Meetings

May meeting to feature 325+ papers

More than 1,300 persons are expected to participate in the 74th annual meeting of the American Oil Chemists' Society to be held May 8-12, 1983, at the Chicago Marriott Hotel.

More than 325 technical papers will be presented representing the latest research on all aspects of fats and oils – from processing of oil-bearing materials through production of edible and nonedible products to the effect of dietary fat on human health. Abstracts begin on Page 676. There will be 50 technical sessions during the 3½-day technical program. To provide more time for technical presentations and to reduce the number of concurrent sessions, organizers have decided not to hold a plenary breakfast on Wednesday. The awards made the past few years during the Wednesday breakfasts will instead be presented during the plenary breakfast on Monday, May 9.

One of the largest exhibits held during an AOCS national meeting will be featured. The exhibit gives registrants a chance to view the latest equipment, supplies and services available to the industry. The opening reception on Sunday evening, May 8, will be held in the exhibit area. Exhibits will be open to give registrants the opportunity for a leisurely visit at a time that does not conflict with any technical sessions or committee meetings.

A keynote address on "Technology and Business – The Growing Partnership," will be given at the Monday morning breakfast session by A.W. Woelfle, chairman of Kraft Inc. and a vice-chairman and director of Dart & Kraft Inc. Woelfle has headed Kraft operations in Europe and in the United States.

Three commercial tours will be offered during the Chicago meeting. One will be to the Chicago Board of Trade. A technical session on pricing of vegetable oils is scheduled Monday afternoon, with the Board of Trade visit scheduled for Tuesday morning. The tour will include a brief audio-visual presentation on what the Board of Trade is and how it operates, followed by an opportunity to watch the trading floor from the visitors' gallery. The Board of Trade opened its new grain trading floor last year. The soybean, soybean oil and soybean meal trading activity affects oilseed and oilseed product prices around the world. Another tour will be to Interstate Foods where frying fats are manufactured for institutional use. A third tour will be to a prominent Chicago bakery, the Sara Lee firm. Details of tour arrangements will be provided in the packet. The tours are optional, but persons who wish to participate must register for each tour. This registration may be done at the Chicago meeting.

The committee meetings will be held from Sunday, May 8, through Wednesday, May 11. A tentative schedule is published in this issue of *JAOCS*; the final schedule will be published in the program distributed at the meeting. Technical and administrative committees will be meeting to consider subjects from analytical methodology to the state of the society's finances, as well as planning future meetings. All committee meetings are open to anyone who wishes to attend, except for the Examination Board which considers confidential information when assessing qualifications of applicants to be referee chemists.

Three social events are scheduled to provide time for informal conversation. In addition to the aforementioned mixer on Sunday, May 8, and breakfast on Monday, May 9, there will be a Chicago in the 1920s theme party on Wednesday evening, May 11. There will be food and entertainment, but unlike the customary banquet, there will be no assigned seating and the evening is designed as a participatory event. Further details will be provided in registrants' information packets at the meeting.

The AOCS Placement Center will open on Sunday, May 8, for job applicants and potential employers to register. Interviews will be scheduled starting Monday, May 9.

Persons who plan to travel to Chicago by air are reminded that United Airlines, the official airlines for the meeting, is offering fares at least 30% below normal coach rates. Persons wishing to use United should call, or have their travel agents call, 800 521-0810 (in Michigan, 800 482-0243) and use the American Oil Chemists' Society meeting code number, 7332. United will ticket you at the lowest price seat available for the dates you wish to travel.

The spouses' program includes attendance at the Sunday evening mixer, Monday plenary breakfast and Wednesday evening event. In addition, spouses will have a special program. A spouses' hospitality tea will be held Sunday afternoon, May 8. On Monday, May 9, after the plenary breakfast, there will be a local tour in Chicago visiting some of the city's historic fashionable residences. On Tuesday, May 10, there will be a bus tour to Geneva in the nearby Fox River Valley. The restaurant where lunch will be served was once a blacksmith's shop.

Exhibitors

BAUERMEISTER INC. (Booth 603). Address: 3951 Senator St., Memphis, TN 38118.

BERICO INDUSTRIES INC. (Booth 510). Information will be available on fuel efficient Berico Soybean/Sunflower Process Driers featuring cleaned recycle air system, insulation, tapered column design with "Turn-Flo" column mixing action for production capacity to 320 tons per hour and outstanding process efficiency with low noise levels in 24-hr duty cycle. Cleanliness, safety and long life are inherent design features. Address: PO Box 12285, 10551 Barkley–Suite 412, Overland Park, KS 66212.

BRINKMANN INSTRUMENTS CO. (Booth 204). Rancidity analyzer, electronic balances and scales and rotary evaporators will be on display. Address: Cantiague Road, Westbury, NY 11590.

THE CAMBIAN ENGINEERING GROUP LTD. (Booth 405). A model of the unique "campro" deodorizer will be on display. The exhibit will include a presentation of the full range of services that Cambrian supplies to the oilseed and associated industries and some new process technology developed by the process group. Address: 2465 Cawthra Rd., Unit 112, Mississauga, Ontario L5A 3P2, Canada.

CROWN IRON WORKS CO. (Booths 502 & 504). Crown Iron Works Company designs and manufactures solvent extraction equipment. Photos, brochures and technical literature will be on display. Address: 1229 Tyler St. N.E., PO Box 1364, Minneapolis, MN 55440.

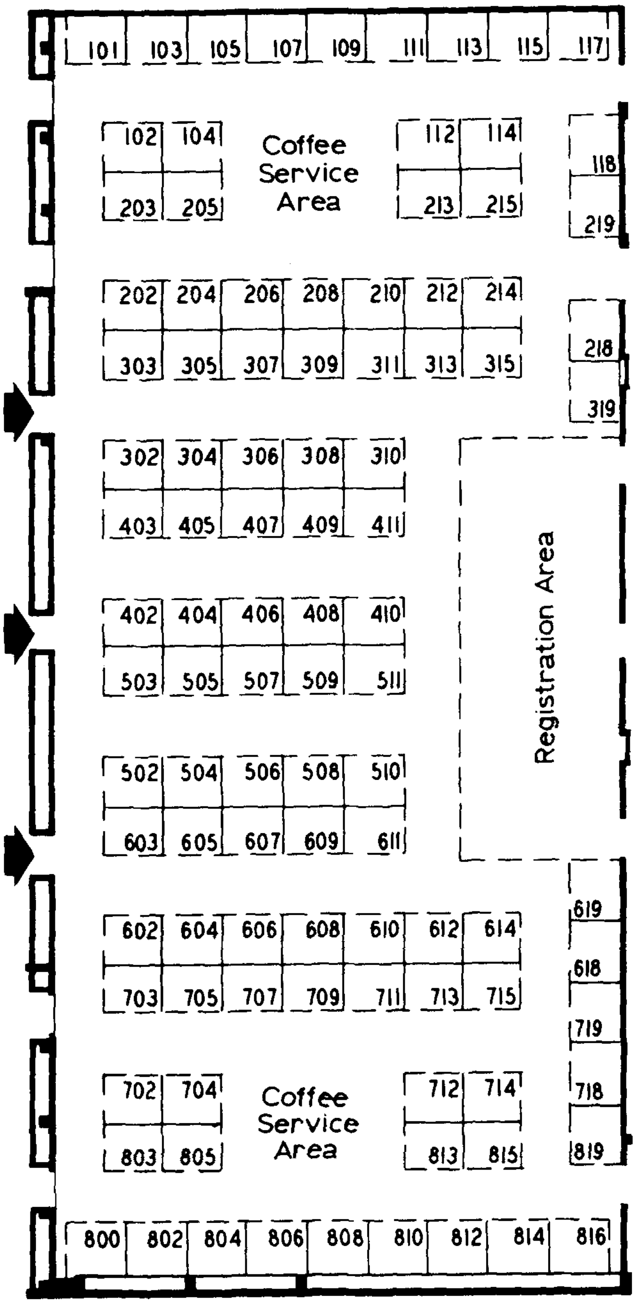
CANOLA COUNCIL OF CANADA (Booths 605 & 607). The thematic display will emphasize canola seed oil while other uses of canola oil products will be featured through samples and graphics. Technical material will be provided to registrants interested in this alternative vegetable oil recently available to the U.S. industry. Address: 301-433 Main Street, Winnipeg, Manitoba R3B 1B3, Canada.

DICKEY-john CORPORATION (Booth 707). DICKEY-john will exhibit its latest near infrared analysis instrument for the process laboratory–The Instalab 800. This new instrument features greater versatility and more usable memory than any previous model. Also shown will be the UL-listed equipment temperature monitor and the full line of process automation systems. Address: PO Box 10, Auburn, IL 62615.

THE DURIRON COMPANY INC. (Booth 402). Durco's Filtration Systems Division will exhibit its full line of filtration equipment, systems and controls including QUADRA PRESS plate and frame filter, pressure leaf filters, tubular filters, up-flow sand filters, sanitary leaves, polypropylene plates, etc. Address: 425 N. Findlay St., Dayton, OH 45402.

EASTMAN CHEMICAL PRODUCTS (Booth 307). Information on Tenox Antioxidants will be available. Address: 1133 Avenue of the Americas, New York, NY 10036.

ELLIOTT AUTOMATION CO. INC. (Booth 407). Micro-2000 Flow Computers and Process Computers will be on display along with Elliott Automation's latest High Level User Programmed Computers for process control and loss monitoring applications. Address: 10903 Brooklet Dr., Houston, TX 77099.



Grand Ballroom – 7th Floor, Chicago Marriott

EMI CORPORATION (Booths 313 & 315). Slides and literature describing EMI soybean extraction and refining systems, award-winning edible protein processing systems, plant pictures and process flow sheets for solvent extraction of oilseeds, fats and oils refining, fatty acid production processes and complete plants as offered by EMI will be featured. EMI catalogs will be available. Address: 3166 Des Plaines Avenue, Des Plaines, IL 60018.

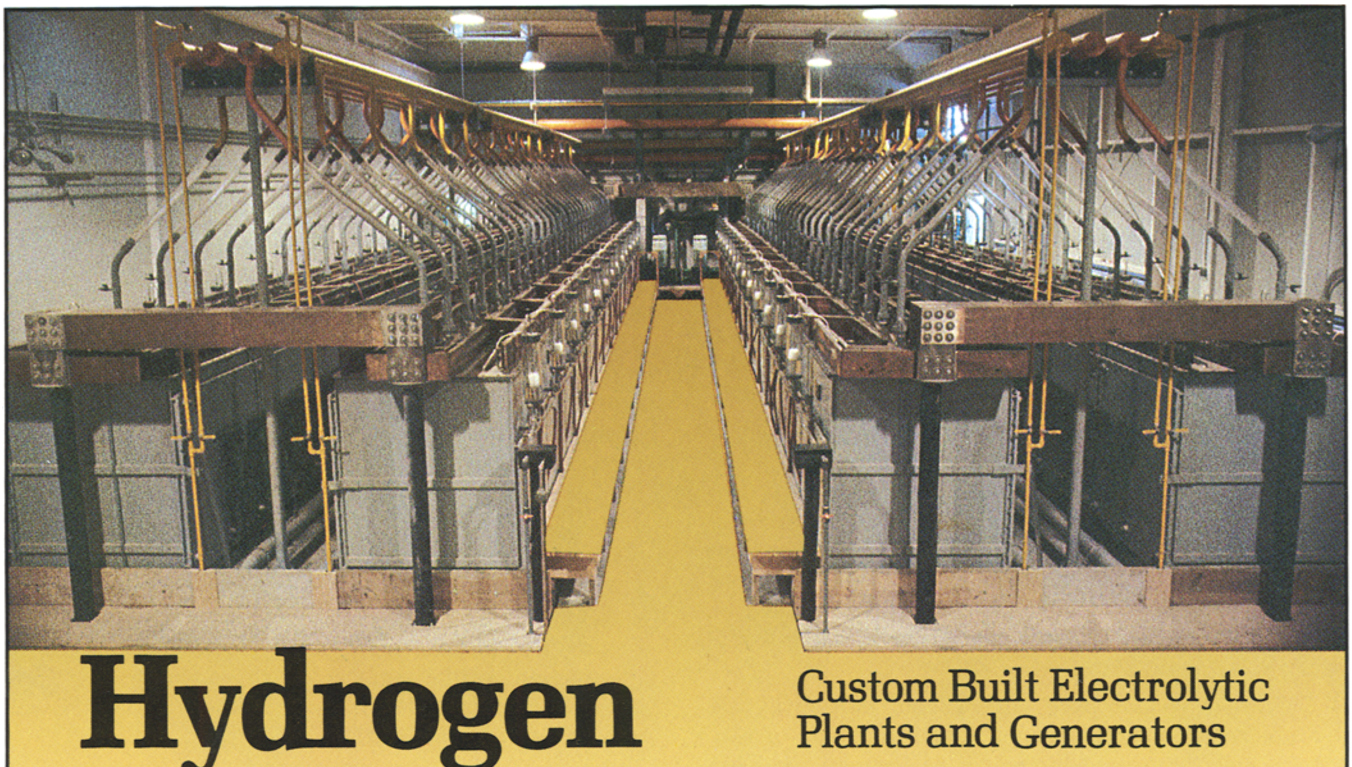
FILTROL (Booths 203 & 205). Filtrol's exhibit will feature a broad spectrum of bleaching earths (widely used in refining oils of animal, vegetable, or mineral derivation) from complementary facilities in Jackson, Mississippi (Filtrol), and Winnipeg, Canada (Pembina Mountain Clays). Technical and Sales personnel will be available to assist oil refiners with adsorption-related inquiries. Address: 300 Lakeside Dr., Room 1128KB, Oakland, CA 94643.

FOXBORO COMPANY (Booths 206, 208 & 210). Foxboro will exhibit the 99UC Series Unit Controller for process monitoring and control; the MIRAN 973 Infrared Process Analyzer for on-line composition and control; the E83 Series Vortex Meter for metering steam, water and hydrogen; the 870 Series pH Sensors and Transmitters for control of waste stream, acid oil process and decant tank oil recovery. Address: Dept. 120E, Mansfield, 38 Neponset, Foxboro, MA 02035.

THE FRENCH OIL MILL MACHINERY CO. (Booths 408, 410, 509 & 511). Model machinery will be on display showing the complete range of equipment and services offered. Representatives will be available to discuss your individual requirements in the field of oilseed processing. Address: 1035 W. Greene St., Piqua, OH 45356.

GB FERMENTATION INDUSTRIES INC. (Booth 704). GBFI will be exhibiting a line of Maxatase® enzymes for use in powder and liquid laundry detergents and whose function is to break down various proteins to form water soluble products. Other enzymes which will be exhibited have applications in the food industry in the areas of starch processing, baking, esterase-lipase, flavor enhancement and others. Address: PO Box 241068, Charlotte, NC 28224-1068.

GROEN DIV./DOVER CORP. (Booth 404). Literature and photographs describing Groen's new chilling and plasticiz-



ing system for lard, shortening and margarine. Completely different approach eliminates costly, motorized worker units and also introduces a modern, more efficient refrigeration system that requires lower capital investment, plus operating energy costs reduced by as much as 80%. Address: 1900 Pratt Blvd., Elk Grove Village, IL 60007.

H.L.S./U.S.O.P. (Booths 718, 719 & 819). Address: Asia House, 4 Wiezman Street, PO Box 33636, Tel Aviv, Israel.

IBM INSTRUMENTS INC. (Booth 805). The PC20 series instruments offered by IBM Instruments Inc. are microprocessor-controlled pulsed NMR analyzers that can be used for relaxation time studies of materials either during or at the end-point of manufacture. Typical applications are moisture, oil, protein and fat content, liquid versus solid; bound water versus free water. Address: PO Box 332–Orchard Park, Danbury, CT 06810.

IDREX INC. (Booths 212 & 214). Pressure Precoat Filters for bleaching, hydrogenation and winterization showing how these lines may be computerized with standard microprocessor technology using the Idrex filter systems will be on display. Address: 1018 Lambrecht Rd., Frankfort, IL 60423.

INDUSTRIAL FILTER & PUMP MFG. CO. (Booths 612 & 614). Illustrations will show the entire equipment line featuring the Type 122 horizontal pressure leaf filters, Type 112, 152, 114D, 116, 118 and 123 filters and systems will be included with oil skimmers, ion exchange and pollution abatement equipment. Address: 5900 Ogden Ave., Cicero, IL 60650.

KRUPP INDUSTRI-UND STAHLBAU (Booths 602 & 604). Krupp Industri- und Stahlbau, the Harburg Works, will show their developments in the field of food industry equipment by means of color slides and photomurals. Address: Franz-Schubert Strasse 1-3, 4100 Duisburg 14, West Germany.

McCLOSKEY SCIENTIFIC INDUSTRIES INC. (Booths 213 & 215). On display will be the Edible Oil Colorimeter which measures red and yellow values, chlorophyll content and addition of β-carotene in oils. An "in-line" process control version of the Edible Oil Colorimeter will also be displayed. Address: PO Box 69, Newfoundland, NJ 07435-0069.

METTLER INSTRUMENT CORP. (Booth 306). Analytical and precision balances, automatic filtration and density systems and thermal analyzers will be featured. Address: PO Box 71, Hightstown, NJ 08520.

MILTON ROY CO. (Booths 712 & 714). Milton Roy will exhibit a pilot scale supercritical fluid extraction system which operates over a range of ambient to 100 C, atmospheric to 5000 psi. A unique solute load detection system records the amount of entrained extract in the supercritical fluid. Technical information on supercritical fluids will be available. Address: 201 Ivyland Rd., Ivyland, PA 18974.

N. HUNT MOORE & ASSOCIATES (Booths 608 & 610). Address: 3951 Senator St., Memphis, TN 38118.

MULTI-METAL WIRE CLOTH INC. (Booth 503). The booth will display photos of various filters, samples of filter leaves and literature on all Multi-Metal products. Address: 501 Route 303, Tappan, NY 10983.

NATIONAL SUNFLOWER ASSOCIATION (Booth 304). Functional properties and nutritional advantages of sunflower oil will be distributed. Stop by for a sunflower snack. Address: PO Box 2533, Bismark, ND 58502.

NEUMUNZ, INC. (Booth 611). Address: 117 Fort Lee Rd., Leonia, NJ 07605.

NOVO LABORATORIES INC. (Booth 403). Novo Laboratories, Inc., the world leader in industrial enzymology, will feature its enzyme products designed for the detergent and edible oil industries. Among the products featured are Alcalase®, Neutrase® and Cellulase®. Address: 59 Danbury Road, Wilton, CT 06897.

NU-CHEK-PREP INC. (Booth 202). Fatty acids and ester homologs, triglycerides, diglycerides, monoglycerides, acid chlorides, fatty nitriles, fatty alcohols, fatty acetates, cholesteryl esters, hydrocarbons, alkyl-methane, sulfonates, soaps, fatty acid anhydrides, wax esters, GLC and TLC standard reference mixtures will be featured. Address: PO Box 172, Elysian, MN 56028.

PACIFIC SCIENTIFIC COMPANY (Booth 302). The Pacific Scientific Company Model 51A Near-Infrared Spectrophotometer as well as the Model 102 Near-Infrared Analyzer and Computer Terminal will be displayed. These instruments provide near-infrared analyses of oil. They provide laboratory accurate results in seconds and are easy to operate. Stop by the booth for literature and a demonstration of these reliable and accurate instruments. Address: 2431 Linden Lane, Silver Spring, MD 20910.

PALM OIL RESEARCH INSTITUTE OF MALAYSIA (Booth 505). Information on palm oil regarding its production, characteristics, utilization, production and export statistics will be provided through posters and audio visual presentation. Samples of palm oil, its various products and PORIM technology booklets shall be displayed. Address: 18th Floor, Angkasa Raya, Jalan Ampang, Kuala Lumpur, Malaysia.

C.A. PICARD (Booths 709 & 711). Wear parts for over 15 makes of screw presses and extruders such as Anderson, French, Rosedowns, Krupp and Masiero will be featured. Information will be available on custom-made wear parts to your design and specifications. Address: 305 Hill Brady Rd., Battle Creek, MI 49015.

POS PILOT PLANT CORPORATION (Booth 311). POS Pilot Plant Corporation provides pilot scale processing, on a fee for use basis, for food and feed process development. POS Laboratories and plant are operated by experienced scientific staff trained in cereal grain research, protein and lipid chemistry and food processing. Address: University of Saskatchewan Campus, Saskatoon, Sask. S7N 2R4, Canada.

PRATER INDUSTRIES, INC. (Booths 409 & 411). Address: 1515 S. 55th Ct., Chicago, IL 60650.

ROSKAMP MFG. INC. (Booth 305). Photographs and literature will be available on the new Mark III Flaking Mill which describes the infrared scanner system that releases roll pressure when grain flow stops, new high torque belt drive, also stainless steel housing with easy access to cheek plates above rolls and scrapers beneath, all on 28 x 52 or 28 x 62 mills. Address: 616 Grand Blvd., Cedar Falls, IA 50613.

L.A. SALOMON & BRO. INC. (Booth 310). Tonsil bleaching earths and Norit activated carbons for the processing of edible and inedible fats and oils will be featured. The use of bentonite clays to maintain waste water and to line ponds, lagoons and tank farms will also be highlighted. Technical literature will be available. Address: PO Box 828, Port Washington, NY 11050.

SIMON-ROSEDOWNS LTD. (Booths 506 & 508). A panel display system will feature the current design, manufacture procurement and financial package available to the world's oilseed processing industry. Specialists will be available to discuss new product development in screw pressing and edible oil refining as well as Rosedowns complete range of contracting services. Address: Cannon Street, Hull HU2 0AD, England.

TECHNICON INDUSTRIAL SYSTEMS (Booths 713 & 715). Demonstrations will feature the rapid analysis of edible oils for solid fat index, iodine value and neutral oil loss using InfraAlyzer 400L. The analysis involves syringe injection of sample tempered to 65 C and results for all three parameters are obtained in less than 90 seconds. The InfraAlyzer 500 Scanning Near-Infrared Reflectance Analysis for quantitative and qualitative research and development also will be shown. Address: 511 Benedict Ave., Tarrytown, NY 10591.

THE TINTOMETER COMPANY (Booth 303). Instruments for grading and measuring the color of edible oils, fats and tallows, including the Lovibond® AOCS Scale, the new Lovibond® Three-Field FAC Comparator and the new Lovibond® Automatic Tintometer. Address: 206 Packets Court, Williamsburg, VA 23185.

TRAMCO METAL PRODUCTS, INC. (Booth 309). Literature will be available on Tramco chain conveyors including Model "G", RXT, RS, RL, N, RB and SC. Various photographs, literature and flight samples will also be featured. Address: 1011 E. 19th St., Wichita, KS 67214.

UNICHEMA INTERNATIONAL (Booths 218 & 319). Unichema International supplies a range of high quality PRICAT nickel catalysts for the hydrogenation of edible oils and fats for fatty acids. Outstanding features of the PRICAT catalyst range include consistently high activity, resistance to poisoning, a high degree of selectivity and excellent filtration characteristics. Address: PO Box 2, 2800 AA Gouda, The Netherlands.

UOP PROCESS DIVISION (Booth 308). UOP Process Division will display the Sustane® line of food-grade antioxidants, including BHA, BHT, TBHQ, propyl gallate and a variety of liquid antioxidant blends. Color product brochures, specification sheets and other technical literature will be available. Sample requests will be accepted. Address: 20 UOP Plaza, Des Plaines, IL 60016.

WURSTER & SANGER, INC. (Booths 703 & 705). Catalogs, technical literature, plant photographs and process flowsheets reflecting the complete capabilities of Wurster & Sanger as process engineers for the fats and oils industry will be featured. W&S custom builds plants for oilseeds, glyceride fats and oils, fatty acids, glycerine and their byproducts. Samples of products from W&S processes will be displayed. Address: 222 West Adams St., Chicago, IL 60606.

CHICAGO MEETING COMMITTEE

Arnold Gavin
General Chairman

Timothy L. Mounts
Program

David C. Tandy
Registration

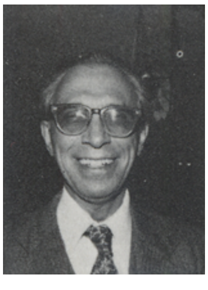
Jack Suriano
Finance

W.C. Zievers
Golf tournament

Edward H. King
Exhibits
(Photo not available)

George Kreutzer
Advisory

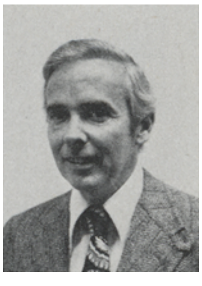
R.A. Reiners
Publicity



Robert Husch
Entertainment

Joan Gavin
Spouses' program

Bart A. Greenwell
Plant tours



William McPherson
Hotel

AOCS awards

AOCS awards during the meeting in Chicago will recognize outstanding research, scholarship, analytical proficiency, service and publications.

Many recipients of awards were known in mid-February, as this article was being prepared, and are identified in the articles that follow.

But other recipients will not be known until just before the meeting. Among these are the participants in the Smalley Check Sample Program, in which certificates are presented to the most proficient analysts in a variety of check sample series. Their names will be printed in the awards program distributed at the meeting and in the July issue of *JAOCS*.

The recipient(s) of the AOCS Award of Merit will be announced at the meeting. This award recognizes outstanding service to AOCS over a period of time.

Also to be announced at the meeting will be the recipient of the Soap and Detergent Association award for the best technical publication of 1982 to appear in the Soaps and Detergents section of *JAOCS*.

van Dorp to be cited

Dr. David A. van Dorp, known for his research on essential fatty acids and prostaglandins, will receive the 1983 Supelco AOCS Research Award in Chicago.

Dr. van Dorp, retired from the Unilever Research Laboratories in Vlaardingen, The Netherlands, discovered the biochemical link between the essential fatty acids arachidonic acid, dihomo-γ-linolenic acid and prostaglandins. His research has helped speed understanding of the physiological function and relationships between essential fatty acids and prostaglandins.

The award, sponsored by Supelco Inc., will be presented during the plenary breakfast on Monday, May 9. The award consists of a plaque and an honorarium of $3,000. Dr. van Dorp's acceptance address will be presented at 1 p.m. Monday.

His contributions to the chemical synthesis of essential fatty acids has been termed "indispensable" for the study of the relationship between their structure and physiological activity.

Before joining Unilever, van Dorp was with Organom N.V. where he performed the first synthesis of vitamin A-acid and vitamin A. He was with Organon from 1941 until 1959 when he joined the staff at Vlaardingen, where the work on EFA and prostaglandins was pursued. He received the Heinrich Wieland award and was named a professorial fellow of the University of Cardiff in 1968; in 1973 he became a member of the Koninklijke Nederlands Akademie van Wetenschappen; and in 1980 received the golden medal of the Golden Jubilee International Congress on Essential Fatty Acids and Prostaglandins in Minnesota.

8 Honored Students selected

Eight graduate students from the United States and Canada have been selected to receive 1983 AOCS Honored Student Awards and will be presenting papers in Chicago.

Each honored student receives funds to defray travel and other costs, as well as a free registration. Certificates will be presented during the plenary breakfast on Monday, May 5.

1983 awardees are:

D.S. Boehme, University of Southern California, "Levels of Phospholipid Precursors and Metabolites in Lungs of Fetuses of Diabetic Rats," Session KK – Nutritional Biochemistry, Wednesday afternoon.

D.P. Cistola, Boston University School of Medicine, "Acid Soaps: The Phase Behavior of Anhydrous and Hydrated 1:1 Potassium Hydrogen Dioleate," Session FF – Surface Chemistry, Analysis and Environmental, Wednesday morning.

D.A. Diersen-Schade, Iowa State University, "Effects of Beef, Soy and Conventional Diets on CO_2, Fatty Acid, and Glycerol Synthesis in Young Pigs," Session I – Dietary Proteins and Their Effects on Metabolism and Disease, Monday afternoon.

L.J. Magrum, University of Illinois, "Modulation of Prostaglandin Synthesis in Rat Peritoneal Macrophages Through Dietary Means," Session AA – Nutritional, Physiological, and Biochemical Studies of Omega-3 Fatty Acids and Prostaglandins, Tuesday afternoon.

F. Manganaro, Charles H. Best Institute, Toronto, "A Reiterative Method for Calculation of Triacylglycerol Species in Natural Mixtures," Session HH – Lipid Methodology, Wednesday morning.

D.M. Manning, Pennsylvania State University, "Visual Characterization of Cocoa Butter Crystals," Session HH – Lipid Methodology, Wednesday morning.

R.J. Rodriguez, Oregon State University, "Structural Requirements for Diverse Sterol Functions in Saccharomyces Cerevisae," Session KK – Nutritional Biochemistry, Wednesday afternoon.

C.A. Taylor, Colorado State University, "Effects of Dietary Linoleate on Eicosanoid Synthesis in Rat Platelets," Session AA – Nutritional, Physiological and Biochemical Studies of Omega-3 Fatty Acids and Prostaglandins, Tuesday afternoon.

Kim to get Potts award

Heassook Kim, a graduate student at Rutgers, has been chosen to receive the second annual Ralph H. Potts Memorial Fellowship, to be presented during the AOCS annual meeting in Chicago. The award consists of a scroll and a $1,000 honorarium.

Ms. Kim will present a paper on "Isolation and Identification of the Volatile Flavor Compounds in Commercial Soybean Lecithin" during the Ralph Potts Memorial Symposium on Wednesday. The symposium honors the late Mr. Potts who did his pioneering work on fatty acid processing with Armak whose headquarters is in Chicago.

Ms. Kim is a native of Korea, receiving her bachelor's and master's degrees from Seoul National University.

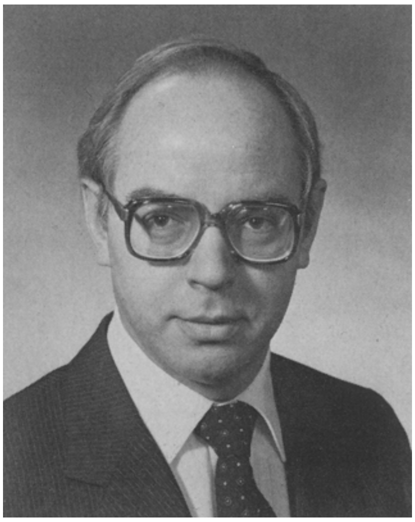
The initial recipient of the Potts award, Nikolas Sotirhos, in 1982 in Toronto, also was a graduate student from Rutgers.

FOSFA to hold palm oil session

FOSFA has announced a one day Symposium on Palm Oil to be held Wednesday, May 4, at the Leatherhead Food Research Association in Leatherhead, Surrey, England.

Topics will include agronomy, production, processing, trading and end uses. Registration fee is £50 for FOSFA or Leatherhead Food Research Association members and £75 for all others, plus value added tax. Details are available from D.S. Dixon at FOSFA's offices, 24 St. Mary Axe, London EC3A 8ER, UK (tele: 01-283 5511).

Smouse to head AOCS



Two decades ago, in 1963, the AOCS Governing Board approved a program to recognize outstanding graduate students in fats and oils by inviting them to attend AOCS national meetings, which the governing board hoped might influence the students to become active AOCS members once they had graduated.

Next month during the AOCS' 74th annual meeting, Thomas H. Smouse will become the first person to complete the chain from an Honored Student in 1964 to the AOCS President.

The pathway for Tom and his parents' white-face Hereford beef farm in Pennsylvania to the head of the oil chemists is routed through New Jersey, Texas and Missouri. The pathway is filled with beneficial coincidences, although coincidence is perhaps the wrong word, for Smouse's abilities to analyze a program, develop a research approach to a solution, and then to carry out that research, have opened many doors, some before he really expected or wanted them to open.

When high school chemistry did not prove as difficult as peer group rumors predicted, he decided to combine his agricultural background with chemistry in college. He became a student of Dr. Howard O. Triebold in the Agricultural and Biological Chemistry Department at The Pennsylvania State University, in University Park, Pennsylvania. Dr. Triebold, an associate of A.E. Bailey, emphasized fat and oil chemistry, and the biochemistry majors were expected to do better than others in that portion of the curriculum.

Upon graduation in 1958, Smouse accepted an offer from Nabisco, at their new Research Center in Fair Lawn, New Jersey. The following year, he and his high school sweetheart, Elizabeth Madore, were married. He recalls this year was filled with many trips from Fair Lawn to University Park where Elizabeth was completing her B.S. degree in Business Education. Tom worked at a variety of analytical tasks for Nabisco until one day his supervisor showed him, as one of the most recent college graduates to join the research center, a new analytical instrument and asked if he knew what it was and how it could be applied to quality control. "I told them it was a vapor fractometer, but I wasn't sure how it worked," Smouse recalls. Nabisco assigned Tom the task of determining how best to use the instrument—now known as a gas chromatograph—to monitor the quality of incoming soybean oil.

In seeking ways to use the new instrument, he read some interesting papers on soybean oil stability written by Dr. Stephen S. Chang, who had recently joined nearby Rutgers, the State University of New Jersey. A chance encounter at a dinner meeting in New York City gave Tom a chance to outline some proposed modifications in Dr. Chang's technique. Steve invited Tom to Rutgers to discuss the proposals and to visit the fat and oil laboratory.

Tom had been thinking of returning to graduate school and had been accepted by several schools, but with a wife and son to support, finances were a problem. Steve offered Tom more than another major northeastern university had offered. Thus Tom Smouse and Steve Chang teamed up to do pioneering research that is considered today among the basic works in the field of soybean oil flavor reversion.

It was while in graduate school at Rutgers that Tom joined AOCS. He also began helping prepare abstracts for *JAOCS*. In 1964, he received the Honored Student Award. Smouse received his doctorate in 1965 and that same year agreed to be the publicity chairman for the AOCS 1966 national meeting in Philadelphia, Pennsylvania.

"Tom Smouse was one of the best graduate students I have ever had," Dr. Chang, now head of the Food Science Department at Rutgers, says. "He is a conscientious, systematic, constant worker. His laboratory techniques are excellent."

When he received his doctorate in 1965, Dr. Smouse accepted a position with the Campbell Soup Company in Camden, New Jersey, which offered him a higher salary than he had requested. "I pointed out to the director of research that they were offering more than I had requested," Smouse says. "He said, 'We expect to get more from you' ". With a wife and two children—a son and a daughter—to support, Smouse accepted.

Dr. Smouse's graduate work had made him visible to the fats and oils industry and people were saying good things about him and his research work. During the AOCS 1966 meeting in Philadelphia, he was "coincidentally" invited by Anderson Clayton's Robert R. Allen to walk together to one of the society's functions. Bob used the walk to talk to Tom and Allen decided he wanted Smouse for the firm's new W.L. Clayton Research Center being built in Richardson, Texas. Six months later, he approached Tom about moving. Eventually, Smouse accepted, becoming one of the original staff members on the center's Exploratory and Applied Research team at the new research center. It was in Texas that the Smouse family was completed with the birth of a second son.

But his travels were not over. In the late 1970s, Ralston Purina recruiters, seeking a replacement for a recently retired fat and oil researcher, came calling. The St. Louis firm had been told Smouse was the best man for the job they had open. At first Tom said he wasn't interested, but eventually the challenge was too intriguing. Ralston is primarily known for its farm animal feed and pet food products, but in producing the soy protein for its feeds, it also produces and sells crude soybean oil, crude-degummed soybean oil, lecithin, toasted soybean meal, and a variety of isolated soy proteins. Smouse is manager of lipid science in the firm's Protein Technologies Division at its World Headquarters at Checkerboard Square. And, as is the case with most private research positions, that is about the most he can say about his job and what research he is presently conducting.

While in Texas, Tom had become involved in AOCS national activities. He served as Program Chairman for the 1975 meeting in Dallas. He began to get involved in technical and administrative committee work, including the Finance Committee. When he moved to St. Louis in 1977, he was immediately recruited to serve on the local committee for the 1978 annual meeting to help with the technical program and to be the hotel chairman.

In 1978, Smouse was elected a member-at-large of the Governing Board. He then served three terms as the National Treasurer before being elected Vice-President approximately a year ago.

His service on technical and administrative committees has provided a broad perspective of society activities. He's interested in seeing younger members given more opportunity in responsible positions, in continuing improved work by technical committees, and in providing better technical meetings for AOCS members.

He has seen the society grow from being predominantly a society of U.S. oil chemists' to one which covers the globe in its members, its technical programs, and its world conferences. Every major society around the world that is addressing research in fats and oils has benefited by the world conferences that have been cosponsored with our society. His work as chairman of the National Program Planning Committee has seen the development of new technical interest groups in the society such as the division of oilseed protein products, and soaps and detergents. In recent years, the biochemists and medical researchers have become more involved in our technical programs at the national meetings. In addition, the nutritional aspects of fats and oils have become more important and there is a trend toward more research being reported in these fields and less work in the areas of fat and oil processing. He believes if the Society is to continue to grow, its officers must provide leadership by addressing the desires of new research interest groups in providing a place and a forum for these new groups to become active. Great organizations become such by having its leaders set objectives which address the needs of its members, he says. This principle is one that Tom hopes actively to pursue in developing the society in 1983.

The Smouses' two older children—Thomas Madore and Deirdre Anne—are both students at Southeast Missouri State University, majoring in accounting-finance and advertising (fashion), respectively. The youngest, Robert Hadley, attends junior high school in suburban St. Louis and takes great pride in his Texan birth. With two of three children in college, Elizabeth recently accepted a teaching position at a local private high school in Webster Groves.

The coming year will be a busy one for Tom. He will be AOCS President during the 75th anniversary meeting next spring in Dallas. Dr. Smouse is one of the youngest presidents in AOCS' history. That's recognition not only of his professional competence and accomplishments, but the contributions he has made to AOCS during the past two decades since he first became active while still a graduate student.

TENTATIVE COMMITTEE SCHEDULE

Day and Committee	Time
SUNDAY, May 8	
Governing Board	8 a.m.—noon
Referee ad hoc	1—3 p.m.
Nuclear Magnetic Resonance	2—4 p.m.
Examination Board	3—6 p.m.
Hydrogenated Oils	3—4 p.m.
Membership Admissions	3—4 p.m.
Education	4—6 p.m.
Technical Safety and Engineering	4—6 p.m.
Monographs	4—5 p.m.
Aflatoxin	5—6 p.m.
MONDAY, May 9	
Public Relations	10—11 a.m.
1984 Annual Meeting	11—noon
Soap and Detergent Steering	noon—2 p.m.
1985 Annual Meeting	1—2 p.m.
1984 World Conference	2—4 p.m.
Lipids Advisory Board	3—5 p.m.
Membership Development	3—4 p.m.
Dibasic Acids	3—4 p.m.
Advertising	4—5 p.m.
Commercial Fats and Oils Analysis	4—5 p.m.
Atomic Absorption Spectroscopy	4—5 p.m.
Flavor Nomenclature	4—6 p.m.
Nutrition	5—6 p.m.

Local Sections	5–6 p.m.
Energy Conservation	5–6 p.m.
Cellulose Yield	5–6 p.m.
TUESDAY, May 10	
Publications	8–10 a.m.
Chromatography	8–9 a.m.
Bleaching Methods	8–9 a.m.
Fiber Determination	9–10 a.m.
1983 World Conference	10–11 a.m.
Seed and Meal Analysis	10 a.m.–noon
Investments subcommittee	2–3 p.m.
Finance	3–4 p.m.
Edible Fats (Smalley)	3–4 p.m.
Smalley Check Sample Program	4–6 p.m.
National Program Planning	4–6 p.m.
International Relations	4–5 p.m.

Awards Administration	5–6 p.m.
WEDNESDAY, May 11	
Meeting Logistics	8–10 a.m.
Mycotoxins	8–10 a.m.
1985 World Conference	11 a.m.–noon
Protein and Co-Products	noon–2 p.m.
Uniform Methods	2–4 p.m.
Environmental Regulation (NPPC subcommittee)	3–4 p.m.
Environmental	4–5 p.m.
AOCS Foundation	4–5 p.m.
Oilseed Proteins (NPPC subcommittee)	4–5 p.m.
THURSDAY, May 12	
Governing Board	10 a.m.–4 p.m.

Abstracts

Unless indicated by *, first name given is speaker.

SESSION A Plant Lipids I Monday a.m.

1

THE NATURE OF PLANT FATTY ACID SYNTHETASES. Paul K. Stumpf, Department of Biochemistry and Biophysics, University of California, Davis, CA 95616.

Although the structure of procaryotic and eucaryotic fatty acid synthetase (FAS) systems have been investigated intensely, the nature of the plant FAS systems was only recently elucidated in a number of laboratories. The picture that emerges is that the higher plant FAS systems are very similar to those associated with the enteric bacteria such as *E. coli*, i.e., the enzymes in higher plants are (a) nonassociated, (b) localized in specific organelles. Thus, in the leaf cell, the leaf FAS is associated with the chloroplasts; in the seed, in the proplastids. The higher plant FAS system has one set of enzymes that participate in the construction of the C_{18} hydrocarbon chain with one exception. Thus the β-ketoacyl-ACP synthetase I catalyzes the condensation of malonyl-ACP with acetyl-ACP to myristoyl-ACP, whereas β-ketoacyl-ACP synthetase II specifically catalyzes the condensation of malonyl-ACP to palmitoyl-ACP to form stearoyl-ACP. The implications of these observations will be discussed. (Supported in part by NIH Grant #29415-01.)

2

BIOSYNTHESIS OF PHOSPHATIDYLGLYCEROL IN CHLOROPLASTS. J.B. Mudd and S.A. Sparace, ARCO Plant Cell Research Institute, 6560 Trinity Court, Dublin, CA 94568.

The biosynthesis of phosphatidylglycerol by mitochondria and endoplasmic reticulum from higher plants has been known for some time. Although phosphatidylglycerol is the major phospholipid of chloroplasts, earlier attempts to measure synthesis by the isolated organelle were negative. Proposals have been made that the phosphatidylglycerol of the chloroplast must be made in other organelles and transported to the chloroplast, by phospholipid exchange proteins, for example. While using ^{14}C-glycerol-3-phosphate as a precursor for lipid synthesis in isolated chloroplasts, we noticed that a small percentage of the radioactivity was found in phosphatidylglycerol. Modifications were made to the reaction mixture to improve the reaction. The presence of Mn^{2+} as well as Mg^{2+} is a critical modification which allows as much as 25% of the incorporated label to be found in phosphatidylglycerol. The mitochondrial and endoplasmic reticulum systems for phosphatidylglycerol synthesis are greatly stimulated by detergents such as Triton X-100. In contrast, the chloroplast system is totally inhibited by very low concentrations of Triton X-100. The phosphatidylglycerol synthesized by the chloroplast has been digested by phospholipases to determine positions of labeling. When the radioactive precursor was ^{14}C-glycerol-3-phosphate, digestion of the biosynthetic product by either phospholipase C or phospholipase D indicated equal labeling of the backbone and head group glycerol moieties. When the radioactive precursor was ^{14}C-acetate, the two acyl moieties were shown to be equally labeled by phospholipase A_2 and Rhizopus lipase digestion. The radioactive fatty acid at position 2 was essentially all 16:0, whereas at position 1 there was 18:1 and 18:2. The finding of 18:2 at this position is some indication that phosphatidylglycerol may be a substrate for fatty acid desaturation.

3

COOPERATION BETWEEN THE TWO ENVELOPE MEMBRANES DURING GALACTOLIPID BIOSYNTHESIS IN PEA CHLOROPLASTS. Jaen Andrews, Kenneth Cline and Kenneth Keegstra*, Department of Botany, University of Wisconsin, Madison, WI 53706.

Galactolipids are the major lipids in all chloroplast membranes and therefore a major lipid in green tissues. The chloroplast envelope is the site of assembly of galactolipids. Our recently developed procedure for separating the two membranes which comprise the chloroplast envelope has allowed us to investigate the role of each membrane in galactolipid synthesis. For pea chloroplasts, our current evidence indicates that the early stages involving the synthesis of diacylglycerol from fatty acids and glycerol 3-phosphate occur in inner envelope membrane. However, our present evidence indicates that the galactosylation steps occur in the outer envelope membrane. The implications of these conclusions for galactolipid biosynthesis and membrane biogenesis will be discussed.

4

REGULATION OF PHOSPHOLIPID SYNTHESIS IN CASTOR BEAN ENDOSPERM. Thomas S. Moore, Jr., and George D. Troyer, Department of Botany, Louisiana State University, Baton Rouge, LA 70803.

The regulation of phospholipid metabolism and utilization in plant tissues has received little attention. The situation in postgermination castor bean (*Ricinus communis* L. var. Hale) endosperm appears to be complex. The total amounts of most of the phospholipids of this tissue remain constant or decrease over an 8-day period. Specifically, phosphatidylcholine slowly decreases over that period, with the exception of a slight increase at day 4. Meanwhile, CDPcholine: diacylglycerol cholinephosphotransferase activity is low until day 2 and then increases (10-fold) to a peak at day 4. These data suggest a balance between degradation and synthesis of phospholipids in this tissue, but efforts to detect phospholipases have met with little success. The relative maximum activities of the phospholipid-synthesizing enzymes are in proportion to the relative amounts of phospholipid produced, with the exception of CDPdiacylglycerol: inositol phosphatidyltransferase, which, under optimal in vitro conditions, demonstrates an apparent V_{max}=35 nmol/hr/mg protein. For cholinephosphotransferase the value is ca. 20 nmol/hr/mg protein, but the level of phosphatidylcholine in the tissue is much higher than that for phosphatidylinositol. Such data suggest regulation beyond simply differences in enzyme levels. We have begun attempts to purify certain phospholipid synthesizing enzymes. Cholinephosphotransferase can be partially "solubilized" through the use of Na-cholate. However, 60-80% of the activity is lost. Other detergents eliminate the activity at very low concentrations. Efforts to purify and characterize this enzyme will be described. (Supported by NSF grants PCM78-06817 and PCM-8025006.)

5

ACYL CARRIER PROTEIN DURING SEED DEVELOPMENT OF SOYBEANS. John B. Ohlrogge and Tsungmin Kuo, Northern Regional Research Center, ARS, USDA, 1815 N. University Street, Peoria, IL 61604.

Between 20 and 50 days after anthesis, the rate of lipid biosynthesis by soybean seeds increases dramatically (> 10 fold). As the seed reaches maturity, lipid synthesis declines. We are investigating whether these developmental changes are brought about by transcription-translation controls or by posttranslational mechanisms. *E. coli* acyl-ACP synthetase can be used as a sensitive assay for plant acyl carrier protein (ACP). Prior to assay, soybean extracts must be heated and salt fractionated to remove interfering activities. Measurement of ACP at various stages of seed development has indicated that ACP activity per seed increases markedly in association with the in vivo increase in lipid synthesis. Therefore de novo synthesis or activation of fatty acid biosynthetic proteins can at least partially account for the activation of the oil storage process. However, as the seed reaches maturity and lipid biosynthesis declines, acyl carrier protein activity per seed remains high. These data suggest that desiccation or lack of substrates rather than decreased fatty acid synthetase cause the decline in lipid production. In the mature seed we found that greater than 95% of the ACP is in the cotyledons, less than 5% is in the axis, and less than 1% is in the seed coat. The highest specific activity of ACP (per dry weight of tissue) in developing soybean seeds is 2-4-fold higher than in young soybean leaves or roots.

SESSION B Dietary Factors Affecting Lipid Metabolism Monday a.m.

6

SUPPRESSION OF CHOLESTEROGENESIS BY PLANT CONSTITUENTS. W.C. Burger, A. Qureshi and C. Elson*, Department of Nutritional Sciences, University of Wisconsin, 1415 Linden Drive, Madison, WI 53706.

Adding 100 g of a byproduct of the commercial barley pearling process or 40-50 g garlic paste or 2.5 g powdered ginseng root to one kg of standard mash effected a 20% lowering of the plasma cholesterol of chicks fed the experimental diet. Hepatic 3-hydroxy-3-methylglutaryl CoA (HMG CoA) reductase and cholesterol 7 α-hydroxylane (chol 7 α-hyd) activities were decreased 50%. Fatty acid synthetase (FAS) and pentose phosphate enzyme activities were elevated only in the group fed the barley byproduct. Weight gains of experimental chicks matched those of controls. These results prompted us to fractionate the three materials in order to obtain indications of the chemical natures of the active agents. The dried solubles obtained from seral extractions of each material with solvents of increasing polarity were fed at levels equivalent to those indicated above. The petroleum ether solubles of each material suppressed FAS activity; the methanol and water solubles and the residue of the barley product each doubled FAS activity. Suppressors of HMG-CoA reductase and chol 7 α-hyd were present in the solubles of each material and in the garlic residue. The petroleum ether and methanol solubles of each material most effectively lowered the plasma cholesterol concentration, a lowering restricted to the LDL-cholesterol fraction. Chromatographic separation of the petroleum ether solubles of the barley byproduct yields several fractions, one of which suppresses HMG CoA reductase and another which promotes weight gain. Spectra of the HMG CoA suppressors in the solvent solubles suggest that the plant materials contain variously conjugated forms of a suppressor. These findings are discussed with reference to reports that semipurified diets support higher plasma cholesterol levels than do their crude counterparts.

7

CHOLESTEROL METABOLISM IN RELATION TO AGING AND DIETARY FAT. Jacqueline Dupont, Food and Nutrition Department, 107 MacKay Hall, Iowa State University, Ames, IA 50011.

Studies, using rats, of effects upon mortality and cholesterol metabolism as affected by dietary fat saturation will be reviewed. Cholesterol synthesis and turnover in males and females have been reported to differ in relation to sex and age more than to dietary fat saturation. In rats and humans, serum cholesterol is known to increase with age and the relationship to dietary fat is not readily discernible. Mechanisms for the increase with age will be discussed in relation to regulation of cholesterol synthesis, turnover, conversion of bile acids, and peripheral tissue metabolism.

8

EICOSANOID METABOLISM IN RELATION TO DIETARY FATS AND OTHER NUTRIENTS. Jacqueline Dupont and Melvin M. Mathias, Food and Nutrition Department, 107 MacKay Hall, Iowa State University, Ames, IA 50011.

Evidence that fatty acid content of the diet is involved in regulation of eicosanoid metabolism will be reviewed. Effects of deficiency and excess of linoleate in the diet upon synthesis of prostaglandins and thromboxane in rats and humans will be presented. The effects of γ-linolenic acid and *trans* fatty acids will be reviewed. Functions of prostaglandins in relation to zinc status will be reviewed. Evidence for the involvement of vitamin E and alcohol in eicosanoid metabolism will be presented.

9

THE POSSIBLE ROLE OF OXIDIZED STEROLS IN THE DEVELOPMENT OF ATHEROSCLEROSIS. Fred A. Kummerow, Ross P. Holmes, T. Takagi and Dennis Leszczynski, Burnsides Research Lab, 1208 W. Pennsylvania Ave., Urbana, IL 61801.

Dietary sources of oxidized sterols have been shown to accelerate the accumulation of foam cells and degenerated cells in the intima layer of the coronary arteries of animal models. We have found that the coronary arteries of piglets from mothers which had been fed the commercial level of two million IU of cholecalciferol (vitamin D_3)/ton of ration contained a significantly higher number of foam cells and degenerated cells than piglets from mothers fed 300,000 IU of vitamin D_3/ton of ration or 97/2180 and 42/2119 counts, respectively. The level of vitamin D in the serum of piglets from mothers fed 2 million IU of vitamin D_3/ton of ration was in the same range as the average serum vitamin D level in man or 30 and 27 ng/ml, respectively. The autoxidized derivatives of cholesterol such as 25,OH and 7-keto cholesterol also increased lipid deposition in the ascending aorta as compared to chicks fed 1% cholesterol. Degeneration of smooth muscle cells was quite apparent, especially in the thickened intima and inner media. The oxidized sterols seem to increase the fluidity of membranes which may stimulate calcium uptake into the intimal cells and contribute to their degeneration. For example, 25,OH vitamin D is believed to increase the incorporation of polyunsaturated fatty acids into the brush border membranes in the intestinal tract which increases membrane fluidity and stimulated calcium uptake.

10

EFFECTS OF DEFINED FORMULA DIETS ON SERUM LIPIDS OF HEALTHY SUBJECTS. Jean T. Snook, 265 Campbell Hall, 1787 Neil Avenue, The Ohio State University, Columbus, OH 43210.

Serum total cholesterol (TC), high density lipoprotein cholesterol (HDL-C) and triglyceride (TG) levels were studied in healthy male and female subjects fed for one-week periods a control diet of normal foods (NF) with 42% of energy as fat, principally butterfat, and then in random order nutritionally complete liquid formulas. Compared to NF, liquid diets with 32% of energy as corn oil lowered TC by 24-27%, HDL-C by 10%, and TC:HDL-C by 13-19%. Isotonic liquid diets with 34% of energy as polyunsaturated and medium chain TG (MCT) lowered TC by 12-20% and HDL-C by 10-17%, did not consistently affect TC:HDL-C, and raised TG by 26-43%. Diets with peptides and amino acids and 10% of food energy as safflower and MCT oil lowered TC by 10-23%, lowered HDL-C by 24-35%, doubled TG, and raised TC:HDL-C by 6-23%. When three formulations of the low fat, high carbohydrate (74% of energy) diet were ingested for 3 weeks, these lipid effects persisted. Esterified but not free TC was reduced in subjects' sera. Free and esterified HDL-C were both reduced. Ability of subjects' sera to activate lipoprotein lipase from milk was not affected by treatment with the low fat diets. (Supported in part by a grant from Ross Laboratories.)

11

DIETARY FIBER EFFECTS ON LIPID ABSORPTION AND METABOLISM. Constance Kies, Room 316, Ruth Leverton Hall, University of Nebraska, Lincoln, NE 68583-0807.

Decreased absorption of dietary fat and decreased reabsorption of bile salts from the gastrointestinal tract have been credited to result in decreased blood serum lipids and a decreased incidence of atherosclerosis and coronary heart disease. Epidemiological evidence is the basis of much of this theory. Responses in terms of changes in fecal fat excretion, bile acid excretion and blood serum lipids of human subjects in controlled research situations to variations in level of dietary fiber have been mixed. Dietary fibers as a class of substances have only the single characteristic of being relatively resistant to digestion in the upper gastrointestinal tract. Since these materials include substances with a wide range of chemical and physical characteristics, it is not surprising that wide variations in physiological response to their inclusion in the diet should be elicited. Such extrinsic factors as particle size, degree of hydration prior to consumption, and food media containing the fiber source all contribute to the poor predictability of the physiological-biochemical response on the basis of chemical composition of the dietary fiber fed. In addition, intrinsic factors relative to the animal model used or to specific individuals (human or animal) within the specie may affect the outcome of such studies. By careful control of these extraneous variables, it should be possible to define more exactly the relationships between dietary fiber and blood serum lipid levels. (Supported by Nebr. Agric. Expt. Station Project 91-024, USDA, CSRS Regional Project W-143 and by Ross Laboratories, Columbus, Ohio.)

SESSION C Emulsions and Microemulsions I Monday a.m.

12

EMULSIFICATION OF NONMINERAL OILS: EFFECT OF TYPE AND SOURCE. K.J. Lissant, c/o Petrolite Corp., 369 Marshall Ave., St. Louis, MO 63119.

A group of vegetable and animal oils were tested for their ability to form emulsions with water in the presence of a series of emulsifiers. The variation of optimum emulsifier with oil source and treatment history of the oil is determined. Where possible, oil composition is correlated with behavior.

13

COALESCENCE OF WATER-IN-SHALE OIL EMULSIONS. V.B. Menon and D.T. Wasan, Department of Chemical Engineering, Illinois Institute of Technology, 10 W. 33rd Street, Chicago, IL 60616.

Water-in-shale oil emulsions are formed during the extraction and cleaning of shale oil. The present study deals with the effect of chemical additives, i.e., demulsifying agents on the rates of coalescence and flocculation of water-in-shale oil emulsions. A photomicrographic technique was used to study the interdroplet coalescence behavior of a 10% water-in-shale oil emulsion in the presence of a demulsifier. Both the flocculation and coalescence rate constants were determined as a function of the demulsifier concentration, temperature and agitation rate. The interfacial properties of the water/shale oil interfaces, viz. the interfacial tension and the interfacial viscosity, were also measured in the presence of chemical additives. The interfacial viscosity showed a direct correlation with the rate of coalescence while the interfacial tension did not. These results suggest that the film drainage between the coalescing drops is responsible for the coalescence of these emulsion systems.

14

NONIONIC SURFACTANT CONCENTRATION EFFECTS IN OIL-IN-WATER EMULSIONS. D. Fairhurst, M.P. Aronson and F.D. Goddard, Union Carbide Corporation, Ethylene Oxide Derivatives Div., Tarrytown Technical Center, Tarrytown, NY 10591.

A striking influence of emulsifier concentration has been observed during a study of oil-in-water emulsions stabilized with a number of nonionic surfactants. An upper and lower concentration range exists, outside of which it is not possible to produce a stable emulsion. Different types of instability occur at these specific emulsifier concentrations. At the lower concentration, which can be quite accurately defined, the major instability is creaming because of flocculation of the oil droplets. At the upper concentration, which is also well defined, one of two types of instability are observed. The first occurs with more water-soluble surfactants and is identified as a rapid flocculation and creaming without any separation of free oil. A second, quite different, instability results with surfactants having higher oil solubility. It involves extremely rapid coalescence and separation of free oil. The instabilities appear to arise for different reasons. Their critical nature, role and importance to an understanding of emulsion stability will be discussed.

15

EMULSIFICATION OF OIL IN WATER. Marcel Loncin, Institut für Lebensmittelverfahrenstechnik, Kaiserstr. 12, University D 7500 Karlsruhe, West Germany.

An emulsion of oil in water consists of at least two phases and three components: water as a continuous phase, oil as a dispersed phase and surfactant used as an emulsifier. Various other components like stabilizers can also be added. The evaluation of the emulsification process can be achieved by measurement and mathematical expressions (various moments) of the size distribution of the droplets before and after treatment. The forces involved in the emulsification process are almost exclusively shear forces and normal forces (cavitation). The former play a major role in colloid mills, the latter in high pressure homogenizers. The results are also influenced by the coalescence of the newly dispersed droplets. It has been shown that the dynamic behavior of the emulsifier, especially the rate of migration towards the newly formed interfaces, plays a major role in most emulsification processes. This migration is a function of the operational conditions and also of the chemical structure of the emulsifier(s). The share of energy input which is actually used for the disruption of oil droplets is always extremely low (less than 0.1%). Suggestions are made in order to improve the yield of the emulsification processes in general.

16

INFLUENCE OF VISCOSITY OF THE INTERNAL PHASE ON RHEOLOGY OF EMULSIONS.

I. Layrisse, INTEVEP S.A., Caracas, Venezuela.

Abstract not available at press time.

17

MICROEMULSIONS INCORPORATING AROMATIC HYDROCARBONS. INFLUENCE OF THE COSURFACTANT ALCOHOL ISOMERY.

Marc Clausse, Elizabeth Poquet, Luc Nicolas-Morgantini, Jacques Poulicard and Abdallah Zradba, IURS, Avenue Philippon, 64000 Pau, France.

So-called microemulsion systems can be formed by mixing, in the presence of suitable surface active agents, water with indifferently aliphatic or aromatic hydrocarbons. A phase diagram study of microemulsions incorporating various aromatic hydrocarbons has been carried out, the aim being to investigate the influence of the chemical structure of the alcohol (cosurfactant), combined with the anionic surfactant sodium dodecylsulfate to form the surface active mixture. A pronounced influence of the alcohol chemical structure was thus evidenced. In the case of straight-chained alkanols with carbon number n_a ranging from 2 to 10, it has been possible to define a threshold value n_c of n_a. For $n_a \leqslant n_c$, the microemulsion domain forms a unique area that spans over broad composition regions of the diagram and increases as n_a increases, (type U systems). For $n_a > n_c$, the microemulsion domain consists of two disjointed areas that are separated by a region of long-range-ordered media, (type S systems). Both of the regions shrink as n_a increases. These results are consistent with previous observations, performed on microemulsion systems incorporating aliphatic hydrocarbons. For $n_a \leqslant n_c$, it was observed that the alcohol isomery has only negligible effects upon the microemulsion domain that remains of the U type. In contrast, for $n_a > n_c$, striking alterations of the microemulsion domain were seen upon varying the alcohol isomery, especially when $n_a = n_c + 1$. The substitution of an isomeric pentanol for another, starting with 2-methyl-2-butanol and ending with 1-pentanol, induces a progressive transition from the type U case to the type S one. This progressive transition is mainly characterized by the apparition of hybrid configurations of the microemulsion domain that then consists of two subdomains connnected by a channel, (type U* systems). For $n_a > n_c + 1$, similar situations were observed in a few cases, but the alcohol isomery influence appears to be weaker. Experiments showed that transport phenomena within the monophasic domain are greatly influenced by the configuration of the monophasic domain, thence by the alcohol chemical structure. This general result can be interpreted in the light of data available as concerns microemulsion structure and internal interactions. For some type U* systems, a detailed study has been made of the phase behavior over the composition region adjacent to the monophasic channel. Diphasic systems have been evidenced that consist of an upper isotropic phase in equilibrium with a lower birefringent one.

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PHASE DIAGRAMS AND TRANSPORT COEFFICIENTS OF MICROEMULSION SYSTEMS. INFLUENCE OF THE COSURFACTANT ALCOHOL CHEMICAL STRUCTURE AND OF THE SURFACTANT/COSURFACTANT RATIO.

Marc Clausse, Abdallah Zradba and Luc Nicolas-Morgantini, IURS, Avenue Philippon, 64000 Pau, France.

The so-called microemulsions are macroscopically monophasic, fluid, normally transparent and isotropic media made up of water, hydrocarbon and adequate amphiphilic compounds. Most of the microemulsions commonly investigated incorporate as amphiphiles combinations of an ionic surfactant with a cosurfactant which is generally an alcohol. The surfactant/cosurfactant ratio k being given, the four-component system phase behavior can be investigated, at constant temperature and pressure, in a triangular pseudoternary phase diagram. By varying k, it is possible to describe the phase behavior inside the entire volume of the phase tetrahedron. This general method has been applied to the study, at T = 25 C and under atmospheric pressure, of water/sodium dodecylsulfate/primary alkanols/*n*-dodecane quaternary systems, the emphasis being put on those incorporating 1-pentanol. The boundaries of the monophasic areas, (microemulsion domains), were determined, as well as those of the composition ranges over which the occurrence of birefringent media was observed. The configuration of the pseudoternary phase diagram monophasic areas depends strikingly upon the cosurfactant chemical structure and, especially in the case of 1-pentanol, upon the surfactant/cosurfactant ratio k. The three-dimension monophasic regions delimited inside the phase tetrahedron appear to be the spatial extensions of the water/surfactant/alcohol ternary diagram monophasic regions. Over the birefringent regions, three types of systems were put into evidence, i.e., upon increasing the water content, diphasic media consisting of an upper isotropic phase in equilibrium with a lower birefringent one, (i/g); monophasic birefringent media, (g); diphasic media consisting of an upper birefringent phase in equilibrium with a lower isotropic one, (g/i). In the 1-pentanol case, it was clearly shown that the four-component i/g, g and g/i subregions are extensions of the water/sodium dodecylsulfate/1-pentanol ternary phase diagram. Correlatively, it was found that transport phenomena, such as the low frequency electrical conduction, are strikingly influenced by the system composition, which most probably reflects the diversity that characterizes microemulsion structure and/or internal interactions. In situations where the monophasic domain consists of a unique area spanning over broad composition ranges of the pseudoternary phase diagram, the microemulsion electrical conductive behavior appears to be of the percolative type, which is not the case when the monophasic domain consists of two disjointed subdomains that are separated by a birefringent zone. This correlation between microemulsion transport properties and domain configuration seems to be a general and significant one.

SESSION D Vitamins and Antioxidants Monday a.m.

19

VOLATILE CONSTITUENTS FROM GLYCEROL-TRIS-*cis*-9,*cis*-15-OCTADECADIENOIC ACID HEATED (192 C) IN AIR.

E. Selke, 1815 N. University Street, Peoria, IL 61604.

Isolinoleic acids, hydrogenation products of linolenic acid, are attributed to be precursors of "hydrogenation odor." Glycerol-tris-*cis*-9,*cis*-15-octadecadienoic acid, an isolinoleic acid isomer, was synthesized to investigate what volatiles and associated odors would be formed when subjecting the model compound to cooking oil temperature. Volatiles from the heated (192 C) synthesized oil were collected, separated, quantified and identified by gas chromatography-mass spectrometry-computer technique. Major volatiles observed indicate each of the double bonds (9-10 and 15-16) in the model dienoic acid oxidize and produce volatiles unique to each double bond position. The 15-16 isolated double bond oxidizes and forms the 14, 15, 16, and 17 monohydroperoxides, which presumably are the precursors of the following four major observed volatiles: 2-pentenal (7.7%), 2-butenal (9.4%) and ethanal (1.8%), respectively. The 9-10 isolated double bond oxidizes to form the 8, 9, 10, and 11 monohydroperoxides, which are the expected precursors of the following volatiles: 2,8-undecadienal (5.6%), 2,7-decadienal (7.5%), 6-nonenal (7.7%), 5-octenal (1.8%), 3-octene (4.7%) and 3-heptene (4.9%), respectively. These latter six compounds are analogous to the major volatiles, two hydrocarbons and four aldehydes, observed from oxidized triolein. A C-17 diene hydrocarbon (0.8%) was also noted as a major volatile. Its presence is consistent with identification of similar long-chain hydrocarbons from heated tristearin and triolein.

20

CAPILLARY GC ANALYSIS OF HEADSPACE VOLATILES FROM VEGETABLE OILS.

J.M. Snyder and E.N. Frankel, Northern Regional Research Center, Agricultural Research Service, US Department of Agriculture, Peoria, IL 61604.

Eight different vegetable oils obtained commercially were analyzed for volatiles by capillary gas chromatography. Volatiles generated in a Perkin Elmer headspace sampler were automatically injected onto a 30 m Durabond-5 capillary column. Only a small number of volatiles of low intensity were present in the fresh samples which varied in peroxide values from 1 to 3. Several major peaks were evident in the oils aged 8 days at 60 C with peroxide values ranging from 5 to 30. Identification of the GC peaks was tentatively based on the relative retention time of reference compounds and by GC-MS. Major volatiles common in each of the vegetable oils included butane, pentane, hexanal, heptenal and 2,4-decadienal.

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FLAVOR STABILITY OF SOYBEAN OILS BASED ON INDUCTION OF GAS CHRÓMATOGRAPHIC VOLATILE COMPOUNDS. K. Warner, L. Kuster and E.N. Frankel, Northern Regional Research Center, ARS, USDA, 1815 N. University, Peoria, IL 61604.

The lack of reliable analytical methods to predict the flavor stability of vegetable oils increases the need for correlation studies between sensory and chemical tests. Previous work showed good correlations between volatile compounds detected by gas chromatography (GC) and flavor scores. A direct GC analysis was applied to measure the flavor stability of soybean oils after aging at 60 C. Prominent peaks identified by GC-MS included: pentane, hexanal, 2-heptenal, 2,4-heptadienal, 2-decenal and 2,4-decadienal. Induction periods calculated for the formation of volatiles showed the oils with the tertiary butylhydroquinone (TBHQ) + citric acid combination, with the citric acid only and with no additives to have inductions of 9, 5, and 0 days, respectively, for total volatiles. Pentane, 2,4-decadienal and total volatiles were most related to deteriorative changes and produced characteristic induction curves. Correlation coefficients of volatiles with flavor scores were also high. This study showed that flavor stability can be predicted by determining induction periods based on GC volatiles analysis and such determinations can complement sensory evaluations.

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EFFECTS OF PHOSPHATIDYLCHOLINE ON THE FLAVOR STABILITY OF OIL DURING STORAGE. D.B. Min and T. Stasinopoulos, 122 Vivian Hall, 2121 Fyffe Road, Columbus, OH 43210.

Soybean oils were treated with 5 levels of L-distearoyl phosphatidylcholine (0, 100, 200, 300, and 400 ppm) and 3 levels of ferric ion (0, 0.5 and 1 ppm) to study the effects of these treatments on the flavor stability during storage. The flavor stability of oil was evaluated for peroxide value, oxygen absorption and volatile flavor compounds in the headspace using a gas chromatographic method. The results were statistically analyzed by analysis of variance. Linear regression equations were developed to predict the flavor compounds formed and absorbed oxygen in oils containing different levels of phosphatidylcholine and ferric ions. The effects of 5 different levels of phosphatidylcholine were dependent upon the concentration of ferric ion. When the ferric ion added was 0, there were no significant effects of different levels of phosphatidylcholine on the flavor stability of oil. However, as the concentration of added iron increased, the effects of different levels of phosphatidylcholine increased. That is, when the added iron level was 1 ppm, the higher the phosphatidylcholine concentration added, the better the flavor stability of oil was. The results indicated that phosphatidylcholine works as a metal chelator.

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PROTECTION OF TOCOPHEROLS IN DEODORIZER DISTILLATE WITH TBHQ ANTIOXIDANT. D.F. Buck, Building 230, Eastman Chemical Products, Inc., PO Box 431, Kingsport, TN 37662.

Deodorizer distillate is a valuable byproduct for refiners of vegetable oils. This distillate may contain substantial amounts of tocopherols which can be recovered for the production of natural vitamin E (d-alpha-tocopherol). The value of deodorizer distillate to producers of vitamin E is dependent upon the concentration of tocopherols in the distillate. Tocopherols are known to be susceptible to oxidative deterioration during production, storage, and transport. These oxidative changes can significantly lower the value of deodorizer distillate. The antioxidant properties of TBHQ antioxidant are well documented and it is generally recognized as the most effective antioxidant for vegetable oils. Previous laboratory tests have shown that the addition of TBHQ to crude vegetable oils increased the concentration of tocopherols in the deodorizer distillate obtained from treated oils. The objective of this experiment was to determine if TBHQ would protect tocopherols when the antioxidant was added directly to the deodorizer distillate. Results of this experiment will be reported. An economic analysis of TBHQ treatment will also be presented.

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ANTIOXIDANT ACTIVITIES OF ALPHA-TOCOPHEROL AND TERTIARYBUTYL HYDROQUINONE (TBHQ) IN SOYBEAN OIL. D.B. Min and T. Stasinopoulos, 122 Vivian Hall, 2121 Fyffe Road, Columbus, OH 43210.

Soybean oils of factorial experiments having 4 levels of alpha-tocopherol (0, 0.1, 0.2 and 0.4%) and 4 levels of TBHQ (0, 50, 100, and 150 ppm) were evaluated to study the antioxidant activities of tocopherols and TBHQ and their interactions. The antioxidant activities were evaluated by measuring the oxygen disappearance and volatile flavor compounds in the headspace of oil stored in gas-tight bottles using a gas chromatographic method. Results indicated that the higher the alpha-tocopherol content in the oil was, the faster were the rates of oxygen disappearance and the slower the rates of the formation of volatile compounds in the oil. This indicates that alpha-tocopherol works as an antioxidant by reacting with oxygen to form alpha-tocoquinone. In the case of TBHQ, the higher the TBHQ content in the oil was, the slower were the rates of oxygen disappearance and flavor compounds formation. This suggests that TBHQ works as an antioxidant by donating protons to free radicals of fats to interrupt the chain radical propagation.

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Withdrawn.

SESSION E Oilseed Processing I Monday a.m.

26

OILSEEDS HANDLING AND PREPARATION PRIOR TO SOLVENT EXTRACTION. N. Hunt Moore, N. Hunt Moore & Associates, Inc., 3951 Senator St., Memphis, TN 38118.

Topics to be discussed include the cleaning of soybeans prior to process drying; the present method of drying soybeans to facilitate easy hull removal for the production of high protein meal; the latest method of air recirculation for energy efficiency in process drying; the conventional methods of dehulling with emphasis on the energy savings; the latest innovation in the drying, dehulling and conditioning of soybeans by use of the fluid bed drier; the use of microwave vacuum process in the drying and conditioning of soybeans; the cracking of soybeans with high capacity mills with special corrugations to give ideal particle size distribution for efficient dehulling; the flaking of soybeans with high capacity mills; and the toasting of hulls with conventional toasters and with the new toaster/cooler equipment.

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PROCESSING OF OILSEEDS USING FLUIDIZED BED TECHNOLOGY. Helmut R. Bartesch, Escher Wyss GmbH, D7980 Ravensburg, West Germany.

There are numerous steps in oilseed processing where the product is heated, conditioned, dried and cooled. Different installations are used in these steps, e.g., stack dryers, stack coolers, rotary dryers and coolers, shaft dryers and coolers, rotary and stack conditioners. One disadvantage of this system is, because of a wide variation in retention time, production of a nonhomogenous product. Further, these steps do not make optimal use of energy. In this paper, using the example of soybean processing, it is shown that the following process steps have been improved by using fluid bed installations: meal drying/cooling, conditioning of cracked beans, dehulling and conditioning. The fluid bed treatment ensures an even retention time for each particle and hence a homogenous product. Fluid bed treatment makes full use of available energy by the precise and rapid control of the process and through recirculation of hot fluidization gases. Particular advantage is presented through the newly developed dehulling and conditioning process. In contrast to the current process for dehulling and, later on, conditioning, the fluid bed process is continuous with the beans heated once, cracked hot, then the hulls are separated and beans conditioned. Compared to present processing, this means the elimination of one heating/cooling stage and of the tempering tanks, providing savings in equipment and energy costs.

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HEAD-END AND TAIL-END DEHULLING. Willi Fetzer, Buhler Brothers Ltd. Engineering Works, Department DM-41, Ch-9240 Uzwil, Switzerland.

Head-end and tail-end dehulling systems are discussed including yield, investment costs, and energy consumption. A comparison of the European and US methods of using head-end and tail-end dehulling is provided. A combination of front-end and tail-end dehulling systems is shown, including the results in yield. Power consumption and investment costs are presented in comparison to front-end dehulling.

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EXTRACTION OF OIL FROM PALM FRUIT. Kurt G. Berger, Palm Oil Research Institute of Malaysia, 18th Floor, Angkasa Raya Bldg., Jalan Ampang, Kuala Lumpur, Malaysia.

Palm oil is obtained from the fruit flesh of *Elaeas Guineensis*. Whole bunches of ripe fruit are harvested and brought to the oil mill. Processing involves sterilization, mechanical removal of fruit from the bunch and mechanical breakdown of the fruit structure followed by expression of the oil in a screw press. Oil mixed with water and fruit debris is purified in settling tanks and centrifuges, dried and stored. Oil yield represents 22% of the fresh fruit bunch and kernels a further 5%. The solid wastes are the empty fruit bunch, the press fiber and the nut shells. Empty bunches are incinerated, whereas fiber and shell are used to fire the mill boilers. The liquid effluents are mixed and usually treated by anaerobic/aerobic fermentation until fit for discharge. Various treatment systems will be described. Quality control in the oil mill concentrates (a) on minimizing deterioration of the oil by hydrolysis and by oxidation, and (b) on optimizing oil yield by frequent measurements of oil losses.

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MECHANICAL OIL EXTRACTION. Dean K. Bredeson, French Oil Mill Machinery Co., 1035 W. Greene St., Piqua, OH 56356.

Competitive pieces of equipment for full-pressing and prepressing oilseeds are described. "Enhanser" machines to treat seeds before solvent extraction consideraly increase the capacity of the solvent extraction system.

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SOLVENT EXTRACTION. Paul L. Christensen, Archer Daniels Midland Co., Corn Sweetners Division, 4666 Faries Parkway, Decatur, IL 62525.

The subject as presented at the 1976 AOCS World Conference is reviewed. The basic theory of solvent extraction is historically developed, and applied to current processes and equipment. New concepts and innovations, including computer (MP) control, are presented and related to energy and other operating efficiencies.

SESSION F Autoxidation I Monday a.m.

32

STEREOCHEMISTRY OF BICYCLOENDOPEROXIDES DERIVED FROM METHYL γ-LINOLENATE. David E. O'Connor, Edward D. Mihelich and Milton C. Coleman, The Procter & Gamble Company, Miami Valley Laboratories, PO Box 39175, Cincinnati, OH 45247.

We have investigated the autoxidation of methyl 9-hydroperoxy-*cis*-6-*trans*-10-*cis*-12-octadecatrienoate, which leads to stereoisomers of dinor-PGG$_1$, presumably by the sequence shown in the scheme. Five of the eight possible diastereoisomers have been isolated and their structures, as well as those of their corresponding triols, have been established. The two C-13 epimers of the endo,endo substituted bicycloendoperoxide accounted for well over half the total bicyclic peroxide fraction, and the two C-13 epimers of the exo,exo substituted ring system were also formed in significant amounts. A single C-13 epimer having the natural PGG ring stereochemistry was also isolated as a minor component. These results show there is significant stereoselectivity in this radical cyclization reaction, just as we had observed in our earlier work with an α-linolenate-derived hydroperoxide. The reaction favors the formation of bicycloendoperoxides having *cis* substituents rather than the natural prostaglandin stereochemistry.

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ANALYSIS OF AUTOXIDIZED FATS BY GAS CHROMATOGRAPHY-MASS SPECTROMETRY: VIII. VOLATILE THERMAL DECOMPOSITION PRODUCTS OF SECONDARY OXIDATION PRODUCTS. E.N. Frankel, W.E. Neff and E. Selke, Northern Regional Research Center, Agricultural Research Service, US Department of Agriculture, Peoria, IL 61604.

Secondary oxidation products are important sources of volatiles because of their susceptibility to further decomposition. Volatiles from the thermal decomposition of hydroperoxy cyclic peroxides were identified by capillary gas chromatography followed by mass spectrometry. By using a synthetic model saturated hydroperoxy cyclic peroxide, the thermal cleavage reactions were elucidated. Main cleavage occurred between the peroxide ring and the carbon-bearing hydroperoxide group. Hydroperoxy cyclic peroxides and dihydroperoxides from autoxidized and photosensitized oxidized methyl linolenate produced volatiles that were generally similar to those from corresponding monohydroperoxides. New volatiles identified included methyl 8-(2-furyl)-octanoate, methyl ketones and conjugated diunsaturated aldehyde esters. The general fragmentation observed between the peroxide ring and the hydroperoxide-bearing carbon is sufficiently predictable that it can be used as a useful tool for the structural characterization of hydroperoxy cyclic peroxides. This work provides direct evidence that secondary oxidation products are important precursors of volatile oxidation products that may affect the flavor of foods containing polyunsaturated lipids.

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SECONDARY AUTOXIDATION PRODUCTS IN MODEL SYSTEMS AND IN BIOMEMBRANES. Guey-Shuang Wu, Robert A. Stein, James F. Mead and Ronald N. McElhaney, Lab. of Biomedical and Environmental Sciences, 900 Veteran Ave., Los Angeles, CA 90024.

In the autoxidation of linoleic acid, the secondary reactions of hydroperoxide to form products with mono-, bi- and multifunctional groups can generally be regarded as originating from the following three processes: (a) degradation of hydroperoxide to form radicals that results in epoxidation and hydrogen abstraction, (b) the rearrangement of hydroperoxide, and (c) the addition of the peroxy radicals to the conjugated diene system of the hydroperoxide. Our recent findings on the autoxidation of various systems, including monolayers, bilayers and mycoplasma membranes indicate that the importance of each of the above three processes differs considerably in each system. In the liquid phase autoxidation of linoleic acid, the secondary reactions appear to be less selective and all of the possible products deriving from above three processes are generally found. In linoleic acid monolayers, however, the epoxidation and rearrangement processes were found to be more favorable and the major products isolated were epoxide and hydroxyepoxy compounds. In both soybean phosphatidylcholine (PC) liposomes and mycoplasma membranes, the addition reaction to give trihydroxyoctadecenoates prevailed throughout the entire incubation period. The incorporation of saturated fatty acid in the model membranes makes the rearrangement reaction more favorable, thus increasing markedly the production of hydroxyepoxy compounds in both monolayers and soybean PC liposomes. The presence of oleic acid intermixed with linoleic acid, as in the case of egg PC liposomes, gives rise to oleic acid hydroperoxide presumably from the abstraction reaction. The hydroperoxide degradation product, ketooctodecadienoate was also found in egg PC liposomes. The selection of a particular course of the reaction in these systems seems to depend largely on the following two factors: (a) the arrangement of the lipid molecules in the system, and (b) the type of the fatty acid present in proximity to linoleic acid.

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THE EFFECTS OF ANTIOXIDANTS ON THE NATURE OF PRODUCTS FORMED IN AUTOXIDATION REACTIONS OF POLYUNSATURATED FATTY ACIDS.

D.T. Coxon, K.E. Peers and H.W.-S. Chan, Chemistry and Biochemistry Division, ARC Research Institute, Colney Lane, Norwich, Norfolk NR4 7UA, England.

Studies of autoxidation of polyunsaturated fatty acids in the presence of antioxidants have shown that there can be significant differences in the proportions and types of products produced in "inhibited" autoxidations as compared with control autoxidations in the absence of an antioxidant. The autoxidation of methyl linolenate has been used as a model system with which to study the effects of both natural and synthetic antioxidants on product formation. The antioxidants studied included α-, γ-, and δ-tocopherol, α-tocotrienol, 2,2,5,7,8-pentamethylhydroxychroman (PHMC), 2,6-di-*tert*-butyl-4-methylphenol (BHT), 3-*tert*-butyl-4-hydroxyanisole (BHA), 3,5-di-*tert*-butyl-4-hydroxyanisole (DBHA), mono-*tert*-butylhydroquinone (TBHQ) and propyl gallate. Of all these, α-tocopherol produced the most dramatic effects on product formation and at high concentrations could be used to control oxidation reactions to produce high yields of monohydroperoxides without secondary reactions occurring. This effect has been used synthetically to prepare pure hydroperoxides from methyl linolenate, methyl arachidonate and some synthetic triglycerides. When tested at high concentrations, all the antioxidants used dramatically affected the distribution of products formed, but even at low concentrations subtle changes in products were noticeable. A mechanistic explanation of these effects will be presented and the possible significance of this selective oxidation which can be brought about by antioxidants will be discussed in relation to off-flavor development in products containing polyunsaturated lipids.

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PHOTOSENSITIZED OXIDATION OF METHYL LINOLEATE MONOHYDROPEROXIDES.

W.E. Neff, E.N. Frankel, E. Selke and D. Weisleder, Northern Regional Research Center, Agricultural Research Service, US Department of Agriculture, Peoria, IL 61604.

Previous studies of lipid secondary oxidation products were extended to six-membered hydroperoxy cyclic peroxides from the singlet oxygenation of monohydroperoxides from autoxidized methyl linoleate. The oxidation mixture was fractionated by silicic acid chromatography with diethyl ether: hexane mixtures and selected fractions were separated by polar phase HPLC. Products characterized by TLC, GLC, UV, IR, NMR, and MS included: (I) 9-hydroperoxy-10,13-epidioxy-11- and (II) 13-hydroperoxy-9,12-epidioxy-10-octadecenoates, 8,13- and 9,14-dihydroperoxy-octadecadienoates and keto compounds. The six-membered hydroperoxy cyclic peroxides are apparently due to Diels-Alder addition of singlet oxygen to 9- and 13-hydroperoxides after isomerization of the conjugated diene systems to the *trans,trans* configuration. Dihydroperoxides may be derived from the 9- and 13-hydroperoxides by free radical oxidation. The thermal decomposition of the six-membered hydroperoxy cyclic peroxides at 200 C produced methyl 9-oxononanoate from I and hexanal from II as the major volatiles. Other volatiles included 2-pentyl furan, pentane and 4-oxo-2-nonenal from I and methyl furan-octanoate and methyl 9,12-dioxo-10-dodecenoate from II.

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THERMAL OXIDATION OF LIPIDS IN MONOLAYERS. Lung-Bin Hau and W.W. Nawar, Department of Food Science and Nutrition, University of Massachusetts, Amherst, MA 01003.

There have been several studies in which fatty acids adsorbed on silica gel surface were used as models for investigating the autoxidation of membrane lipids. The monomolecular nature of the binding on silica was established by Porter and coworkers and Mead and coworkers. Mead's group further concluded that the number of molecules adsorbed corresponds to isolated non-hydrogen bonded silanol groups and is insensitive to chain length and degree of unsaturation of the adsorbed substrates. In contrast, our present work in which different substrates were studied indicated that the number of moles adsorbed per unit area of silica decreased as the chain length increased. The binding was also sensitive to different functional groups. For the same chain length the amount adsorbed was in the following order: alcohol > acid > ester > triglyceride whereas the binding strength (binding constant) was as follows: triglyceride > acid > ester > alcohol. For the autoxidation studies, Mead and coworkers reported that oxidation of linoleic acid in monolayer forms predominantly epoxy compounds and that the reaction is first order. In the present study, thermal oxidation of certain lipid systems adsorbed on silica is examined with emphasis on decomposition products. Samples of linoleate and linolenate, both adsorbed and in bulk, were heated at 80 C and 180 C for different periods of time and their decomposition products analyzed by GC-MS. The major differences identified so far between the bulk and monolayer were quantitative. When the substrates were adsorbed on silica, the amount produced of ethyl 9-oxo-nonanoate was much larger and that of ethyl octanoate much smaller, than in the case of bulk oxidation. Pentenal produced from 18:3 was also formed in larger amounts in the case of monolayer oxidation. A discussion of possible mechanisms responsible for the behaviors will be presented.

SESSION G Chemical Synthesis Monday a.m.

38

CONVENIENT SYNTHESIS OF UNSATURATED 1-^{13}C FATTY ACIDS. Alfred M. Ajami and SunShine Yuan, Tracer Technologies, Inc., 276 Third Street, Cambridge, MA 02142.

The increased utilization of tracer labeled unsaturated fatty acids in clinical nutrition studies prompted our search for improved methods to synthesize multigram quantities of these materials. We have adapted the well known microscale scheme for the preparation of ^{14}C labeled alkyl carboxylic acids involving $^{14}CO_2$ carbonation of an α-lithiated carboxylate ester and selective decarboxylation of the unlabeled carboxyl in the resulting malonate. Thus, reaction of *t*-butyl oleate with lithium diisopropylamide and exposure to excess $^{13}CO_2$ (90 mol% ^{13}C) afforded the *t*-butyl hemiester malonate salt. Careful protonation and treatment with diazomethane gave *t*-butyl 2-^{13}C-carbomethoxyoleate in 70% yield based on $^{13}CO_2$ on a 20-g scale, after purification by preparative HPLC. Removal of the *t*-butyl group in refluxing toluene with *p*-toluenesulfonic acid catalyst, isolation of the hemiester and pyrolytic decarboxylation at 265 C under argon furnished methyl oleate in 80% yield, again after preparative HPLC. We found this material to be indistinguishable from authentic methyl oleate by thin layer and gas chromatography. Its NMR spectrum was consistent with theory, and infrared analysis showed less than 5% 9,10-*trans* isomer. The chemical purity was at least 98%, but evaluation of the isotopic enrichment indicated a 10% loss of ^{13}C during pyrolysis, presumably because of partial transesterification between the ^{13}C-carbomethoxy group and the labile free carboxyl. The 1-^{13}C ester was converted into oleic acid, which then served as precursor to $^{13}C_3$-triolein and to mixed triglycerides containing varying proportions of 1-^{13}C-palmitic acid. In summary, our scheme represents a more viable approach to stereochemically pure 1-^{13}C-fatty acids, in contradistinction to the assembly of disubstituted acetylenic-1-^{13}C acids and stereocontrolled hydrogenation to the *cis* isomer. Our route is even more applicable to the rapid preparation of 1-^{13}C-linoleic and other labeled polyunsaturated acids, whose bench-scale synthesis by more conventional means is especially laborious.

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SYNTHESIS OF DEUTERIUM LABELED METHYL 6,9,12-OCTADECATRIENOATES. Henry Rakoff and Edward A. Emken, Northern Regional Research Center, Agricultural Research Service, US Department of Agriculture, Peoria, IL 61604.

Methyl *cis*-6,*cis*-9,*cis*-12-octadecatrienoate-15,15,16,16-d_4 (1) and the corresponding *cis,cis,trans* isomer were obtained from the Wittig coupling between hexyl-3,3,4,4-d_4-triphenylphosphonium bromide (2) and methyl 12-oxo-*cis*-6,*cis*-9-dodecadienoate (3). Compound 2 was prepared from 3-hexynol by catalytic deuteration of the corresponding tetrahydropyranyl ether and intermediate formation of the bromide. Compound 3 was obtained, through the intermediate dioxanyl and dimethoxy derivatives, from the Wittig coupling of methyl 9-oxo-*cis*-6-nonenoate (4) with [2-(1,3-dioxan-2-yl)ethyl] triphenylphosphonium bromide (5). Compound 4 was obtained in a similar fashion, from the Wittig coupling of methyl 6-oxohexanoate (6) with compound 5. Compound 6 was obtained, through several steps, from the ozonolysis of cyclohexane. Geometric isomers formed during each of the Wittig reactions were separated by silver resin chromatography.

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SYNTHESIS OF DEUTERIUM LABELED STEREOSPECIFIC PEANUT OIL TYPE TRIGLYCERIDES. August V. Bailey and John L. White, Southern Regional Research Center, ARS, USDA, PO Box 19687, New Orleans, LA 70179.

Deuterium labeled stereospecific triglycerides of the type found in peanut oil were synthesized using deuterium labeled fatty acids. The fatty acids were oleic and linoleic, the predominant unsaturated fatty acids in peanut oil, and behenic, a 22-carbon atom saturated acid which is reported to be found almost entirely in the 3-position of the *sn*-triglyceride. The deuterium labeled fatty acids were prepared as follows: *cis*-9-Octadecenoic acid-8,8,11,11-d_4 was synthesized in a five-step procedure starting with oleic acid. Similarly, *cis*-13-docosenoic acid-12,12,15,15-d_4 was prepared starting with erucic acid and subsequently deuterated with D_2 using a rhodium catalyst to obtain docosanoic acid-12,12,13,14,15,15-d_6. Docosanoic acid-13,14-d_2 was prepared directly from erucic acid by similar deuteration and the rhodium catalyst. Optically active 1,2-isopropylidene-*sn*-glycerol can be prepared in good yield starting from D-mannitol. Selected fatty acid triglycerides were then synthesized from the 1,2-isopropylidene-*sn*-glycerol with the use of appropriate blocking groups to direct the fatty acid moiety to the desired 1,2, or 3-*sn*-glycerol position to give the desired stereospecific triglyceride.

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IMPROVED METHODS FOR THE SYNTHESIS AND PURIFICATION OF ACYLGLYCEROLS. Robert G. Jensen, Dept. of Nutritional Sciences, U-17 University of Connecticut, Storrs, CT 06268.

We have synthesized several triacylglycerols with a published method for acylation which employs a mono- or diacylglycerol, the desired free acid, 4-(dimethylamino)pyridine and dicyclohexylcarbodiimide. Yields are good, reaction times are short and pyridine and acid chlorides are not required. Flash chromatography, in which low pressures (2-5 psi), columns of silicic acid and rapid flow rates of solvent (2 in./min) are utilized, was applied to the purification of reaction mixtures from the preparation of acylglycerols. We have purified several triacylglycerols in ca. 20 min with this method. Our detailed results, the advantages of these methods and other newer relevant procedures will be discussed.

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SYNTHESIS AND POLYMORPHISM OF 3-ACYL-*sn*-GLYCEROLS. Dharma R. Kodali and Trevor G. Redgrave, Biophysics Institute, Boston University School of Medicine, 80 East Concord St., Boston, MA 02118.

Previous studies have been confined to 2-monoglycerides or racemic 1-monoglycerides. In this investigation, optically active 3-acyl-*sn*-glycerols with 10-24 even numbers of acyl carbon atoms were synthesized from 1,2-isopropylidene-*sn*-glycerol. Because of their low solubility, the protecting ketal group was removed from the longer chain acyl derivatives ($>C_{18}$) of isopropylidene by applying them to silica gel and then exposing to HCl gas at -75 C. Purity of these compounds was checked by TLC and ^{13}C NMR. The polymorphism of each compound was studied with differential scanning calorimetry (DSC). The DSC data of the first heating showed that these compounds generally had a single melting transition. Subsequent reheatings showed multiple transitions for some members of the series. Two main transitions have been found for these compounds during cooling. This is interpreted to mean that the compounds during cooling from the melt formed firstly an unstable packing mode and then transformed to a more stable form. Both transitions were exothermic. The first transition from the melt was reversible. The linear increase in the temperature of fusion indicated that these compounds were probably isostructural in a more stable crystal form. Similarly, the temperature of first crystallization was linear through the series, indicating the possibility that the unstable forms were also isostructural.

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ADDITION OF AROMATIC COMPOUNDS TO OLEIC ACID CATALYZED BY HETEROGENEOUS ACID CATALYSTS. Hitoshi Kohasi and Thomas A. Foglia, Eastern Regional Research Center, US Department of Agriculture, ARS, 600 E. Mermaid Lane, Philadelphia, PA 19118.

The addition of aromatic compounds to the double bond of oleic acid has been studied with heterogeneous solid acid catalysts. For example, in the presence of an acid clay catalyst (bentonite), phenol reacted with oleic acid to give an alkylbenzene addition product in 96% yield. When toluene was used as the aromatic reactant in the above reaction, however, the yield of addition product was < 2%. In this instance, the major reactions observed were elaidinization and migration of the double bond of oleic acid. The addition of phenol to oleic acid in > 95% yield also was accomplished with the use of a sulfonic acid ion-exchange resin catalyst. This same catalyst also catalyzed the addition of toluene and benzene to oleic acid to give alkylbenzene type addition products in 82% and 22% yield, respectively. In the latter instances the major side-products formed were the γ and δ-stearolactones. Capillary gas chromatographic analyses of the alkylbenzene addition products obtained showed them to be mixtures of positional isomers. The isomer distributions were subsequently determined by the combined use of gas chromatography-mass spectrometry.

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CHOLESTEROL SIDE-CHAIN MANIPULATIONS: SYNTHESIS OF 20-ISO-CHOLESTEROL AND (25R)- AND (255)-26-HYDROXYCHOLESTEROL. Henry W. Kircher and Fumiko U. Rosenstein, Nutrition and Food Science Department, University of Arizona, Tucson, AZ 85721.

(20S)-3β-Acetoxybisnorchol-5-en-21-al was partially isomerized to the (20R)-isomer with KOtBu and the mixture treated with vinyl MgBR to give a mixture of (20 R,S; 22R,S)-3β-acetoxychol-5-en-22-ols. Reaction with ethyl orthoproprionate and propionic acid gave a mixture of ethyl (20 R,S; 25R,S)-3β-acetoxycholesta-5,22E-dien-26-oates that could be readily separated by crystallization and $AgNO_3$ column chromatography into oily ethyl (20R; 25R,s)-3β-acetoxycholesta-5,22E-dien-26-oates and their (20S; 25R, S)-isomers. This mixture was reduced to the 22-dihydroesters, which were in turn hydrolyzed and reacted with dihydropyran to give the 3β-THP ethers. These were reduced with $LiAlH_4$ to the mixture of (25R,S)-20-iso-3β-THP-26-diols, tosylated, reduced again with $LiAlH_4$ to 20-iso-cholesterol 3-THP ether and thereby eliminating chirality at C_{25}, and hydrolyzed to 20-iso- cholesterol with aqueous acid (mp 153-4 C, lit:154 C (Rodd), acetate mp 94-95.5 C, lit:124-5 C), separates from cholesterol by GLC and $AgNO_3$ TLC (as acetate). The ester was separated by fractional crystallization into the less soluble ethyl (20S, 25R)-3β-acetoxycholesta-5,22-dien-26-oate (mp 129-130 C) and the more soluble (20S, 25S)- isomer (mp 82-3 C). These esters were reduced to the 22-dihydroderivatives over Pd/C and these were in turn reduced with $LiAlH_4$ to (25R)-26-hydroxycholesterol (mp 176-177.5 C, $[\alpha]_D$ -27°, diacetate mp 128-9 C) and (25S)-26-hydroxycholesterol (mp 175-6 C, $[\alpha]_D$ -42°, diacetate mp 100-102 C).

SESSION H Plant Lipids II Monday p.m.

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COMPARTMENTATION OF LIPID SYNTHESIS IN THE DEVELOPING CASTOR OIL SEED. J.A. Miernyk and D.T. Dennis, Department of Biology, Queen's University, Kingston, Ontario, Canada K7L 3N6.

Sixty percent of the dry weight of the mature castor oil seed (*Ricinus communis* L.) is lipid. The acyl components of both the storage triglycerides, and the organelle membranes are synthesized in specialized nongreen plastids within the endosperm. These plastids contain all of the glycolytic and pentose-phosphate cycle enzymes (less glucose-6-P dehydrogenase), the pyruvate dehydrogenase complex, acetyl-CoA carboxylase, acyl carrier protein and fatty acid synthetase. The plastid glycolytic and pentose-phosphate activities exist as isozymes distinct from the cytosolic pathways. We have recently verified the enzyme localization data by a series of isotope incorporation studies. Isolated, intact plastids do not incorporate sucrose or glucose-6-phosphate into chloroform/methanol (2:2, v/v) soluble products. In order of increasing magnitude, they do incorporate fructose, glucose, 3-phosphoglycerate, acetate and pyruvate into lipids. The incorporation of pyruvate is unaffected by 1 mM α-cyano-4-hydroxycinnimate. The incorporation of 3-phosphoglycerate is inhibited by 0.1 mM pyridoxal-5′-phosphate. The incorporation of acetate is unaffected by 50 $\mu g\ ml^{-1}$ avidin or by 450 μM cerulenin. We propose that photosynthetically produced sucrose is transported from the leaves to the developing endosperm of the seeds. The sucrose is then cleaved by invertase in the cytosol. The resulting hexoses are transported into the plastids, metabolized through glycolysis to pyruvate, then to acetyl-CoA and finally to stearic acid. These plastids are capable of the initial desaturation step, yielding oleic acid. Oleic acid is exported from the plastids, either to be hydroxylated in the endoplasmic reticulum and ultimately stored as triricinolean in the lipid bodies, or to be further desaturated in some other compartment and incorporated into the phospho- and glycoglycerides which make up the membranes of the plastids as well as other organelles. We are presently examining the final products of plastid fatty acid synthesis, and the subcellular localization of the enzymes of complex lipid synthesis in the developing castor oil seed. (Supported by the NSERC of Canada.)

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DETERMINING THE BIOLOGICAL BASIS FOR LOWER POLYUNSATURATED FATTY ACID CONCENTRATION IN SOYBEANS. R.F. Wilson, B.A. Martin and J.W. Burton, 4124 Williams Hall, Crop Science Dept., NC State University, Raleigh, NC 27650.

Soybean Glycine max (L.) Merr. genotypes with a high concentration of oleic acid and low levels of polyunsaturated fatty acids have been developed through recurrent mass-selection breeding methodology. These genotypes have been utilized to explore the genetic and biochemical basis for alterations in glycerolipid fatty acid composition during seed development. Recent studies have shown that the fatty acid composition of glycerolipids formed in the seed of experimental genotypes between 0-20 and 45-75 days after flowering were similar to that in the control genotype, i.e., high levels of polyunsaturated fatty acids. During the period of greatest triacylglycerol accumulation (20-45 days after flowering), however, glycerolipids formed in the experimental germplasm were enriched in oleic acid. A positive correlation was found between the acyl-composition of phospholipid and triacylglycerol molecular species during the various periods of seed development. To assess the nature of the dichotomy in lipid metabolism observed in the experimental genotypes, diacylglycerol acyltransferase (EC 2.3.1.20) was partially purified and characterized from developing soybean seed. The subcellular localization of that enzyme was primarily in the fractions enriched with oleosomes and plastids but not the fractions containing the endoplasmic reticulum. Glycerolipid analysis of the organelles revealed that only the plastid fraction from the experimental line contained phospholipids with high concentrations of oleic acid. In other experiments, the fatty acid composition of seed from the scion was not altered by reciprocal grafts between the experimental and control genotypes. A lethal albino genotype also was grafted to the control rootstock for seed production. Polyunsaturated acyl content was higher in the albino seed than the control. At this time, genetic investigations suggest that traits for high oleic acid concentration are under nuclear gene control. The effect of controlled environmental conditions upon the expression of the traits will be discussed.

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SHORT-CHAIN FATTY ACID BIOSYNTHESIS IN DEVELOPING *Cuphea* SEEDS. Michael Pollard and P.K. Stumpf, Plant Cell Research Institute, ARCO Solar Industries, 6560 Trinity Court. Dublin, CA 94568.

The chain lengths of fatty acids found in vegetable oil triacylglycerols show a large variation, and can be classified as short (C_8 to C_{14}), normal (C_{16} and C_{18}), or long (C_{20} to C_{24}). The biosynthesis of normal and long-chain fatty acids is well researched, but the mechanism of short-chain fatty acid biosynthesis is unknown. We have used seeds of the genus *Cuphea*, which contain large amounts of short-chain acids, to investigate this problem. A cell-free extract from developing *Cuphea* seeds was obtained which could synthesize either normal or short-chain fatty acids from malonyl-CoA, depending on incubation conditions. Comparative experiments using cell-free extracts from developing oilseeds which contain only C_{16} and C_{18} acids showed the same result (i.e., either normal or short-chain acids could be synthesized, depending on assay conditions). These and other results will be discussed in terms of probable mechanisms for short-chain fatty acid biosynthesis in maturing oilseeds.

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THE ROLE OF MEMBRANE EXPANSION IN THE EFFECTS OF UNDISSOCIATED ACIDS. Judith B. St. John and Patricia C. Jackson, USDA, ARS, AEQI, Room 237, B-001, BARC-W, Beltsville, MD 20705.

Undissociated forms of organic acids such as formic, acetic, propionic, 2,4-dinitrophenol (DNP), and anesthetics increase the permeability of barley roots (*Hordeum vulgare*) to ions. Effects on permeability are paralleled by changes in the relative amounts of the principal fatty acids from barley root membranes. The proportions of palmitic, stearic, and oleic acids increase and proportions of linoleic and linolenic acids decrease. Only the undissociated forms of the organic acids are effective. The effects on membrane lipids and permeability are immediate. Hydrostatic pressure of ca. 10 atmospheres applied during the exposure prevents the effects of anesthetics and undissociated DNP. Prevention of the effects by pressure suggests a causal association of membrane expansion with the responses. This implies that undissociated forms of organic acids control membrane fatty acid composition and ion permeability by an initial conformational action on the membrane.

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MOLECULAR ANALYSIS OF CARDIOLIPIN FROM *Chlamydomonas reinhardtii* 137^+. David R. Janero, Department of Physiological Chemistry, Johns Hopkins University School of Medicine, Baltimore, MD 21205.

Cardiolipin (1′,3′-di-O-[3-*sn*-phosphatiydl]-*sn*-glycerol) has recently been localized to the inner membrane of the plant mitochondrion (Bligny and Douce, BBA, 617:254 [1980]) as a seemingly exclusive mitochondrial phospholipid in the plant cell. We have obviated the technical difficulty of obtaining purified mitochondria from plant cells by directly isolating and purifying the trace (ca. 0.5% total cell lipid) amounts of cardiolipin from the phototrophic green algaa *Chlamydomonas reinhardtii* 137^+ (wild-type). In order to characterize this phosphoglyceride chemically, we have quantitatively analyzed the associated acyl groups by argentation and gas liquid chromatographies. *Chlamydomonas* cardiolipin has an ester group unsaturated-to-saturated ratio of 2.4. The prevalence of unsaturated fatty acyl chains makes cardiolipin one of the most highly unsaturated phospholipids of the alga. Monoenoic and dienoic acids comprise some 68% of the unsaturated acyl groups and are present in various positional isomers along with lesser amounts of trienoic and tetraenoic fatty acids. Together, 16-carbon and 18-carbon acyl chains constitute over 70 mol% of the major fatty acids, prominent among which are palmitic, stearic, and linolenic acids. The importance of 16- and 18-carbon fatty acids in *Chlamydomonas* cardiolipin is qualitatively reminiscent of both the cell as a whole and the chloroplast thylakoids, although quantitatively the acyl profile of cardiolipin is distinctive as compared to the profiles of the cell lipids and the lipids of the photosynthetic lamellae. At the subcellular level, cardiolipin is not detectable in a fraction of thylakoid membranes prepared by differential and density gradient centrifugations. This investigation, as the first molecular analysis of cardiolipin from a green alga, broadens the details of cardiolipin biochemistry in the green plant cell.

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TRIACYLGLYCEROL STRUCTURAL AND SPECIES CHANGES IN MATURING PEANUTS. Timothy H. Sanders, National Peanut Research Laboratory, 600 Forrester Drive, Dawson, GA 31742.

Quantity, fatty acid composition, structure and species distribution of triacylglycerols in peanut oil changed as peanuts matured. Weight percent of triacylglycerols increased from 85.3 to 95.8% over eight distinct maturity stages. Mole percentage of oleic acid increased while behenic acid decreased from 5.2 to 2.0%. Stereospecific analysis revealed changes at each position on the molecule with the greatest changes occurring at the *sn*-3 position. Silver nitrate-TLC demonstrated significant changes in the distribution of most triacylglycerol species as peanuts matured.

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GLYCERIDE STRUCTURE VARIATION IN SOYBEAN AND OAT TRIGLYCERIDES. W.P. Pan and E.G. Hammond, Department of Food Technology, Iowa State University, Ames, IA 50011.

A rapid method was developed to screen the glyceride structure of individual plants to test for genetic variation. Lipids extracted from a plant are fractionated by thin layer chromatography, if necessary to obtain pure triglycerides. The triglycerides are hydrolyzed on a thin layer plate with pancreatic lipase and separated according to the method of Dutta et al. (J. Chromatogr. 154:39 [1978]). The mono and diglycerides are isolated and the monoglycerides are analyzed as representative of the *sn*-2 position. The diglycerides are reacted with phenyldichlorophosphate (Brockerhoff, J. Lipid Res. 6:10 [1965]) and the phospholipids are hydrolyzed on a thin layer plate with Cobra venom and separated according to the method of Dutta and Das (J. Chromatogr. 173:379 [1979]). The lysophosphatide is analyzed as representative of the *sn*-1-position. The *sn*-3-position is calculated by difference. The method was applied to 48 soybean (*Glycine max*) and 47 *Glycine soya* strains and 60 oat *Avena sativa* and 43 *Avena sterilis* strains. The wild relatives of oat and soybean showed no more genetic deviation from the common pattern than the cultivated varieties. No individuals with radical deviation from the common pattern were discovered.

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LIPIDS IN STEMS OF TWO PRICKLY PEAR CACTI. Henry W. Kircher and Abdul Mageed Mohamed, Nutrition and Food Science Department, University of Arizona, Tucson, AZ 85721.

Large cladodes, variously called joints, stems or pads, of two prickly pear cacti, *Opuntia ficus-indica* and *Opuntia phaeacantha* (*O. engelmanni*), contain ca. 2.5% of their dry weight as ether-soluble lipids. Examination of the lipids by Sigel TLC with 4 solvents of increasing polarity (80:20:1 petroleum ether/ether/HOAc, 60:40 hexane/ethyl acetate, 90:10:1 $CHCl_3$/MeOH/HOAc, 7:2:5 *n*-BuOH/EtOH/28% NH_3) revealed 7 colored components (carotenes and chlorophylls) and 15 additional components after the plates were developed with H_2SO_4 and heat. The composition of some of the components (sterol esters, other esters, triterpenes, sterols, free fatty acids, acyl sterol glycosides, sterol glycosides and glyco and phospholipids) was determined after their separation by column chromatography, acid or base hydrolysis, and identification of the fragments.

SESSION I Dietary Proteins and Their Effect on Metabolism and Disease Monday p.m.

53

PROTEIN EFFECTS IN ATHEROSCLEROSIS. David Kritchevsky, The Wistar Institute, 36th Street at Spruce, Philadelphia, PA 19104.

The first purely nutritional study of diet and atherosclerosis was conducted by Ignatowski in the early 1900s and was carried out to investigate the influence of protein. Until recently, protein effects on atherosclerosis were not studied in a regular or concerted manner. In the 1920s, Newburgh and his students showed that diets containing casein or beef were atherogenic for rabbits. Meeker and Kesten (1940) were first to compare animal (casein) and vegetable (soy) protein and showed the latter to be less atherogenic. In the last 10 years, Carroll has shown that there is a wide range of cholesterolemic effect among both animal and plant proteins. Our studies using a semipurified, cholesterol-free diet have shown that casein is more cholesterolemic and atherogenic than soy protein, but the results are influenced by the type of fiber present in the diet. We have hypothesized that the effect of a protein may be a function of its lysine/arginine (L/A) ratio. Addition of enough lysine to soy protein (L/A, ca. 1) to raise its lysine/arginine ratio to that of casein (L/A, ca. 2) increases the cholesterolemic and atherogenic potential of the soy protein. When three proteins of similar lysine content but different L/A ratios were fed, their atherogenic effect was directly correlated with their L/A ratio. The proteins used were fish (L/A, 1.44); casein (L/A, 1.89) and whole milk protein (L/A, 2.44). (Supported, in part, by HL-00734; HL-03299 and USDA-SEA #59-2426-0-1-479-0.)

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THE EFFECT OF DIETARY VEGETABLE AND ANIMAL PROTEIN ON THE ETIOLOGY OF CHOLESTEROL GALLSTONE FORMATION IN THE HAMSTER. Annemarie Richmond and George Liepa, Department of Nutrition and Food Sciences, Texas Woman's University, PO Box 24134, TWU Station, Denton, TX 76204.

The effect of dietary protein on gallstone formation and biliary constituents was studied using 30 male golden Syrian hamsters. Lithogenic diets containing 20% animal (casein in pelleted or powdered form) or vegetable (cottonseed in pelleted form) protein were fed for 35 days. Gallstone formation was significantly ($p<0.01$) greater in the two groups of casein-fed animals (63 and 90%) when compared to cottonseed protein-fed animals (0%). Bile components (bile acids, phospholipids and cholesterol) were determined in absolute concentrations (μmol/mL) and calculated in relative concentrations (molar %). Cholesterol was the only bile constituent that was significantly ($p<0.05$) higher in absolute concentration in the casein-fed animals, when compared to cottonseed protein-fed animals. When bile constituents were expressed as relative concentrations, cholesterol and phospholipids were significantly ($p<0.01$) higher in casein-fed animals than in cottonseed protein-fed animals. Relative bile acid concentrations were found to be significnatly ($p<0.01$) higher in animals fed the diet containing cottonseed protein. Serum cholesterol and high density lipoprotein cholesterol concentrations were not found to be significantly different in any of the three dietary treatment groups.

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THE EFFECTS OF DIETARY PROTEINS ON SERUM AND BILIARY CONSTITUENTS AND GALLSTONE FORMATION IN THE HAMSTER. Anne M. Duffy and George U. Liepa, Texas Woman's University, Department of Nutrition and Food Sciences, TWU Station, PO Box 24134, Denton, TX 76204.

The effects of dietary proteins on serum and biliary constituents and gallstone formation in the hamster were investigated. Sixty male hamsters four to six weeks of age weighing 60 ± 5 g were used in this study. Hamsters were randomly assigned to a control group or to one of four experimental groups. Purina Rat Chow 5012 was fed to the control group. The experimental diets contained proteins from one of the following sources: casein, soy isolate A, soy isolate B, or soy concentrate. Weight gain was consistent with all diets, with casein-fed animals having the lowest final weight. Gallstones were produced only in the casein-fed group. Total serum cholesterol concentration was significantly different between all experimental groups ($P<0.01$) with the concentration of the casein-fed group higher than the concentration of the three soy-fed groups. High density lipoprotein (HDL) cholesterol concentration was significantly different between all experimental diet groups ($P<0.01$) with the soybean isolate A group showing the highest concentration. The concentration of HDL_2-cholesterol was significantly higher among the three soy diets than it was in the casein-fed group, with the soybean isolate B group exhibiting a significantly higher concentration ($P<0.05$) than the soy concentrate diet group. Biliary cholesterol concentration was highest among the casein-fed animals and lowest among the soybean isolate A-fed animals, although no significant difference existed. Absolute and relative concentrations of bile acids were significantly different between all groups ($P<0.01$). The three soy groups exhibited higher ($P<0.01$) concentrations of bile acids than the casein group. Negative correlations existed between percent bile acid concentration and both percent biliary cholesterol concentration and percent phospholipid concentration. Absolute and relative concentrations of bile acids were also positively correlated with biliary calcium. Biliary calcium concentration was significantly lower ($P<0.01$) in the casein-fed group.

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EFFECTS OF DIETARY ANIMAL AND VEGETABLE PROTEINS ON SERUM AND BILIARY LIPIDS, AND GALLSTONE FORMATION IN THE HAMSTER. Mary Anne Sullivan and George U. Liepa, Texas Woman's University, Department of Nutrition and Food Sciences, TWU Station, PO Box 24134, Denton, TX 76201.

The objective of this study was to determine the effects of various dietary animal and vegetable proteins on serum and biliary constituents and gallstone formation in the hamster. Eighty-four hamsters (60 ± 5 g) were randomly assigned to either a control group or to one of six experimental groups. The control group was fed Purina Rat Chow 5012. The experimental diets were composed of 20.0% protein which was ca. 90.0% pure. Three animal proteins (casein, bovine albumin, and egg albumin) and three vegetable proteins (soy, cottonseed, and peanut) comprised the experimental diets. Weight gain was positive in all diets throughout the 63-day feeding period. Gallstones were present in 16.7% of the animal protein-fed hamsters, whereas the vegetable protein-fed hamsters exhibited gallstone incidence of only 2.8%. Evaluation of total serum cholesterol concentrations showed significant differences ($p<0.01$) with the casein-fed hamsters having a higher cholesterol concentration than either of the other two animal protein-fed groups ($p<0.01$). Concentration of HDL- and HDL_2-cholesterol was different among groups ($p<0.01$), with the animal protein-fed groups of hamsters having a significantly lower HDL-cholesterol concentration ($p<0.01$) than the vegetable protein-fed hamsters. Concentration of VLDL-LDL cholesterol was greatest in the casein group. Percent biliary cholesterol concentration was significantly different ($p<0.01$) between groups with the casein-fed animals showing the highest concentration of percent biliary cholesterol. Percent biliary phospholipid concentration was significantly different ($p<0.01$), with the animal protein-fed hamsters significantly higher ($p<0.01$) than the vegetable protein-fed hamsters. Percent bile acid concentration was elevated ($p<0.01$) with the vegetable protein diets. As a result, cholesterol precipitation into gallstones was inhibited. Strong negative correlations exist between percent bile acids and both percent phospholipid ($r = -.98$) and percent biliary cholesterol ($r = -.74$). The strongest correlation between total serum cholesterol and any of the lipoprotein subclasses of cholesterol exists between total serum cholesterol and both HDL-cholesterol ($r = .76$) and HDL_2-cholesterol ($r = .54$).

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EFFECTS OF BEEF, SOY, AND CONVENTIONAL DIETS ON CO_2, FATTY ACID, AND GLYCEROL SYNTHESIS IN YOUNG PIGS. Deborah A. Diersen-Schade, Donald C. Beitz and Norman L. Jacobson, Department of Animal Science, Iowa State University, Ames,IA 50011.

Previous work in our laboratory demonstrated that young pigs fed a diet containing soybean oil and soy protein isolate gained less body weight but deposited more fat than did pigs fed ground beef as the source of fat and protein. Thus, a study was designed to examine the effects of similar soy- and beef-based diets, as well as conventional corn and soybean meal-based control diet, on CO_2, fatty acid, and glycerol production in several tissues of young pigs. Twenty-one 4-week-old male pigs were fed a beef-based, soy-based, or control diet (7 pigs/diet) for eight weeks and then were slaughtered. Pigs were pair-fed the diets to equalize intake of calories, protein, minerals, and vitamins. Fat of beef, soy, and control diets contributed 42%, 42%, and 9%, respectively, of calorie intake. At slaughter, samples of liver, ileal mucosa, and subcutaneous and perirenal adipose tissues were incubated in Krebs-Ringer bicarbonate buffer containing 5 mM glucose. Rates of CO_2, fatty acid, and glycerol production were determined by using U-^{14}C-glucose as tracer. Fatty acid synthesis in liver and ileal mucosa was low and not affected by diet. Diet did not affect CO_2 or glycerol synthesis in ileal mucosa; liver from soy-fed pigs, however, had greater rates of CO_2 and glycerol synthesis. Soy- and beef-fed pigs had lower rates of CO_2 and fatty acid synthesis in both adipose tissues and of glycerol synthesis in subcutaneous adipose tissue than did controls. These three synthetic activities in adipose tissues of soy- and beef-fed pigs, however, were similar. Our results, therefore, demonstrate that the greater fat content of soy and beef diets suppressed the metabolic activity of adipose tissue; source of dietary fat and protein, however, had no effect. (Supported in part by the Iowa Beef Industry Council.)

HONORED STUDENT PRESENTATION

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INFLUENCE OF DIETARY PROTEIN ON CHOLESTEROL METABOLISM. Jon A. Story and David Kritchevsky, Department of Foods and Nutrition, Purdue University, Stone Hall, West Lafayette, IN 47907.

Differences in the cholesteremic and atherogenic effects of animal and vegetable proteins have been theorized to be caused by alterations in cholesterol turnover and pool size. Casein has been shown to result in larger cholesterol pools and significantly lower levels of oxidation of cholesterol than soy protein when fed to rabbits as part of a semipurified, cholesterol-free diet. In a recent experiment we fed rabbits semipurified diets with soy protein, casein, soy protein with added lysine (to equal the lysine/arginine ratio of casein) or casein with added arginine as sources of protein and compared these diets with a commercial ration. In addition to serum cholesterol levels and aortic atheroma, we measured fecal neutral and acidic steroid concentrations by gas liquid chromatography. Casein resulted in much lower levels of both acidic and neutral steroid excretion than soy protein. Addition of lysine to soy protein reduced excretion of acidic (63%) and neutral steroids (29%) in comparison to soy protein alone, whereas arginine added to casein caused an increase in excretion of both (14% and 76%, respectively). Changes in steroid excretion in response to soy protein and casein and alterations in their lysine/arginine ratio indicate an alteration in cholesterol balance.

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THE EFFECT OF DIETARY PROTEIN ON THE RETENTION OF CALCIUM AND PHOSPHORUS AMONG ANIMALS OF DIFFERENT AGES. Fang-Chuoh Liu, Nancy DiMarco* and George Liepa, Department of Nutrition and Food Sciences, Texas Woman's University, PO Box 24134, TWU Station, Denton, TX 76204.

Forty immature (3-month old) and 40 mature (9-month old) male rats were obtained for this study. The rats in each age group were divided into three subgroups, and assigned to either a control diet (20% casein used as the source of dietary protein) or one of the two experimental diets (20% soybean protein or 20% cottonseed protein used as the source of dietary protein). When the effect of various dietary proteins on calcium and phosphorus retention was examined, no significant difference was found among immature and mature rats. This suggested that neither 20% animal protein (casein) nor 20% vegetable protein (soybean or cottonseed) would affect the retention of calcium and phosphorus by rats. When calcium and phosphorus retention was examined using animals of different age groups, the mature rats showed significantly less retention of calcium and phosphorus than immature rats. This trend was not affected by the type of protein fed. This might be expected since mature animals would need less calcium and phosphorus as compared to immature, actively growing animals.

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MAINTENANCE REQUIREMENTS AND EFFICIENCY OF GAIN OF RATS FED WHEAT GERM AND CASEIN. Elizabeth B. Mills and Nancy L. Canolty*, Department of Foods and Nutrition, University of Georgia, Dawson Hall, Athens, GA 30602.

Linear regression analyses were used to relate body weight gains (y) and feed intakes (x) of rats fed for 21 days diets containing 10% protein supplied as wheat germ or casein. The regression equations obtained were $y=0.31(\pm 0.02)x-24.21$ ($r^2=.96$) for wheat germ and $y=0.37(\pm 0.03)x-32.73$($r^2=.92$) for casein. The daily maintenance requirement, the intake that resulted in zero body weight gain, was calculated for each diet by setting y equal to zero and solving for x, then dividing by 21. An intake of 3.73 g/day maintained body weight when the diet contained wheat germ compared with 4.26 g/day when the diet contained casein. A comparison of the slopes of the regression lines show the wheat germ diet was used 83% as efficiently as the casein diet to promote body weight gain. A comparison of maintenance requirements, however, shows that the wheat germ diet was used as efficiently as the casein diet to maintain body weight. The results of this study indicate that there are differences in the relative efficiency with which diets are used for maintenance and for gain. An assessment of the differences in the utilization of diets for these two processes should be evaluated when nutritional qualities of diets are compared (Supported by NIH Research Grant No. 28544 and Georgia Experiment Station Project 732.)

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MUTAGENIC POTENTIAL OF AFLATOXIN RELATED DECONTAMINATION BYPRODUCTS RESULTING FROM AMMONIATION OF COTTONSEED MEAL. L.S. Lee, D.L. Park, S.R. Hayworth, T.E. Lawlor, S.P. Koltun and A. Ciegler, USDA, ARS, Southern Regional Research Center, 1100 Robert E. Lee Blvd., PO Box 19687, New Orleans, LA 70179.

To date, ammoniation as a decontamination process for aflatoxin has not received FDA approval, partly because little is known of the decontamination products formed from aflatoxin during ammoniation. A joint research effort is underway by FDA and USDA to determine the fate of aflatoxin during ammoniation of contaminated cottonseed meal under conditions approximating those approved for commercial ammoniation of non-aflatoxin contaminated meal. Uniformly labeled $[^{14}C]$-aflatoxin B_1 was added to 22.7 kg of meal (14% moisture) that contained ca. 4000 μg naturally incurred aflatoxin B_1/kg. Distribution of radiolabel was used to trace modification of aflatoxin B_1 following treatment with 4% ammonia at 40 psi, 210 F, for 30 min. Duplicate 2 kg samples of the ammoniated meal were fractionated. Over 90% of the label was detected in meal following initial air-drying. Ca. 25% of the label was extracted from the air-dried meal by methylene chloride with 65% remaining the residue. Ca. 5% was extracted from this residue with methanol. Weak acid released 10% radiolabeled material from the residue after methanol extraction, but no label was recovered as aflatoxin B_1. All unchanged labeled and nonlabeled toxin (4 μg total A_fB_1/kg of ammoniated meal) was recovered as a single band from preparative thin layer chromatography of the methylene chloride extract. In control nonammoniated meals, 90% of the radiolabeled material was accounted for in the methylene chloride extract. Fractions of ammoniated meals containing radiolabel are being tested by the Ames procedure to determine their mutagenic potential. Results obtained will be reported.

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THE EFFECT OF DIETARY COTTONSEED PROTEIN ON SERUM AND SECRETORY IgA LEVELS IN INDIVIDUALS WITH DOWN'S SYNDROME. Kathleen M. Lawson, Carol B. Frankmann, Herbert A. Fritsche and Alice N. Milner, Dept. of Nutrition and Food Sciences, 1130 M.D. Anderson Blvd., Houston, TX 77030.

The purpose of this study was to determine whether a diet in which 50% of the protein is provided by glandless cottonseed would have an effect on serum and secretory levels of immunoglobin A (IgA) in Down's syndrome individuals. Eight institutionalized females (18-30 yr) were equilibrated on a 1400-1800 kcal, 60 g protein diet consisting of usual menu items for one week. For the next three weeks, they received a similar diet in which 50% of the protein was provided by glandless cottonseed. During the fifth week, they returned to the equilibration diet. At the end of weeks 1, 4, and 5, serum levels of IgA, IgG, and IgM were determined. In addition, saliva samples were analyzed for the presence of secretory IgA. Serum IgA was elevated in 6 of the 8 subjects (75%) at the end of the equilibration period. By the end of week 4, serum IgA levels had fallen, and approached the normal range. During week 5, serum IgA levels continued to fall and by the end of the week had reached the normal range; the change from the equilibration period was statistically significant ($p=0.03$). Determinations were again done 3 months after the subjects returned to their usual diet, and serum IgA levels were again elevated in the same 6 subjects; the change from week 5 was statistically significant ($p=0.03$). Secretory IgA was present in all suitable samples at each determination, but quantitative values were not available. Thus, the impact of diet on this parameter could not be determined. Mean serum IgG and IgM levels were normal at all determinations and did not change significantly. Thus, it appears that the changes in serum IgA in these subjects cannot be attributed to infection or illness, but rather to the diet.

SESSION J Emulsions and Microemulsions II Monday p.m.

63

CRYSTALLIZATION PHENOMENA IN EMULSIFIED AQUEOUS SALINE SOLUTIONS. Danièle Clausse, Issam Sifrini and Marc Clausse*, Laboratoire de Thermodynamique et Energétique, IURS, Avenue Philippon, 64000 Pau, France.

Since the pioneering work of Vonnegut (1948), emulsion or suspension type media frequently have been used as means to investigate either nucleation processes in or temperature- or pressure-dependent properties of undercooled melts. The main advantage of this experimental method, often referred to as the "droplet technique", lies in the fact that the liquid phase to be investigated is partitioned into a multitude of individual tiny droplets. In such a situation, the foreign particles present in the bulk liquid sample before its partition are isolated among a very small fraction of the total droplet population so that a large majority of droplets may undergo homogeneous nucleation. The "droplet technique" has been applied to the study of the crystallization of NaCl or NH_4Cl aqueous solutions. These melts formed the disperse phase of water in-oil-type emulsions whose continuous phase was either paraffin oil, the surfactant being lanolin, or methyl-cyclopentane or -cyclohexane, the surfactant being then Span 65. Series of emulsified saline solution identical samples were stored in temperature-controlled chambers where they were maintained at storage-temperatures θ_c included between the macroscopic saline solution freezing depression point T_e and the corresponding homogeneous nucleation temperature T_H, ($T_H < \theta_c < T_e$). The dispersed phase crystallization degree of advancement was recorded by determining through differential scanning calorimetry the amount of frozen melt in samples chosen at random in each series and extracted at regular time intervals from the temperature-controlled chamber. Whichever the suspending medium, sigmoidal crystallization curves were recorded. This means that, at the beginning of the θ_C-storage process, both the crystallization advancement and rate of advancement remain almost equal to zero. Past a time t_0 that can be defined as the crystallization-onset time, the crystallization rate of advancement first increases, then decreases until it eventually becomes null again. Memory effects were evidenced, as proved by the fact that the nucleation process in emulsions obtained by melting solid suspensions, (resulting from the disperse phase complete freezing at θ_C), occurs at temperatures which are higher than the T_H recorded during an initial steady cooling. All these results are consistent with and generalize data previously obtained on emulsions incorporating pure water as the disperse phase. In addition, new experimental facts were evidenced that could be of significance for the knowledge of crystallization phenomena in disperse systems. Experiments clearly showed that emulsified saline solutions having completed their freezing while stored at θ_C and subsequently submitted to a progressive rewarming exhibit a melting behavior totally different from what is observed in the case of similar samples whose previous freezing was achieved by means of a steady cooling down below T_H. One of the most surprising facts is that part of the frozen disperse phase of θ_C-stored emulsions may melt at T = 0 C, the normal melting point of pure ice. This suggests that the state of frozen w/o emulsions depend upon the freezing process, (monothermal vs steady cooling process), and can be interpreted in terms of the freezing process influence on the morphology of the emulsified aqueous phase droplets.

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DIFFUSION MEASUREMENTS IN MICROEMULSIONS. Reginald P. Seiders, N.S. Dixit and Raymond A. Mackay, Research Division, Chemical Systems Laboratory, Aberdeen Proving Ground, MD 21010.

An understanding of the internal structure of microemulsions and the transport properties of solutes dissolved in them are important for the application of these fluids to studies of chemical reactions and interactions at microscopic oil/water interfaces. As one component of this effort, we have measured diffusion coefficients in microemulsions by a variety of techniques. We report here the results of such measurements by means of both quasielastic light scattering (QLS) and by means of polarography. In the latter, the diffusion coefficient of an electroactive probe is measured at a polarizable electrode. One significant result of this work is that for oil-in-water microemulsions of aqueous micelles for which a diffusion coefficient can be determined by QLS, identical results are obtained using an oil-soluble electroactive probe. The results of these and other measurements will be presented, and their implications with respect to microemulsion structure will be discussed.

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DIACID ®, A HYDROTROPE OF DIFFERENT STRUCTURE. Stig E. Friberg and Tony Flaim, Chemistry Department, University of Missouri/Rolla, Rolla, MO 65401.

Hydrotropes are solubilizers that show extreme efficiency at high concentration in water. Their action has been explained from the perturbance of the packing in lamellar liquid crystal by their compact structure. A commercial hydrotrope, DIACID ®, has a different structure with two straight hydrocarbon chains in tandem. Its hydrotropic action is explained, based on determination of the conformation in different association structures.

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NONLYOTROPIC LIQUID CRYSTALS. Stig E. Friberg and M. Elnokali, University of Missouri/Rolla, Rolla, MO 65401.

Abstract not available at press time.

67

THE INFLUENCE OF SURFACTANT TAIL-BRANCHING ON THE LIQUID CRYSTAL/MICROEMULSION PHASE TRANSITION. W.H. Wade, L. Fortney, R.S. Schechter, University of Texas, Austin, TX.

Abstract not available at press time.

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MICROEMULSIONS: REACTION KINETICS, MICROSTRUCTURE AND POTENTIAL APPLICATIONS. D.O. Shah, C. Manohar and R. Leung, Chemical Engineering Department, University of Florida, Gainesville, FL 32611.

Microemulsions can be defined as thermodynamically or kinetically stable isotropic dispersions consisting of microdomains of oil and/or water surrounded by the interfacial film of surface-active molecules. In general, such systems form spontaneously upon addition of all components irrespective of the order of mixing. Microemulsions consisting of benzene, sodium dodecyl sulfate, 2-propanol and water were investigated using electrical conductivity, viscosity and ultrasonic absorption measurements. The results indicated the existence of three distinct regions in the single phase microemulsion area of the phase diagram. These regions are classified as water-in-oil (w/o), phase inversion (PI) and oil-in-water (o/w) microemulsions, each with its well defined microstructure. The transition from one microstructure to another occurs as the water/oil ratio is increased. Further support for these changes in the microstructure was obtained by studying the following reaction $AgNO_3 + NaCl \rightarrow AgCl + NaNO_3$ in these microemulsions using stopped-flow apparatus. Two identical microemulsion samples were prepared, one containing $AgNO_3$ and the other containing NaCl. These two microemulsions were mixed in the stopped-flow apparatus and the precipitation reaction due to the formation of AgCl was measured. Here again, the reaction rates showed 120-500% increase at two values of water/oil ratio exactly corresponding to where the transition from w/o to PI and PI to o/w microemulsion was observed. The possible mechanism for the enhancement of reaction rates at the phase transition is proposed. It is suggested from the reaction kinetics and the physical measurements that large fluctuations occur when the phase separation or the formation of a new phase takes place. It was concluded from this study that the microstructure of the microemulsion changes even within the single-phase isotropic area of the phase diagram and that specific microstructures may have potential applications in enhancing the reaction rates. Microemulsions with desired microstructure are prime candidates for catalysis in liquid medium, for controlling grain size in photographic emulsions and for the formation of metal clusters as catalysts.

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Title not available at press time.
H.T. David, University of Minnesota, Minneapolis, MN.

Abstract not available at press time.

SESSION K Pricing Vegetable Oil and Fats Monday p.m.

70

GROWTH OF SOYBEAN OIL MARKET AND USES OF PRICING. Daniel G. Kelly, Kelly Commodities Inc., 141 W. Jackson Blvd., Suite 1650, Chicago, IL 60604.

In 1949, the major futures market in vegetable oils was the New York Produce Exchange where cottonseed oil was traded. Among the various and many edible oils traded, soybean oil was possibly the least desirable but the most versatile. The fact that soy oil traded at a considerable discount to its competitors naturally encouraged research to enhance its usefulness in products such as margarine. As the standard of living in this country increases due to greater per-capita consumption of red meat, poultry and scientific feeding, using a high protein, caused the size of the soybean crop in this country to expand rapidly. This phenomenon occurred later in Europe as its per-capita income increased and people exposed to American diets (because of the presence of American troops and supporting personnel) consume more meat and poultry. As the demand for meal increased dramatically both domestically and foreign export oil became a distinct byproduct and in considerable surplus. PL 480 was of considerable assistance to our domestic oilseed processors as it provided emerging and poor countries with currency incentives to purchase our surplus vegetable oil. One of the results of this combination of events was to keep animal feed relatively cheap and was obviously a tremendous boom to the US consumer. With a liquid futures market in Chicago, processors were able to sell meal for consumption and "hedge" their oil in the futures market. This in turn supplied a constant market for soybeans and encouraged the farmer to increase production.

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"CASH" VEGETABLE OIL BROKERAGE. W.K. Simeral, W.M. Simeral & Company, Inc., Windsor Office Plaza, Suite 120, 210 W. 22nd St., Oak Brook, IL 60521.

The cash brokerage house is an information exchange in the world of physical commodities. Cash brokers provide the daily contact between buyers and sellers and the information necessary to establish the final FOB or delivered price of the commodity. However, unlike the futures exchange, which is primarily a mechanism to provide price protection (hedging), and only occasionally is used actually to merchandise the physical commodity, the cash broker deals with the myriad of details involved in the final price, shipment, quantity, quality, terms of payment and mode of transportation. The majority of a cash broker's effort is to collect and disseminate information on cash bases, which are the premiums or discounts to the futures market for specific FOB or delivery points. These bases reflect real supply and demand as well as transportation considerations. Most of my talk will concern itself with an explanation of a cash basis; what can change it; and how this information is collected and disseminated, resulting in merchandizing the physical vegetable oil.

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PRICING EDIBLE OILS. John G. Reed Jr., Archer Daniels Midland Co., PO Box 1470, Decatur, IL 62525.

Soybean oil is by far the most prominent edible oil in the world. More soybean oil is produced in the USA than in any other country or in the EEC. Approximately 20% of world soybean oil production is exported from the USA, Brazil, the EEC, and Spain to importing countries all around the world. The soybean oil futures market at the Chicago Board of Trade provides a valid and widely used reference price for soybean oil buyers and sellers all around the world. Because prices of several other edible oils tend to fluctuate at reasonably predictable relationships to soybean oil, the soybean oil futures market also provides a satisfactory reference price for traders of cottonseed oil, palm oil, and sunflowerseed oil. Examples of the pricing mechanism will be provided.

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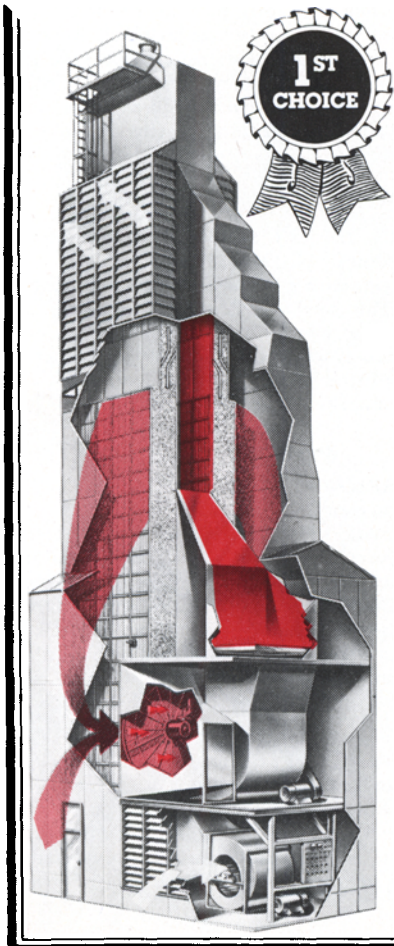
FUNCTION OF THE REFINER (PRICING) WHOLESALER/RETAILER. D. Melendy, Lever Bros. Co., 390 Park Ave., New York, NY 10022.

Since the pricing function in general is a "discovery" process, the pricing function of the refiner is not so different from that of the crusher, except that the refiner is on the opposite side of the fence. The wholesaler or industrial sales portion of the refiner's business is essentially low margin/high competition. There are many refineries with "excess" capacity only too willing to cut a few points in order to gain a sale even at a "loss". The contribution to manufacturing overhead reduces the unit cost for the retail end of the business, making the total business profitable. Retail markets are governed by consumers' tastes, prejudices and willingness/unwillingness to pay a premium for premium goods. Price has its place



where consumers are unable to pay for quality or discern no quality difference between high-priced and low-priced spreads.

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WILL WE HAVE ENOUGH? Peter A. von Eschen, Cargill Inc., 135 S. LaSalle St., Suite 1610, Chicago, IL 60603.

For years, supply has managed to stay ahead of demand. This has occurred despite a doubling of the world's population and some significant increases in per-capita consumption in certain countries. Are the present stocks really burdensome? Future years promise to create additional demand, especially in the developing areas. How important are credit and aid programs in enabling lower income nations partially to satisfy their requirements or how many demand become effective? The coming decades will be both exciting and a little frightening. Some say that by the year 2000 about 6 billion people will be competing for the essentials of life, and the numbers, in an absolute sense, will become even more formidable thereafter.

SESSION L Oilseed Processing 1983 II Monday p.m.

75

MEAL DESOLVENTIZING. Kenneth W. Becker, 38 Prairie Drive, Westmont, IL 60559.

Meal desolventizing accomplishes two purposes in the process simultaneously: solvent recovery and control of the functional properties of the meal. For example, soybean meal for ruminant feed must be toasted sufficiently to inactivate urease. However, soy flours for human use, depending on their ultimate application, are produced from thoroughly toasted to untoasted meal (as measured by nitrogen soluble index). Plant safety depends on thorough desolventizing under all conditions: start-up, emergency and normal shutdown, and operations with good and poor drainage. The amount of solvent retained in the meal should be minimized and the solvent must be recycled back to the process safely and efficiently. The meal produced must be suitable for safe storage under confined conditions to avoid hexane explosion hazards. Several types of current American and European desolventizing systems are illustrated and described in this paper. Also, the necessary design features, instruments, and controls to meet these requirements are presented.

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SOLVENT RECOVERY IN MEAL. Jean-Pierre Wolff, Institut des Corps Gras (ITERG), 10/A rue de la Paix, 75002 Paris, France.

The final hexane content of extracted meal is an increasingly important concern to the oilseed processing industry because of its relationship to safety and environmental considerations. We have compared in our laboratories several methods for the hexane determination and developed a new method, derived from Dupuy's method (head space analysis by GLC), which gives encouraging results. In the GERDOC pilot plant in Pessac, we are studying the influence of several parameters on hexane retention in rapeseed meal. At the pilot plant level, three processes may be used to reduce hexane retention: rapeseed dehulling, rapeseed drying before crushing, and reduction of the length of meal-hexane contact during the extraction procedure itself.

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SOLVENT RECOVERY. Noel Myers, Myers Engineering, PO Box 1493, Decatur, IL 62525.

A brief overview is presented of the economic significance of solvent recovery in the oilseed extraction industry in view of the steep price advance of hexane since 1974 and the likelihood of continuing price increases. The present solvent recovery practices in oilseed plants are outlined with addition of operating techniques since 1976. Also, industry trends are noted in terms of improved equipment. Information is presented on the expected solvent losses in various recovery steps in the normal solvent plant operation. Techniques for measuring solvent losses on vent gas effluent, wastewater effluent and extracted oil production stream are outlined. The areas of greatest solvent loss are the DT meal outlet stream and the various mechanical leaks in the process machinery. Some discussion is presented on the lack of ability better to define the solvent loss associated with meal discharge stream from the DT unit. Various deficiencies are pointed out in testing procedures and a suggestion is made for increased work in the field to substantiate a better value for solvent loss determination in DT meal. This area is suspected to be the major loss source in the average solvent plant of today.

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ALTERNATIVE SOLVENTS FOR OILS EXTRACTION. L.A. Johnson and E.W. Lusas, Food Protein Research and Development Center, FM Box 183, Texas A&M University, College Station, TX 77843-2476.

Hexane is the principle solvent used for extraction of oilseeds. Operating losses of solvent range between 0.2 and 2.0 gal/ton of seed; and a 6-8-fold increase in price in the last decade has made hexane costs a sizeable cost factor in oilseed milling. Occasional scarcities of hexane, and several catastrophic explosions and fires, have further motivated searches for alternative solvents. However, potential replacement solvents differ in their abilities to extract oil, volatility, corrosiveness, toxicity, flammability, and in costs of modifications of current equipment and retrofitting to solvent extraction plants. An ideal solvent should be plentiful, low-cost, easy to remove, and nonhazardous in use and to workers and the surrounding environment. Although some suggested alternative solvents have one or more distinct advantages, such as: abilities to extract triglycerides selectively while leaving phosphatides behind in the meal; or even extracting undesirable compounds like gossypol and aflatoxins, and thus making the meal saleable, they also may have problems of higher solvent cost and energy requirements. The use of such solvents may require modifications in extractor design to operate with more volatile vapors and changes in auxiliary equipment. In some cases, it may be more energy efficient to recover oil from miscella by chilling to take advantage of temperature solubility coefficients, rather than by the traditional process of evaporation. This paper reviews experiences and literature regarding the comparative operating characteristics of hexane and other alkanes, various alcohols, chlorinated hydrocarbons, and other solvents and mixed solvents which have been considered or are being used for extraction of oilseeds. Isopropanol and methylene chloride are particularly attractive.

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SOLVENT PLANT SAFETY. Harold J. Sandvig, Corporate Safety, Cargill Inc., PO Box 9300, Minneapolis, MN 55440.

Solvent plant safety begins with a management commitment to safety and loss control. The need for eductation, training and thorough appreciation of the solvent process and its potential hazards are discussed, as well as where and how solvent extraction operators fail. Steps are outlined to reduce risks, protect life and property, and maintain credibility.

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RECENT SAFETY EXPERIENCES. C. Louis Kingsbaker, C.L. Kingsbaker Inc., 7245 Northgreen Dr. NE, Atlanta, GA 30328.

During the past few years, several oilseed solvent extraction plants have experienced severe explosions and fires causing death, injury and property damage. One city had part of its sewer system destroyed by a hexane explosion resulting from a solvent spill from an extraction plant into the sewer. This paper discusses a few of these incidents and how to prevent future disasters by new plant process designs, operation and safety procedures.

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A LOOK AT THE FUTURE. John E. Heilman, Continental Grain Co., 277 Park Ave., New York, NY 10017.

The general economic situation for the world economy in the future and the outlook for the oilseed processing industry will be considered in trying to evaluate the trends that can be expected in technological development for the industry. The impact of energy supply and cost, regulatory actions, safety consideration, the availability of inexpensive process control computers, and new process technologies that appear to be under development are some of the subjects that will be discussed.

SESSION M Autoxidation II Monday p.m.

82

FORMATION OF MONOHYDROPEROXIDES WITH UNCONJUGATED DIENE SYSTEMS DURING THE AUTOXIDATION OF LINOLEATE. Werner Grosch and Margot Wurzenberger, Deutsche Forschungsanstalt für Lebensmittelchemie, Lichtenbergstraße 4, 8046 Garching, West Germany.

We have investigated whether monohydroperoxides are formed when hydrogen atoms are abstracted from the allylic carbons-8 and -14 during autoxidation of linoleic acid. In initial experiments, the monohydroperoxides isolated from autoxidized methyl linoleate were reduced and chromatographed on silica gel/$AgNO_3$ columns. Besides the major faction which consisted mainly of the well known 9- and 13-hydroxyoctadecadienoates, two minor compounds were observed. On the basis of ^{1}H-NMR and mass spectral data they were identified as the methyl esters of 8- and 14-hydroxy-*cis*-9,*cis*-12-octadecadienoic acids. In addition, experiments have been carried out using phenyl linoleate as substrate. After autoxidation, the monohydroperoxides have been hydrogenated to the corresponding phenyl hydroxy stearates. HPLC and mass spectral investigations of these derivatives have provided evidence that minor quantities of 8-, 10-, 12- and 14-hydroperoxide isomers are formed during autoxidation of phenyl linoleate.

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COMPARISON OF EXTRACTION METHODOLOGIES FOR LIPID OXIDATION PRODUCTS. Suzanna Pinter, Banquet Foods, St. Louis, MO, and E.G. Perkins, Burnsides Research Laboratory, University of Illinois, 1208 W. Pennsylvania Avenue, Urbana, IL 61801.

Thermal oxidation of vegetable oil produces various chemical changes, many of which are of significant importance from the standpoint of flavor, appearance, nutrition and toxicity. This study compared several separation methods for their ability to isolate the major oxidized compounds from thermally oxidized soybean oil methyl esters. A high performance liquid chromatography system (HPLC) was developed to separate the oxidized compounds. Five separation techniques were compared: low temperature crystallization; countercurrent distribution with immiscible phases of 80% aqueous ethanol/hexane and acetonitrile/hexane; and adsorption and partition column chromatography. A Batch type countercurrent distribution using acetonitrile/hexane was the most effective in concentrating the polar products. The greatest amount of higher molecular weight material was also concentrated using this method. The HPLC system developed to separate the oxidized products used a C-18 column with a linear gradient from 50% aqueous acetonitrile to 85% aqueous acetonitrile, at a rate of 5%/min. A UV detector set at 210 nm was used.

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CHEMILUMINESCENCE: A NEW TOOL FOR FOOD ANALYSIS? Joseph A. Fioriti and Rex J. Sims, General Foods Corp. Technical Center, 250 North Street, White Plains, NY 10625.

Although chemiluminescence is a well known and documented phenomenon, its application to the analysis of foods is a recent development. This review will describe some of its theoretical aspects, the equipment used, as well as some of its most recent applications. These will include the use of chemiluminescence in monitoring fats and oil deterioration. Results obtained using breakfast cereals, bread, chewing gum and other food materials will also be described. An assessment of its utility in a food laboratory will be given.

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A QUICK METHOD FOR MEASURING PEROXIDES IN FOODS. C.W. Fritsch, J.W. Zurawski and J.B. Fine, General Mills, Inc., 9000 Plymouth Ave. N., Minneapolis, MN 55427.

The determination of peroxide formation in foods requires the extraction of fat. To obtain a representative fat sample without affecting the peroxide concentration is difficult for most foods and impossible for some. For foods with lipids containing some linoleic acid, peroxidation was measured without the extraction of fat. The peroxides were cleaved by adding to the food sample a boiling solution of 5% ferrous sulfate in 10% sulfuric acid. After 5 min, the concentration of *n*-hexanal in the vapors above the reaction mixture was determined by gas chromatographic analysis. Good correlation was obtained between the peroxide values of different corn oil samples added to a model food system and the amount of hexanal determined by the above procedure. The method was found extremely useful for evaluating lipoxygenase activity in grains.

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OXIDATIVE STABILITY OF PEANUT OIL FROM DIFFERENT MATURITY LEVELS. J.A. Singleton and H.E. Pattee, PO Box 596, Raleigh, NC 27650.

The oxidative stability of fats used in foodstuffs is of prime importance to the food industry. Oxidative degradation of fats leads to a variety of compounds; organic peroxides, alcohols, aldehydes and ketones. The oxidative state of fats can be measured by several static methods; however, the susceptibility of fats to oxidation can probably be best expressed in terms of oxidation stability. Peanut oils from different maturity levels have been subjected to autoxidation of 120 C with oxygen and measuring the conductance of trapped volatiles in distilled water. The length of the induction period is correlated to the stability of the fat.

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PHOTOOXIDATION OF THE FATTY ACIDS: ENHANCEMENT WITH THE ANTIOXIDANTS AND POLYHALOGENATED BIPHENYLS. M.K. Logani, B. Shah and R.E. Davies, The Center for Photobiology, Skin and Cancer Hospital, Temple University Health Sciences Center, Philadelphia, PA 19140.

Environmental ultraviolet radiation, primarily of solar origin, is generally conceded to be the primary etiologic agent for common forms of human skin cancer. In recent years, there has been accumulating evidence that antioxidant supplemented diets provide considerable protection against photocarcinogenesis. The inhibitory action of antioxidants is believed to act through free radical quenching, thus preventing lipid peroxidation of cellular membranes. In order to determine whether or not the antioxidants can prevent photooxidation of lipids, the effect of butylated hydroxytoluene (BHT), butylated hydroxyanisole (BHA), tocopherol, and tocopherol acetate on photooxidation of the fatty acids was studied. Irradiation ($\lambda > 320$ nm) of methyl linoleate with unfiltered black light (10 fluorescent tubes, 20 watt each) showed less than 1% consumption. A marked increase in the photooxidation (18%) of methyl linoleate was observed in presence of BHT. Similarly, consumption of methyl linolenate and arachidonate was much lower with black light alone (15.5 and 19.8%, respectively) in comparison to when BHT was present (57.9 and 67.6%, respectively). Conversely, BHA and tocopherol acetate as such did not show any significant effect but greatly enhanced the photooxidation when hexabromobiphenyls were also present. Hexabromobiphenyls by themselves did not show any notable effect on the photooxidation. Since polybromobiphenyls are present widely as environmental pollutants and tend to accumulate in subcutaneous fat, the observation that these compounds can greatly enhance the photooxidation of fatty acids in presence of the antioxidants could have significant biological implications.

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INVESTIGATION OF CATFISH OIL QUALITY BY DIRECT GAS CHROMATOGRAPHY. A.J. St. Angelo, M.G. Legendre, H.J. Dupuy and G.J. Flick Jr., Southern Regional Research Center, PO Box 19687, New Orleans, LA 70179.

Underwater agriculture, or more simply, aquaculture, has been a rapidly growing industry in the southern part of the United States during the past few years. One of the primary aquatic species being grown commercially in the southern states is the catfish. In January 1982 there were ca. 74,000 acres of water in the production of catfish, with ca. 67% of that total in the state of Mississippi. The diet used in catfish farming has been altered to include high protein feeds for rapid and economic growth of the fish. These diets contain feedstufffs, such as animal byproducts, fish, and oilseed meals. These diets may account for the fact that today's processed catfish contain more bodyfat than those from ten years ago. Since the catfish supply is presently greater than the demand, storage of catfish fillets is necessary. These two factors, diet and storage, are conducive to promoting catfish off-flavors. The Southern Regional Research Center has initiated studies on the identification of compounds associated with various types of off-flavor in pond-raised catfish. As part of this ongoing research, we have developed a procedure for measuring the relative rancidity of crude catfish oils without removing the interfering substances that usually accompany such oils. This paper will describe these conditions and the results obtained on the assessment of catfish oil quality.

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SEMIAUTOMATED DYNAMIC HEADSPACE ANALYSIS OF VEGETABLE OIL VOLATILES. Jeremiah Roberts, CPC International, Best Foods Division, Research and Engineering Center, 1120 Commerce Avenue, Union, NJ 07083.

Semiautomated Teckmar DHC-1, and Hewlett Packard Model 7685A purge and trap sampler instruments were utilized in dynamic headspace analysis of vegetable oil volatiles. Instrument comparison, application, data analysis and recommendations for quality control of oils will be discussed.

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CHIA (*Salvia* SP.) AS A SOURCE OF LIPID ANTIOXIDANT. Dan E. Pratt and Maria Silvia de Lima Taga, Department of Foods and Nutrition, Purdue University, West Lafayette, IN 47907.

Methanolic and aqueous extracts of hexane defatted chia seeds possess potent lipid antioxidant activity. Lipids and other hexane soluble components were extracted from finely ground chia seeds. Defatted seeds subjected to methanolic and aqueous extract yielded solutions that were very potent as lipid antioxidants. Chia seed extracts were heated at 100 C for 45 min in 2N HCl (in methanol) to hydrolyze phenolic glycosides and phenolic esters. Nonhydrolyzed and hydrolyzed extracts were streaked on preparative cellulose TLC plates and developed in 15% acetic acid. Phenolic antioxidant components were subsequently separated by TLC. Isolated antioxidants were identified by TLC, GLC, and UV spectral analyses. GLC analyses were conducted on trimethylsilyl derivatives using bistrimethylsilyl-trifluoro-acetamide as the silylating reagent. The major antioxidant activity of the unhydrolyzed extract was due to flavonol glycosides, chlorogenic acid (7.1×10^{-3} mol/kg of seed), and caffeic acid (6.6×10^{-3} m/kg). Major antioxidants of the hydrolyzed extracts were flavonol aglycones-kaempferol (1.13×10^{-3} m/kg), quercetin (2.0×10^{-4} m/kg) and myricetin (3.1×10^{-3} m/kg)- and caffeic acid (1.35×10^{-2} m/kg). Other phenolic acids were present in chia seeds but in lower concentrations and/or lower antioxidant activity. Two methods were used to measure antioxidant activities. One was based measuring bleaching of β-carotene in the coupled oxidation of β-carotene and linoleic acid in the presence of added antioxidants; the other was to measure the rate of oxidation, by peroxide values, of linoleic acid on storage with added isolated antioxidants. In the former method, the rate of carotene bleaching was inversely proportional to antioxidant activity.

SESSION N Pharmacological Role of Lipids I

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BIOLOGICAL EFFECTS OF PEROXIDIZED POLYUNSATURATED FATTY ACIDS. Hubert S. Mickel, 12A Soldiers Field Park, Boston, MA 02163.

Peroxidation of polyunsaturated fatty acids, either enzymatically or by autoxidation, produces compounds with extensive biological effects. In earlier work, we presented a hypothesis of damage to white matter of the brain in multiple sclerosis and in perinatal telencephalic encephalopathy, based upon a lipid peroxidation mechanism. Recent work lends support to that hypothesis. Investigation of resuscitation of the brain following cardiac arrest and in anoxic encephalopathy models in experimental animals demonstrate that a profound reduction in blood flow to the brain occurs within 90 min after restoration of normal circulation. This low blood flow status to the brain is prevented by calcium uptake blockers and is associated with the enzymatic release of arachidonic acid by brain tissue. It is possible that thromboxanes or other highly vasoactive compounds are formed by peroxidation of arachidonic acid, and that these compounds result in reduced blood flow to the brain. There is also the problem of peroxidation of *trans* polyunsaturated fatty acids, which are formed as a byproduct of the hydrogenation of oils. These compounds are less susceptible to peroxidation or autoxidation than corresponding *cis* polyunsaturated fatty acids, but more susceptible than saturated or monounsaturated compounds. However, *trans* fatty acids are placed in the alpha position of phospholipids and triglycerides, instead of the beta position, as are most *cis* polyunsaturated fatty acids. Since *trans* fatty acids tend to be metabolized similar to saturated fatty acids, their presence in body tissues creates the possibility for an increased level of random free-radical production, resulting from autoxidation.

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EFFECTS OF FATTY ACIDS ON INTESTINAL TRANSPORT.
Helmut V. Ammon, 500 West National Avenue, Wood, WI 53193.

When long-chain fatty acids in micellar solutions are perfused through the human intestine, they alter electrolyte and water transport. Five mM oleate abolishes absorption and 10 mM oleate induces secretion of Na, Cl and water in the jejunum, 2 mM oleate reduces absorption of water and electrolytes in the colon. Similar effects have been observed during jejunal perfusion with linoleate, linolenate and glycerol-monoolein. Thus, the effect is not limited to ionized amphipaths. The changes in water and electrolyte transport are accompanied by a reduction in the absorption of organic solutes such as glucose, xylose and amino acids. The effects of oleate in the human jejunum can be blocked by adding cholesterol or β-sitosterol to the perfusion solutions. Since cholesterol had only a minimal effect on the monomer concentration of oleate and because cholesterol protects membranes against detergents in other systems by stabilizing their lipid bilayers, we postulate, that this in vivo effect of cholesterol is due to its ability to stabilize the lipid bilayer of the enterocyte cell membranes. The mechanism by which fatty acids alter intestinal transport is only incompletely understood. Stimulation of cyclic-AMP, ehancement of mucosal permeability and mucosal damage have been proposed as explanations by other investigators studying hydroxy fatty acids or dihydroxy bile acids. We were able to reproduce the effects of fatty acids on the intestinal transport of electrolytes, water and organic solutes by combining cyclic-AMP mediated fluid secretion (cholera toxin) and enhancement of mucosal permeability by amphotericin B in the rat intestine. The effect of fatty acids on intestinal transport explains the diarrhea associated with steatorrhea. The effect is probably due to the detergent properties of fatty acids. The protective effect of cholesterol suggests that biliary cholesterol may play an important role in the protection of the intestine from the adverse effects of biological detergents.

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CHARACTERIZATION OF THE LIPID AND PROTEASE ACTIVATED FORMS OF PYRUVATE OXIDASE.
Lowell P. Hager, Michael Recny and Gary Leisman, Biochemistry Department-B4, 415 Roger Adams Laboratory, University of Illinois, 1209 West California Street, Urbana, IL 61801.

Pyruvate oxidase (pyruvate:cytochrome b_1 oxidoreductase E.C. 1.2.2.2.) is a peripheral membrane enzyme found in *Escherichia coli*. The enzyme is a tetramer consisting of 4 identical subunits having an individual molecular weight of 60,000. Each subunit contains one tightly bound molecule of flavin adenine dinucleotide. The enzyme catalyzes the oxidative decarboxylation of pyruvate to acetate, carbon dioxide and reduced FAD and requires thiamin pyrophosphate and a divalent metal cation for activity. The natural electron acceptor for the reduced enzyme is a cell membrane associated electron transport system including both ubiquinone-6 and cytochrome b_1. When pyruvate oxidase is assayed for activity in the presence of lipids or detergents, the specific activity is increased more than 20-fold. Activation is thought to be due to a conformational change in the enzyme which is induced by lipid binding. Anionic amphiphiles are better activators than neutral or cationic amphiphiles for a given chain length, suggesting that there may be a positive charge at or near the lipid binding site. [^{14}C]-Lauric acid has been introduced as an affinity label by covalent attachment to the enzyme using a water-soluble carbodiimide crosslinking reagent. The peptides resulting from extensive tryptic digestion of the affinity-labeled enzyme complex have been separated by reverse-phase HPLC using a C18-ODS column. Two radioactive peaks were observed and the corresponding peptides isolated. In the presence of substrates, the enzyme may also be activated by mild proteolysis which reduces the subunit molecular weight to ca. 58,000. The small peptide released is not required for activity. Protease activation results in a substantial change in the FAD absorption spectrum, indicative of a shift from a hydrophobic environment to a conformation which is more open and accessible to the solvent. The effect of specific protease cleavage is similar to lipid binding in that the nicked enzyme is fully active in the absence of lipids. Furthermore, lipid activation and protease activation appear to be mutually exclusive. The protease activated enzyme does not bind lipids and lipid activated enzyme is not susceptible to proteolytic nicking. These observations support the hypothesis that both processes, proteolytic nicking and lipid binding result in similar conformational changes which are reflected by the environment of the flavin prosthetic group and lead to a stimulation of enzymatic activity.

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FOUR HYPOGLYCAEMIC COMPOUNDS THAT INHIBIT β-OXIDATION: 2(5[4-CHLOROPHENYL]PENTYL)OXIRAN-2-CARBOXYLATE (POCA), VALPROATE, PENT-4-ENOATE AND HYPOGLYCIN. A COMPARISON OF THEIR MECHANISMS OF ACTION.
H.S.A. Sherratt, University of Newcastle-upon-Tyne, England.

We have studied 4 hypoglycaemic compounds that inhibit β-oxidation by different mechanisms. These are all metabolized to unusual acyl-CoA esters. POCA-CoA inhibits carnitine palmitoyltransferase I; 3-oxopent-4-enoyl-CoA, a metabolite of pent-4-enoate, inactivates 3-oxoacyl-CoA thiolases; and methylenecyclopropylacetyl-CoA, a metabolite of hypoglycin, inactivates butyryl-CoA dehydrogenase. By contrast, formation of valproyl-CoA causes nonspecific inhibition of β-oxidation by increasing the acyl-CoA/acetyl-CoA+CoASH ratio in the mitochondrial matrix. POCA and valproate inhibit ketogenesis. Pent-4-enoate and hypoglycin are ketogenic, presumably because they also inhibit utilization of ketone bodies very strongly. With all these compounds, hypoglycaemia in fasted animals is due to impaired gluconeogenesis secondary to inhibition of β-oxidation. POCA is a candidate for the chemotherapy of diabetes. Pent-4-enoate and hypoglycin are poisons. Valproate, the least potent inhibitor, is an effective and widely used antiepileptic drug; its effects on intermediary metabolism may contribute to rare cases of valproate-associated hepatotoxicity. All 4 compounds cause multiple enzyme inhibitions and the goal of a completely specific inhibitor of β-oxidation is still elusive.

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CHOLINERGICALLY MEDIATED HYDROLYSIS OF PHOSPHATIDYLINOSITOL IN THE RAT PAROTID GLAND.
Yoram Oron, Etta Nadler and Monica Lupu, Dept. of Physiology and Pharmacology, Sackler School of Medicine, Tel Aviv University, Ramat Aviv 69978, Israel.

The disappearance of phosphatidylinositol in the rat parotid gland following cholinergic receptor stimulation was studied. The process was followed by measuring the disappearance of ^{3}H-inositol label in gland fragments previously labeled with the radioactive tracer. The incorporation of ^{3}H-inositol followed a linear time course and was enhanced when gland fragments were previously exposed to carbamylcholine and then atropine. The pool of the radiolabel was poorly accessible to exogenous unlabeled inositol and, consequently, a loss of label due to cholinergic stimulation could be demonstrated only after prolonged incubation with an excess of inositol. The cholinergically caused disappearance of the label was rapid (maximal at 15 min of incubation with carbamylcholine). The loss of the label corresponded to the release of radioactivity into the cellular space and the incubation medium. Subcellular fractionation of parotid gland fragments showed a uniform decrease in ^{3}H-inositol label in all the particulate fractions at 15 min of incubation with carbamylcholine. The uniform loss of radioactivity from all the fractions could not be attributed to the equilibrium of the label via the action of phospholipid carrier proteins, since changes in the specific radioactivity of a particular subcellular fraction (brought by alpha-adrenergic stimulation, or by the rapid incorporation of exogenous ^{3}H-phosphatidylinositol), were only slowly transferred to other subcellular fractions. It is concluded that cholinergic stimulation in the rat parotid results in a uniform disappearance of phosphatidylinositol from all the cellular membranes and does not occur in any particular fraction. This finding has important implications on the proposed mechanism of stimulus-related changes in cell-membrane Ca^{2+} permeability.

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INVESTIGATIONS ON LIPID ASSOCIATIONS USING MYELIN TUBE FORMATION. Eugène Neuzil and Jeanne Fourche, Laboratoire de Biochimie, Université de Bordeaux II, 146, rue Léo Saignat, 33076 Bordeaux, France.

Myelin forms (MF) are readily observed under the microscope when a fragment of lecithin is immersed in water: the tubes which appear to sprout out from the interface into the water phase are formed by a series of coaxial cylinders separated by thin films of water; this lamellar structure explains both the fluid character and the growth of MF. The basic structure of the tubes corresponds to an oriented bilayer of phospholipid molecules; MF may thus be considered as simple models of biological membranes. Myelin tubes are also formed when a droplet of oleic acid (or of a related unsaturated fatty acid) is surrounded by aqueous ammonia. A systematic study of the influence of various nitrogenous cations on the ordered packing of the fatty anions showed the outstanding place of different hydrazine compounds, a fact which led us to study the hitherto undescribed group of hydrazinium soaps. The observation of myelin tube formation is finally applied to investigating the occurrence of molecular associations between sterols and fatty anions. Positive results were obtained not only with cholesterol but also with other sterols (a) possessing both a free 3β-OH group and a planar structure; (b) devoid of supplementary methyl groups (lanosterol); (c) having no additional hydrophilic group on the aliphatic chain, a structural feature which suppresses the amphiphilic character. In the system sterols/Na oleate/water, MF are obtained with several naturally occurring membrane sterols (cholestanol, zymosterol, β-sitosterol, stigmasterol, fucosterol . . .) and with some biological equivalents or phylogenic precursors of cholesterol (cycloartenol, α-amyrine, bacterio-hopane tetrol . . .).

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SIGNIFICANCE OF LIPIDS OF SCOTOCHROMOGENIC MYCOBACTERIA FOR THEIR IDENTIFICATION, TAXONOMY, AND IMMUNOSTIMULATING PROPERTIES. M. Mára, J. Julák, Z. Miková and C. Michalec, Laboratory for Medical Microbiology and Immunology, Charles University, Faculty of Medicine, Studničkova 7, 128 00 Praha 2, CSSR.

In 22 collection strains of scotochromogens (pigmented, non-pathogenic, slowly growing mycobacteria), the characteristic markers of organisms identified by biochemical tests as *M. gordonae* were the presence of 2-methyltetradecanoic acid and absence of tuberculostearic acid (determined by GC-MS), as well as growth in cords. These markers were absent in *M. flavescens* and *M. scrofulaceum*. Moreover, the pattern of mycolic acids (by one- and/or two-dimensional TLC of free acids) differed among these three species and from other mycobacteria. *M. gordonae* did not contain greater amounts of petroleum ether-extracted components (crude cord-factor according to Bloch) than the "non-cord" *M. flavescens* and *M. scrofulaceum*, but had greater amounts of mycolic acids in extracts. The immunostimulating potency of scotochromogens was found in mice infected by Listeria monocytogenes. This potency did not depend on the total lipids content of mycobacteria, but it depended on the ratio of two main spots in the mycolic acids pattern. The preventative as well as therapeutic antitumor potency (sarcoma 180 in mice) did not differ significantly among mycobacterial species, but some strains of *M. gordonae* seem to be more suitable for the immunotherapy of tumors.

98

MEMBRANE-BOUND PROTEINS AS PROBES OF THEIR PHOSPHOLIPID ENVIRONMENTS. David Zakim and Yehosua Hochman, 151K/Veterans Administration Medical Center, 4150 Clement St., San Francisco, CA 94121.

The lipid environments of membrane-bound proteins can be integral components of their regulatory apparatus. It is important to define these interactions not only as a first step in understanding the regulation of such proteins, but also because the properties of membrane-bound proteins could serve as probes of local environments in membranes. Enzyme-phospholipid interactions modulate several properties of UDP-glucuronyltransferase (GT) in liver microsomes. Activity of GT in intact, untreated microsomes, and several kinetic properties unrelated to catalytic steps, are altered when microsomes are treated with detergents or phospholipases; and the function of pure, delipidated forms of GT is determined by the type of phospholipid used to reconstitute activity. Especially interesting is that GT in intact microsomes has non-Michaelis-Menten kinetics and is sensitive to allosteric activation by UDP-N-acetylglucosamine (UNAG). These properties disappear after disruption of microsomes with detergents and phospholipases, and are absent from pure, delipidated GT. The data pose the question: what type of phospholipid environment reconstitutes a form of GT with properties similar (or identical) to those of enzyme in intact, untreated microsomes? GT with non-Michaelis-Menten kinetics and sensitivity to activation by UNAG is reconstituted by adding GT to bilayers of phosphatidylcholine that are in a gel phase. Warming the bilayers to the temperature for the gel-to-liquid crystalline phase transition is associated with an abrupt change from non-Michaelis-Menten kinetics to Michaelis-Menten kinetics and a loss of sensitivity to activation by UDP-N-acetylglucosamine. Since reconstitution of pure GT with "physiologic" properties can be accomplished with some, but not all, phospholipid environments, it seems reasonable to conclude that the function of GT in intact microsomes is a probe of its lipid environment. Thus, we conclude that GT in intact microsomes at 37 C is present in a gel-phase phospholipid. This result is contrary to expectations, based on experiments with exogenous probes (fluorescence NMR, ESR) and calorimetry, and suggests that some of the phases in a microsome are not susceptible to detection by exogenous probes. Detailed information about the heterogeneity of organization of microsomal phospholipids may be obtainable only by purification of integral proteins whose function appears to depend on interactions with microsomal phospholipids, followed by development of model systems that duplicate the properties of these proteins as they exist in intact, untreated microsomes. (This work was supported by a grant from the National Science Foundation, No. PCM8204270).

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PHOTOLABELING FROM INSIDE THE BILAYER REVEALS FACTORS AFFECTING PROTEIN INSERTION. Bernadine J. Wisnieski, Dept. of Microbiology and The Molecular Biology Institute, University of California, Los Angeles, CA 90024.

Photolabeling with the glycolipid probe 12-(4-azido-2-nitrophenoxy)-stearoyl-1-^{14}C-glucosamine has allowed us to identify the domains of protein toxins which penetrate the membrane bilayer. Studies have been done with both artificial and biological membrane targets. The proteins analyzed include cholera toxin ($A_1A_2 5B$), ricin toxin (AB), and the membrane attack complex of human complement (C5b-9). Our experimental protocol allows us to monitor the kinetics of protein insertion and to determine whether factors which affect toxicity, such as pH or temperature, operate at the level of insertion. We have found that both subunits or ricin toxin can penetrate the bilayer, even when isolated and tested individually. In addition, ricin A subunit binding and penetration is apparently not receptor mediated (not blocked by galactose; does not require ganglioside GM_1 in vesicle studies). Ricin subunit penetration continues at 0 C but at a slower rate than at 37 C. With cholera toxin and complement proteins, we have found that the extremely rapid insertions that occur at 37 C are completely blocked at 0 C. At permissable temperatures, only the A_1 subunit of cholera toxin inserts. During assembly, all five terminal components of complement insert, but when C9 is added to vesicles containing preassembled C5b-8, C9 inserts as rapidly as has been measured (5 sec) and displaces all previously inserted components. Use of thrombin-cleaved C9 has allowed us to localize the inserting domain as a region in the carboxy-terminal half of C9 (C9b). Lytic poly-C9 complexes built up by a heat aggregation method, in the absence of C5b-8, are likewise only anchored through the C9b portion of the molecule. At present we are trying to identify the photolabeled regions of the A_1 subunit of cholera toxin and of the ricin A and B chains (all are sequenced). We intend to relate these domains to 3-D structures to see if conformational changes are involved in the entry processes. Use of defined lipid vesicles has been very helpful in these studies because they enable us to examine the role of membrane structure and composition on the protein insertion processes involved in membrane biogenesis, toxin assembly and entry.

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INFLUENCE OF BOND LOCATION ON THE EFFECTIVENESS OF ACYL CHAINS. William E.M. Lands, Dept. of Biological Chemistry, 1853 W. Polk, A-312, Chicago, IL 60612.

An auxotrophic mutant of *E. coli* that is unable to synthesize or oxidize unsaturated fatty acids is a useful tool for examining the consequences of specific alterations in acyl chain structure. These cells respond to very slight geometrical and positional differences in the structure of acyl chains, discriminating among *cis,trans*, acetylenic and cyclopropane groups. Studies of the contribution of the acyl chain to membrane fluidity and to metabolic regulation indicated different conditions in which either the former or the latter may dominate cell growth. The acyl chain contribution to fluidity appears to limit cell growth only when there is sufficient cAMP in the cells. In this latter situation, only the physical features of the fatty acid isomers seems to influence cell yields and the model system provides a rough index of the degree to which a given isomer can contribute to membrane fluidity. On the other hand, with limited cellular cAMP levels, the highly specific discrimination by the mutant reflects the ability of certain isomers to release the cells from catabolite repression.

Session O Enzymatic Reactions in Flavor Development — I Tuesday a.m.

101

OXYGEN-ISOTOPE EFFECT IN ENZYMATIC CLEAVAGE REACTION OF 13-L-HYDROPEROXYLINOLEIC ACID TO HEXANAL. Akikazu Hatanaka, Tadahiko Kajiwara and Jiro Sekiya, Department of Agricultural Chemistry, Faculty of Agriculture, Yamaguchi University, Yamaguchi 753, Japan.

An oxygen-isotope effect was first observed during the cleavage reaction of ^{18}O-labeled 13-L-hydroperoxylinoleic acid into *n*-hexanal by hydroperoxide lyase (E_2'') solubilized with Tween 20 from tea chloroplasts. The incubation of the unlabeled hydroperoxide (6 μmol) with solubilized E_2'' (1 mL) for 10 min at 35 C, resulted in 1.2 μmol of hexanal formation, whereas 0.5 μmol of hexanal was formed from the ^{18}O-labeled hydroperoxide. This finding is supported by monitoring the course of the reaction with decrease at 234 nm; the unlabeled hydroperoxide cleaved faster ca. 2.6 times than the ^{18}O-labeled hydroperoxide did. A significant difference was found between the percentage of ^{18}O-C of TMS ether derivative from the recovered hydroperoxide after incubation of the ^{18}O-labeled hydroperoxide and that of the peroxide for the substrate; the purity of ^{18}O-C of the recovered hydroperoxide increased after incubation. With tea chloroplasts and homogenate of tea leaves and watermelon seedlings, hexanal formation from the labeled hydroperoxide was 44-54% of that from unlabeled hydroperoxides.

102

THE BIOSYNTHESIS OF JASMONIC ACID: A PHYSIOLOGICAL ROLE FOR PLANT LIPOXYGENASE. Brady A. Vick and Don C. Zimmerman, Department of Biochemistry, North Dakota State University, Fargo, ND 58105.

Isotope labelling studies with linolenic acid and the pericarp of *Vicia faba* L. have shown that linolenic acid is the biosynthetic precursor to jasmonic acid, a 12-carbon monounsaturated fatty acid containing a cyclopentanone ring. Intermediates which have been isolated and characterized are: 13-hydroperoxylinolenic acid, formed by lipoxygenase catalysis; 12-oxo-phytodienoic acid, resulting from a hydroperoxide cyclase enzyme reaction; 12-oxo-phytoenoic acid, in which the ring double bond was saturated by a reductase enzyme; dihomojasmonic acid, formed by the loss of four carbons from the carboxyl end of 12-oxo-phytoenoic acid, presumably by β-oxidation; and jasmonic acid, the final product resulting from the cleavage of two additional carbons from the carboxyl end of the molecule. Jasmonic acid has recently been identified as a plant growth regulator which promotes senescence. A physiological role for plant lipoxygenases in plant growth regulation has now been established.

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SEASONAL CHANGES IN THE FOUR ENZYME ACTIVITIES CONCERNING WITH FORMATION OF VOLATILE C_6-COMPOUNDS FROM LIPIDS IN TEA PLANTS. Jiro Sekiya, Tadahiko Kajiwara and Akikazu Hatanaka, Department of Agricultural Chemistry, Faculty of Agriculture, Yamaguchi University, Yamaguchi 753, Japan.

Volatile C_6-compounds such as hexanal, hexanol, *cis*-3-hexenal, *cis*-3-hexenol and *trans*-2-hexenal are products of a sequential degradation of plant lipids and are flavor components characteristic to row tea leaves. These compounds were produced in summer leaves much more than in winter leaves. We examined the activities of four enzymes, lipolytic acyl hydrolase (LAH), lipoxygenase, hydroperoxide lyase (HPO lyase) and alcohol dehydrogenase (ADH), of tea leaves (*Thea sinensis* cv. Yabukita) throughout the year. LAH and lipoxygenase show high activities in summer leaves and low or no activities in winter leaves. On the other hand, HPO lyase activity was slightly higher in winter leaves than in summer leaves, but even in summer leaves the activity was sufficient to convert formed 13-hydroperoxides of linoleic and linolenic acids to C_6-aldehydes. Thus the activity changes in LAH, lipoxygenase and HPO lyase can elucidate seasonal changes in total amounts of C_6-aldehydes. ADH activity pattern shows low activity in summer leaves and high in winter leaves. Based on the analysis of tea leaf essential oil, the ratios of alcohols to aldehydes were low in summer leaves and high in winter leaves. ADH activity changes are consistent with the results of essential oil analysis. In conclusion, seasonal changes in the amounts of C_6-aldehydes and C_6-alcohols formed are correlated to seasonal changes in the enzyme activities.

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THE FORMATION OF 1-OCTEN-3-OL IN MUSHROOMS. Deutsche Forschungsanstalt für Lebensmittelchemie, Lichtenbergstrabe 4, 8046 Garching, West Germany.

The unsaturated alcohol (-)-1-octen-3-ol contributes significantly to the flavor of edible mushrooms. A method has been developed by which 1-octen-3-ol can be rapidly and quantitatively analyzed. Using this method, variations in the rate of 1-octen-3-ol formation with mushroom type and storage time have been demonstrated. Experiments with ^{14}C-labeled linoleic acid indicated that mushrooms contain an enzyme system which oxidatively cleaves this substrate into 1-octen-3-ol and 10-oxo-*trans*-8-decenoic acid. The enzyme system was solubilized and enriched by precipitation and gel chromatography. Full experimental details and results to date will be reported.

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MEMBRANE-ASSOCIATED, ENZYME-CATALYZED LIPID PEROXIDATION IN MUSCLE. H.O. Hultin, University of Massachusetts Marine Station, Box 128 Lanesville, Gloucester, MA 01930-5828.

A microsomal fraction can be isolated from muscle tissue that carries out an enzymic-catalyzed peroxidation of the membrane lipids. Iron and NAD(P)H are absolute requirements for this lipid peroxidation, and it is enhanced by compounds such as ADP or ATP. The microsomal fraction from chicken muscle utilizes NADPH better than NADH, whereas the fish system has an almost absolute requirement for NADH. Separation of proteins from fish microsomes has been accomplished by fractional solubilization with detergents, isoelectric focusing, and polyacrylamide gel electrophoresis. The peroxidative activity of the membrane has been assigned to a single band of protein on the electrophoretic gel representing some 2% of the membrane protein. The fish muscle microsomal fraction shows a high rate of lipid oxidation at low temperatures compared to the avian. It is not known at this time whether this is due to the enzymes or to the nature of the lipid substrates. Fish muscle microsomal systems retain a considerable portion of their activity in the frozen state; the extent of oxidation is inversely related to the temperature. Hydrolysis of the lipids of the fish membrane by phospholipase A_2 causes inhibition of both enzymic and nonenzymic lipid oxidation processes. Potent antioxidative systems of both high and low molecular weight are found in the supernatant fraction of the fish muscle and may play a role in controlling the rate of oxidation in vivo.

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ELIMINATION OF LIPOXYGENASE ISOZYMES FROM SOYBEAN BY GENETIC SELECTION. N.C. Nielsen, J.R. Wilcox and C.S. Davies, Agronomy Department, Purdue University, West Lafayette, IN 47907.

Soybean lines lacking lipoxygenase-1, lipoxygenase-2 and lipoxygenase-3 have been identified using electrophoretic and immunological techniques. Null-alleles for lipoxygenase-1 ($1X_1 1X_1$) and lipoxygenase-3 ($1X_3 1X_3$) are inherited as single gene recessives and appear to be unlinked. Lines bearing the $1X_2 1X_2$ genotype have only recently been identified and progeny from crosses designed to study the genetic inheritance of this allele are now being grown. Seeds bearing the genotype $1X_1 1X_1 1X_3 1X_3$ are viable and produce plants which appear normal. The lipoxygenase null-alleles are being introduced into well adapted agronomic material, as well as into a line which has a low linolenic acid content (ca. 3%). The latter line was obtained by mutation breeding and the low 18:3 level has remained stable through several generations of selfed progeny. The molecular basis for the loss of lipoxygenase activity is also being investigated.

Session P New Protein Sources — I Tuesday a.m.

107

FUTURE PROSPECTS FOR THE USE OF WINGED BEAN PROTEIN SOURCES. John W. Erdman Jr. and S. Sri Kantha, 567 Bevier

Hall, 905 S. Goodwin Avenue, University of Illinois, Urbana, IL 61801.

Despite the high protein content in its ripe seeds, tubers and leaves, in the range of 29.3-39.0, 3.0-15.0 and 5.0-7.6% (fresh weight), respectively, and the high quality of that protein, the winged bean *Psophocarpus tetragonolobins* remained somewhat obscure as a food source until about ten years ago. In the last decade, this legume has received increasing attention from scientists due to its potential multidimensional use as a utilizable protein source in the humid tropics. This review presents information largely published during the last ten years on the nutritional literature of winged bean. This review covers the following aspects related to protein: (a) classification of winged bean proteins; (b) nutritional properties, including the antinutritional components of the winged bean protein; (c) protein quality; (d) functional properties; and (e) protein-based food products. Since the oil content of the winged bean seeds range from 15.0 to 20.4%, the use of winged bean as a potential oil seed crop is discussed. Some questions that have not been given adequate attention by researchers to date are elaborated upon and relevant areas of needed research are identified.

108

CRAMBE MEAL AS A PROTEIN SOURCE FOR FEEDS. Kenneth D. Carlson and Harvey L. Tookey, Northern Regional Research Center, Agricultural Research Service, US Department of Agriculture, Peoria, IL 61604.

Crambe abyssinica may be grown as a source of seed oil containing 55-60% erucic acid to fill a long-term, technologically important US industrial market. Until the recent worldwide trend toward low or "zero" erucic acid varieties of rapeseed, this market was filled by imported high-erucic-acid rapeseed oil. Like other Cruciferae, crambe seeds contain glucosinolates that limit the feeding value of the defatted meal, which contains 25-31% protein (with hulls; 46-58% protein without hulls) and have a favorable amino acid composition in terms of lysine and sulfur-containing amino acids. A number of processing methods have been explored for improving the feed value of crambe meal. These include conventional prepress/solvent and solvent extraction of the oil, and less conventional processes involving chemical treatments, water or aqueous solvent extractions of the glucosinolates, or heat treatments of various types including microwave processes. Feeding trials with conventionally processed meals resulted in FDA approval of these types of meals as protein supplements in beef cattle rations. Nutritional quality of unconventionally processed meals has been evaluated in rat or chick feeding experiments. These studies and the status of crambe as a protein source in feeds will be reviewed.

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POTENTIAL OF WILD OATS AS A HIGH PROTEIN FOOD. Frank W. Sosulski, Department of Crop Science & Plant Ecology, University of Saskatchewan, Saskatoon, Saskatchewan, S7N 0W0, Canada.

Wild oats are a common weed in cultivated crops and substantial quantities are separated with other weed seeds during grain cleaning operations. It is possible to obtain weed fractions which are primarily wild oats and these fractions can be dehulled and processed much as is done with domestic oats. When the hulls are removed, the groat is found to contain over 20% protein as well as 8-9% of lipids and 55% of starch. The proteins are balanced in essential amino acid content, being high in lysine and sulfur-containing amino acids. The neutral lipids constitute 87% of the crude oil fraction, the fatty acid composition being 14% palmitic, 47% oleic and 37% linoleic acids. In total, the wild oat groat represents an excellent nutritional package which should be utilized in infant and dietary foods where its low allergenicity and high protein content offer advantages over other protein sources.

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IMPROVED USE OF DISTILLERS' GRAINS AND OTHER ALCOHOL FERMENTATION BYPRODUCTS IN FOODS AND FEEDS. J.S. Wall, Y.V. Wu, G.N. Bookwalter, R.J. Bothast and A.A. Lagoda, Northern Regional Research Center, Agricultural Research Service, US Department of Agriculture, 1815 North University Street, Peoria, IL 61604.

The widespread acceptance of ethanol as a liquid fuel supplement and economic concessions to protomote utilization of surplus grains by fermentation have increased availability of distillers' grains and other high-protein byproducts of alcohol production. To reduce alcohol costs, three objectives of byproduct utilization are being targeted: (a) lower energy requirements and costs in drying and processing; (b) broader feed markets; and (c) food uses. After distillation, the stillage contains only 9% solids, of which 70% insolubles can be removed by screening and centrifugation to yield corn distillers' grains (CDG). The corn distillers' solubles (CDS) solution containing 2% solids must be evaporated. Considerable savings in cost and energy can be achieved when CDS solutions are recycled several times into subsequent fermentation media or concentrated by ultrafiltration and reverse osmosis. CDG is high in protein (26%), lipid (12%) and crude fiber (14%), but the protein is poor in lysine and has low digestibility and solubility. For ruminants, these properties result in rumen bypass and increased protein utilization. For growing swine, CDG must be mixed with equal amounts of soy meal. Dry milling and sieving CDG concentrates protein in the fine fractions. Acceptable specialty breads containing 10% CDG have been prepared. About 7% CDG can be incorporated into corn-soy-milk blended foods with acceptable PER and fiber content for children.

111

HYPERPRODUCTION OF SPECIFIC PROTEINS THROUGH RECOMBINANT DNA TECHNOLOGY. Klaus M. Herrman, Department of Biochemistry, Purdue University, West Lafayette, IN 47907.

Animal diets based on corn and other cereal grains are limited in nutritional value by their content in certain amino acids such as lysine and tryptophan. Although recombinant DNA technologies, some time in the future, may allow construction of genetic variants of these grains that satisfy all nutritional requirements, a more feasible approach today is to use the available technology to synthesize by fermentation such feed supplements as amino acids. We have used recombinant DNA technologies to construct several strains of the bacterium *Escherichia coli* with the potential to produce in large quantities the aromatic amino acids phenylalanine, tyrosine, and tryptophan. In order to measure the actual amounts of amino acids produced by these microorganisms under various conditions, we use nuclear magnetic resonance spectrocopy of whole bacterial cells. This is a new noninvasive technique that yields directly in vivo metabolic information without influencing or disturbing the metabolism of the organism at all. The combination of gene splicing techniques with whole cell NMR, first done at Purdue, represents today's most powerful analytical tool for investigations of microorganisms with fermentation potential.

Session Q Surfactants: Performance and Evaluation – I Tuesday a.m.

112

CONSUMER TESTING – FORCE OR FARCE? A.H. Gilbert, Lever Bros. Research, Edgewater, NJ. Abstract not available at press time.

113

AN APPROACH TO FORMULATING COLD WATER LAUNDRY PRODUCTS. Ted P. Matson and Michael F. Cox*, Conoco Inc., PO Box 1267, Room 148 RDW, Ponca City, OK 74603.

Optimum laundry formulations for cold water detergency performance were determined by evaluating trilinear mixed active systems. Temperature and hardness effects were studied on several different soils and substrate combinations. The effect of builder type on the optimum formulation was also examined. Triangular charts graphically illustrate these optima and allow for superimposition of cost lines for determination of cost/performance.

114

CHEMICAL STUDIES OF ZEOLITE CONTAINING DETERGENTS. Ramon A. Llenado, Procter & Gamble Ivorydale Technical

Center, Cincinnati, OH 45217.

Sodium type A zeolite is a synthetic crystalline aluminosilicate that has been recently developed and commercially introduced as a detergent builder. This paper describes a number of studies done to characterize zeolite A as a cost-effective partial replacement for phosphate. Solution studies of zeolite A are presented, e.g., hardness exchange, and the effect of cobuilders, surfactants, and other electrolytes; and the results are correlated with detergency. Solid state properties, e.g., particle size, crystallinity, degree of hydration, are also related to detergency. The talk concludes with some studies demonstrating material safety and favorable biodegradation fate.

115

REDEPOSITION OF NATURAL SOILS IN A HOME LAUNDRY TEST. George C. Feighner, Scientific Services, 5 Fir Court, Oakland, NJ 07436.

A procedure for measuring the redeposition of natural soils onto clean fabrics was developed. Laundry bundles of paired articles from typical homes were divided and washed under controlled conditions using the pair of laundry products being compared. Large swatches of fabrics (unsoiled) were included in the laundry load. After washing and drying, small swatches of the test fabrics were cut out for measurement of reflectance and judging by a panel. Twenty repetitive cycles were run. The results demonstrate that the procedure will discriminate between similar products. Conditions used for the test gave very high levels of soil removal as was shown by the amount of soil removed from standard soiled swatches included in the laundry load. The effect seen in this test is similar to the overall soil build-up which occurs on articles compared in the Laundry Bundle Test ASTM D-2960. However, the bundle test is a very time-consuming procedure, whereas the test described here can be run at the rate of several cycles per day.

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OPTIMIZATION OF NONIONIC SURFACTANTS FOR HARD-SURFACE CLEANING. Ted P. Matson and Michael F. Cox*, Conoco Inc., PO Box 1267, Ponca City, OK 74603.

The performance of nonionics in hard-surface cleaning was evaluated as a function of molecular weight and ethylene oxide content. Various nonionic homologs were tested on several soils and soil substrates. The effects of blending and dilution were also examined. Results show molecular weight to be very important to hard-surface cleaning. Lower molecular weight nonionics averaging in the C_6-C_8 range show optimum performance. Ethylene oxide content is also important, particularly under dilute concentrations. A trade-off exists between performance at low concentration and nonionic water solubility.

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QUALITATIVE AND QUANTITATIVE EVALUATION OF ENZYMES IN HOUSEHOLD LAUNDRY PRODUCTS USING SOIL TEST CLOTHS. Brian P. Flynn and Marjorie L. Besemer, Purex Industries, 24600 S. Main St., Carson, CA 90745.

Several test cloths have been developed which provide a relatively easy means for qualitative determination of both protease and amylase in detergents, bleaches and other laundry products using detergency measurement techniques. With suitable controls, quantitative measurement of enzyme content is possible. The effects of wash temperature, enzyme concentration, type of builder, type of surfactant, wash time and water hardness on soil removal are discussed. Comparisons are also made between these cloths and commercially available soil test cloths.

118

THE USE OF ENZYMES IN POWDERED DETERGENTS, REVIEW AND FUTURE DEVELOPMENTS. Gert H. de Raaff, Gist-Brocades N.V., Wateringseweg 1, 2611 XT Delft, Holland.

This paper describes the developments of detergent enzymes throughout the 1970s as well as the expected developments in the coming years. Alkaline proteases were introduced in the late 1960s to improve the performance of detergents. These proteases are generally used in European detergent formulations and find an increasing acceptance in the USA. Over the last 15 years, the safety in the use of proteases has been greatly enhanced by the introduction of enzyme granulates and the subsequent improvement thereof. New developments in granulation and encapsulation technology are presented. Whereas up to now, the major enzyme used in detergents has been of the alkaline protease type, such as Maxatase®, new proteases and amylases are expected to become relatively more important in the coming years. Performance of high-alkaline protease and conventional alkaline protease are shown, notably under US washing conditions. Amylase performance is also discussed.

Session R Applications of Supercritical Fluids — I Tuesday a.m.

119

SOLUBILITIES OF SEED OILS IN SUPERCRITICAL CO_2 AS A FUNCTION OF TEMPERATURE AND PRESSURE. John P. Friedrich and James H. Johnson, Northern Regional Research Center, ARS, USDA, 1815 N. University Street, Peoria, IL 61604.

Contrary to previous theory, at temperatures above 60 C the solubility of seed oils increases dramatically with increasing pressure above 10,000 psi. The apparent maximum solubility, as determined from extraction of the flakes or ground seed, is mass transfer controlled and varies with seed type, configuration and morphology. Below this apparent maximum, all extracted seed triglycerides exhibited the same equilibrium solubilities under identical conditions of temperature and pressure. The rapid response of solubility to temperature and/or pressure allows much faster extraction rates and provides more economical methods of oil recovery. Because CO_2 is relatively incompressible at high pressure, recompression (pumping) costs are greatly reduced and the oil can be recovered by slightly reducing the pressure at constant temperature. Alternatively, reducing the temperature at constant pressure also affords good oil recovery.

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EFFECT OF MOISTURE AND PARTICLE SIZE ON THE EXTRACTABILITY OF OILS FROM SEEDS USING SUPERCRITICAL CO_2. J.M. Snyder*, J.P. Friedrich* and D.D. Christianson*, Northern Regional Research Center, Agricultural Research Service, US Department of Agriculture, Peoria, IL 61604.

Extractions of vegetable seeds with supercritical carbon dioxide were carried out at constant temperature (50 C) and pressure (8000 psig) while varying the moisture level and particle size. Extractions of soybeans were examined extensively; other seeds studied included peanuts and cottonseed. The rate of extraction and ultimate oil yields were quite low with cracked soybeans; however, good extraction rates and nearly theoretical oil yields were obtained from ground or thinly flaked (<0.010") seeds. Moisture levels between 3% and 15% had little effect on extractability. Oil composition was not influenced by either parameter. Scanning electron microscopy was used to study seed structure before and after extraction with supercritical CO_2.

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SOLUBILITY PARAMETERS OF SUPERCRITICAL FLUIDS FROM PRESSURE-VOLUME-TEMPERATURE DATA. Robert L. Eissler, Joseph M. Ritter and John P. Friedrich, Northern Regional Research Center, Agricultural Research Service, US Department of Agriculture, Peoria, IL 61604.

The solubility parameter is of great practical value in predicting solubilities in systems at atmospheric pressure and room temperature. Through empirical expression, the estimation of these parameters allows extension of the concept to some supercritical fluids. The true solubility parameter is related to the internal pressure which can be directly determined from pressure-volume-temperature data. With a program written in Fortran IV and literature data, the solubility parameter for supercritical carbon dioxide has been computed at temperatures ranging from 40 to 100 C and for pressures up to 21,000 psi. Parameter values determined for supercritical CO_2

directly from pressure-volume-temperature data are somewhat lower than those given by the usual empirical expression for corresponding conditions. It appears possible to compute solubility parameters for other supercritical fluids in the proper temperature and pressure range by slight modifications of the computer program.

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GENERALIZED EXTRACTION CONDITIONS FOR THE CRITICAL FLUID PROCESSING OF OILS AND OLEOPHILLIC COMPOUNDS. J.W. King, 211 Sunset Terrace, Crystal Lake, IL 60014.

Rigorous examination of the available literature data and its correlation utilizing a combination of a reduced states/solubility parameter approach has permitted the formulation of generalized experimental conditions for extracting and fractionating industrially important oils and their constituents. Such an approach permits the evaluation of both the chemical nature of the gas as well as the magnitude of compression on the solvent power of the critical fluid. Results will be presented that show the strong dependence of the equilibrium solubility and hence the quantity of oil extracted on the gas solubility parameter. Modest yields of oil can be obtained at reduced densities in the range of 1.5-1.7; however, maximum yields are realized only at reduced densities approaching 2.0. Hence, for the extraction of such oils as soybean, sunflower, copra, and corn, the solubility of the gas phase must lie between 6-8 Hildebrands, a value which compares favorably with prefered liquid extractants. Reported deodorization schemes utilizing propane and CO_2 occur at much lower gas densities, usually yielding solubility parameters in the range of 2-4 Hildebrand units. Selective fractionation of oil constituents can be accomplished when the solubility parameter of the gaseous phase is adjusted between 3 and 7, where individual solutes commence migration at specific "threshold pressures." Such behavior has permitted the partial fractionation of sterols from steryl esters and the separation of the triglyceride fraction from the diglycerides. Discrete solubility maxima will be noted for pure solutes such as stearic acid and steryl esters dissolved in critical fluids having reduced solubility parameters approaching unity. Finally, the advantage of incorporating an entraining agent into the critical fluid will be rationalized on the basis of regular solution theory and illustrated for specific systems in which increases of the order of 2 $(cal/cc)^{1/2}$ are possible.

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CALORIMETRIC DETERMINATION OF HEATS OF MIXING OF SUPERCRITICAL CO_2 WITH SEVERAL ORGANIC LIQUIDS. Reed M. Izatt, John L. Oscarson and James J. Christensen, Thermochemical Institute, 267 FB, Brigham Young University, Provo, UT 84602.

A flow calorimetric procedure has been used to determine heats of mixing over the entire mole fraction range of several fluids (CO_2 and freons) near their critical points with several different hydrocarbons. A significant feature of these data is the large exothermic heat of mixing associated with reactions near the critical locus of the fluids being mixed. The procedure used and the information about the reacting species which can be obtained will be described. Flow calorimetry is also useful in detecting two phase regions and in determining the mole fractions at which these occur. Possible application of the results to understanding solvent properties of supercritical fluids will be discussed.

Session S Operating Expertise in Oil Processing Tuesday a.m.

124

SOYBEAN OIL. David R. Erickson, American Soybean Association, PO Box 27300, St. Louis, MO 63141.

The growth and present stature of soybeans and soybean oil production and utilization in the world and in the USA is presented. The composition of soybeans and soybean oil is compared with other common vegetable oils. The current and optimal processing practices of extraction, degumming, neutralization (caustic and physical), hydrogenation, and deodorization are discussed. Where appropriate, new and innovative approaches will be introduced. Utilization of soybean oil is covered, followed by a historical and present view on the subject of soybean oil flavor. Present and future nutritional considerations of soybean oil concludes the presentation.

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COTTONSEED OIL. G.C. Cavanagh, Ranchers Cotton Oil, PO Box 2596, Fresno, CA 93745.

A brief review of the significant innovations and patents that resulted in cottonseed oil becoming one of the stable worldwide sources of edible vegetable oil is presented. This is followed by a report on the current state of the art for refining cottonseed oil, including conventional refining, miscella refining and winterization, and viable alternatives for physically refining cottonseed oil.

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CANOLA OIL. Theodore K. Mag, Canada Packers Inc. Research Centre, 2211 St. Clair Ave. W., Toronto M6N 1K4, Canada.

Canola is a registered trademark of the Canola Council of Canada for the seed, oil and meal derived from rapeseed cultivars low in erucic acid and low in glucosinolates. The name "canola" denotes a significant quality improvement over oil and meal derived from previously grown seed. Conversion to canola cultivars on a commercial scale started in 1976; in 1981, ca. 87% of the brassica-based oil crop was of canola quality. Processing of canola oil follows that of other vegetable oils very closely. Water degumming, alkali refining, bleaching, hydrogenation and deodorization are the standard processing steps. Suitable modifications, such as the use of phosphoric acid as a pretreatment for alkali refining and the use of acid-activated clay, especially suited for chlorophyll removal, take account of differences to other oils. No significant changes in this approach have occurred in the past few years. New developments are now under way in degumming technology. Processes were developed which produce crude oil at phosphorus concentrations below 50 parts per million. The production of this specially degummed oil is expected to lead to significant economies in alkali-refining and soapstock acidulation, and improve the possibilities for physical refining of the oil.

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SUNFLOWER OIL. Edward J. Campbell, Archer Daniels Midland Co., Decatur, IL 62525.

The presentation will cover sunflower oil, its fatty acid composition and analytical characteristics; its uses, its application in products and the advantages and problems associated with its use. Specific processing conditions, including flow diagrams, to produce satisfactory finished products are discussed. The presentation emphasizes developments since 1976, anticipated changes in technology and a forecast of changes that may lie ahead.

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PLANT PRODUCTION OF HYDROWINTERIZED SOYBEAN OIL. D.C. Tandy and N.M. LeBard, c/o EMI Corporation, 3166 Des Plaines Avenue, Des Plaines, IL 60018.

Partial hydrogenation and winterization of refined soybean oil is an important step to produce a stable ingredient for use in a variety of oil products including salad dressings, cooking oils and mayonnaise. The hydrogenation step is used to eliminate the linolenic acid which has been credited with causing the flavor reversion common to soybean oil, and when this hydrogenated oil has been winterized, the resultant product will meet the required cold test and will not cloud when stored for a prolonged period at refrigeration temperatures. This paper will discuss the plant production of hydrowinterized soybean oil with particular emphasis on a recent installation that contained new features to conserve energy and produce higher yields. The typical process was modified to preheat each incoming batch with the previous completed batch and direct expansion of ammonia was used for cooling in the winterizing system for additional energy conservation. In addition, the stearin and liquid oil fractions were separated in a special filter designed to "squeeze" the stearin cake to provide increased yield of liquid oil and reduced loss in the cake.

129

ALTERNATIVES IN SOAPSTOCK UTILIZATION. John B. Woerfel, 141 McGuire Cove, Clarksdale, MS 38614.

Soapstock is a valuable byproduct from the alkali refining of edible oils. Methods of processing at the refinery to make it suitable for use as an animal feed ingredient or for further industrial processing are discussed. Utilization as a feed fat and as an industrial raw material are reviewed.

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A REVIEW OF SAFETY HAZARDS IN EDIBLE OIL PROCESSING. Joseph Anglin, PSI Process Systems, Inc., 4466 Elvis Presley Blvd., Suite 300, Memphis, TN 38116.

Considerable progress has been made in the last five years in engineering and designing safer edible oil processing plants. Many improvements have been made to reduce injury or loss of life through process automation. Although this greatly reduces exposure to dangerous conditions, many hazards still exist. It has been established that 80-90% of all industrial accidents are a result of unsafe acts rather than unsafe conditions. This paper will deal with each step of the edible oil process reviewing the potential hazards that face plant personnel. A brief review will be presented of existing safety hazards involved in the bulk handling of chemicals, tank car cleaning and loading, refining, bleaching, hydrogenation, deodorization, and maintenance.

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THE MULTIPLE PIPE CONTINUOUS BLEACHING SYSTEM. K. Weber, Extraktionstechnik GmbH, Hamburg, Germany.

The multiple pipe contibleach system introduced 15 years ago in refineries and having been built more than 20 times with capacities from 50 to 300 tpd has been developed continuously to improve bleaching clay and energy savings. The theoretical basis of this almost unique bleaching system is described as well as the results obtained with a large variety of oils. Considerations are given to the flexibility, changing of parameters and this influence on oils to be treated. Particular emphasis is given to the possibility of heat recovery and the incorporation in existing refineries.

Session T Developments in Silver Ion Chromatography Tuesday a.m.

132

DEVELOPMENT OF ARGENTATION SEPARATIONS OF LIPIDS. C.R. Scholfield, 1116 W. Moss, Apt. 7-B, Peoria, IL 61606.

Based on earlier studies of Ag-olefin complexes, argentation methods for separation of methyl esters and of triglycerides by countercurrent distribution and by column and thin layer chromatography were first introduced about 20 years ago. Chromatographic methods with either $AgNO_3$-silica mixtures or silver ion on exchange resins as stationary phases have since been improved until now they are among the most useful methods for lipid separations. Techniques include both preparative methods and analytical high performance separations. The development of these methods will be summarized and some needs and possibilities for future improvements suggested.

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ACETONITRILE AS ELUENT IN ARGENTATION CHROMATOGRAPHY. W.J. DeJarlais, R.O. Adlof and E.A. Emken, Northern Regional Research Center, Agricultural Research Service, US Department of Agriculture, Peoria, IL 61604.

A disadvantage of the liquid column chromatography of unsaturated esters on supported silver salts, whether by silver ion on cation exchange resin (silver resin) or silver nitrate on silica, is the inconveniently long retention times of the more unsaturated esters. With silver resin chromatography using methanol or acetone as solvents, elution times of polyunsaturated esters may be shortened by the technique of partial argentation resin chromatography (or PARC) in which silver ions partially replace the sodium or hydrogen ions of a macroreticular exchange resin. Such columns give poor separations of esters of a wide range of unsaturation. Esters of less unsaturation than optimum for the column have too little retention for good resolution, while esters of greater unsaturation have retention times longer than desired on the column. A number of columns would therefore be required for such ester mixtures. By use of solvent programming with mixtures of acetonitrile in methanol, it was found possible to use one fully saturated silver resin column to separate esters having large differences in unsaturation. An advantage of this solvent combination is its compatability with UV detection. Thus, the separation of methyl oleate, linoleate, linolenate and arachidonate can be achieved within 3 hr by programming from 0 to 15% acetonitrile in methanol. Preparative separations (up to 800 mg/min) have been made using isocratic mixtures of acetonitrile and methanol or acetone and refractive index for detection. For example, methyl linoleate has been separated from safflower oil methyl esters. In the separation of unsaturated esters on silver nitrate on silica where benzene has frequently been used, we found that acetonitrile used as modifier in hexane serves very well in controlling retention while allowing UV detection.

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FID RESPONSES OF GEOMETRICAL FATTY ACID ISOMERS WHEN ANALYZED BY $AgNO_3$ THIN LAYER CHROMATOGRAPHY (IATROSCAN-CHROMAROD) AND BY GAS LIQUID CHROMATOGRAPHY. J-L. Sebedio, T.E. Farquharson and R.G. Ackman, Canadian Institute of Fisheries Technology, Technical University of Nova Scotia, PO Box 1000, Halifax, Nova Scotia B3J 2X4, Canada.

A separation of methyl oleate (*cis*-18:1Δ9), elaidate (*trans*-18:1Δ9) and stearate (18:0) was obtained on Chromarods-S impregnated with silver nitrate, using a mixture of benzene and hexane as the solvent system. The FID responses for the Iatroscan analyses of the *cis* and *trans* isomers of methyl esters of 18:1Δ6, 18:1Δ9 and 18:1Δ11 were studied at concentrations ranging from 0.5 μg to 20 μg using methyl 18:0 as internal standard. The response of each *cis* and *trans* isomer was found to be linear in the range of 3-20 μg. However, the FID correction factor for the Iatroscan analysis was greater for the *cis* than for the *trans* isomer, the opposite of the results obtained when calculating the FID correction factor in gas liquid chromatographic analyses. The difference can be attributed to the types of complexes formed in absorption of the *cis* and *trans* isomers on the silver-nitrate rods. The main applications of the $AgNO_3$-TLC/FID technique are: the determination of *trans* content in common vegetable oil margarines, the separation of geometrical isomers of dienoic fatty acids in these and in partially hydrogenated marine oils, and the quantitation of the *trans,trans*-methylene-interrupted dienoic fatty acids in partially hydrogenated vegetable oils.

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SILVER-π COMPLEX CHROMATOGRAPHY IN THE ISOLATION AND PURIFICATION OF DITERPENE RESIN ACIDS. Duane F. Zinkel, Forest Products Laboratory, USDA, Forest Service, PO Box 5130, Madison, WI 53705.

Some of the earliest applications of silver-π complex chromatography were in the field of terpenes. For diterpene resin acids, the technique has largely been auxiliary to the other methods, providing another dimension in separation and purification. In the early 1960s, thin layer chromatography was applied to resin acids, successfully separating the two similar conjugated abietadienoic acid methyl esters, methyl palustrate and methyl levopimarate. At that time, these two esters could not be analyzed in admixture by gas chromatography. Column chromatography with silver nitrate on silica or alumina has been used to isolate and purify a large number of resin acid methyl esters including the numerous isomers of the monoene resin acids. Argentation chromatography with silver in the form of silver sulfonate resins allows separations of free resin acids and is not limited to esters as with silver impregnated absorbants. Examples of the various argentation methods are discussed.

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ISOLATION OF INTACT PHOSPHATIDYLCHOLINE PLASMALOGEN BY ARGENTATION- OR REVERSED-PHASE HPLC. William N. Marmer and Thomas A. Foglia, Eastern Regional Research Center, US Department of Agriculture, ARS, 600 E Mermaid Lane, Philadelphia, PA 19118.

Two different experimental approaches to the HPLC isolation of intact plasmalogens were the objects of investigation. The first approach took advantage of the uniquely electron-rich functionality of the plasmalogens – the vinyl ether double bond. This functionality has the ability to coordinate with such charge-transfer electrophiles as silver ion. A cation-exchange type HPLC column (sulfonic acid bonded to silica) was used to effect a separation of plasmalogen of bovine heart phosphatidylcholine (PC). Complete exchange of all active sites of the column with silver ion (Ag^+/PC = 4000) led to complete retention of PC. By charging the column with small increments of Ag^+, on the other hand, an effective Ag^+/PC ratio was established (=80) and the PC was separated into fractions according to the degree of unsaturation. Plasmalogen fractions eluted last and remained intact during the process. The use of an analogous system with mercuric ion led to on-column hydrolysis of the plasmalogen. The second approach to plasmalogen isolation took advantage of subtle differences in the hydrophobicity of the vinyl ether side-chain from the acyloxy counterpart. On a C-18 reversed-phase HPLC column, bovine heart PC was separated into a number of molecular species, one prominent fraction of which was intact plasmalogen. These instances of plasmalogen isolation are to our knowledge the first ever to have been reported.

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PURIFICATION OF TRIGLYCERIDES BY SILVER RESIN CHROMATOGRAPHY. R. Adlof and E.A. Emken, Northern Regional Research Center, Agricultural Research Service, US Department of Agriculture, Peoria, IL 61604.

Triolein, trilenolein, and trilenolenin were prepared by the sodium methoxide catalyzed interesterification of triacetin with the appropriate methyl ester. Yields ($\sim$70%) were higher than the coupling of the acid chloride and glycerol. This procedure also generated less byproducts than the *p*-toluene sulfonic acid catalyzed esterification of the fatty acids by glycerol (higher temperatures required). Multigram quantities of the prepared triglycerides were separated from their methyl esters on a 40 X 470 mm Michel-Millercolumn packed with $\sim$700 mL of silum-saturated XN1010 cationic resin. The solvents used were 100% acetone for oleate, 8.5% acetonitrile in acetone for linoleate, and 15% acetonitrile in acetone for linolenate. Silver resin chromatography was also used to separate triolein from oleic acid, trilenolein from linoleic acid and trilinolenin from linolenic acid. The unreacted fatty acid/esters are readily recovered for use in subsequent triglyceride synthesis.

Session U Pharmacological Role of Lipids – II Tuesday a.m.

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EFFECTS OF FATTY ACID DERIVATIVES UPON RELEASE OF EXTRACELLULAR ENZYMES FROM BACTERIA. J.R. Chipley*, F. Atchley and J.J. Kabara, United States Tobacco Co., Research and Development Division, Nashville, TN and Department of Biomechanics, Michigan State University, East Lansing, MI 48824.

The antimicrobial activity of certain fatty acids and their corresponding esters is well documented. Many derivatives of fatty acids have been prepared and screened in order to study the relationships of chemical structure to antimicrobial activity. From these studies, the potential of nitrogen-containing fatty acid compounds, alkyl amides and amines, was recognized. Yeasts and gram-positive bacteria are the most sensitive to these agents. Previous studies have involved determining the minimum inhibitory concentrations of fatty acid derivatives for microorganisms. The present study was designed to measure the effects of these compounds upon the release of extracellular enzymes from bacteria. Several genera of gram-positive and gram-negative bacteria were grown in defined media with and without added fatty acid derivatives. Formation of extracellular enzymes was monitored either by assaying cell-free supernates or by plating bacterial suspensions onto solid media containing the appropriate substrate. Cells were harvested from liquid media, washed, and disrupted with a French Press. Cell Walls were isolated, purified, and lipids extracted. Fatty acids were esterified and analyzed by gas liquid chromatography. Significant differences were observed both in the quantities of enzymes secreted into media and in the fatty acid content of isolated cell walls. Data from the present study indicate that changes in the permeability and/or composition of cell walls and membranes may occur as a result of bacterial growth in the presence of fatty acid derivatives.

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COMPARISON OF ANTIBACTERIAL PROPERTIES OF LAURICIDIN AND BHA AGAINST ANTIBIOTIC-RESISTANT AND SENSITIVE *Staphylococcus aureus* AND *Pseudomonas aeruginosa*.

D.V. Vadehra and V. Wahi, Department of Microbiology, Panjab, University, Chandigarh, India.

The minimum inhibitory concentrations (MIC) of antibiotic-resistant (clinical isolate, R) and antibiotic-sensitive (standard strains, S) of *Pseudomonas aeruginosa* were 160 and 75 μg/mL for lauricidin and the values for BHA were 115 and 145 μg/mL, respectively. However, the MIC values for antiobiotic-sensitive and antibiotic-resistant strains of *Staphylococcus aureus* were much lower: these were 10 and 20 μg/mL for lauricidin and 140 and 110 μg/mL for BHA. Differences in the slopes of death times curves were also observed and the values were 1.42, 2.90, 1.08 and 2.06, respectively, for *P. aeruginosa* R and S and *S. aureus* R and S with lauricidin. Similar studies with BHA gave the values of 2.57, 1.36, 2.80 and 1.60, respectively. The differences between R and S cells are probably due to the differences in permeability, as there was more leakage of the intracellular contents in the R cells than in the S cells. The involvement of the membrane as the target of action was also confirmed by the extensive leakage of hemoglobin from human and animal erythrocytes. Lauricidin also caused a 10% decrease in the specific activity of succinic, isocitrate and malate dehydrogenase. BHA, however, caused little or no change in the activity of these enzymes. It is not clear if this decrease has any relationship with the mode of action of the test compounds. The potential of lauricidin as antibacterial agent particularly for external application in antiseptic creams is quite evident because of their activity on suppurative organisms such as *S. aureus* and *P. aeruginosa*. However, these organisms under induced conditions in the laboratory became resistant to the action of lauricidin.

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INHIBITION OF *Staphylococcus aureus* IN A MODEL SAUSAGE SYSTEM BY MONOGLYCERIDES.

Jon J. Kabara, Department of Biomechanics, College of Osteopathic Medicine, East Fee Hall, Michigan State University, East Lansing, MI 48824.

A sterile agar-meat sausage system was used as a model food system and seeded with *Staphylococcus aureus*. Two new monoglycerides, which are GRAS emulsifiers, caused both static and cidal effects on *S. aureus*. When compared to potassium sorbate, both Lauricidin® and Lauricidin®812 were more active. The presence of lactic acid was necessary for optimal biocidal activity. Inhibitory effects were generally greater on "anaerobic" than "aerobic" growth. These results indicate that special monoglyceride emulsifiers like Lauricidin® can be used to create environments in foods hostile to microorganisms without added preservatives. A review of Lauricidin® as an important new emulsifier to protect food will be presented.

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ANTIMICROBIAL PROPERTIES OF LAURICIDIN IN MECHANICALLY DEBONED CHICKEN, MINCED FISH AND CHICKEN SAUSAGE.

Robert C. Baker, Winnie Poon, Donna Kline and Dharam V. Vadehra, Department of Poultry and Avian Sciences, 200 Rice Hall, Cornell University, Ithaca, NY 14850.

Aerobic plate counts on Plate Count Agar at 25 C were used to determine the time required to reach a microbial spoilage level of 1.0×10^7 CFU/g, for mechanically deboned chicken meat, minced fish and chicken sausage stored at 2 C. The storage times were 5, 8 and 9 days, respectively. Addition of citric acid (0.2%), ascorbic acid (0.2%) or lauricidin (250 ppm) alone extended the shelf-life by 0-2 days. The combination of lauricidin and citric acid or lauricidin and ascorbic acid extended the time required to reach a microbial spoilage level for mechanically deboned chicken meat by as much as 7 days, minced fish by as much as 4 days and chicken sausage by 8 days.

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MONOGLYCERIDE INHIBITION OF *Mycoplasma pneumoniae*.

R.D. Fletcher and A.C. Albers, 645 Salk Hall, University of Pittsburgh, Pittsburgh, PA 15261, J.N. Albertson Jr., USAMBRDL, Frederick, MD, and J.J. Kabara, Michigan State University, East Lansing, MI 48824.

It has been reported that long-chain lipids inhibit certain bacteria and long-chain alcohols inactivate mycoplasma. It was of interest to determine if specific monoglycerides would inactivate *M. pneumoniae*. The *M. pneumoniae* were grown in a Difco mycoplasma broth supplemented with 20% horse serum, 10% yeast extract, 0.5% glucose and 0.004% phenol red. Cultures were incubated at 37 C and growth was monitored by the change in percentage transmittance at 560 nm. Monoglycerides from 8 to 18 carbon-chain lengths were tested. It was determined at 37 C for 5 days that monolaurin (12:0), 80 μg/mL, and monomyristin (14:0), 80 μg/mL, produced 46% and 60% inhibition, respectively; one degree of unsaturation, e.g., monoolein (18:1), 80 μg/mL, increased inhibition to 85%. In contrast, two unsaturated bonds, monolinolein (18:2), 80 μg/mL, produced no inhibition. Of the monoglycerides tested for *M. pneumoniae* inhibition of the monoolein was most active with 16, 46 and 98% inhibition at 50, 75 and 100 μg/mL, respectively. The *M. pneumoniae* were also grown in the presence of 0.1 μg/mL tetracycline with and without 75 μg/mL monoolein. This low concentration of tetracycline produced no inhibition; however, with the monoolein the percentage inhibition was 75. This may suggest that the monoglycerides affect membrane permeability.

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NEUTRALIZATION OF ANTIBACTERIAL PROPERTIES OF LAURICI BHA BY TWEENS.

D.V. Vadehra, V. Wahi and J. Keswani, Department of Microbiology, Panjab University, Chandigarh, India.

See page 755.

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FATTY ACIDS OR ESTER DERIVATIVES AS CARIOSTATIC AGENTS.

Rachel A. Schemmel and Jon J. Kabara, Michigan State University, Dept. of Food Science & Human Nutrition, East Lansing, MI 48824.

Review of the literature supports the concept that diets high in fat content tend to be less cariogenic than fat-free diets. This cariogenic lowering property of lipids is more pronounced in diets containing fatty acids or fatty acid esters. Numerous studies have demonstrated that fatty acids or fatty acid esters show in vitro antimicrobial properties. Saturated fatty acids or ester derivatives reach optimal antimicrobial activity with chain lengths of 12 or fewer carbons. Those with longer chain length are less active. This review focuses on the cariostatic properties of fatty acids and their ester derivatives with an emphasis on those microbial active lipids which contain chain lengths of 9-12 carbons. Glycerol monolaurin (GML) is an effective cariostatic agent. In at least 5 different experiments conducted in our and other laboratories (Williams et al., Archs. Oral Biol. 1982, in press), rats which were fed diets containing 2% GML had significantly fewer smooth surface and sulcal carious units than rats fed control diets. The basic diets (control) into which 2% GML was added varied. When granular sugar was substituted for powdered sugar in NIH diet 2000, the incidence of caries was lower in both controls and rats fed diets with GML. When control diets contained no fat, the relative cariostatic effect of GML was greater than when control diets contained 2% hydrogenated vegetable fat. Plaque formation was also lower in rats fed diets with 2% GML or 2% lauric acid than control diets which contained alphacel or linoleic acid or nonanoic acid. The potassium salt of nonanoic acid also has cariostatic properties (Hayes and Berkovitz, Archs. Oral Biol. 24:663 [1979]).

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EFFECT OF CHOLESTEROL ON OLEATE-INDUCED INCREASE IN CHOLESTEROGENESIS IN HEPATOCYTES.

Edward H. Goh, Section of Pharmacology, Medical Sciences Program, Indiana University School of Medicine, Bloomington, IN 47405.

It was previously observed that oleic acid concurrently stimulated the synthesis and efflux of endogenous cholesterol of perfused rat livers. This oleate-induced increase in cholesterogenesis was reduced by unpurified exogenous cholesterol. Chemically pure cholesterol, however, has been found by others to be ineffective in reducing cholesterogenesis not stimulated by oleate. In view of this, the effect of pure exogenous cholesterol on the oleate-induced increase in cholesterol synthesis was investigated. Freshly isolated rat hepatocytes (50 mg cell protein) were incubated in Krebs-Henseleit buffer (5 mL), pH 7.4, containing glucose, albumin, oleic acid (2mM), and 194, 389, or 649 nmol of purified cholesterol labeled with ^{3}H-desmosterol. ^{3}H-Desmosterol permitted estimates to be made of the influx of exogenous cholesterol through hepatic microsomes by the conversion of ^{3}H-desmosterol to ^{3}H-cholesterol by the microsomes. With this tracer, it was observed that the influx of exogenous cholesterol through the microsomes was elevated by increasing amounts of exogenous cholesterol even though cholesterogenesis, measured by the activity of HMG-CoA reductase, was similar to that in experiments without added exogenous cholesterol. These observations suggest that the influx of exogenous cholesterol may not be sufficient to reduce the oleate-induced elevation in the synthesis of cholesterol in hepatocytes incubated under this condition.

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EXAMINATIONS ON ANTITUMOR, IMMUNOLOGICAL, AND PLANT-GROWTH INHIBITORY EFFECTS OF MONOGLYCERIDES OF CAPRYLIC, CAPRIC, AND LAURIC ACIDS AND RELATED COMPOUNDS.

Jon J. Kabara, Michigan State University, Department of Biomechanics, East Fee Hall, East Lansing, MI 48824, Masanori Ohkawa, Tetsuro Ikekawa, Tatsuhiko Katori and Yoshihiro Nishikawa*, Kanazawa University, Japan.

Recently, Japanese authors of this paper have reported that various synthetic fatty acid esters of carbohydrates can exert some interesting biological activities such as antitumor, immunopotentiating, and plant-growth inhibitory effects. In the present study, monoglycerides of caprylic, capric, and lauric acids (lauricidins A, B, and C, respectively) and related compounds were subjected to the same bioassays as those employed previously for the carbohydrate esters. When the plant-growth inhibitory effect (abscisic acid-like activity) was examined by Nitsch's straight growth test of Avena coleoptiles, it was found that lauricidin B could exhibit a marked activity, which was comparable to that observed previously with the D-glucose-1-laurate, giving the inhibition ratio higher than 90% at the concentration of 500/3 ppm with or without addition of Tween 20. Under similar bioassay conditions, lauricidins A and C were moderately effective, whereas monostearin and the triglycerides corresponding to the abovementioned monoglycerides were completely or nearly ineffective. The in vitro cytotoxic effects of the lauricidins were tested by the cell culture method, using two leukemia cell lines, L-5178Y and L-1210 (inoculum siza, 1.0×10^5 cells/mL). The results indicated that all the lauricidins were somewhat effective in inhibiting the growth of both the tumor cells. Among the three, lauricidin C gave the lowest IC_{50} value against either leukemia (62 and 50 mcg/mL against L-5178Y and L-1210, respectively). We will also present the results on the in vivo antitumor activities, as well as on the immunological effects (e.g., effect on the phagocytic response of the reticuloendothelial system and effect on the delayed-type hypersensitivity to sheep red blood cells), elicited by administration of the lauricidins and related glycerides into mice.

Session V Enzymatic Reactions in Flavor Development — II

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LIPID HYDROLASES AS INITIATIORS OF FLAVOR DEVELOPMENT.

H.M. Henderson and N.A.M. Eskin, Departments of Food Science & Food Nutrition, University of Manitoba, Winnipeg R3T 2N2, Manitoba, Canada.

Lipid hydrolases are responsible for the release of fatty acids from triglycerides and phospholipids. This paper will discuss the biochemical properties of lipid hydrolases isolated from fababeans and green peas in relation to their role in the development of off-flavor.

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CLEAVAGE OF METHYL HYDROPEROXYLINOLEATES INTO VOLATILES BY EITHER RADICAL β-SCISSION OR LEWIS ACID CATALYSIS: VOLATILES FROM LEWIS ACID CATALYSIS RESEMBLE THOSE FORMED BY HYDROPEROXIDE LYASE.

H.W. Gardner, R.D. Plattner and E. Selke, Northern Regional Research Center, USDA, ARS-NCR, CSF Lab, 1815 N. University Street, Peoria, IL 61604.

It is well known that production of volatile compounds from fatty hydroperoxides can proceed via β-scission of oxy radicals from homolysis of the hydroperoxide. In addition, acid catalysis also can lead to formation of a less complex mixture of volatiles by a decidedly different mechanism. The β-scission of radicals from hydroperoxides is theorized to occur via two pathways. Peroxy radicals cleave at the C-O bond, allowing subsequent rearrangement of one isomeric hydroperoxide into another, whereas oxy radicals lead to cleavage of the C-C bond on either side of the carbon bearing the oxy radical. Heating fatty hydroperoxides to 220 C in the injection port of a gas chromatograph is a convenient way to initiate radical formation, and subsequently to separate the volatiles produced. By this method, we examined volatiles produced from methyl 13-hydroperoxylinoleate, methyl 9-hydroperoxylinoleate and methyl 12,13-epoxy-9-hydroperoxy-*trans*-10-octadecenoate. Major volatiles were attributed to C-C cleavage from β-scission of oxy radicals, whereas minor volatiles were indicative of other processes. On the other hand, treatment of methyl 13-hydroperoxylinoleate with BF_3, a Lewis acid, in anhydrous ether led to formation of hexanal and methyl 12-oxo-*trans*-10-dodecenoate as the only cleavage fragments. These products resemble those formed from decomposition of 13-hydroperoxylinoleate by the enzyme, hydroperoxide lyase. Thus, acid catalysis may have mechanistic implications regarding action of the enzyme.

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OXIDATIVE DECOMPOSITION PRODUCTS FROM THE HUMAN RED BLOOD CELL MEMBRANE.

F.J. Bunick and W.W. Nawar, Dept. of Food Science and Nutrition, University of Massachusetts, Amherst, MA 01003.

Recently, lipid oxidation studies have begun to explore the oxidation processes that occur in biological membranes. Many of these studies deal with models vastly simpler than the membranes to which the results are extrapolated. In an effort to examine autoxidation in an authentic biological membrane, we have chosen the red blood cell membrane in the form of the erythrocyte ghost as a substrate. Early studies with ghosts in parallel to a lipid extract of ghosts showed that under high oxidizing conditions (80 C/O_2/2 wk), each preparation produced some unique oxidation products. Present studies build on this work by equalizing oxygen uptake between lipid preparations in air from 80 to 40 C. O_2 uptake profiles are markedly different in that the bulk phase oxidation is completed within 5 days, whereas the ghosts require about one month. Also, a pronounced induction period is seen in the ghost studies at 40 C. The production of CO_2 and CO with time is being followed and will be presented for both lipid preparations, as will the identification of a variety of volatile and nonvolatile oxidative products. Hexanal, ethyl hexanoate and ethyl octanoate appear to dominate the volatile pattern in these systems. The most abundant nonvolatiles produced are free fatty acids and cholesterol esters. Unique to the oxidized ghosts is a class of compounds whose R_f and staining characteristics suggest they are waxes. Phosphatidylethanolamine and serine were found to be the most labile lipid classes, disappearing almost completely. Time course reaction of the phospholipids will be presented.

Total fatty acid analysis of the samples after saponification show several regions by TLC which correspond to polar derivatives of the FFA especially the mono- and dihydroxylated isomers. Identification of these and other compounds via GC-MS and microchemical analysis will be presented.

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ROMANO CHEESE-LIKE FLAVOR DEVELOPED BY FUNGAL LIPASE AND THE STUDY OF ITS VOLATILE FATTY ACIDS COMPOSITION. Stephen S. Chang, Kuo-Chung Mark Lee, An-Shun Huang, Huang Shi and Chi-Tang Ho, Dept. of Food Science, New Jersey Agricultural Experiment Station, Cook College, Rutgers, The State University, New Brunswick, NJ 08903.

An excellent Romano cheese-like flavor was generated from a butterfat emulsion, which was treated by the crude lipase prepared from *Candida rugosa* (A.T.C.C. No. 14,830). The reaction of the lipase with the butterfat emulsion comprising 20% butterfat and 1.5% Tween 80 in pH 7.5-7.7 buffer solution was held at 37 C for 3 hr and then aged at room temperature for 3 days to complete the flavor generation. The volatile flavor components of the butterfat emulsion and of a commercial brand, Stella, cow's milk made, 5 months' aged Romano cheese were isolated to study their flavor identity. Their acidic volatile compounds were analyzed by gas chromatography, and identified by mass spectrometry. Results show a good resemblance between these two samples. Both contained eight major short-chain fatty acids, from acidic acid to decanoic acid, and the relative concentrations of their fatty acids were very close. Butyric acid was the major component in both samples. However, the total volatile fatty acids content of butterfat emulsion was much higher, about twice that of the commercial Romano cheese. (New Jersey Agricultural Experiment Station No. K-10412-1-83).

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CHEMICAL/BIOCHEMICAL PROPERTIES OF PEANUTS FROM BIOREGULATOR-TREATED PLANTS. E.J. Conkerton, D.C. Chappital and R.L. Ory, Southern Regional Research Center, ARS, USDA, PO Box 19687, New Orleans, LA 70179.

Bioregulators (plant growth regulators) are being used to change growth patterns of plants; for example, to reduce plant size, reduce water requirements, increase cold tolerance, and/or induce early maturity. As these effects are noted, it becomes necessary to monitor the effects of the bioregulator on other portions of the plant. The data reported here were obtained from analyses of a series of peanuts harvested from plants treated with a bioregulator at selected times during the growth cycle. Peanuts from treated plants had protein, carbohydrate and metal profiles similar to those from untreated plants. There was, however, a significant decrease in the lipoxygenase activity of peanuts from treated plants compared with that from untreated plants. The possibility of extending the shelf-life of peanuts and peanut products by this type of treatment will be discussed.

Session W New Protein Sources — II Tuesday p.m.

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EVALUATION OF SOY PROTEIN ISOLATE AS A GRAS FOOD INGREDIENT. F.R. Senti, Life Science Research Office, FASEB, 9650 Rockville Pike, Bethesda, MD 20814.

Soy protein isolate was among the generally recognized as safe (GRAS) food ingredients evaluated by the Select Committee on GRAS Substances of the Federation of American Societies for Experimental Biology. The factors and relevant data considered in that evaluation of the health aspects of soy protein isolate will be reviewed. The Committee considered protein quality, mineral metabolism and bioavailability of trace minerals, vitamin requirements, trypsin inhibitor and lysinoalanine content, as well as nitrite and the possibility of nitrosamine formation in spray-dried isolates. Several multigeneration studies of rats fed soy protein isolate failed to indicate evidence of toxicity. Nitrogen balance, in most studies with humans, was similar for isonitrogenous diets based on methionine-fortified soy protein isolates and proteins of animal origin. The population subgroup consuming the largest amount (per unit body weight) of soy protein isolate was infants fed soy isolate-based formulas. Growth rate of infants fed such formulas was similar to those of infants fed formulas based on cow milk. The Committee recommended that food grade specifications be developed for soy protein isolate including provisions for acceptable levels of lysinoalanine, nitrite and nitrosamines. Evidence from studies with experimental animals and humans of soy protein isolate, properly prepared and supplemented, provided no cause for concern at current levels of use or levels that might reasonably be expected in the future. The Committee recognized the need to review its conclusions as new information becomes available.

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VARIATION IN AND GENETICS OF CERTAIN BIOLOGICALLY ACTIVE COMPONENTS OF SOYBEAN SEED. Theodore Hymowitz, Department of Agronomy, University of Illinois, Urbana, IL 61801.

Several thousand accessions of soybeans in the US Department of Agriculture soybean collection were screened for variation in Kunitz trypsin inhibitor, seed lectin, β-amylase and lipoxygenase-1. Nulls for all four components of seed were located in various accessions. In the homozygous recessive state, none of the four components are produced in seed. The four components of seed do not appear to be vital to the species since null seeds germinate normally and the subsequent plants grow, flower and produce seed just like typical soybeans. The availability of soybean genotypes lacking these seed components should be of particular interest to the soybean industry for the development of soybean products with (a) improved nutritional quality; (b) protein of altered functional characteristics; and (c) perhaps improved flavor.

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TOFU AND TEMPEH AS POTENTIAL PROTEIN SOURCES IN THE WESTERN DIET. Hwa L. Wang, Northern Regional Research Center, 1815 N. University, Peoria, IL 61604.

In recent years, a growing interest in foods of plant origin, especially plant protein foods, has become evident. A large number of low-technology, oriental soy foods have appeared in the American market outside the oriental community. The most popular one is tofu, an exceedingly versatile soybean product. Tempeh, another protein food, has also attracted a lot of attention. Tempeh has not yet been accepted to the extent that tofu has, but it is becoming the hamburger-alternative for vegetarians, now numbering 10-15 million in the USA. According to information published by the Soyfoods Center of California, the number of non-oriental tofu producers in North America rose from zero in 1975 to 181 in 1981. It was estimated that 26,000 tons of tofu were produced in 1981 as compared to 6,500 tons in 1979. Total annual retail sales in 1981, including tofu, tempeh, soymilk, soynut, soy sprout, miso, and soy sauce, were ca. $391 million. Tofu is made by curdling the protein with a calcium or magnesium salt from a water extract of whole soybeans. It is a highly hydrated, gelatinous product with a soft, smooth texture and a bland taste. Therefore, tofu can easily be incorporated with other foodstuffs and used in nearly every culinary context, from salad to dessert and breakfast foods to burgers. Tempeh is made by fermenting boiled soybeans with *Rhizopus oligosporus*. After 20-24 hr at 30 C, the beans are covered with white mycelia that bind the beans together to form a firm cake. It can be sliced, seasoned, and cooked by frying, roasting, or baking — just like meat. The technical aspects of making these products will be discussed.

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SWEET POTATO PROTEIN. William M. Walter Jr., USDA-ARS, 322 Schaub Hall, Department of Food Science, NC State University, Raleigh, NC 27650.

The sweet potato ranks sixth in worldwide production among plant food crops. Certain varieties are available which yield in excess of 5×10^4 kg/hectare. Crude protein content of sweet potato cultivars ranges from 2 to 9% (dry basis), depending upon horticultural practices and environmental factors. The crude protein content of widely grown US cultivars generally lies between 5 and 7% (dry basis) at harvest. Crude protein includes significant amounts (10-30%) of nonprotein nitrogen (NPN) mainly as asparagine, glutamic acid and aspartic acid. The amino acid pattern of purified protein compares favorably with the FAO reference protein. Total sulfur and lysine are the limiting amino acids. Rat feeding studies have shown that the protein efficiency ratio (PER) for isolates and concentrates is equal to the PER for ANRC reference casein. Cooked, oven-dehydrated flour from "Centennial" and "Jewel" cultivars had PER values of 2.2 and 1.8, respectively (corrected to a casein PER of 2.5). A more drastic dehydration process used to prepare "Centennial" flour caused the PER value of the flour to fall from 2.2 to 1.3. Although the amino acid pattern was identical to that of "Centennial" oven-dried flour, lysine availability was significantly lowered. Thus, modification of lysine occurred during processing, which produced acid hydrolyzable (chemically available), yet biologically unavailable lysine derivatives, resulted in a lowered PER value.

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NEW SEMIARID CROPS AS PROTEIN RESOURCES. R. Becker, R.N. Sayre and R.M. Saunders, Western Regional Research Center, Agricultural Research Service, US Department of Agriculture, 800 Buchanan Street, Berkeley, CA 94710.

The worldwide population pressures and accompanying increased demands on water supplies and cultivatable land has forced a reevaluation of traditional agriculture techniques and crops. Underutilized semiarid lands are becoming candidates for crop production using stress tolerant plants. Desert legume trees and shrubs such as species of *Prosopis*, *Acacia*, *Cercidium*, *Leucaena*, *Olneya*, and *Geoffroea* fix nitrogen and could be sources of seed protein, forage, or biomass. Seeds from desert legume perennials have a high potential as protein producers. Some members of the grass family are adapted to arid and/or saline conditions and produce nutritious grain; for example, saltgrass, seagrass, channel millet, and some varieties of traditional crops such as barley and wheat. Other diverse plants such as buffalo gourd, some cactus, desert palms, and amaranth are potential new protein-containing crops also suited for semiarid lands.

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PRODUCTION OF PROTEIN AND VOLATILE FATTY ACIDS IN THE FERMENTATION OF BLACKSTRAP MOLASSES BY *Eubacterium ruminantium*. Ketan I. Mehta and C.D. Callihan, Department of Chemical Engineering, Louisiana State University, Baton Rouge, LA 70803.

Production of protein and volatile fatty acids by anaerobic digestion of blackstrap molasses was investigated. Fermentation of blackstrap molasses by *Eubacterium ruminantium* isolated from ruminant fluid was studied in a chemostat. A constant temperature of 37 C was maintained. This study focused on the kinetics of growth of the pure culture. The maximum rate of cell production was found when the pH and retention times were 6.2 and between 5 and 7 hr, respectively. The average cell yield was 12.6% and carbohydrate conversion was from 82 to 99%. Volatile fatty acids were also produced with *n*-butyric acid being the predominant product. Other products were acetic and propionic acids. Six different kinetic models were used to fit the experimental data. The kinetic parameters obtained for the Monod model were μ_{max} = 0.21 hr^{-1}, K_S = 0.19 g/L; and k_d = 0.007 hr^{-1}.

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EFFECT OF THE OIL EXTRACTION PROCESS ON THE QUALITY OF DEFATTED LUPINE FLOUR. L.E. Camacho and D.F. Owen, Macul 5540, PO Box 15138, Santiago 11, Chile.

The effect of different oil extraction processes at a pilot plant level on some quality factors of defatted lupine flour was evaluated. The general objective of the study was to obtain defatted lupine flour that could be used as a protein extender of human foods that undergo further heat treatments such as baking or extrusion. Whole kernels of sweet lupine (*Lupinus albus* var. Astra) with 32.8% protein (N X 6.25), 12.8% crude oil and 0.04% alkaloids, were used as raw material. The kernels were heated for 15 min in a retort with live steam injection at 120 C (15 psi) and in a hot air dryer at 70 C and 90 C for 30 min. All samples were dehulled, flaked and extracted with commercial hexane for an effective total contact time of 8 hr. After the oil extraction, the flakes were desolventized by direct steam injection for 10 min and by direct exposure to sun. Those samples desolventized by steam were dried overnight at 30 C. Finally, the treatments were pulverized in a Rietz Mill using a mesh of 0.016 in. The protein solubility at a pH range of 5.5-8.0, flour yields, proximate analysis and sensory characteristics were evaluated. Defatted lupine flour presented a final average protein content of 47.8% and 0.02% alkaloids; therefore, it was concluded that a fraction of the bitter compounds are lost with the hull. It was finally concluded that, under the conditions of this study, a prior heating at 90 C for 30 min, desolventization by direct live steam injection, and a pH in the range of 6.5-7.5, was the best process for obtaining defatted lupine flour of high quality, high protein solubility and adequate flour yields.

Session X Oilseed/Oil Processing Roundtable Tuesday p.m.

No abstracts. Panel participants will answer questions asked by the audience.

Session Y Applications of Supercritical Fluids – II Tuesday p.m.

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WHY DON'T PEANUTS WORK? Val Krukonis and R.T. Kurnik, Phasex Corporation, #1 Mill, 85 Factory Street, Nashua, NH 03060.

A variety of botannicals, seeds and beans are being tested for their response to supercritical fluid extraction. Emphasis is being directed to many of these materials because of cost, product improvement, and human and environmental safety considerations. The potential for producing seed oils, flavors, and beverage products via supercritical fluid extraction is being studied at a number of industrial and government laboratories. Removal of oil from peanuts using supercritical carbon dioxide has also been tested, but raw (and roasted) peanuts cannot be extracted readily, with only ca. 2% of the oil (of an available 50%) removed at conditions of 5000 psi and 55 C. Cell wall diffusion resistance is responsible for the inability to "de-oil" whole peanuts; however, if the cell walls are ruptured, the oil can be extracted (by both organic solvents and supercritical carbon dioxide). During the supercritical carbon dioxide extraction sequence, which includes the pressurization and depressurization steps, whole peanuts are comminuted; if in a second extraction sequence this comminuted material is extracted at the same conditions as those which resulted in the comminution, all the oil is removed, even though the comminuted pieces are larger than the cell size. The phenomena in operation during the supercritical fluid extraction of whole peanuts were observed in a sight glass, and the results of rapid-frame, still photography and high-speed, movie photography will be presented.

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PROCESSING OF COTTONSEED OIL OBTAINED BY EXTRACTION WITH SUPERCRITICAL CARBON DIOXIDE. G.R. List, J.P. Friedrich and J. Pominski, Northern Regional Research Center, Agricultural Research Service, US Department of Agriculture, 1815 N. University Street, Peoria, IL 61604.

Flaked cottonseed was extracted with supercritical carbon dioxide (SC-CO_2) at temperatures ranging from 50 to 80 C and pressures of 8,000-15,000 psig. The crude oils were characterized for color, free fatty acid, total gossypol, phosphorus, refining loss and unsaponifiable matter, and compared to hexane prepress and expeller produced commercial crude oils. Extraction of cottonseed with SC-CO_2 offers several advantages over conventional extraction methods including lighter colored crude oil, less refining losses, and lower caustic soda requirement for the refining operation. Preliminary data show that the gossypol content of SC-CO_2-extracted crude oil is markedly lower than that of hexane prepress or expeller crudes. Flavor and oxidative stability of SC-CO_2– and conventionally extracted oils were investigated and the results will be presented and discussed.

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OPTIMIZING CARBON DIOXIDE EXTRACTION FOR SPECIAL PRODUCTS: PYRETHRUM. Marc Sims, Consulting Chemical Engineer, 2935 Pine Avenue, Berkeley, CA 94705.

The selectivity, safety and low cost of CO_2 make it an ideal commercial solvent for extracting many natural materials. However, the complexity of natural materials requires a process study for each to find the conditions which give the highest yield and purity for the lowest equipment and operating costs. An example process study is presented for producing the CO_2 extract of the insecticidal pyrethrum flower. The cost factors which are generally applicable to all CO_2 extraction processes are discussed.

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MODULAR PILOT PLANTS FOR SUPERCRITICAL EXTRACTION RESEARCH. Ravi Randhava and David Goltermann, Xytel Corporation, 801 Business Center Drive, Mt. Prospect, IL 60056.

Interest in supercritical extraction (SCE) research has grown dramatically during the past few years, both in the USA and abroad. This has naturally created an urgent need for bench-scale systems and pilot plants. As always, scientists are looking for cost-effectiveness, flexibility, computerization and fast availability. This paper describes how Xytel's modula pilot plant technology can be applied to meet these requirements at savings of 25-30% over conventional techniques. Two examples are presented: first, a general purpose computer-controlled pilot plant for supercritical extraction of selected compounds from edible liquids; and second, a computer-controlled system for supercritical extraction of highly viscous residual matter produced by conventional crude oil cracking.

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SYSTEMS FOR SUPERCRITICAL CO_2 EXTRACTIONS. James H. Love, WSE, Inc., Engineers, Consultants, Fabricators, Agents, PO Box 471, La Grange, IL 60525.

In the evaluation of supercritical extraction processes with CO_2, it is advisable to include considerations of the sources, availability, pricing structure and equipment for distribution and supply of the solvent. Plant locations, distribution systems, storage and supply facilities, pumping and compression equipment, flow, temperature, and pressure control systems are critical to the process. Many different layouts are possible for single and multiple extractor vessel systems, each with its own associated equipment and instrumentation requirements. Engineering of a particular system must take into consideration the availability and cost of the components required, because this technology is capital intensive.

Session Z Surfactants: Performance and Evaluation – II Tuesday p.m.

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EFFICACY OF LOW MOLE ETHOXYLATES IN SOLVENT-BASED PRESPOTTERS. H.L. Benson, Shell Development Company, PO Box 1380, Houston, TX 77001.

Studies have been conducted at ambient temperature on the effects of hydrophobe molecular weight and low EO/ROH mole ratios of alcohol ethoxylates for removal of nonpolar stains from polyester/cotton fabric. Optimum prespotting/washing results against dirty motor oil and a TFI oil/carbon mixture have been achieved for solvents containing 10% ethoxylates with an EO/ROH ratio between 2 and 3. A qualitative relationship appears to exist between these results and the rapid solubilization rates for oil/ethoxylate blends in low cloud point surfactant systems.

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SECONDARY ALKENE BENZENE SULFONATE–AN ECOLOGICAL AND ECONOMICAL ALTERNATIVE. Trautmann and Jürges, Hoechst AG, ATA TH - D 562, Postfach, D-6230 Frankfurt 80, West Germany.

Because of the changed ecological situation, the tetrapropylene benzene sulfonate (ABS) has been replaced by the linear alkene benzene sulfonate (LAS), which shows an improved biodegradebility. Hoechst has developed another anionic surfactant, the secondary alkene sulfonate (SAS) – the biodegradebility of SAS is still better than that of LAS. SAS is produced by a full continuous process, based on well defined raw materials (*n*-paraffine, SO_2, O_2). Based on this highly sophisticated process, the SAS shows specific properties like high purity (which means no byproducts – an unique quality standard) which means the same excellent quality standard over long periods. In relationship to LAS, the SAS in general has the same detergency and the same foam properties; on the other hand, SAS offers the following specific advantages: (a) Improved water solubility in combination with solubilizing properties. SAS can be regarded as a surfactant with hydrotrope characteristics and as a hydrotrope with surfactant properties. These advantages are used in the whole range of liquid detergents, especially in high concentrated formulations. (b) The superior performance of SAS in chlorine-containing detergents, e.g., in liquid bleach, all-purpose cleaner and sanitizers can be demonstrated. Specific synergism with other surfactants are shown. (c) The utilization of SAS during the production of heavy duty powders via spray-drying processes offers economical advantages because of a high solid content of the slurry; the throughput can be increased in addition to energy saving. (d) Good toxicological and dermatological data are the reasons for the usage of SAS in personal care products. All other fields of an anionic surfactant are of course covered by the SAS too. Up to now, the SAS has gained a remarkable market share in the whole detergent market in Europe. A plant is under construction in the USA.

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PRIMARY ALKANE SULFONATES. Anna M. Koberda and Joseph R. Wechsler*, Stepan Chemical Company, Edens & Winnetka, Northfield, IL 60093.

Terminal alkyl sulfonates have been known for some time, going back to 1913 when Reychler, McBain, and Twitchell prepared them independently by oxidation of the corresponding mercaptans. Later, in the 1930s, Reed and Tartar, as well as some other researchers, applied the Strecker technique of reacting alkyl halides with sodium or ammonium sulfite, with moderate yield. A more modern technique was developed in the 1960s and 70s with the advent of commercial alpha olefins, based on free radical reactions initiated by peroxides. Numerous patents using such techniques were filed in that time period, particularly in Germany. In spite of ths wide interest, this type of surfactant never gained commercial acceptance, presumably because of its strange solubility characteristics, which limit its conventional usage. In the course of our work, we uncovered several unusual features relating to the mechanism of reaction and to the physical properties of various derivatives of this class of surfactant.

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METHYL GLUCOSIDE/TRIGLYCERIDE ALCOHOLYSIS PRODUCTS, THEIR PREPARATION AND CHARACTERIZATION. C. Deane Roth, A.E. Staley Mfg. Co., 2200 East Eldorado St., Decatur, IL 62525.

Methyl-α-D glucoside (MeG) is a polyol produced from renewable resources (corn) by published and patented procedures. It is presently produced in semicommercial quantities, and it will be available in commercial quantities in mid 1983. Its cyclic structure is unique among polyols. Its four hydroxyls show varying chemical reactivities which facilitate the preparation of chemical intermediates. One such family of intermediates is made by the alcoholysis (or alcohol interchange) of MeG with triglycerides. These were described in the early 1950s as intermediates for conversion into coating products such as alkyds or oil modified urethane resins. With the current availability of MeG, these end uses are again being actively explored. Other end uses should be considered for these intermediates because these molecules contain distinct polar/nonpolar segments. Among these uses are emulsifiers, surfactants, mold release agents, and plasticizers. An experimental design (Box-Behnken 3) was carried out to explore the preparation of this intermediate. The variables chosen were MeG/triglyceride equivalents ratio, catalyst (Li_2CO_3) level, and addition or omission of previously prepared alcoholysis product. Analysis of these data showed the equivalents ratio had the most significant effect upon methanol solubility and viscosity of the intermediate. Four of these 15 experiments were further analyzed for glucoside ester/glyceride ester distribution by gas chromatography of the trimethylsilyl derivates. These results are included as well as a detailed alcoholysis procedure.

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THE PREPARATION AND PROPERTIES OF 1,2 BUTYLENE OXIDE AND ETHYLENE OXIDE BLOCK COPOLYMER SURFACTANTS. Irving R. Schmolka* and Bongsub Kim*, BASF Wyandotte Corporation, 1609 Biddle Avenue, Wyandotte, MI 48192.

A series of novel nonionic surface active agents, the BUTRONIC^{TM} polyols, has been prepared from 1,2 butylene oxide and ethylene oxide. Starting with a low molecular weight water-soluble glycol initiator, and in the presence of an alkaline catalyst, 1,2 butylene oxide is added to form a series of water-insoluble hydrophobic compounds. Ethylene oxide is added in incremental amounts to each base, to form the final nonionic surfactant. These vary in molecular weight from 750 to over 15,000, and are liquids, pastes or solid grades. The products include members that are either oil-soluble or water-soluble. Pour points or melting points vary from a low of -19 C to a high of 65 C. An examination of their physical properties reveals that several members exhibit outstanding foaming or thickening properties. The foaming properties are compared with commercial high foaming nonionics. The advantages over, and differences with, other nonionic gelling agents for water are detailed.

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OXYETHYLATED SULFONAMIDES AS NONIONIC SOIL-WETTING AGENTS. Thomas J. Micich and Warner M. Linfield, Eastern Regional Research Center, USDA, 600 East Mermaid Lane, Philadelphia, PA 19118.

Initial studies of nonionic soil-wetting agents derived from aromatic sulfonamides were made to determine the structures exhibiting the best wetting properties toward peat moss and cotton skeins. Several N-alkylbenzenesulfonamides of the type $RC_6H_4SO_2NHR'$, where R is hydrogen or *para-t*-butyl and R′ is an alkyl group containing 4-10 carbon atoms, were prepared in good yield from a benzenesulfonyl chloride and excess aliphatic amine in dichloroethane. The sulfonamides were treated with ethylene oxide at < 50 psi to form polydisperse adducts containing 2-20 mol ethylene oxide/mol sulfonamide. Thus, each series showed a range of wetting properties and water solubility. Optimum wetting properties were found with peat moss and cotton skeins for adducts containing 6-12 mol ethylene oxide and derived from sulfonamides where R′ contains 6-8 carbon atoms and where R is a *t*-butyl group. This ethylene oxide content corresponds to cloud points above 0 C and minimal surface tensions. The widest range of good wetting properties with changing ethylene oxide content was found with adducts derived from N-alkyl-*t*-butylbenzenesulfonamides.

Session AA Nutritional Physiological and Biochemical Studies of Omega-3 Fatty Acids and Prostaglandins Tuesday p.m.

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POSSIBLE BENEFICIAL EFFECTS OF THE LINOLENATE CLASS (n-3) OF FATTY ACIDS. William E.M. Lands, Dept. of Biological Chemistry, University of Illinois at Chicago, 1853 W. Polk, A-312 CMW, Chicago, IL 60612.

The cyclooxygenase activity that converts polyunsaturated fatty acids to prostaglandins can catalyze the oxygenation of many different acids in vitro. Results from in vitro and in vivo studies help emphasize that prostaglandin biosynthesis in tissues is normally suppressed by the lack of sufficient amounts of both the hydroperoxide activator and nonesterified substrate. A release from this suppression is the basis for many pathophysiologic phenomena. The relatively high concentration of lipid hydroperoxide activator needed to initiate oxygenation of the n-3 class of acids (relative to the n-6 class) tends to prevent their conversion in vivo where hydroperoxide levels are generally lower than obtained in vitro. Thus for normal tissues we can predict a selective formation of dienoic prostaglandins (from n-6 precursors) and not trienoic prostaglandins (from n-3 acids). An additional consequence of this result is that the n-3 class of acids serve as competitive inhibitors of prostaglandin biosynthesis from the closely related n-6 polyunsaturated fatty acids. In this way, the n-3 class of polyunsaturated fatty acids may aid the normal suppression of prostaglandin formation and diminish the severity of pathophysiologic events due to unbalanced formation of dienoic prostaglandins from the n-6 fatty acids. Several examples of experimental results with animals and humans indicate that dietary intake may have significant effects.

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CONSEQUENCES OF FEEDING n-3 POLYUNSATURATED FATTY ACIDS CONTAINING DIETS TO RATS AND RABBITS. Jan Kloeze, Edward Haddeman, Gerard Hornstra and Paulus M. Verschuren, Unilever Research Laboratorium, PO Box 114, 3130 AC Vlaardingen, The Netherlands.

We studied the effects of various dietary fats (including those rich in polyunsaturated fatty acids (PUFA) of either the n-3 or the n-6 family) in rats and rabbits on fatty acid incorporation in phospholipids (PL) of blood platelets and the vessel wall and subsequent metabolism to prostanoids as well as the effects on arterial thrombosis (rat) and atherosclerosis (rabbit). Timnodonic acid (TA; 20:5 n-3) as well as 22:5 and 6 n-3 were incorporated in PL in both species, mainly at the expense of arachidonic acid (AA), except in rabbit platelets where linoleic acid was replaced. Formation of prostanoids by platelets and aorta wall was depressed by the presence of TA in the phospholipids and correlated positively with the AA content of the PL, except again in rabbit platelets. In rats, the obstruction times (OT) of aorta protheses (arterial thrombosis model) correlated negatively with both TXA_2 and PGI_2 formation by stimulated platelets and incubated aorta pieces, respectively. In rabbits, the degree of aorta atherosclerosis shows a similar negative correlation with TXA_2 and PGI_2 formation, in vitro. The TXA_2/PGI_2 ratio was not found to be changed by diet manipulations. Prostanoids of the 3 series could not be detected, although we were able to show that TA was available at least in platelets. Rabbits fed for 18 months a semisynthetic diet containing 32 en% of fish oil with 8 en% added sunflowerseed oil (to prevent linoleic acid deficiency) showed deviations in some serum enzyme activities pointing to liver damage. Postmortem examinations confirm this as extensive lipogranulomas filled with metabolically inert residues of cellular material (lipofuscin) were found in the livers. Similar lesions were found in mesenterial lymph nodes. These results indicate that some reserve is justified in recommending a widespread use of large amounts of oils rich in n-3 PUFA as a panacea against IHD.

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CONCERTED STIMULATION AND INHIBITION OF DESATURATION, CHAIN ELONGATION AND ESTERIFICATION OF ESSENTIAL FATTY ACIDS BY CULTURED NEUROBLASTOMA CELLS. Harold W. Cook, Joe T.R. Clarke and Matthew W. Spence, Rm. C-R1, 5849 University Avenue, Dalhousie University, Halifax, Nova Scotia, B3H 4H7, Canada.

The formation of polyunsaturated acyl chains of complex lipids from the essential fatty acids, linoleate and linolenate, in mammalian cells involves several reactions including activation, desaturation ($\Delta6$, $\Delta5$ and $\Delta4$), chain elongation and esterification to phospholipid and triacylglycerol. Our experiments showed that Neuroblastoma (NIE-115) cells in culture rapidly incorporated exogenous linoleic and linolenic acids suspended as albumin complexes in the medium. The major products of conversion of these acids (20:4 from 18:2(n-6) and 20:5 and 22:5 from 18:3(n-3)) were preferentially esterified to phospholipids. Lesser amounts of intermediates were esterified primarily or equally to triacylglycerol with extremely small (< 1%) amounts of any label in the free fatty acid pool. The effects of unlabeled exogenous fatty acids (e.g., 40 μM 18:2(n-6), 18:3(n-6), 18:3(n-6), 20:3(n-6), 20:3(n-3), 20:4(n-6), *trans*-18:2(n-6), 18:1 (n-9), *trans*-18:1(n-9) or 16:0) on the conversion of 2 μM $[1\text{-}^{14}C]$ 18:2(n-6) or 18:3 (n-3) and on accumulation of products and unaltered substrates in phospholipids and triacylglycerol were examined after incubations of 2-24 hr. With $[1\text{-}^{14}C]$ 18:2, formation and esterification of 20:4 to phospholipid was: (a) stimulated 4-8 fold by 18:2(n-6), 20:3(n-6) or 20:4(n-6); (b) inhibited by 18:3 (n-3) on *trans*-18:2(n-6); and (c) little altered by the other fatty acids. Specific but less marked effects were observed with $[1\text{-}^{14}C]$ 18:3(n-3). Thus, our observations indicate that: (a) stimulation by certain fatty acid involves accumulation primarily of the esterified end-product with much less increase in intermediate accumulation; (b) activity is not decreased by attempts to "trap" intermediates by pool dilution; and (c) at least from a regulatory standpoint, free 20:4 cannot be the final product of the sequence of reactions. These observations support a closely coordinated or concerted enzyme system for directed synthesis of esterified polyunsaturated acyl chains such that, once the substrate acid is committeed to production of a specific product, the entire sequence of reactions may proceed.

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ON THE ROLE OF EICOSANOIDS AND THEIR DIETARY PRECURSORS IN ATHEROSCLEROTIC DISEASE. A.L. Willis, D.L. Smith, M. McCarry, B. Nagel and I. Mahmud, Institute of Pharmacology and Metabolism, Syntex Research, 3401 Hillview Avenue, Palo Alto, CA 94301.

From both epidemiological and intervention studies, it is well documented that increased dietary intake of polyunsaturated over saturated fat exerts protection against occlusive coronary artery disease. High uptake of saturated fat is invariably associated with atherosclerosis, which not only predisposes to platelet thrombus formation, but is itself propagated by the release of factors from platelet thrombi. We have studied the effects of various fatty acids and their eicosanoid oxidation products in two systems thought to be important in atherogenesis and thrombogenesis. These are proliferation of vascular smooth muscle cells (studied mainly in tissue culture) and aggregation of platelets. We confirmed and extended the work of Cornwell's group (Lipids 14:194 [1979]) to show that submicrogram concentrations of PGE_1 and its precursor (dihomo-γ-linolenic acid, DHLA) could inhibit proliferation of rabbit vascular smooth muscle cells grown in culture. Similar findings were observed with arachidonic acid (AA) and some of its eicosanoid products, including 5-HETE and LTB_4. Aggregation and release of platelet constituents is inhibited by PGE_1 (derived from DHLA) and both PGI_2 and PGD_2 (derived from AA). On the other hand, PGH_2 and TXA_2 (unstable eicosanoids also derived from AA) cause intense vasoconstriction and both platelet aggregation and release of platelet constituents. Although it is a very poor substrate for cyclooxygenase, eicosapentaenoic acid (EPA) can, under some conditions, be converted to PGI_3 and to PGD_3 which inhibit platelet aggregation. In every case, the platelet inhibitory effects of the PG would be expected to reduce release of proatherosclerotic growth factors for vascular smooth muscle. We found that among several fatty acids tested, DHLA was the most potent inhibitor of platelet aggregation in human or animal platelets. This effect is largely mediated via its conversion to PGE_1, which elevates cyclic AMP. EPA, adrenic acid and docosahexanoic acid also had some inhibitory properties. These and other results will be discussed in relation to the eicosanoid precursor role of the polyunsaturated fatty acids present in vegetarian-type and marine-type diets which are known to protect against occlusive coronary artery disease.

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ABNORMAL ESSENTIAL FATTY ACID LEVELS IN PATIENTS WITH ATOPIC ECZEMA: SUCCESSFUL TREATMENT WITH EVENING PRIMROSE OIL (EFAMOL). D.F. Horrobin, M.S. Manku, S. Wright and J.L. Burton, Efamol Research Institute, PO Box 818, Kentville, Nova Scotia, B4N 4H8, Canada.

Platelets from patients with atopic disorders (eczema, asthma, allergies) are known to make smaller amounts of prostaglandins (PG) than normal and to be more than normally susceptible to drugs which inhibit PG synthesis. Skin from atopic patients does not form PG normally in response to niacin. A possible cause for these observations is reduced availability of the PG essential fatty acid precursors, dihomogammalinolenic acid (DGLA) and arachidonic acid (AA). Essential fatty acid levels were measured in the phospholipid fraction from the plasma of 50 patients with atopic eczema. Linoleic acid levels were significantly elevated whereas levels of its metabolites, gamma-linolenic acid (GLA), DGLA and AA were all highly significantly reduced. These results suggest a defect in the conversion of linoleic acid to GLA by the enzyme delta-6-desaturase (D6D). If this defect is important in causing the disease, then bypassing the proposed defect by administering GLA should lead to clinical improvement. Human milk contains substantial amounts of GLA but for practical purposes the only available source is evening primrose oil (Efamol), the seed oil of *Oenother biennis* which contains ca. 9% of GLA and 72% of linoleic acid. 60 patients with atopic eczema were therefore studied in a double-blind, placebo-controlled, crossover trial of Efamol in atopic eczema. Half the patients received Efamol for 12 weeks followed by placebo for 12 weeks, while the other half received the treatments in reverse order. Three dose levels of Efamol, 2g, 4g and 6 g per day, were used. The lowest dose had no significant effect, but the two higher doses produced highly significant improvements in itching, redness, scaling and overall skin involvement by both patient and doctor assessments. Levels of GLA, DGLA and AA were all significantly elevated by the treatment, but even after 12 weeks Efamol had not fully restored normal levels. We propose that atopy may be due to a partial genetic defect in D6D function. Our observations explain the defects in PG synthesis in platelets and skin in atopic patients and also the protection against atopy afforded by human milk but not other milk products.

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ALPHA LINOLENIC ACID METABOLITES AND IMMUNOCOMPETENT CELLS. Patricia V. Johnston and Lisa A. Marshall, Burnsides Research Laboratory, Department of Food Science, University of Illinois at Urbana-Champaign, 1208 W. Pennsylvania Avenue, Urbana, IL 61801.

A brief review of the functions of immunocompetent cells will be followed by a discussion of the metabolic fate of dietary α-linolenic acid (18:3ω3) in these cells and the implications for their role in immunity. The discussion will center on two aspects of the influence of the metabolites, namely, their modulating effect on the capacity of the cells for synthesis of prostaglandins and related metabolites, and their effect on the microviscosity of the cell membrane in quiescent and stimulated cell populations. Studies showing that increases in the dietary level of 18:3ω3 relative to linoleic acid (18:2ω6) leads to a decrease in arachidonic (20:4ω6) and an increase in eicosapentaenoic (20:5ω3) acid deposition in splenocytes and other immunocompetent cells will be described. The effect of the changed fatty acid patterns on prostaglandin synthesis will be discussed with regard to the competition for the cyclooxygenase. Studies on the changes taking place in the membrane phosphoglyceride fatty acid patterns and their effect on membrane fluidity in lymphocytes during stimulation by mutagens will be reviewed. Our recent spin-labeling studies on cells from rats fed different levels of 18:3ω3 will be described. The results will be discussed from the point of view of some functions underlying the essentiality of α-linolenic acid.

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MODULATION OF PROSTAGLANDIN SYNTHESIS IN RAT PERITONEAL MACROPHAGES THROUGH DIETARY MEANS. L.J. Magrum and P.V. Johnston, 205 Burnsides Research Laboratory, Department of Food Science, University of Illinois at Urbana-Champaign, 1208 W. Pennsylvania Avenue, Urbana, IL 61801.

The ability of ω3 fatty acids to inhibit the synthesis of prostaglandins (PG) was first demonstrated by Culp et al. (Prostaglandins Med. 3:269 [1979]). Our laboratory and others have since established that the consumption of diets rich in ω3 fatty acids is associated with decreased PG synthesis in platelets (Hwang and Carroll, Am. J. Clin. Nutr. 33:590 [1980]) and immunocompetent cells (Marshall and Johnston, Lipids 17:905 [1982]) of rats. The macrophage, a cell central to the reactions of cellular immunity, is known to synthesize high levels of PG and is reported to regulate activities of other immune cells as well as some of its own through a feedback mechanism involving PG. We have conducted experiments to determine whether dietary α-linolenic acid interferes with PG synthesis in th macrophage, and if so, how this influences macrophage function. Male weanling Sprague-Dawley rats were fed ad libitum for 8 weeks purified diets containing 10% by weight fat which contained either a 3:1 or 1:42 ratio of α-linolenic to linoleic acids. Peritoneal macrophages were harvested, isolated from other peritoneal cells, and either cultured for functional studies and PG synthesis assays or extracted for fatty acid analysis. The phospholipids of macrophages from rats fed the higher amount of α-linolenic acid showed significant increases in ω3 fatty acids and decreases in ω6 fatty acids. In addition, they showed significantly decreased synthesis of PGE$_1$ and E$_2$ upon stimulation with zymosan. In vitro studies showed that the ability of the macrophage to synthesize PG could be increased or decreased by culturing cells with a complex of either arachidonic (20:4ω6) or timnodonic (20:5ω3) acids and fat-free bovine serum albumin. Effects of increased ω3 fatty acid composition and decreased PGE$_1$ and E$_2$ synthesis on macrophage function will be described.

Honored Student Presentation.

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DIETARY EFFECTS OF MENHADEN OIL ON FATTY ACID COMPOSITION AND THE ARACHIDONIC ACID CASCADE IN RAT PLATELETS. Norberta W. Schoene and Dario Fiore, USDA, ARS, BHNRC, Lipid Nutrition Laboratory, Beltsville, MD 20705.

Arachidonic acid pools in rat platelets are altered considerably in one week by diets containing n-3 fatty acids found in menhaden oil. The percentage of arachidonic acid in platelet phospholipids decreased by one-half after rats were fed a purified diet with 4% menhaden oil and 1% corn oil as the source of lipid. Little change in the percentage of linoleic acid occurred but the percentage of the n-3 fatty acid (eicosapentaenoic acid) increased, indicating that this fatty acid competes with arachidonic acid for incorporation into phospholipids. This rapidity in replacement of a n-6 fatty acid by a n-3 fatty acid is related both to turnover of platelets and phospholipid turnover in circulating platelets. A combination of HPLC and RIA methods were used to study the arachidonic acid cascade from endogenous substrate in platelets stimulated with thrombin. Platelets were prepared from two groups of rats fed for one week either the menhaden oil diet or a control diet containing corn oil alone.

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ESSENTIAL FATTY ACID DEFICIENCY IN EXPERIMENTAL DIABETES. R.T. Holman, S.B. Johnson, J.M. Gerrard and D.M. Brown, The Hormel Institute, University of Minnesota, 801 16th Avenue, N.E., Austin, MN 55912.

Male rats were maintained on a chow diet or on a semisynthetic diet containing either safflower oil or cod liver oil. Subgroups of these were rendered diabetic by injection of streptozotocin. When the diabetes had been of more than 100 days duration, the experiments were terminated, and heart, liver, kidney, abdominal aorta and serum lipids were extracted, the phospholipids isolated as a class and the fatty acid patterns measured by capillary GLC. In the rats fed chow diet, the patterns of PUFA indicated an anomalous EFA deficiency, with minor variations in the several tissues. The phenomenon was essentially the same in rats fed semisynthetic diet, but the safflower and cod liver oil diets influenced the patterns of the PUFA as well.

Session BB Pharmacological Role of Lipids — III Tuesday p.m.

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EFFECTS OF DIETARY LINOLEATE ON EICOSANOID SYNTHESIS IN RAT PLATELETS. Melvin M. Mathias and Cynthia A. Taylor, Colorado State University, Gifford Building, Dept. of Food Science & Nutrition, Ft. Collins, CO 80523.

Arachidonic acid, the precursor of prostaglandins (PG) is synthesized from dietary linoleic acid. We have studied the effects of amount of linoleate in diet on PG synthesis in rat platelets employing multipoint schemes achieved using saturated fats, unsaturated fats, or combinations of these to produce a range of linoleate levels. Early work showed relative linearity in PG synthesis with increasing linoleate; then, more recently, high linoleate (29% linoleate calories) decreased synthesis of the eicosanoid thromboxane B2 (TXB$_2$). Obviously, the relationships between dietary levels of this essential fatty acid and PG synthesis are complex. To investigate these effects further, male Sprague-Dawley rats were fed one of 8 semipurified diets containing, by weight, 19% protein, 50% carbohydrate, and 21% fat. The culinary fats and polyunsaturated/saturated combinations used yielded percent energy as linoleate of 0.0, 0.4, 2.3, 9.0, 23.0 and 31.0. Rats were fed these diets for 4 months, then were sacrificed in the fed state under light ether anesthesia. Coagulating blood was drawn via the juglar vein and incubated at 37 C for 10 or 40 min. At the end of the incubation period, PG synthesis was stopped with 4.2mM aspirin and serum was obtained and assayed for PGE$_2$, PGE$_1$, PGF$_{2a}$, and TXB$_2$ by radioimmunoassay. Platelet derived levels of PGE$_2$, PGE$_1$, PGF$_{2a}$, and TXB$_2$ increased as linoleate increased from 0.0% to 0.4%; however, they remained relatively linear thereafter. Synthesis approximately doubled in the 40-min incubated samples as compared to the 10-min samples. In all cases, eicosanoid production was lower in rats fed hydrogenated coconut oil (0% linoleate) than in those fed a fat-free diet (also 0% linoleate), indicating a more pronounced essential fatty acid deficiency induced by hydrogenated coconut oil.

Honored Student Presentation.

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PERMEATION OF AMPHIPHILIC SOLUTES ACROSS LIPID BILAYERS. John Bramhall, Microbiology & Immunology Department, Medical School, University of California, Los Angeles, CA 90024.

Permeation across lecithin bilayers has been studied using rapid-mixing, stopped flow techniques with a group of structurally related amphiphilic dyes. Permeation occurs in three discrete kinetic phases: a rapid, superficial adsorption of dye to membrane, translocation across the center of the bilayer followed, finally, by release at the opposite side. Translocation has been identified as the slowest step, by several orders of magnitude, for the amphiphiles studied. Charged solutes show a maximum rate of translocation at a temperature coinciding with the gel to liquid-crystalline phase transition (Tc). Neutral solutes show no such maximum, and translocation rates increase continuously with temperature. The data suggests that translocation of charged amphiphiles is rate-limited by the rate of copermeation of counterions which restore electrical balance. Using one dye in particular, N-5-dimethylaminonaphthalene-1-sulfonyl glycine, differences in behavior have been identified between the inner and outer membrane monolayers of small single-shelled lecithin vesicles. This dye also reveals that the inner monolayer suffers temperature-dependent structural changes at temperatures well below Tc. Rate constants for translocation range from 10^2 to 10^{-4} sec^{-1} for the solutes studied, and the activation energies for the process are ca. 100 kJ/mol. Rates are strongly influenced by the physical state of the lipid bilayer, as well as by the size and polarity of the permeating amphiphile.

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EFFECT OF DIETARY LECITHIN ON LIPID METABOLISM IN RATS. Mei Ling W. Chang and Margaret A. Johnson, Carbohydrate Nutrition Laboratory, Beltsville Human Nutrition Research Center, ARS, USDA, Building No. 307, Room No. 328, Agricultural Research Center-East, Beltsville, MD 20705.

Blood cholesterol is known to be associated with atherosclerosis. Dietary lecithin (Lec) lowers blood cholesterol in men as well as in rats. Dietary Lec depressed lipogenic enzyme (glucose-6-phosphate dehydrogenase, 6-phosphogluconate dehydrogenase and malic enzyme) activities in the liver of the rat and also lowered rat liver total lipid. Liver cholesterol concentration was markedly lower in the

Lec-fed than in the control animal. These decreases were observed in rats after a feeding for 14 days as well as in rats fasted and refed for 2 days. Further investigations indicated that these effects of Lec were not due either to the action of its polyunsaturated fatty acids or to any other fragment of the Lec molecule. Recently, a study was initiated to investigate the effect of Lec on the degradation of cholesterol in tissues. Rats were fed a cholesterol-4-^{14}C diet for 2 days and then continuously fed the same diet without labeled cholesterol for 12 days more. One group of rats was killed after day 3 of feeding (G1) and served to quantitate the cholesterol in the tissues and another group was killed after day 14 of feeding (G2). The excretion of radioactive sterol was greater in the Lec-fed than in the control group during the period of isotope intake and, in contrast, the radioactivity in the liver and serum was significantly less in the Lec-fed than in the control group. However, the deposition of cholesterol in the skin was about the same in both diet groups. From the comparison of G1 with G2, radioactive sterol disappeared in all tissues studied, but there were differences in the rates of disappearance among tissues and between diets. The loss of radioactivity was faster in Lec-fed, especially in the skin, than in the control. The excretion of endogenous neutral sterol (% of total sterol) was much greater in Lec-fed than in the control, 27.5 ± 2.9 and 12.9 ± 0.9%, respectively. This might indicate that dietary Lec affected catabolic pathways of endogenous cholesterol. In summary, Lec depressed lipogenic enzyme activities in the liver, inhibited cholesterol absorption, increased cholesterol disappearance and lowered serum and liver cholesterol levels.

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BIOPHYSICAL CHARACTERIZATION OF DIETARY LIPID INFLUENCES ON IMMUNE RESPONSIVENESS. Dorothy A. Adams and Kent L. Erickson*, Department of Human Anatomy, University of California, School of Medicine, Davis, CA 95616.

Previous investigations indicate that dietary fat can modify several parameters of immune status in neonatal mice such as response to T-cell mitogens, the percentage of immunoglobulin (Ig) positive cells, and serum immunoglobulin levels. The purpose of these current studies was to determine the influence of dietary fat concentration and saturation on antibody response in mice. Dietary fat did not influence the number of IgM or IgG-bearing lymphocytes after primary or secondary immunization with sheep red blood cells. Likewise, there was no difference in the number of Ly 1.2, Ly 2.2 or Thy 1.2 bearing cells among the dietary groups. In contrast, both IgM and IgG plaque forming cell (PFC) responses were greater for those mice fed a diet adequate in essential fatty acids than those fed a fat-free diet. Both IgM and IgG PFC responses after primary immunization increased in mice fed the saturated fat (SF) diet and decreased in mice fed the polyunsaturated fat (PUF) diet as compared with the controls. A similar pattern was observed for IgG PFC response after secondary immunization. These changes in PFC response were inversely related to the levels of linoleic acid in the whole lymphocyte as well as isolated plasmalemma. Nevertheless, the mechanism by which dietary lipids modulate immune response is known. To understand the molecular interactions involved, we are examining the motional properties of membrane components by biophysical methods. Fluorescence polarization of lipophilic probes in lymphocytes was decreased in mice fed 8% PUF but not in lymphocytes from other groups. However, the fluorescence lifetimes did not remain constant, therefore interpretation of the polarization data is equivocal. Preliminary high resolution ^{1}H NMR has indicated a possible shift in the distribution of phosphatidylcholine in the membrane bilayer. Spectral changes observed by ^{31}P NMR indicate alterAtion in the motional properties of phospholipid headgroups in situ on the membrane surface as a function of dietary manipulation. We conclude that lipids can modulate the level of immune responsiveness; furthermore, this may be related to changes in membrane fluidity. (Supported by NCI, DHHS grant CA 30273 and the National Live Stock Meat Board).

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EFFECT OF PHOSPHOLIPIDS ON THE CONTROL OF NUCLEAR DNA TEMPLATE RESTRICTION. Francesco Antonio Manzoli, Instituto di Anatomia Umana Normale, Università di Bologna, Via Irnerio 48, 40126 Bologna, Italy; Nadir Mario Maraldi, Università di Ancona; and Silvano Capitani*, Università di Ferrara, Italy.

Phospholipids have been identified as minor components in the chromatin of a number of sources. They undergo significant changes related to cell growth, differentiation and malignant transformation. Functional evidences indicate that they affect the thermal stability of DNA and nucleohistones, and modify the activity of DNA and RNA polymerase in both bacterial and eukaryotic systems, so that they show the features of potential template-regulating molecules. In isolated rat liver nuclei, anionic phospholipid vesicles increase the endogenous RNA polymerase activity and give rise to an extensive euchromatization, whereas opposite effects are obtained with neutral vesicles. The changes of transcriptional activity seem to depend on the interaction of the lipid molecule with the nuclear components and may be related to a different removal of repressor proteins, which can also account for the transition of the chromatin structure.

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THE MODE OF ACTION OF CHOLESTERYL 14-METHYLHEXADECANOATE IN PROTEIN SYNTHESIS. Zdena Tuháčková and Jan Hradec*, Department of Biochemistry, Oncological Institute, Na Truhlářce 100, 180 00 Prague 8, Czechoslovakia.

Evidence was provided by our several papers that cholesteryl 14-methylhexadecanoate (CMH) plays an important role in protein synthesis. It is a constituent of aminoacyl-tRNA synthetases, peptide initiation and elongation factors and of ribosomes. The enzymic activity is significantly decreased if it is removed by extraction or digestion with cholesterol esterase and normal activity can be restored by the addition of pure CMH. This lipid intereacts in a specific way with the binding site for aminoacyl-tRNA. Labeled CMH prepared in this laboratory becomes bound by peptide initiation and elongation factors as a specific allosteric modifier changing the conformation of protein-synthesis factors and thus modulates the activity of their binding sites. This modulation apparently involves the interaction of this lipid with the phosphroylation of protein-synthesis factors. Autocatalytic phosphorylation of protein-synthesis factors recently discovered in this laboratory affects the binding of aminoacyl-tRNA probably by a competition for the same binding site. The participation of CMH in these reactions may thus explain the molecular mechanisms of the involvement of this lipid in the translation of the genetic message.

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ANTITUMOR AND ANTILEUKEMIC PROPERTIES OF SYNTHETIC ALKYL-LYSOPHOSPHOLIPIDS (ALP) IN VITRO. Wolfgang E. Berdel, Ulrich Fink, Anneliese Reichert and Johann Rastetter, Division of Hematology and Oncology, Department of Medicine I, Technical University, Munich, Federal Republic of Germany.

ALP are synthetic analogs of the naturally occurring ester-linked 2-lysophosphatidylcholine (2-LPC). Some of these ether-linked lysophospholipids show cytostatic and cytotoxic properties when incubated with cells of various human solid tumors and leukemias in vitro. ALP inhibit the uptake of radiolabeled thymidine in cells of both permanent lines and single cell suspensions of freshly explanted solid tumors as well as various human leukemias. Solid tumors of more than 15 different histologies, various acute leukemias and blastic crisis of chronic myelogenous leukemias have been tested. Generally, 1 μg/mL ALP was found to be the lowest effective concentration. In the majority of tests, a clear dose response relation was observed between 1 and 30 μg/mL. A minimum incubation period of 12 hr was necessary, and full efficacy with incorporation rates less than 10% of the controls was reached after incubation periods > 48 hr. Leukemic cells and cells of permanent in vitro lines were found more sensitive than cells of freshly explanted solid tumors. Only the ether-linked ALP but not the ester-linked 2-LPC showed activity in the dose range between 1 and 30 μg/ml. Results of trypan blue dye exclusion test were closely correlated with thymidine incorporation in cells from solid tumors and leukemias. These results indicate that ALP exert not only antiproliferative but also cytotoxic activity. Furthermore, tumor cells and leukemic cells revealed severe membrane defects in microscopic examinations and scanning electron microscopy. Several observations indicate that the involvement of an alkyl-cleavage-enzyme defect of neoplastic cells is one possible molecular basis for the antineoplastic activity of ALP in vitro: (a) The cytotoxic activity is closely linked to the ether-bond of the molecule. (b) Treatment of ALP with a preparation of alkyl-cleavage-enzyme from rat liver microsomes destroyed almost all of the cytotoxic properties of the ALP (in cooperation with F. Snyder). (c) Some authors have found a selectivity in the cytotoxic action of ALP within a certain dose range since nonneoplastic cells are less sensible.

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THE INACTIVATION OF BACTERICIDAL FATTY ACIDS BY AN ENZYME OF *Staphylococcus aureus*. Frank A. Kapral and Joel E. Mortensen, Department of Medical Microbiology and Immunology, 5072 Graves Hall, The Ohio State University, Columbus, OH 43210.

Staphylococcus aureus is a bacterium capable of causing a family of distinct diseases in the human. Some infections, such as boils, are relatively benign, whereas pneumonias, bone infections, or the toxic-shock syndrome are severe. Regardless of the site of infection, the organism typically tends to form lesions which are localized (abscesses) and in which various toxins are produced. These toxins, when disseminated, account for the symptoms associated with the different disease states. Recently, it was shown that an important mechanism whereby the host controls growth or destruction of the staphylococci within abscesses is by the production of a group of staphylocidal fatty acids (SFA). Subsequently, it was found that some staphylococcal strains can produce a factor capable of inactivating the SFA and therefore studies were begun to determine how this was accomplished. Staphylococci were grown in trypticase soy broth at 37 C/24 hr. The filter-sterilized culture supernatant (source of the factor) was reacted with either pure fatty acids or fatty acid mixtures obtained from staphylococcal abscesses. Separation of the reaction products by TLC and their identification by mass spectroscopy revealed that the factor was an enzyme capable of esterifying a variety of unsaturated long-chain fatty acids. The enzyme is destroyed by protease K and is inactivated at 60 C/hr. Esterification is optimal at pH 6 and at 37-40 C, and does not require divalent cations. Fatty acids can be esterified to either methanol, ethanol, isopropanol, acetone, or cholesterol, but not to certain other mono-, di-, or polyhydric compounds. The enzyme is strongly inhibited by triglycerides and less so by diglycerides, provided that these lipids contain unsaturated fatty acid residues in the molecule. These results indicate that some *S. aureus* strains produce an esterifying enzyme which may afford the organism protection against the SFA under conditions existing within abscesses.

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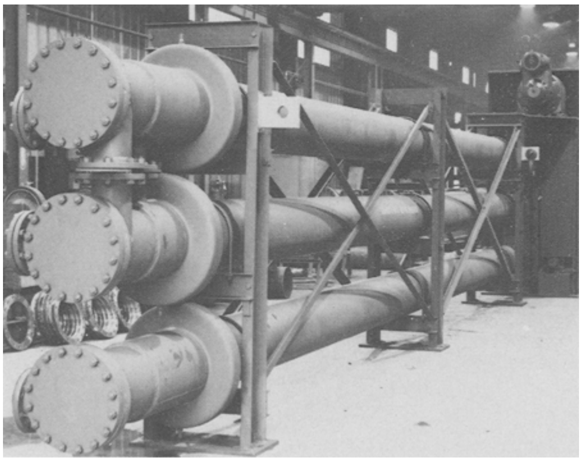
THE RECENT TREND IN USAGE OF FATS AND OILS AS FUNCTIONAL INGREDIENTS IN THE BAKING INDUSTRY – NUTRITIVE VALUE. O.K. Chung and Y. Pomeranz, US Grain Marketing Research Laboratory, 1515 College Avenue, Manhattan, KS 66502.

This presentation reviews the recent trend in usage of fats and oils in baking industry. Fats are essential ingredients in baking. Amounts and types of fats vary depending on types of baked goods. Insofar as fats and oils are concerned, a revolutionary change has taken place in the US baking industry during the last decade. Utilization of shortening in bread and cake baking decreased from 1972 to 1977 by 22% (from 956 million lb to 741 million lb) and of lard



by 54% (from 266 million lb to 122 million lb). Utilization of shortening in all baked goods including cookies and crackers was 1422 million lb (34% of total) in 1972 and 1158 million lb (27% of total shortening consumption) in 1977, based on a report by S.S. Jackel in 1980 (Baker's Dig. 54:32). The trend is now to replace the plastic fats in baked goods with liquid vegetable oils and also to reduce total usage of fats and oils. In order to maintain vegetable oils as functional ingredients in baked goods, a small amount of surfactant(s) is added. Thus, nutritive values, especially food energy and the fatty acid balance, of baked goods would be changed by the recent trend in usage of fats and oils as functional ingredients in the baking industry. The role of baked goods as sources of fats and oils in meeting dietary goals and recommendations will be discussed.

Session CC Tall Oil Tuesday p.m.

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TALL OIL ACIDULATION – STATE OF THE ART. Wilford W. Keyes, 609 Poinciana Drive, Gulf Breeze, FL 32561.

As introduction, a brief definition of tall oil, and its relative position in world fatty acid and rosin commodity markets is given. The history of various tall oil acidulation methods is outlined. The analyses of tall oils from various geographical areas are given, and typical reasons for the quality variations are discussed. The effect of various acidulation methods on the quality of tall oil and its acidulation byproducts is detailed. Several novel methods of acidulation have been tried in an effort to minimize sulfur in the brine and lignin phases that must be returned to the pulp mill liquor recovery cycle. In conclusion, a detailed discussion of acidulation methods in current use, giving the advantages and disadvantages of each is given.

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TALL OIL SOAP ACIDULATION PROCESSES. Faustino L. Prado, Baymont Engineering Company, 10051 5th Street North, St. Petersburg, FL 33702.

When the acidulation of tall oil soap (Kraft black liquor skimmings) to manufacture crude tall oil was developed in Scandinavia early in the century, the only method then available was the batch or "cook" method. The original batch processes were labor intensive and featured little instrumentation. In contrast with early production methods, today one can find modern acidulation plants with large capacity, high reliability, good quality control, and low labor demands. This paper will survey the present acidulation process, compare their relative advantages and disadvantages, and show a flow diagram for each. Particular emphasis will be given to economic considerations. The following processes will be specifically considered: (a) batch acidulation/batch gravity decanting, (b) continuous acidulation/batch gravity decanting, (c) continuous acidulation/continuous gravity decanting, and (d) continuous acidulation/continuous centrifugal decanting. Other methods, which are no longer used will be mentioned, but will not be discussed in detail.

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A COST-EFFICIENT AUTOMATED SEMICONTINUOUS TALL OIL ACIDULATION PROCESS. J.P. Krumbein, Reichhold Chemicals, Inc., PO Box 1433, Pensacola, FL 32596.

Automated batch type skimmings acidulation plants provide a cost-effective and flexible tall oil process offering comparatively low capital investment and low operating costs. Automation is achieved by the use of timer operated metering pumps and automated reactor temperature control to acidulate the skimmings. Continuous gravity operation is employed to separate the oil-salt cake water phases. A soap washing step is used to remove black liquor from the skimmings prior to acidulation. Four automated batch plants of the type described in this paper are now in successful operation.

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USE COMPARISON OF TALL OIL FATTY ACIDS. H.G. Arlt, Arizona Chemical Co., 16-00 Route 208, Fair Lawn, NJ 07410.

This paper will review the source refining and utilization of tall oil fatty acids. The similarities with other vegetable source fatty acids will be established. Special emphasis will be placed on physical and chemical properties of tall oil fatty acids and correlation of properties with utility. Tall oil fatty acids are produced from black liquor soap which is a byproduct of the Kraft pulping of pine wood. The soap is acidified and refined to produce high purity mixtures of straight-chain C-18 unsaturated fatty acids similar to those derived from various seed oils. The minor differences in the fatty and nonfatty acid components of tall oil and seed oil fatty acids result as a consequence of source isolation and refining. The uniformity, availability, and chemical properties of the tall oil fatty acids result in key uses such as dimer acids, epoxy plasticizers and polymerization emulsifiers.

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MODERN TECHNIQUES FOR EVALUATING ALLOYS IN FRACTIONAL DISTILLATION TOWERS. Earle Fritz, Union Camp Corporation, PO Box 2668, Savannah, GA 31402.

The most common problem facing the design and process engineer is the choice of material of construction as it relates to corrosion. This is especially true for fatty acid distillation towers. After installation, feedstocks and processing conditions change from those originally specified, frequently resulting in a more aggressive corrosive atmosphere. The use of retractable corrosion probes allows the monitoring of corrosion of several species of metals at the same location in the distillation towers. It is also possible to evaluate the potential for crevice corrosion, galvanic corrosion, and the effect of the surface condition of the metal. Temperature as well as concentration of fatty acids can be correlated to the actual corrosion occurring in the distillation column and internals. By using these probes along with fixed corrosion coupons and iron material balance in the process streams, it is possible to set operating parameters that minimize the potential for continuing corrosion.

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PRODUCTION OF TALL OIL FATTY ACIDS VIA A MODERN DAY DISTILLATION PROCESS. Elliott Shimley, Marketing – Tall Oil & Specialty Chemicals, Georgia-Pacific Corporation, 133 Peachtree Street N.E., Atlanta, GA 30303.

This paper examines the experience of Georgia-Pacific Corporation in building and operating a Luwa process plant to process crude tall oil from sulfate pulping operations. The five-stage process and its fractioning sequence are described. Comments and caveats regarding the operation of each stage are provided, as are overall comments on the process's viability for small capacity operations. Also discussed are the primary advantages of the Luwa process. The second portion of this paper examines the products derived from the process. Included are descriptions of the properties and marketplace applications of tall oil fatty acids, tall oil rosin, heads, pitch and distilled tall oil.

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MODERINZATION OF EXISTING TALL OIL STEAM DISTILLATION PLANTS. William J. Hartnett, Foster Wheeler SPEC, Inc., 110 South Orange Ave., Livingston, NJ 07039.

Recent changes in the cost of energy and pricing of raw materials have caused producers, and subsequently design engineers, to reevaluate the use of steam distillation in the production of tall oil rosin and fatty acids. This paper will attempt to show that steam distillations can be made substantially more attractive by the addition of process heat recovery systems for improved thermal efficiency and partial or complete replacement of trays with modern packings to improve product recovery.

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AUTOMATIC SS OVERLAY: A COST-EFFECTIVE ALTERNATIVE FOR RENEWING FATTY ACID TOWERS AND PRESSURE VESSELS. John Hartemink, Alloy Cladding – Div. of Digi-Data Corp., R.R. 13 Box 843, Ft. Myers, FL 33908.

Automatic, stainless steel weld overlay is a cost-effective and viable method to extend the operational life of fatty acid and tall oil towers and other pressure and vacuum vessels. This paper will discuss the specially designed submerged arc welding equipment Alloy Cladding has designed and used, details on the kinds of vessels which can be overlaid with this equipment and the history of overlay. It will also review some of the essential requirements which must be defined prior to contracting for an overlay including variables such as chemistry, percent of bead overlap and the thickness of the deposit. Finally, it will run through a typical job sequence and discuss average production statistics.

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APPLICATION OF FLEXIPAC® (MELLAPAC®) TO EXISTING TALL OIL RECTIFICATION COLUMNS. C.S. Brown, Koch Engineering Co., Inc., 161 E. 42nd St., New York, NY 10017.

FLEXIPAC, a high efficiency, low pressure drop oriented tower packing, has now been used for several years in the distillation operations for the production of tall oil derived fatty acids and rosin. Pilot plant studies and commercial installations will be discussed, with specific reference to pressure drop, efficiency of separation and the benefits that are derived from the use of this packing to replace trays or dumped packing in existing columns. The principal benefit – the reduction or even elimination of carrier steam – will be discussed. Also covered, will be practical aspects of installation of the packing, auxiliaries required, maintenance and materials of construction. FLEXIPAC, the trade name of Koch Engineering Company, is licensed from Sulzer Brothers of Switzerland who market the same product under the trade name MELLAPAK in Europe, Asia and other areas.

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METERING DIFFICULT CHEMICALS IN A TALL OIL ACIDULATION PROCESS. R.E. Clements, Clements & Associates, Inc., PO Box 28747, Memphis, TN 38128.

One of the most critical points in any tall oil plant is the sulfuric acid metering. Methods of metering are reviewed on the basis of accuracy required, types of equipment available, and typical individual cost. A typical metering system is examined from the point of acid supply, through the metering circuit to entry into the reactor. The system is described in engineering terms with sample calculations demonstrating friction drop, pipe sizing, and the relative energy requirements when the pipe size is changed. Although no conclusions are drawn on which system is most practical, the controlling parameters are defined so that those at the individual plant can reach their own conclusion.

SESSION DD Lipoproteins and Membranes Wednesday a.m.

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CALIBRATION OF THE ANALYTIC ULTRACENTRIFUGE (AnUC). F.T. Lindgren, V.G. Shore, G.L. Adamson, L.A. Glines and T.S. Kahlon, Donner Laboratory, Lawrence Berkeley Laboratory, University of California, Berkeley, CA 94720.

The analysis of lipoproteins involves reproducible methods for isolation, characterization and quantification of lipoproteins. With quantitative refinement in the specific refractive increments, the analytic ultracentrifuge may provide a more stable absolute standardization for lipoprotein and lipoprotein subfraction analysis. We have used a Beckman standard calibration wedge routinely to establish and maintain calibration, after a drive change or any manipulation or adjustment of the optical system. Usual changes are less than 1–2% of the previous calibration. The calibration used for our computer analysis of schlieren lipoprotein patterns is that for corresponding time periods. Since this method has never been independently validated, we chose to construct a special boundary cell consisting of a 2½° centerpiece scribed one-third from the top on both sides. One side is one-third filled with 1.47% sucrose, and the other is filled completely with distilled H_2O. During acceleration to ca. 10,000 rpm, a sharp boundary is formed which diffuses with time. With standard magnification, the calibration wedge gives a rectangular area between the scribed lines and the vertical deviation of 114.68 cm^2, corresponding to 0.007638 Δn. The extrapolated 0 time area of the sucrose boundary was 32.03 cm^2, giving a $\Delta n = 0.002130$. Independent precision refractometry (Na_D line) between water and the sucrose solution gave a $\Delta n = 0.002108$ or within 1% of the wedge value. Substituting a Hg source (as used in the AnUC) gave a Δn within the error of measurement, i.e., ± 0.00002 Δn, or ±1% of the above Na_D line Δn value. Evaluation of specific refractive increment (SRI) requires precise lipoprotein mass measurements. To achieve this we employed CHN elemental analysis (accurate to less than 1%) and total lipid and protein composition analysis. Also since lipoprotein fractions are isolated in the presence of the serum small molecule background containing glucose, amino acids, etc., all fractions were dialyzed against the NaBr salt background of $\rho_{20} = 1.0631$ g/mL and 1.2030 g/mL as used for AnUC of LDL and HDL, respectively. Results of 0.00140 and 0.00132 for total LDL and HDL, respectively, compare with 0.00154 and 0.00149 Δn/g/100 mL as presently used. Lower values obtained from schlieren analysis in the analytical ultracentrifuge, as compared with refractometry, probably reflect nonfloating HDL and LDL of densities close to 1.20 g/mL and 1.061 g/mL, respectively.

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COUPLED SECRETION OF VERY LOW DENSITY LIPOPROTEIN APOPEPTIDES AND ACYLGLYCEROLS BY THE LIVER CELL. David R. Janero, Patricia Siuta-Mangano and M. Daniel Lane, Physiological Chemistry, 725 North Wolfe Street, Baltimore, MD 21205.

Primary cultures of estrogen-induced chick liver cells have been used to investigate the relationships among very low density lipoprotein (VLDL) apoprotein synthesis, the assembly of lipid with the VLDL apopeptides, and the secretion of the VLDL particle. Hepatocyte monolayers in lipid-free medium were pulsed for 2.5 min with either [^{3}H]leucine or [^{3}H]palmitate and were then chased for 8.5 hr with fresh lipid-free medium either containing 10 μM cyclohexamide or not. At this concentration, cycloheximide inhibits cellular protein (and VLDL apopeptide) synthesis by $>$ 98% within 30 sec without impairing the secretion of VLDL apoprotein chains completed prior to the cycloheximide treatment. During the chase, parallel aliquots of media from both the [^{3}H]leucine- and [^{3}H]-palmitate-labeled cultures were taken, and the VLDL was immunoprecipitated therefrom to assess the appearance of VLDL [^{3}H]-apoproteins and [^{3}H]lipids in the medium. In both the absence and presence of cycloheximide, 3 hr are required for ∿95% of the pulse-labeled VLDL [^{3}H]apoprotein B to clear the cells and be secreted. Without cycloheximide, [^{3}H]triglyceride and [^{3}H]phospholipids specifically associated with VLDL apoproteins continue to be secreted over the course of the 8.5-hr chase. The cycloheximide-treated cells do not secrete VLDL [^{3}H]lipids after 3 hr into the chase, i.e., after the cells have secreted their content of VLDL apoprotein synthesized prior to the cycloheximide block. The lipid secreted up to 3 hr is associated with the apopeptide chains completed prior to cycloheximide treatment but not yet secreted. We conclude that hepatic apoprotein synthesis is essential for the assembly and secretion of the VLDL acylglycerols and plays a decisive regulatory role in the control of VLDL biogenesis. (Supported by NIH AM-06706 (DRJ), GM-00184 (PS), and AM-14574/5 (MDL).)

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PLASMA LIPID AND LIPOPROTEIN RESPONSE OF HUMANS TO BEEF FAT, COCONUT OIL AND SAFFLOWER OIL. W. Insull Jr., J.L. Probstfield, A. Silvers, L.W. Scott, M.L. Shorney, A.M. Gotto Jr., R.D. Wood, B.C. O'Brien and Raymond Reiser, Department of Biochemistry and Biophysics, Texas A&M University, College Station, TX 77843-2128.

The purpose of this study was to compare human plasma lipid and lipoprotein response to dietary beef fat (BF) and coconut oil (CO), fats customarily linked as "saturated," in dietary recommendations for prevention of coronary heart attacks. Safflower oil (SO) was used as the unsaturated control oil. Twelve free living normolipidemic men aged 25.6 ± 3.5 (SD) years consumed centrally prepared lunches and dinners of common foods having 40% fat calories, 60% of which was of the test fats. The test fats were isocalorically substituted, and each was ingested for five weeks in random sequences with intervening five weeks of ad libitum diets. Breakfast during the test periods was low in fat and high in carbohydrate. The average plasma lipid and lipoprotein cholesterol (C) responses to the the fats in mg/dl ± SD were: total C:BF 150 ± 28, CO 163 ± 34, and SO 135 ± 20; triglycerides:BF 87 ± 23, CO 68 ± 16, and SO 75 ± 29; HDL C:BF 41 ± 11, CO 47 ± 11, and SO 44 ± 10; LDL C:BF 96 ± 33, CO 100 ± 41, and SO 79 ± 16; and VLDL C:BF 17 ± 19, CO 5.6 ± 5.6, and SO 16 ± 10. The low TG and VLDL C responses to CO is attributable to its high content of fatty acids of less than 14 carbon acids, ca. 80%. Since much of these are absorbed via the portal system, they may produce a low level of chylomicrons. BF and SO have none of these acids. The customary grouping of BF with CO as "saturated" in dietary recommendations for prevention of coronary heart disease overlooks their differences in absorption, transport and metabolism. Eventually these differences are expressed in different plasma lipid and lipoprotein concentrations. Thus, BF should not be equated with CO as saturated fats for their lipidemic and atherogenic effects.

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SYNTHETIC LYSOPHOSPHOLIPID ANALOGS AND THEIR USEFULNESS IN MEMBRANE STUDIES. Wolfgang J. Baumann, S. Parthasarathy, R. Murari, The Hormel Institute, University of Minnesota, 801 – 16th Avenue, N.E., Austin, MN 55912; and M.M.A. Abd El-Rahman*, Department of Chemistry, Alexandria University, Alexandria, Egypt.

Monochain choline and ethanolamine phospholipids, in which the glycerol backbone was replaced by a short-chain diol, were synthesized. The lysophospholipid analogs were used to probe the structural specificity of various lysophospholipid-mediated membrane processes independent of rapid lysophospholipid turnover. The choline phospholipids were prepared from the respective diol monoesters or monoethers by condensation with 2-bromoethyl dichlorophosphate in ether followed by nucleophilic displacement of the bromine with trimethylamine. The ethanolamine phospholipids were synthesized from monoradyl diols by condensation with 2-phthalimidoethyl dichlorophosphate in THF and removal of the phthalimido group with hydrazine. The diol-derived choline phospholipids mimicked lysolecithin in their physical effects on erythrocytes and other cells. Lysophospholipid-mediated stimulation or inhibition of various membrane-bound enzymes, such as diacylglycerol cholinephosphotransferase, was more structure specific. We found that the cytolytic and enzyme-modulating effects of lysolecithin and its analogs were counteracted by cholesterol. This lysolecithin-cholesterol antagonism may be attribted to the ability of cholesterol to prevent the reorganization of the membrane and the formation of more labile lysolecithin-rich membrane domains by stabilizing the lysophospholipid in a lamellar arrangement.

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DOPAMINE RECEPTOR FUNCTION IN NIE-115 NEUROBLASTOMA: EFFECTS OF MANIPULATING MEMBRANE FATTY ACIDS. M.G. Murphy, Dalhousie University, Department of Pharmacology, Sir Charles Tupper Medical Building, Halifax, Nova Scotia B3H 4H7, Canada.

The effects of polyunsaturated fatty acids (PUFA) on dopamine receptor function are being investigated in NIE-115 neuroblastoma cultured in PUFA-supplemented media, by radioligand binding studies and intracellular cAMP determinations. The dopamine agonist, [^{3}H]ADTN (5–10 nM) and antagonist, [^{3}H]spiroperidol (1–5 nM), bind to NIE-115 with a high degree of specificity (108.3 ± 32.6 (mean ± SEM, N=5) and 115.8 ± 29.3 (N=7) fmol specifically bound/mg protein, respectively). Binding of both radioligands was enhanced (>130% control values) when cells were cultured with 20:4 (n-6) (50 μM). [^{3}H]Spiroperidol binding was even higher in 18:2 (n-6)-supplemented cells; however, growth in 18:3 (n-3) reduced binding (<75% control), particularly at low concentrations of ligand. Basal levels of intracellular cAMP were higher (1.5–2.5 fold) in cells cultured with either 18:2 or 18:3, with the most pronounced effect being observed in the 18:2 cultures. Incubation (15 min, 37 C) with dopamine (10–100 μM) resulted in 2–4 fold increases in cAMP levels in control and 18:3-supplemented cells, whereas adenylate cyclase in cells grown with 18:2 was much less sensitive to dopamine stimulation. These results suggest that membrane receptor function is affected by polyunsaturated fatty acids, and that functional state is fatty-acid specific.

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UPTAKE AND METABOLISM OF LIPID VESICLES FROM SEAWATER BY JUVENILE PACIFIC OYSTERS, *Crassostrea gigas*. Robert S. Parker and Daniel P. Selivonchick, Division of Nutritional Sciences, N205B MVR, Cornell University, Ithaca, NY 14853.

Ingestion and metabolism of liposomes by juvenile Pacific oysters *(Crassostrea gigas)* were studied by several methods in an effort to assess their potential as encapsulating agents. Liposomes composed of egg phosphatidylcholine/cholesterol/stearylamine (7:1:2) formed readily and appeared stable in synthetic seawater. Radiotracer studies with liposomes containing [4-^{14}C] cholesterol or [1-^{14}C] dipalmatoyl phosphatidylcholine (DPPC) showed uptake of up to 40% of the available dose in 24 hr. Most label appeared in epithelial cells of ducts and tubules of the digestive diverticula, as shown by autoradiography. Fluorescence microscopic examination of oysters fed fluorescein isothiocyanate (FITC)-tagged liposomes or liposomes with encapsulated FITC-tagged albumin revealed tissue distribution similar to that observed with radiotracer studies. Radioactivity from encapsulated ^{14}C-labeled glucose or amino acids appeared predominantly in water-soluble or acid-precipitable material, respectively. Label from [1-^{14}C]DPPC was redistributed into triglycerides, phosphatidylethanolamine, and choline phosphonolipid, and appeared to involve transacylation rather than de novo synthesis. The data indicates uptake of intact liposomes followed by intracellular breakdown and redistribution of liposomal material. Therefore, these lipid vesicles may serve as a useful delivery system for nutritional or toxicological studies involving bivalves or other filter-feeding organisms. (Conducted at Oregon State University through the Oregon Agricultural Experiment Station.)

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HEPATIC ASSEMBLY OF VERY LOW DENSITY LIPOPROTEIN APOPROTEINS AND GLYCEROLIPIDS IN THE ABSENCE OF APOPEPTIDE GLYCOSYLATION. David R. Janero and M. Daniel Lane, Department of Physiological Chemistry, The Johns Hopkins University School of Medicine, Baltimore, MD 21205.

The major and only glycosylated apoprotein of chick very low density lipoprotein (VLDL) is apoprotein B; the "C" apopeptides are not glycosylated (J. Cell Biol. 73:332 [1977]). We have employed chick hepatocytes in primary culture to investigate the role of VLDL apopeptide glycosylation in the regulation of VLDL biogenesis. To this intent, hepatocyte monolayers were incubated for 4.5 hr in lipid-free medium either with or without 0.1 μg/mL tunicamycin, thereby, in the former case, blocking further cellular protein (and apoprotein B) glycosylation and allowing secretion of all intracellular synthesized apoprotein B already glycosylated. The monolayers were then labeled for 2.5 hr with [^{3}H]palmitate in fresh, lipid-free medium with or without tunicamycin, in accord with prior treatment. After labeling, the lipids specifically associated with secreted VLDL were isolated by immunoprecipitation and were analyzed chromatographically and radiochemically to quantify the [^{3}H]palmitate incorporated into the VLDL acylglycerols. The total amount of [^{3}H]palmitate, as well as its distribution among the various glycerolipid types, was identical in secreted VLDL containing either glycosylated or unglycosylated apoprotein B. In both cases, the "C" apopeptides were assembled into VLDL and were secreted normally. Fine-structural examination of the two types of VLDL particles revealed no morphological difference between them. These studies demonstrate that the state of apoprotein B glycosylation does not influence the assembly of VLDL apopeptides B and "C" with the major VLDL acylglycerols, the secretion of the lipids in specific association with the VLDL apoproteins, or the fine-structure of the secreted VLDL particle. Thus, aglycoapoprotein B can serve as a structural and functional component of hepatic VLDL. (Supported by NIH AM-06706 (DRJ) and AM-14574/5 (MDL).)

SESSION EE Protein Chemistry and Interactions Wednesday a.m.

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NATIVE AND INDUCED CONFORMATIONAL MODES IN OILSEED STORAGE PROTEINS. T.J. Jacks, Southern Regional Research Center, USDA, ARS, PO Box 19687, New Orleans, LA 70179.

Conformational modes of oilseed storage proteins have been found to consist of about half aperiodic structures. Whether oilseed processing treatments and exposure to other seed constituents cause conformational changes has been suggested in the early literature but only recently has been examined directly. With immunological, electrophoretic, chromatographic and spectroscopic techniques, responses of proteins to a myriad of agents can be explained by changes in its structural features. Interpretive illustrations will include responses of oilseed proteins to heat, organic solvents, phenolics and peroxides.

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INTERACTION OF PROTEINS WITH SORGHUM TANNINS: MECHANISM, SPECIFICITY AND SIGNIFICANCE. Larry G. Butler, David J. Riedl and Daniel G. Lebryk, Department of Biochemistry, Purdue University, West Lafayette, IN 47907.

The grain of some lines of sorghum contains 2% (dry weight) or more condensed tannin (proanthocyanidins, oligomers of flavan-3-ols). Tannin confers agronomic advantages such as resistance to bird depredation, but diminishes the nutritional value of the grain for nonruminants. The biological effects of tannin are a result of its propensity for binding proteins. Tannins bind proteins through a combination of hydrogen bonding and hydrophobic interactions; an aqueous environment enhances protein binding. In the digestive tract, sorghum tannins can bind dietary proteins and reduce their digestibility, and can bind and inhibit digestive enzymes. Proteins differ greatly in their affinity for tannin; those with highest affinity are large, have an open structure, contain no bound carbohydrate, and are rich in proline. Certain sorghum proteins associate strongly with tannin; they are difficult to remove during tannin purification, and are found combined with tannin in the indigestible residue after in vitro digestion with pepsin. These proteins have been identified as components of kafirin, the alcohol-soluble prolamine fraction of the storage proteins. On germination the seed may sacrifice a portion of these proteins to bind the tannin which might otherwise interfere with metabolism by inhibiting seed enzymes. During seed development, tannin molecules remain too short to effectively precipitate proteins; they lengthen as the seed dries down. The antinutritional effects of sorghum can be eliminated by soaking the grain in dilute aqueous ammonia, but not by cooking. When rats are put on high tannin sorghum diets, their parotid glands undergo hypertrophy and produce a group of unique salivary proteins with extremely high affinity for tannin. These proteins contain over 40% proline and are devoid of sulfur-containing and aromatic amino acids. This metabolic adaptation may protect the rats against tannin by binding and inactivating it immediately on entering the digestive tract.

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PROTEIN-PHYTATE INTERACTIONS IN FOODS. Munir Cheryan and S.S. Deshpande, Department of Food Science, University of Illinois, 104 Dairy Manufactures Building, 1302 W. Pennsylvania Avenue, Urbana, IL 61801.

Phytic acid is present in almost all major plant protein sources. Concern about its presence in foods is due to its effect on mineral bioavailability, presumably as a result of the formation of insoluble mineral-phytate complexes that render the complexed mineral "unavailable" under physiologic conditions. The presence of other charged food components, such as fiber and protein, complicate our understanding of the phenomenon. Phytate interactions with proteins may also affect functional properties. There is usually a significant shift in the pH-solubility profile and it may mask the true effect of divalent cations on protein solubility. Calcium/phytate and phytate/protein molar ratios correlate well with solubility behavior of calcium, phytate and protein in a model soy protein system. Unfortunately, little is known about the nature and extent of protein phytate interactions, especially the effect of processing, as opposed to the phytate content per se, on these interactions. There is also some evidence that phytic acid could act as a potent inhibitor or activator of certain enzymes important in digestive and physiologic processes, by complexing the enzyme, its substrate or minerals affecting the enzyme's activity.

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CALORIMETRIC STUDIES ON PHYTIC ACID SYSTEMS: IONIZATION CONSTANTS. M.A. Marini and W.J. Evans, Northwestern University, Biochemistry Program, 303 E. Chicago Avenue, Chicago, IL 60611.

Potentiometric as well as thermal titrations of phytic acid and its calcium complexes have been conducted using both the batch and titration microcalorimeters. For phytic acid, the experimental values by either method are in excellent agreement. For the calcium complexes, the total number of groups and the total heat evolved are in agreement, but the placement of the curves is different due primarily to the differences in calcium concentration. Binding of calcium by phytic acid is endothermic for the pH range 2–11 whereas the heat of dilution of 1 M $CaCl_2$ is exothermic. The binding at pH 11.16 gives a value of 19.6 kcal/mol. Inspection of the thermal binding curve indicates that a number of step binding constants are involved and that 5.3 mol calcium are bound per mol phytic acid. This value has been confirmed by atomic absorption spectroscopy. Both the thermal and the potentiometric curves are reversible either by the instant injection of acid or base or by continuous titration. Values for the ionization constants (as pK') and the enthalpy of ionization (as ΔHi) have been estimated by computer assisted curve-fitting. These results are the necessary prerequisite data for the study of phytic acid and metal binding to protein systems.

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HEATS OF PRECIPITATION OF ZINC PHYTATE. W.J. Evans, M.A. Marini and C.J. Martin, USDA, ARS, Southern Regional Research Center, 1100 Robert E. Lee Boulevard, PO Box 19687, New Orleans, LA 70179.

The heat of precipitation has been determined for the reaction, in aqueous solution, of zinc ion with the phytate ion. The reaction is endothermic. The equilibrium constant for the reaction has been determined. From the value of the equilibrium constant and the enthalphy change, the entropy change has been calculated. The large, positive entropy change is consistent with the view that when zinc ion reacts with the phytate ion there is a decrease in the hydrophilic character of the phytate ion.

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PHYTATE AND MINERAL PARTITIONING IN AIR CLASSIFIED BEAN FLOUR FRACTIONS. E.J. Tecklenburg, M.E. Zabik, M.A. Uebersax, J.C. Dietz and E.W. Lusas, Department of Food Science and Human Nutrition, Room 139 Food Science Building, Michigan State University, East Lansing, MI 48824.

Navy, pinto, and black beans *(Phaseolus vulgaris)* were dry roasted in a particle-to-particle heat exchanger at 240 C for 1 min. A portion of the roasted beans were ground into whole flour and the remainder were dehulled. The hulls were separated by air aspiration and ground into hull flour. The cotyledons were pin-milled and air classified to yield intermediate, high starch, and high protein fractions. Samples of all fractions were analyzed by inductively coupled plasma emission (ICP) spectroscopy for Ca, Cu, Fe, Mg, Mn, Mo, P, Zn, Na and K. Phytate phosphorous was estimated using the extraction and precipitation method of Lolas and Markakis (1975). As compared to whole navy flour, the protein fraction contained higher amounts of Fe, Mg, P and Zn; whereas Ca was most abundant in the hull flour. Cu, Na and K were more evenly distributed among all fractions. The phytate phosphorus content of whole navy, pinto, and black bean flours were 0.57, 0.50 and 0.56%, respectively. For all bean types, phytate phosphorus was present in the greatest quantity in the protein fraction (0.86–1.06%), followed by the intermediate fraction (0.46–0.54%), the hull flour (0.38–0.44%), and the high starch fraction (0.12–0.32%). The high total and phytate phosphorus content of the protein flour in conjunction with the partitioning of zinc and iron into this fraction suggests that these minerals may bind to phytate, decreasing their bioavailability.

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

A new technique has been developed to produce low-phytate and light-colored protein isolate from hexane-defatted sunflower flour. The technique involves: (a) extraction of the flour with aqueous ethanol (30% ethanol) at 20–25 C; (b) reextraction of the residue from the aqueous alcohol extraction with water containing 0.1% sodium bisulfate or 0.2% sodium borate at pH 8.5, 10–15 C; (c) precipitation of protein in the extract at pH 4.5; and (d) drying of the protein curd after neutralization with sodium hydroxide solution. Elimination of the aqueous alcohol extraction step or alcohol extraction at temperatures higher than 30 C resulted in dark brown protein isolate, whereas the isolate prepared by the conventional procedure was green. Protein isolate obtained by the new technique was greyish white, and contained low phytate and chlorogenic acid as compared to isolates prepared by the conventional method. Comparative structural changes and selected functional characteristics of the isolates prepared by the new and conventional methods are also discussed.

SESSION FF Surfactants: Surface Chemistry, Analysis and Environmental Wednesday a.m.

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THE DETERGENCY MECHANISM OF ROLL-UP, SOLUBILIZATION, AND EMULSIFICATION ON LIQUID SOILS. James A. Wingrave, Conoco Inc., Ponca City, OK 74601.

Experimental studies were performed to deduce the relative significance of different soil removal mechanisms in detergency. The three mechanisms studied were roll-up, solubilization, and emulsification. Surfactants included alcohol nonionics and linear alkylbenzene sulfonates in the presence and absence of hardness and/or builder for several model soils. Another facet of the study was to deduce how well soil removal correlated with lab reflectance readings. In brief, the study showed that all three mechanisms play a significant role in detergency, with the predominating mechanism being dependent on the soil-surfactant-hardness/builder system type.

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BEHAVIOR OF SURFACTANT MIXTURES IN MODEL OILY-SOIL DETERGENCY STUDIES. M.P. Aronson, M.L. Gum and E.D. Goddard, Union Carbide Corporation, Ethylene Oxide Derivatives Division, Tarrytown Technical Center, Tarrytown, NY 10591.

In previous papers we reported the important factors affecting detergency in a model system, viz., mineral oil removal from polyester film. These studies employed single nonionic surfactants. In this paper we examine the effect of employing surfactant mixtures. Ionic surfactants, and nonionic surfactants with relatively long EO chains ($\eta \overset{\sim}{>} 20$), are themselves rather ineffective in oil removal in distilled water and can reduce the roll-up efficiency of an effective nonionic surfactant. This inhibitory effect of the anionic surfactant can be offset in hard water, or in the presence of a sufficiently high concentration of simple salt. Inhibition by the second surfactant cannot be ascribed to its effect on the adsorption of the primary surfactant onto the polyester substrate. However, the observed effects do have a direct analogy in an increase in interfacial tension which the additive causes between the surfactant solution and oil. This finding supports our view that a low o/w tension is a primary requirement for efficient oil removal. It is shown that the observed behavior of the surfactant mixtures can be explained in terms of mixed micelle formation of the two surfactants with attendant changes in their monomer concentration.

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ACID SOAPS: THE PHASE BEHAVIOR OF ANHYDROUS AND HYDRATED 1:1 POTASSIUM HYDROGEN DIOLEATE. David P. Cistola, Donald M. Small, David Atkinson and James A. Hamilton, Biophysics Institute, Boston University School of Medicine, Boston, MA 02118.

Titration of an aqueous solution of a potassium soap with hydrochloric acid at room temperature, results in the formation of either crystals or liquid crystals of a 1:1 fatty acid to potassium soap compound ("acid soap"). We have examined the phase behavior of a hydrated acid soap (1:1 potassium hydrogen dioleate [KHOleate]) as a function of temperature and water concentration using differential scanning calorimetry, hot-stage polarizing microscopy, and X-ray diffraction, and present a two-component phase diagram for this system. Anhydrous KHOleate forms lamellar liquid crystals with a 47 Å periodicity, and decomposes at 47 C to a mixture of liquid fatty acid and soap and crystalline soap. Upon hydration, the chain melting transition (Tc) falls to $\sim$ 20 C at 20 wt% water and then remains fairly constant with increasing water content. Two one-phase liquid crystalline regions are present: a low hydration, a hexagonal type II liquid crystalline phase, and at > 50% water, a lamellar liquid crystalline phase. The hexagonal phase shows angular, striated, and nongeometrical textures by polarizing microscopy; X-ray small-angle reflections index into a 2D hexagonal lattice, and a wide-angle fringe at 4.5 Å indicates liquid chains. The lamellar phase shows oily streak and mosaic textures; X-ray small-angle reflections index into a one-dimensional lamellar pattern, and a 4.5 Å fringe indicates liquid chains. The lamellar phase swells indefinitely with increasing water content, and a plot of d-spacings vs concentration ([1 − c]/c) yields a straight line which intersects the 0% water axis at 47 Å. In contrast with the analogous soap-water phase diagram, the acid soap-water diagram shows the following. (a) The Tc line is ca. 40 C above that for potassium oleate-water mixtures. (b) The liquid crystalline phases occur in a different order of appearance with increasing water content. Acid soaps: hex II → lamellar; soaps: lamellar → hex I. (c) Hydrated acid soaps lack a micellar phase. The high-water region shows continuous swelling of bilayers to d-spacings of > 300 Å.
Honored Student Presentation

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ANALYTICAL METHODS FOR ALPHA SULFO METHYL TALLOWATES. George Battaglini, Jeanette L. Larsen-Zobus and Thomas G. Baker, Stepan Chemical Company, Edens and Winnetka Roads, Northfield, IL 60093.

Recent economic trends have made alpha sulfo methyl tallowates viable alternatives to oil based synthetic detergents in certain applications. Currently available analytical methods to monitor and control product quality are rather limited and sketchy, however, meaning that a substantial amount of methods development has been required. This includes methodology for resolving the three types of sulfonates present, and for the determination of sodium methyl sulfate. This paper describes new methods developed for making these determinations. They include a new two-phase dye transfer titration and a potentiometric ion selective electrode titration for the resolution of sodium alpha sulfo tallowate; and sodium alpha sulfo tallow acid. In addition, a new method involving saponification and two phase dye transfer or potentiometric ion selectrode electrode titrations for the determination of sodium methyl sulfate is described.

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PRIMARY AND ULTIMATE BIODEGRADATION OF AN ALCOHOL ETHOXYLATE AND A NONYLPHENOL ETHOXYLATE UNDER AVERAGE WINTER CONDITIONS IN THE USA. L. Kravetz, H. Chung, K.F. Guin, W.T. Shebs and L.S. Smith, Shell Development Company, PO Box 1380, Houston, TX 77001.

The primary and ultimate biodegradabilities of a commercial alcohol ethoxylate (AE) and a nonylphenol ethoxylate (NPE) have been studied under average winter conditions found in the USA. The AE and NPE were radiolabeled with tritium in their hydrophobes and carbon-14 in their hydrophiles to facilitate obtaining detailed information on the biodegradation of these surfactants. Activated sludge obtained from a domestic waste treatment plant was used as bacterial inocula in closed continuous bench scale aeration units at temperatures ranging from 46 F to 77 F. Although essentially equivalent primary biodegradation occurred at 77 F for these surfactants, at 46 F the primary biodegradation averaged 93% for AE and 84% for NPE. Effluents from the NPE test at 46 F foamed extensively, whereas effluents from the AE test showed no foaming tendencies. Radiotracer data showed that ultimate biodegradation to CO_2 and H_2O was more extensive for AE than for NPE at all temperatures studied. Biodegradation of the hydrophobe of the NPE was appreciably sensitive to low temperature, biodegrading to H_2O and CO_2 to the extent of 29% at 77 F and only 2% at 46 F. In contrast, biodegradation of the hydrophobe of AE was less sensitive to temperature, biodegrading to H_2O and CO_2 to the extent of 79% at 77 F and 76% at 46 F.

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THE CONTAMINATION OF BAR SOAPS UNDER "IN-USE" CONDITIONS. Jon J. Kabara, Department of Biomechanics, College of Osteopathic Medicine, East Fee Hall, Michigan State University, East Lansing, MI 48824.

The importance of handwashing for the control of nosocomial infections was recognized by Semmelweiss over 145 years ago. Evidence is provided for the general supposition that bar soaps harbor microorganisms. A microbiological survey of 26 lavoratories was carried out in a wing of a university office-laboratory building housing ca. 230 people. Six popular bar soaps were found to be contaminated in every case (65/65). Both medicated and nonmedicated soaps yielded two, three or more microorganisms. The amount of colony forming units (CFU) varied from lows of 30–50 CFU to highs of greater than 60,000 CFU. Random bar soap samples unused for 24 and 48 hr still yielded appreciable CFU values. Numerous gram-positive, gram-negative, yeast and fungi were found to cohabit in-use bar soap. Four types of liquid soaps examined under similar in-use conditions were found to remain sterile. The finding that both wet or dry nonmedicated and medicated bar soaps have been shown to harbor viable organisms should alert healthcare personnel to the potential role of bar soaps in nosocomial infection.

SESSION GG Ralph Potts Memorial Symposium—I Wednesday a.m.

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RALPH H. POTTS: HISTORY OF A PIONEER IN CHEMISTRY. R. A. Reck, Armak Co., 801 W. 47th Street, McCook, IL 60525.

Ralph Potts joined Armour & Co. as a chemical engineer in 1922, fresh out of Lehigh University. At that time Armour & Co. produced from fat byproducts lard, soap and glycerin, but they were strongly interested in finding other uses for those extremely inexpensive byproducts. Fortunately, Ralph was on board and was the main cog in the machinery to reach that goal. The first breakthrough was the development of cast-iron stills to convert low-grade fatty acids to quality fatty acids by distillation. These stills were coal-fired, but they did the job. Ralph had some experience in petroleum fractionation, so he knew that with proper modifications these stills could be converted to fractionating capability. The modifications were made by the Armour machine shop and, as a result, the first fatty acid fractionating column was constructed. The column was a piece of brass pipe filled with broken milk bottles as the packing. No great commercial production was obtained, but Ralph's theories were proven. In the early thirties, as some of you will recall, there was a depression, but the demand for fractionated acids was there and the first true commercial fractionating still was put into operation in 1935. At that time, Armour & Co. started a central research facility whose objective was to convert 2¢ per pound tallow to $1.00 per pound chemicals. In fact, one of the objectives was to produce rubber precursors from fats and the rubber could then be used to produce golf balls. The Director of Research, Vic Conquest, and Ralph Potts lived in the same apartment building and there were many long discussions on fatty chemicals while the two of them were sitting on the back porch. The result was the building of a pilot plant in the Stockyards which combined the basic research efforts with the manufacturing knowledge held by Ralph and the Armour Chemical Division. The research on rubber substitutes prepared from fats never worked out, but as a result of high temperature catalytic work, it was found that if one added ammonia to the system, fatty nitriles could be produced in good yields and then reduction of these nitriles produced valuable amines. Mr. Potts designed almost all of the equipment needed to transfer the lab data to manufacturing capability and he also designed, and was instrumental in building, the first large fatty amine plant ever put up. Many of the designs and commercial processes were patented under Ralph's name. Since that time five other plants using the same basic processes have been constructed. In 1971, Armour sold its chemical business to Akzo and the name was changed to Armak. Ralph retired in 1961, but he was quickly hired as a consultant by Armour and continued with Armak in the same capacity until 1980. He never stopped making significant contributions to the fatty chemical industry. His ingenuity and inventiveness will never be equalled.

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CRYSTALLIZATION PROCESSES. F.B. White, 110 South Orange Avenue, Livingston, NJ 07039.

Separation of fatty acids by means of selective crystallization in a solvent is practiced by many. This paper will describe a new process which sharply reduces both capital cost and energy consumption for this separation. The process, developed by Firma Walter Rau in Germany, is continuous and is applicable to a variety of materials such as fats, waxes and aromatic compounds, as well as to aliphatic fatty acids. Solvents for the process may include water, hexane, ketones, alcohols, etc. Feedstock is dissolved in a proportioned amount of solvent. The resulting solution is cooled by flash evaporation to a state of supersaturation. The supersaturated solution, during its brief induction period, has the stability to allow its transfer to crystallizing vessels, without initiating crystallization. Following the induction period, crystallization is completed only 3 min after nucleation starts. After crystals are separated, solvent is recycled from both mother liquor and solid fractions by means of vapor recompression, thereby resulting in an 80% heat recovery. Advantages of the process include: (a) small crystallizers and consequently small solvent hold-up; (b) continuous operation; (c) low energy consumption; (d) crystals have uniform size and are easily separable by sedimentation, filtration or centrifugation; and (e) low capital cost. Typical operating conditions for the separation of tallow fatty acids will be given.

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SULFONATED METHYL ESTERS, THEIR SYNTHESIS, COMPOSITION AND APPLICATION. G.A. Bonner and M.E. Tuvell, Ethyl Corporation, Baton Rouge, LA.

Recently, intensive interest has developed in an effort to identify more cost-effective raw materials for use as detergent feedstocks. One of the more interesting types of these raw materials are methyl esters in the range from methyl laurate to methyl stearate which can be reacted with sulfur trioxide to form an anionic surfactant. Sulfonated methyl esters (SME) have been shown to have excellent detergent properties in a range of water hardness, in addition to having low toxicity and good biodegradability. This paper reviews the two-step sulfonation mechanism as well as recent advances in production and analysis of detergent range SME. These surfactants were also evaluated as actives for both light duty and heavy duty detergents.

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ALPHA SULFO METHYL TALLOWATE: SYNTHESIS AND PROCESS STUDIES. R. Gabriel and T. Szczeblowski, Stepan Chemical Company, Edens and Winnetka, Northfield, IL 60093.

In this investigation a continuous production process was employed to produce excellent quality alpha sulfo methyl tallowate (ASMT). By using special reaction conditions, methyl tallowate was alpha-sulfonated on a commercial scale with minimal product degradation. In addition to the operating conditions used to produce the sulfonic acid in excellent yield, postsulfonation methodology, affording ASMT with excellent color, is described.

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A WASTE MANAGEMENT PROGRAM TO REDUCE COSTS AND OPTIMIZE REGULATORY COMPLIANCE. Jack McVaugh, Armak Company, 300 S. Wacker Drive, Chicago, IL 60606.

In 1980, the hazardous waste provisions of the Resource Conservation and Recovery Act (RCRA) went into effect, causing many companies to formalize and pay closer attention to their hazardous waste management techniques. In early 1981, Armak Company instituted a policy to reduce or eliminate, if possible, the volumes of hazardous wastes generated, and to optimize management of the remaining residues. The policy quickly expanded to include nonhazardous as well as hazardous solid wastes, and finally developed into a coordinated, multimedia waste management program. Initially, generic solid waste management options were listed and ranked according to potential value/cost to the company. A multidisciplinary task force was assembled from various parts of the company to meet on a regular basis, with the goal of determining an optimal management strategy for individual, prioritized waste streams. This waste management optimization program has resulted in significant reductions in operating costs related to environmental compliance, while incurring little or no capital expenditure. Moreover, the use of landfilling for ultimate disposal has been greatly reduced (a goal of the program). Potential liability considerations take part in all decision making, and the company believes the program is working to reduce such liabilities.

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ISOLATION AND IDENTIFICATION OF THE VOLATILE FLAVOR COMPOUNDS IN COMMERCIAL SOYBEAN LECITHIN. Heasook Kim, Chi-Tang Ho and Stephen S. Chang, Department of Food Science, Rutgers, The State University, PO Box 231, New Brunswick, NJ 08903.

Phospholipids have been shown to oxidize easily during heating or prolonged storage. Phospholipids also have been incriminated as playing a major role in the development of warmed-over flavors in poultry, mutton, beef and pork. Soy phosphatidylcholine was found to develop rancid flavors and a bitter taste during storage. Soybean lecithin, a byproduct from soybean oil processing, is an important and widely used food additive. However, soybean lecithin tends to develop an objectionable flavor which impedes its utilization. Researchers generally believe that beany and grassy odors and bitter taste of soy protein products are due to the remaining lipids, especially lecithin. The objective of the research is to isolate and identify the volatile flavor constituents of commercial soybean lecithin. The information obtained from this work may be utilized to eliminate the undesirable flavor of commercial soybean lecithin. It may also be used to elucidate the mechanisms for the formation of objectionable flavor by foods containing phospholipids. Volatile flavor compounds isolated from commercial soybean lecithin were chromatographed into 23 broad fractions. Each fraction was sensory evaluated by an experienced panel. Among them, fraction 12 had a strong lecithin-like flavor. Each fraction was then chromatographed again into subfractions and sensory evaluated. All subtractions were analyzed by GC-mass spectrometry. Numerous compounds such as ketones, aldehydes, lactones and furans were identified. Two interesting compounds, 3,5,5-trimethyl-2-cyclohexenone and 3,5-dimethyl-2-cyclohexenone were identified in the subfractions 12-16 and 12-17 which had a strong lecithin-like flavor. The importance of these compounds in the objectionable flavor of lecithin remains to be determined. Mesityl oxide, a dimerization product of acetone and a known toxic compound, was shown to occupy almost half of the total amount of volatile compounds isolated.

Ralph Potts Memorial Award Presentation

SESSION HH Lipid Methodology Wednesday a.m.

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THIN LAYER CHROMATOGRAPHY/FLAME IONIZATION ANALYSIS OF TRANSESTERIFIED VEGETABLE OILS. B. Freedman, E.H. Pryde and W.F. Kwolek, Northern Regional Research Center, Agricultural Research Service, US Department of Agriculture, Peoria, IL 61604.

A quantitative method for analyzing reaction mixtures containing fatty esters, tri-, di-, and monoglycerides obtained by the transesterification of vegetable oils has been developed. Analyses were performed by TLC/FID chromatography using an Iatroscan TH-10 instrument. Stearyl alcohol served as an internal standard. From plots of area and weight ratios of methyl linoleate, tri-, di-, and monolinolein, linear equations were developed from which response factors for these compounds were calculated. Response factors for ethyl and butyl esters from sunflower oil were similarly obtained. Screening of a number of solvent systems to optimize resolution indicated petroleum ether/diethyl ether/acetic acid (90:10:1) was most satisfactory. The effect of changes of instrument parameters such as scanning speed, hydrogen flow, etc., on resolution, sensitivity, and baseline stability were determined. Calculations of percent composition of transesterified reaction mixtures were made automatically by a computer. A procedure has been developed whereby 30 samples can be analyzed in 2–3 hr.

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A REITERATIVE METHOD FOR CALCULATION OF TRIACYLGLYCEROL SPECIES IN NATURAL MIXTURES. F. Manganaro, J.J. Myher and A. Kuksis, C.H. Best Institute, University of Toronto, Toronto, Ontario M5G, 1L6, Canada.

A method is proposed for obtaining progressively improved estimations of the composition of molecular species of natural triacylglycerols using computer fitting of the data. The estimation begins with a calculation of the fractional proportion of each molecular species based on the 1-random 2-random 3-random distribution derived from a stereospecific analysis of the total triacylglycerol mixture. This distribution is corrected by making use of various other experimental facts, such as the carbon number profile of the triacylglycerols and the carbon number and unsaturation profiles of the separate *sn*-1,2-, *sn*-2,3- and *sn*-1,3-diacylglycerol moieties. The reiterative correction is made by summing the appropriate triacylglycerol species in the random calculation to obtain sums of species corresponding to the known distribution. These sums are divided by the known values to give correction factors, which are then used to derive improved estimates of the proportions of molecular species by dividing the previous estimates of each species by the correction factors. This is done assuming that all species are represented and that the reverse isomer proportions remain unchanged. When all corrections by all sets of data have been made once, the process is repeated (100 cycles) until the new estimates change very little. By means of synthetic mixtures of triacylglycerols of known composition, we have demonstrated that the calculated values tend to converge to a limiting solution. Furthermore, we have been able to verify that the quantitative estimates thus obtained can approximate closely those derived for the major molecular species isolated by reversed phase liquid chromatography and measured directly. The method can be expanded to incorporate additional information (e.g., proportions of reverse isomers) to provide a further refinement.

Honored Student Presentation

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ANALYSIS OF TRIGLYCERIDE SPECIES BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY VIA A FLAME IONIZATION DETECTOR. W.L. Erdahl, F.C. Phillips and O.S. Privett, The Hormel Institute, University of Minnesota, 801 – 16th Avenue, N.E., Austin, MN 55912.

The analysis of triglyceride species by high performance liquid chromatography (HPLC) with a flame ionization detector (FID) by reversed-phase chromatography with gradient and isocratic solvent systems is described. Triglycerides containing acyl groups of critical pairs, *trans* isomers as well as mixtures of normal even and odd chain lengths are separated. Identification is made on the basis of retention time relative to equivalent carbon number and fatty acid composition. Quantitative analysis is made with the flame ionization detector on the basis of proportionalities of peak areas which are related to carbon mass of individual components. The method is demonstrated on standard mixtures of pure triglycerides and several natural fats and oils.

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DIRECT LIQUID INLET LC/MS OF NATURAL TRIACYLGLYCEROLS AND STERYL ESTERS. A. Kuksis, J.J. Myher and L. Marai, Banting and Best Department of Medical Research, University of Toronto, M5G 1L6, Canada.

Triacylglycerol and steryl ester mixtures from plant and animal sources were resolved by HPLC on Supelcosil LC-18 columns using either a gradient of 30–90% propionitrile in acetonitrile or 100% propionitrile as the mobile phase. About 1/100 of the column effluent containing a minimum of 50 ng of each molecular species was admitted to a quadrupole mass spectrometer via a direct liquid inlet interface. The elution profile of the lipid esters was given by the total chemical ionization current. The reversed-phase system allowed the separation of most of the common triacylglycerol species except positional isomers and enantiomers, and of all the steryl esters which, however, overlapped with the triacylglycerols. Individual molecular species of triacylglycerols were identified from the (MH-RCOOH)+ ions, which in the LC/MS mode of operation constituted the base peaks, and from the protonated molecular ions, (MH)+. The relative abundance of the (MH-RCOOH)+ ions allowed the identification of positional isomers such as POO and OPO. The steryl esters, which did not give a molecular ion were identified from the masses of ions generated from their steroid nuclei and recovered from the HPLC column with retention times characteristic of specific fatty acid esters. Cholesteryl linoleate was eluted between palmitoyloleoyl-linoleoyl- and dipalmitoyllinoleoylglycerol, whereas campesterol linoleate emerged as a separate peak between dipalmitoyllinoleoyl and trioleoylglycerol. β-sitosterol linoleate appeared between the peaks of trioleoylglycerol and palmitoyldioleoylglycerol. The steryl esters of oleic and palmitic acids overlapped with other triacylglycerols, while the arachidonates were eluted as separate peaks ahead of the common animal and plant triacylglycerols. The free sterols were eluted with any free diacylglycerols present in the sample. The chemical ionization response differed for the different molecular species of the fatty esters and accurate quantitative work required calibration. The study shows that direct liquid inlet LC/MS provides sensitive detection and an unambiguous identification of the lipid esters in the HPLC effluent, which is not always possible from the retention times.

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CHARACTERIZATION OF PEANUT TRIGLYCERIDE COMPOSITION BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY AND GAS LIQUID CHROMATOGRAPHY. J.A. Singleton and H.E. Pattee, USDA, ARS, SR, North Carolina State University, PO Box 5906, Raleigh, NC 27650.

Triglyceride composition of natural seed oils is very complex and characterization by conventional methodology is tedious and time-consuming. HPLC methodology has been developed which separates triglycerides into groups according to the degree of unsaturation in the molecule and the equivalent carbon number of fatty acids in the triglyceride. Crude oil from mature peanuts was used and generally class separation was achieved on a C_{18} reverse-phase column using a UV detector at 210 nm. Acetonitrile and ethanol were used as the eluting solvents. Each separated group or class was collected, and the carbon number and fatty acid composition determined by GLC.

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TRANSFORMATION ENERGETICS AND THEORETICAL α-FORM STRUCTURES OF TRIGLYCERIDES BY DSC AND COMPUTER MODELING. James W. Hagemann and John A. Rothfus, Northern Regional Research Center, ARS, USDA, 1815 N. University Street, Peoria, IL 61604.

Differential scanning calorimetry studies on saturated single-acid triglycerides have revealed fundamental differences between odd and even chain lengths and between short and long chain lengths. Two β′-forms are common with triglycerides C_{15} through C_{24}, but shorter odd chain length triglycerides C_9–C_{13} exhibit only one β′-form, whereas short even chain lengths C_8–C_{14} exhibit three. Even-chain, single-acid triglycerides larger than C_{21} produce two α-forms, and C_{21} and C_{23} show two β-forms. Apparent energies of phase excitation for α-form transformations show odd-even alternation for short chain lengths but increase linearly with chain length above C_{14}. Changes in melting point patterns, particularly for β′- and β-forms, at C_{14} correlate with the change in apparent phase excitation energy. Comparison of X-ray data with dimensions from space-filling models and agreement between observed entropies of fusion and values calculated from probabilistic models emphasize the importance of extended chain conformation and suggest configurational differences, and possibly different polymorph conversion pathways for odd versus even chain length triglycerides. Because α-form triglycerides can be considered the first of several forms in the conversion pathways leading to stable β-forms, theoretical triarachidin space-filling α-form structures were examined using a computer modeling technique that simulates restricted oscillations of carbon zig-zag planes in synchronous and nonsynchronous modes. Intermolecular minimization procedures determined best-fit positions around a centralized molecule, which enabled calculation of total lattice energy values for nine different hexagonal subcell arrangements. The analysis thus far indicates several equally preferred structure-subcell arrangement combinations for triglyceride α-forms rather than a single crystalline entity.

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VISUAL CHARACTERIZATION OF COCOA BUTTER CRYSTALS. Douglas M. Manning and Paul S. Dimick, 111 Borland Laboratory, The Pennsylvania State University, University Park, PA 16802.

The ability of cocoa butter to undergo polymorphic changes is important because of its affect on product texture and appearance. Polymorphic resolidification of cocoa butter into higher melting forms can destroy the smooth glossy appearance of a confectionary product. The purpose of this investigation was to develop microscopic techniques used to examine cocoa butter crystals and to define the crystalline forms by differential scanning calorimetry. Microscopic methods included scanning electron microscopy (SEM) and polarized light microscopy (PLM). Techniques of preparation differed in that the samples for scanning electron microscopy were free growing crystals. For polarized light microscopy, samples were placed on a slide with a cover slip, thus restricting free crystal growth. The view presented by SEM is a surface reflection view, whereas PLM is a cross-sectional or internal structure view of the crystals. Crystal formation temperatures were preestablished and ranged between 26 and 34 C. The results include visual classification and melting ranges of seven crystalline forms described as 'individual,' 'tempered', 'feather', 'blade', 'spiney', 'needle', and 'irregular'. These are descriptive terms established to denote the various crystals. 'Feather', 'tempered', 'individual', 'spiney', and 'irregular' crystals were analyzed using a differential scanning calorimeter (DSC). Melting curves were run at 20°/min between 15 and 45 C. A technique employing a hoop and polyethylene was used to grow the crystals. Prior to analysis, each crystal was identified and photographed; thus visual structural characteristics could be linked to melting point. Melting ranges of particular crystals are important, but just as significant are the formation temperatures at which the crystal developed. By controlling the formation temperatures, the melting points and polymorphic transition can be indirectly controlled. Unlike previous literature which shows only one or two forms being present in the 32–35 C melting range, this investigation revealed the existence of numerous high melting crystal forms.
Honored Student Presentation

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COMPLEXATION OF RHODIUM (I) SPECIES TO UNSATU-

RATED LIPIDS. R. Aneja, B.T. Golding and C. Pierpoint, Department of Food Science, Clemson University, Clemson, SC 29631.

The principles and applications of argentation in fats and oils are well documented. Complexation of rhodium (I) species to unsaturated lipids shows chemical features and offers opportunities which complement those offered by argentation. Complexation of model 1,4-dienes, particularly 1,5-dialkyl-1,4-dienes is interesting because this functionality is present in natural unsaturated fatty acids. We have shown previously that the structure and ease of formation of their complexes depends on the stereochemical configuration of the 1,4-diene function. The E,E-isomers form complexes such as [(diene) Rh(I)(penta-2,4-dionate)] in which the diene functions as a bidentate ligand. The Z,Z-isomers yield complexes containing two monodentate-diene molecules per Rh(I) and the E,Z-isomers may yield both types of complexes. Complexes of methyl oleate and its E,E-isomer conform to the aforementioned behavior. We have now studied the complexation of (ethene)$_2$ Rh(I)(penta-2,4-dionate) and its hexafluoro derivative with (Z,Z,Z)-octadeca-3,6,9-triene (prepared from methyl linolenate) and with simple triglycerides typified by 1,2-dioleoyl-3-palmitoyl-glycerol, 1,2-dielaidoyl-3-palmitoyl-glycerol and 1,3-dielaidoyl-2-palmitoyl-glycerol. The physical and spectroscopic properties, especially ^{13}C NMR and/or ^{1}H NMR, leading to characterization of 2:1 and 1:1 lipid:rhodium complexes will be discussed.

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HIGH PERFORMANCE LIQUID CHROMATOGRAPHY OF THE TOCOLS IN CORN GRAIN. E.J. Weber, USDA-ARS-NCR, S-320 Turner Hall, University of Illinois, 1102 S. Goodwin Street, Urbana, IL 61801.

The tocols of corn grain have been analyzed by high performance liquid chromatography in three ways: (a) by direct injection of corn oil, (b) after alkaline hydrolysis of germ oil, and (c) after alkaline hydrolysis of the ground grain. Detection of the tocols by fluorometry and by ultraviolet spectroscopy were compared. No tocotrienols were found in germ oil. The relative proportions and the total amounts of the tocol isomers varied greatly among the corn inbreds examined. Although γ-tocopherol has traditionally been considered to be the predominant vitamin E isomer in corn oil, inbreds with higher levels of α-tocopherol than of γ-tocopherol have been discovered. The large genotypic variations in tocols found among the corn inbreds allowed breeding of hybrids with selected proportions of vitamin E isomers.

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CHARACTERIZATION OF COMPOSITION, SPRAY AND ENGINE COMBUSTION OF FOURTEEN VEGETABLE OILS. Thomas W. Ryan III, Timothy J. Callahan and Lee G. Dodge, Southwest Research Institute, 6220 Culebra Road, San Antonio, TX 78284.

The development of diesel fuel specifications has been based on a wealth of empirical data and experience with the fuel/engine systems. A similar data base does not exist for the vegetable oils. This study represents an attempt to start the development of a data base and to propose a preliminary specification for vegetable oil fuels. Fourteen different oils (four different types with 3–4 stages of processing for each type) have been characterized with respect to the properties normally used for vegetable oils as well as those used for diesel fuel. The diesel type spray characteristics of the oils were examined using high-speed motion picture techniques at two different oil temperatures (45 C and 145 C) spraying into an environment maintained at 4.1 MPa and 480 C. The combustion characteristics (rates of heat release) of the oils were determined at eight different speed/load conditions in two different diesel engines (a direct injection engine and an indirect injection engine). A preliminary fuel specification is proposed for use as a basis for further refinement.

SESSION II Petrochemical and Fuel Alternatives from Fats and Oils: Part A—Vegetable Oils as Fuel Alternatives

Wednesday a.m.

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DURABILITY TESTS OF SUNFLOWER OIL AS A DIESEL FUEL. Kenton R. Kaufman and Mariusz Ziejewski, Agricultural Engineering Department, North Dakota State University, Fargo, ND 58105.

Laboratory endurance tests were conducted using sunflower oil in various ways as an alternative fuel for a direct injected diesel engine. The engine was run on a test cycle recommended by the Engine Manufacturer's Association. The sunflower oil was used as a 25% blend in diesel fuel, both with and without fuel additives. The sunflower oil was also used in a nonionic microemulsion with aqueous ethanol. Engine performance was satisfactory. However, engine durability was a problem. Engine inspection after the tests revealed abnormal carbon deposits (a) in the intake ports, (b) on intake and exhaust valves, (c) on the cylinder liner above the ring travel area, (d) on the piston lands, and (e) in the ring grooves. Based on the results of these tests, sunflower oil could not be recommended as an alternative for diesel fuel.

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VEGETABLE OILS AS DIESEL FUEL: PRELIMINARY DURABILITY SCREENING. Carroll E. Goering and Bob Fry, 100 Agricultural Engineering, University of Illinois, 1208 W. Peabody Drive, Urbana, IL 61801.

Microemulsions of soybean oil and alcohol, with and without diesel fuel, have been proposed as possible fuels for diesel engines. Although the microemulsions have been shown to give satisfactory performance in direct-injected diesel engines, there are concerns that such fuels might have adverse effects on engine life. The EMA (Engine Manufacturer's Association) has proposed a variable load-speed cycle to be used in 200-hr engine tests of experimental fuels. The tests are intended to provide preliminary screening and early elimination of fuels that would have an adverse effect on engine life. Fuels passing the test would need further evaluation, including tests conducted by the manufacturers themselves in connection with their engine warranty programs. In the research to be reported, a control system was developed to carry out the EMA cycle on a 3.589 liter, turbocharged, direct-injected diesel engine. The 200-hr screening test was then carried out using No. 2 diesel fuel to provide standards of comparison for subsequent tests. The 200-hr test was also carried out on several microemulsion fuels. Before starting each test, the engine was rebuilt with new parts to eliminate the effects of earlier fuels. The report will document the effect of one or more of the microemulsion fuels on the engine during a 200-hr screening test.

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METHYL, ETHYL AND BUTYL SOYBEAN ESTERS AS A RENEWABLE FUEL FOR DIESEL ENGINES. S.J. Clark, P.G. Pienaar, L. Wagner and M.D. Schrock, Agricultural Engineering Department, Kansas State University, Manhattan, KS 66506.

Recently, there has been a renewed interest in using vegetable oils as a fuel for diesel engines since vegetable oils are a renewable resource that can be produced with a low expenditure of energy. In the past, problems were encountered in using vegetable oil as a diesel fuel due to excessive carbon deposits and lubricating oil thickening. The higher viscosity of vegetable oils compared to diesel fuel is largely responsible for these problems. Transesterification of vegetable oils results in an ester of the oil that has a viscosity very close to diesel fuel. Glycerol is a valuable byproduct of the process. This paper will report on results of research to determine how the fuel properties of soybean oil esters produced from ethyl, methyl and butyl alcohols compare with a standard diesel fuel. Also covered in the paper will be results of 200-hr engine performance and wear tests performed on the three ester fuels and a diesel reference fuel. The engine tests include engine power and efficiency, exhaust emissions, lubricating oil viscosity change as a function of time, lubricating oil metal ion concentration as a function of time and micrometer tests on engine parts carried out prior to and following tests.

Test results show that power level is reduced slightly with the ester fuels. Exhaust emissions are about the same as for the diesel reference fuel. Indication of wear and sludge accumulation were no greater for the soybean esters than for the diesel reference fuel.

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VARIABLES AFFECTING THE YIELDS OF FATTY ESTERS FROM TRANSESTERIFIED VEGETABLE OILS. B. Freedman, E.H. Pryde and T.L. Mounts, Northern Regional Research Center, Agricultural Research Service, US Department of Agriculture, Peoria, IL 61604.

Fatty esters obtained from vegetable oils by transesterification have promising potential as alternative diesel oil fuels because of their improved viscosity and volatility properties compared to triglycerides. Efforts have been directed toward determining the transesterification reaction variables that affect the yield and purity of these esters. The ester content obtained was strongly dependent upon the molar ratio of alcohol/vegetable oil, the type of catalyst (basic or acidic), the reaction temperature, and the degree of refinement of the vegetable oil. Under suitable conditions, almost complete conversions to methyl, ethyl and butyl esters were obtained in 1 hr. At moderate temperatures (32 C), vegetable oils were 99% transesterified in ca. 4 hr with an alkaline catalyst. Transesterification with acid catalysis was much slower than with basic catalysis. The methyl ester contents and yields from refined soybean, sunflower, peanut and cottonseed oils were compared to those from the corresponding crude vegetable oils. Although the crude oils could be successfully transesterified, ester yields were reduced because of gums and extraneous material present in the crude oils.

SESSION JJ General
Wednesday a.m.

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ON-LINE INFRARED COMPOSITION MEASUREMENTS OF MICELLA AND RELATED PROCESS STREAMS FOR INCREASED PRODUCTIVITY. G. DeMattia and J. Blanchard, Burlington Center, 78 Blanchard Road, PO Box 435, Burlington, MA 01803.

The single-beam dual wavelength infrared principle for measurements of oil in hexane (micella) and other downstream product compositions is a useful analytical technique which finds extensive application in oilseed solvent extraction and recovery processes. When interfaced with an appropriate control scheme, the measurement offers a unique, continuous analysis which can result in an optimum use of feedstocks, energy savings and maximum end-product quality. The location of the appropriate measurement instrumentation is determined with respect to key processing variables for ultimate utility of the analyzer and control unit. Sample handling and conditioning systems are incorporated at each distinctive location such that the analyzer is compatible with the various processing parameters encountered throughout the processing stream. The analyzers and associated sampling systems are enclosed such that installations can be made in a variety of electrical area classifications.

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AUTOMATIC KARL FISCHER TITRATION OF MOISTURE IN SUNFLOWER SEED. James A. Robertson, USDA, ARS, Richard B. Russell Agricultural Research Center, PO Box 5677, Athens, GA 30613.

An automatic Karl Fischer (KF) titrator of the motor-driven type was used for the determination of moisture in sunflower seed. A preliminary study of the effect of sample size on KF moisture analysis showed a significant decrease in moisture content with increase in sample size from 1 to 5 g. In the moisture range of 5.5–10.5%, a sample size of 3–4 g gave moisture values corresponding to those obtained by the AOCS official oven method for sunflower seed. Comparison of KF moisture analysis with oven methods on 6 samples with moisture contents ranging from 5.4 to 12.7% showed that KF moisture values were not significantly different from air oven and vacuum oven methods. The standard deviation of a KF determination was typically ± 0.09% moisture content at a moisture content of 8.8%, whereas for oven moistures the standard deviation was ± 0.05%. KF moisture values generally were slightly lower than the air oven moisture values. Using KF and vacuum oven methods to measure moisture contents, sunflower seed were found to lose 6.7% moisture (0.6% moisture from a sample with 8.9% moisture) when grinding the sample with Hyflo Super Cel as in the AOCS official method.

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OIL CONTENT DETERMINATION UTILIZING VARIOUS INSTRUMENTAL ANALYTICAL TECHNIQUES. Raymond F. Bailey, Oxford Inst., Ltd., 62 Tickford Street, Newport Pagnell, Bucks., England.

Oil content determinations are becoming ever increasingly important in the food industry. The last 15–20 years have seen many changes in this area. Instrumental techniques have taken over from standard analytical methods, generally enabling measurement times to be decimated. Resulting in far greater control of processes and consequent financial savings on raw material use. Two of the earlier instrument techniques which came to prominence in the late 1960s were continuous wave nuclear magnetic resonance (NMR) and pulsed wave nuclear magnetic resonance; these have been followed more recently by near infrared (NIR). The paper will set out and show the advantages and disadvantages of these techniques relative to one another and with respect to the more conventional standard methods.

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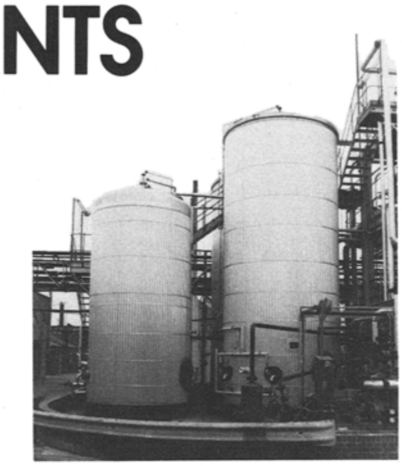
PREDICTION OF VISCOSITY VALUES AS A FUNCTION OF IODINE VALUE AND TEMPERATURE. J. Mikle, A.H. Chen*, P.J. Wan and D.D. McIntire, W. L. Clayton Research Center, 3333 N. Central Expressway, Richardson, TX 75080.

For engineering and design purposes, the viscosities of triglycerides at high temperatures have to be determined with accuracy.



Viscosity data at temperatures above 300 F, simultaneously taking into consideration the IV (iodine value) as well, is scarce. Viscosities of SBO (soybean oil) and its hydrogenated derivatives were found to be highly correlated to the temperature and IV. A mathematical model was generated for predicting the viscosities of SBO and the stocks resulting from its hydrogenation, at various temperatures. Iodine values ranged from 62.7 to 131.8, temperatures from 200 F to 425 F. The model is particularly useful when mass, heat and momentum transfer is considered in hydrogenation, steam refining/deodorization.

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EFFECT OF PROPIONIC ACID ON AFLATOXIN ANALYSIS OF STORED GEORGIA DENT CORN SAMPLES. Odette L. Shotwell, Glenn A. Bennett, William F. Kwolek and C.W. Hesseltine, Northern Regional Research Center, ARS, USDA, 1815 N. University Street, Peoria, IL 61604.

In 1981, 75 corn samples were collected from four areas in Georgia. The collection was not made in such a manner as to be representative of the 1981 Georgia corn crop. Every sixth ear was husked and placed in an oven to be dried the day of collection. The rest of the corn was shipped without husking to Peoria in cardboard boxes. When undried, unhusked ear samples arrived in Peoria, they were husked and randomly separated into five equivalent samples. One set of 75 samples was shelled and dried as soon as possible to avoid further aflatoxin formation. One other set of 75 samples was stored 6 weeks before shelling and drying. The remaining three sets of ear samples were placed in plastic bags with 5%, 2%, and 1% Monoprop (1 part propionic acid plus 1 part versite) and stored 6 weeks before shelling and drying for analysis. The samples dried in Georgia before shipping had an average total aflatoxin level of 198 ng/g. Samples shelled and dried immediately after arrival had an average level of 640 ng/g. Samples shelled and dried after 6 weeks' storage had average aflatoxin levels of 595 ng/g. Samples stored 6 weeks in the presence of 5%, 2%, and 1% Monoprop (2.5%, 1%, and 0.5% propionic acid) had average toxin levels of 342 ng/g, 350 ng/g, and 376 ng/g, respectively.

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REMOVAL OF AFLATOXIN BY PHYSICAL REFINING. Aurelia Anghelescu, John M. Hasman and Leopold R. Strecker, Best Foods Research and Engineering Center, 1120 Commerce Avenue, Union, NJ 07083.

Damaged and moldy oil-bearing materials such as seeds and nuts, unlike typical commodities of commercial quality, may contain aflatoxins. Hence, the possibility exists that crude oils derived from these toxin-containing materials may also be contaminated. It is known that conventional alkali refining of aflatoxin-contaminated crude oils removes the toxins effectively resulting in fully detoxified finished oils. Recently, a physical process in which caustic treatment was eliminated became a viable alternative for the refining of various vegetable oils. A model study was carried out to determine the efficiency of removal of aflatoxin by consecutive physical refining steps: degumming, bleaching and steam refining-deodorization. Crude corn oil, to which from 100 to 1000 ppb aflatoxin levels were deliberately added, was used during these investigations. It was found that the bleaching step is the most effective for removal of aflatoxins. As little as 1% activated bleaching clay can detoxify these highly contaminated oils. In addition, it was found that degumming reduces the initial aflatoxin content in crude oil by ca. 40%. Consequently, the physical refining process results in fully detoxified oil, comparable to the conventional, alkali refined oil.

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POSSIBILITIES AND LIMITS OF ANALYTICAL METHODS TO THE DETECTION OF ADULTERATION IN VEGETABLE OILS. P.Y. Vigneron, Lesieur Cotelle and Associes, BP 89, 59412 Coudekerque, France.

The control of authenticity of fats and oils requires the use of several methods of analysis. As a matter of fact, fatty acid composition cannot always be used to detect an adulteration at first sight, and one has to resort to more specific analysis such as determination of sterols, tocopherols and some triglycerides (trilinolein, dilinoleolinolenin, trilinolenin). As the purpose is to detect low levels of adulteration, reliable analytical techniques such as gas liquid chromatography using glass capillary columns and high performance liquid chromatography are used. It is essential to establish preliminarily tables of composition of oils extracted from mature seeds from different geographic areas of production in order to find out unambiguously the type and level of adulteration. Different examples of blended vegetable oils are studied, particularly relating to peanut, sunflower and olive oils.

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FRACTIONAL CRYSTALLIZATION AND GAS CHROMATOGRAPHY ANALYSIS OF FATTY ACIDS AS A MEANS OF DETECTING BUTTERFAT ADULTERATION. R.S. Farag, F.A. Ahmed, F.M. Hewedy, S.H. Abo-Raya and H.H. Khalifa, Director of Central Laboratory, Faculty of Agriculture, Cairo University, Giza, Egypt.

A method has been devised which gives the distribution of saturated and unsaturated fatty acids of pure and adulterated cow and buffalo ghee with lard or margarine. It involves fractionation of pure and adulterated butter fat into fractions by fractional crystallization. The composition of the fatty acids liberated by the hydrolysis of each of the fractions were determined by gas chromatography. Adulteration of cow and buffalo ghee with various levels of lard or margarine caused significant changes in certain fatty acids, i.e., 22:0, 18:1, 18:0 and 16:0. 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 certain fatty acids. The techniques used in these systematic analyses of fat adulteration have fulfilled the requirements for development of more routine procedures.

SESSION KK Nutritional Biochemistry
Wednesday p.m.

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ASSESSMENT OF HUMAN LUNG MATURITY IN UTERO BY SODIUM HYDROXIDE. Eric J. Sing, Apartment 608, 1062 Bryn Mawr, Chicago, IL 60660.

Phosphatidylcholine was a major lung surfactant. Insufficient development of the surfactant in neonates was often associated with the respiratory distress syndrome. A sodium test was developed and performed on 49 human amniotic fluid samples of various weeks (16–40) of gestation in normal human pregnancies to assess the lung maturity. Approximately 1 mL of unspun amniotic fluid was placed in a 100 X 13 mm test tube and one pellet (ca. 0.2–0.3 g) of sodium hydroxide was added. The mixture was gently tapped with one finger for 30 sec. Bubbles which are not stable or which broke down within 15 sec indicated lung maturity and the test was considered to be positive. Stable bubbles forming in the solution indicated lung immaturity and the test was considered to be negative. No respiratory distress syndrome was observed with a positive test. The positive sodium hydroxide test indicated that the lecithin/sphingomyelin ratio was more than 2.0. In general, the test became positive at 36 weeks of gestation in normal human pregnancy. The results of the sodium hydroxide test indicated the maturity or immaturity of the fetal lung within one minute. Any doctor, nurse or midwife can perform this test at the bedside. Some attempt has been made to correlate the sodium hydroxide test with other lung maturity tests and the results will be presented. In conclusion, the sodium hydroxide test is useful in predicting the risk of neonatal respiratory distress. This work was done at Northwestern University in 1980.

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LEVELS OF PHOSPHORYLATED PHOSPHOLIPID PRECURSORS AND METABOLITES IN LUNGS OF FETUSES OF DIABETIC RATS. D.S. Boehme, C.M. Roberts and S.P. Bessman, University of Southern California, School of Medicine, Department of Pharmacology and Nutrition, 2025 Zonal Avenue, Los Angeles, CA 90033.

Female rats were injected via the tail vein with streptozotocin, STZ, 45 mg/kg, or saline. Average nonfasting 72-hr postinjection blood glucoses were 353 mg/dl (178–513 mg/dl) for the STZ animals and 130 mg/dl (93–149 mg/dl) for the controls. From night 4 on, the females were housed with males until conception was confirmed by presence of sperm in the vagina. At 19 and 21 days' gestation and at 2 days after birth, lung samples were removed from the offspring, and extracted in perchloric acid to obtain the acid soluble phosphorylated precursors and metabolites of phospholipids. These compounds were resolved on a 25 cm column of AGMP-1 chloride, with a linear gradient of 10 mM ammonium borate, pH 10.0, to 50 mM ammonium borate, pH 9.0, containing 100 mM ammonium chloride. Quantitation of all fractions was determined by phosphate analysis.
Honored Student Presentation

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LIPID PEROXIDATION IN REVERSIBLY AND IRREVERSIBLY SICKLED ERYTHROCYTES. Salil K. Das* and C. Rajagopalan Nair*, Department of Biochemistry, Meharry Medical College, Nashville, TN 37208.

It is well known that in sickle cell anemia, the majority of sickled erythrocytes assume normal, biconcave, discoid shape and resume oxygen transport under the influence of hyperbaric oxygen. These erythrocytes are designated as reversibly sickled cells (RSC). In severe cases of the disease, some erythrocytes fail to return to normal shape even after prolonged exposure to oxygen and are called irreversibly sickled cells (ISC). Hemoglobin in ISC is fully oxygenated and remains unaggregated in the presence of oxygen, yet fails to function normally. We have reported (Das and Nair, Brit. J. Haematol. 44:87 [1980]) in sickled cells, that the red cell membrane is a primary locus of cell damage. The purpose of this study is to determine whether a difference in erythrocyte membrane lipid peroxidation exists between RSC and ISC. To evaluate this, we measured superoxide dismutase, catalase and glutathione peroxidase activity as well as endogeneous malonaldehyde, lipid peroxidation potential of fractionated sickled cells and compared with controls. The ISC were separated from RSC by linear BSA density gradients. The biochemical parameters were measured as described (Das and Nair, 1980). Sickled erythrocytes had increased SOD, and reduced catalase and glutathione peroxidase activities compared to normal erythrocytes. RSC had higher SOD and lower glutathione peroxidase and catalase activity than ISC. However, while both RSC and ISC had higher SOD, RSC had essentially equal glutathione peroxidase and catalase activity compared to normal erythrocytes, and ISC had significantly lower glutathione peroxidase and catalase activities. RSC had negligible amount of malonaldehyde as did normal erythrocytes, although ISC contained significant amounts of endogeneous malonaldehyde. The peroxidation potential of RSC was equal to that of normal erythrocytes, whereas ISC had a lower peroxidation potential. This suggests that ISC had undergone considerable higher degree of peroxidation than RSC. (This study was supported by Grant RR-08037 from the National Institute of Health and Grant GR-3624 from the State of Tennessee.)

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RESTRICTION OF MATERNAL FOOD INTAKE AND THE β-OXIDATION OF FATTY ACIDS BY DEVELOPING RAT HEARTS. Nirmala K. Menon, Govind A. Dhopeshwarkar and James F. Mead, Laboratory of Biomedical and Environmental Sciences, 900 Veteran Avenue, Los Angeles, CA 90024.

The capacity of the heart to degrade and utilize fatty acids is higher during the suckling period than at the fetal or postweaning stages. We studied the effect of a restricted maternal diet on the β-oxidation of fatty acids by the hearts of the suckling progeny. Control pregnant rats were fed a stock diet. For the experimental group, food was restricted to half of the control intake on the 7th day of pregnancy and continued through lactation. The pups on the restricted diet were significantly smaller than the control. There were no changes in either the fatty acid composition or the total soluble proteins (μg/mg heart) of the myocardium. At postnatal days 7, 14 and 21, the β-oxidation of [1-^{14}C]palmitate by heart homogenates was determined in the presence of ATP, CoA and carnitine. At postnatal day 21, the production of 1-$^{14}CO_2$ was decreased by 60% in the group on the restricted diet. Consequently, the possibility of an inhibition of activation or intramitochondrial transport of fatty acids by heart mitochondria was studied in vitro using [1-^{14}C]palmitate, [1-^{14}C]palmityl CoA and [1-^{14}C]palmityl carnitine. With [1-^{14}C]palmitate, the rate of 1-$^{14}CO_2$ produced was 2463.92 ± 317.02 cpm/mg protein/min for the control and 1681.58 ± 91.21 for the restricted diet group. When [1-^{14}C]palmityl CoA was the substrate, the oxidation rate of the heart mitochondria from the experimental group increased to 3927.99 ± 974.25, equal to the control value of 3907.40 ± 1067.20. With [1-^{14}C]palmityl carnitine, the rates of β-oxidation for the control and restricted diet groups were 4782.08 ± 771.83 and 4908.18 ± 1033.76 respectively. Our results show that restriction of maternal food intake inhibits the β-oxidation of fatty acids by the developing heart and this inhibition is due to a decrease in palmityl CoA synthetase activity.

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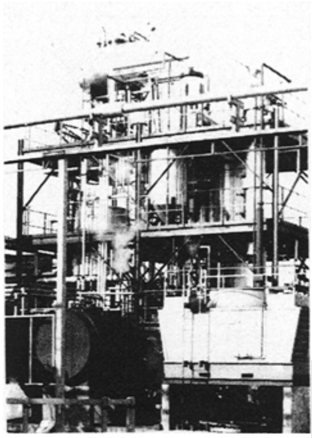
IRON ABSORPTION BY THE ANEMIC RAT AS INFLUENCED BY BEEF TALLOW, CORN OIL, SALMON OIL, VITAMIN E AND BUTYLATED HYDROXY. Dennis T. Gordon, 224 Eckles Hall, Department of Food Science and Nutrition, University of Missouri, Columbia, MO 65211.

Many dietary factors can affect Fe bioavailability. The purpose of this experiment was to examine the effect of different types and levels of dietary lipids, vitamin E and butylated hydroxy toluene (BHT) on the ability of the anemic rat to absorb Fe. Hemoglobin (Hb) was depleted by feeding male growing rats a semipurified diet (American Institute Nutrition-AIN) low in Fe. Animals were then divided into 36 groups of 5 animals each with a mean Hb of 6.6 g/dl. Beef tallow, molecularly distilled corn oil and salmon oil were substituted in the AIN diet at levels of 5, 10 and 20%, replacing D-glucose. All test diets contained 25 μg Fe/g ($FeSO_4 7H_2O$) and were



provided to animals for 14 days. Hemoglobin change was the evaluated response. The greatest increase in Hb was observed in animals consuming beef tallow, 6.32 g/dl, followed by corn oil, 5.84 g/dl and salmon oil 5.46 g/dl (LSD critical mean value P 0.05=0.82 g/dl). Increasing dietary lipid levels from 5 to 10 to 20% caused Hb concentrations to decrease from 5.96 to 5.93 to 5.73 g/dl, respectively. Each type and level of dietary lipid was incorporated into diets with increasing levels of vitamin E. The mean change in hemoglobin for animal groups which had 0, 50 or 200 mg vitamin E/kg diet were 5.80, 6.21 and 5.61 g Hb/dl, respectively. At the 20% dietary lipid level, diets containing 0.02% BHT in the fat/oil had a significantly higher ($P<0.05$) increase in Hb, 5.73 g/dl, compared to the change in Hb observed in animals consuming the same diets without BHT, 4.38 g/dl. Results indicate that lipid unsaturation and not dietary lipid level can reduce Fe bioavailability. Dietary vitamin E appears to have no effect, while BHT added to the fat/oil has a positive influence on Fe bioavailability.

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STRUCTURAL REQUIREMENTS FOR DIVERSE STEROL FUNCTIONS IN *Saccharomyces cerevisiae.* Russell J. Rodriguez and Leo W. Parks, Department of Microbiology, Oregon State University, Corvallis, OR 97331-3804.

We have shown that the growth of sterol auxotrophic yeast on cholestanol is precluded unless minute quantities of sterol are also present. Contaminating sterol in most cholestanol preparations or excess sterol in the inoculum used in growth studies is adequate to provide the required sterol. We interpret the results to mean that sterols have a bulk structural role and a second function having high sterol specificity. A wide range of sterols and stanols have been analyzed for their ability to satisfy bulk activity and the high-specificity functions in the sterol auxotroph, RD5-6. While many sterols and stanols satisfy the bulk requirement, only those compounds possessing a C-5,6 unsaturation, or capable of being desaturated at C-5, fulfill the high-specificity requirement. Unsaturation in the A ring renders the sterols or stanols unsuitable for either function. The presence of the C-28 methyl group of ergosterol allows for greater ease of C-5 desaturation, such that some sterols lacking the C-28 methyl were incapable of supporting growth while identical sterols with the C-28 methyl were growth supportive. Evidence is presented on the functional moieties required of sterols to satisfy the bulk and high-specificity requirements. These data are extended to a possible role for the C-28 methyl group of ergosterol in yeast.

Honored Student Presentation

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COMPARATIVE STUDIES OF THE EFFECTS OF *cis-* AND *trans-*OCTADECENOATE ON STEROL METABOLISM IN RATS. Michihiro Sugano, Midori Watanabe, Kikuko Ryu, Young-J. Cho and Takashi Ide, Laboratory of Nutrition Chemistry, Kyushu University School of Agriculture 46-09, Higashi-ku, Fukuoka 812, Japan.

The effects of *trans* fats on sterol metabolism were examined using dietary fats with a comparable amount of octadecenoate but differing in the geometry. Male rats were fed diets containing 5–20% olive oil (or camellia oil) or partially hydrogenated corn oil for about one month. Linoleic acid contents were kept equivalent. *Trans* fat compared to *cis* fat showed no untoward effects on growth parameters and was in no way cholesteremic. On feeding cholesterol-free diets, dietary fat-type unmodified concentrations of bile acid and cholesterol in the bile. There was possibly a trend toward higher fecal excretion of both neutral and acidic steroids, but the effects on steroid compositions were indefinite. Differences in fecal output disappeared on cholesterol-enriched diets. Specific activity of hepatic and intestinal HMG-CoA reductase and hepatic cholesterol synthesis in vitro tended to increase moderately by *trans* fat feeding, whereas hepatic cholesterol 7α-hydroxylase activity elevated markedly. These results favor the view that *trans* octadecenoate interferes with intestinal absorption of both cholesterol and bile acid. Though dietary fat is thought to enhance colonic carcinogenesis presumably by stimulating production of bile acids, the significance of the observed effects should be considered with meticulous care.

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INVESTIGATIONS OF THE EFFECT OF GLUCOCORTICOIDS ON THE PRODUCTION OF LEUCOTRIENES AND HETES BY HUMAN LEUKOCYTES. J.K. Beckman, A.R. Brash and John A. Oates, Department of Pharmacology, Vanderbilt University, School of Medicine, Nashville, TN 37232.

Glucocorticoids have been reported in the rabbit and rat peritoneal leukocytes to induce the synthesis and release of a peptide (alternatively named macrocortin or lipotropin) which inhibits phospholipase activity. Activation of phospholipases is a key step in the sequence of events in leukocytes leading to the production of lipoxygenase-derived metabolites of arachidonic acid which stimulate inflammatory responses. It has thus been postulated that glucocorticoids might be of benefit in therapy for certain allergic disorders. In the present study we have stimulated human white cells with melittin, a bee venom-derived peptide which activates phospholipases. Lipoxygenase products, including leukotrienes and HETEs were measured. The effects of various intervals of preincubation of the cells with the glucocorticoid, hydrocortisone, prior to stimulation by melittin, were then assessed. In addition, the media derived from cells incubated in the presence or absence of selected levels of hydrocortisone was assayed for phospholipase inhibitory activity using purified enzymes.

SESSION LL Protein Chemistry: Functionality and Processing Effects Wednesday p.m.

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FUNCTIONAL PROPERTIES OF DRY BEAN *(Phaseolus vulgaris* L.) PROTEIN CONCENTRATES. S.S. Deshpande and Munir Cheryan, Department of Food Science, 104 Dairy Manufacturing Building, 1302 W. Pennsylvania Avenue, Urbana, IL 61801.

Functional properties of protein concentrates prepared from five dry bean *(Phaseolus vulgaris* L.) cultivars, viz., Viva Pink, Small White, Great Northern, Light Red Kidney, and Cranberry, were evaluated. The protein contents ranged from 65.71 to 71.70% on as-is basis. Water and oil absorption capacities ranged from 3.1 to 4.3 and 2.1 to 2.5 g/g protein, respectively. Minimum protein concentrations required for gelation were 5 to 7% (w/v). At 70 C, mean gelation times for proteins decreased with increasing concentration. Addition of Ca^{2+} ions lowered the time required for the gelation of proteins. Solubility of bean proteins was minimal at pH 4.0. Dry bean proteins had good foaming properties. Emulsifying activities of 0.5% (w/v) protein solutions ranged from 65.5 to 82.4%. Dry bean protein emulsions were fairly stable to heat. Effects of pH on foaming and emulsion properties will be discussed.

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UTILIZATION OF FIELD PEAS AS A PROTEIN SUPPLEMENT IN FOODS. Barbara P. Klein and Martha A. Raidl, Department of Foods and Nutrition, University of Illinois, 905 S. Goodwin, Urbana, IL 61801.

Legume seeds, such as soy and other pulses, are widely used as protein sources in the human diet. Field peas are generally consumed directly as the seed, but recent advances in technology suggest that protein concentrates and isolates can be produced by relatively simple methods (e.g., air classification). Differences in composition among legume products influence their functionality as well as their nutritive value. Acceptability of field pea products is limited because of undesirable organoleptic characteristics, in spite of improved functional effects, in food systems. Pea flours and concentrates have been used for protein enrichment of baked products and for meat extenders. Studies of the volatile compounds produced during cooking and baking of foods with pea supplementation indicate differences in the distribution of volatile carbonyl compounds in pea and other grains and legumes. Differences in enzyme activities in peas may contribute to the functional properties. This review will encompass studies of chemical composition, enzyme distribution and activity, processing methodology, functional properties and utilization of field pea products in food systems, particularly bread production. The future potential of field peas as a high protein supplement in the human diet will be discussed.

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FUNCTIONALITY OF SOY PROTEINS IN BAKED PRODUCTS. S.L. Melton, Food Technology and Science, University of Tennessee, PO Box 1071, Knoxville, TN 37901.

Several forms of soy protein products (defatted soy flour, full-fat soy flour, lecithinated soy flour, refatted soy flour, soy concentrates and soy isolates) are used successfully in the commercial production of one or more bakery products, including white bread and buns, variety breads, doughnuts and all types of cakes. In the United States, these soy protein products are utilized for their functional properties and/or as a replacement for higher priced ingredients rather than to improve the protein content and quality of the food product. The need for special functional properties in soy proteins which replace higher priced ingredients or add a desirable quality to a baked product has resulted in several commercial soy protein products engineered for specific uses. Processing of soy protein products can be varied to produce variation in their solubility, dispersibility, water holding capacity, fat absorption, whipping ability, thickening and gelling characteristics, emulsifying capacity and emulsion stabilization. Certain functional characteristics of available soy protein products will be reviewed in relation to their performance in baked products.

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EFFECT OF PROTEIN RECOVERY METHODS ON EMULSIFYING PROPERTIES OF TOMATO SEED PROTEIN CONCENTRATE. S. Latlief and D. Knorr*, Alison Hall, Department of Food Science and Human Nutrition, University of Delaware, Newark, DE 19711.

The potential of tomato seed proteins as functional food ingredients was investigated. It was further attempted to tailor protein functionality through examining the effect of protein recovery conditions on protein concentrate functionality. Tomato seed protein concentrates were produced by coagulating the proteins after alkaline extraction from ground tomato seeds. A 3 X 3 X 3 matrix of coagulation conditions was applied using different protein coagulants (citric acid; citric acid/hydrochloric acid, 50:50, hydrochlorid acid), three levels of flocculating agent addition (0 mg chitin, 250 mg chitin/L protein water, 500 mg chitin/L protein water) and various coagulation temperatures (25 C, 60 C, 95 C) to investigate the effect of process conditions on protein concentrate functionality. The evaluation of protein functionality revealed significant differences among the freeze dried samples. The coagulation temperature was the primary factor affecting both emulsion ability and emulsion stability. Samples coagulated at ambient temperature possessed superior emulsion properties than protein concentrates coagulated at 60 C and 95 C. The application of different coagulating agents showed a significant interaction effect with the coagulation temperature. Flocculating agent addition had a minimal effect on emulsifying properties of the tomato seed protein concentrates. The data obtained stress the complexity of the effects of processing on protein functionality and indicate the potential of obtaining tailored functional protein concentrates directly from protein sources without the need of further modification.

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MODIFICATIONS OF ILLINOIS PROCESS FOR THE ELABORATION OF PEANUT/SOY BEVERAGE. L.E. Camacho and M.P. Steinberg, Macul 5540, PO Box 15138, Santiago 11, Chile.

Several modifications of the Illinois process for soybean beverage were made to obtain a peanut/soy beverage, using the edible losses of the roasting peanut process. Acceptable organoleptic characteristics with emphasis in decreasing chalkiness, low cost and nutritional value closer to cow milk, were the desired characteristics. To decrease the typical chalkiness of legume beverages, the addition and method of application of tricalcium phosphate was essayed. Modifications on the incorporation and temperature of water, grinding stages, and the method of application of the sugar:salt blend, were also considered for the same goal. The roasting degree of peanuts and the trials of several milk flavorings to improve the flavor and aroma of the beverage, were evaluated. To reach a nutritional value closer to cow milk, the initial blend of soy and peanut was calculated in basis to a fat:protein ratio of 1. Protein contents of 3, 3.5, 4 and 5%, and the addition of both DL-methionine and L-acetylmethionine were studied. The treatments were evaluated by sensory analysis. A consumer study of acceptability with 112 persons chosen randomly within the student population of University of Illinois, was also made. The optimal final process consisted of: separate blanching of medium roasting degree peanut and dehulled soybean in water with 0.05% $NaHCO_3$ for 30 min, addition of sugar:salt blend and 0.305% of tricalcium phosphate by sprinkling, grinding at three stage in the Rietz Mell with a third of the water at boiling temperature incorporated on each stage and mesh of 3/16, 3/32 and 0.23 in, respectively, addition of L-acetylmethionine in a 2% total protein basis, and double homogenization at 3500/500 psig and 190 F each. A better flavor was obtained by addition of a chocolate formula prior to homogenization. The final product had a fat:protein ratio of 1, 3.7% protein and pH 7. The peanut/soy beverage was highly rated by 63% of the consumers, and was defined by presenting a nutty flavor.

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BIOLOGICAL EVALUATION OF SOYBEAN MEALS PROCESSED BY ISOPROPYL ALCOHOL EXTRACTION OF SOYBEAN FLAKES. J.L. McNaughton and E.C. Baker, USDA, ARS, SR, South Central Poultry Research Laboratory, PO Box 5367, Mississippi State, MS 39762.

Hexane is used extensively in the soybean oil extraction process. Isopropyl alcohol (IPA) is safer, is more available, and the vapors are considered less toxic than hexane. Previous investigators have shown potential energy savings when oilseeds are extracted with aqueous alcohols, such as IPA, because of the nondistillation recovery of the oil. Soybean flakes were extracted with aqueous IPA at 77 C in a Kennedy countercurrent continuous extractor at a retention time of 71 min. Broiler chickens from 1 to 28 days of age were fed diets that contained soybean meal extracted with 85% IPA in a 3:1 solvent-to-meal ratio (S:M), 87.7% IPA in a 2:1 S:M, 90.5% IPA in a 2:1 S:M, and hexane in a 2:1 S:M. Corn-soybean meal diets were formulated to contain 19% protein and 3200 kcal metabolizable energy per kg of diet. All other nutrients were added to meet or exceed the broiler's requirements. Each extracted soybean meal was desolventized-toasted to reduce trypsin inhibitor and urease. Trypsin inhibitor values ranged from 1.3 to 4.2 mg/g of sample, which is below the value previous investigators have determined adequate for optimum monogastric protein utilization. Feed efficiencies were unaffected by dietary treatment. Body weights were greater for chickens fed diets containing soybean meals extracted with 85% IPA in a 3:1 S:M, 87.7% IPA in a 2:1 S:M, and hexane, as compared to chickens fed soybean meals extracted with 90.5% IPA in a 2:1 S:M. Experimental results indicate that IPA is adequate for extracting soybean oil, but a maximum of 87.7% IPA solution should be used.

SESSION MM Ralph Potts Memorial Symposium—II Wednesday p.m.

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Title unavailable at press time.
N.O.V. Sonntag, consultant, Red Oak, TX.
Abstract not available at press time.

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LIQUID DETERGENT SOFTENER ANTISTAT FORMULATIONS "LDSA". Moneeb Zakaria and James K. Whitehead, Armak Company, 8401 W. 47th Street, McCook, IL 60525.

The concept of introducing a laundry product which provides both detergency and softening has been a very attractive one for the laundry products manufacturers for many years. The chemical nature of popular detergents being anionic and the softener bases being cationic made this task difficult to achieve. With the advent of synthetic nonionic detergents, this incompatibility problem was no longer an issue and it was possible to formulate products that are efficient as both detergents and softeners. The detergents selected for Armak's formulations have provided improved detergency over a wide range of fabrics and soils. The use of Armak's unique and diversified cationic softener bases resulted in stable, compatible formulations with added detergency and good softening and antistatic properties. Comparative evaluations against commercially available LDSA products were made and demonstrated Armak's formulations excellent performance.

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ALPHA SULFO METHYL TALLOWATE IN HEAVY DUTY LAUNDRY DETERGENTS. Kelly M. Chambers and Carl P. Cullotta, Stepan Chemical Company, 22 W. Frontage Road, Northfield, IL 60093.

The detergency of ASMT in heavy duty laundry formulations has been investigated due to the price stability and availability of its tallow-derived feedstocks. Terg-o-meter and wash/wear testing were used to evaluate its performance against commercially used surfactants on a variety of fabrics under different wash conditions. Stain removal efficacy as well as other performance characteristics of ASMT were also examined. Results show ASMT to be an excellent and effective alternative to petroleum-derived surfactants in heavy duty laundry detergents.

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NMR METHODS FOR THE PROFILING OF FATTY AMINE REACTIONS. Edward H. Fairchild and Floyd E. Friedli, Sherex Chemical Company, 5777 Frantz Road, Dublin, OH 43017.

The catalyst-promoted reductive conversion of fatty nitriles to primary and secondary amines is a method of wide commercial utility. In order better to understand the mechanism of these sometimes capricious reactions, we have examined a variety of conversions (different conditions and different catalysts) using both proton and carbon-13 NMR methods. The NMR spectrum provides a great deal of structural information without perturbing the mixture in any way. Minimal sample handling means that labile intermediates can often be observed without decomposition. Sequential sampling provides an additional variable, time, to assist the analyst in sorting out the component spectra in the spectra of complex reaction mixtures. Reaction dynamics for a variety of components can rapidly be obtained from a single set of samples. The strengths and weaknesses of both proton and carbon spectral methods will be discussed.

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GAS CHROMATOGRAPHIC SEPARATION OF LONG-CHAIN FATTY NITRILES AND LONG-CHAIN ACID AMINES. Chu-nan Wang and Lincoln D. Metcalfe, Armak Company, Research Laboratories, 8401 W. 47th Street, McCook, IL 60525.

A method is described for the chromatographic separation of long-chain fatty nitriles and long-chain acid amides on a cyanopropyl-phenylsilicone columns. It was found that better separations on saturates and unsaturates were obtained for these compounds using a cyano column than with any method previously reported.

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ANALYSIS OF METHYL ESTERS OF DIMER ACIDS BY HPLC. Azhar A. Shah and Nancy A. Meyer, Emery Industries, 4900 Este Avenue, Cincinnati, OH 45232.

Dimer acids produced by catalytic dimerization of tall oil fatty acids and oleic acids are of great commercial value and find many important uses, such as in the preparation of polyamides, polyesters, etc. Commercial dimer acids as produced are a complex mixture of monomer, dimer, and trimer acids of various structures and may also include higher polymers. An accurate determination of their composition is important for quality control as well as end use. Techniques for separation and quantitation of methyl esters of monomer, dimer, and trimer acids by liquid-solid chromatography are presented. The components are separated on a preparative "CN" column and various fractions collected. After evaporation of solvent, the fractions are weighed and composition determined. Recovery from the columns is of the order of 99+%. Preliminary data on the various structures of the dimer acids are also presented. This technique also provides unique fingerprint profiles of various types of commercial dimer acids available in the market which is of significant value in identifying the type of dimer acid.

SESSION NN Hydrogenation Wednesday p.m.

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BEHAVIOR OF PLATINUM AND PALLADIUM CATALYSTS IN SOYBEAN OIL HYDROGENATION. John D. Ray, Best Foods Research and Engineering Center, 1120 Commerce Avenue, Union, NJ 07083.

A detailed study of Pt and Pd catalysts on carbon supports will be presented. The effects of temperature, hydrogen pressure and catalyst concentration were examined for each catalyst for the hydrogenation of soybean oil. Both catalysts are several times more active than nickel catalysts but have different selectivity and isomerization rates. At certain operating conditions, the amount of *trans* isomerization is low for Pt catalyst; however, the selectivity is also low. Palladium has higher selectivity and produces *trans* isomers at nearly the level of nickel catalysts. Reaction models and a consideration of the economics of the catalysts will also be presented.

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EMPIRICAL MODELING OF HYDROGENATION OF SOYBEAN OIL. John D. Ray, Best Foods Research and Engineering Center, 1120 Commerce Avenue, Union, NJ 07083.

Operating variables that control the hydrogenation process have a complex relationship to final hardened oil produced. A number of empirical models were generated by fitting data from a series of statistically designed laboratory hydrogenation experiments. The power-series equations facilitate predictions of hydrogenation results for the responses: reaction time, rate of reaction, *trans* isomer content, and selectivity. Thus, knowing reaction conditions of temperature, hydrogen pressure, catalyst concentration, agitation level and final iodine value, results of the hydrogenating soybean oil can be predicted. Response/surface plots assist in the selection of operation conditions that will give desired product in reasonable time. The effects of catalyst concentration and agitation were found to be more significant than expected on *trans* content which in turn influences the melting characteristics of the hardened oil. Pressures above 25 psig were found to have little effect toward increasing *trans* isomer content, although pressure was very important in determining reaction rate. Reaction temperature is seen as the most important determinate of *trans* isomer content for a given iodine value. Generally, 50–60% *trans* isomers are predicted by the model for all reasonable operating conditions. These kinds of predictions can assist in scale-up operations and in determining the optimum operating conditions to run production hydrogenations.

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PARTIAL HYDROGENATION TO PRODUCE LOW-*TRANS* UNSATURATED OILS. J.A. Heldal, Laboratory of Industrial Chemistry, University of Trondheim, Trondheim, Norway.

Considerable interest has been given in the last 10–20 years in developing hydrogenation catalysts that give low *trans* isomerization and high selectivity for polyunsaturates. These efforts have been justified economically because decreased *trans* unsaturation will decrease losses during winterization of partially hydrogenated vegetable oils, and nutritionally because of still unknown effects of large intakes of *trans* isomers in human diets. Also, decreased *trans* unsaturation changes the physical properties of oils, and may influence the oxidaton and flavor stability of hydrogenated products. A review is given of different catalytical systems known to give low *trans* products. The activity, selectivity and specific isomerization (% *trans*/Δ IV) are discussed for the most important homogeneous and heterogeneous catalysts. The influence of processing variables (temperature, pressure, catalyst concentration) and type of process (batch, continuous) are also considered.

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COMPARISON OF HOMOGENEOUS AND HETEROGENEOUS PALLADIUM HYDROGENATION CATALYSTS. J.A. Heldal and E.N. Frankel, Laboratory of Industrial Chemistry, University of Trondheim, Norway.

Mechanistic and kinetic studies of Pd-catalyzed hydrogenation at atmospheric pressure and 30–100 C were carried out with methyl sorbate, linoleate and conjugated linoleate. Homogeneous Pd-catalysts and Pd-acetylacetonate [$Pd(acac)_2$], in particular, were significantly more selective than Pd/C in the hydrogenation of sorbate to hexenoates. The main monoene was *trans*-2-hexenoate. Relative rate constants for the different parallel and consecutive reactions, determined by computer simulation, indicated that the low selectivity of Pd/C can be attributed to a significant direct reduction of sorbate to hexanoate. The similar behavior of $PdCl_2$ to that of Pd/C suggests that Pd(II) was initially reduced to Pd(0). Valence stabilization of $PdCl_2$ by adding DMF or a mixture of Ph_3P and $SnCl_2$ increased the selectivity but decreased the activity. Stabilization of $Pd(acac)_2$ with triethylaluminum (Ziegler catalyst) gave an increased activity but decreased selectivity. The kinetics of methyl linoleate hydrogenation showed that although $Pd(acac)_2$ was only half as active as Pd/C, their respective diene selectivity was similar (10.4 and 9.6). The much greater reactivity of conjugated linoleate compared to linoleate toward $Pd(acac)_2$ suggests the possible formation of conjugated dienes as intermediates that are rapidly reduced and not detected in the liquid phase during hydrogenation.

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CONTINUOUS SLURRY HYDROGENATION OF SOYBEAN OIL WITH COPPER-CHROMITE CATALYST AT HIGH PRESSURES. S. Koritala, K.J. Moulton Sr., E.N. Frankel and W.F. Kwolek, Northern Regional Research Center, Agricultural Research Service, US Department of Agriculture, Peoria, IL 61604.

Soybean oil was hydrogenated continuously with copper-chromite catalyst in a 120-ft tubular reactor. A series of hydrogenations was performed according to a statistical design varying processing conditions such as oil flow (0.5, 1.0 and 2.0 L/hr), reaction temperature (180 and 200 C), hydrogen pressure (1100 and 4500 psi) and catalyst concentration (0.5 and 1.0%). Analysis of variance showed that linolenate selectivity and isomerization were not affected by change in pressure, temperature or catalyst concentration. As expected, increase in temperature, pressure, or catalyst concentration resulted in increased hydrogenation. Increasing the oil flow rate at 1100 psi gave higher reaction rates, possibly because of increased turbulence within the reactor. At the higher pressure, hydrogenation increased when flow rate was increased from 0.5 to 1.0 L/hr. To hydrogenate large volumes of vegetable oils at high pressure to a given IV, continuous reaction with a selective catalyst such as copper chromite may offer economic advantages over batch hydrogenation.

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ULTRASONIC HYDROGENATION OF SOYBEAN OIL. K.J. Moulton Sr., S. Koritala and E.N. Frankel, Northern Regional Research Center, Agricultural Research Service, US Department of Agriculture, Peoria, IL 61604.

The rate of hydrogenation of soybean oil with either copper chromite or nickel catalysts increased more than a hundredfold with the aid of ultrasonication. With ultrasonic energy, 87% hydrogenation of linolenate in soybean oil was obtained in 8.6 sec at 115 psig H_2 with 1% copper chromite at 181 C and 77% hydrogenation with 0.025% nickel. Without ultrasonic energy, only 59% linolenate hydrogenation was obtained in 240 sec with copper chromite at 198 C and 500 psig H_2 and 68% linolenate hydrogenation in 480 sec with nickel at 200 C and 115 psig H_2. In a continuous reaction system, the selectivity with copper chromite catalyst for linolenate reduction was somewhat lower when ultrasonic energy was applied. This innovation may offer an important advantage in increasing the activity of commercial catalysts for fats and oil hydrogenation, particularly for copper chromite.

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HYDROGENATION PRACTICE. Herman J. Beckmann, Harshaw Chemie B.V., PO Box 19, DeMeern, The Netherlands.

This paper deals with such topics as the changes in the molecular dimensions of a triglyceride during hydrogenation and the effect of catalyst structure on selectivity and filterability and the effect of sulfur on activity and isomerization, the prevention of aromatics formation during hydrogenation of highly unsaturated oils, explanation and prevention of green coloration of oil, the effect of phosphatides on selectivity and *trans*-isomer formation. Heat saving equipment and process control are also discussed.

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HYDROGENATION PLANT DESIGN AND OPERATION. Joseph Anglin, Philip Bollheimer and R.E. Clements, PSI Process Systems, Inc., 4466 Elvis Presley Boulevard, Suite 300, Memphis, TN 38116.

This paper will detail the design and operation considerations of a modern vegetable oil hydrogenation plant. Hydrogenation theory will not be addressed, but rather the practical aspects of plant design and operation will be emphasized. Topics discussed include convertor design, safety, catalyst reuse, heat recovery, catalyst and polish filtration, and instrumentation and control. The effect of these design considerations on capital costs, energy use and ease of operation will be shown.

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THERMAL PROPERTIES OF HIGHLY HYDROGENATED SOYBEAN FAT. P.J. Wan and A.H. Chen, Anderson Clayton Foods, W.L. Clayton Research Center, 3333 N. Central Expressway, Richardson, TX 75080.

Thermal properties of a highly hydrogenated soybean fat with iodine value (IV) of 4.9 was studied using a differential scanning calorimeter (Perkin Elmer, DSC-4). The specific heat, heat of fusion, and the rate of crystal transformation were measured between 0 and 80 C with a cooling or heating rate from 5 C/min to 320 C/min. From these thermal data, ways of handling the fat flakes during and after the process will be discussed.

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IMPROVING YOUR ON-STREAM FACTOR WITH LIQUID HYDROGEN SUPPLY. George F. Diehl, Mary E. Buffington and David P. Bhasin, Air Products and Chemicals, Inc., PO Box 538, Allentown, PA 18105.

A reliable high-purity hydrogen supply is essential to an edible or inedible oil refinery. Hydrogen may be generated internally or purchased from a merchant hydrogen producer. Hauled-in liquid hydrogen supply can improve the on-stream factor of hydrogenators. Liquid hydrogen can (a) serve the entire hydrogen needs of the plant, (b) supplement existing on-site generator capacity, or (c) provide back-up to hydrogen generators during equipment outages. Alternatives are given of the types of liquid hydrogen supply systems and the associated equipment (cryogenic, vaporization and control) and utilities required. The considerations that are involved in selecting a liquid hydrogen supply system as a primary or supplementary source are presented. Case histories are included to illustrate actual use.

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NICKEL, OILS AND FATS RECOVERY FROM USED NICKEL CATALYST. Mario Calebotta and Juan Luis Gautier, Departamento de Quimica, Universidad de Santiago, Casilla 5659 Santiago 2, Chile.

Recovery of Ni, oils and fats from a used nickel catalyst obtained from hydrogenation plant has been achieved by treatment with Si, Al, Fe silicates. The fats extraction was carried out employing classical organic solvents in a continuous reactor. Fluorescence analysis did not detect nickel ions in the liquid phase. Gas chromatographic analysis showed that percentages of methyl esters are not changed with respect to original oil. The solid phase containing the adsorbed cations was treated with 20% H_2SO_4 (P/P) at 95 C. All the cations were separated from nickel by selective precipitation and checked by atomic absorption. The quantitative recovery of Ni was accomplished by DC galvanostatic method over stainless steel cathode. A laboratory cell for reduction was designed. The cathodic conditions such as current density, pH, temperature, electrode arrangement were studied. Working at 13 mA/cm^2, 100% of nickel ions are reduced from the electrolyte during 28 hr. Boric acid was employed as an additive in order to avoid the faradic yield decrease due to hydrogen evolution. The cathodic yield was estimated by gravimetric and electrochemical measurements. The chemical characteristics of electrolytical nickel are almost of 100% purity.

SESSION OO Petrochemical and Fuel Alternatives from Fats and Oils: Part B—Vegetable Oil Carriers for Crop Production Chemicals Wednesday p.m.

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SOYBEAN VS PETROLEUM OIL ADJUVANTS IN SOYBEAN WEED CONTROL. W.L. Barrentine, H.R. Hurst and J.E. Dale, Delta Branch, MS Agricultural and Forestry Experiment Station, PO Box 197, Stoneville, MS 38776.

Soybean oil and petroleum oil adjuvants (oil/surfactant 87:13% wt/wt) were evaluated under field conditions with herbicides applied preplanting soil incorporated (ppi), preemergence (pre), or postemergence (poe), in soybeans. Results show that the choice of adjuvant, i.e., soyoil or petroil blends depends on the herbicide, target weed, and spray volume. Trifluralin applied ppi at 1.12 kg/ha in water at 56 L/ha with a spinning disc applicator (SDA) with or without soyoil adjuvant gave 66% seedling johnsongrass [*Sorghum halepense* (L.) Pers.] control, but conventional application in water alone at 187 L/ha gave 97% control. Pre application of metolachlor at 4.5 kg/ha gave 90–97% johnsongrass control with or without the adjuvants at 56 L/ha or without adjuvant at 187 L/ha. Hemp sesbania [*Sesbania exaltata* (Raf.) Cory] control by acifluorfen (Tackle) + X-77 or soyoil adjuvant poe, at 0.14 kg/ha + 0.5% (v/v) was 99% and 35% with petroil adjuvant. Rhizome johnsongrass control was 85% with sethoxydim at 0.28 kg/ha applied poe in soyoil without adjuvant, 10% in water, and 50% with soyoil or petroil as adjuvants (1.25% v/v) at 9.4 L/ha. Control of several morningglory (*Ipomoea* sp.) species, prickly sida (*Sida spinosa* L.), and hemp sesbania was not enhanced by the addition of soyoil or petroil adjuvants when applied aerially at 9.4 L/ha and 47 L/ha or at 47 L/ha and 140 L/ha with conventional hydraulic nozzle ground equipment.

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THE USE OF VEGETABLE OILS IN ULV INSECTICIDE APPLICATIONS. Dan F. Clower, Department of Entomology, Life Sciences Building, Louisiana State University, Baton Rouge, LA 70803.

This paper presents the results of a 2-year study to determine the value of vegetable (soybean/cotton seed) oils as carriers for insecticides applied to cotton. The performance of ultralow volume aerial applications containing either cottonseed or soybean oil were compared to conventional applications of water-based aerial sprays. During the two-year research program, four pyrethroid and one organophosphate insecticide were tested for efficacy against cotton insect pests when applied in vegetable oil. Additionally, the on-target deposit characteristics of the two application techniques were compared in one test. Insecticide residues resulting from the first and final applications were sampled at 4, 24, 72 and 120 hr post-treatment with separate samples taken at each date from the top and bottom portions of the plants. External and internal leaf residues for each sample were also determined by appropriate procedures.

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CURRENT USE AND EFFICACY OF VEGETABLE OIL AS A CARRIER FOR APPLICATIONS OF INSECTICIDES. R.G. Luttrell and Roy Reid, Department of Entomology, Drawer EM, Mississippi State, MS 39762.

The use of vegetable oil as a carrier for insecticide sprays has recently received considerable attention and is rapidly being accepted by cotton farmers and consultants in the Mid-South. The concurrent development of synthetic pyrethroid insecticides, which are highly toxic to insects at extremely low rates, and the improvement of spray application equipment, particularly that related to ultralow volume (ULV) applications, stimulated the interest in using vegetable oil as a carrier. Acceptance of vegetable oil as a carrier for insecticide sprays is closely related to the development of reduced volume, both ULV and LV, applications of insecticides. A chronological development of the reduced spray volume-vegetable oil concept of insect control is presented in this paper. Although the use of reduced volume applications of insecticides in vegetable oil is an extremely interesting and popular concept, the actual biological efficacy and potential limitations of the application method have not been adequately documented. We have initiated studies to define more accurately the biological efficacy of reduced volume-vegetable oil sprays for control of cotton insect pests. These studies were conducted in 1981 and 1982. We plan to continue our investigations in both small and large plot field studies in 1983. In all of our studies reduced volume-vegetable oil sprays are compared to standard volume-water sprays. Data are collected on efficacy, canopy penetration and droplet characteristics. Results of initial studies and plans for future research are included in this paper.

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COTTONSEED OIL AS A CARRIER FOR PYDRIN® INSECTICIDE FOR COTTON BOLLWORM CONTROL. Max M. Sckerl, Shell Development Company, PO Box 3871, Houston, TX 77001.

Ultralow volume (ULV) Pydrin® insecticide treatments using cottonseed oil as the carrier were compared to Pydrin® treatments using water as the carrier for insect control in cotton. Two years' data from large plot yield trials have shown that ULV treatments resulted in comparable insect control at labeled rates when compared to conventional treatments. Likewise, cotton yield was as good or better on the ULV plots compared to the conventional plots. When lower than labeled rates were compared, the ULV treatments consistently resulted in better insect control and consequently higher cotton yields than the conventional treatments. These data as well as results from over a million acre commercial ULV applications of insecticides using cottonseed or soybean oil as the carrier, confirm that ULV treatments are efficacious for insect control in cotton.

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VEGETABLE OILS AS CARRIERS FOR PESTICIDES. R.S. Freedlander, Biological Research Center, ICI Americas, Inc., PO Box 208, Goldsboro, NC 27530.

Today's farmer has the option of selecting either water or oil as a pesticide diluent for crop spraying. University, industrial, and independent agriculturalists have been carefully researching these alternative methods and have noted that both routes have inherent advantages as well as inherent disadvantages. The role of the formulation chemist in this scenario is to provide the field researcher with optimum formulas in order that appropriate use patterns for the different techniques can be defined. Such development calls for a basic understanding of the physicochemical properties of various formulations upon dilution into the appropriate carrier. Whereas water dilutions require careful consideration of emulsification properties, oil dilutions mandate a firm grasp of solution science. During the past decade, scientists within the Plant Protection Division of ICI and its US subsidiary, ICI Americas Inc., have been evaluating the use of oil, particularly vegetable oil, for crop spraying. Another existing avenue of formulation research involving oils which we have been exploring evolves around ICI's new electrodynamic sprayer termed ELECTRODYN^{TM}. In this novel spray system, the pesticide formulation flows through a high voltage nozzle such that it is subjected to an intense electric field. The charged liquid atomizes as it leaves the nozzle and is propelled to the crop target. Formulation criteria for optimum sprayer performance are defined by both the electrical and viscoelastic properties of the liquid. Laboratory studies have demonstrated that refined vegetable oil meets our specifications as a primary diluent for many of our formulations.

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DRIFT PROFILE OF WATER AND OIL DILUTED AERIAL SPRAYS. Sidney G. McDaniel, Bruce M. McKay, Robert L. Houston and Larry D. Hatfield, FMC Corporation, 2964 Terry Road, (A-4), Jackson, MS 39212.

During 1980, FMC Corporation conducted research to examine the drift characteristics of two types of aerial spray: reduced volume Pounce 3.2EC applied in one quart of vegetable oil/acre and high volume Pounce 3.2EC applied in 3 gal of water/acre. Results of this study indicated that there was no significant difference ($\alpha = 0.05$) between the two types of aerial application when airborne drift was measured over the downwind, one-half mile test area. Drift profiles were most accurately described by negative exponential regression equations, in which oil-phase sprays averaged a greater negative slope compared to water-phase sprays. This inferred that the reduced volume oil-phase spray droplets were leaving airborne status at a faster rate when compared to high volume water-phase droplets. Mylar deposition data showed that the two types of application were strikingly similar, although initial displacement of the smaller oil droplets were skewed to the right, and both methods approached minute amounts at 200 ft downwind. Cascade impactor data for droplet/particle size categories of ≥ 7.2 microns and < 7.2 microns followed the same trend as obtained from high volume air sampler data on one-half mile downwind, although a high degree of variability existed. Both devices captured less airborne active ingredient from the reduced volume oil-phase application when compared to the high volume water-phase application. From this study, we conclude that reduced volume applications using a nonvolatile vegetable oil are not more drift prone than high volume water-phase application and, in fact, may offer an advantage against long range drift into nontarget areas.

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REDUCED VOLUME APPLICATONS OF PESTICIDES ON VEGETABLE OILS. Walter J. Walla, Room 118B, Plant Sciences Building, Texas A&M University, College Station, TX 77843.

Applications of a pesticide in a vegetable oil carrier applied at a volume of one quart or more per acre is referred to as a reduced volume application (RVA-Oil). During 1982, Texas cotton producers treated 4.5 million acres (sprayed acres) with synthetic pyrethroid-cottonseed oil at 1.5 quarts/acre total volume. Total volume vegetable oil sales in Texas were 1.125 million gal with a dollar value of .84 million. Additional research into the use of herbicides and fungicides could result in a rapid increase in the agricultural market for vegetable oils. Research has shown that half-life of certain pesticides is increased dramatically when applied in an oil carrier. Increased residual activity is due to slower degradation by UV light, and a reduction in evaporative losses. Increased spray technology is necessary to generate uniform droplet sizes from agricultural aircraft to prevent off-target movement and ensure adequate coverage necessary for proper pest control.

SESSION PP Jojoba
Wednesday p.m.

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INTRODUCTORY REMARKS: AN OVERVIEW. Noel D. Vietmeyer, National Academy of Sciences, 2101 Constitution Avenue, N.W., Washington, DC 20418.

The conversion of jojoba from a wild desert plant to a cultivated crop is now in progress. In the USA, Mexico, Israel and other countries, universities, corporations, and private research laboratories have underway a considerable research effort designed to understand the characteristics of the shrub and the market potential of its products. It is now safe to conclude that jojoba can be grown in plantation cultivation. American farmers have already established 26,000 acres of commercial jojoba plantations. Mexican farmers have ca. 12,000 acres planted and Israel, Brazil, Australia and other countries are also establishing plantations. Jojoba oil contains no triglycerides; it is made up of wax esters. No known plant produces a comparable oil. In principle, jojoba oil could become a basic feedstock for the chemical industry. Lubricants, emulsifiers, plasticizers, protective coatings, foam inhibitors, corrosion inhibitors, cosmetics, polishes, and transformer fluids are some of the potential uses that have been proposed for this new product.

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COMMERCIAL CULTIVATION OF JOJOBA: CURRENT STATUS AND PROJECTED YIELDS. Carole Ann Whittaker, 3420 E. Shea Boulevard, #125, Phoenix, AZ 85028.

Certain conditions under which jojoba exists as a native plant are not conducive to obtaining stable or high yields of jojoba seed. Plantation sites must be selected for temperature requirements, availability of water, soil type and terrain. Most plantations to date have been developed using seed from native plants as propagating stock which has resulted in a high degree of genetic diversity and large differences in plant characteristics. Selections are currently being made for superior cultivars which can be cloned by rooted cuttings or tissue culture techniques. A summary of jojoba acreage currently under cultivation in the USA is given by planting date and geographic location. Estimated yields of jojoba oil are given for minimum and maximum extraction efficiencies in order to develop a projection for the supply of jojoba oil available to the oil markets in the period 1983–1995.

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CHEMICAL PROPERTIES AND TRANSFORMATIONS OF JOJOBA OIL. Jaime Wisniak, Department of Chemical Engineering, Ben Gurion University of the Negev, Beer Sheva 84105, Israel.

The growing interest in developing the shrub jojoba *(Simmondsia chinensis)* stems from the unusual properties of the oil that can be extracted from its seeds. Jojoba seeds contain an average of 50% by weight of a practically colorless, odorless liquid wax composed primarily of straight-chain monoesters of C_{20} and C_{22} alcohols and acids with one double bond each in the alcohol and acid moiety. Jojoba oil is subject to a variety of transformations including sulfurization, sulfur-chlorination, phosphonation, hydrogenation and ester reduction. The properties of the oil make it suitable as a transformer oil and as an ingredient in the manufacture of pharmaceuticals and cosmetics. Sulfurized and phosphonated jojoba oil offer excellent possibilities as a lubricant for high temperatures and pressures. Hydrogenation of jojoba oil produces a hard white wax with high melting point and properties competitive with beeswax and candililla, carnauba, and spermacetti waxes. Ester reduction of jojoba oil provides a unique source of C_{20} and C_{22} straight-chain alcohols which may be useful in the manufacture of detergents, wetting agents, dibasic acids, long-chain ethers, hydroxy ethers and sulfated products.

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VARIABILITY IN OIL CONTENT OF JOJOBA SEEDS. S.C. Anderson and W.H. O'Brien, Cargill, Inc., PO Box 9300, Minneapolis, MN 55440.

Jojoba is a new potential crop in the Southwestern USA. The seeds are high in oil, which is a potential replacement for sperm whale oil. Since efforts at domestication of the plant are recent and little breeding work has been done on it, a brief study of the variability in oil content of individual seeds was made to get some idea of the selection potential for improving the oil content. Individual seeds analyzed by NMR varied from 23 to 62% oil. This range should afford a good opportunity to improve average oil content by a selection breeding program.

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JOJOBA OIL AS A POTENTIAL LUBRICANT–AN OVERVIEW. Ron Estefan, Southwest Research Institute, 6220 Culebra Road, San Antonio, TX 78284.

Possible uses of jojoba oil in the lubricant industry will be discussed with emphasis on automotive applications. Potential use of the oil as a lubricant base stock, blend, additive and functional fluid will be presented. An overview of current lubricant markets and comparisons between petroleum and synthetic lubricants in these markets will also be discussed. Areas of research and testing of jojoba oil thus far as both a lubricant and additive will be outlined. Finally, current requirements and suggestions for additional research and testing of jojoba oil in the lubricant industry will be discussed.

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JOJOBA OIL—A COMPONENT IN COSMETIC FORMULATION TECHNOLOGY. Henry Libby, Libby Laboratories, Inc., Berkeley, CA 94710.

Discussion of jojoba oil as a component in cosmetic products requires not only a basic organizational framework but also a methodical approach to the numerous pertinent formulations that involve chemists in the cosmetic and pharmaceutical industry. A physicochemical classification is presented based on the polarity of single phase systems and an arbitrary organization of the several multiphase systems in terms of this same principle. On this basis, cosmetic products can be assigned to a simple classification. Jojoba oil can be included and evaluated as a single variable of each product classification in terms of the general properties and unique characteristics of jojoba oil. A summary includes discussion of products which are currently being marketed and a critical review of evaluation of these cosmetics in relation to the properties of jojoba oil.

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JOJOBA SEED MEAL AS AN ANIMAL FEED. Anthony J. Verbiscar and Thomas F. Banigan, Anver Bioscience Design, Inc., 160 East Montecito Avenue, Sierra Madre, CA 91024.

Jojoba seed meal contains four cyanomethylenecyclohexyl glucosides that contribute to its toxicity, including simmondsin, simmondsin 2′-ferulate, 5-desmethylsimmondsin and 4,5-didesmethylsimmondsin. These cyano compounds occur in the seed meal at total levels as high as 11%. Simmondsin, the major toxicant, and the seed meal are more toxic to rodents and poultry than to ruminants. A palatability factor causes animals to shun diets containing the seed meal. However, treatment of jojoba seed meal with selected strains of *Lactobacillus acidophilus* lowers cyano toxicant levels by 95% in three weeks, and improves palatability. The treated seed meal has a crude protein level of 28–30% and is accepted in livestock diets at 5–10% additive levels. *L. acidophilus* detoxified jojoba meal can be prepared by an ensilage process and used in cattle, sheep and poultry diets. It is most suitable for cattle rations, perhaps for dairy cows, where ruminant microorganisms complete the detoxification of residual simmondsin in jojoba seed meal.

Poster Session Wednesday p.m.

P1

LYSOLECITHIN AS PRECURSOR OF PHOSPHATIDYLCHOLINE IN HEPATIC LIPOPROTEIN SYNTHESIS. Wolfgang J. Baumann, S. Parthasarathy and A. Rosalind Marita, The Hormel Institute, University of Minnesota, 801 – 16th Avenue, N.E., Austin, MN 55912.

We have shown that systemic hypolipidemic drugs are potent inhibitors of phosphatidylcholine synthesis by rat liver microsomes, particularly by the lysolecithin acyl-transferase (LLAT) pathway. Increasing effectiveness in LLAT inhibition was observed in the series clofibric acid (CPIB), SaH-42-348, tibric acid, S-321328, WY-14643, S-8527 and DH-990 with 50% inhibitory concentrations ranging from 9 mM (CPIB) to 40 μM (DH-990). The order of effectiveness of the drugs in inhibiting LLAT in vitro correlated well with the drugs' known hypolipidemic potency in vivo, suggesting that inhibition of hepatic lysolecithin reacylation may result in impaired lipoprotein synthesis. The importance of the LLAT route in the synthesis of lipoprotein phosphatidylcholine was demonstrated on perfused rat liver. We could show that lysophosphatidyl-[^{14}C-methyl] choline was an effective precursor of phosphatidylcholine of lipoproteins, particularly of HDL. Choline-labeled lysolecithin was incorporated into phosphatidylcholine of lipoproteins ten times more effectively than was labeled choline. In the presence of hypolipidemic drugs, perfused liver was unable to synthesize lipoprotein phosphatidylcholine. The data suggest that lysolecithin reacylation is a major route of phosphatidylcholine synthesis for lipoproteins in liver and that inhibition of this pathway by hypolipidemic drugs interferes with lipoprotein assembly.

P2

EFFECT OF CYCLOPROPENOID FATTY ACIDS ON MEMBRANE COMPONENTS OF LIVER FROM RAINBOW TROUT *(Salmo gairdneri)*. Mark A. Einerson, Henry W. Schaup and Daniel P. Selivonchick*, Department of Food Science, Oregon State University, Corvallis, OR 97330.

The effects of cyclopropenoid fatty acids (CPFA) on membrane components of liver from rainbow trout were studied by several methods. 9,10-Methylene-^{14}C sterculic acid was used to determine the incorporation of CPFA into microsomal membrane phospholipids. At 72 hr after intraperitoneal injection of the radiolabeled CPFA livers were removed, microsomes prepared, and lipid extracted and analyzed. Radioactivity was found predominantly in choline (57%) and ethanolamine (22%) phospholipids. Only small amounts of radiolabel were found in other microsomal lipids. Phospholipase A_2 treatment of purified choline and ethanolamine phospholipids showed radioactivity preferentially esterified to the one position of the glycerol backbone. Two-dimensional polyacrylamide gel electrophoresis (PAGE) was used to assess the effects of dietary CPFA on protein composition of liver microsomal and plasma membranes. Microsomes from fish treated with 50 and 300 ppm CPFA showed a consistent difference in proteins in the 37,000 dalton range. These proteins consistently appeared as a group of from 4 to 6 proteins in CPFA gels, while only 2–4 proteins were present in the control gels. Plasma membrane proteins from CPFA treated animals showed an increase in proteins within a molecular weight range of 93,000 to 125,000 daltons. To determine if the spatial arrangement of membrane proteins could be altered by CPFA crosslinking studies with dimethyl 3,3′-dithiobispropionimidate-2HCl (DTBP), a bifunctional crosslinking reagent, were initiated in untreated animals. After treatment of microsomes with DTBP two groups of proteins were observed; a high molecular weight group of crosslinked aggregates not resolvable by PAGE and a group of low molecular weight proteins with components that decreased with increasing levels of DTBP. These data will be discussed in terms of membrane disruption induced by CPFA and cellular toxicity.

P3

SERUM LIPIDS AND LIPOPROTEINS IN RABBIT FED SEMIPURIFIED DIETS CONTAINING VARYING PROTEIN AND CARBOHYDRATE SOURCES. John E. Bauer, Box J-144, JHMHC, University of Florida, Gainesville, FL 32610.

Feeding trials of male New Zealand white rabbits were carried out with cholesterol-free semipurified diets containing casein or soy protein and sucrose or dextrose protein and carbohydrate sources. Three-month old rabbits, initially matched for size, maintained their body weights during the 12-week dietary period. Animals fed the casein-sucrose (CS) diet rapidly became hypercholesterolemic, but those fed the casein-dextrose (CD) diet became hypercholesterolemic more slowly. By contrast, in rabbits fed either a soy protein-sucrose (SS) diet or a soy protein-dextrose (SD) diet, low normal plasma cholesterol levels were maintained for the 3-month period. Gross aortic lesions were absent in all groups of rabbits, yet analysis of serum lipoproteins after 12 weeks showed the excess cholesterol in the casein-fed animals to be present mainly in the intermediate and low density fraction (d=1.006–1.009 g/mL and d=1.019–1.063 g/mL). Compositional analysis of the lipoproteins found very low density lipoprotein (d=1.006 g/mL, VLDL) of rabbits fed the CS and CD diets to be relatively cholesterol-enriched and triglyceride-poor. In the soy protein fed group, VLDL with a triglyceride content more like that for chow fed animals was observed. The type of dietary protein and carbohydrate used in this study affect the composition VLDL. These changes may be important in the development of atherogenesis in rabbits fed similar diets for longer periods.

P4

GC-MS ASSAY OF F PROSTAGLANDINS METABOLITE IN URINE. A. Ferretti, V.P. Flanagan and J.M. Roman, Lipid Nutrition Laboratory, BHNRC, USDA, Room 122, Bldg. 308, Beltsville, MD 20705.

A gas chromatographic-mass spectrometric method for quantitative determination of 9α,11α-dihydroxy-15-oxo-2,3,4,5,20-pentanor-19-carboxyprostanoic acid, the major urinary metabolite of F prostaglandins (PGF-M), is proposed. The metabolite was analyzed as the dimethyl ester-*O*-methyloxime-*bis*-trimethylsilyl ether derivative. Quantification was achieved by GC-MS with multiple ion analysis. The internal standard, which was added to the urine at the beginning of the analysis, consisted of a mixture of (underivatized) diethyl ester + monoethyl ester-δ-lactone of PGF-M. These two species were converted to the 1-methyl-20-ethylester derivative of the metabolite during the analytical process. Linear standard curves were obtained in the range 5–70 ng of injected prostaglandin. The method comprised extraction with Amberlite XAD-2, methylation, chromatography over octadecasilyl-silica, delactonization, remethylation, chromatographies over SiO_2 and Lipidex-5000, followed by methoximation, trimethylsilylation, and instrumental analysis. Interassay coefficient of variation, for analysis of 4 identical urine specimens, was 7% and intraassay coefficient of variation ranged from 3.2 to 6.0%. Specificity, accuracy and precision of the method were verified by recovery of the metabolite from several urine pools. The recovery of authentic, underivatized PGF-M was 107.3 ± 5.7 (mean ± SE, N=9). (We are indebted to Dr. U.F. Axen and Dr. J.E. Pike, The Upjohn Co., for supplying synthetic PGF-M.)

P5

MICROCOMPUTER IN THE LIPID LABORATORY. Herbert J. Dutton, The Hormel Institute, University of Minnesota, 801 – 16th Avenue, N.E., Austin, MN 55912.

Application of a microcomputer will be demonstrated with programs such as (a) "Cataly" (AOCS Recommended Practice Tz lb-79–Selectivity of Hydrogenation Catalysts); (b) "Journal" (an article filing and retrieval system); (c) "Diene" (a matrix solution for analysis of dienoic fatty acid mixtures in hydrogenated products). Problems and potentialities of the microcomputer in the lipid laboratory will be discussed.

P6

ANALYSIS OF STEROLS OF SOME VEGETABLE OILS BY CAPILLARY GAS LIQUID CHROMATOGRAPHY. C-S.J. Shen, P. Yasaei, M. Aldridge and A.J. Sheppard, HFF-268, Division of Nutrition, Bureau of Foods, FDA, 200 C Street, S.W., Washington, DC 20204.

The determination of sterol composition is a useful tool for the identification of vegetable oils. In the present study, the use of capillary gas chromatography on a 15-m SE-54 fused-silica open tubular column for the analysis of sterols of several vegetable oils, including soybean, cocoa bean, sunflower and tobacco seed, is reported. Vegetable oil was extracted from each sample and then saponified. The individual sterols were analyzed as butyrate derivatives. The gas chromatographic conditions were as follows: helium flow rate, 0.74 mL/min; column temperature, 250 C; injector and detector temperature, 300 C; split ratio, 1/81. Three major sterols, beta-sitosterol, campesterol and stigmasterol, were present in all oils. Several minor sterols, tentatively identified as Δ^7-stigmasterol, Δ^5-avenasterol and Δ^7-avenasterol, were also detected. Cholesterol represented from 5 to 9% of the unsaponifiable fraction in the tobacco seed oils but less than 1% in the other oils. The sterol composition of these oils as determined by capillary column was compared to that obtained by packed column gas chromatography. The capillary column, which provided a better separation power than the packed column, is more desirable for the analysis of the complex mixture of sterols in vegetable oils.

P7

DETERMINATION OF AIRBORNE ODOR COMPONENTS BY TENAX-GC ADSORPTION, THERMAL DESORPTION CAPILLARY GC-MS. Kenneth J. Welch, Mail Station 056, S.C. Johnson and Son, Inc., Racine, WI 53403.

Our laboratory is frequently requested to determine the airborne organic compounds, such as fragrances or malodors, being emitted from a variety of sources. To meet this goal, the well established methods for porous-polymer preconcentration were combined with high-resolution gas chromatography-mass spectrometry (GC-MS). In a specialized sampling apparatus, metered air is drawn across the odor source and through a metal cartridge containing Tenax-GC. The metal cartridge is placed into a desorption unit (Chemical Data Systems 320), and slowly heated (10 min) to 265 C. The organic compounds are desorbed and reabsorbed on a smaller column containing Tenax-GC. The second column is rapidly heated (1 min) to 265 C. The organic compounds are passed through a heated transfer line to the GC-MS (Finnigan 4023) where they are focused at the head of a cool (30 C) fused-silica capillary column (0.25 mm X 50 m Se-30). The organic compounds are finally separated via temperature programming and identified through a combination of mass spectral appearance and Kovat's retention index. The performance of the concentrator system approximates that of normal syringe injections. The time necessary to obtain a robust sample varies according to the odor source. For example, foods require several hours of sampling, whereas soaps and shampoos need only a few minutes. The additional criterion of a Kovat's index (KI) has improved the performance of the spectral identification process. The KI parameter assists the automated library search system by disregarding those library spectra with KI values outside the retention region being studied. In addition, a KI can be of some help when manual interpretations are encountered. The odor constituent of some flowers, fruits and vegetables have been examined as well as the perfumes from soaps and shampoos. The permeation of membranes and package materials was easily studied with this technique.

P8

TRIACYLGLYCEROL COMPOSITION OF EVENING PRIMROSE OIL. Y.S. Huang and M.S. Manku, Efamol Research Institute, PO Box 818, Kentville, Nova Scotia B4N 4H8, Canada.

Studies from our laboratory have shown that gamma-linolenic acid (GLA) is ca. 170-fold more effective in lowering plasma cholesterol level than linoleic acid (LA), the major constituent of most polyunsaturated oils. GLA is the first product of LA metabolism via the essential fatty acid pathway and is formed by the actions of the delta-6-desaturase (D-6-D). Many factors, such as diabetes, aging, viral infections, *trans* fatty acids and atopic disorders, interfere with D-6-D function. Thus, direct provision of GLA could have an important role in nutrition. However, GLA is rare in foods, being found for practical purposes only in human milk. The only other substituted natural source of GLA is a seed extract of the evening primrose plant, which contains 72% LA and 8% GLA. The present study was undertaken to examine the acylglycerol structure of evening primrose oil. The triacylglycerols were purified by thin layer chromatography (TLC) and fractionated into 7 classes according to the degree of unsaturation by argentation-TLC. The quantity and fatty acid composition of each fraction was determined by gas liquid chromatography after transesterification of the fatty acid moiety into methyl esters using heptodecanoic acid an an internal standard. The stereospecific distribution of the fatty acids in each fraction was determined after pancreatic lipase hydrolysis, synthesis of phenyl-phosphatides and release of lysophenyl-phosphatides by phospholipase A2. Our study shows there were two highly unsaturated triacylglycerol fractions which represented 20.3% of total triglycerides in evening primrose oil and which contained most of the GLA. The 2-position of the triglycerides in evening primrose oil was dominated by LA (76%) and followed by oleic acid (14%) and GLA (9%). GLA was distributed in all 3 positions, and in each molecule GLA-containing triacylglycerol was associated with at least one mole of LA.

P9

THE FATTY ACID CONTENT OF FRUIT AND VEGETABLE LIPIDS. John L. Weihrauch and Janet Kerr, USDA, HNIS, CNC, Federal Building, Room 300, Hyattsville, MD 20782.

Data on the fatty acid content of fruits and vegetables from the published and unpublished literature have collated for release in the updated expanded sections of Agriculture Handbook No. 8, "Composition of Foods; Raw-Processed-Prepared." The total lipid content of most fruits and vegetables is between 0.1 and 0.5%, and hence, under normal conditions they do not contribute significantly to total dietary lipid. However, the fatty acid composition has been studied in conjunction with keeping quality and off-flavor development in vegetables such as potatoes. Under some unusual conditions a knowledge of the quantities of especially the essential fatty acids is desirable. On several occasions we have had inquiries from hospital dieticians in cases where patients on self-imposed lopsided vegetarian or fruitarian diets were among others suspected of suffering from essential fatty acid deficiency. The fatty acids are given in our handbooks as the amount of the free acid in g/100 g of food. In this paper the values are expressed as the weight percent of each fatty acid methylester relative to the total fatty acid methylester mixture present in the lipid and as the amount of each fatty acid (as the free acid) in mg/g of lipid. Frequently the fatty acid composition varies considerably among the anatomical parts of given plants. Parts such as seed, fruit pulp, leaf or root may have distinct fatty acid patterns. Differences and similarities will be discussed. Suggestions for further research will be made.

P10

HYDROCARBONS OF PEANUT AND CORN OIL. R.E. Worthington, H.L. Hitchcock, L.G. Pounds, J.L. Harper and D.M. Wilson Jr., Department of Food Science, University of Georgia Agricultural Experiment Station, Experiment, GA 30212.

The nonacylglycerol fraction of seed oils consists of a variety of classes of compounds including hydrocarbons. The hydrocarbon content is generally less than .2% of the total oil and consequently small amounts of hydrocarbon contaminants derived from the environment during the handling and storage of seeds, oil processing, and analytical procedures employed in isolating hydrocarbons from the triacylglycerol matrix, will greatly influence the apparent hydrocarbon spectrum of seed oils. In this study, hydrocarbons were isolated and quantitated by a combination of preparative gravity-flow column chromatography, thin layer chromatography and gas chromatography. An internal standard, *n*-hexacosane, was added to oil samples prior to the initial separation by column chromatography. Blank runs were made to insure that the internal standard, chromatographic materials, and solvents were free from hydrocarbon impurities. Corn oil samples (Mazola, Kroger) were obtained from the local market; peanut oils from two commercial varieties of peanuts were prepared in the laboratory with a Carver press. The two peanut oils contained .02% total hydrocarbon and of this amount squalene accounted for 72 and 84%, respectively. The remaining hydrocarbon consisted of numerous compounds present in trace amounts and unresolved material that caused chromatographic base-line evaluation. Corn oil samples contained ca. .03% total hydrocarbon. Squalene ($C_{30}H_{50}$) accounted for 74% of total hydrocarbon in Mazola oil and 44% in Kroger oil. The remainder of the corn oil hydrocarbons consisted of a cluster of peaks eluting after squalene. Positive ion chemical ionization mass spectrometry revealed $C_{29}H_{46}$, three isomers of $C_{29}H_{48}$, and two isomers of $C_{28}H_{46}$.

P11

RELATIVE COMPOSITION AND DISTRIBUTION OF THE LIPID IN SIX COMMON OAT VARIETIES. Mark H. Love and Masood

Dehghan, 110 MacKay Hall, Ames, IA 50011.

Six common varieties of oats *Avena sativa* were studied: Cherokee, Lang, Noble 001 and 003, Stout, and Multiline E77. Water saturated *n*-butanol was the most efficient solvent system for total lipid extractions. Extracts were partitioned into $CHCl_3$/MeOH/Water (2:1:0.75). Extracted lipids were separated into three classes by silicic acid chromatography yielding neutral lipids (72%), glycolipids (18%) and phospholipids (10%). The relative distribution of 23 subclasses from these three major classes were quantitatively measured using reflectometric densitometry. Fatty acid analyses of each major class were determined by gas liquid chromatography. Linoleic acid was the major fatty acid in all lipid classes and varieties. The unsaturated to saturated ratio (u/s) varied from class to class and variety to variety. The range for neutral lipids was 3.2–5.2; for glycolipids, 2.7–3.4; and for phospholipids, 1.2–1.7.

P12

THE IONIZATION AND PHASE BEHAVIOR OF AQUEOUS FATTY ACIDS. David P. Cistola, Donald M. Small and James A. Hamilton, Biophysics Institute, Boston University School of Medicine, Boston, MA 02118.

Potentiometric titration curves were obtained at 25 C for dilute aqueous potassium oleate and potassium decanoate. The titration curve for 0.03 M potassium oleate (KOl) revealed two plateau regions from which apparent pK values of 9.5 and 7.2 were obtained; these values correspond to fractional degrees of ionization (α) of 0.82 and 0.34, respectively. At high pH (α=1.0), the 0.03 M KOl solution was micellar and optically clear. With the addition of a small amount of HCl, the sample (α=0.97) became turbid; this turbidity increased with added HCl until α=0.16, at which point an oil phase became visible at the surface. The turbidity resulted from the formation of a lamellar liquid-crystalline phase of aqueous potassium hydrogen dioleate, an acid-soap complex. Calculations of the surface area per charge for this phase at half-ionization (α=0.5), using the measured pH value and the Gouy-Chapman model for charged interfaces, yielded a value (31 $Å^2$/charge) which was much less than the value determined independently by analysis of X-ray diffraction data at 20 C (68 $Å^2$/charge). For comparison, potassium decanoate (KC_{10}) was titrated at a concentration below its critical micellar concentration. The potentiometric titration curve for this system differed significantly from the KOl curve; the KC_{10} curve showed only one plateau with an apparent pK (α=0.5) of 6.8. However, like aqueous KOl, aqueous KC_{10} became turbid with added HCl because of the formation of a lamellar liquid-crystalline phase. Calculations of the surface-area per charge for this phase, using the pH value at α=0.5 and the Gouy-Chapman model, yielded a value (68 $Å^2$/charge) which agreed with the value obtained by analysis of X-ray diffration data for 1:1 potassium hydrogen dioleate at 20 C. Thus, the Gouy-Chapman model appears to be applicable to purely lamellar liquid-crystalline systems containing fatty acids and soaps, such as dilute aqueous potassium decanoate/decanoic acid.

P13

EFFECT OF STABILIZERS ON ROOM ODOR OF HYDROGENATED AND UNHYROGENATED SOYBEAN OIL. K. Warner and T.L. Mounts, Northern Regional Research Center, 1815 N. University Street, Peoria, IL 61604.

Soybean oils, before and after hydrogenation with copper and nickel catalysts, were heated to 190 C for different periods and evaluated by a trained panel for room odor characteristics. The effects of additives were investigated with citric acid, methyl silicone, tertiary butylhydroquinone (TBHQ) and a polymeric antioxidant in various combinations. The methyl silicone + citric acid combination had the greatest effect in lowering odor intensity of the heated oils, followed by the citric acid + methyl silicone + TBHQ combination. As heating times increased, the odor intensity of methyl silicone-treated oils remained fairly constant, while the intensity of all other oils decreased from original strong levels. Methyl silicone was the most effective additive in decreasing objectionable odors in soybean oil and in hydrogenated soybean oil.

SESSION QQ Fatty Acids in Metabolism Thursday a.m.

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TOTAL FATTY ACIDS OF ADULT HUMAN BRAIN. Leon L. Gershbein, K. Baburao, Aldo F. Pedroso and Gloria G. Arellano, 5659 West Addison Street, Chicago, IL 60634.

Lipids extracted with chloroform/methanol from whole brain removed at autopsy from persons with minimal brain pathology were saponified and the fatty acids processed and analyzed by GC. Attention was directed to the unsubstituted acids and the composition deduced did not contain the hydroxy-acids. The more prominent acids and their % ± SD comprised 16:0 (19.3 ± 1.18), 18:0 (22.2 ± 3.41) and 18:1 (27.0 ± 4.24) for 27 specimens. The fatty acids from acid hydrolysis of the brain lipids simulated the latter in composition. On the basis of sex (17 males), none of the differences for 25 component acids showed any significance by analysis of variance. Thus far, no remarkable differences in the same acids can be inferred according to age, two groups being compared, 27-60 yr (10 cases) and 61-87 yr (17 cases). The current approach is being applied to geriatric correlations in regard to age and brain pathology, since the procedures allow for the workup of many specimens, the data being a prelude toward the study of the lipid classes and employing brain sampled from various areas.

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FATTY ACID COMPOSITION OF CHOLESTERYL ESTERS IN MILK OF MOTHERS OF PREMATURE AND FULL TERM INFANTS. Joel Bitman, D.L. Wood, US Dept. of Agriculture, Beltsville, MD 20705; N.R. Mehta, P. Hamosh and Margit Hamosh, Georgetown University Medical School, Washington, DC 20007.

Milk was obtained on postpartum days 2-3 (colostrum) and days 7, 21, 42 and 84 from mothers of 18 very premature (VPT, 26-30 wk gestation age), 28 premature (PT, 31-36 wk) and 6 term (T, 37-40 wk) infants. Lipids were extracted in chloroform/methanol and analyzed by thin layer (TLC) and gas liquid chromatography (GLC). Fatty acid composition of cholesteryl esters (CE) was determined by GLC after isolation of CE by preparative TLC and hydrolysis. Amounts of 18:3, 20:3 and 20:4 of VPT (5.6%) and PT (6.2%) colostrum were considerably higher than T colostrum (1.8%). Fatty acid composition of CE of VPT, PT and T milk was similar at subsequent time periods. Fatty acids esterified with cholesterol in wt % were: decanoic, 0.5; lauric, 2.3; myristic, 3.0; palmitic, 14.7; palmitoleic, 4.9; stearic, 9.3; oleic, 32.8; linoleic, 27.8; linolenic, 1.5; eicosatrienoic, 1.1; arachidonic, 2.3. Unsaturated fatty acids contribute 70 wt % of fatty acids in CE, considerably higher than in milk triglycerides. The greatest difference occurred in 18:2 content, which was 27.8% in CE and only 13.0% of total fatty acids in milk. The results suggest that unsaturated fatty acids are associated preferentially with the cholesteryl ester fraction and that the fatty acid composition of cholesteryl esters differs from the composition of total milk lipid.

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ESSENTIAL FATTY ACIDS PROTECT AGAINST CARBON TETRACHLORIDE-INDUCED LIVER DAMAGE IN THE RAT. S.C. Cunnane and D.F. Horrobin, Efamol Research Institute, PO Box 818, Kentville, Nova Scotia B4N 4H8, Canada.

Injection of carbon tetrachloride (CCl_4) into rats is well known to induce accumulation of triglycerides (TG) in the liver. Linoleic acid (LA) desaturation is also impaired. The latter effect may be partly responsible for the overall liver damage, and therefore may be prevented by supplemental essential fatty acids inducing gamma-linolenic acid (GLA). Male Wistar rats (125-150 g) were fed a control diet or a diet supplemented with evening primrose oil (5%-EPO) from Efamol Ltd., London, England, which contains 72% LA and 9% GLA. After one week, CCl_4 (500 μL) was given by stomach tube and the rats killed 24 hr later. Liver, plasma and erythrocyte lipids were extracted (Folch method), the fractions separated by TLC and their fatty acid compositions determined by GLC. The liver weight/body ratio was increased by 55% ($p < 0.01$) in control rats after CCl_4 but only 39% into the EPO-treated rats (different from control at $p < 0.05$). Liver total lipids increased from 24 to 48 mg/g after CCl_4 in control rats ($p < 0.01$) but only increased from 31 to 33 mg/g in the EPO-supplemented rats (different from control at $p < 0.01$). The main fatty acid changes were in the liver TG were CCl_4 increased LA by 21% ($p < 0.01$) and decreased arachidonic acid by 59% ($p < 0.01$) in controls. In the EPO-supplemented group, CCl_4 increased LA as in controls but arachidonic acid was only decreased 38% (different from the controls at p 0.01). These results suggest that the significant changes in lipid metabolism induced by CCl_4 which cause an accumulation of TG in the liver and a greatly increased linoleic acid/arachidonic acid ratio in liver TG are partly preventable by prior supplementation with LA and GLA in the form of EPO. The mechanism of this effect is currently under investigation.

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INHIBITION OF ARACHIDONIC ACID SYNTHESIS BY ISOMERIC OCTADECENOIC ACIDS.

Larry D. Lawson, Ralph T. Holman and Eldon G. Hill*, The Hormel Institute, University of Minnesota, 801 16th Avenue, N.E., Austin, MN 55912.

Partially hydrogenated soybean oil (ICTO) was fractionally crystallized to produce concentrates of isomeric *trans* octadecenoic acids (ITO) and isomeric *cis* octadecenoic acids (ICO). All three fats were fed to young rats such that all diets contained 21% fat and 1.3% (w/w) linoleic acid. Analysis of liver lipids of ICTO fed rats revealed a decrease in arachidonic acid in phospholipid, phosphatidylcholine, phosphatidylinositol, cholesterol ester and triglycerides by 35, 45, 35, 55 and 75%, respectively, when compared to beef tallow controls. Concurrently, $18{:}2\omega6$, $20{:}3\omega6$, $20{:}5\omega3$ and $20{:}3\omega9$ were elevated. Similar effects were observed in heart, testis, brain and nerve, but to a much smaller extent. The effects of the ITO or ICO diets on inhibition of $20{:}4\omega6$ synthesis were much smaller than that of the ICTO diet.

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ENZYMATIC HYDROLYSIS IN VITRO OF THERMALLY OXIDIZED OILS.

J.C. Alexander and H. Yoshida, Dept. of Nutrition, University of Guelph, Guelph, Ontario N1G 2W1, Canada.

Three commercially refined vegetable oils (soybean, sunflower, and corn) were heated at 180 C for 50, 70 and 100 hr with aeration. Four classes of compounds (monomers, dimers, trimers and polymers) formed from the acylglycerols were separated from the oils by column chromatography on silica gel, and further verified by thin layer chromatography. Each fraction, after analyses for general properties, was subjected to a time course study of hydrolysis by pancreatic lipase over a 30-min period. The acylglycerol monomers were hydrolyzed at least as rapidly as the corresponding original oils. However, the acylglycerol dimers and trimers were less readily hydrolyzed. After 70 hr of heating, the hydrolysis rate for the dimers was only about half that of the monomers, and the rate for the trimers was in turn about one third that of the dimers. The polymers were the least hydrolyzed and showed no further reaction after 5 min. The reduction in enzymatic hydrolysis of isolated fraction from thermally oxidized oils indicates structural differences related to formation of polar compounds and polymerization products. Adverse effects on animals from feeding these materials can be attributed partly to inhibition of hydrolysis.

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PROSTAGLANDIN HYDROXYLATION BY ISOZYMES OF CYTOCHROME P-450.

D.R. Koop, D. Kupfer, A.D. Theoharides, K.P. Vatsis and M.J. Coon, The University of Michigan, Ann Arbor, MI 48109.

The isozymes of liver microsomal cytochrome P-450 (P-450_{LM}) catalyze the oxygenation of prostaglandins, fatty acids, and steroids as well as a variety of foreign compounds, including carcinogens, drugs, and insecticides. The hydroxylation of PGE_1, PGE_2, and PGA_1 was shown to occur in a reconstituted rabbit liver microsomal enzyme system containing phenobarbital-inducible isozyme 2 or 5,6-benzoflavone-inducible isozyme 4 of P-450, NADPH-cytochrome P-450 reductase, phosphatidylcholine and NADPH. Significant metabolism of prostaglandins by isozyme 2 occurred only in the presence of cytochrome b_5. Under these conditions the maximal rate of PGE_1 hydroxylation was obtained with a 1:1:2 molar ratio of reductase to cytochrome b_5 to P-450. Apocytochrome b_5 or ferriheme alone was without effect, while reconstituted cytochrome b_5 led to activities similar to those obtained with the native cytochrome. P-450 isozyme 2 catalyzed the conversion of PGE_1, PGE_2, and PGA_1 to the respective 19- and 20-hydroxy metabolites in a ratio of ca. 5:1 and displayed comparable activities toward the three prostaglandins as judged by the total products formed. Isozyme 4 of P-450 differed from isozyme 2 in that it catalyzed prostaglandin hydroxylation at a substantial rate in the absence of cytochrome b_5, was regiospecific for position 19 with all of the prostaglandins, and had an order of activity of $PGA_1 > PGE_1 > PGE_2$. The addition of cytochrome b_5 gave about a 25% increase in the rate of PGE_1 hydroxylation and an appreciably greater enhancement in the extent of all of the isozyme 4-catalyzed reactions, the stimulation being greatest with PGE_2 (3-fold) and least with PGA_1 (1.6-fold). Cytochrome b_5 was required for maximal metabolism of all the prostaglandins but had no effect on the regiospecificity of P-450 isozyme 4 or on the order of activity of the individual substrates. More recently, we have found that isozymes 3a, 3b, and 3c of P-450_{LM} are only weakly active, but that isozyme 6, isolated from animals chronically exposed to ethanol, is the most active of any of the cytochromes tested. 19-Hydroxy-PGE_1 is formed, along with a major, less polar metabolite which remains to be identified. These reactions in large part represent catabolic pathways which help control the level of circulating prostaglandins, but in some instances, as suggested by others, may lead to products with enhanced or different biological activities.

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METABOLISM OF *trans* FATTY ACIDS IN ISOLATED PERFUSED RAT LIVER.

Takashi Ide and Michihiro Sugano*, Laboratory of Nutrition Chemistry, Kyushu University School of Agriculture 46-09, Higashi-ku, Fukuoka 812, Japan.

The metabolic fate of geometrical isomers of unsaturated fatty acids is still not well understood. In this study, hepatic metabolism of *t*-fatty acids was compared with *c*-fatty acids in perfused rat liver. Isolated liver was perfused with continuous infusion of either oleic, elaidic, linoleic or linoelaidic acid as an albumin complex. Both *t*-acids compared to *c*-acids increased ketone body production to a similar extent. Although *c*-acids stimulated triglyceride secretion, *t*-acids virtually did not. Hence the secretion of not only triglyceride, but cholesterol and phospholipid VLDL was markedly low. In liver lipids, relatively more *t*-acids were esterified to triglyceride and cholesteryl ester than to phospholipid and the magnitude of incorporation was somewhat greater in elaidate than in linoelaidate. In the perfusate, incorporation into phospholipid and cholesteryl ester was comparable to that into corresponding liver lipids, whereas in triglyceride it was ca. 2-fold high for both *t*-acids. Thus, though the secretion rate was low, fatty acids with *trans*-configuration seem to be secreted preferentially as triglyceride in relation to other lipids similar to the case of *cis*-counterparts. The decrease in VLDL secretion on perfusing *t*-acids presumably represents the relative restriction of the fatty acid substrate for formation of VLDL due to the faster oxidation rate.

SESSION RR Extrusion Technology
Thursday a.m.

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FOOD PROCESSING APPLICATIONS OF TWIN-SCREW EXTRUSION.

A. Feldbrugge, General Foods Technical Center, 250 North Street, White Plains, NY 10625.

Twin-screw extrusion is an emerging technology in food product processing. Twin-screw extruders have been used to produce texturized plant proteins; expanded cereal, pet food, and snack products; biscuits and flatbreads; and to process doughy and gumlike materials. This paper presents an overview of current applications.

The design and operating principles of the several available twin-screw extruder configurations, including corotating and counter-rotating, and intermeshing and nonintermeshing, screws are discussed. Differences between twin-screw extruders and the more conventional single-screw cooker-extruders are described, together with comparative advantages and disadvantages.

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DYNAMIC MECHANICAL PROPERTIES OF TEXTURIZED DEFATTED SOY FLOUR. Javier Arce, Vincent Sweat and Kenneth Diehl, 1912 Carl Road, Apt. #254, Irving, TX 75061.

Using a rectangular die and a capillary rheometer, texturized defatted soy flour extrudate was obtained at different shear rates and time-temperature histories. These samples were then analyzed for the dynamic modulus, phase angle, and anisotropy using sinusoidal excitation of 5 Hz. The mechanical properties were also correlated to a previous study of protein solubilities in water, water and buffer solution, the last solution plus mercaptoethanol and the third solution plus sodium dodecyl stearate. The dynamic modulus was a function of time, of heating and the direction of the test. The phase angle was a function of time, shear rate, and also the direction of the test. In general, as time elapsed, the modulus of elasticity increased and the phase angle decreased. Shear rate slightly decreased the phase angle. The direction of the test (anisotropy) was significant for the dynamic modulus and phase angle, but it did not change as expected. The mechanical properties correlated very well to the buffer soluble protein and mostly to the insoluble protein.

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CORN PROTEIN CONCENTRATE: EXTRUSION STUDY. Y.C. Jao, A.H. Chen and W.E. Goldstein, Miles Laboratories, Inc., PO Box 932, Elkhart, IN 46515.

Functional properties of corn protein concentrate derived from Miles dextrose plant byproduct were evaluated through laboratory Brabender extruder and a Wenger X-25 extruder. Three physical parameters of the extrudates, namely the bulk density of dry extrudates, water content and hardness after rehydration, were used as criteria for textural comparison. Effect of pH on the texture of extrudates from both soy flour and its corn protein concentrate mixture was examined. Results from both laboratory and pilot-plant study indicated that corn protein concentrates prepared from both aqueous and ethylacetate extraction are more suitable for extrusion applications than the one prepared from hexane extraction.

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PRINCIPLES OF PREDICTION OF TWIN-SCREW EXTRUDER OPERATION. Larry D. Schopf, Baker Perkins, Inc., PO Box 1718, 1200 W. Ash Street, Goldsboro, NC 27530.

The most common type of twin-screw extruder used in the food industry is the corotating fully intermeshing type. These extruders are able to provide good mixing, high energy input, a self-wiping action, and a relatively positive conveying action. In addition, the screw configurations on these extruders can easily be changed to provide extensive variations in residence time, energy input mixing, and conveying efficiency. This paper will cover the principles behind the functionality of these various types of screw elements as well as the effect of screw rpm and die design on a variety of different food products. These products will include texturized vegetable protein and other grain and grain blends having high oil and protein content. Some mathematical and theoretical models that can be applied to the various types of screw elements and to die design will also be developed. It will be shown how this information can be used to help predict results and determine the best extruder set-up to accomplish a specific task.

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TEXTURAL AND CHEMICAL PROPERTIES OF EXTRUDED COWPEA MEAL. R.D. Phillips and M.B. Kennedy, Department of Food Science, University of Georgia Agricultural Experiment Station, Experiment, GA 30212.

Starchy legumes are little used for the production of manufactured foods in spite of their relatively high protein quality and a proximate composition which resembles that of cereal grain/oilseed meal combinations. A systematic study of the extrusion cooking of cowpea meal was undertaken using a lab scale extruder equipped with a 509 X 19 mm barrel, a 5.1 compression ratio screw and a 22 X 5 mm rod die. Initial feed moisture was 20, 30 and 40%, and barrel temperatures were 150, 175 and 200 C. A constant screw speed of 180 rpm was employed. The resulting extrudates exhibited a wide range of textural properties as measured by tensile and shear tests. Protein solubility and starch gelatinization were also found to be a function of extrusion parameters. Mathematical models describing the interrelationships between these variables have been developed.

SESSION SS Packaging
Thursday a.m.

303

PACKAGING CONSIDERATIONS AND TESTS FOR EDIBLE OIL PRODUCTS. Ronald G. Moore, Anderson Clayton Foods, 3333 North Central Expressway, Richardson, TX 75080.

Manufacturers of edible fats and oils use many different types of materials and containers to package their products. Changes in these packages are made from time to time for various reasons such as to reduce costs, to take advantage of new materials, or to meet competitive pressures. When changes are contemplated, many factors must be considered and several tests must be performed before final changes can be made. This paper will review these factors and tests. The various test methods will be detailed and alternate methods will be given. Several case histories or package changes will be given to illustrate the necessary requirements.

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THE COMPOSITE CAN AND ITS APPLICATION TO FATS AND OILS PACKAGING. Calvin G. Hill, Sonoco Products Co., PO Box 160, Hartsville, SC 29550.

Constructed with two steel end closures and spirally wound layers of plastics, aluminum foil and paperboard, the composite can plays a major role in fats and oils packaging. Two current applications are for institutional cooking oil and retail solid shortening. The composite can's acceptability is due primarily to two attributes, product protection and cost effectiveness. With respect to the former, data will be presented which exhibit the can's ability to provide product protection during storage and distribution. Considered in this data will be the can's strength properties which allow multiple pallet warehouse stacking as well as resistance to abuse during shipment. Also considered will be the can's barrier materials which retard oxygen and moisture permeation and thereby help maintain expected shelf-life. The can's cost effectiveness, as data will show, results primarily from the combining of thin layers of barrier materials with relatively low cost, high strength paperboard. In addition, the can's comparatively large number of components enhances cost effectiveness by providing many areas where there exist long-term cost reduction potential.

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PLASTIC CONTAINERS FOR EDIBLE OIL PRODUCTS. S.W. Go, W.J. Kollen and S.A. Jabarin*, Owens-Illinois, Inc., One SeaGate 2E-NTC, Toledo, OH 43666.

It is commonly known that edible oils are sensitive to exposure to oxygen. Therefore, efforts to package them in plastic containers successfully must consider the permeable nature of plastics and the level of sensitivity of the product to oxygen gain. The paper presented here discusses the considerations necessary for packaging edible oil products in plastic containers. Initially, a brief review of literature is presented with respect to the protection required. This is followed by discussions of mechanical, thermal and barrier properties required of plastics used for containers in this application. Additionally, the effects of processing such an orientation on the properties of various plastics are presented. Specifically, orientation can improve mechanical strength, barrier to oxygen and thermal resistance. Barrier properties are discussed with respect to type of plastic, multilayer structures and coatings. Container performance as it relates to shelf-life is dependent on shape, size and wall thickness. Finally, plastic containers with potential for packaging edible oil products are compared.

SESSION TT Processing—General Thursday a.m.

306

THE PACING TECHNOLOGIES IN THE FATS AND OILS INDUSTRY. Alegria B. Caragay, Arthur D. Little, Inc., 15 Acorn Park, Cambridge, MA 02140.

The US fats and oil industry is a mature industry. To revitalize the industry, new opportunities for growth must be creatively explored. The shifting trends in technology, which will play a vital role in shaping the fats and oils industry of the future, will be discussed. Technologies can be classified into one of three categories, i.e., base, key and pacing. The base technology is well known and is often the technology upon which the industry was founded. The key technologies are those which provide competitive advantage and product differentiation and are generally still under active development within the industry. The pacing technologies are those in an early stage of development and have major potential for the future. Some, but not all, of the pacing technologies of today will be the key technologies of tomorrow. The pacing technologies to be discussed will include processing, biotechnology, and those directed at developing new products to create new uses and to satisfy unmet consumer needs.

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IMPROVED QUALITY TRIGLYCERIDE OILS VIA SODIUM BOROHYDRIDE PURIFICATION. Samuel F. Heleba, Richard A. Mikulski, John Hickman and Michael M. Cook*, THIOKOL/Ventron Division, 150 Andover Street, Danvers, MA 01923.

High quality triglyceride oils were produced by incorporation of sodium borohydride (SBH) in the caustic refining step of the normal oil processing sequence. Addition of low levels of sodium borohydride (250-1000 mg SBH/kg triglyceride) at this stage results in oils having lower peroxide contamination, improved flavor, odor, color, and stability. Sodium borohydride was conveniently introduced in the aqueous caustic refining solution as SWS®, a commercially available solution of 12% $NaBH_4$ and 40% NaOH in water. The contact and temperatures afforded in the normal caustic refining operation were sufficient for borohydride reduction of the peroxide and other contaminants in the oil. Analysis of the purified oil confirmed that no boron species were present even at the highest SBH purification levels. Optimization of both the SBH and the bleaching clay levels, used in the subsequent processing step, resulted in both higher quality oils and potential gains in reducing other processing times and associated costs.

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AN AQUEOUS ETHANOL EXTRACTION PROCESS FOR COTTONSEED OIL. R.J. Hron Sr. and S.P. Koltun, Southern Regional Research Center, PO Box 19687, 1100 Robert E. Lee Blvd., New Orleans, LA 70179.

A bench-top process for the extraction of cottonseed flakes with aqueous ethanol has been developed. The process consists of meat conditioning, flaking, drying and extracting with boiling aqueous ethanol (95% by volume) at atmospheric pressure. The resulting miscella is chilled producing an emulsion containing precipitated solids. The heterogeneous solution is filtered, coalesced and separated with a phase separator. The oil phase, which contains ca. 10% volatiles, quickly separates out and is stripped to produce a light crude oil. The miscella phase, containing ca. 3% oil and 1% hexane insolubles, is reheated and recycled through the extractor. The marc is pressed and desolventized to produce a meal having a residual oil content less than 1%.

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SYSTEMS AND POSSIBILITIES TO ACHIEVE 80% HEAT RECOVERY IN SEMICONTINUOUS DEODORIZERS. K. Weber, Extraktionstechnik GmbH, Postfach 7603 69, D-2000 Hamburg 76, Germany.

Semicontinuous deodorizers offering advantages to the refinery producing blends of oil are less economic than the continuous units in terms of energy consumption. Usually, a heat recovery of only ca. 50% is achieved, compared to more than 80% in continuous units. Two different systems of heat recovery are introduced which can be used to improve the heat recovery rate above 80% in semicontinuous units. Particular emphasis is given to the subject of oil/oil contamination. The possibilities of incorporating such systems in existing units are discussed. Operational costs are compared.

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PHYSICAL (STEAM) REFINING—ADVANTAGES AND LIMITS FOR SOFT OILS. Z. Leibovitz and C. Ruckenstein*, H.L.S. Ltd., PO Box 193, Petah-Tikva 49101, Israel.

This paper will cover: a description of physical refining methods actually used in the edible oil industry; introduction of these methods for soft oils; advantages and limits; stability of physically refined oil; yields and consumptions; practical examples of the results for soybean, sunflower, maize and peanut oil; conditions for bleaching, deacification and deodorization of degummed oil with low phosphorus content; consumptions and flowsheets; byproducts and their uses; and ecological problems.

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PHYSICAL VS CAUSTIC REFINING OF SOYBEAN OIL: A COMMERCIAL SCALE COMPARISON. Marco Antonio Rivas and Sergio M. Sarmiento, De Smet Mexico, S.A. de C.V., Florencia 37-4 Piso, México D.F. 06600, Mexico.

El Palmito has a caustic refining plant and a physical refining plant. The company's normal policy calls for physical refining for every lot of oil that can be thus treated; other oils, such as cottonseed or badly damaged soybean oil, are to be chemically neutralized. For the purpose of this report, a portion of each lot of physically refinable soybean oil was caustically refined, the balance being physically refined. Comparisons were made between both processes, covering the following points: (a) economics—yields and consumptions (reagents, energy, water); (b) product quality—FFA, peroxide value, AOM, color, and organoleptic evaluation.

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DIRECT SOLVENT EXTRACTION OF SUNFLOWER AND WET-MILLED CORN GERM. Mario Bernardini and Renato Sassoli, Costruzioni Meccaniche Bernardini C.M.B., S.p.A., Via dei Castelli Romani 2, 00040 Pomezia (Rome), Italy.

Direct solvent extraction of high-oil content seeds is made possible by the Direx system. This technique eliminates the prepressing step, with consequent economic advantages and higher quality of the end-products. Among the various Direx plants which work successfully for different types of oilseeds, the most interesting results are those achieved by an Italian company processing sunflower and a European branch of a US group processing wet-milled corn germ. The technique of the Direx system is illustrated and the operating results of the two plants are examined on the basis of one year of steady production. Finally, an economic comparison is presented between the Direx and the conventional system of prepressing and solvent extraction.

SESSION UU Animal Fats Thursday a.m.

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RENDERING SYSTEMS FOR PROCESSING ANIMAL BYPRODUCT MATERIALS. William H. Prokop, National Renderers Association. These systems are divided into two classes: (a) edible rendering of animal fatty tissue into edible fats and proteins for human consumption, and (b) inedible rendering of animal byproduct materials into animal fats and proteins for animal feed and other nonedible applications. The inedible rendering process consists of two basic steps: "cooking" or moisture removal by evaporation, and separation of the melted fats from the protein solids. The basic rendering process involves the use of batch cookers. In recent years, continuous rendering systems which utilize continuous cooking have replaced many batch systems. These continuous systems are described. A continuous low-temperature system is described for edible rendering. This system features two stages of centrifuges: (a) a horizontal, solid-bowl centrifuge for separation of protein solids from the liquid; and (b) a disc centrifuge for separation of the edible fat from the water phase.

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MEAT FAT UNLOADING AND STORAGE. Joe Klonowski, Bunge Edible Oil Corp., PO Box 765, Kankakee, IL 60901.

The intent of this discussion is to outline the principles of meat fat unloading the storage. Lard (hog fat) and tallow (beef fat) handling will be discussed. The principles will be presented vis-à-vis soybean oil procedures. The primary discussion points will be temperature, agitation, USDA control, lot-to-lot variations, and supplier-to-supplier variations.

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REFINING BLEACHING AND HYDROGENATING MEAT FATS. E.G. Latondress, Davy McKee Corporation, 10 S. Riverside Dr., Chicago, IL 60606.

Meat fats are most often steam refined. This has been the accepted practice for at least 35 years. Meat fats are caustic refined for a few specialized products. The caustic refining conditions differ from those used for vegetable oils primarily in the amount of mixing used after the addition of caustic. Bleaching of meat fats is easily accomplished. Most meat fats are light in color and require clarification more than bleaching. The green color of tallows containing large amounts of chlorophyll is easily removed with activated earth. Meat fats are hydrogenated to develop the SFI curves needed for various products and also hydrogenated to saturation for use as plasticizing agents for lard and shortenings. The hydrogenation of lard and tallow is not as complicated as that of most vegetable oils because the original fat is more saturated and the reaction has fewer possible routes to follow.

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MEAT FAT FORMULATION. Frank R. Kincs, Bunge Edible Oil Corporation, PO Box 192, Kankakee, IL 60901.

Lard and tallow are used extensively in shortenings either as the sole source of triglycerides or in conjunction with other vegetable oils. Fatty acid profiles are ideal for good plasticity in bakery products. Specific functionality is dictated by the crystalline habits of the two fats. Both products are used in deep fat frying either for specific flavor attributes or for stability reasons. Economic considerations are an ongoing factor. Formulation with meat fats are complicated by compositional variations at the crude oil stage. To adjust for these changes, the use of partially hydrogenated meat fats and/or vegetable oils is commonly employed. This paper will discuss technical considerations in formulating products for several common applications.

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FINISHED PRODUCT HANDLING AND STORAGE. John B. Woerfel, 141 McGuire Cove, Clarksdale, MS 38614.

Oil and fat products require care in handling, shipping and storage to ensure that they reach the housewife, restaurant or food processor in satisfactory condition to perform functionally in food preparation. Preferred practices depend upon a number of factors including product formulation, packaging, end use and conditions of use. In the case of bulk shipments, food processors may actually be performing the final manufacturing steps required to make a functional product. Conditions applicable to variety of products, both packaged and bulk, are discussed.

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USE OF ANIMAL FATS IN FEEDS. H.L. Fuller, University of Georgia, Athens, GA 30602.

Animal fats, and feed grade fats in general, serve three distinctly different purposes in livestock and poultry feeds. First, they contribute greatly to the physical attributes of the feed, e.g., lubrication, palatability, reduction of dustiness and agglomeration. Secondly, they provide essential fatty acids to the extent that these nutrients are not satisfied by the residual fat in the basal dietary ingredients. Thirdly, by far the greatest amount of supplementary fat is used as a concentrated source of energy. Fats contain 2.25 times as much energy as carbohydrates so their use provides greater flexibility in feed formulation. By providing more energy with less weight, it becomes possible to increase the density of energy and nutrients in the feed. It has also been shown that when feed is supplemented with fat, feed efficiency is usually improved more than would be expected on the basis of equivalent metabolizable energy value of the ingredients replaced in the formula. This has been attributed to a synergistic effect between the added fat and the nonfat portion of the diet with respect to the absorption of both. In addition, the metabolizable energy value of fat underestimates its *net* energy value because of its lower heat increment. Other attributes have been demonstrated for supplemental fats under special conditions. For instance, when fat is added to the preparturition diet of sows at relatively high levels, the survival rate of piglets is improved. In other work at the University of Georgia, the use of supplemental fat in broiler rations was shown to alleviate the effects of heat stress in young chickens. An improvement in egg size by the addition of fat, isocalorically, to the diet of young pullets has also been demonstrated.

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MEAT FAT USAGE IN FATTY CHEMICALS. R.A. Reck, Armak Company, 300 S. Wacker Drive, Chicago, IL 60606.

By far the largest production of meat fats and oils comes from tallow, estimated at 10 billion lb per year. Other meat triglycerides, such as poultry fat, hog and sheep, also end up as meat oils. The largest chemical user of these raw materials is the soap industry, but this will not be discussed in this paper. The first chemical production is the splitting of the triglyceride into fatty acids and glycerine. The glycerine is recovered and purified and then used in numerous products. The estimated production of glycerine from meat triglycerides is 200M lb. The fatty acids produced from meat fats and oils generally fall into the C14-18 chain length distribution, with the C18 chain length being saturated or unsaturated. The acids can be used as such or may be separated by crystallization into the saturated or unsaturated components. Also, the acids can be saturated into higher melting products by hydrogenation. Another large use for the meat-produced triglycerides is their conversion into glycerine and esters, usually methyl, by transesterification with methanol. Again, the glycerine is purified and sold and the methyl esters of the fatty acids are usually converted to alcohols with corresponding chain lengths by hydrogenation. Esters of the fatty acids are also a large market. Generally speaking, the esters are derived from monofunctional alcohols or polyfunctional alcohols. Hydrogenated tallow fatty acids are used in the production of large quantities of metallic salts. The main products are aluminum, zinc and calcium stearates. The nitrogen derivatives of fatty acids can be prepared directly from the triglycerides or from the monoesters or from the fatty acids. From the monoesters or triglycerides, the initial reaction to introduce the nitrogen is with an amine, such as diethanolamine or a polyamine, such as diethylenetriamine. The other method of introduction of the nitrogen atom is by reacting the fatty acid with ammonia at high temperature to produce nitriles. The nitriles can then be converted to literally hundreds of amine derivatives.

SESSION VV Heated Fats Thursday a.m.

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HIGH PERFORMANCE GEL PERMEATION CHROMATOGRAPHY (HPGPC) OF HEATED FAT COMPONENTS. Constantina Christopoulou and E.G. Perkins, Burnsides Research Laboratory, University of Illinois at Urbana-Champaign, 1208 W. Pennsylvania Avenue, Urbana, IL 61801.

The application of HPGPC with small particle semigrid, highly cross-linked styrene/divinylbenzene copolymers with small pore sizes to the separation of heated fat components was studied. The effect of swelling solvents, tetrahydrofuran, chloroform and others was evaluated to determine the effect of apparent pore size on the separation efficiency obtained. For each series of packings, Biobeads SX4, 8, 12, a plot of K_{av} vs molecular weight distribution (log) was made and the relative location of monomers, dimers and higher molecular weight oxidation products determined. Three-dimensional plots of K_{av} vs swelling solvent (pore size) vs log MW allow the selection of resin and solvent combination for optimization of separation. Fractions collected from the columns were then subjected to analysis by high temperature GLC, NMR and mass spectrometry to aid in their characterization.

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ANALYSIS AND CHARACTERIZATION OF HEATED OLIVE OIL COMPONENTS BY HIGH PERFORMANCE REVERSE PHASE CHROMATOGRAPHY (HPRC), AND GC-MS. A.H. El-Hamdy, Al-Fateh University, E.N. Frankel and E.G. Perkins, Burnsides Research Laboratory, University of Illinois at Urbana-Champaign, 1208 W. Pennsylvania Avenue, Urbana, IL 61801.

The application of HPRC to the analysis of heated olive oil triglycerides and methyl esters showed distinct bands that indicate "fingerprint" areas for analytical as well as quality control purposes. A clear difference between heated and unheated olive oil was found using an octadecyl bonded stationary phase (Supelcosil LC-18) packed in 4.6 X 250 mm stainless column and acetonitrile/methanol mixture (1:1, v/v) for methyl esters and acetonitrile/acetone (36.4: 63:6, v/v) for triglycerides, Cyclic monomers were resolved completely from their "normal" counterparts. The presence of a ring in a molecule changes the elution time, but the extent of this change is determined by the degree of substitution and position of the double bond(s) in the molecule. This is indicated by the elution of saturated cyclic C18 monomer ahead of stearate, monounsaturated, cyclic monomer, ahead of oleate and diunsaturated cyclic monomer ahead of linoleate. GC-MS of HPRC fractions indicated the presence of saturated and unsaturated furans, hydroxystearate, saturated, monounsaturated, and diunsaturated cyclic monomers as well as aromatic esters. Although no effort was taken to determine the effect of hydroxyl or keto groups on the HPRC elution behavior, the results showed that these groups have a greater effect in decreasing the relative residence time that does a double bond.

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CYCLIC FATTY ESTERS: SELECTIVE HYDROGENATION AND REDUCTION OF 9-(6-PROPYL-3-CYCLOHEXENYL)-8-NONENOIC ACID OR ITS METHYL ESTER. R.A. Awl and E.N. Frankel, Northern Regional Research Center, Agricultural Research Service, US Department of Agriculture, Peoria, IL 61604.

Diunsaturated, C-18 cyclic fatty acid methyl esters (CFAME) were previously synthesized (Lipids 17:414 [1982]) as model derivatives of cyclic fatty acids (CFA) formed in heat-abused vegetable oils for characterization and biological evaluation. The propyl substituted, diunsaturated CFAME (1) was selectively hydrogenated and reduced to prepare two monounsaturated, positional isomers with the double bond located either in the ester substituent (monoene II) or in the ring (monoene III). Capillary GLC showed that each positional isomer was a mixture of *cis* and *trans* ring isomers. The ring double bond in diene I was readily hydrogenated with various metal catalysts with no formation of any cyclohexene isomer III. Platinum oxide poisoned with Ph_3P was the most selective catalyst examined for converting diene I to monoene II. Diimide reduction was the only method found to reduce the double bond in the ester substituent of I. This diimide reduction was facilitated when diene I was *trans*-isomerized with *p*-toluenesulfinic acid. Because this chemical reduction was not selective, it was necessary to separate the cyclohexene isomer III from isomer II by argentation HPLC. The two isomeric monoenes were characterized by GC-MS, capillary GLC, microozonolysis, IR, and NMR. The new information obtained in this study will form the basis for improved methodology to analyze products of thermal oxidation in oils used for cooking.

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OCCURRENCE OF CYCLIC FATTY ACID MONOMERS IN FRYING OILS USED FOR FAST FOODS. E.N. Frankel, Northern Regional Research Center, ARS, USDA, Peoria, IL 61604; L.M. Smith*, C.L. Hamblin, R.K. Creveling and A.J. Clifford, Departments of Food Science and Technology and Nutrition, University of California, Davis, CA 95616.

Cyclic monomers were analyzed by gas chromatography in commercial samples of frying oils obtained in this country and in the Middle East. Samples were collected from fast foods outlets in California and Illinois after varying periods of usage. Samples from Egypt and Israel were obtained from street vendors frying vegetable patties (known as "fallafel") in open air stands. The United States samples ranged from 0.1 to 0.6% in cyclic monomers, and from 1 to 8% polar/noneluted thermal oxidation materials. The Middle East samples showed significantly more heat abuse with values for cyclic monomers from 0.2 to 0.7% and polar materials ranging from 2 to 22%. Previous work of Iwaoka and Perkins with rats (Lipids 11:349 [1976]) showed that incorporation of 0.15% cyclic fatty acid methyl esters in low protein diets containing 15% corn oil caused accumulation of liver lipid.

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BIOLOGICAL EFFECTS OF THERMALLY OXIDIZED FATS. J.C. Alexander, Department of Nutrition, University of Guelph, Guelph, Ontario N1G 2W1, Canada.

When heat is applied to fats during the preparation of foods in frying operations, the formation of potentially toxic derivatives by thermal oxidation depends on a number of factors including type of fat used, temperature, exposure to oxygen, and duration of heating. Animals given these used fats in their diet have shown reduced feed efficiency, poor growth, fatty livers, altered lipid metabolism, and pathological lesions in various organs. Many volatile and nonvolatile compounds are formed during heating, some of which may be toxic, depending on level of ingestion. Heated fats can be fractionated to concentrate the unnatural components to provide a means of assessing biological effects with tissue cultures or animal models, and experimental results will be discussed. In general, observations have shown that the conditions for practical frying procedures usually produce low levels of toxicants, and possible hazard to the consumer would be related to a substantial intake. An adequate balance of required nutrients in our diet on a regular basis will help to reduce adverse effects from thermally oxidized frying fats.

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A STUDY OF THE NONVOLATILE RADIOLYTIC PRODUCTS FROM UNSATURATED FATS. Shan-Shan Sheu and W.W. Nawar, Department of Food Science and Nutrition, University of Massachusetts, Amherst, MA 01003.

Irradiation is becoming increasingly attractive as an alternative method of food preservation. In a previous presentation, we reported detailed results of a study of the volatile decomposition products from fats by irradiation, as compared to those produced by heating. A striking observation was the much simpler pattern of radiolytic products in the case of unsaturated systems, i.e., oleate, linoleate and linolenate. It was suspected that these systems may give rise to cyclic and polymeric products in preference to smaller molecules. The prupose of the present study was to investigate the nonvolatile fraction of the decomposition products from unsaturated substrates. Oleic acid, ethyl oleate, triolein, linolenic acid and ethyl linolenate were either heated in air at 180 C for 1 hr or irradiated with 25 Mrad under vacuum at ambient temperature. Separation and identification of the nonvolatile decomposition products was accomplished via TLC, GPC, GC, urea adduct fractionation, various microderivatization and mass spectrometry. The patterns of compounds produced from the two treatments was distinctly different both qualitatively and quantitatively. In general, heating produced more polar compounds such as those containing hydroxy, aldehydic and ketonic functional groups. Both monomeric and dimeric products were isolated from the heated samples with the monomeric products predominating. In the case of irradiated samples, on the ohter hand, less oxygenated compounds could be detected and dimers accounted for the major portion of the irradiated products. Specific details of identification for each of the substrates with the two different treatments will be presented.

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PURIFICATION OF USED DEEP-FRYING OILS. W.P. Pan, S.Y. Chiu and T.C. Chen, Food Industry R & D Institute (FIRDI), PO Box 246, Hsinchu 300, Taiwan.

Deep-fat frying is one of the most popular methods in Chinese food preparation. The rancid deep-frying oil not only causes adverse effects to the flavor, color and texture of fried products, but also may be harmful to human health when consumed in excessive amount. The current work was undertaken to seek a simple and handy method by adding appropriate chemicals (mostly on GRAS list) as to purify the used deep-frying oils during Chinese food preparation. Based on the selected rancidity parameters such as (a) peroxide value (PV), (b) TBA value, (c) oxirane content, (d) free fatty acid (FFA) content, and (e) AOM (active oxygen method), it was found that adding chemicals when the oil was cooled to 185-190 F, after stirring for 15 min and properly filtered, NaOH, activated clay and charcoal could effectively reduce PV; MgO, NaOH could remove FFA; silicic acid, silica gel 60, activated carbon, NaOH, $Mg_2O_8 \cdot Si_3$ and charcoal could lower TBA values; stannous chloride could drastically eradicate epoxide while increase PV; activated clay and charcoal still proved to be the best bleaching agents for used frying oils. The synergism of these chemical purifiers and the stability (e.g., AOM) of the purified frying oils will also be presented.

Late Abstract

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NEUTRALIZATION OF ANTIBACTERIAL PROPERTIES OF LAURICIDIN AND BHA BY TWEENS. D.V. Vadhera, V. Wahi and J. Keswani, Department of Microbiology, Panjab University, Chandigarh, India.

Lauricidin, a food grade emulsifier, has been shown to possess antibacterial properties by a number of workers. The antibacterial properties are enhanced by the addition of other agents such as EDTA and BHA. In our attempts to increase its antibacterial properties with other surfactants, we noticed that Tween 20, 60 and 80 completely neutralized the activity of lauricidin. Similarly, Brij-35 was also able to neutralize its activity, but Triton X-100, in general, did not neutralize the inhibitory property of lauricidin. In contrast, all the three agents (Tweens, Brij-35 and Triton X-100) neutralized the antimicrobial properties of BHA. The extent of neutralization was related to concentration ratios between the antimicrobial agents and the test surfactant as well as the test organism. A concentration of 1 mg/mL of lauricidin was completely neutralized by 0.5% of Tween 80 when the test organism was *S. aureus*, while a concentration of 1% was required for *P. aeruginosa*. The neutralization concentrations of Brij-35 were 0.1% for *S. aureus* and 0.5% for *P. aeruginosa*. The antimicrobial properties of BHA (1 mg/mL) against *S. aureus* and *P. aeruginosa* (antibiotic-sensitive strain) were neutralized by 0.1% of Tween-80, Brij-35 and Triton X-100. For *P. aeruginosa* (antibiotic-resistant strain), the neutralization concentrations were 0.25%, 0.1% and 1% for Tween-80, Brij-35 and Triton X-100, respectively. The exact mechanism of action of the neutralizing agents is not known and is being investigated.