMENT OF QUALITY CONTROL PROCEDURES. G.R. List, Northern Regional Research Center, U.S. Dept. of Agriculture, 1815 N. University St., Peoria, IL 61604.

The research laboratory has played a major role in the development of quality control procedures for edible fats and oils. Historically, this research can be traced in part to the need for basic information on the composition, processing, and flavor stability of edible soybean oil. In this review of basic contributions made by research laboratories, emphasis will be placed on methods for evaluating crude, partially processed and finished oil quality by organoleptic, instrumental and chemical tests.

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DIETARY LIPID MODULATION OF IMMUNE RESPONSIVENESS IN MICE. Kent L. Erickson, Dept. of Human Anatomy, Univ. of California, School of Medicine, Davis, CA 95616.

The effects of dietary fat concentration and saturation on the development of immune responsiveness were studied. Mice were subjected to dietary manipulation either prenatally and postnatally, or after weaning. The weights of lymphoid organs were significantly influenced by dietary fat, whereas those of other organs were not. Serum levels of IgG_1 and IgG_2, but not IgM or IgA increased in mice fed the polyunsaturated (PUF) diet compared to levels in mice fed the saturated fat (SF) diet. T-cell responses to mitogens were influenced by both saturation and concentration of dietary fat; the changes were reflected in the lymphocyte and not cell numbers. In contrast, dietary fat affected the percentage of splenic B-cells, but not the levels of B-cell transformation. Blastogenesis of lymphocytes from diet-manipulated mice in response to alloantigens from control mice was significantly greater for those fed a diet adequate in essential fatty acids (EFA) than those fed a fat-free diet. As the concentration of dietary fat increased, responses decreased. Cytotoxicity mediated by allogenic splenic or peritoneal lymphocytes against melanoma cells was greater for mice receiving diets with only EFA than for those receiving diets with no fat. Small increases in dietary PUF, however, resulted in decreased cytotoxicity, whereas significant suppression of cytotoxicity was observed when the dietary fat concentration was greater than 8%. Thus, high levels of fat, particularly PUF, suppress lymphocyte functions whereas low levels intensify this response. We conclude that lipids can modulate the level of immune responsiveness; however, the exact mechanism by which this occurs remains to be determined. (Supported by NCI, DHHS grant CA 30273 and the National Live Stock and Meat Board.)

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SOYBEAN OIL EMULSION DECREASES THE CAPACITY OF MONONUCLEAR PHAGOCYTES TO PRODUCE COMPLEMENT. Robert C. Strunk* and Kathleen Kunke, National Jewish Hospital and Research Center/National Asthma Center, Denver, CO.

Soybean oil emulsified with egg yolk phospholipid (Intralipid) (IL) had been used extensively in infants and adults as a source of essential fatty acids and fats of parenteral nutrition. Biopsy and autopsy studies of patients who have received this material have demonstrated the presence of lipid vacuoles in macrophages throughout the reticuloendothelial system. Because a major function of these cells is synthesis of complement (C) components, we have studied the effect of ingestion of soybean oil emulsions on C synthesis by macrophages and by blood monocytes, the precursors to tissue-derived macrophages. Guinea pig (GP) peritoneal macrophages incubated in vitro with IL, as low as 2.3 mg/dl, ingested IL and had a decreased capacity to synthesize the second (C2) and fourth (C4) components of C. The decrease in C synthesis was *not* due to a decrease in cell viability and was not associated with a decrease in production of total protein or lysozyme. The decrease in C synthesis by cells incubated with IL for 4 hr was similar to the decrease in production by cells incubated with IL for 48 hr. In similar studies, human peripheral blood monocytes incubated in IL, 19 or 38 mg/dl, produced significantly decreased amounts of C2 when compared to controls. Similar to GP cells, the effect of IL on the monocytes was selective for C2 and the production of lysozyme, β-glucosaminidase or PGE_2 was not altered. Unlike the GP cells, the inhibition of C2 production by monocytes was reversible: C2 levels returned to normal after removal of IL; cells stimulated with opsonized zymosan produced levels of C2 comparable to stimulated control cells, despite the continued presence of IL within the cells; and cells incubated with arachidonic acid, in addition to IL, produced C2 as well as control cells. It is possible that a general increase in fat metabolism in response to the ingestion of IL nonspecifically consumed arachidonic acid, decreasing its availability as a substrate for a cell product that is important in production of C2. It is likely that this product is not PGE_2, because production of this arachidonic acid metabolite was not affected by IL. As the effects on C2 production were seen with concentrations of IL commonly seen in plasma of infants receiving IL iv, this study has implications for the clinical use of oil emulsions in parenteral nutrition.

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LIPOSOMES AS VEHICLES FOR VACCINES: ADJUVANTICITY AND EFFICACY AS PROTEIN CARRIERS. Roberta L. Richards*, Walter Reed Army Inst. of Research, Loren I. Alving, California Inst. of Technology, Joel Moss, National Institutes of Health, Benoy

Banerji, Medical Univ. of So. California, and Carl. R. Alving, Walter Reed Army Institute of Research, Walter Reed Army Medical Center, Washington, DC 20012.

Liposomes (synthetic phospholipid vesicles) have been proposed as both adjuvants and immunologically inert carriers of antigens in vaccines. We have studied the immunogenicity of a protein (cholera toxin, or CT) bound to liposomes through its receptor (ganglioside G_{M1}) or encapsulated within liposomes lacking G_{M1}. Immunization of rabbits with CT bound to G_{M1}-containing liposomes enhanced serum anti-CT production 18-fold over immunization with CT alone. The addition to the liposomes of lipid A from Gram-negative bacterial lipopolysaccharide increased anti-CT production over 600-fold above that obtained in the absence of liposomes. The CT bound to G_{M1}-containing liposomes had the added advantage of having less than 1/10,000 as much cytotoxicity in a human fibroblast assay as did CT alone. CT does not bind to preformed liposomes lacking G_{M1}, but when present during the swelling of such liposomes, as much as 1/2 of the liposome-associated CT was exposed on the outside of the liposomes. Thus, the CT associated with liposomes lacking G_{M1} was only partially encapsulated, and that which was exposed retained its toxicity. This partially encapsulated CT was as immunogenic as was CT bound to G_{M1}-containing liposomes. We conclude that liposomes can be very effective adjuvants and can serve as carriers for protein antigens, with the potential to reduce antigen toxicity, as well.

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ROLE OF MEMBRANE LIPIDS IN THE IMMUNOLOGICAL KILLING OF TUMOR CELLS: I. TARGET CELL LIPIDS. Seymour I. Schlager*, Dept. of Microbiology, University of Notre Dame, Notre Dame, IN 46556, and Sarkis H. Ohanian, Natl. Cancer Inst., NIH.

The properties of tumor cells that may be associated with their ability to resist or escape from humoral or cell-mediated immune (CMI) attack have been investigated. P815 mouse mastocytoma cells cultured for 17 hr with metabolic inhibitor drugs (adriamycin, actinomycin D, puromycin) were increased compared to controls in their susceptibility to killing by antibody (Ab) plus complement (C). Conversely, tumor cells cultured with insulin or hydrocortisone were increased in their resistance to Ab-C killing. The drug and hormone effects were dose- and temperature-dependent and reversible; these effects on the susceptibility of the cells to Ab-C killing correlated with the ability of the cells to synthesize complex cellular lipids and fatty acids, but not with cellular DNA, RNA, protein, or carbohydrate synthesis or with the distribution or expression of antigen on the cell surface. Further, drug and hormone treatment affected cell lipid and fatty acid composition: tumor cells rendered sensitive to Ab-C killing after drug treatment were decreased in their total lipid content, in their cholesterol:phospholipid mole ratio, and were increased in the unsaturated fatty acid content of neutral lipids and phospholipids. Hormone-treated resistant cells showed the opposite effects. In contrast, the ability of drug- or hormone-treated tumor cells to resist CM killing did not correlate with their ability to incorporate radioisotopically labled precursors of DNA, RNA, protein, or complex carbohydrate synthesis, or with total cellular lipid synthesis. However, tumor cell susceptibility to CMI attack did correlate with the synthesis and composition of specific complex cellular lipids. Tumor cells that were most susceptible to CMI attack were enriched in their content of highly polar phospholipids (lecithin and sphingomyelin); these cells demonstrated a markedly reduced net negative cell surface charge density. Again, hormone-treated cells made more resistant to CMI attack showed the opposite results. These data suggest: (a) the lipid composition of tumor cell membranes may be of fundamental importance for the ability of the cells to resist humoral and CMI attack; (b) the metabolic properties of tumor cells that are associated with their sensitivity to humoral vs CMI attack are different; and (c) different physical properties of cell membranes that are influenced by cellular lipid and fatty acid composition (fluidity vs cell surface charge density) may be responsible for the differences in tumor cell susceptibility to humoral vs cellular immune attack.

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ROLE OF MEMBRANE LIPIDS IN THE IMMUNOLOGICAL KILLING OF TUMOR CELLS: II. EFFECTOR CELL LIPIDS. Seymour I. Schlager*, Dept. of Microbiology, Univ. of Notre Dame, Notre Dame, IN 46556, and Monte S. Meltzer, National Cancer Inst., NIH.

Peritoneal macrophages (MØ) from mice become cytotoxic after incubation in lymphokine (LK)-rich supernatants of antigen-stimulated spleen cell cultures. Tumoricidal activity is evident with MØ treated with LK for 4 hr, becomes maximal after 8-12 hr incubation and decreases to control levels by 24-36 hr. To gain insight into LK-induced functional changes, the lipid composition of MØ cultures was analyzed by high pressure liquid chromatography. MØ were cultured in LK in medium with 10% serum for 0-36 hr. At various time points, cultures were washed and incubated with tumor target cells; concomitantly, the lipid fraction of similarly treated MØ was extracted. LK induced marked changes in MØ lipid composition: cellular content of cholesterol (CHOL) and polyunsaturated fatty acid content of cellular lipids increased 5-10 fold after 8 hr when the cells showed maximal tumoricidal activity. Cellular lipid and fatty acid content returned to control levels by 24 hr when the MØ had lost tumoricidal activity. These changes were not observed with equal numbers of MØ cultured in control supernatants. MØ cultured in LK in medium with 10% delipidized serum showed little or no increase in total CHOL content, yet these LK-activated cells were strongly cytotoxic. Onset of tumoricidal activity by activated MØ in delipidized serum was accompanied by increases in cellular free CHOL content with a corresponding depletion in CHOL esters; an increase in the unsaturated fatty acid content of cellular lipids was also observed in these cells. Both increases returned to control levels by 24 hr. In contrast, MØ from mice genetically unresponsive to LK treatment showed no tumoricidal activity or changes in lipid or fatty acid composition after treatment with LK. As a further probe, MØ activated for tumor cytotoxicity in vivo with a number of different immunostimulants were also analyzed for their lipid composition; these effector cells showed similar increases in cellular CHOL and unsaturated fatty acid content when the cells were maximally tumoricidal; nontumoricidal inflammatory MØ showed no such changes. These results suggest that tumoricidal activity by MØ activated in vivo or by LK in vitro appears to be linked to characteristic changes in the effector cell lipid and fatty acid content. These changes may be fundamental for the ability of the MØ to express or regulate its tumoricidal activity.

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THE SPECIFIC ROLE OF PHOSPHOLIPIDS AND NEUTRAL GLYCOLIPIDS IN MYXOVIRUS-INDUCED MEMBRANE FUSION. Richard T. Huang, Institut für Virologie, Justus Liebig Universität Giessen, Frankfurter Strasse 107, D-6300 Giessen, FRG.

Myxoviruses (influenzavirus and paramyxovirus) enter host cells by 2 successive steps consisting of attachment and fusion between viral and cellular membranes. The initial attachment is thought to occur through specific interaction of neuraminic acid of cellular membrane with the hemagglutinin protein of influenzavirus or the hemagglutinin-neuraminidase complex of paramyxovirus. The following step of membrane fusion is mediated by the hydrophobic projections of viral glycoproteins present at the termini of the HA_2-segment of the hemagglutinin and the fusion protein, but the cellular counterparts involved in this fusion step have not been yet considered. We used techniques of reconstituted membranes, competitive hemolysis inhibition and fluorescence energy transfer to characterize cellular receptors responsible for membrane fusion. Choline-containing phospholipids (sphingomyelin and lecithin), as well as several glycolipids terminating in galactose were found to be major participants in membrane fusion. Other lipids did not seem to interact strongly with the viral envelopes. It could further be shown that the surface glycoproteins of cellular membrane did not directly participate in the fusion process. The results obtained indicate the existence of a group of lipids responsible for the myxovirus-induced membrane fusion and show that this fusion involves specific recognition of certain phospholipids and neutral glycolipids.

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INCREASING UTILIZATION EFFICIENCY OF WORLD PROTEIN RESOURCES. Morton Satin, Industrial Grain Products, PO Box 6089, Montreal, Quebec H3C 3H1, Canada.

A large proportion of the world's population does not receive an adequate supply of well-balanced food protein. This has been variously ascribed to an insufficient food supply, the improper distribution of food because of economic or political considerations, a lack of nutritional knowledge, or poor social conditions. Regardless of specific cause, this critical problem still exists and has served as the motivation for considerable research activity and intervention programs in the area of food and agriculture. Research activity has taken the form of an extremely wide variety of work ranging from genetic engineering to assorted levels of so-called appropriate technology. A middle ground technology that has proved successful in many intervention programs is that of composite flours. The system described uses a computer programming method to develop blends of protein supplements that complement native sources of protein while maintaining the traditional organoleptic appeal of common foods. Through this technique, the utilization efficiency of many protein sources can be improved. Experience with this system also provides a broader insight toward the development of lesser known protein materials and processing methods.

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THE NECESSITY FOR FUTURE OILSEED PROCESSING TECHNOLOGY TO YIELD NONDENATURED PROTEINS. E.D.

Murray* and S.D. Arntfield, Food Science Department, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada.

The oilseed crops (e.g., soybeans, canola, sunflower) annually produce extremely large quantities of protein; however, only relatively small amounts of protein from these sources are used directly in food applications. With the increasing pressures of production efficiency, nutrition and economics being applied to animal protein products, it would appear that the future bodes well for plant proteins if these materials can be provided in forms acceptable to consumers. Usually, in almost all food applications, a native protein is essential in order to obtain a specific desired functionality. Although processed legume and cereal proteins are relatively easy to produce in a native state, such is not the case for oilseed proteins. This situation will surely impede the exploitation of oilseed proteins in food uses. Native and denatured protein materials will be compared with a view to emphasizing the need for new oilseed processing technology designed to yield nondenatured proteins.

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BIOENGINEERING AND OILSEED PROTEINS. C.A. Bock, POS Pilot Plant Corp., 118 Veterinary Road, University of Saskatchewan Campus, Saskatoon, Saskatchewan S7N 2R4, Canada.

There are, at present, several methods for producing protein concentrates and isolates from oilseed meals. Many of the improvements in the composition of the proteins and oils from oilseed crops have come from the plant breeders, however, and the current state-of-the-art of plant breeding will be reviewed. Bioengineering will be viewed in this instance as the manipulation of genetic material and its introduction into a host by the use of an "engineered" microorganism: the benefits and possibilities for the oilseed industry for such manipulations will be discussed. Engineered microorganisms might be used to ferment meal proteins to produce improved protein. For example, the production of a fungal mass suitable for extrusion into a mushroom-like product is already a reality. In view of the need to increase protein yields from crops, the possibilities of applying this type of technology to biomass from oilseed crops will be explored.

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RHEOLOGICAL ASSESSMENT OF FUNCTIONAL PROPERTIES OF OILSEED MEAL PROTEINS. Marvin A. Tung* and Brian D. Ladbrooke, University of British Columbia, Department of Food Science, Suite 248, 2357 Main Mall, Vancouver V6T 2A2, Canada.

The rheological properties of oilseed meal proteins are of considerable pertinence in the processing of high-protein ingredients and provide criteria for application of functional protein ingredients in formulated foods. This paper emphasizes the relevance of rheological testing in clarifying the physicochemical nature of the protein which permits prediction of functional behavior under a variety of conditions, as experienced in complex food systems. An instrumental texture profile analysis using an Instron tester reveals the complex interaction between experimental variables when frankfurters are supplemented with soy or canola protein isolates. At a more fundamental level, a description of the viscoelastic nature of meal protein gels is obtained from nondestructive dynamic testing. In these experiments, a Weissenberg rheogoniometer fitted with a temperature control attachment was used to follow changes in the loss tangent as a function of temperature during protein gelation. The loss tangent indicates the proportion of viscous and elastic components contributing to the structure of the dispersion and decreases in value as the gel network forms and the material becomes more elastic in nature.

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EFFECT OF RECOVERY METHODS ON THE FUNCTIONALITY OF VEGETABLE PROTEINS. Dietrich Knorr, Department of Food Science & Human Nutrition, University of Delaware, Newark, DE 19711.

The effects of protein coagulants and coagulation conditions (pH, temperature) as well as dehydration methods and dehydration conditions (temperature of drying medium, pH of coagulate) on the functionality of protein concentrates recovered from food processing waste effluents is presented. Special attention is given to protein solubility, fat binding and water binding capacity of potato, rice bran, tomato seed and soy protein concentrates. Baking properties and textural properties of protein-fortified breads are also given. The multiple interactions between protein recovery and protein functionality are shown and the potential for tailoring protein concentrates with desired functionality by selecting specific protein recovery procedures is discussed.

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CORRELATION BETWEEN APPARENT VISCOSITY OF EXTRUDED DEFATTED SOY FLOUR AND DIE SHEAR RATE. Bor-Wen Huang and Henry G. Schwartzberg, Food Engineering Department, University of Massachusetts, Amherst, MA.

The apparent viscosity of extruded defatted soy flour containing 30, 35 and 40% moisture was estimated by measuring pressure drops across extruder dies and the discharge rates of extrudate. Two die diameters and extruder rpm ranging from 5 to 130 were used to obtain a wide range of die shear rates. A linear relationship between the logarithm of apparent viscosity and the logarithm of die shear rate was obtained. Exponent values for a power law rheological model were calculated by measuring the slopes of these lines. These exponents range from 0 to 0.33 at die temperatures below 140 C and thus the apparent viscosity was almost inversely proportional to the shear rate. Such behavior can be characteristic of slippage at the die wall and suggests that, below 140 C, the soy extrudate resembled a concentrated suspension of a solid in a fluid. Because the shear rate and residence time in the extruder barrel are correlated, we have not been able to separate the influence of these 2 variables. Thirty percent M.C. defatted soy flour was extruded using die and metering section temperatures at 100, 120, 140 and 150 C. Identical relationships between apparent viscosity and die shear rate were obtained at die temperatures of 100 and 120 C. However, when die temperatures higher than 120 C were used, the apparent viscosity decreased. Moreover, at a die temperature of 150 C, the apparent viscosity changed radically and became Newtonian, i.e., independent of die shear rate when the die shear rate was below 30 sec^{-1}.

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WITHDRAWN

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UNUSUAL LIPID COMPOSITION OF AN OBLIGATE PSYCHROPHILIC BACTERIUM. Toshi Kaneda, Biology Group, Alberta Research Council, 11315–87 Ave., Edmonton, Alberta T6G 2C2, Canada.

A psychrophilic *Flavobacterium*, isolated from a soil of the Canadian Arctic, grew actively in the temperature range of 5-18 C but lost viability overnight at room temperature. De novo fatty acid synthetase of this organism was found to be similar to that of other bacteria having branched-chain fatty acids as major cellular fatty acids. The lipids of the organism were fractionated and identified by thin layer chromatography, gas liquid chromatography and mass spectrometry. The organism contained only one major phospholipid which was identified as phosphatidylethanolamine. The total fatty acids of the organism were separated into 3 classes: saturated, unsaturated and hydroxyl. Saturated fatty acids were the largely branched-chain type of iso- and anteiso-series. Unsaturated fatty acids were Δ^4- and Δ^9-isomers. Hydroxyl fatty acids were 3- and 4-hydroxyl isomers. The physiological significance of these unusual fatty acids in relation to the psychrophilic nature of the organism will be discussed.

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SATURATED, CYCLOPROPANE, MONOETHYLENIC AND POLYETHYLENIC BRANCHED-CHAIN FATTY ACIDS OF INSECT GUT-DWELLING FLAGELLATED PROTOZOANS. Wallace R. Fish, George G. Holz, Jr., and David H. Beach*, Department of Microbiology, SUNY, Upstate Medical Center, Syracuse, NY 13210.

Trypanosomatid flagellates of the genera *Phytomonas* and *Herpetomonas*, all parasites of the guts of various insects, carried out the de novo biosynthesis of a variety of even- and odd-numbered, iso and anteiso, saturated and unsaturated, C_{14}-C_{22} fatty acids. When they were grown axenically in a chemically defined and lipid-free medium, as much as 85% of their total fatty acids were branched. Among these fatty acids were novel even-numbered, iso-branched, polyunsaturated forms with 2-5 methylene-interrupted double bonds (iso-$C_{18}\Delta^{6,9}$, iso-$C_{18}\Delta^{9,12}$, iso-$C_{18}\Delta^{6,9,12}$, iso-C_{20}-$\Delta^{5,11,14}$, iso-$C_{20}\Delta^{5,8,11,14}$, iso-$C_{22}\Delta^{4,7,10,13,16}$), and an iso-$C_{19}$ cyclopropane fatty acid (iso, *cis*-9,10-methyleneoctadecanoic acid). Identifications were based on combinations of chromatographic,

chemical degradative and spectrometric (IR, PNMR, MS) procedures. The subject trypanosomatids are recommended as model organisms with which to study the influences on eukaryotic cell membrane functions of combinations of branches, cyclopropane rings and multiple double bonds in the fatty acyl groups of phospholipids.

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LIPID AND FATTY ACID COMPOSITION IN LARVAE OF *CRASSOSTREA VIRGINICA* DURING DEVELOPMENT. Fu-Lin E. Chu*, Kenneth L. Webb and Beverly B. Casey, Virginia Institute of Marine Science, Gloucester Point, VA 23062.

In order to observe the changes of lipid and fatty acid composition in larvae during development, the lipid and fatty acid composition of straight hinge (24-hr-old), 3-day, 6-day, 8-day and "eyed" larvae were determined by thin layer chromatography and gas liquid chromatography, respectively. Preliminary results from the analyses of lipid composition indicated that no qualitative change of lipid composition occur in larvae during development. There were some quantitative changes of fatty acid composition; the percentage of polyethylenic fatty acids were lower in younger larvae than in older larvae. The amount of total saturated fatty acids decreased in both the neutral and the polar fractions. Changes in the proportion of C-12, C-14, C-16 and C-18 saturated fatty acids were also observed. This paper will deal with variations in lipid class and fatty acid compositions of oyster larvae during development, in order to assess the nutritional significance of changes in lipids.

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BIOCHEMICAL CHARACTERIZATION OF THE MICROSOMAL LIPIDS OF *CARCHARIAS TAURUS*. A.O. Emokpae and G.E. Anekwe*, Department of Biochemistry, College of Medicine, University of Lagos & Nigerian Institute for Oceanography & Marine Research, Lagos, Nigeria.

Liver microsomes of *Carcharias taurus*, a common shark in Nigerian waters, incorporated [2-^{14}C]acetate into all the major classes of lipids. There was relatively greater incorporation into the neutral lipids than into the polar lipids. Saponification of the total neutral lipids fraction followed by petroleum ether extraction yielded the nonsaponifiable fraction (NSF). Alumina chromatography of the NSF yielded 3 major moieties of this fraction—the hydrocarbon fraction (21.29 wt % of the NSF), a sterol fraction (26.45 wt %) and the coenzyme fraction (52.26 wt %). Squalene was the major component of the hydrocarbon (34.26%), followed by pristane (12.75%); cholesterol was the predominant sterol (89.29%), but 1-hexadecyl glycerol ether and long-chain alcohols were present as minor constituents of this fraction. Vitamin A and coenzyme Q_{10} accounted for 87.8 and 12.2%, respectively, of the major coenzyme fraction. It is apparent from the present findings that *C. taurus* lipids conformed, to a substantial extent, to the general pattern in sharks in that its liver contained large amounts of the more unusual lipids such as hydrocarbons, that are not commonly found in appreciable amounts in other marine organisms. These unusual lipids are involved in buoyancy regulation. Class identification of the lipids was checked by ultraviolet spectral determination which showed characteristic absorption bands for the different compounds. Final characterization and proof of structure of the lipids was achieved by mass spectrometry. Electron microscopic examination of the liver microsomes revealed the presence of numerous and very large lipid droplets and provided evidence for the purity of the microsomes.

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EFFECTS OF VITAMIN B_{12} DEFICIENCY ON FATTY ACID PATTERNS ON LUNG PHOSPHATIDYLCHOLINE. James J. Peifer, Department of Foods and Nutrition, University of Georgia, Dawson Hall, Athens, GA 30602.

Dipalmitoyl phosphatidylcholine (PC) is the predominant phospholipid and surfactant in lung alveoli. Palmitic acid (16:0) is also most concentrated in PC of the liver and brain, and 16:0-rich PC accumulates the greatest amounts of odd-numbered fatty acids (ONFA), both 15:0 and 17:0, in vitamin-B_{12}-deficient rats (Peifer and Lewis, 1981). This report describes the effects of B_{12} deficiency on incorporation of ONFA into lung PC of rats. Groups of 3-5 rats were fed high-protein (24%) diets for 8 months. With our experimental conditions, the B_{12}-deprived rats developed a severe deficiency as evidenced by their mean daily excretion of 2,077 μmol of methylmalonic acid in the urine. Lung PC fatty acids of the controls included: 45.2% of 16:0 and 15.3% of 18:0; 1.1% and 1.4% of 15:0 and 17:0, respectively; 4.4% and 6.0% of 18:2 and 20:4, respectively. The B_{12} deficiency promoted a 3-fold increase of 15:0, but not 17:0, in lung PC. Daily supplements of 300 mg of 15:0 during last 10 days of the experiment promoted further increases of 15:0 in lung PC. The B_{12}-deficient rats also had proportionally greater amounts of both 18:2 and 20:4 in this lung phospholipid.

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USE OF UNSAPONIFIABLE MATTER FOR DETECTION OF GHEE ADULTERATION WITH OTHER FATS. R.S. Farag* and F.A. Ahmed, Biochemistry Dept., Faculty of Agriculture, Cairo University, A.A. Shihata, Chemistry Dept., Helwan University, S.H. Abo-Raya, Food Science and Technology Dept., Faculty of Agriculture, Cairo University, and A.F. Abdalla, Agronomy Dept., Faculty of Agriculture, Cairo University, Giza, Egypt.

Gas liquid chromatography (GLC) was used for the detection of lard and margarine admixture to buffalo and cow ghee. The chromatograms of the unsaponifiable matter could be divided into 2 parts representing hydrocarbons and sterols. Hydrocarbons were fractionated by GLC into 3-6 different compounds, depending on the lipid origin. The sterols were cholesterol and β-sitosterol. The content of cholesterol in lipid samples was in the following decreasing order: cow > buffalo > lard > margarine. With β-sitosterol, the concentration order was margarine > buffalo > cow > lard. The ratios of total hydrocarbons to total sterols in the unsaponifiable matter for margarine and lard differed the most for the various lipids. Adulteration of cow and buffalo ghee with various levels of lard or margarine caused significant changes in the unsaponifiable compounds. It is possible to determine the extent of admixture of lard or margarine to either cow or buffalo ghee by applying a simple regression equation for each unsaponifiable component. Hence, an examination of unsaponifiable matter appears to provide a rapid and simple laboratory method for the detection of ghee adulteration.

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LIPID COMPOSITION OF MILK OF MOTHERS OF PREMATURE AND FULL-TERM INFANTS. Joel Bitman* and D.L. Wood, U.S. Department of Agriculture, Beltsville Agricultural Research Center, Beltsville, MD 20705, and Margit Hamosh, P. Hamosh and N.R. Mehta, Georgetown University Medical School, Washington, DC 20007.

Milk was collected with an electric breast pump from mothers of 18 very premature (VPT, 26-30 wk gestation age), 28 premature (PT, 31-36 wk) and 6 term (T, 37+ wk) infants. Samples were taken from an entire breast collection on day 2-3 (colostrum), and at 1, 3, 6 and 12 wk postpartum. Total lipids were extracted in chloroform/methanol and percentage fat determined gravimetrically. Lipid composition was determined by quantitative densitometry after separation into classes (phospholipids, monoglycerides, free fatty acids, cholesterol, 1,2-diglycerides, 1,3-diglycerides and triglycerides) by thin layer chromatography (TLC). Fat content for 154 milk samples was 2.80 g/dl gravimetrically and 2.66 g/dl by TLC densitometry (r=0.85). The fat content of VPT milk (3.29 g/dl) was significantly higher at 1 wk than PT (2.30 g/dl) and T (2.36 g/dl) milk, whereas there were no differences at later lactation periods. Milk phospholipids were separated by TLC into classes (sphingomyelin, phosphatidylcholine, -serine, -inositol and -ethanolamine) and measured quantitatively. The fatty acid composition of the milk fat and of the phospholipids and cholesteryl esters were determined by gas liquid chromatography of fatty acid methyl esters. Data will be presented on the variations in the lipid composition of milk as a function of length of lactation and as a function of gestation age.

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PHOSPHOLIPID COMPOSITION AND STEROL EFFLUX FROM L-929 CELLS. Young-sun Son* and Chester E. Holmlund, Department of Chemistry, University of Maryland, College Park, MD 20742.

When L-929 fibroblasts are grown on a synthetic medium supplemented with 10% delipidized serum (DLS), sterol requirements for cellular reproduction are met by de novo synthesis of domesterol, the most abundant sterol in this cell line. Apolipoproteins present in the DLS can serve as acceptor molecules and can promote efflux of cellular sterol. Analysis by gas liquid chromatography indicates that about 2.5 μg sterol/mg cellular protein is excreted into fresh medium containing DLS within 12 hr, and then the amount slowly increased to 3.5 μg sterol/mg cellular protein over a 72-hr incubation period. Cellular sterol content is maintained at about 12 μg sterol/mg protein over this period. If dipalmitoylphosphatidylcholine (16:0 PC) is added at 2×10^{-5} M together with fresh medium, sterol excretion continues steadily and amounts to 32 μg sterol/mg cellular protein by 72 hr. Over this time period, the cellular sterol content is maintained at 11-13 μg sterol/mg cellular protein. The amount of sterol excreted in the presence of DLS and added phospholipid is influenced by the concentration, and by the fatty acid and base composition, of the phospholipid. The relative activity among the diacylphosphatidylcholines tested is as follows: 16:0 > 15:0 > 18:2. Among the dipalmitoylphosphatidyl compounds

tested, choline was more active than glycerol, which in turn was more active than ethanolamine. The most active phospholipid was a bovine sphingomyelin, which contained a mixed fatty acid content. A bacterial cardiolipin was also active.

HONORED STUDENT PRESENTATION

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COMPOSITIONAL CHANGES OF PERIPHERAL NERVE GLYCOLIPIDS WITH DEVELOPMENT AND WALLERIAN DEGENERATION. Jeffrey K. Yao* and Peter James Dyck, Lipid Biochemistry Lab, Peripheral Nerve Center, 812 Guggenheim Bldg., Mayo Clinic, Rochester, MN 55905.

The role of glycolipids in peripheral nerve myelinogenesis and regeneration after degeneration was investigated. The cerebroside, sulfatide and their respective fatty acid compositions of rat sciatic endoneurium were examined at various ages during development and at various times after nerve crush. The endoneurial cerebroside and sulfatide contents in developing rats had exceeded 50% of the adult values (~130 μg/mg dry wt) before day 20. At day 20, the nonhydroxy fatty acids 22:0, 24:0 and 24:1, which are characteristic of myelin glycolipids, had increased from <5% to 15-30% each whereas 16:0, 18:0 and 18:1 had decreased proportionately. In the α-hydroxy fatty acid fraction, 24:0 had already reached ~50% of total fatty acids of cerebroside by day 12. These findings suggest that the biosynthesis of glycolipids and the fatty acid elongation preferentially occur at the time when the peripheral nerve is undergoing active myelination. The concentration of endoneurial glycolipids decreased appreciably 6 days after crush injury. A maximal decrease of cerebroside and sulfatide contents (43 and 51% of controls, respectively) was observed at 12 days. By the time that nerve fiber regeneration had reached a fiber composition approaching normal (180 days), both the cerebroside and sulfatide contents had returned to near control values. A similar change with nerve degeneration and regeneration was also found for the fatty acids 22:0, 24:0 and 24:1 of glycolipids. Therefore, the maximal reduction of glycolipids is associated temporally with axonal degeneration and, particularly, with myelin conversion to sudanophilic lipid. These alterations in glycolipid composition relating to different stages of nerve development, degeneration and regeneration should be taken into account in interpreting alterations in peripheral nerve disease.

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EFFECT OF DIETARY FATTY ACIDS ON LIPID COMPOSITION AND DESATURASE ACTIVITY IN CHICKEN LIVER MICROSOMES. B.H. Simon Cho, H.E. Moore Heart Research Foundation, 503 S. Sixth St., Champaign, IL 61820.

Studies were conducted to investigate the hepatic microsomal lipid composition and desaturase activity from chicks fed diets containing a different fatty acid for 3 weeks. An individual fatty acid (lauric, myristic, palmitic, stearic, oleic or linoleic acid) was fed to chicks at a 14% level with 1% corn oil and 24% casein in the diet. A low-protein diet (12% casein) was included with lauric and linoleic acids. The microsomal cholesterol content was generally higher in chicks fed lauric, myristic and linoleic acids. Compared to the low-protein diet, high dietary protein resulted in higher cholesterol levels in chicks fed lauric acid, whereas this trend was reversed in chicks fed linoleic acid. Phospholipid and triglyceride levels showed no noticeable differences between groups, regardless of dietary fatty acid or protein levels. The fatty acid composition of total microsomal lipids revealed that saturated fatty acid did not accumulate in the liver microsomes from any of the dietary groups. On the other hand, microsomal oleic and linoleic acids were significantly increased in groups fed those fatty acids. The arachidonic acid content was relatively constant (10%) in all groups. The in vitro microsomal conversion of stearic acid to oleic acid was much higher in groups fed saturated fatty acid than in groups fed unsaturated fatty acid and was in the order of: saturated fatty acid > oleic acid > linoleic acid. The level of stearic acid desaturation was fairly similar in those groups which were fed a saturated fatty acid with high protein; however, low-protein diet caused a marked decrease in stearic acid desaturation in chicks fed lauric acid, whereas the effect of dietary protein level was insignificant in chicks fed linoleic acid.

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THE EFFECT OF LOCAL ANESTHETICS ON CHOLESTEROL ESTERIFICATION AND ACCUMULATION IN CULTURED CELLS. F.P. Bell*, Diabetes and Atherosclerosis Research, The Upjohn Co., Kalamazoo, MI 49001, and G.H. Rothblat and M. Bamberger, Medical College of Pennsylvania.

The local anesthetic lidocaine inhibited cholesterol esterification in cultured cells derived from tissues of various species including rodent, man and monkey. The addition of 1.5 mM lidocaine to cells in culture reduced by 20-50% the esterification of added [^{3}H] cholesterol, [^{14}C] oleate and endogenous fatty acids synthesized from [^{14}C] acetate. In Fu5AH rat hepatoma cells incubated with hyperlipemic serum lipoproteins, lidocaine increased the unesterified cholesterol mass of the cells but resulted in a decrease in cellular cholesterol ester mass. By using hyperlipemic serum lipoproteins containing labeled cholesterol of known specific activity, it was demonstrated that the influx of exogenous unesterified cholesterol by the cells was constant whereas its incorporation into cholesteryl esters was reduced in a dose-dependent fashion by lidocaine. Lidocaine may be useful as a tool for selectively altering the unesterified and esterified cholesterol contents of cells.

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GENETIC IMPROVEMENT OF SOYBEAN OIL. Keith J. Smith, American Soybean Association, 777 Craig Road, PO Box 27300, St. Louis, MO 63141.

Soybean oil is unique in that it contains more linolenic acid than does cottonseed, sunflower, corn, safflower, or the other minor vegetable oils used in the U.S. Linolenic acid has been blamed for most of soybean oil's flavor stability problems. Research to improve the quality of soybean oil has been underway since the mid-1940s. This presentation will review: the importance of linolenic acid reduction; results of soybean breeding programs designed to reduce linolenic acid levels; environmental factors altering fatty acid levels; physiological development of the seed and its relationship to linolenic acid levels, and will set the stage for the symposium.

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THE POTENTIAL FOR MODIFICATION AND STABILIZATION OF SOYBEAN OIL USING SUBSTITUTED PYRIDAZINONES. D.E. Terlizzi*, J.B. St. John and M.N. Christiansen, Beltsville Agricultural Research Center, USDA, AR, Beltsville, MD 20705.

A series of experiments was undertaken to determine the effectiveness of substituted pyridazinones in reducing the linolenic acid content of soybean oil. A greenhouse study was designed using soil-drench application to evaluate influence of growth medium (soil or Jiffy mix), pyridazinone type (SAN-6706, SAN-9789 or BASF 13 338) and pyridazinone concentration (5, 25 or 50 ppm) or general vegetative damage, seed weight and fatty acid composition of seed oil. Seed fatty acid composition was found to vary significantly with medium-type and pyridazinone-type and was further modified with increasing concentration. SAN-6706 at 5 and 50 ppm in soil reduced linolenic acid levels in seeds whereas similar treatment in Jiffy mix increased linolenic acid. Increased linolenic acid levels were also observed in BASF 13 338- and SAN-9789-treated plants with increases in pyridazinone concentration, resulting in increased linolenic acid. Folar application was also examined in a greenhouse experiment in an effort to by-pass the strong interactions observed with the pyridazinones and growth media. SAN-6706, SAN-9789 and BASF 13 338 were applied at ca. 10 days after flowering using 1% ethanol and 0.01% Tween 20 as surfactants. Only BASF 13 338 at 5 ppm significantly reduced the linolenic acid content of soybean oil. Combined results of laboratory, greenhouse and field studies suggest the substituted pyridazinones may be of value in the manipulation of soybean oil fatty acid composition, as well as in the inhibition of certain destabilizing factors.

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PROGRESS IN BREEDING FOR SOYBEAN OIL WITH LOW LINOLENIC ACID. E.G. Hammond* and W.R. Fehr, Department of Food Technology, Iowa State University, Ames, IA 50011.

The reduction of linolenic acid in oil crops by plant breeding has proved to be a laborious process requiring thousands of analyses. Progress in reducing linolenic acid content is made in small steps, and care is required to distinguish genetic reduction from variation caused by environmental conditions. Analysis time has been reduced by crushing the seed in a hydraulic press that will process 12 samples at one time, and by computerizing control of the gas chromatographic injection and computation. To estimate environmental effects, seed from promising plants is grown along with controls in plots of multiple environments. The most rapid progress has been made by treating soybeans with the mutagen ethyl methanesulfonate. The beans are soaked for 8 hr in ca. 0.025 M ethyl methanesulfonate, washed and planted wet in a field in moist soil. Depending on the variety, 7-60% of the seeds treated in this way produce a plant. About 10-15% of the plants with the lowest linoleic acid are chosen for testing in replicated plots. Soybean strains vary in their response to mutagens, and it seems that soybeans will need to be exposed to several cycles of mutagen treatment and selection to achieve the linolenic acid levels desired. Some progress also has been made by crossing low-linolenic-acid strains and searching the progeny for individuals with lower levels of linolenic acid than the parents. The lowest linolenic acid level produced by crossing and selection has been about 4.7%. By treating these low-linolenic-acid strains with mutagens, levels of about 3.5% have been reached.

Selection for low linolenic acid also has resulted in selection for increased oleic and reduced linoleic acids. Oils from these selections have increased flavor stability compared to common soybean oil. The low-linolenic-acid strains have poor agronomic properties, and the low-linolenic trait will need to be transferred to vigorous, productive plants.

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EFFECT OF GENETIC SELECTION ON LIPID METABOLISM IN SOYBEANS. R.F. Wilson, 4124 Williams Hall, USDA-ARS and Crop Science Department, North Carolina State University, Raleigh, NC 27650.

Recurrent selection methodology for increased levels of oleic acid and decreased concentrations of polyunsaturated fatty acids has demonstrated significant progress toward developing soybean germplasm with improved flavor quality. It is apparent, however, that genetic control of polyunsaturated fatty acid synthesis in soybean seed is not a simply inherited trait. It is highly probable that several different genes affect the desired changes in soybean fatty acid composition. In addition, the products of those genes may alter the synthetic activities of enzymes at specific points within the glycolipid metabolic pathways that lead to triacylglycerol biosynthesis. Exploration of the biochemical differences between selected genotypes has provided evidence to suggest that: genetic manipulation has altered the desaturase reaction for linoleic acid synthesis; the desaturase system uses phospholipid intermediates; phospholipids are metabolized to form diacylglycerol, a substrate for triacylglycerol biosynthesis; and there is no apparent diacylglycerol substrate specificity for diacylglycerol-acyltransferase. Hence, the observed changes in triacylglycerol composition during seed development may result from changes in phospholipid biosynthesis. Attempts are being made to determine the subcellular localization of triacylglycerol biosynthesis and the nature of the synthetic pathway. These experiments will increase our understanding of the complex nature of lipid biosynthesis in soybeans, and also demonstrate the specific relationships between genetic and biochemical differences in lipid metabolism by selected genotypes.

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SOYBEAN GERMPLASM EVALUATION—SEARCH FOR LOW-LINOLENIC LINES. Robert Kleiman* and James F. Cavins, Northern Regional Research Center, ARS, USDA, 1815 N. University St., Peoria, IL 61604.

More than 5,000 soybean samples from both the northern and southern soybean germplasm collections have been analyzed for their fatty acid compositions. Rapid esterification techniques have been developed in preparation for subsequent gas chromatography. Samples from maturity groups I through IX and from the wild collection were analyzed. Although fatty acid composition is known to be linked to environmental conditions (higher temperatures can result in lower linolenic acid levels), 9 of the 12 samples found to have less than 5% linolenic acid were in maturity groups I-III. The lowest found to date is 4.2% 18:3. A strong negative correlation has been found between the concentrations of 18:1 and 18:3. However, in a number of the low-linolenic acid lines, normal oleic acid concentrations were found with slightly higher than the usual linoleic acid observed.

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CHANGES AND LIMITATIONS OF BREEDING FOR IMPROVED POLYENOIC FATTY ACIDS CONTENT IN RAPESEED. Gerhard P. Röbbelen, Institute of Agronomy and Plant Breeding, University of Goettingen, Fed. Rep. Germany.

Beause of evident interdependences in the biogenetic substrate flow, zero erucic rapeseed oil is marked by both increased linoleic (18:2) and linolenic acid (18:3) contents. Notwithstanding, this 22% of 18:2 is too low for nutritional value and the 12% of 18:3 is too high for technical reasons. Therefore, monogenic mutants have been selected after chemical induction, producing as much as 35% 18:2 and as little as 3% 18:3. The agronomic performance of these genotypes, however, is considerably reduced compared to the original cultivar. Recurrent selection for higher yield was of little effect, too. By measuring ethane formation after cellular decompartmentation, thylakoid membranes of mutants were also shown to contain less 18:2 than normal. But, at present, any explanation as to the site and kind of the crucial metabolic restraint is speculative.

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CARBON DIOXIDE FLOODING FOR ENHANCED OIL RECOVERY: PROMISE AND PROBLEMS. F.M. Orr, Jr.*, J.J. Taber and J.P. Heller, New Mexico Petroleum Recovery Research Center, New Mexico Institute of Mining and Technology, Socorro, NM 87801.

Of the enhanced oil recovery methods currently being considered for application to many of the nation's older oilfields, carbon dioxide (CO_2) flooding may offer the greatest potential for additional oil recovery. In this paper, we review field experience to date and document the recent surge in field activity. The physical mechanisms by which CO_2 contacts and mobilizes crude oil are reviewed. Influence on the displacement process of factors such as the phase behavior of CO_2-crude oil mixtures, swelling of oil by dissolved CO_2, and reduction of oil viscosity are considered. Adverse effects of the viscous instability which occur when very low viscosity CO_2 displaces more viscous oil and water are discussed. Advantages and disadvantages of 3 potential methods for controlling the mobility of CO_2 are reviewed: thickening CO_2 with polymeric additives, reduction of CO_2 mobility by high-water saturations, and use of surfactants to generate foam-like emulsions of water and CO_2. Finally, a brief assessment of the future of CO_2 flooding research and practice is offered.

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SURFACTANT-ENHANCED STEAM DRIVES FOR HEAVY OIL RECOVERY. R.E. Dilgren* and K.B. Owens, Shell Development Co., PO Box 481, Houston, TX 77001.

Steam/noncondensible gas foam formulations were developed to reduce steam mobility in the steam-drive process as applied to heavy oil reservoirs with little or no dip. The steam/noncondensible gas foam process is intended to reduce or minimize the gravity layover problem in such reservoirs. Candidate surfactants for the steam/noncondensible gas foam process not only should be good foamers in porous media at elevated temperatures, but should also display hydrolytic and thermal stability and preferably low adsorption on the reservoir minerals. Several classes of anionic surfactants have shown promise in steam/noncondensible gas foam formulations. Commercially available dodecylbenzene sodium sulfonate, both branched side-chain and straight side-chain, as well as α-olefin sulfonates in the C_{16}-C_{18} range, proved effective to varying degrees. The α-olefin sulfonates appeared to be the most cost-effective of the surfactants studied in laboratory tests.

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APPLICATION OF SURFACTANTS IN THE PETROLEUM INDUSTRY. Richard C. Nelson, Shell Development Co., PO Box 481, Houston, TX 77001.

Surfactants are used in many segments of the petroleum industry —from exploration and production (e.g., lignosulfonates and aryl sulfonates in drilling muds, naphthalene sulfonates and glycoheptonates in cements) to refined products (e.g., amines and amides in gasoline, aryl sulfonates and salicylates in lube oils). Despite continuing decreases in U.S. oil production, increased drilling activity and deeper wells portend modest growth for surfactants used in oil production. The trend toward better fuel economy from smaller engines portends little growth in surfactants for refined products. By far the greatest potential for large increases in surfactant utilization by the petroleum industry lies in enhanced oil recovery. In micellar-polymer flooding, surfactants (e.g., petroleum and synthetic sulfonates, alcohol and alkylphenol alkoxylates and alkoxysulfates) release trapped oil by lowering interfacial tension. In many types of enhanced oil recovery, foams stabilized by surfactants (e.g., ethoxylates, aryl sulfonates, aryl ethoxyalkyl sulfonates) are being studied by improving oil recovery through better mobility control. If this research proves successful, surfactant-stabilized foam may replace the polymer in micellar-polymer flooding and may be used to improve oil recovery efficiency in steam, carbon dioxide and caustic flooding.

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THE USE OF INORGANIC SACRIFICIAL AGENTS IN COMBINATION WITH SURFACTANTS IN ENHANCED OIL RECOVERY. James S. Falcone*, Paul H. Krumrine and George C. Schweiker, The PQ Corporation, 280 Cedar Grove Road, R&D Center, PO Box 258, Lafayette Hill, PA 19444.

The effectiveness of the use of surfactants in chemically enhanced oil recovery processes is dependent on many factors. Uncontrollable factors such as reservoir parameters and minerology, as well as the nature of the crude petroleum, influence the choice of the chemical process and finer variations within the chosen technology. Each reservoir offers a different set of problems. When the use of a given surfactant is indicated, one attempts to further optimize the activity of this surfactant by modifying the chemistry of the reservoir system. Cost aside, maintenance of optimal surfactant activity is essential to minimize the oil/water interfacial tension. Also, loss of surfactant activity due to adsorption on substrate material is particularly disadvantageous because rock water wetting ability may be decreased. The use of alkaline, weak acid anions, such as sodium silicate, phosphate and carbonate, to enhance surfactant effectiveness has been studied. These sacrificial agents can reduce hardness cation activity in solution and compete with surfactant for active sites on the reservoir rock surface. Core flood results show that there is an inverse correlation between surfactant retention in the core and residual oil recovery. They also suggest

that surfactants may be recovered for reinjection by the optimal use of sacrificial agents, in particular, the sodium silicates.

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A STUDY OF SURFACTANT FLOODING AT HIGH SALINITY AND HARDNESS. J. Novosad*, B. Maini and J. Batycky, Petroleum Recovery Institute, 3512 33rd St. NW, Calgary, Alberta T2L 2A6, Canada.

Many surfactants have been patented for their potential use as agents for enhanced oil recovery by surfactant flooding. However, in field applications, petroleum sulfonates of molecular weights between 350 and 500 g/mol have been used almost exclusively. One of the greatest difficulties encountered in the application of petroleum sulfonates has been their poor solubility in reservoir brines, particularly those of higher salinity and high divalent ion contents. Removal of these ions from the reservoir by preflushing with a soft brine is usually impractical due to ion-exchange phenomena, or impossible due to a lack of fresh water sources. A number of chemical compounds have been suggested for use as cosurfactants having the goal of making petroleum sulfonates more compatible with reservoir fluids. While most of the research in this area deals with fairly pure compounds as cosurfactants, this paper summarizes work performed at PRI which has used commercially available surfactant materials. Some of these have the potential to act as effective cosurfactants to petroleum sulfonates in high salinity and high hardness environments. The types of compounds considered included low-molecular-weight alcohols, ethoxylated acetylenic glycols, phosphate esters, polyethanoxyalkyl ether, nonylphenol ethoxylate, ethoxylated fatty alcohol, sulfated ethoxylated lauryl alcohol, polyethoxylated vegetable oil and alkylether sulfate. The brine selected for the experiments was 80,000 ppm total dissolved solids (TDS) with a ratio of Na:Ca:Mg cations of 20:2:1. A mineral oil and pure alkanes have been used as the hydrocarbon phase. The data obtained included solubilities, phase behavior, interfacial tensions, displacement characteristics in Berea cores, viscosities, adsorption and retention. Summaries of results and examples of the combinations of surfactants and cosurfactants are reported in detail.

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ENHANCED OIL RECOVERY CHEMICAL NEEDS. Barry M. O'Brien, Exxon Chemical Americas, PO Box 3272, Houston, TX 77001.

The chemical industry is becoming increasingly aware of the many potential opportunities for surfactants and polymers in enhanced oil recovery (EOR). Perhaps it is less aware of the technical, economical and resource constraints which must be overcome if these markets are to develop. Beginning with a basic overview of EOR processes, the presentation then focuses on the need for surfactants and polymers which are effective and stable under conditions of high temperature and/or high salinity. Information is presented on volume requirements and costs for EOR injection fluids. The impact of economics and limited manpower resources on the timetable for EOR development is discussed briefly.

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POLYENE FATTY ACID COMPOSITION OF HEART MUSCLE PHOSPHOLIPIDS MODIFIED BY AGING, DIET AND CATECHOLAMINES. S. Gudbjarnason, Science Institute, Univeristy of Iceland, Dunhaga 3, Reykjavík, Iceland.

Alterations in fatty acid composition of phospholipids in rat heart muscle were examined in relation to age, dietary fat and catecholamine stress. Aging was accompanied by replacement of linoleic acid (18:2n6) by arachidonic acid (20:4n6) in phosphatidylcholine (PC) and replacement of linoleic acid by docosahexaenoic acid (22:6n3) in phosphatidylethanolamine (PE). Dietary corn oil (10% w/w) increased arachidonic acid in PC at the expense of linoleic acid, whereas dietary cod liver oil (10% w/w) increased docosahexaenoic acid, replacing the n6 fatty acids. Repeated administration of norepinephrine caused significant but reversible alterations in polyene fatty acid composition of PC and PE. A decrease in linoleic acid and an increase in docosahexaenoic acid were observed in these phospholipids during stress, whereas arachidonic acid decreased in PE and increased in PC during the same period. Dietary cod liver oil increased mortality during overstimulation with isoproterenol whereas dietary hydrogenated fish oil was without effect. Control rats had significantly lower mortality during isoproterenol stress when receiving vitamin E supplements.

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BIOLOGICAL PROPERTIES OF SOME POLYUNSATURATED FATTY ACIDS WITH ONE *TRANS* DOUBLE BOND. U.M.T. Houtsmuller, Unilever Research Laboratorium, Vlaardingen, The Netherlands.

All essential fatty acids (EFA) have *cis* double bonds in the (n-6) and (n-9) position. Additional skipped *cis* double bonds may change the EFA properties quantitatively, but not qualitatively. However, introduction of an extra *trans* double bond in the (n-13) position results in a fatty acid (columbinic acid) with peculiar properties: (a) it is incorporated unchanged into all complex lipids, notably at the 2-position of phospholipids, (b) prostaglandin-like products are not formed from this fatty acid; moreover, it inhibits PG-formation from arachidonic acid, (c) it cures EFA-deficiency symptoms that are due to structural insufficiencies, but has no effect on—or aggravates—symptoms that are the consequence of deficiencies in prostaglandin synthesis. Other isomeric and analogous fatty acids, all having next to the (n-6,9) *cis* double bonds one or more *cis* or *trans* ones in various positions, exhibited to a lesser extent the same effects. These results indicate that it is an oversimplification to take all fatty acids with *trans* double bonds together as one single group with identical properties; different types should be identified and appreciated separately.

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EFFECTS OF PARTIALLY HYDROGENATED VEGETABLE AND MARINE OILS ON MITOCHONDRIAL FUNCTION, MEMBRANE PHOSPHOLIPID FATTY ACIDS AND MICROSOMAL DESATURASE ACTIVITY IN THE RAT. Rolf Blomstrand* and Lennart Svensson, Dept. of Clin. Chem., Huddinge Univ. Hospital, S-141 86 Huddinge, Sweden.

Male weanling Sprague-Dawley rats were fed diets containing 20% (w/w) peanut oil (PO), partially hydrogenated peanut oil (HPO), partially hydrogenated Norwegian capelin oil (HCO), partially hydrogenated herring oil (HHO) and rapeseed oil (RSO) for 70 days. The partially hydrogenated diets were supplemented with 4.6 Cal % of linoleic acid. A preparative group separation of *cis* and *trans* isomers of monounsaturated fatty acid methyl esters was achieved according to chain length by reverse-phase HPLC. The different fractions containing *cis* and *trans* forms of monounsaturated fatty acid methyl esters were analyzed for their contents of positional isomers using glass capillary gas chromatography. The preparative step in the HPLC was also used analytically for the determination of the ratio between the *cis* and *trans* monounsaturated fatty acids. The partially hydrogenated oils were characterized and the distribution of the positional and geometrical isomers of monounsaturated fatty acids in different phospholipids of heart and liver mitochondria was estimated with the described technique. The relative distribution of positional *trans*-isomers of octadecenoic acid as a percentage of total *trans* octadecenoic acids in the 1-position of phosphatidylcholine and phosphatidylethanolamine from cardiac mitochondria isolated from rats, fed the different diets, has been determined. The influence on the ATP synthesis of isolated rat heart mitochondria by the different experimental diets was followed. There was a general tendency to a depressed ATP synthesis in isolated rat heart mitochondria from rats fed rapeseed oil, high in erucic acid, and from rats fed partially hydrogenated herring oil. Furthermore, we have studied the influence of dietary long-chain monoene fatty acids and *trans*-fatty acids on the rat liver microsomal activity of Δ^5 and Δ^6 desaturases in relation to the fatty acid composition of the microsomes. There was a tendency toward decreased Δ^6 and Δ^5 desaturase activities in liver microsomes from rats fed partially hydrogenated marine oils compared to rats fed peanut oil. The complex relationship between the dietary *trans*-fatty acids and the microsomal desaturase activity will be discussed.

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HYDROGENATED VEGETABLE OIL FATTY ACID ISOMERS: INCORPORATION INTO INDIVIDUAL LIPID CLASSES OF HUMAN TISSUES. John B. Ohlrogge* and Edward A. Emken, Northern Regional Research Center, U.S. Dept. of Agriculture, 1815 N. University St., Peoria, IL 61604.

Hydrogenated vegetable oils contain 15-20 different *cis* and *trans* positional isomers of oleic acid. We have recently reported that essentially all of these unusual fatty acid structures are present in human tissue total lipid extracts. To determine if the positional isomers are selectively distributed, we have now analyzed individual lipid classes from human heart, liver, plasma and red blood cells. *Trans*-18:1 isomers were found to be present in all lipid classes analyzed. The neutral lipid classes (triglyceride and cholesterol esters) contained higher levels of *trans*-18:1 than the phospholipids. Analysis of the *trans* and *cis* double bond distribution in heart and liver phosphatidylcholine has revealed a trend toward accumulation of isomers with double bonds near the methyl terminus relative to isomers with double bonds near the carboxyl. In addition, the double bond patterns have provided evidence for selective metabolism of the *cis*-10 and *trans*-14 octadecenoate isomers. Comparison of the distribution of *trans* double bond positions in adipose tissue with their patterns in butter and hydrogenated vegetable oils allows an estimate to be made of the relative contribution of these 2 sources of *trans* isomers to human diets. For subjects analyzed in this study, we estimate that at least 90% of the *trans* isomer intake originates from industrially hydrogenated vegetable oils.

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COMPETITIVE DEPOSITION OF 8-, 10- AND 12-*TRANS*- VS 9-*CIS*-OCTADECENOATE IN THE LAYING HEN. Alan C. Lanser, Northern Regional Research Center, 1815 N. University St., Peoria, IL 61604.

Tritium-labeled *trans*-8- (8*t*-18:1-^{3}H), *trans*-10- (10*t*-18:1-^{3}H), and *trans*-12-octadecenoate (12*t*-18:1-^{3}H) isomers were fed as paired mixtures with carbon-14-labeled *cis*-9-octadecenoate (9*c*-18:1-^{14}C) to laying hens. Competitive deposition into major lipid classes of egg yolk was determined by examining isotopic ratios. The hen preferentially incorporated 9*c*-18:1-^{14}C into yolk triglycerides at the combined 1- and 3-acyl positions and at the 2-acyl position over each of the *trans* isomers. Yolk phosphatidylethanolamine displayed selection for the *trans* isomers in the order 12*t*- > 8*t*- > 10*t*-18:1-^{3}H. Each *trans* isomer was incorporated into this lipid class to a greater extent than 9*c*-18:1-^{14}C. Phosphatidylcholines contained more 12*t*-18:1-^{3}H but less of the 8*t*- and 10*t*-18:1-^{3}H isomers than 9*c*-18:1-^{14}C. The *trans* isomers were concentrated at the 1-acyl position of phospholipids and discriminated against at the 2-position. Yolk cholesteryl esters preferentially contained 12*t*-18:1-^{3}H but discriminated against the 8- and 10-*trans* isomers. Radiochromatograms of yolk lipids indicated that chain shortening occurred during metabolism of each of the *trans* isomers. Elongation and desaturation of the 10*t*-18:1-^{3}H was observed. Deposition of 8*t*- and 10*t*-18:1-^{3}H compared to 9*c*-18:1-^{14}C in specific organ lipids was also observed and will be discussed.

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BIOSYNTHESIS OF OCTADECADIENOIC ACIDS FROM OCTADECENOIC ACIDS PRESENT IN PARTIALLY HYDROGENATED VEGETABLE OIL. Larry D. Lawson*, E.G. Hill and R.T. Holman, The Hormel Institute, University of Minnesota, 801 16th Ave. NE, Austin, MN 55912.

Rats were fed an essential fatty acid deficient (EFAD) diet containing 8% partially hydrogenated vegetable oil (PHVO) as the sole fat source. The fat contained 45% *trans* 18:1 isomers, 27% *cis* isomers, 2% 18:2 *cis,trans* isomers and 2% 18:2 *cis,cis* isomers. The liver phospholipid fatty acid methyl esters were found to contain up to 3% 18:2 *cis,trans* and 3% 18:2 *cis,cis* fatty acids. The 18:2 *cis,trans* and 18:2 *cis,cis* isomers were isolated and purified by preparative GLC and argentation thin layer chromatography. Double bond positions were identified from the products of ozonolysis and reduction, with some confirmation by capillary GLC. Several positional isomers for both 18:2 *cis,trans* and 18:2 *cis,cis* were shown to exist which were not present in the diet. Most of the *cis,cis* isomers found were those which are produced in animals fed a fat-free diet (18:2ω7, 18:2ω9, 18:2ω10). However, the 18:2 *cis,trans* isomers found were mostly Δ5 and Δ9 desaturation products of *trans* 18:1 isomers. In conclusion, these results show that EFA-deficient rats can and do desaturate monoenoic fatty acids present in dietary PHVO to dienoic fatty acids.

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SUPPRESSION OF POLYUNSATURATED FATTY ACID METABOLSIM IN RATS BY DIETARY PARTIALLY HYDROGENATED VEGETABLE OIL OVER TWO GENERATIONS. E.G. Hill, L.D. Lawson and R.T. Holman, Hormel Institute, University of Minnesota, 801–16th Ave. NE, Austin, MN 55912.

Weanling rats from stock mothers and from mothers fed 18% partially hydrogenated soybean oil plus 2% corn oil (PHSO + CO) were fed the PHSO + CO diet for 10 wk, after which the PHSO was removed from the diet. A third group of weanling rats from stock mothers was fed an essential fatty acid deficient (EFAD) diet containing 18% PHSO plus 2% hydrogenated coconut oil (PHSO + HCNO) for 10 wk, after which the PHSO was removed from the diet. At several time points before and after removal of PHSO from the diet, liver phospholipid fatty acids were measured. The 18:2 of single (1G) generation PHSO + CO fed rats was elevated by 50% and in second generation rats (2G) to 75% above control (2% CO) rats. Removal of PHSO from the diet of 1G rats caused a gradual decrease of 18:2 to control values by 3 months. However, removal of PHSO from the 2G rats resulted in a large lipid decrease (50%) of 18:2 which persistently remained significantly below control values. In EFAD rats fed PHSO + HCNO, the 18:2 was double that of control (2% HCNO) rats, and the 20:3ω9 was nearly half that of control rats; both reached control values within 3 months after removal of PHSO from the diet. We conclude that isomeric fatty acids present in PHSO inhibit rat liver desaturase and that the degree of inhibition is even greater in second generation rats.

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DIETARY SURVEY IN PREGNANCY IN A LOW SOCIOECONOMIC GROUP. M.A. Crawford, Wendy Doyle and D. Kuhn, Department of Biochemistry and Nutrition, Nuffield Laboratories of Comparative Medicine, Zoological Society of London, Regent's Park, London NW1, U.K.

Essential fatty acids (EFA) are required for early brain development. We have studied weighed food intakes and circulating EFA in 76 mothers in a low socioeconomic group to examine those at risk to low birth weight, and to define the relative importance of protein, dietary fats and energy. The mean protein intake was 66.9 g and was above the Recommended Daily Allowance (RDA) in each trimester. Only 6% of the mothers met the RDA of 2,400 kcal. The intakes of mothers with infants born below 2,500 g were significantly lower in energy, fat and pyridoxine intakes, but not in protein.

Birth weight group	<2500 g Mean	(n=9) SE	>2500 g Mean	(n=62) SE	p
Energy, MJ (kcal)/day	6.0(1446)	0.95	7.2(1723)	0.4	<0.001
Protein, g/day	61.7	5.2	67.8	1.7	N.S.
Fat, g/day	62.1	5.0	72.6	1.7	<0.025

Maternal and fetal blood analyses at term showed that the availability of EFA correlated with birth weight; e.g., maternal plasma cholinephosphoglyceride:

Birth weight	n	Linoleate	SE	Arachidonate	SE wt%
<2501	7	14.2	1.7	6.87	1.01
2501-2850	11	16.3	2.58	8.97	0.96
2581-3000	10	18.3	1.82	7.42	0.62
3001-3500	13	20.8	0.82	8.73	0.33
3501-5000	9	20.0	0.65	9.23	0.48

Placental perfusion studies and analysis of maternal and fetal blood showed that the placenta was exporting arachidonate to the fetus in preference to linoleate. Maternal blood at midterm had a higher proportion of arachidonate in the phosphoglycerides than at term, suggesting that the rate of its synthesis from linoleate might not keep pace with the placental utilization and export.

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COMPARATIVE EVALUATION OF 6 METHODS OF SOLVENT EXTRACTION WITH RESPECT TO NEUTRAL AND POLAR LIPIDS IN MEAT. M.R. Sahasrabudhe* and B.W. Smallbone, Food Research Institute, Agriculture Canada, Ottawa, Ontario K1A 0C6, Canada.

Samples of ground beef containing 3 levels of fat (>5%, 15% and >20%) were extracted for total fat by 4 methods of wet extraction with solvents (chloroform + methanol, hexane + isopropanol, ethyl alcohol + ethyl ether) and 2 methods of Soxhlet extraction of freeze-dried material (petroleum ether and chloroform + methanol). The extracted lipids were purified by biphasic separation with chloroform + methanol + water (2:1:0.8) and fractionated into neutral and polar lipids by silicic acid column chromatography. Chloroform + methanol-based solvents extract more total lipid than that extracted by petroleum ether. The difference is partly accounted for by the extraction of polar lipids in chloroform + methanol.

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POSSIBILITIES FOR BETTER PRECISION OF THE ANALYSIS OF SHORT-CHAIN FATTY ACIDS. Giovanni Bigalli*, Robert D. Houseal, Jr., and Dennis R. Eichelberger, Hershey Foods Corp. Research Dept., 1025 Reese Ave., Hershey, PA 17033.

The accuracy and precision of short-chain fatty acids analyses have been significantly lower than for the rest of the members of the homologous series. In a previous study, volatility was demonstrated not to be the primary cause, and other factors such as chromatographic conditions affect quantitation more directly. This report presents further studies of the causes that affect precision and presents the evaluation of specific methodology and conditions that minimize this problem. The nature of the compounds and the proximity of the solvent in the chromatogram demands better understanding and special considerations during the analysis. These details will be discussed.

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DETERMINATION OF *TRANS* FATTY ACIDS IN MILKFAT. L. deMan*, Food Specialties Co. Ltd., Ajax, Ontario, and J.M. deMan, University of Guelph, Guelph, Ontario, Canada.

Milkfat is extremely complex, with about 500 different fatty acids reported in the triglycerides. Seasonal variation results in higher unsaturated fatty acid levels in summer than in winter. Rumen microbes hydrogenate unsaturated feed lipids to yield a mixture of geometrical and positional isomers which are transmitted to the milk. Total isolated *trans* fatty acids in milkfat reported in the literature range from 2 to 11% with maximal values in summer and minimal values in winter. A study was undertaken about the use of AOCS method Cd 14-6 for the determination of isolated *trans* levels in milkfat. The triglycerides of milkfat were analyzed using trielaidin as a standard and milkfat methyl esters were analyzed

using methyl elaidate as a standard. Loss of the methyl esters of the short-chain fatty acids was corrected by means of analysis of the fatty acid composition by gas liquid chromatography. The levels of *trans* found by using the triglycerides was considerably higher than by using the methyl esters. Infrared (IR) spectra of pure triglycerides of saturated fatty acids showed measurable absorption at 965 cm^{-1} whereas methyl esters of saturated and *cis* unsaturated fatty acids did not. Use of the IR method for analysis of *trans* isomers in milkfat triglycerides appears to be unsatisfactory.

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POLAR CAPILLARY GLC OF MOLECULAR SPECIES OF DIACYL, ALKYLACYL AND ALKENYLACYLGLYCEROL MOIETIES OF PHOSPHOLIPIDS. J.J. Myher* and A. Kuksis, Banting and Best Department of Medical Research, 112 College St., Toronto, Ontario M5G 1L6, Canada.

Our previously described method for separating diacylglycerols by gas chromatography on a short capillary column coated with SP-2330 (cyanopropyl silicone) has now been extended to the separation of the TMS or t-BDMS ethers of diacyl, alkylacyl and alk-1-enylacylglycerols released from natural glycerophospholipids by hydrolysis with phospholipase C (*B. cereus* or *Cl. welchii*). The silyl ethers are separated by GLC at 250 C on a 10-m open tubular column coated with SP-2330, using hydrogen as carrier gas. The molecular species are resolved according to carbon number and degree of unsaturation, and the alkylacyl and alk-1-enylacylglycerols are eluted earlier than the corresponding diacyl glycerols. At 250 C, the relative retention times are 0.52, 0.57 and 1.00 for the TMS ethers of 1-hexadec-1-enyl-2-oleoyl-, 1-palmityl-2-oleoyl- and 1-palmityl-2-oleoyl-*sn*-glycerol, respectively. Although good resolution is obtained for total diradylglycerol mixtures a complete separation of molecular species requires a preliminary segregation of the diacyl, alkylacyl and alkenylacylglycerols, as obtained by TLC using borate-impregnated silica gel plates (chloroform/acetone, 75:2). Applications of the method are illustrated by analyses of the diradylglycerol moieties of the phosphatidylcholines and phosphatidylethanolamines isolated from the total lipids of rat heart, rat kidney and bovine erythrocytes.

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HIGH PERFORMANCE LIQUID CHROMATOGRAPHY OF LIPIDS USING UV-DETECTION. Bengt G. Herslöf*, KabiVitrum AB, PO Box 121 70, S-102 24 Stockholm, Sweden, and Timothy J. Pelura, KabiVitrum Inc., c/o Food Sci. Dept., Cook College, Rutgers Univ., PO Box 231, New Brunswick, NJ 08903.

HPLC analyses of lipid material are generally done using refractive index detection because of the lack of strong UV-absorbing chromophores in most lipids. The possibilities of using UV-detection on such compounds at short wavelengths (200-220 nm) are discussed in this paper. Chromophores, such as the ester group, can be effectively used in spite of their comparatively weak UV-absorbance. Examples of HPLC on different types of lipids, e.g., triglycerides and fatty acids, will be discussed. The solvent systems in this chromatography are of great importance, especially in reversed-phase systems where ternary mixtures can be very useful and efficient in separating highly nonpolar lipids. The quantitative aspects of the UV-detector will be discussed and compared with other detection systems available.

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ANALYSIS OF LIPIDS BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY VIA FLAME IONIZATION DETECTOR AND MASS SPECTROMETRY. Warren L. Erdahl, Frederick C. Phillips, W. Robert Anderson and Orville S. Privett*, The Hormel Institute, University of Minnesota, 801 16th Ave. NE, Austin, MN 55912.

An apparatus is described for the detection and identification of the lipid classes by HPLC in conjunction with a flame ionization detector coupled with mass spectrometry. The general principle of the analysis is to separate the lipid classes by HPLC and analyze them simultaneously by flame ionization detector and chemical ionization mass spectrometry. The system is demonstrated on common lipid classes from natural sources.

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ANALYSIS OF DOLICHYL PHOSPHATE BY HIGH PRESSURE LIQUID CHROMATOGRAPHY. N. Chaudhary*, D.J. Freeman, J.W. Rip and K.K. Carroll, Department of Biochemistry, University of Western Ontario, London, Ontario N6A 5C1, Canada.

Dolichol consists of a series of isoprenoid alcohols containing 14-27 isoprene units, of which only the α-unit is saturated. They occur in mammalian tissues as free alcohols and fatty acyl esters, or as phosphorylated forms and their glycosylated derivatives. The phosphorylated forms serve as carriers of oligosaccharides in the biosynthesis of asparagine-linked glycoproteins. Dolichyl phosphate is thought to comprise only a small part of the total dolichol pool and its availability in tissues may be a rate-limiting factor in glycoprotein synthesis. A method developed previously in our laboratory for analysis of dolichol by high pressure liquid chromatography (HPLC) (Freeman et al., *Lipids* 15:191-193, 1980) was unsuitable for analysis of dolichyl phosphate because of incomplete recoveries during extraction from tissues and irreversible absorption on HPLC columns. These difficulties have been overcome by including phosphoric acid in the solvents used for extraction and chromatography. Tissues were extracted with chloroform/methanol (9:1) containing 20 mM phosphoric acid. The extract was washed with water and chromatographed on a silicic acid column to obtain a fraction enriched in dolichyl phosphate. This fraction was eluted with chloroform/methanol (9:1) after elution of neutral lipids with chloroform. The dolichyl phosphate was then analyzed by reverse-phase HPLC, using an RP-18 column and gradient elution with methanol and isopropanol, the latter containing 10 mM phosphoric acid. The first gradient was from 95 to 65% methanol for 5 min, and the second from 65 to 20% methanol over 15 min at a flow rate of 2 mL/min. Eluates were monitored by a variable wavelength detector set at 210 nm. Retention times for dolichyl phosphate ranged from 10 to 20 min. Individual homologs were separated and could be measured to a level of about 50 ng. Using this method, rat liver was found to contain 1.5-3 μg of dolichyl phosphate/g wet wt, amounting to less than 5% of total liver dolichol. Rat liver microsomes contained 64 ng/mg protein, or about 40% of total microsomal dolichol. These results are in agreement with the concept of microsomes as the major site of glycoprotein biosynthesis. (Supported by the Medical Research Council of Canada.)

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SEPARATION OF ISOMERS OF FATTY ACID METHYL ESTERS BY HPLC USING A SILVER-LOADED ALUMINOSILICATE COLUMN. T. Grossberger, Best Foods, a Div. of CPC International, 1120 Commerce Ave., Union, NJ 07083.

Silica gel (Whatman Partisil-10) was converted to sodium aluminosilicate by refluxing with aluminum nitrate and sodium hydroxide. The aluminosilicate was packed into an HPLC column (25 cm × 4.1 mm) by Whatman. The column was converted to the silver functionality by pumping through it a 1% $AgNO_3$ solution in methanol for 18 hr. The silver ions displace the sodium, and the silver aluminosilicate produced does not lose any silver when it is washed with additional methanol. The resulting column shows a high degree of selectivity for *cis* vs *trans* isomers. The relative retention (α) of *cis* isomers vs the corresponding *trans* isomer is greater than 2. For positional isomers, the order of elution for Δ6 through Δ11 is in reverse order (i.e., Δ11 before Δ9). This is the reverse of the order of elution from capillary GC columns coated with highly polar phases (SP2340, OV275). This makes the 2 techniques complementary because components that are not well resolved in one system can be resolved in the other. A preliminary separation of the silver-loaded HPLC column followed by capillary GC analysis of the separated fractions results in a more complete characterization of the isomers present in hydrogenated oils.

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RETENTION BEHAVIOR OF TRIGLYCERIDES ON A REVERSE-PHASE COLUMN USING PSEUDOPHASE LIQUID CHROMATOGRAPHY. J.A. Singleton* and H.E. Pattee, USDA, ARS, SR, North Carolina State University, PO Box 5906, Raleigh, NC 27650.

Surface-active agents are amphilic substances containing both a hydrophobic and a hydrophilic moiety. These substances can be added to a mobile phase in reverse-phase chromatography to further modify phase composition. Ionic surfactants were added to a non-aqueous mobile phase to investigate the effect of a pseudophase on the capacity factors of triglycerides on a reverse-phase column. Solute retention generally decreased with increased concentration of surfactant after presaturation of the column with pseudophase. Exceeding the critical micelle concentration of the surfactant resulted in decreased resolution of closely related triglyceride groups in peanut oil, and skewing of peaks became prominent in the more hydrophobic solutes (C_{60} triglycerides containing saturated fatty acid moieties). Triglycerides of known composition and natural triglyceride mixtures were used as test probes. Possible mechanisms of solute retention will be discussed.

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NONSPECIFIC LIPID TRANSFER PROTEINS AS PROBES OF MEMBRANE STRUCTURE AND FUNCTION. Richard C. Crain, U-125 Biochemistry and Biophysics Section, The University of Connecticut, Storrs, CT 06268.

Proteins that accelerate phospholipid transfer between membranes have been isolated from plant, animal and yeast cells. Recently, we purified 3 proteins from beef liver that catalyze the transfer of most phospholipid classes. These nonspecific lipid transfer pro-

teins (NS-TP) have been useful in studying lipid asymmetry and transbilayer movement in both natural and artificial membranes. Incubation of isotopically labeled and nonlabeled membranes in the presence of NS-TP caused the transfer of 2 kinetically distinct pools of labeled phospholipid to the nonlabeled membranes. The phospholipid localized in the outer monolayer was rapidly transferred whereas that localized in the inner monolayer was slowly transferred. The rate of transbilayer movement can be calculated from the latter. For small unilamellar vesicles containing PtdCho/PtdEtn/PtdIno (45:45:10, mol/mol), a nearly symmetric phospholipid distribution occurred and the rate of translocation was slow ($t_{1/2}$ > 3 days). In rat erythrocyte membranes, however, the distribution of PtdCho, PtdEtn and sphingomyelin was asymmetric. All sphingomyelin, 63% of PtdCho, and little PtdEtn were in the outer monolayer. The half-time for transbilayer movement of PtdCho was about 5 hr. Incubation of NS-TP with unilamellar vesicles and biological membranes has also been used to produce a net change in phospholipid composition of either rat liver mitochondria or microsomes. In the first case, incubation with PtdCho vesicles and NS-TP resulted in net increase in PtdCho with little change in other mitochondrial lipids. In the second case, incubation with PtdCho vesicles and NS-TP caused increased microsomal PtdCho content and decreased PtdEtn and PtdIno contents. If PtdCho-specific transfer protein was included instead of NS-TP, no change in phospholipid class composition occurred. Modifications of phospholipid composition of microsomal membranes by appropriate choice of vesicle lipid composition and transfer protein specificity have been used to examine the dependence of glucose-6-phosphate phosphohydrolase activity on the microsomal phospholipid composition. The possible involvement of PtdEtn has been indicated.

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USE OF FLUORESCENT PHOSPHOLIPID ANALOGS IN STUDIES ON PHOSPHOLIPID TRANSFER PROTEINS. P. Somerharju* and K.W.A. Wirtz, Laboratory of Biochemistry, State University of Utrecht, Padualaan 8, PO Box 80.054, NL-3508 TB Utrecht, The Netherlands.

A series of fluorescent phospholipids (PC, PE, PI, PG and PA) containing a parinaroyl residue in the *sn*-2-position has been synthesized. Vesicles prepared of these lipids display a low level of fluorescence due to efficient self-quenching. We have made use of this property to construct both a phospholipid transfer assay and a binding assay for phospholipid transfer proteins. In the assay, vesicles consisting of a parinaroyl phospholipid are mixed with an excess of unlabeled vesicles. The low fluorescence intensity of the probe molecules is maintained as there is no mixing of the labeled and unlabeled lipid molecules. However, when a proper transfer protein is added, a time and protein concentration-dependent increase in fluorescence is observed. This increase is due to the insertion of the labeled molecules into the unlabeled, i.e., nonquenching acceptor membranes, through the action of the transfer protein. In addition to the initial rate of fluorescence increase, which is a measure for the transfer activity, other useful information can be obtained from the progress curve. For instance, addition of unlabeled lipids into the labeled donor membrane results in sigmoidal curves if the unlabeled lipid has a higher affinity for the transfer protein than the labeled lipid. This behavior will be demonstrated for the brain transfer protein which has higher affinity for PI than for PC. In the binding assay, vesicles consisting of a parinaroyl phospholipid are titrated with a purified transfer protein. If the protein can form a true complex with the lipid, the fluorescence will increase (due to the high fluorescence of the protein-bound label) as a function of protein concentration with normal saturation characteristics. From the fluorescence titration curve, the number of lipid binding sites in the protein molecule can be calculated.

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MODULATION OF PHOSPHOLIPID TRANSFER PROTEIN ACTIVITY. George M. Helmkamp, Jr., Department of Biochemistry, University of Kansas Medical Center, 39th and Rainbow Blvd., Kansas City, KS 66103.

The transfer of phospholipid molecules between biological and synthetic membranes is facilitated by the presence of soluble catalytic proteins. From bovine brain is isolated a phospholipid transfer protein which specifically accelerates the intermembrane flux of phosphatidylinositol (PF) and phosphatidylcholine (PC). A typical assay system consists of 2 populations of phospholipid bilayer vesicles—a donor membrane and an acceptor membrane—which are mixed in the presence of transfer protein and subsequently separated to analyze the extent of phospholipid movement. A series of tertiary amine local anesthetics, when added to the assay system, decreased the rates of protein-catalyzed PI and PC transfer. The potency of inhibition, dibucaine > tetracaine > lidocaine > procaine, was identical to that observed for a wide variety of anesthetic-dependent membrane phenomena. The half-maximal inhibition PI transfer activity by dibucaine was observed at a concentration of 0.18 mM, significantly lower than the concentration of 1.9 mM required for half-maximal inhibition of PC transfer activity. It was therefore possible to modulate the multiple activities of the bovine brain phospholipid transfer protein by different sensitivity to local anesthetics. The phospholipid transfer activities of the bovine brain protein were also sensitive to inhibition by alkylating agents. Thus, *N*-ethylmaleimide (1 mM, pH 7.4) abolished 94% and 81%, respectively, of PC and PI transfer activities. Iodoacetate (1 mM, pH 7.4) and iodoacetamide (1 mM, pH 7.4) were less effective, giving rise to 10-20% losses in activity. These results are discussed with respect to the interaction of bovine brain phospholipid transfer protein with phospholipid molecules and membrane surface. (This work has been supported by grant GM 24035 from the U.S. National Institutes of Health.)

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PHOSPHOLIPID TRANSFER PROTEINS IN THE LUNG SURFACTANT SYSTEM. Roger H. Lumb, Biochemistry Group, Western Carolina University, Cullowhee, NC 28723.

The lung surfactant system provides a unique tissue for studying the synthesis, packaging, storage and secretion of phospholipid. Surfactant phospholipid, primarily disaturated phosphatidylcholine (PC), is synthesized on the alveolar type II cell endoplasmic reticulum and is then accumulated in lamellar bodies for later release by exocytosis into the alveolar subphase. We have demonstrated a correlation between PC transfer activity and the lung specific alveolar surface area in vertebrate lung-soluble fractions. We examined sheep lung-soluble fraction for phospholipid transfer activity and have purified and characterized proteins that catalyze the transfer of disaturated PC, unsaturated PC, phosphatidylglycerol and phosphatidylinositol. Some of these proteins are highly specific for PC or phosphatidylglycerol and some are less specific. Activity of the PC-specific proteins correlates with the developmental appearance of lamellar bodies in the fetal lamb lung. A family of transfer proteins also exists in rat lung. PC transfer is 4-fold and phosphatidylglycerol transfer is 6-fold higher in soluble fraction of isolated alveolar type II cells than of whole rat lung; these cells also possess a protein that is highly specific for phosphatidylglycerol transfer.

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THE USE OF RESONANCE ENERGY TRANSFER TO STUDY THE KINETICS OF AMPHIPHILE TRANSFER BETWEEN VESICLES. J. Wylie Nichols* and Richard E. Pagano, Carnegie Institution of Washington, Department of Embryology, 115 W. University Pkwy., Baltimore, MD 21210.

Resonance energy transfer between 7-nitro-2,1,3-benzoxadiazol-4-yl (NBD) acyl chain-labeled lipids (the energy donors) and (lissamine) Rhodamine B-labeled phosphatidylethanolamine (*N*-Rh-PE) (the energy acceptor) was used to monitor the rate of transfer of NBD-labeled lipids between 2 populations of small vesicles. When both fluorescent lipid analogs were incorporated into the same donor vesicle at ∿1 mol %, NBD-fluorescence was quenched by the *N*-Rh-PE due to resonance energy transfer. Addition of nonfluorescent acceptor vesicles to these donor vesicles resulted in an immediate and continuous change in NBD-fluorescence due to the transfer of the NBD-lipids, but not the nonexchangeable *N*-Rh-PE (*Biochemistry* 20:4920) [1981] to the acceptor vesicles. Thus, by continuously monitoring NBD-fluorescence intensity, both the rate of transfer and equilibrium distribution of NBD-labeled lipids could be determined. Using this technique, we found that the kinetics of transfer of NBD-labeled lipids were accurately predicted by a model based on the diffusion of soluble monomers as a function of both the acceptor and donor vesicle concentrations and the respective on-rate, off-rate, and affinity constants. By application of this model, we demonstrated that these rate constants for a given amphiphile depended on the structure of both its polar and nonpolar regions and on the lipid composition of the vesicle. In addition, when 2 vesicle populations had different off-rates for a given amphiphile, the half-time for equilibration was dependent on their concentration ratio. For the special case when acceptor vesicles were in excess, the half-time was solely dependent on the off-rate from the donor vesicles, and when the donor vesicles were in excess, the half-time was solely dependent on the off-rate from the acceptor vesicles.

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MODE OF ACTION OF PHOSPHOLIPID TRANSFER PROTEINS. T.E. Thompson, Department of Biochemistry, University of Virginia, Charlottesville, VA 22908.

Although it is generally believed that phospholipid transfer proteins act as carriers in the aqueous phase for lipid transferred between bilayer systems, recent work on model systems suggests that this need not be the case. Studies of the relatively slow transfer

of phospholipids between bilayer systems in the absence of transfer proteins show that this process is characterized by half-times for transfer that range from 2 to 45 hr. In addition, these studies indicate that the inter-bilayer transfer process is rate-limited not by the aqueous phase mass transfer step, but by the rate at which lipid molecules leave the donor bilayer. Thus, in order to accelerate transfer, an increase in this off-rate constant is required. The presence of a carrier protein which could increase the number of lipid molecules in transit through the aqueous phase could have no effect on the rate of the overall process. This analysis suggests that phospholipid transfer proteins need not necessarily be carrier proteins which bind lipid in the aqueous phase. Rather, transfer proteins need only interact transiently with lipid bilayers in such a way as to increase the off-rate constant for component lipid molecules. (This work was supported by USPHS NIH grants GM-14628 and GM-23573.)

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FACILE FORMATION OF KETONES FROM β-KETO ESTERS UNDER ANHYDROUS CONDITIONS. R. Aneja*, Department of Food Science, Clemson University, Clemson, SC 29631, A.P. Davies and G. Eaton, Unilever Research, Colworth Lab., Sharnbrook, Bedford, U.K.

Alkyl ketones are important ingredients of cheese flavors. In the classical procedure for their synthesis from monoalkyl- and dialkylacetoacetic esters, these β-keto esters are hyrolyzed by dilute alkali followed by acidification to the corresponding β-keto acids which undergo decarboxylation. We have hypothesized and experimentally realized a new procedure which causes facile C-C cleavage resulting in elimination of the alkyl carboxylate residue from β-keto esters without hydrolysis. The β-keto ester is reacted with the sodium derivative of propane-1,2-diol in an excess of anhydrous propane-1,2-diol as the solvent. For instance, ethyl *n*-dodecyl acetoacetate reacted at 60 C for 15 min gave pentadecan-2-one (yield 95%).

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AUTOMATED AOM TEST FOR FAT STABILITY. J.M. deMan, Department of Food Science, University of Guelph, Guelph, Ontario, Canada N1G 2W1.

The AOM or Swift test (AOCS method Cd 12-57) suffers from the disadvantage of requiring constant attention and this presents difficulties with samples of long AOM times. Several automated versions of the test have been described in which the endpoint is determined by sensing the production of formic acid which is swept from the reaction vessel. A method is described in which the endpoint detection is achieved by measurement of conductivity. The precision of the method is considerably better than that specified for the AOCS procedure. The endpoint of various oils was not obtained at the same peroxide value. A variety of oils was examined and peroxide values at the endpoint were: corn oil 160, soybean oil 135, shortening 100, sunflower oil 150, canola oil 80.

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DETERMINATION OF VEGETABLE OIL FLAVOR QUALITY BY PURGE AND TRAP ANALYSIS. Jerome N. Geske* and Gary G. Spyres, A.E. Staley Mfg. Co., 2200 E. Eldorado St., Decatur, IL 62525.

A simple and versatile GC procedure using a modified commercial purge and trap sampler has been developed and applied to determining the flavor quality of vegetable oils. A 500-mg sample of oil was heated to 200 C and purged with helium at 50 mL/min for 20 min. The volatile components were trapped on a Tenax® trap maintained at room temperature. The Tenax® trap was rapidly desorbed at 200 C, sweeping the volatiles through a heated transfer line onto a GC column of 8% Poly MPE on Tenax® thermostated at 40 C. Chromatography was achieved by temperature programming the oven from 40 C to 240 C. Good correlations were observed for peak areas of 7 volatile compounds and taste panel flavor scores of vegetable oils. The automated aspect of the purge and trap sampler allowed the analysis of 1 sample/hr with excellent reproducibility and a minimum of operator attention.

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VOLATILE PROFILES OF FATS AND OILS EMPLOYING AUTOMATED DIRECT GAS LIQUID CHROMATOGRAPHIC PROCEDURE. J.L. Gensic*, Bernard F. Szuhaj and Joseph G. Endres, Central Soya Company, Inc., Fort Wayne Nat'l Bank Bldg., Fort Wayne, IN 46802.

A system is described for automating the direct gas chromatographic method for examining volatile profiles of vegetable oils reported earlier by Dupuy (*JAOCS* 50:340, 1973). The system couples an external inlet system to a microprocessor-based gas chromatograph to provide automatic control of the analysis cycle (e.g., sampling temperatures and times, valve switching and GC operating parameters). Automation of the analysis cycle provides consistent control over sampling and analysis to provide rapid and reproducible volatile profiles. Manual control is eliminated and frees the analyst for other tasks. Volatile profile analysis is used to monitor protected oil quality. Volatile profiles provide an objective measurement of oil quality and removes the subjectivity of flavor panels. Automated volatile profile analysis also provides a flexible system which enables modification of operating parameters for handling various sample types.

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ISOLATION AND CHARACTERIZATION OF THE NATURAL ANTIOXIDANTS FROM ROSEMARY. Stephen S. Chang and Chi-Tang Ho*, Department of Food Science, Rutgers State University, PO Box 231, New Brunswick, NJ 08903, and James W. Wu, Mrs. Paul's Kitchens.

A new, improved method has been developed for the preparation of a natural antioxidant from rosemary leaves with activity greater than BHA and equal to BHT. In some applications, the natural antioxidant thus prepared was separated into 16 fractions by liquid chromatography, using silicic acid as an absorbent and gradient elution. The 2 fractions with the highest antioxidant activity were further fractionated by HPLC. The fraction with the most antioxidant activity was further fractionated by reverse-phase HPLC. Among the pure fractions obtained, one was identified by IR, MS and NMR as carnosol, which is an active antioxidant, but with poor solubility. The other fraction identified by IR, MS and NMR was ursolic acid, which is not an antioxidant. The most active fraction was a brown, viscous liquid which has an excellent solubility in oil. The structure elucidation of this component will be discussed.

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THE QUANTITATIVE EFFECTS OF CHELATE, PROOXIDANT AND OXYGEN CONTENT ON OIL FLAVOR STABILITY DURING STORAGE. David B. Min* and Jye Wen, Department of Food Science and Nutrition, 2121 Fyffe Road, Columbus, OH 43210.

Soybean oils were treated with 4 levels of iron (0, 0.3, 3 and 15 ppm), 5 levels of citric acid (0, 10, 50, 100 and 150 ppm) and 4 levels of oxygen content (2.5, 4.5, 6.5 and 8.5 ppm) to study the effects of these treatments on the oil flavor stability during storage. The flavor stability of oil was evaluated by measuring (a) the rate of dissolved free oxygen in oil and (b) the rate of flavor compounds formation. The results were statistically analyzed to study the quantitative effects of citric acid, dissolved free oxygen and iron by analysis of variance. Multiple linear regression equations were developed to predict the flavor compounds formed and the disappeared dissolved free oxygen in oils containing different levels of citric acid, iron and dissolved free oxygen during storage. The effects of 4 different levels of iron on the flavor stability were significantly different from each another at the 5% level. When the oil contained more than 3 ppm of iron, the higher the added citric acid content, the better the oil flavor stability. The effects of 5 different levels of citric acid were significantly different from each other on oil flavor stability at the 5% level. Four different levels (2.5, 4.5, 6.5 and 8.5 ppm) of dissolved free oxygen were also significantly different from each other on oil flavor stability at the 5% level.

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FLAVOR AND OXIDATIVE STABILITY OF HYDROGENATED AND UNHYDROGENATED SOYBEAN OIL: EFFICACY OF PLASTIC PACKAGING. K. Warner and T.L. Mounts*, Northern Regional Research Center, 1815 N. University St., Peoria, IL 61604.

Soybean oils were packaged in polyvinyl chloride, acrylonitrile, clear glass and amber glass bottles. Flavor stability of the oils was evaluated by a trained sensory panel. Efficacy of nitrogen packaging of oils in plastic bottles was evaluated in long-term storage tests relative to the same oils in glass bottles with nitrogen in the headspace. Two-, 3- and 4-way analyses of variance were used to determine statistical significance of differences in flavor scores and peroxide values. Hydrogenated and unhydrogenated oils showed similar patterns of flavor deterioration regardless of container or type of aging. In accelerated light exposure tests, oils in plastic bottles showed flavor and oxidative stability that was equivalent to the same oils in clear glass bottles. Packaging in the amber glass bottle provided, as expected, significantly improved oil stability during light exposure tests. In accelerated storage tests at 60 C with air in the headspace, sensory evaluation and peroxide determination showed no effect due to type of bottle in which the oil was packaged. Oils in plastic bottles with nitrogen in the headspace had flavor and oxidative stability equal to those in glass bottles with nitrogen during long-term storage. These investigations indicate that packaging of soybean oils in polyvinyl chloride or acrylonitrile bottles is a viable alternative to packaging in clear glass bottles.

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INVESTIGATION OF 1-DECYNE FORMATION IN COTTONSEED OIL FRIED FOODS. Lucy L. Fan*, Jiunn-Yann Tang and Alan Wohlman, Frito-Lay, Inc., Research Dept., 900 N. Loop 12, Irving, TX 75061.

1-Decyne has been identified in oxidized cottonseed oil and was previously thought to originate from oleic acid. However, we have recently demonstrated that 1-decyne is a degradative product from photooxidation of cyclopropenoid fatty acids (CPFA) naturally present in cottonseed oil. Products containing photooxidized cottonseed oil have the distinct off-flavor of 1-decyne. Unrefined cottonseed oil contains from 1 to 2% CPFA but commercial cottonseed oil is reported to contain 0.2-0.45% CPFA and a trace amount of chlorophyll. Experiments have been conducted to identify the factors involved in 1-decyne formation. Reactions have been performed under the following conditions: (a) in the dark or under light; (b) with or without removal of CPFA from cottonseed oil; (c) in the presence or absence of singlet oxygen quenchers, e.g., Dabco and β-carotene; (d) in the presence or absence of hydroperoxide reducing agent triphenylphosphine; and (e) with or without photosensitizers, e.g., chlorophyll. Furthermore, 1-decyne has been identified by GC/MS and sensory evaluation. In a model study, methyl sterculate was used as a substrate for studying 1-decyne formation under photosensitized oxidation conditions. In conclusion, we have demonstrated that 1-decyne is formed by the photooxidation of CPFA using chlorophyll as a photosensitizer. Based on these results, a mechanism for 1-decyne formation is proposed.

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QUANTIFICATION AND IDENTIFICATION OF VOLATILES FROM TRILINOLENIN HEATED IN AIR. E. Selke* and W.K. Rohwedder, 1815 N. University Ave., Peoria, IL 61604.

Headspace volatiles derived from trilinolenin heated to 192 C in air were collected, separated and identified using a microroom-GS/MS-computer system. Data from 4 analyses indicated about 100 volatiles were present. Of these volatiles, 35 have been identified, and their combined GC peak areas contributed 85% to the total integrated chromatographic area. Primary volatiles identified included: ethanal (2%), pentene (3%), ethanol (3%), acrolein (19%), propanal (7%), ethyl furan (1%), 2-butenal (9%), 2-pentenal (4%), 2,4-heptadienal (24%) 4,5-epoxy-2-heptenal (3%) and decatrienal (2%). Most of the primary and some of the minor volatiles are predicted from the decomposition of the 6 linolenin hydroperoxides. However, the concentrations of the predicted volatiles do not reflect the proportions expected from cleavage of autoxidized linolenate monohydroperoxides. Primary and minor volatiles also are present that are unrelated to the classical hydroperoxide decomposition hypothesis, which suggests that trilinolenin and some of the volatile compounds undergo further oxidation.

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ANTIOXIDANT ACTIVITY OF SODIUM NITRITE IN MEAT. M. Zubillaga, T.A. Foglia and G. Maerker*, USDA/ARS/ERRC, 600 E. Mermaid Lane, Philadelphia, PA 19118.

It is recognized that addition of sodium nitrite to processed meats provides protection against lipid oxidation, although sodium nitrite itself is not an antioxidant. Little is known about the effectiveness of the antioxidant activity imparted by sodium nitrite or about the mechanism by which this effect is achieved. The current work was undertaken to develop information on these questions. Fresh ground beef was treated with 156 ppm of sodium nitrite and stored at 4 C for up to 3 wk in air-permeable wrappings. Untreated portions were packed and stored similarly. Samples were withdrawn periodically and analyzed for peroxide and TBA values and for residual nitrite. Comparison of results showed that the free nitrite content of the treated samples decreased rapidly within 48 hr whereas TBA values remained low and constant over a period of up to 3 wk. The TBA values of the untreated controls increased constantly over the same period. Similar results were obtained with samples treated with sodium nitrite (or untreated) and heated to 70 C before storage. From these data, it appeared that the meat that had been treated with nitrite contained one or more moiety having antioxidant activity. To determine whether the indicated antioxidant activity resides in the lipid portion of the nitrite-treated samples, fresh ground beef was treated as just described and the polar and neutral lipids were isolated separately. The antioxidant activity of the polar lipid fractions was evaluated by a published procedure. In this procedure, the enzymatic oxidation of linoleic acid is indicated by bleaching of β-carotene present in the system. The retardation of this bleaching action is a measure of antioxidant activity. The data suggest that antioxidant activity is present in polar lipids derived from nitrite-treated meats.

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LINOLEIC ACID OXIDATION CATALYZED BY AMADORI COMPOUNDS IN AQUEOUS MEDIA. R.S. Farag*, Y. Ghali and M.M. Rashed, Biochem. Dept., Faculty of Agriculture, Cairo University, Giza, Egypt.

This investigation was undertaken to prepare amadori substances from the reaction between various monosaccharides with amino acids to study their anti- or prooxidant effect on linoleic acid oxidation. The various sugars showed great variation in their reactivity to form amadori substances. The pH of the reaction mixture also played an important role on amadori compounds production. The measurement of oxygen uptake of the various model systems showed that the rate of hydroperoxide formation with time was typical of an autocatalytic reaction. Considerable variation in the rates of linoleic acid oxidation in comparison to the control experiments were observed. The model systems DL-alanine/D-xylose and L-proline/D-xylose were highly antioxidant and may be applied in preserving lipids. The products of the model systems DL-cysteine-HCl/D-glucose and DL-cysteine-HCl/galactose possessed a slight antioxidant effect, whereas a slight prooxidant behavior was observed in the model systems containing DL-cysteine-HCl with D-xylose, L-arabinose and D-fructose. No correlation was found between either the chemical structure of various amino acids, sugars or the absorbance of the amadori solutions and the antioxidant behavior.

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CHEMICALS, FUELS AND MATERIALS FROM WHOLE PLANTS. Marvin O. Bagby, Northern Regional Research Center, S&E, USDA, 1815 N. University, Peoria, IL 61604.

Plant sources of high-energy chemicals and materials competitive with synthetic petrochemicals already enjoy considerable commercial acceptance. These resources include tall oil, naval stores, seed oils, plant oils, and waxes. However, less than 0.1% of the nearly 300,000 known plant species have significant commercial acceptance in the world. We anticipate that numerous species can be identified and exploited as sources of chemicals, fuels and strategic materials. Consequently, the U.S. Department of Agriculture has determined oil and hydrocarbon contents of 500 species and has identified nearly 70 with promising amounts of plant chemicals. More than 20 species consist of at least 5% oil and nearly 12 yield greater than 2% isoprene polymers. These soluble components could serve as important chemical feedstocks.

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INTERPENETRATING POLYMER NETWORKS FROM TRIGLYCERIDE OILS CONTAINING SPECIAL FUNCTIONAL GROUPS. L.H. Sperling* and J.A. Manson, Materials Research Center, Coxe Laboratory 32, Lehigh University, Bethlehem, PA 18015.

While most triglyceride oils contain only double bonds as functional groups, a few of these oils are endowed with special functionalities. Two such oils are castor oil, which contains hydroxyl groups, and vernonia oil, which contains epoxy groups. These oils can be reacted with many chemical reagents yielding polyurethane or polyester networks. For example, both of these oils react with sebacic acid (itself derived from castor oil) to form soft elastomeric materials. When combined with another polymer network such as polystyrene cross-linked with divinyl benzene to form interpenetrating polymer networks (IPN), tough plastics or elastomers result, depending on the overall composition. Two methods of synthesis have been developed: (a) the sequential IPN synthesis, in which the oil is polymerized to completion first, then swollen with the second monomer, followed by polymerization of the second monomer; (b) the simultaneous interpenetrating network (SIN) synthesis, in which both the oil and the second monomer are mixed and polymerized simultaneously, but by different mechanisms, usually by condensation and additional routes so that interference is minimal. The interrelationships among synthesis, morphology and mechanical behavior will be explored. Although some emphasis is on impact-resistant plastics, rubbery products suitable for shoe heels, e.g., and containing more oil, will also be discussed.

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CROP ORIGIN OILS AS ADDITIVES TO HERBICIDES. John D. Nalewaja, Department of Agronomy, North Dakota State University, Fargo, ND 58105.

Herbicide phytotoxicity has often been increased by the addition of an oil or a surface-active agent to the spray mixture. Phytobland petroleum oils were developed as additives to enhance weed control with atrazine applied postemergence to corn which has a high tolerance for atrazine. Thus, the increased atrazine action with the oil additive did not cause injury to corn. Oil additive usage may increase in the future with the development of new postemergence herbicides and integrated weed control systems. Crop origin oils used in place of petroleum oils as additives to herbicides would help conserve the limited supply of petroleum oil. Research was con-

ducted both in the field and laboratory to evaluate linseed oil and other crop origin oils as additives to various herbicides at North Dakota State University. Emulsifiable linseed oil applied at 2.3 L/ha was equally effective as 9.3 L/ha of petroleum oil (crop oil) and more effective than 2.3 L/ha petroleum oil with 20% surfactant (Amoco crop oil concentrate) in enhancing weed control with atrazine. Emulsifiable linseed oil as an additive to cyanazine enhanced weed control and reduced injury to corn compared to petroleum oil additives. A water-soluble linseed oil (concrete-causing compound) was more effective than emulsifiable linseed or petroleum as an additive to bentazon for red-root pigweed control. Research has indicated that the effectiveness of an oil additive for weed control was influenced by the weed, crop and herbicide. The function of the oil additive with postemergence herbicides was to enhance uptake by plants, reduce the washing effect of a rain shortly after application, reduce vapor loss of herbicide, and increase retention of spray by plants. Oils from various crops have been generally similar in enhancing the action of herbicides. Research is needed to evaluate various crop origin oil with all postemergence herbicides and to determine the characteristic of an oil which influences its effectiveness as an additive to various herbicides for specific weeds in crops.

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REDUCING DUST BY USE OF VEGETABLE OIL. F.S. Lai, U.S. Grain Marketing Research Lab., 1515 College Ave., Manhattan, KS 66502.

Control of the grain dust emitted during grain handling is badly needed to improve air quality and industrial safety. Unfortunately, cost-effective control measures for dust have yet to be established. Although separation of dust from dust-laden air by bag filters or electronic precipitators can be effective, the costs of installation, operation and maintenance for such equipment are high. This type of dust control allows explosive mixtures to occur. Moreover, the energy required by current methods of removing dust from the air may exceed the energy required to remove the grain. Application of edible vegetable oil to grain on a pilot scale has been tested at the U.S. Grain Marketing Research Laboratory. The results indicate that dust emission from corn treated with 0.04% soybean oil was reduced to 6.7% of that emitted from corn without soybean oil treatment. The figure was 5.4% for wheat. The degree of reduction suggests that the methods can be applicable in the grain industry. Wheat, corn and soybean were treated with 0.02-0.10% deodorized soybean oil to reduce grain dust emission during handling in a commercial grain elevator. Grain handled without the oil additive served as control. The oil additive was applied as the grain was being handled and the amount of dust emitted was measured. Dust emitted during handling of the grain was reduced with as little as 0.02% added oil. Finally, the cost of applying the vegetable oil was estimated.

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PLASTICIZERS FROM MODIFIED VEGETABLE OILS. E.H. Pryde, Northern Regional Research Center, U.S. Dept. of Agriculture, 1815 N. University St., Peoria, IL 61604.

Of the 2 billion lb of plasticizers produced in the U.S., about 86% are benzenoid (e.g., dioctyl phthalate) and 14% are nonbenzenoid (e.g., epoxidized soybean oil). The benzenoid plasticizers have been consumed in such large quantities throughout the world that they have become ubiquitous environmental contaminants. They also are suspect with regard to subtle toxicological effects, and extensive testing programs have been undertaken both by government agencies and by the chemical industry. It is appropriate, therefore, to examine what further contributions the fats and oils industry could make to plasticizer markets. Many of the fat-based plasticizers, such as epoxidized oils, have excellent solubility. One method for increasing functionality of vegetable oils is to perform the oxo or hydroformylation reaction with rhodium catalyst. Rhodium is unique in introducing the formyl group at each of the double bonds in polyunsaturated fatty esters, and in doing so at temperatures and pressures much lower than required by conventional cobalt carbonyl catalysts. Once formed, the formyl group is easily transformed into acetal, hydroxy esters or carboxylates, all of which have been shown to have some desirable properties for plasticizer use. These compounds need extensive toxicological and biodegradability tests before they can be approved for commercial use, but they probably can perform better in these properties than the benzenoid compounds.

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DESIGN OF A 50,000-LB/HR SOLAR STEAM PLANT. D.J. Allen* and A.C. Gangadharan, Foster Wheeler Solar Development Corp., 12 Peach Tree Hill Road, Livingston, NJ 07039.

Solar thermal systems using parabolic trough collectors are now commercially available. Some of these systems are being built to supply steam for sale to industrial companies; other systems are undergoing final testing and will be offered shortly for sale at fixed prices. In this paper, a modular solar thermal system capable of generating 5,500 lb/hr steam will be described. Particular emphasis will be placed on the retrofitting of plants with such systems, the installation of multiple modules to generate 50,000 lb/hr steam, and the economics of installing solar thermal systems at various points in North America. Alternatives to parabolic trough collectors for generating steam with solar energy will be discussed.

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CRYSTALLIZATION AND PULVERIZATION OF FAT AND FAT-LIKE SUBSTANCES. E.-W. Muench and Wolfgang Stein*, Fried, Krupp GmbH, Krupp Industrie -und Stahlbau Werk Horburg, Seevestrasse/Bohnhofsinsel, D2100 Hamburg 90, Federal Republic of Germany.

Crystallization and pulverization of fats together with several variables will be discussed. The basic layout of the plant and its main components will be described. The feasibility of operating such a plant will be considered.

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RECENT DEVELOPMENTS IN ELECTROLYTIC GENERATION OF HYDROGEN. Arnold F. Hufnagl, The Electrolyser Corp., 122 The West Mall, Toronto, Ontario M9C 1B9, Canada.

Major development projects have been initiated in several countries with the objective of significantly reducing the cost of electrolytic hydrogen. Progress is being made in improving electrical efficiency and reducing the capital investment required per unit of hydrogen production capacity. Large programs in Europe, the U.S., Canada and Japan are now moving toward engineering demonstration of improved equipment design and performance. The major developmental programs will be reviewed, highlighting the objectives, technical approaches, and progress for the advancement of electrolytic hydrogen technology, as well as the implications for on-site generation of hydrogen.

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SOLVENT EXTRACTION OF SPENT CLAY. Guy L. Posschelle, De Smet U.S.A. Corp., Atlanta, GA.

Not counting the processing of spent clay simultaneously with oilseed in an existing solvent extraction plant, the practical system known to the industry defats the clay with systematic countercurrent extraction while the cakes are still in the filters that are used in the bleaching process. This system presents the disadvantage of introducing solvent into a normally nonexplosion-proof designed refinery and oversizes the filter surfaces. A brief analysis is made on the practical ways to overcome these handicaps, obtaining an entirely continuous and automatic system. Another approach is to handle the oily cake discharge from bleaching filters into a separate, explosion-proof protected area. The clay has to be slurried in order to permit the extraction with a nonpolar solvent. However, conventional oilseed extractors or filters with vertical leaves surfaces cannot be used. A description is made on how to solve the problems caused by the settling of clay in the miscella and of the use of modified, horizontal leaf filters with special discharge devices, or continuous belt filters used as extractors. Advantages and drawbacks of each system are discussed.

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APPLICATION OF SUPERCRITICAL FLUID EXTRACTION. Alegria B. Caragay* and Christopher P. Eppig, Arthur D. Little, Inc., 15 Acorn Park, Cambridge, MA 02140.

Supercritical fluid extraction has been emerging from the laboratory as a viable process substitute in many areas where conventional solvent extraction has previously been used. In this study, supercritical fluid extraction has been applied to the recovery of avocado oil from avocado pulp, with and without drying the pulp before processing. The effect of process parameters on oil recovery, such as temperature, pressure and moisture content, will be discussed. A comparison of the quality of the oil obtained from the "raw" pulp and the pre-dried pulp will also be presented.

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PROCESSING OF EDIBLE OILS OBTAINED BY EXTRACTION WITH SUPERCRITICAL CARBON DIOXIDE. G.R. List*, J.P. Friedrich and D.D. Christianson, USDA Northern Regional Res. Center, 1815 N. University St., Peoria, IL 61604.

Full-fat soy flakes and wet-milled and dry-milled corn germ were extracted with supercritical carbon dioxide (SC-CO_2) at 50 C and 8,000 psi. The resulting crude oils were analyzed for fatty acid composition, trace metals, phosphorus, tocopherol, unsaponifiable matter, free fatty acids, color and refining loss, and compared to oil obtained by hexane extraction. The SC-CO_2-extracted oils were caustic-refined, bleached and deodorized in the laboratory to yield

salad oils and were compared to hexane-extracted oils processed under similar conditions. Organoleptic evaluations showed that SC-CO_2-processed soybean oils have high flavor scores and initially are equal to their hexane counterparts. After accelerated storage, SC-CO_2-extracted oils had flavor scores equal to or better than hexane-processed oils. From a processing standpoint, SC-CO_2 possesses several advantages over hexane extraction, including lower refining losses and elimination of the degumming step, because phospholipids have limited solubility in SC-CO_2. However, because phospholipids retard oxidation in crude oil, SC-CO_2-extracted oil may require more exact storage and handling conditions than normal. Processing of corn germ with SC-CO_2 possesses some advantages over hexane by affording lighter-colored oil, lower refining losses and improved flavor. Organoleptic evaluation of finished oils from wet- and dry-milled crudes will be presented and the results will be discussed.

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CONTINUOUS ACIDULATION OF SOAPSTOCK AND RECOVERY OF ACID OIL. T.K. Mag*, D.H. Green and A.T. Kwong, Canada Packers Inc., Research Centre, 2211 St. Clair Ave. W., Toronto, Ontario M6N 1K4, Canada.

Existing processes and the need for improvements will be reviewed. A new continuous system will be described consisting of equipment for acidulating the soapstock, decanting the bulk of acid oil from the acid water and treating the acid water in a coalescer for further separation of emulsified acid oil. Fatty material concentrations in the acid water of less than 150 ppm can be achieved. The acid water is then neutralized for discharge to municipal sewers. The emphasis will be on operating results from a pilot-process using a variety of soapstocks.

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CHEMICAL SPECIES CONTRIBUTING TO THE DE-EMULSIFYING ABILITY OF BACTERIAL CELL SURFACES. William L. Cairns*, Richard Rumble and Naim Kosaric, Chemical and Biochemical Engineering, Faculty of Engineering Science, The University of Western Ontario, London, Ontario, Canada N6A 5B9.

The hydrophobic/hydrophilic nature of bacterial cell surfaces is a contributing factor to the versatility of bacterial surfaces to act as de-emulsifiers of a wide variety of synthetic and commercially important emulsions. Increasing hydrophobicity of the bacterial surfaces is often associated with an enhanced ability to break oil-in-water emulsions. Cell surface hydrophobicity increases with culture age in the case of several studied bacterial species. The increasing hydrophobicity continues well into the "endogenous metabolism" phase of growth, suggesting that cell lysis and liberation of intracellular hydrophobic components which reassociate with the outer cell surface may be responsible for the increased hydrophobicity. The results of studies which evaluate the contribution of this hydrophobic chemical species to de-emulsification by bacterial cell surfaces will be presented.

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EMULSIFICATION EVALUATION OF BACTERIA USING HYDROPHILIC-LIPOPHILIC BALANCE (HLB) VALUES. J.E. Zajic* and W. Seffens, Department of Biological Sciences, The University of Texas at El Paso, El Paso, TX 79968.

Various bacteria produce surface-active agents which assist the microorganisms in degrading and utilizing hydrocarbons. The surface properties of these bacteria influence their ecological effectiveness at biodegradation of pollutant oil in aquatic habitats and their pathogenicity toward plants and animals. These attributes have huge economic impact in terms of treating oil pollution and in the control of disease. Biosurfactants from bacteria are also attractive in product formulations requiring nontoxic or specialized emulsifiers and detergents. Hydrophile-lipophile balance (HLB) evaluations of surfactants, commonly used for industrial emulsifiers, are demonstrated to be applicable to bacteria. Presented are HLB values for bacterial species together with correlations to emulsification, adsorption at interfaces and partitioning of cells between oil and water. Implications concerning pathogenicity in plants and humans are discussed.

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PRODUCTION OF SURFACTIN FROM *BACILLUS SUBTILIS*. D.G. Cooper*, McGill University, Montreal, C.R. Macdonald, University of Guelph, S.J.B. Duff and N. Kosaric, University of Western Ontario.

Surfactin is a lipopeptide produced by *Bacillus subtilis*. This compound is very surface-active. For example, it lowers the surface tension of water from 72 mN/m to 27 mN/m. It is a stable compound and relatively easy to isolate from the culture medium. It is produced by *Bacillus subtilis* grown on a soluble carbon source. Most biosurfactant-producing organisms require an immiscible hydrocarbon substrate to generate a reasonable yield of product. The amount of surfactin produced is normally fairly low (usually less than a 10-fold excess of the critical micelle concentration). The yield can be dramatically increased by addition of metal ions to the medium. Only 2 metal cations were found to have a positive effect on surfactin production (Mn^{2+} or Fe^{3+}). The addition of iron salts, up to 10^{-3} mol/L, increased the production of surfactin by an order of magnitude. Manganese had an even larger effect and a much smaller amount was required (10^{-6} mol/L). The yield of surfactin was also greatly improved by continuously removing the foam produced during a fermentation. The product inhibits further production, but is concentrated in the foam. Thus, continuous product removal allows a larger over-all yield of surfactin.

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THE INTERACTION OF EMULSAN WITH HYDROCARBONS. D.L. Gutnick, Z. Zosim and E. Rosenberg, George S. Wise Faculty of Life Sciences, Tel Aviv University, Tel Aviv, Israel.

The growth of microorganisms on hydrocarbons is generally accompanied by the emulsification of the carbon source in the aqueous media. In the case of the hydrocarbon-degrading bacteria *Acinetobacter calcoaceticus* RAG 1, this process is brought about by a high molecular weight (MW ≈ 10^6), water-soluble extracellular bioemulsifier termed emulsan. Emulsan is a *d*-galactosamine-containing polyanionic (pK′3.05) polysaccharide in which both acetate and long-chain fatty acids are bound via O-acyl and N-acyl linkages. Emulsan is initially released from the cell surface as a protein complex; removal of the protein yields a polymer, termed apoemulsan, which retains emulsifying activity. Studies on the interaction of emulsan and apo-emulsan with hydrocarbons reveal several interesting properties: (a) hydrocarbon substrate specificity—the polymer works best in the presence of a mixture of aliphatic and cyclic or aromatic hydrocarbons; (b) emulsion stability—in addition to enhancing the formation of emulsions, emulsan stabilizes preformed emulsions at weight ratios of oil to emulsan as high as 800:1; (c) reversibility—emulsions stabilized by emulsan separate by creaming, rather than by coalescence. The creams (emulsansols) readily disperse in water to yield emulsions which exhibit the same characteristics as the original emulsions; (d) emulsan binding at the oil-water interface—immunological analysis of emulsansols demonstrate that emulsan concentrates at the oil-water interface independent of the pH of the aqueous phase; (e) binding of cations at the oil-water interface—an aqueous solution of emulsan differs from emulsan which is bound to an oil droplet in that the latter binds cations such as Rhodamine B. This hydrocarbon-mediated cation binding is pH-dependent, decreasing rapidly below the pK′ of emulsan.

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SELECTING BIOSURFACTANTS FOR ENHANCED OIL RECOVERY (EOR): AN INTRODUCTION TO AN APPROACH INVOLVING STRUCTURE-FUNCTION CORRELATIONS. William L. Cairns*, Joan M. Wood and Naim Kosaric, Chemical and Biochemical Engineering, Faculty of Engineering Science, The University of Western Ontario, London, Ontario, Canada N6A 5B9.

Not all surfactants are suitable for EOR. A number of properties have been suggested in the literature as being desirable for any surfactant which might contribute to EOR. These properties are summarized and the known pure biosurfactants are surveyed for classes which might possess the desired properties. Data are presented on how the desired properties vary for the pure biosurfactants compared to the mixtures of biosurfactants which are frequently produced during culturing. An attempt is made to illustrate how our current program of correlating structural chemistry of biosurfactants with their functional properties can complement screening programs for selection of biosurfactants with potential for EOR.

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BIOLOGICAL DE-EMULSIFICATION OF COMPLEX PETROLEUM EMULSIONS. Neil C.C. Gray, Ann L. Stewart*, William L. Cairns and Naim Kosaric, Chemical and Biochemical Engineering, Faculty of Engineering Science, The University of Western Ontario, London, Ontario, Canada N6A 5B9.

In the past, this laboratory has studied several bacteria (i.e., *Corynebacterium petrophilum*, *Nocardia amarae*, *Rhodococcus aurantiacus*) which were found to be de-emulsifiers of simple, defined model oil-in-water (O/W) and water-in-oil (W/O) emulsions. Preliminary characterization studies revealed that this activity was associated with the cell surface of the bacteria; therefore, they could be used as de-emulsifiers either in a viable or nonviable form. Studies using petroleum field emulsions (O/W and W/O) indicated that the bacteria were able to act as de-emulsifiers; the rate of de-emulsification varied with a number of biological parameters including culture age, growth medium, pH, temperature, bacterial

concentration, contact time and length of agitation period. The basic composition of the field emulsion has also been examined and correlated to the rates of de-emulsification. Various commercial de-emulsifiers and flocculating agents were tested with and against the bacterial de-emulsification system. From these studies, a preliminary cost analysis has been undertaken comparing the commercial and bacterial agents.

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SUBSTRATE-DEPENDENT AND GROWTH TEMPERATURE-DEPENDENT CHANGES IN TYPES OF WAX ESTERS PRODUCED BY *ACINETOBACTER* SP. H01-N. Jacqueline L. Ervin, John Geigert* and Saul L. Neidleman, Cetus Corp., 600 Bancroft Way, Berkeley, CA 94710.

The effects of substrate (C_{16}-C_{20} *n*-alkanes, C_2 and C_3 acids) and growth temperature (17-32 C) on the wax esters produced by the bacterium *Acinetobacter* sp. H01-N were examined by means of fused-silica capillary gas chromatography. For the *n*-alkene substrates, the chain lengths of the wax esters formed were directly related to the chain length of the substrate: C_n *n*-alkene → C_{2n}, C_{2n-2} and C_{2n-4} wax esters. The ratio of mono- and diunsaturated components to saturated components increased with increasing chain length of the *n*-alkane substrate. For the C_2 and C_3 acids, the chain lengths of the wax esters formed were C_{30}-C_{36}, even numbers only for acetate, and even plus odd numbers for acetate plus propionate. Although bacteria have the ability to alter both the proportion of unsaturation and the chain length of the wax ester components in response to temperature changes, *Acinetobacter* sp. H01-N exclusively increased only the proportion of unsaturation at lowered temperatures of growth. These microbial-produced wax esters bear a close chemical resemblance to those of sperm whale and jojoba oil.

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OIL REFINERY LOSS MONITORING AND CONTROL SYSTEMS. Peter F. Elliott, Elliott Automation Company Inc., 10903 Brooklet Dr., Houston, TX 77099.

There's more to loss monitoring than meets the eye and the author of this paper will review basic concepts, theoretical technology, and practical application of that technology to accurately determine oil refinery losses. Early loss monitoring methods using tank gaging and tank weight measurement systems have been largely superceded by today's automated on-line methods to measure oil refinery losses with computerized flow-measurement systems. Practical methods have been developed to simplify the installation and continued operation of the flowmetering system so that many years of output can be obtained with only minimal attention to service. The key to long service is attention to detail in the design stages and determination by the plant manager and refinery manager to do the job properly and not cut any corners. Success leads to success and refinery personnel quickly take for granted a technology that only a few years ago was regarded as impossible to implement. Computerized caustic dilution systems are now on-line as a logical next step to controlling oil refinery losses. The caustic dosing is, of course, the most critical process variable effecting oil refinery losses, but amazingly, almost no oil refineries have caustic dosing systems that take advantage of today's technology. To wind up this paper, an advanced method to control caustic dosing will be described.

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AN INTEGRATED CONTROL AND INFORMATION SYSTEM APPLIED TO AN EDIBLE OILS PLANT. E.W. Ralph, Procter & Gamble Engineering Division, 6250 Center Hill Road, Cincinnati, OH 45224.

Digital electronics has provided many new, low-cost control devices. This paper deals with how these devices have been integrated into a system to meet the control and information needs of an edible oils plant. The application uses a distributed hierarchical control approach with the following basic functions: (a) control of process equipment such as pumps, agitators and divert valves; (b) control of continuous process variables such as flow, temperature and pressure; (c) monitoring of tanks–both temperature and level. The system includes a computer-based information and advanced control system. The computer maintains an integrated data base of all process variables, process equipment status, analytical results, current pumping activity and current production. The system provides operator displays, operator reports, management reports and operator logs. The system also allows the user to meet special needs by writing additional Fortran-based programs.

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OIL RECOVERY TECHNIQUES. William T. Wall, Jr., Marketing Manager-Industrial Waste Group, and William M. Throop, Manager-Market Development, Envirex Inc., A Rexnord Co., Waukesha, WI.

The fats and oils industry in the U.S. and in Canada discharges over one-half billion gal of wastewater daily (1), mostly discharging to municipal wastewater treatment plants (from U.S. Department of Commerce Publication MC72). Although there are wide variations in industry segments, a number of common unit operations contribute to these wastewater flows. The distribution of discharge water in the plant can be grouped into 3 categories: ca. 55% process water, 30% condenser cooling water and 15% boiler feedwater. Actual operating experiences and comparative data from several recent installations are presented. The treatment train, involving equalization, acidification, gravity separation, chemical flocculation and polishing with dissolved air flotation, is reviewed, along with design variables that are considered to most effectively meet desired effluent requirements.

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ELIMINATION OF AIR AND WATER POLLUTION BY DOUBLE-STAGE SCRUBBER. Anthony Athanassiadis, Extraction De Smet NV, Antwerp, Belgium.

This new scrubbing system has been developed in view of entirely eliminating air pollution caused by water cooling towers during oils or fats deodorization. Also, thanks to this process, water effluent is minimized. Already in industrial application since last year, this sytem is based on the action of 2 scrubbers placed in series. The first scrubber is a conventional one, whereas the second uses concentrated, cooled brine circulating in closed-loop circuit as condensing media. Thorough purification of water vapors is thus achieved before gas from the deodorizer enters into the high vacuum boosters. As a practical result of this special scrubbing process, the condensing water of barometric condensers can be entirely recycled and this water is cooled by clean water in a surface heat exchanger that does not require any maintenance for cleaning.

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MIXING–DESIGN AND SCALE-UP FOR NON-NEWTONIAN FLUIDS. A. Dhruv, Anderson Clayton Foods, 3333 N. Central Expressway, Richardson, TX 75080.

Concepts of various mixing parameters, i.e., average and maximal shear rates for different vessel geometries, Reynolds number, Power number, impeller pumping rate per batch volume, power per batch volume and blend time, are presented. For purposes of process design involving mixing, the concept of correlating chemical engineering coefficients (heat/mass/reaction rate), and hence, process results to mixing parameters rather than specific vessel/impeller geometry or impeller rotational speed is described. Differences in significance of these parameters in Reynolds and turbulent range, and their interpretation and use with non-Newtonian fluids are discussed. Selection of a mixing parameter that has the most significant effect on a required process result as a scale-up criterion is recommended. The above process of correlating mixing parameters and process results, using it for process design and scaling it up on the basis of the most significant mixing parameter was successfully used for designing and scaling up a process for an imitation cheese product. Various implications on the relationships between mixing parameters, process results and product characteristics are illustrated for the above product and its process.

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OIL PROCESSING–PROCESS SAFETY. Robert C. Meyer, Procter & Gamble Co., Engineering Division, 6300 Center Hill Road, Room E2N29B, Cincinnati, OH 45224.

This paper will address the potential safety hazards in the shortening and oil processes and the design and operating considerations that can be used to minimize risk. Each of the following major processing areas will be included: (a) bean handling and storage, (b) solvent extraction, (c) refining and bleaching, (d) hydrogenation, and (e) deodorizing. For each of these areas, examples of the types of hazards will be reviewed. When possible, the examples will include actual case histories of industrial accidents in order to illustrate the potential consequences of these accidents. Ideas will be presented on how to minimize the risk of accident in each of the aforementioned process areas. Although not intended to be comprehensive, both design considerations and operating procedures will be included.

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AQUEOUS PROCESSING OF LUPINES. J.M. Aguilera, M.F. Gerngross and E.W. Lusas*, Food Protein R&D Center, FM Box 183, Texas A&M University, College Station, TX 77843.

Full-fat flours from sweet and bitter lupines (*Lupinus sp.*) were water-extracted and fractionated into protein concentrates and cream (oil) at pilot-plant scale. Concentrates produced ranged from 7 to 80% in protein content, with oil contents between 3.7 and 8.0%. The cream contained 50-80% oil. Alkaloid content of concen-

trates from sweet lupines was below 0.01%. Significant reduction in alkaloid concentration was achieved in bitter lupines by washing with acidified water. Aqueous processing (AP) proved to be a very attractive technique for separating protein, oil and water-soluble alkaloids in one step. AP can be readily adapted to milk-drying plants and avoids the problems of petroleum-based solvents.

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ABRASIVE DRY MILLING OF COWPEAS. R.D. Phillips and M.S. Chhinnan*, Department of Food Science, University of Georgia, Georgia Experiment Station, Experiment, GA 30212.

Cowpeas with wrinkled, tightly adhering seed coats are favored for most food applications in West Africa. Traditionally, they have been decorticated by soaking to loosen the seed coats, followed by manual rubbing. Dry milling peas to meal or flour has many advantages over wet processing, but has met with limited success. This is due to the difficulty of removing dry testa components which leads to poor recovery of edible material. Several approaches to achieving improved recovery rates have been investigated in this study. The central operation was removal of seed coats by abrasion. One scheme used a device composed of an abrasive disk rotating in a closely fitting, abrasive-lined cylinder. Following abrasion, residual eyes were loosened by impacting in a mill and were separated by aspiration. The second scheme used a high velocity stream of abrasive particles impinging on seeds held in wire mesh container. Trials were also conducted in which the seeds were heat-treated prior to abrasion. This treatment considerably shortened the required abrasion time. These techniques yielded cotyledon pieces which were almost totally free of seed coat and eye. Yields and fraction compositions were compared to those from the dry milling of a variety with smooth, loosely adhering seed coats. Such comparisons were also made with blackeyed peas subjected to wet milling. Compositions of the various cotyledon fractions did not differ greatly from each other, whereas seed coat (bran) fractions differed in tannin and fiber content.

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GAS LIQUID CHROMATOGRAPHIC SEPARATION OF PHENOLIC ACIDS IN OILSEED AND LEGUME FLOURS. Kazimierz J. Dabrowski and Frank W. Sosulski*, Dept. of Crop Science, Univ. of Saskatchewan, Saskatoon, Sask. S7N 0W0, Canada.

The stability of silylated derivatives of simple phenolic acids and the precision of the GLC determination of these seed components were investigated. Tetrahydrofuran was better than methanol for the extraction of phenolic acids whereas methyl heptadecanoate proved superior to *n*-tetracosane as the internal standard. Phenolic acids in defatted meals and flours were extracted and fractionated into free, soluble esters and insoluble-bound phenolic compounds. In rapeseed, the proportions of phenolic acids in these fractions were about 75, 1,000 and 5 mg/100 g flour with *cis*- and *trans*-sinapic acids being the major phenolic acid or aglycone in each fraction. The distributions of phenolic acids among the solubility fractions of soybean and other oilseeds and legumes were also determined.

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SUPPLEMENTATION OF BAKERY ITEMS WITH HIGH-PROTEIN PEANUT FLOUR. Robert L. Ory* and Edith J. Conkerton, Biochemistry Research, Oilseed and Food Laboratory, PO Box 19687, New Orleans, LA 70179.

Peanuts were defatted with hexane to produce high-protein peanut flours with 55-60% protein, depending on the cultivar being examined. The peanut flour was used to supplement wheat flour at levels of 10, 13, 15, 20 and 55% (of the wheat flour) in bread, cookies and all-peanut flour muffin. In general, the high solubility of peanut proteins tends to increase moisture retention in the baked products compared to nonsupplemented controls. Net increase of protein in baked items varied from 4% increase for 10% peanut flour bread to over 40% for the all-peanut flour muffins. Other physical and chemical properties of these food products will be presented to increase the possible applications of peanut flour in supplemented food products.

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COMPOSITIONAL, PHYSICAL AND SENSORY CHARACTERISTICS OF AKARA PROCESSED FROM COWPEA PASTE AND NIGERIAN COWPEA FLOUR. Kay H. McWatters, Department of Food Science, Georgia Station, Experiment, GA 30212.

The cowpea (*Vigna unguiculata*) is a primary food legume and a leading source of protein in West Africa. Paste made from soaked, dehulled, milled blackeye peas forms the basis of popular dishes such as steamed moin moin and deep-fat-fried akara. Recent efforts to reduce the extensive time and effort required at present to prepare cowpea paste have focused on the use of (a) light-skinned peas which lack pigmentation in the hilum and do not require dehulling and (b) pre-milled meal or flour. The quality of akara prepared from traditionally processed blackeye paste, from soaked but not dehulled cream peas (Dixiecream cultivar), and from a commercial Nigerian cowpea flour was compared. Akara from blackeye and cream pea paste was higher in moisture and oil content and lower in protein and carbohydrate content than akara made from the flour. Gardner color values for lightness and yellowness of akara were similar for all treatments. Sensory scores for appearance, color and aroma were not significantly different for akara prepared from paste or flour. Texture and flavor scores were significantly lower for akara made from flour than from either of the pastes. Akara from blackeye or cream pea paste was more tender, requiring significantly less force to compress and shear, than akara from flour. Improvements in processing should encourage increased cowpea use worldwide.

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NUTRITIONAL AND PHYSIOLOGICAL RESPONSE OF RATS TO DIETS CONTAINING WHOLE DECORTICATED AND DECORTICATED-STEAMED COWPEAS. R. Dixon Phillips* and Joy G. Adams, Department of Food Science, University of Georgia Agricultural Experiment Station, Experiment, GA 30212.

Whole cowpeas which had been ground, decorticated and ground, and decorticated, ground and steamed for 1/2 hr at atmospheric pressure were incorporated into diets as the sole source of protein (10% of the diet) and fed to groups of weanling Sprague-Dawley rats for 4 weeks. Other groups received diets containing ANRC casein, textured soy flour and durum wheat flour. Diets also contained 8% cottonseed oil, 5% mineral mix, and 1% vitamin mix and corn starch to 100%. Body weights and feed intakes were determined weekly. Feces were collected during the last week of the study. Feces and diets were analyzed for nitrogen by Kjeldahl assay, for Ca, Fe and Zn by atomic absorption spectroscopy, and for P by a colorimetric procedure. At sacrifice, the liver, pancreas and testicles were removed from rats receiving cowpea diets and from a group whose weights closely matched those on cowpea diets, but which had been fed standard diets. PER (computed weekly) of whole and decorticated cowpeas improved steadily over the assay period, although changes were not significant ($p \leq 0.05$). Other PER showed no consistent time trends. Decorticating and steaming improved PER values with the greatest differences observed early in the assay period. Apparent protein digestibility of cowpea proteins increased from 73% for the whole pea to 78% for the decorticated and steamed peas. Values for casein, TVP and durum wheat flour were 94, 85 and 89%, respectively. Apparent absorption of calcium, phosphorus and zinc, and iron was much higher from the cowpea diets than from TVP or durum wheat diets and, in most cases, than from casein diet. Surprisingly, mineral absorption from cowpea diets decreased with decortication and with steaming. Although the differences were not significant, the (average relative) testicle weight was smallest and pancreas weight largest for the group receiving whole peas whereas the converse was true for the group receiving decorticated steamed peas.

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EFFECT OF TEMPERATURE, TIME, AND MOISTURE TREATMENT ON SOME NUTRITIONAL AND FUNCTIONAL PROPERTIES OF COWPEA PROTEINS. R. Dixon Phillips* and Leo G. Mendoza, Department of Food Science, University of Georgia, Georgia Experiment Station, Experiment, GA 30212.

Finely ground (<200 mesh) flour from decorticated Mississippi silver skin cowpeas was equilibrated with water vapor for 0, 8 and 24 hr, resulting in total moisture contents of 7, 19 and 25%. These flours were each subjected to heat treatment at 100, 125 and 150 C for 4 time periods which ranged from 15-120 min for low moisture-low temperature samples to 0.5-7 min for high moisture-high temperature samples. Changes in trypsin inhibitor activity, protein solubility (0.1 M phosphate buffer, pH 7), and in vitro protein digestibility were measured as a function of treatment conditions. Trypsin inhibitor was quite labile, being rapidly reduced from 11 units/mg in the untreated flour to undetectable levels at all treatments in which temperature was $\geq$ 125 C or moisture was $\geq$ 19%. In vitro protein digestibility exhibited an increase under lower temperature-moisture conditions (from 81 to 83%) which was largely independent of heating time and which may have been due in part to destruction of trypsin inhibitor. Under intermediate moisture-temperature conditions (100 C-19% H_2O, 125 C-7% H_2O) digestibility rose to 84%, again independently of heating time. Under the more severe conditions of temperature and moisture content, digestibility initially increased, then decreased with time to values ($\sim$79%) that were lower than those from untreated flour ($\sim$81%). Nitrogen solubility was decreased according to the moisture level and temperature of the flour. At 100 C and 7% or 19% H_2O, moderate decreases in solubility over the heating periods were observed (from 65 to 56 and to 50%, respectively). At higher moistures and temperatures, solubility rapidly decreased to the

minimal detectable level, i.e., to ∿12% in 0.5 min at 150 C-25% H_2O.

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SUBSTITUTION OF SOY FOR BEEF AND FISH IN HUMAN DIETS: IMPACT ON SEVERAL NUTRITIONAL PARAMETERS. C. Kies* and H.M. Fox, Dept. of Human Nutrition and Food Service Management, University of Nebraska, Lincoln, NE 68583.

Use of soy-based products as partial or total replacements for animal products in western diets is an area of economic, political and scientific interest. In earlier studies in this laboratory, protein quality of extruded defatted soy meal in comparison to beef was evaluated using bioassay techniques involving human adults and adolescents. The objective of the current project was to assess the nutritional impact of substituting commercially available, soy-based products for meat and fish in mixed food diets of healthy adult women. Ten adult women were maintained on a laboratory-controlled diet based on ordinary foods for 8 weeks. The same foods were fed each day. Using a cross-over design, subjects received in randomized order the controlled diet with tuna fish (lunch) and ground beef (dinner) for 4 weeks and the controlled diets with soy-concentrate-based products substituted for the beef and tuna for 4 weeks. Subjects made complete collections of urine and stools for the entire experiment. Fasting venous blood samples were drawn at the beginning of the study and at the end of each week. Urine, feces and blood were analyzed for a variety of constituents of concern in assessment of nutritional status. Mean blood or blood serum values of subjects while receiving the meat-fish diet or soy diet based on preliminary data were: triglycerides, 84 and 80 mg/dl; total cholesterol, 176 and 148 mg/dl; high density lipoproteins, 60 and 58 mg/dl; iron, 99 and 80 μg/dl; total iron binding capacity, 350 and 398 μg/dl; hemoglobin, 13.2 and 13.0 g/dl; hematocrit, 39.2 and 38.9%; blood urea nitrogen, 13 and 13 mg/dl; and total protein, 7.4 and 7.4 g/dl, respectively. (Nebr. Agric. Expt. Station 91-024 and USDA C.S.R.S. W-143.)

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THE COMPARATIVE EFFECT OF DIETARY ANIMAL AND VEGETABLE PROTEIN ON GALLSTONE FORMATION AND BILIARY CONSTITUENTS IN THE HAMSTER. George U. Piepa* and Susan Mahfouz, PO Box 24134, TWU Station, Department of Nutrition and Food Sciences, Texas Woman's University, Denton, TX 76204.

A gallstone-inducing diet containing 74.3% sucrose, 20.0% protein, 5.0% mineral mix, 0.5% vitamin mix and 0.2% choline chloride was used to examine how various dietary proteins (casein, soybean and cottonseed) effect gallstone formation and production of key biliary constituents in the hamster. Casein, as the protein source, produced gallstones in 100% of the animals; however, with the substitution of soybean or cottonseed as the protein source, gallstone incidence was dramatically reduced to 32 and 0%, respectively. In an effort to ascertain the mechanism or mechanisms responsible for gallstone formation, the 3 primary biliary constituents, bile acids, phospholipid and biliary cholesterol and serum cholesterol were quantitatively measured. Biliary cholesterol was elevated with all experimental diets compared to standard rodent chow diet. When casein was the protein source, biliary cholesterol was increased 4-fold whereas soybean and cottonseed yielded 3- and 2-fold increases, respectively. Additionally, this research indicates that serum cholesterol can be reduced by substituting vegetable proteins in the diet. This study suggests that the substitution of vegetable for animal protein in the diet can dramatically decrease gallstone formation in the hamster. A lowering of the concentration of biliary cholesterol in an absolute and relative manner appears to be partially responsible for the decrease in cholesterol gallstone formation.

P1

DETERGENT SPRAY TOWER EFFLUENT RECYCLE SYSTEM. Norman C. Foster and Burton Brooks, The Chemithon Corporation, 5430 W. Marginal Way SW, Seattle, WA 98106.

Recycle of effluent gases from a detergent spray drying tower was investigated. It was found that ca. 50% of the effluent gas from the tower could be recycled back to the tower furnace. Fuel consumption was reduced. Higher tower operating temperatures resulted in increased drying capacity. The effluent clean-up system size was reduced. Theoretical calculations and pilot plant data are compared to operating experience in 2 full-sized plants.

P2

EFFECT OF POLYUNSATURATED ALCOHOLS ON BACTERIAL GROWTH. J.R. Gilbertson*, 559 Salk Hall, University of Pittsburgh, Pittsburgh, PA 15261, R.J. Crout, University of W. Virginia, R.H. Connamacher, D. Platt and H. Langkamp, University of Pittsburgh.

Fatty acids, particularly polyunsaturated moieties, are growth inhibitors for gram-positive bacteria. However, their antimicrobial activities can be altered by changes in the composition of the culture media. Thus, one would expect that, in vivo, there would be a variation in the effectiveness of the free fatty acids. Other studies indicate that long-chain alcohols occur naturally in mammalian and bacterial cells. They have a low toxicity for mammals and are structurally similar to the free fatty acids. Thus, one might expect polyunsaturated long-chain alcohols to be antimicrobial agents. In one instance in which the antimicrobial effect of lauryl alcohol was evaluated, inclusion of this moiety in the culture media inhibited the growth of a number of gram-positive bacteria. Considering these observations, the effect of primary alcohols of varying chain length and degree of unsaturation on bacterial growth was assessed. The unsaturated alcohols linoleyl and linolenyl effectively inhibited bacterial growth. Of the saturated alcohols evaluated, only lauryl and myristyl alcohols inhibited growth, but at concentrations much higher than required for the unsaturated alcohols. All gram-positive organisms tested were sensitive to linolenyl alcohol; gram-negative bacteria were not. Linoleic and linolenic acids were inactive as antibacterial agents when administered at the same concentration. Repeated exposure of *Strep. mutans* BHT to linolenyl alcohol produced no change in the sensitivity of the organism to the alcohol. Significant amounts of linolenyl alcohol were found in the bacterium but linolenic acid could not be detected. It is proposed that the alcohols dissolve in the cell membrane, acting as molecular spacers. This decreases the hydrophobic association of the acyl chains of the phospholipids, resulting in an increased membrane permeability. This suggestion is supported by the increased amount of tetracycline taken up by bacteria exposed to linolenyl alcohol in contrast to stearyl alcohol.

P3

LIPID-DEGRADING ENZYMES IN LEGUMES: AN OVERVIEW. H. Michael Henderson, Department of Food Science, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada.

Lipid-degrading enzymes are implicated in undesirable flavor development during postharvest storage of fresh or unblanched frozen vegetables. Continuing studies are concerned with the following legumes: fababeans (*Vicia faba minor*), peas (*Pisum sativum*), lentils (*Lens esculenta*) and lupins (*Lupinus albus*). These crops may become significant sources of dietary protein, but in every case, the low lipid content is still sufficient to be implicated in postharvest quality deterioration. In these studies, lipoxygenase was the first enzyme to be identified, partially purified and biochemically characterized, followed by corresponding studies on lipolytic enzymes in fababeans and peas. Such hydrolytic enzymes demonstrated were lipase, phospholipase D, and 2 enzymic deacylating activities, i.e., the hydrolysis of *p*-nitrophenyl fatty acyl esters and of phosphatidylcholine (PC). The PC activity suggests the presence in fababeans and peas of phospholipase A and/or B activities. The objective of this study is an understanding of the role of enzymes in the postharvest degradation of endogenous lipids in legumes, with a view to overcoming flavor problems through the control of enzymic lipid degradation. The results from this study should show how PC could be completely degraded enzymically into its 5 component parts, and a pathway common to fababeans and peas is proposed for the sequential action of hydrolases and lipoxygenase on endogenous lipids in postharvest conditions.

P4

FATTY ACID PROFILING FROM MULTIPLE TISSUE SAMPLES: I. SYSTEMATIC TISSUE HANDLING, LIPID EXTRACTION AND CLASS SEPARATION, AND GC ANALYSIS. Robert J. Maxwell* and William N. Marmer, Eastern Regional Research Center, U.S. Department of Agriculture, ARS, 600 East Mermaid Lane, Philadelphia, PA 19118.

A systematic procedure was developed to allow the detailed fatty acid profiling of both the neutral and polar lipid classes isolated from over 100 related bovine muscle and adipose tissues. Lipid class separation was accomplished concomitantly during the extraction of the tissues by our previously developed dry column method, which allowed a detailed analysis of minor, but important, fatty acids associated with the polar fraction. This avoided the problems incurred during typical analyses of fatty acids from unseparated *total* lipid extracts, in which the contribution by the polar lipid's fatty acids is diluted by the overwhelming presence of the neutral lipid's fatty acids. Neutral lipids were derivatized to fatty acid methyl esters (FAME) by a standard procedure. To protect against hydrolysis of plasmalogens in the polar fraction and the resulting contamination of FAME with artifacts, a modified esterification

procedure was developed. FAME profiles then were obtained for almost 500 runs on a high resolution capillary GC equipped with an automated sampler-injector and a BASIC-programmable computer. Run programs for unattended GC operation will be described. Individual reports were stored on magnetic tape for later analysis. Peak identification was accomplished by peak enhancement techniques using standard FAME. Using this overall procedure, quantitation and peak identification were obtained for both major and minor fatty acid constituents from bovine tissue.

P5

FATTY ACID PROFILING FROM MULTIPLE TISSUE SAMPLES: II. SYSTEMATIC DATA HANDLING AND INTERPRETATION: COMPARISON OF BOVINE LIPID COMPOSITION VS DIETARY REGIMEN. William N. Marmer*, Robert J. Maxwell and John C. Phillips, Eastern Regional Research Center, U.S. Department of Agriculture, ARS, 600 East Mermaid Lane, Philadelphia, PA 19118.

The methodology described in the previous abstract was continued to allow a statistically valid consolidation and interpretation of the almost 500 separate fatty acid profiles of 2 studies. One study sought to determine differences in fatty acid composition encountered from tissue to tissue within a single dietary regimen (grain) and within the same tissue from regimen to regimen (grain vs wheat-pasture forage). Another study sought to detect compositional differences induced by incorporation of monensin into the diet. Analysis of polar lipid fractions separate from neutral lipid fractions allowed the amplification of differences seen among the minor, though biologically significant, fatty acids. The complexity of the fatty acid GC pattern precluded automatic identification by programmed time window. Instead, assignments were made manually on a modified computer-generated report that calculated relative retention times. Peak area data by peak number were transferred into a larger computer for statistical analysis. Initial manipulation of the data confirmed the precision of the initial procedures for tissue handling, lipid extraction, derivatization and GC analysis, and pinpointed items that needed further editing. Then, for each study, lipid profiles were statistically compared, neutral and polar separately. In one study, comparisons within a single (grain) regimen were made among all samples of semitendinosus (ST), longissimus dorsi (LD), and psoas major muscle and between subcutaneous (SQ) and kidney knob adipose tissues. In both studies, comparisons between dietary regimens were made for all samples of a single muscle (ST or LD) and for all samples of SQ tissue.

P6

HYDROCARBONS, STERYL ESTERS AND FREE STEROLS OF PEANUT AND CORN OIL. R.E. Worthington, Department of Food Science, University of Georgia Agricultural Experiment Station, Experiment, GA 30212.

The non-acylglycerol fraction of seed oils consists of a variety of classes of compounds that together usually make up 3% or less of oil weight. Some of these classes of compounds may be isolated and quantified by saponification of the oil and extraction of nonsaponifiables whereas other classes of compounds are destroyed by this treatment. In this study, steryl esters, free sterols and hydrocarbons were isolated and quantified by a combination of preparative column and thin layer chromatography and gas chromatography after the addition of cholesteryl heneicosanoate, cholesterol and *n*-hexacosane as internal standards. Corn oil samples (Mazola, Kroger) were obtained from the local market; peanut oil samples were prepared in the laboratory from commercial varieties of peanuts (Florunner, Starr). Average percentage values (±1 standard deviation) obtained for hydrocarbons, steryl esters and free sterols were: Florunner – 0.36 ± .004, .074 ± .0005, .15 ± .003; Starr – .03 ± .001, .051 ± .0005, .13 ± .002; Mazola – .039 ± .004, 1.42 ± .04, .37 ± .008; Kroger – 0.39 ± .003; .95 ± .04, .32 ± .004. Squalene was the major hydrocarbon and constituted 59 and 53% of total hydrocarbons in Florunner and Starr peanut oils and 59 and 34% of total hydrocarbons in Mazola and Kroger corn oils, respectively. The remaining hydrocarbon fraction consisted of a complex mixture of compounds, including both even- and odd-carbon-number hydrocarbons with the even-carbon-number compounds predominating. β-Sitosterol was the major sterol in all fractions and together with campesterol, stigmasterol, and Δ^5-avenasterol made up 90-95% of all sterols. Steryl esters of peanut oil contained higher proportions of linoleic acid and long-chain acids (C_{20}-C_{24}) than did whole oil. Corn oil steryl esters also contained a higher proportion of linoleic acid than whole oil.

P7

CHOLESTEROL AND CHOLESTERYL ESTER CONTENTS OF HUMAN MILK DURING 16 WEEKS OF LACTATION. R.G. Jensen*, R.M. Clark, A.M. Ferris, M.B. Fey and P.B. Brown, Dept. of Nutritional Sciences, University of Connecticut, U-17, Storrs, CT 06268.

Milk samples were collected from 10 mothers at 2, 6, 12 and 16 wk postpartum. The total contents of one breast was taken with the Egnell pump and the lipids were extracted by the Folch method. Total lipids were determined gravimetrically. The cholesterol and cholesteryl ester contents were analyzed by gas liquid chromatography. The contents of these compounds at 2, 6, 12 and 16 wk were: total lipid (%); 3.87, 4.08, 4.59 and 5.18, total cholesterol (mg/100 mL); 11.01, 9.72, 10.29 and 10.37, and cholesteryl esters (mg/100 mL); 1.28, 1.56, 1.8 and 2.97. The marked increase in total lipid content was not accompanied by an increase in amount of cholesterol.

P8

THE LECITHIN (PHOSPHOLIPID) CONTENT OF FOODS. John L. Weihrauch*, Nalini Narasimhan and Young-Sun Son, USDA, HNIS, CNC, Federal Building, Room 301, Hyattsville, MD 20782.

Reports have linked ingested choline and lecithin with the elevation of plasma choline and brain choline and acetylcholine levels, the improved memory and learning in animals and, in some cases, in man, and with the improvement in the condition of some patients having neurological disorders. This increased research has uncovered the need for reliable data on the lecithin content of foods. In response to this need, the U.S. Department of Agriculture has initiated a search of the literature on the lipid classes in foods. Preliminary data show that eggs, meats, organ meats, legumes and cereals, and their milled products, are good sources of dietary lecithin. For example, the lecithin content of 100 g of eggs, pork liver, pork kidney, lean beef, wheat flour and soybeans is about 3,000, 2,900, 2,300, 700, 1,200, and 2,000 mg, respectively. Few data were found in the published literature for most foods, except for some legumes and some cereal grain products. Interlaboratory differences and differences in analytical methodology contributed most to the variability in the data.

P9

BOVINE PULMONARY SURFACTANT. F. Possmayer*, N. Smith and S.F. Yu*, Dept. of Obstetrics & Gynecology, University of Western Ontario Hospital, Winderemere Road, London, Ontario N6A 5A5, Canada.

Normal lung function is dependent on the presence of a specialized material, the pulmonary surfactant which stabilizes the alveolus by reducing the surface tension at the air-tissue interface. Lack of sufficient pulmonary surfactant at birth is associated with the development of the Neonatal Respiratory Distress Syndrome (N.R.D.S.) the major cause of perinatal morbidity and mortality in North America. Treatment of premature neonates suffering from N.R.D.S. with lipid extracts of bovine pulmonary surfactant leads to a marked improvement in gaseous exchange. Lipid extracts of bovine lung surfactant contain 97% phospholipid and 3% neutral lipid. Cholesterol accounts for the major proportion of the neutral lipids. The phospholipid fraction is composed of 80% phosphatidylcholine, 10% phosphatidylglycerol and smaller amounts of phosphatidylethanolamine, sphingomyelin, phosphatidylinositol and phosphatidic acid. Phosphatidylcholine and phosphatidylglycerol contain a high proportion of palmitate, but this was not observed with the other glycerolipids. Suspensions of natural bovine surfactant or protein-depleted lipid extracts exhibit similar abilities in reducing the surface tension of a pulsating bubble to 25-30 dynes/cm at maximal radius (0.55 mm) and 0 dynes/dm at minimal radius (0.4 mm). These results are consistent with the view that the proteins associated with natural bovine surfactant are not essential for the expression of surfactant activity and it should be possible to produce wholly artificial surfactant from synthetic and semisynthetic lipids. (Supported by grants from the Canadian Medical Research Council and The Toronto Sick Childrens' Hospital Foundation.)

P10

THE SYNTHESIS OF PHOSPHATIDYLCHOLINE FROM EXOGENOUS 1-[^{14}C] PALMITOYL-*SN*-GLYCEROPHOSPHORYLCHOLINE AND [^{14}C] ARACHIDONIC ACID IN UNSTIMULATED AND AGGREGATING HUMAN PLATELETS. B.J. Holub*, D.E. Agwu and V.G. Mahadevappa, Department of Nutrition, University of Guelph, Guelph, Ontario N1G 2W1, Canada.

The synthesis of phosphatidylcholine (PC) from exogenous 1-[^{14}C] palmitoyl-*sn*-glycero-3-phosphorylcholine (1-[^{14}C] palmitoyl GPC) or [^{14}C] arachidonic acid was studied in both unstimulated and aggregating human platelets. For the purposes of simultaneously measuring PC synthesis and thrombin-induced platelet aggregation, incubations were conducted at 37 C with magnetic stirring in siliconized tubes inserted into a Payton Dual Channel Aggregator. Within 30 sec of stimulating platelet aggregation by the addition of thrombin to platelet suspensions (0.2 U/mL), the rate of incorporation of [^{14}C] arachidonate into platelet PC was markedly increased. This indicates that an enhanced formation of arachidonoyl-PC from exogenous arachidonic acid and endogenous 1-acyl GPC occurs in

association with thrombin-induced platelet aggregation. In contrast, the rate of incorporation of exogenous 1-[^{14}C] palmitoyl GPC into platelet PC was not significantly different in unstimulated, compared to aggregating, platelets. (This work was supported by the Medical Research Council of Canada.)

P11

PENTOBARBITAL SLEEPING TIME AND MEMBRANE LIPIDS. R.C. Aloia, Dept. of Anesthesiology, Loma Linda Univ. Med. Ctr. and Veterans Admin. Hosp., Loma Linda, CA, W. Mlekusch, Dept. of Medical Chemistry, Univ. of Graz, Graz, Austria, B.J. Brandstater, Dept. of Anethesiology, Loma Linda Univ. Med. Ctr., and J.A. Meyer, Anesth. Serv., Veterans Hosp., Loma Linda, CA.

The role of dietary fats in modulating barbiturate-induced sleeping time was investigated in mice fed a stock diet (CHOW) or one containing partially hydrogenated coconut oil (PHCO). Sleeping time was recorded on the 48th day of the experiment after injection of pentobarbital. Mice fed the PHCO diet slept significantly longer than those fed the stock diet. At the time of the experiment, liver lipids from mice fed PHCO contained slightly less phosphatidylethanolamine and slightly more phosphatidylinositol than did those from CHOW-fed mice; the ω9 acids were higher, and ω3 and ω6 acids lower in the PHCO-fed animals. Similar changes in ω3 and ω9 acids were observed in brain lipids. Alterations in barbiturate-induced sleeping time may result from changes in the membrane milieu of endoplasmic reticular enzymes responsible for metabolism of pentobarbital or from an altered sensitivity of brain membranes to the drug.

P12

SOME CHARACTERISTICS OF RAPESEED OIL AND MEAL. Yehia G. Moharram, Food Science and Technology Department, Faculty of Agriculture, Alexandria University, M.M. Mostafa and E.H. Rahma, Food Science and Technology Department, Faculty of Agriculture, Monoufeia University.

The oil and meal of rapeseed cultivated recently in Egypt were evaluated. The seed contained 40.3% and 25.8% crude oil and crude protein, respectively. The crude oil was composed of 7 classes, 7 triglyceride fractions, and contained 19% erucic, 35% oleic, 27% linoleic and 7.5% saturated fatty acids. The meal had relatively high levels of lysine, methionine, threonine, valine and histidine. The results of water and fat absorption, emulsification and foaming capacities, and stability of rapeseed meal revealed it to have good functional properties.

P13

SYNTHESIS OF 1-*O*-ALKYL [ALKYL-1',2'-^{3}H]-2-ACETYL AND 1,2-DIPALMITOYL [2-PALMITOYL-9,10-^{3}H]-*SN*-GLYCERYL-3-PHOSPHORYLCHOLINE. Un Hoi Do and David G. Ahern, New England Nuclear Corp., Lipids Department, 575 Albany St., Boston, MA 02118.

Two physiologically important ^{3}H-labeled phospholipids have been prepared for metabolic studies and identified by chromatographic, spectroscopic and enzymic techniques. 1-*O*-Alkenyl-2-acetyl-*sn*-3-phosphorylcholine (GPC) was prepared by deacylation of beef heart plasmalogen phosphatidylcholine (PC) with tetramethyl ammonium hydroxide followed by acylation of the resulting plasmalogen lyso PC with acetyl chloride in the presence of N,N-dimethylaminopyridine. 1-*O*-Alkenyl-2-acetyl GPC was reduced with $^3H_2$ gas over palladium oxide to give 1-*O*-alkyl [alkyl-1',2'-^{3}H]-2-acetyl GPC. 1,2-Dipalmitoyl [2-palmitoyl-9,10-^{3}H] GPC was obtained by the reduction of 1-palmityl-2-palmitoleoyl GPC which had been prepared by acylation of L-α-1-palmitoyl lyso PC with palmitoleoyl chloride.

P14

OBSERVATIONS ON THE ACYLATION OF 1-PALMITOYL-GLYCEROPHOSPHORYLCHOLINE WITH FATTY ACID ANHYDRIDES. R.W. Evans*, M.A. Williams and J. Tinoco, Department of Nutritional Sciences, Morgan Hall, University of California, Berkeley, CA 94720.

A widely used method for the preparation of phosphatidylcholines involves the acylation of lysophosphatidylcholine or glycerophosphorylcholine with fatty acid anhydride in the presence of the sodium salt of the fatty acid. In our studies, we analyzed the conditions of acylation using linoleyl anhydride and 5 μM of 1-palmitoyl-glycerophosphorylcholine (LPC) which was prepared from L-α-dipalmitoylphosphatidylcholine using the phospholipase A_2 activity of snake venom (*Crotalus adamanteus*). Fatty acid anhydrides were prepared by an established procedure using the reaction with dicyclohexylcarbodiimide. After acylation and thin layer chromatography, determination of the levels of phosphatidylcholine and LPC gave the following results: (a) levels of fatty acid salt above 5 μM did not improve the yield; 2.5 μM was a little less effective than 5 μM; (b) >80% acylation was obtained in the presence of 6.25 μM of anhydride; (c) yields at acylation temperatures of 70 and 50 C were similar but higher than that at 30 C; (d) acylation ceased within 1 hr at 70 and 50 C and within 2 hr at 30 C. The same procedures were also used to acylate larger samples of LPC (up to 80 μM) with over 20 different fatty acid anhydrides ranging in chain length from 12 to 24 and containing from 0 to 6 double bonds. The method was successful for all the anhydrides except those formed from 2 very long chain saturated acids: 22:0 and 24:0. (This work was sponsored by USPHS grants AM12024 and AM10166.)

P15

DIFFICULTIES IN USING THE IATROSCAN FOR THE QUANTIFICATION OF COMPONENTS OF A LIPID MIXTURE. R. Thomas Crane, Steven C. Goheen, Edward C. Larkin and G. Ananda Rao*, Hematology Research Laboratory (151H), VA Medical Center, Martinez, CA 94553.

The Iatroscan has previously been used for qualitative analyses of lipid composition. This instrument uses chromarods (quartz rods coated with silica gel) for the separation of lipids by thin layer chromatography. Levels of lipids are measured by flame ionization detection. More recent studies have indicated that this method may be useful for quantitative assessments of various components of tissue lipids. In these studies, response factors have been determined for several lipid classes. However, these are uncertain since they vary significantly among reports. For example, in one study, the response factor for cholesterol esters was twice that of fatty acids whereas in another study, they were the same. Furthermore, the values for the response factor of fatty acids differed by 50% in the 2 studies. In the earlier paper, weight percentages of cholesterol, tristearin, stearic acid and cholesterol ester coincided with their peak areas which suggested that their response factors were identical. On the other hand, in the later study, response factors for these compounds ranged from 0.66 to 1.57. In an attempt to resolve these discrepancies and to develop a rapid quantitative assay of lipid components, we determined the response factors of various neutral and phosphoglycerides, fatty acids, fatty acid methyl esters, cholesterol and cholesterol palmitate. The response factors of these compounds were markedly different. They were found to allow the descending order: cholesterol palmitate, cholesterol, phosphatidylcholine, mono-, di- and triglycerides, phosphatidylserine, free fatty acids, lysolecithin, sphingomyelin and phosphatidylethanolamine. Response factors varied from 1.9 to 0.4 based on palmitic acid with a response factor of 1.0. Fatty acid methyl esters had response factors which varied from 0.45 (methyl pentadecanoate) to 0.9 (methyl behenate). All the above factors were calculated using 5-μg samples. Response factors also varied with the amount of lipid analyzed for all lipid classes studied. For example, the response factor for tripalmitin varied from 0.39 ± 0.06 (SD) for 1 μg spotted to 1.06 ± 0.11 for 10 μg. After repeated use of the rods, response factors became unreliable since they varied with the position of the spot on the rod. Qualitative lipid analyses are therefore more difficult than suggested previously. Whether components of unknown lipid samples can be accurately quantitated using this technique remains to be determined. (This work was supported by the Veterans Administration.)

P16

CAPILLARY GAS LIQUID CHROMATOGRAPHY OF CHOLESTERYL ESTERS. Norman B. Smith, Department of Biophysics, Health Sciences Centre, The University of Western Ontario, London, Ontario N6A 5C1, Canada.

Separation of cholesteryl esters (CE) by capillary gas liquid chromatography (GLC) was investigated. GLC on nonpolar capillary columns coated with OV-1 was performed with a narrow bore (0.2 mm id) 22-m fused silica column (0.11-μm film thickness; hydrogen inlet pressure, 20 psi; temperature program, 130-285 C at 30 C/min, then 285-330 C at 1.5 C/min) using the splitless injection technique, and with a wide bore (0.3 mm id) 15-m bonded phase, fused silica column (0.1-μm film thickness; hydrogen inlet pressure, 2-3 psi; temperature program, 100-255 C at 30 C/min, then 255-320 C at 1.5 C/min) using the cool on-column injection method. Both OV-1 columns resolved the CE principally on the basis of carbon number, but separation of the saturated esters from the unsaturated esters also occurred. The CE retention times were greater with the wide bore column than the narrow bore column, but peak resolution was better on the narrow bore column. GLC with on-column injection on the wide bore column, however, provided a much greater sensitivity, especially for the higher molecular weight CE (carbon nos. 43-47), with a lower limit for measurable peaks of about 500 pg; this enhanced sensitivity was achieved probably because on-column injection ensures a quantitative transfer of the sample from the needle to the column. Capillary GLC of CE on a 7-m glass column (0.25 mm id) coated with the polar phase, Silar 10C, was also studied (helium inlet pressure 20 psi; temperature program 150-219 C at 30 C/min, then 219-230 C at 0.5 C/min; splitless injection). Separation of CE according to degree of unsaturation was achieved.

Capillary GLC of intact CE is particularly useful in studies in which the esters are available for analysis only in ng amounts, e.g., from small individual atherosclerotic lesions, and therefore cannot be readily derivatized prior to GLC. (Supported by the Ontario Heart Foundation and the Medical Research Council of Canada.)

P17

ACCUMULATION OF ERUCIC ACID IN RAT ADRENAL AND OVARY: A TIME-COURSE STUDY. Brian L. Walker, Department of Nutrition, University of Guelph, Guelph, Ontario N1G 2W1, Canada.

Inclusion of high levels of erucic acid in the diet of the rat results in substantial deposition of this acid, as its cholesteryl ester, in the adrenal and ovary. Unlike the heart, these 2 tissues retain high concentrations of erucate as long as the dietary source is maintained. In the weanling male rat, cholesteryl erucate accounted for over 30% of total cholesteryl esters after only 4 days of feeding high-erucic-acid rapeseed oil. A maximal concentration of about 38% was observed after 10-12 days. Cholesteryl oleate and eicosenoate also accumulated rapidly, but the polyunsaturated esters 20:4n-6 and 22:4n-6 declined on a mole % basis. On an absolute weight basis, all of these esters increased, but the increases in 20:4 and 22:4 were slower than those of the monoenes. Similar results were obtained with female weanlings, but the increase in cholesteryl erucate was more rapid and the final concentration was greater than in the male rat. In the females, the absolute concentration of 20:4 and 22:4 was only transient. Ovarian cholesteryl erucate in weanling females accounted for ca. 29% of total ovarian cholesteryl esters after 7 days of rapeseed oil feeding; it increased slightly between 27 and 33 days of feeding and then remained constant. The increase in adrenal cholesteryl erucate in mature female rats occurred more slowly than in the weanlings, reaching a maximum after 12 days. This was again accompanied by a decline in the mole % of the 20:4 and 22:4 esters; these esters did increase with time on an absolute basis. In ovaries from mature females fed rapeseed oil, cholesteryl erucate and eicosenonate increased rapidly with time, with the cholesteryl erucate reaching a maximal concentration in 5 days; cholesteryl arachidonate constituted a constant proportion of ovarian cholesteryl esters during 22 days of rapeseed oil feeding. Overall, cholesteryl erucate deposition in adrenals was rapid, particularly in the case of female weanlings.

P18

THE EFFECT OF SELECTED ANTIOXIDANTS ON THE STABILITY OF VIRGIN OLIVE OIL. A.K. Kiritsakis*, Higher Technical Education School, (KATEE) Salonika, Greece, and L.R. Dugan and C.M. Stine, Michigan State University.

The effect of the antioxidants butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), tertiary butylhydroquinone (TBHQ) and propyl gallate (PG) on the stability of 3 different samples of virgin olive oil was studied. The antioxidants were tested either alone or in different combinations at different levels of concentration. The experiments were done under accelerated conditions (oven test) and under long storage conditions. For the long-storage studies, samples were stored at room temperature (20-28 C) in the dark, and in light, and at 50 C in the dark. Peroxide value, diene conjugation and thiobarbituric acid (TBA) tests were conducted to measure the oxidation of olive oil. Under accelerated conditions, the antioxidants increased the stability of the oil, but their effectiveness varied among the 3 different samples of olive oil used. Olive oil stored at room temperature in the dark did not undergo any significant oxidative deterioration during the 22-wk storage period. Therefore, the antioxidants used had no effect. This is understandable, as chlorophyll acted as an antioxidant in the dark. On the other hand, olive oil with or without antioxidants stored at room temperature in the light underwent a high degree of oxidation. Results obtained from peroxide value, diene conjugation and TBA tests correlated well in this experiment. The addition of antioxidants to olive oil stored at 50 C exhibited a beneficial effect. Potency of the antioxidants under these conditions was in the following order: TBHQ > BHT > BHA. This held true even when the amount of TBHQ used was half as much as that of BHT or BHA. The combinations of TBHQ with BHA and BHT provided good results, but they never exceeded the results obtained by using TBHQ alone.

P19

SOME EFFECTS OF DEEP-FAT FRYING ON LIPIDS OF FAST FOODS. L.M. Smith*, A.J. Clifford, R.K. Creveling, C.L. Hamblin and W.L. Dunkley, Departments of Food Science and Technology and Nutrition, University of California, Davis, CA 95616.

This study evaluated the changes in cooking oils and shortenings, as well as the changes in the fatty acid composition, of selected food items cooked by deep-fat frying. Total lipids were extracted from chicken and fish pieces, french fries, doughnuts, potato chips and several snack foods. In addition, fresh and used cooking oils and shortenings were obtained from fast-food restaurants in California. The lipid content of each type of food varied among different commercial sources. All samples were analyzed for fatty acid composition by gas chromatography. Fatty acid compositions of french fries, doughnuts, chicken and fish pieces were affected by the amount and the fatty acid profile of lipids in each uncooked food as well as by the composition of the cooking oil. There was little variation in the fatty acid profiles of several brands of potato chips but marked variation among corn and cheese snack foods. Several different physical and chemical analyses were made on the fresh and used oils. For quality assessment of used oils, the methods varied in convenience, equipment required, cost, sensitivity and reproducibility. Changes in dielectric constant, percentage of polar materials and smoke point correlated well with each other and with frying usage. The results show wide variations in the fatty acid composition of commercially used cooking oils and deep-fat fried foods. (Supported by the Greater Los Angeles Affiliate, American Heart Association.)

P20

CONVERSION OF USED FRYING OIL AND FAT TO A FUEL FOR DIESEL ENGINES BY TRANSESTERIFICATION. Martin J. Nye, Department of Chemistry, University of Guelph, Guelph, Ontario N1G 2W1, Canada.

Previous work in this laboratory has shown that rapeseed oil can be converted to a fuel for diesel engines with much reduced viscosity by reacting the triglycerides with methyl, ethyl or butyl alcohol to give esters. The present project is concerned with investigating the feasibility of converting used frying oil or fat into diesel fuel by a similar process. Used oils were donated by the University cafeterias, and were either solid animal fat or semisolid hydrogenated soybean oil. Good yields of the esters were obtained, but in all cases, varying degrees of solids were present at room temperature. After filtration, all the fuels performed as well as and better than rapeseed oil in engine tests. Although long-term results are not yet available, the lower viscosity and higher volatility of the new fuels should lead to fewer long-term engine problems. Also, the higher saturation of the fats should give rise to higher calorific value of the fuel and lower decomposition of the crankcase oil into which it has leaked during normal running conditions.

P21

TESTING VARIOUS FATTY ACID ESTERS AS DIESEL FUELS. William E. Klopfenstein*, Department of Biochemistry, and Hugh S. Walker, Dept. of Mechanical Engineering, Kansas State University, Manhattan, KS 66506.

Vegetable oils show considerable variation in their fatty acid compositions. We have undertaken a study to determine whether any of the common fatty acids which are found in most vegetable oils are especially desirable as diesel fuels. We prepared methyl esters of commercial grades of lauric, myristic, palmitic, stearic, oleic, linoleic and linolenic acids. In addition, ethyl and butyl esters of oleic acid were prepared. Triolein and some common vegetable oils were used as comparison fuels. Number 2 diesel fuel was used as a control. The fuels were tested in a single-cylinder diesel engine running at rated speed and load, and fuel consumption was measured. In general, the fuel consumption was higher with the esters than with #2 diesel. Fuel consumption appeared to decrease with increasing chain length and unsaturation of the fatty acid. Monoesters of the fatty acids are less viscous than the vegetable oils and therefore more closely resemble diesel fuel in their properties.

P22

"HYAMINE" TITRATION RESPONSES TO ALCOHOL AND ETHOXYLATED ALCOHOL SULFATES AND ALKYL ARYL SULFONATES USING METHYLENE BLUE, BROM CRESOL GREEN AND MIXED INDICATOR TWO-PHASE TECHNIQUES. F.C. Veatch*, J.L. Hoyt and D.L. Carson, Conoco, Inc., Research & Development Dept., PO Box 1267, Ponca City, OK 74603.

The most commonly used 2-phase titration techniques with "HYAMINE" 1622 titrant are compared. The responses of each dye to 3 types of surfactant, alcohol and ethoxylated alcohol sulfates and alkyl aryl sulfonates, are shown graphically, with special emphasis on the low molecular weight "cut-off" point. With the tables and graphs generated in this report, predictions for applicability, response and low molecular weight cut-off can be made.

P23

THE QUANTITATIVE DETERMINATION OF BHT IN SOAP PRODUCTS BY CAPILLARY GAS CHROMATOGRAPHY. M.M. Goldstein*, K.S. Molever, W.P. Lok and A.F. Miller, Research and Development Dept., Armour-Dial Co., Scottsdale, AZ 85260.

A simple and rapid procedure is described for the isolation,

silylation, and capillary gas chromatographic (GC) quantitation of the BHT content in soap bars, fatty acids and related intermediates. BHT is determined by blending sample with DMF in the presence of 2,4-di-*t*-butylphenol internal standard, filtering the mixture, silylating an aliquot with BSTFA and quantitating by capillary GC using flame ionization detection. The silyl derivatization and nonpolar capillary column (10-m, SP-2100, fused silica) provided resolution of BHT from certain fragrance component interferences. The method has a detection limit of ca. 10 ppm. Soaps fortified with BHT showed recoveries of 97.2 ± 3.8% at the 200-ppm level and 92.3 ± 2.3% when spiked at the 75-ppm level. The effect of bar soap storage time on BHT content is also demonstrated.

4

BIOLOGICAL ROLE OF FATS AND OILS. Jon J. Kabara, Department of Biomechanics, East Fee Hall, College of Osteopathic Medicine, Michigan State University, East Lansing, MI 48824.

An increased understanding of the role lipids have in a wide area of biological functions has developed during the past decade, with details presented at various AOCS national meetings. Because of the diverse nature of fats and oils, their roles need to be summarized; and the recognition of additional uses for the ubiquitous substances needs to be addressed. The involvement of lipids in the processes of health and disease necessitates that we bring some global concepts to bear, at least as first approximations, for a working hypothesis. Although the role of fats and oils has been discussed in a special AOCS seminar (Chicago, 1981), as it relates to heart disease and cancer, the need to enlarge upon these and other themes exists: exploration of lipid function in membranes, drug metabolism, dental caries, and enzyme systems, for example, should be considered. Additionally, the role of dietary fats should be understood at several levels: as specific chemicals and not in a generic sense; their occurrence in certain foods; their bio-availability; and, finally, their pharmacological or biological effects, whereas past emphasis has been on caloric value alone. New approaches to optimizing health conditions, as well as control or reversal of certain types of disease, are now available because of the manner in which many clinical conditions are affected by dietary fats. Beyond their role in nutrition, fatty acids and their simple derivatives have potential for being considered in the design of new germicide and insecticide systems. Specific examples for understanding the broad spectrum of the biological role of fats and oils will be given. The conclusions reached, based both in the literature and on the presenter's personal experience, will be of interest to basic and clinical scientists and to processors and users of dietary fats and oils. The responsibility of the research scientist and industry to the ultimate consumer of fats and oils will be emphasized.