Welcome

AOCS Members and Guests,

Welcome to the Valley of the Sun. The annual meeting of AOCS, slated for May 8–12, 1988, will be held for the first time in Phoenix, Arizona.

Technical program chairman Neil Widlak has arranged an outstanding program of over 300 papers. If you are interested in omega-3 fatty acids, surfactants and detergents, pharmacological effects of lipids, processing of oilseeds, proteins or biotechnology, you should attend this meeting.

A high point of the meeting will be the Flavor Chemistry of Lipid Foods Symposium, slated for Monday and Tuesday, May 9–10, in honor of Stephen S. Chang.

The golf tournament will be held at the Tournament Players Club, the site of the Phoenix Open, on Sunday morning, May 8. Prizes will be given for low net, low gross, longest drive and nearest to the pin, for both men and women. Send in your registration form because tee times are limited. A registration booth for both golf and tennis will be set up in the Sheraton Hotel on Saturday afternoon, May 7. Buses will depart the Sheraton on Sunday morning.

The tennis tournament will be held at the Arizona Biltmore Hotel on Sunday morning, May 8. Prizes will be given. Check the registration booth in the Sheraton Hotel on Saturday afternoon.

The opening mixer will be held Sunday evening in the exhibit area of the Convention Center. We are sure you will want to join us Monday night for the optional event, a narrated tour of Phoenix, with a steak dinner at Rawhide, an Arizona 1880s town. The Fourth Annual Fat People's Fun Run and Walk will be held Tuesday morning early enough for you also to attend the technical program.

We suggest you attend the optional Wednesday evening social event, "A Taste of the Southwest." There will be displays of handicrafts and decor native to this area and a wide variety of food, drink, dancing and entertainment.

Another first for AOCS will be a financial seminar Wednesday morning. The seminar will provide information for people who are planning for retirement or for their children's college education. All attendees are invited to attend this seminar.

All spouses are invited to the Sunday afternoon tea. Monday will feature a tour of the Valley, including lunch and a tour of model homes in Troon Village. On Tuesday, trollies will shuttle participants to the legendary shopping areas of Scottsdale. Wednesday is open, with time to attend the financial seminar or visit other area attractions.

In the Valley of the Sun, dress is casual, comfortable and Western, even in the technical meetings. Days are warm; desert nights turn cool.

We look forward to seeing you in Arizona.

Sincerely,

Arnold M. Gavin
General Chairman

1988 meeting features 300 talks

More than 1,500 persons are expected to attend AOCS' 79th annual meeting, to be held in Phoenix, Arizona, May 8–12, 1988. Featured will be approximately 300 talks in three days of technical sessions. The meeting will include 42 technical sessions as well as poster presentations. All technical sessions, committee meetings, exhibits and social events will be held at the Phoenix Civic Plaza. The Hyatt Regency Phoenix and Sheraton Phoenix are co-headquarters hotels for the meeting.

Timothy Mounts (left), incoming AOCS president, and Robert Hastert (center), current AOCS president, will be among the featured speakers at the 1988 annual meeting. Neil Widlak (right) is technical program chairman for the meeting.

An opening mixer will be held Sunday, May 8, from 6:30 to 8:30 p.m. in Hall E, the Exhibit Hall. Hors d'oeuvres and drinks will be provided. Non-registrants also may attend by purchasing tickets for $25 in the registration area Sunday afternoon.

On Monday morning, technical registrants and spouses are invited to attend the 7:30 a.m. business meeting breakfast in the Phoenix Civic Plaza Ballroom. The full breakfast will be followed by various reports on the society. Tickets are required for the breakfast. Non-registrants may purchase tickets in the registration area. The cost is $15.

In addition, a keynote talk by David H. Swanson of Central Soya Co. Inc. and the presentation of the Supelco/AOCS Research Award to Konrad Bloch will be part of the breakfast session. Swanson, president and chief executive officer of Central Soya Co. Inc., gave the Protein and Co-Products Section talk at the 1987 AOCS annual meeting. Following Swanson's talk, attendees can hear the Supelco/AOCS Research Award address by Bloch. This talk is slated for 9:30 a.m. and will be held in the same room as Monday morning's Session E, Effect of Dietary Omega-3 Fatty Acids I, chaired by Joyce Beare-Rogers of the Bureau of Nutritional Sciences, Canada.

Another special offering Monday morning will be an oilseed outlook session with speakers from USDA's Foreign Agricultural Service, Merrill Lynch Capital Markets, *Oil World*, Oilseeds International Ltd. and Iowa State University. Thomas Applewhite, editor of *JAOCS*, will chair the session.

The optional social event for the evening will be a narrated tour of Phoenix, with a steak dinner at Rawhide. Tickets are required.

Special technical interest discussion groups will meet between noon and 2 p.m. Tuesday. Topics offered, and group leaders, will be chromatography, John Callahan; flavor, Jerry Roberts; processing, Robert Becker; environmental issues, Jorge Castellanos and Dave Berner; and sodium analysis in foods, Frank McGovern. The groups are open to all who are interested.

Also, on Tuesday morning, there will be two tours offered. One will be a visit to a potato chip factory in Goodyear. The second will be a trip to Jojoba Growers & Processors' Apache Junction jojoba oil extraction facility. Tickets can be purchased in the registration area until 5 p.m. Monday. The cost is $15.

In addition to regular technical sessions, offerings Tuesday will include approximately two dozen poster presentations, scheduled from noon to 5 p.m. in the exhibit hall.

The inauguration of new officers and presentation of all other awards will be held at a noon luncheon Wednesday, May 11, in the ballroom of the Phoenix Civic Plaza. The incoming AOCS president will speak and the other new officers will be installed and introduced. A full meal will be served.

Among the awardees to be recognized at this event are recipients of the AOCS Award of Merit, Honored Students Award, Ralph Potts Memorial Award and the Smalley Cooperative Check Sample Program awards.

Instead of a traditional banquet, this year's meeting will feature "A Taste of the Southwest" Wednesday evening. This social event will include displays of handicrafts and decor native to the area and a wide variety of food, drink and entertainment. Tickets are required and may be purchased in the registration area. The cost is $35 per person.

In addition, individuals who have qualified for the AOCS President's Club and Honor Roll by recruiting new members for the society since the 78th Annual Meeting in New Orleans have been invited to a reception on Tuesday evening. Admission is by invitation only. Qualified individuals who have not received an invitation are asked to inquire at the AOCS Service Center desk. President's Club and Honor Roll members are identified by a special ribbon distributed in the registration packets.

On Thursday, May 12, the Finance Coordinating Committee, the Administrative Coordinating Committee and the Governing Board meetings are the only activities scheduled.

Program highlights

Sunday, May 8	
Buses, golf tournament (Sheraton)	6:30 a.m. (tee-off 7:30 a.m.)
Buses, tennis tournament (Sheraton)	8:15 a.m. (9 a.m. start)
Spouses' tea	2:00 - 4:30 p.m.
Registration	2:00 - 6:30 p.m.
Exhibits	2:00 - 8:30 p.m.
Opening Reception	6:30 - 8:00 p.m.
Monday, May 9	
Registration	7:00 a.m. - 5:00 p.m.
Business Breakfast	7:30 a.m.
Spouses' Program	
Continental Breakfast (Civic Plaza)	8:00 a.m.
Buses depart from the Civic Plaza	9:30 a.m.
Exhibits	9:00 a.m. - 5:00 p.m.
Supelco AOCS Research Award acceptance address	9:30 a.m.
Technical program begins	10 a.m.
Protein & Co-Products Section Address	11:00 - 11:45 a.m.
Protein & Co-Products Section Luncheon	Noon - 2:00 p.m.
Technical program resumes	2:00 p.m.
Buses depart from Sheraton & Hyatt hotels for social event at Rawhide	6:00 p.m.
Tuesday, May 10	
Buses depart, Fat People's Run	6:00 a.m.
Registration	8:00 a.m. - 5:00 p.m.
Technical program begins	8:30 a.m.
Exhibits	9:00 a.m. - 5:00 p.m.
Buses, plant tours	Morning
Spouses' Program (buses depart)	9:30 a.m.
Technical interest discussions	Noon - 2:00 p.m.
Poster presentations	Noon - 5:00 p.m.
Technical program resumes	2:00 p.m.
Canadian Section Reception	5:30 - 6:30 p.m.
Desert Southwest Reception	5:30 - 6:30 p.m.
NorCal Reception	5:30 - 6:30 p.m.
North Central Reception	5:30 - 6:30 p.m.
Northeast Reception	5:30 - 6:30 p.m.
South Central Reception	5:30 - 6:30 p.m.
Southwest Reception	5:30 - 6:30 p.m.
Surfactants & Detergents Reception	5:30 - 6:30 p.m.
President's Club Reception, by invitation only	Evening
Wednesday, May 11	
Registration	8:00 a.m. - 5:00 p.m.
Technical program begins	8:00 a.m.
Financial seminar	9:00 a.m. - Noon
Exhibits	9 a.m. - 1:30 p.m.
Awards/inaugural lunch	Noon
Technical program resumes	2 p.m.
A Taste of the Southwest	7:30 - 11:30 p.m.

Short courses

Three short courses will be held during the four days before the 1988 annual meeting opens in Phoenix, Arizona. The courses will be held May 4–7, 1988, at The Pointe resorts, Phoenix.

Topics are Introduction to Fats and Oils Technology; Lecithins: Sources, Manufacture and Uses; and Application of Pulsed NMR Techniques in Food Analysis.

Opening receptions for each course will be held Wednesday, May 4, at 6:30 p.m. Technical sessions will begin Thursday morning, May 5.

The purpose of the Introduction to Fats and Oils Technology short course is to provide fundamental information on fats and oils for new professionals in the field. Topics range from chemistry and engineering principles in fats and oils technology to oilseed handling and crushing, quality assurance and control, nutrition and future technology. Chairing the short course are Anthony H. Chen of 3I Corp. and Peter J. Wan of Kraft Inc. The course will be held at The Pointe at Tapatio Cliffs.

The short course on Lecithins: Sources, Manufacture and Uses, to be held at The Pointe at Squaw Peak, will review the basic chemistry of lecithin, its availability and uses in food and nonfood applications. Bernard F. Szuhaj of Central Soya Co. Inc. will chair the course. Featured will be sessions on nomenclature, chemistry and sources; sources, separation and modification; manufacture, analysis and applications; food applications and nutrition; and nonfood applications.

The short course on Applications of Pulsed NMR Techniques in Food Analysis also will be held at The Pointe at Squaw Peak. The focus will be the latest information on the application of pulsed NMR techniques in food analysis. Attendees will have the opportunity during the afternoon sessions to practice the theory learned in technical sessions. Chairing the short course are V.K.S. Shukla of Arhus Oliefabrik and Giovanni Bigalli of Hershey Food Corp.

Spouses' events

On Sunday, all Spouses' Program participants are invited to the spouses' hospitality room in the Phoenix Civic Plaza between 2 and 4:30 p.m. for refreshments and an opportunity to meet other participants.

On Monday, a continental breakfast will be served beginning at 8 a.m. in the spouses' hospitality room at the Civic Plaza. Buses will leave the Civic Plaza at 9:30 a.m. for the tour of the Valley of the Sun.

On Tuesday, buses will leave the Civic Plaza at 9:30 a.m. for Scottsdale shopping areas.

A financial session on "Investment, Tax and Retirement Planning or Life After Tax Simplification" will be held Wednesday from 9 a.m. until noon at the Civic Plaza. Among the areas to be discussed are what financial planning includes, accumulation planning, fringe benefits, business continuity, estate planning and the financial team.

Protein section

The Protein and Co-Products Section this year will feature a speaker and luncheon on Monday, May 8. The speaker, scheduled for 11-11:45 a.m., will be Donald C. Beitz, professor in the Nutritional Physiology Group, Department of Animal Science, at Iowa State University. He will speak on "Effect of Dietary Protein on Atherosclerosis."

The section's luncheon is set for noon following the talk. Luncheon tickets must be purchased by 5 p.m. Sunday, May 8, in the registration area. The cost of the luncheon is $20 per person.

For the first time, the section also has organized symposia during the technical sessions. They are the following: Session K, Effect of Protein Modification on Functionality, chaired by John E. Kinsella of Cornell University, Monday afternoon; Session R, Structure and Molecular Modeling, chaired by Richard H. Lee of Kraft Inc., and Importance of the Sulfhydryl Group and Thermal Effects on Protein Structure and Function in Food, chaired by Shuryo Nakai of the University of British Columbia, Tuesday morning; Session Y, Molecular Properties of Proteins Important for Emulsification, Foaming and Gelation, chaired by Charles V. Morr of Clemson University, Tuesday afternoon; and Session FF, Toxic Compounds in Vegetable Proteins, chaired by Irvin E. Liener of the University of Minnesota at St. Paul, Wednesday morning.

Section parties

Eight AOCS sections will hold cocktail parties Tuesday, May 10, from 5:30 to 6:30 p.m., to provide an opportunity for current members to meet and for potential section members to become acquainted. The Canadian, Northeast, North Central, South Central, Desert Southwest, Southwest, NorCal and Surfactants & Detergents Sections will meet.

The receptions will take place at the Sheraton Phoenix Hotel. Tickets to the section cocktail receptions may be purchased in the registration area. Tickets will identify the room in which each reception will be held.

Sports events

The Fourth Annual Fat People's Fun Run and Walk will be held Tuesday morning, May 10. Buses will depart at 6 a.m. Tuesday to take participants to the five-kilometer course. The run begins at 6:30 a.m., and everyone should be finished before the day's technical program begins.

The event is supervised. Prizes will be awarded, and t-shirts will be distributed to early registrants. A light breakfast will be served.

Tickets are required. Runners/walkers who did not pre-register for this event may do so in the registration area. The fee is $15 per person.

Also, there will be golf and tennis tournaments on Sunday morning, May 8. The golf tournament will be held at the Tournament Players Club, with first tee-off at 7:30 a.m. Buses will depart at 6:30 a.m. from the Sheraton Hotel. Prizes will be given.

The tennis tournament will start at 9 a.m. Sunday at the Arizona Biltmore Hotel. Prizes also will be given. Buses will leave at 8:15 a.m. from the Sheraton.

A registration booth for both the golf and tennis events will be set up in the Sheraton Hotel on Saturday afternoon, May 7.

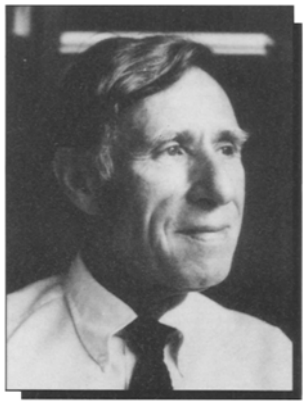
Student awards

Five students will be recognized as AOCS honored students at the annual meeting in May in Phoenix.

The awardees are Patricia Clark of the Department of Food Science, University of Arkansas; Vincent D'Souza of the Department of Food Science, University of Guelph; Craig Miller of the Department of Dermatology, University of California at Davis; Behroze Mistry of the Department of Food Science and Nutrition, Ohio State University; and Steven Pind of the Department of Biochemistry, University of Toronto.

The honored students will present technical papers during the meeting and will be recognized at the awards/inaugural luncheon slated for noon on Wednesday, May 11.

Donors who have helped make the Honored Student awards possible for the Phoenix meeting include Akzo Chemie America, Best Foods/Division of CPC International Inc., Canada Packers Inc., Cargill Inc., CasChem Inc., Central Soya Co. Inc., Colgate-Palmolive Co., The French Oil Mill Machinery Co., Gerber Products Co., Kraft Inc., Nu-Chek-Prep Inc., Procter & Gamble Co., Shell Chemical Co., Somes-Nick & Co., Union Camp Corp. and U.S. Borax Research Corp.



Konrad E. Bloch

Supelco Award

Konrad E. Bloch of Harvard University, who received the Nobel Prize in Medicine and Physiology in 1964 for research in the biosynthesis of cholesterol and metabolism of fatty acids, has been selected to receive the 1988 Supelco AOCS Research Award at the Phoenix meeting in May.

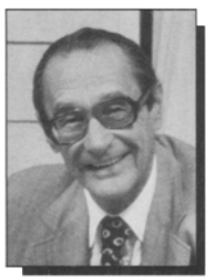
The award consists of a plaque and a $4,000 honorarium plus expenses up to $1,500. Bloch will give his acceptance speech at 9:30 a.m. Monday in the room for Session E, Effects of Dietary Omega-3 Fatty Acids. He will be awarded his plaque and check during the business meeting breakfast Monday morning.

The award is funded by Supelco Inc. of Bellefonte, Pennsylvania.

Bloch, 76, was born in Neisse, Germany. He began his research career in Switzerland, where he worked on the phospholipids of tubercle bacteria. That work brought him to the attention of Rudolph Anderson at Yale University, who invited him to come to the U.S. He entered graduate school at Columbia University and received his doctorate in biochemistry in 1938. From Columbia, he went on to work at the University of Chicago and later, at Harvard University.

His accomplishments have included the delineation of the pathways of sterol and cholesterol biosynthesis, the discovery and elucidation of the mechanisms used in unsaturated fatty acid biosynthesis, fundamental contributions to the understanding of the regulatory mechanisms involved in lipid biosynthesis in both bacteria and eukaryotes and many demonstrations of the specific roles that lipids play in processes such as photosynthesis, membrane structure and function and cellular metabolism. He has published more than

Cahn



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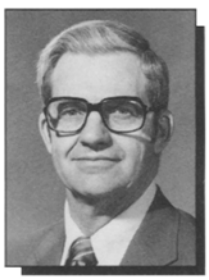

Matson

Schick

Merit awards

Four long-time AOCS members active in the surfactants and detergents field will be awarded the 1988 AOCS Award of Merit during the 1988 AOCS annual meeting.

Recipients will be Arno Cahn, president of Arno Cahn Consulting Services of Pearl River, New York; Ted Matson, chief technical officer for Vista Chemical Co.'s surfactants research R&D department; Martin Schick, a consultant based in New York; and Helmut Stupel, who last year retired after 28 years with the Shell group of companies.

The four are being honored for their contributions to the society through their service on the Surfactants and Detergents Steering Committee and action to form the Surfactants and Detergents Section of AOCS.

250 articles on his research.

For his work, Bloch has received a number of awards as well as honorary doctoral degrees from the University of Uruguay, University of Brazil, University of Nancy, Columbia University, Technische Hochschule in Munich, Brandeis University and Hokkaido University.

Potts awardee

John Flygare, a student at Northwestern University, has been selected as the 1988 recipient of the Ralph G. Potts Memorial Fellowship.

He will present a paper on "Stereospecific Alkene Formation Via Peterson Olefination," based on his research, at Session NN Wednesday afternoon, May 11, at the annual meeting.

Flygare, a doctoral candidate in the chemistry department at Northwestern, received his B.A. in chemistry from Carleton College in 1985 and his M.A. in chemistry from Northwestern in 1986. Flygare is a native of Illinois.

The award is named for the late Ralph Potts, a pioneer researcher on fatty acids and nitrogen derivatives. The award fund was established by Akzo Chemie America, the successor firm to Potts' original employer, the Armour organization.

Job placement

AOCS will provide a job exchange and placement service during its annual meeting in Phoenix. This activity, located in the AOCS Service Center area, is designed to bring together employers and job applicants in subject areas served by AOCS.

This service is offered free to applicants who are AOCS members or to nonmembers who have registered for the meeting. There will be a $10 handling fee for nonmembers wishing to participate who have not registered for the meeting. There is no fee for employers to list jobs.

Applicants and employers are encouraged to send copies of resumes and job descriptions to AOCS headquarters, PO Box 3489, Champaign, IL 61821-0489, before May 1. Those who have not done so by that date are asked to provide at least five copies of these items at the AOCS Service Desk during the meeting.

The AOCS Service Desk will open at 2 p.m. on Sunday, May 8. Employers and job applicants should check with staff at the AOCS Service Desk after they have completed meeting registration.

Meeting exhibit

The annual exposition by suppliers of equipment and services to the fats and oils industry will be held in conjunction with the annual meeting in Phoenix.

Firms that had reserved exhibit space (booth number in parentheses) as of mid-February include the following:

Amafilter B.V. Holland, c/o Moret Enterprises, 2811 Green Mountain Ln., Escondido, CA 92025, USA (Booth 520). For over 40 years, Amafilter B.V. has provided development, construction and installation of vertical and horizontal tank, vertical plate and pressure filter systems. Amafilter supplies the edible oil industry with installations worldwide for the filtration of pressed, bleached, winterized and hydrogenated oils.

Amano International Enzyme Co., 120 E. Ogden Ave., #118, Hinsdale, IL 60521, USA (326). Amano, active in industrial enzymology since 1947, will present 15 microbial lipases, as well as 25 other industrial enzymes. These lipases are applicable for use in detergents, chemical synthesis, transesterification and flavor production in various food products.

American Colloid Co., 5830 Mt. Moriah, Suite 5, Memphis, TN 38115, USA (327 and 426). The company's acid-activated bleaching clay will be displayed.

Anderson International Corp., 6200 Harvard Ave., Cleveland, OH 44105, USA (103). This exhibit will feature Mega Series expeller presses, vegetable oil extruders and the W.C. Cantrell Bauer line of separating equipment. Photos, brochures and technical literature will be on display.

Armstrong-Hunt Inc., 2081 E. Ocean Blvd., Stuart, FL 34996, USA (111). Armstrong-Hunt manufactures heavy-duty heating and cooling coils for process applications. Features include embedded fin designs and all-welded construction. The company specializes in high-pressure/temperature applications, stainless steel construction and removable, cleanable coil sections.

Brinkmann Instruments Inc., Cantiague Road, Westbury, NY 11590, USA (321). Brinkmann Instruments will exhibit its line of Metrohm titrators and the Metrohm Rancimat.

Bruker Spectrospin, 555 Steeles Ave. E., Milton, Ontario L9T 1Y6, Canada (505, 507 and 509). The Bruker exhibit will feature the Minispec PC 100 series of automated bench-top pulsed nuclear magnetic resonance spectrometers. Food industry applications for the Minispec include solid fat index in edible oils, total fat determinations and oil determinations in oil-bearing seeds.

The Cambrian Engineering Group Ltd., 2200 Argentia Rd., Mississauga, Ontario L5N 2K7, Canada (501 and 503). Models, photographs and description material on the "campro" line of oil processing equipment will be displayed. Also available will be information on new approaches developed for Far East licensees, and preliminary information on new technologies being developed.

CEM Corp., PO Box 200, Matthews, NC 28106, USA (502). CEM Corp. will introduce a six-minute microwave Kjeldahl digestion. The Kjel-FAST is designed to provide percent protein for process control, with precision and accuracy comparable with the standard Kjeldahl digestion method. Also exhibited will be a rapid moisture analyzer and oil and fat extraction system.

Centrico Inc., 100 Fairway Ct., PO Box 178, Northvale, NJ 07647, USA (521 and 523). Centrico Inc. represents Westfalia Separator for the U.S. and Canada. Photos, brochures and technical literature will be available. A new high-capacity Westfalia refining centrifuge will be displayed.

Crown Iron Works Co., PO Box 1364, Minneapolis, MN 55440, USA (115). Crown Iron Works Co. designs and manufactures solvent-

extraction equipment. Photos, brochures and technical literature will be on display.

De Smet USA Corp., 2839 Paces Ferry Rd., Suite 640, Atlanta, GA 30339, USA (511). De Smet specializes in designing and supplying processes and machinery for the agro and food industry with emphasis on oilseed crushing and vegetable oil refining processes. De Smet also supplies turnkey plants.

Eastman Chemical Products, 1133 Ave. of the Americas, New York, NY 10036, USA (415). Eastman will provide information on monoglyceride and tenox antioxidants.

Eirich Machines Inc., PO Box 550, Maple, Ontario L0J 1E0, Canada (108). Representatives from Eirich will be available to discuss processing equipment and mixers.

EMI Corp., 3166 Des Plaines Ave., Des Plaines, IL 60018, USA (200 and 202). Representatives at the booth will be Arnold Gavin, David Tandy and Bill McPherson. Slides and literature will describe EMI physical refining systems, edible protein processing systems, plant pictures and process flowsheets for solvent extraction of oilseeds, fats and oils refining, fatty acid production processes and complete plants. Catalogs will be available.

Equipment Engineering, 757 E. Murry St., Indianapolis, IN 46227, USA (508). Equipment Engineering specializes in the sale and remanufacture of high-speed vertical and decanter centrifuges, as well as quality, American-made replacement parts, custom-engineered electrical controls, field service, preventative maintenance and training sessions. Purchase and trade-in of centrifuges are available.

Florida Industrial Filters Inc., 1367 Highland Ave., PO Box 873, Dunedin, FL 34697-0873, USA (323). Florida Industrial Filters will show filter equipment for various stages in edible/vegetable oil processing and replacement filter elements for different filter types.

The Foxboro Co., Dept. 120/N30-1E, Foxboro, MA 02035, USA (201, 203, 300 and 302).

French Oil Mill Machinery Co., 1035 W. Greene St., Box 920, Piqua, OH 45356, USA (400). Representatives will be available to discuss oilseed processing machinery. French manufactures the entire line of preparation, extraction and meal-handling equipment. Offerings include energy-efficient, high-capacity equipment for both full pressing and prepressing, as well as solvent extractors, counter-current desolventizer-toasters, meal dryer-coolers and DTDC. Models of these machines will be on display.

G. Mazzoni S.p.A., PO Box 421, Busto Arsizio 21052, Italy (420 and 422). General literature, advertising material, photographic panels and small-scale model plants will be on display.

International Bio-Synthetics, PO Box 241068, Charlotte, NC 28224, USA (514 and 516). International Bio-Synthetics will display its detergent enzymes such as Maxatase, Maxocal and Maxamyl.

Harshaw/Filtrol Partnership, 30100 Chagrin Blvd., Cleveland, OH 44124, USA (401 and 403). Information will be available on a broad line of Filtrol clay products and Harshaw hydrogenation catalysts used in refining and processing edible and inedible oils. Featured will be fast-filtered clay, including new Grade 105 SF. Technical representatives will be available to discuss specific products and applications.

Industrial Filter & Pump Mfg. Co., 5900 Ogden Ave., Cicero, IL 60650, USA (214 and 216). Industrial Filter & Pump Mfg. Co. will display an array of filtration equipment featuring Type 122 and 114D fully automated filtration systems. Process applications include crude oil bleaching, hydrogenation, winterizing, polish and tank loading.

Kalsec Inc., PO Box 511, Kalamazoo, MI 49005, USA (522).

Laporte Inorganics, PO Box 2, Moorfield Road, Widnes, Cheshire

WA8 0JU, England (303). The range of Fulmont activated bleaching earths will be represented by Laporte Inorganics of Great Britain. Information on the product range and their applications in the oils and fats industry will be available as well as the latest research work on the functioning of bleaching earths.

Leybold Vacuum Products Inc., 5700 Mellon Rd., Export, PA 15632, USA (118). Industrial vacuum pumps and vacuum pumping systems for laboratories, pilot plants and full-scale processing facilities will be on display.

Libra Laboratories Inc., 44 Stelton Rd., Piscataway, NJ 08854, USA (222). Quick Test Kits certified by Libra Laboratories are designed for rapid analysis of fats and oils. Also featured will be "Food Service for Products and Foodservicer," a laboratory service for optimizing process, products and distribution of oil-based foods.

Linde Division, Union Carbide Corp., Tarrytown Technical Center, Tarrytown, NY 10591, USA (110 and 112). Industrial gases and technologies for the fats and oils industry will be displayed. Emphasis is on hydrogen for hydrogenation processes and nitrogen for inverting.

Manville, Filtration and Minerals, PO Box 519, Lompoc, CA 93438-0519, USA (220). Manville's exhibit will feature filtration technology and a broad range of products including Celite diatomite filter aids and adsorbents used in the production and refinement of oils.

Medallion Laboratories, 9000 Plymouth Ave. N., Minneapolis, MN 55427, USA (519). Medallion Laboratories, an analytical lab specializing in food industry applications, will have literature available on its services.

Mettler Instrument Corp., Box 71, Princeton-Hightstown Road, Hightstown, NJ 08520, USA (517). Mettler Instrument Corp. will exhibit its new auto titrators, as well as thermal analysis and density meters.

Miles Laboratories Inc., 1127 Myrtle St., Elkhart, IN 46514, USA (500). Miles Laboratories will feature its line of enzymes and detergent ingredients including alpha-anylase and protease in liquid and granular forms as well as citric acid and sodium citrate.

N. Hunt Moore & Assoc. Inc., 3951 Senator St., Memphis, TN 38118,

USA (221, 223, 320 and 322). This exhibit will feature Escher Wyss soybean preparation systems, Champion soybean meal and hull-processing equipment, Lurgi extraction and refining systems, and the Schroeder Kombinator for the processing of margarine and shortening.

Nicolet Instrument Corp., 5225 Verona Rd., Madison, WI 53711, USA (227). The 8200 FT-IR spectrometer will be exhibited to demonstrate infrared QC instrumentation for the analysis of constituents in edible oils. The instrument features preprogrammed quantification methods, simple sample handling and one-button operation.

Novo Laboratories Inc., 33 Turner Rd., Danbury, CT 06810, USA (107 and 109). Novo Laboratories will display its industrial enzymes specifically for fats and oils and detergent applications.

Nu-Chek-Prep Inc., PO Box 295, Elysian, MN, 56028 USA (506). Fatty acids and ester homologs, tri-, di- and monoglycerides, acid chlorides, fatty nitriles, fatty alcohols, fatty acetates, cholesterol esters, alkylmethane, sulfonates, soaps, fatty acid anhydrides, wax esters, standard reference mixtures GLC and TLC will be displayed.

Oil-Dri Corp. of America, 520 N. Michigan Ave., Chicago, IL 60611, USA (510). Oil)Dri, a supplier of specialty minerals for 46 years, will feature Pure-Flo bleaching clays for bleaching edible and inedible oils, fats and oleochemicals.

Oregon Meadowfoam Growers Assoc., 866 Lancaster SE, Salem, OR 97301, USA (515). This exhibit will feature photos, materials and printed handouts on meadowfoam oil, a triglyceride comprised almost completely of fatty acids with chain lengths of 20 and 22 carbon atoms. Samples will be available.

Pacific Scientific Co.-Instrument Div., 2431 Linden Ln., Silver Spring, MD 20910, USA (411). Pacific Scientific will display its NIR spectrophotometers for oilseed analysis.

POS Pilot Plant Corp., 118 Veterinary Rd., Saskatoon, Saskatchewan S7N 2R4, Canada (101). Consisting of four pilot plants and 10 laboratories, POS' oils and oilseed applied facilities provide all dimensions of oil processing, from seed preparation to margarine production. Training programs can be arranged.

Prater Industries Inc., 1515 S. 55th Ct., Chicago, IL 60650, USA (210). Prater Industries will introduce its latest approach to economic meal and hull grinding. The MM5 Mega mill will be exhibited along with a variety of photos illustrating Prater's range of products for the industry.

PSI Process Systems Inc., 1790 Kirby Pkwy., Suite 300, Memphis, TN 38138, USA (121). PSI provides engineers, construction managers and contractors for process engineering, construction and fabrication to producers of food and food products such as sweeteners, beverages, alcohol and edible oils as well as oleochemicals, glycerine and soap. A complete range of process, structural, mechanical instrumentation, electrical and computerized control systems designs will be displayed.

Simon-Rosedowns Ltd., Cannon Street, Hull, N. Humberside HU2 0AD, England (114 and 116). A corporate display and video will feature the latest equipment for screw pressing and oil refining. Graphics will illustrate the new redesigned range of computer-controlled presses and Econoflow deodorizers.

Spectral Data Services Inc., 818 Pioneer, Champaign, IL 61820, USA (513). Spectral Data Services provides multinuclear NMR data-acquisition services. Solution and solid (MASS, CP/MASS, VASS) analysis capabilities are available. Instrumentation includes 360 and 270 MHz instruments.

Süd-Chemie AG Group, Box 828, Port Washington, NY 11050, USA (206 and 208). This display will update the highly active Tonsil bleaching earths and UCI (Girdler) catalysts for the refining and process-

ing of fats and oils. Technical service representatives will be available to discuss products for specific applications.

Tekmar Co., 10 Knollcrest Dr., Cincinnati, OH 45237, USA (421 and 423). Tekmar will display purge and trap concentrators and viscometers.

The Tintometer Co., 309A McLaws Circle, Williamsburg, VA 23185, USA (100 and 102). Color-grading and measuring instruments for edible oils, fats and tallows including the Lovibond AOCS color-scale tintometer, FAC scale, Gardner scale, Model E tintometer, American Oil tintometer and the latest digital readout Lovibond automatic tintometer for Lovibond and AOCS scale with options for chlorophyll and carotene including printer and computer interface will be on display.

Tramco Inc., 1020 E. 19th St., Wichita, KS 67214, USA (229). On display will be the heavy-duty Tramco Model "G," designed to provide years of service under extreme applications. The Model G is built to accommodate large capacities of free-flowing dry materials.

UOP Inc., Biological and Food Products, 25 E. Algonquin Rd., Des Plaines, IL 60017-5017, USA (402). UOP will introduce a line of natural food-grade tocopherol antioxidants. It also will display its 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.

Varian Instrument Group, 10440-2 Pioneer Blvd., Santa Fe Springs, CA 90670, USA (104 and 106). Varian Instruments, manufacturer of gas and liquid chromatographs and associated data systems plus atomic absorption and UV-VIS-NIR spectrophotometers, will feature its services for oil chemists offered by the company's technical support and service engineer staff.

Votator Div. of Cherry-Burrell, PO Box 35600, Louisville, KY 40232, USA (407 and 409). The Votator equipment lines for the fats and oils industry will be shown in photo displays. These will include oil deodorization plants, shortening- and margarine-processing equipment and a thin-film evaporator for drawing lecithin and fatty acid stripping.

Waters Chromatography Div., Millipore, 34 Maple St., Milford, MA 01757, USA (417). Waters Chro-

Exhibit hours

Sunday, May 8
2:00 - 8:30 p.m.
Monday, May 9
9:00 a.m. - 5:00 p.m.
Tuesday, May 10
9:00 a.m. - 5:00 p.m.
Wednesday, May 11
9:00 a.m. - 1:30 p.m.

matography Division will display high performance liquid chromatography (HPLC) instruments with capabilities to analyze edible oils. Typical analyses include fatty acids, mono-, di- and triglycerides, and mocotoxins.

Wurster & Sanger Inc., 222 W. Adams St., Suite 1529, Chicago, IL 60606, USA (117). On display will be catalogs, technical literature, plant and vessel photographs plus process flowsheets reflecting the capabilities of Wurster & Sanger as process engineers for the fats and oils industry. The company custom builds plants for oilseeds, glyceride fats and oils, fatty acids, glycerine and their by-products. Samples will be displayed.

Book exhibit

The following publications will be displayed in the AOCS book exhibit during the annual meeting in May in Phoenix. The list includes books received through mid-February. Order sheets will be available at the exhibit to order books from the publishers. Persons not attending the meeting who wish to buy books should contact the original publishers, not AOCS.

From the American Association of Cereal Chemists (AACC), 3340 Pilot Knob Rd., St. Paul, MN 55121, USA:

Near-Infrared Technology in the Agricultural and Food Industries, edited by Phil Williams and Karl Norris, 1987, $169.

AACC Approved Methods, compiled by the AACC Approved Methods Committee, 1983 (plus current supplements), $245 (includes two hardcover ring binders).

From the American Institute of Chemical Engineers (AIChE), 345 E. 47th St., New York, NY 10017, USA:

Biotechnology Progress, by M.L. Shuler, December 1987, AIChE members $14, nonmembers $50.

Biotechnology Processes—Scale-up and Mixing, by Chester S. Ho and J.Y. Oldshue, 1987, AIChE members $35, nonmembers $70.

From the Association of Official Analytical Chemists (AOAC), 1111 N. 19th St., Suite 210, Arlington, VA 22209, USA:

Official Methods of Analysis of the AOAC, 14th Edition, edited by Sidney Williams, 1984, $148.50.

Journal of the AOAC, Raffaele Bernetti, editor-in-chief, published bi-monthly, $99.50/year.

From ISTA Mielke GmbH, PO Box 90 08 03, 2100 Hamburg 90, West Germany:

Oil World Weekly, edited by Siegfried Mielke, published weekly, DM823.80.

Oil World Annual, edited by Siegfried Mielke, April 1988, DM98.

Oil World—The past 30 years and the prospects for the next 20, edited by Siegfried Mielke, November 1988, DM290.

From McCutcheon's Publications, 175 Rock Rd., Glen Rock, NJ 07452, USA:

McCutcheon's Emulsifiers & Detergents, April 1988, $50.

McCutcheon's Functional Materials, April 1988, $50.

From the Plenum Publishing Corp., 233 Spring St., New York, NY 10013, USA:

Fat Production and Consumption, Vol. 131, by Galli and Fedeli, 1987, $62.50.

Surfactants in Solution, Vol. 4, by Mittal and Bothorel, 1987, $97.50.

Surfactants in Solution, Vol. 5, by Mittal and Bothorel, 1987, $97.50.

Surfactants in Solution, Vol. 6, by Mittal and Bothorel, 1987, $97.50.

Platelet-Activating Factor and Related Lipid Mediators, by Snyder, 1987, $79.50.

The Metabolism, Structure, and Functions of Plant Lipids, by Stumpf et al., 1987, $110.

The Phospholipases (Handbook of Lipid Research, Vol. 5), by Waite, 1987, $59.50.

Prostaglandin and Lipid Metabolism in Radiation Injury, by Walden and Hughes, 1988, $72.50.

From Springer-Verlag New York Inc., 175 5th Ave., New York, NY 10010, USA:

Dense Gases for Extraction and Refining, by E. Stahl, K. Quirin and D. Gerard, 1988, $89.50.

Immobilized Biocatalysts, by W. Hartmeier, 1988 (expected), $25.

Food Chemistry, by H. Belitz and W. Grosch, 1987, $79.50.

Surfactants in Consumer Products, by J. Falbe, 1987, $126.50.

Annual Meeting Technical Paper Abstracts

Session A Monday morning

Surfactants and Detergents I: Fat-Based Surfactants

A1

N-Alkylpyrrolidone Based Surfactants. Robert B. Login, GAF Chemicals Corporation, 1361 Alps Road, Wayne, NJ 07470, and Joseph Niu, GAF Chemicals Corporation.

Pyrrolidone, a planar lactam exhibiting maximum orbital overlap and hence charge separation, is sufficiently hydrophilic to afford surface activity when combined with suitable alkyl hydrophobes. Such compounds function as low HLB auxilliaries in a variety of applications such as foam stabilizing, thickening, wetting and compatabilizing. In addition, pyrrolidone can complex with actives such as phenolics, mercaptans and fragrance components resulting in additional novel applications. Surfadone™ is a commercial example of this class of surfactant.

A2

Acylamino Acid: Characteristic Properties and Applications. Kazutami Sakamoto, Ajinomoto U.S.A., Inc., Glenpointe Centre West, 500 Frank West Burr Blvd., Teaneck, NJ 07666-6894.

Characteristic properties of Acylamino Acid (AAA) as a surface active agent come from multifunctional structures of amino acids. Amino acid residue in the structure of AAA plays a role mainly as a hydrophilic group with the combination of fatty acid residue as a hydrophobic moiety. Based on the difference of numbers and combination of ionic group in the amino acid molecule, every ionic type of surface active AAA's are prepared. AAA's not only have sufficient surface activity as each type of surfactant, but also have superior properties of being extremely mild to skin, substantive conditioning effect upon skin and hair. The amino acid linkage, like a peptide linkage of proteins, may provide a high affinity to the proteins through intermolecular hydrogen bond. An optical active nature of AAA adds another aspect to the self-aggregation of AAA and interaction with proteins. Optically active AAA show highly structured aggregate with asymetrically ordered hydrogen bonding in micell formation and gellation. Natural existence and importance of AAA's, such as acyltaurine in digestive system of invertebrate animals as a substitute for bile acids, are recognized. The history of practical application of AAA's is rather new, yet the significant improvement of amino acid production technology and development of process for AAA synthesis has enabled economical and commercial utilzation of AAA's. Extensive effort for the basic research and development of new application will open further opportunity for the practical application of AAA.

A3

A ^{13}C NMR Study of the Effects of Chain Branching on the Quaternization of Tertiary Amines. Edward H. Fairchild, Sherex Chemical Company, Inc., Box 646, Dublin, OH 43017, and Sheldon R. Schulte, Sherex Chemical Company, Inc.

Quaternization of fatty tertiary amines is practiced widely on an industrial scale. Studies of the kinetics and mechanism of quaternization abound in the literature, but seldom report conditions similar to those used for commercial preparation. Differences in the rates of quaternization of various commercial fatty tertiary amines led us to studies of model branched compounds. The utility of ^{13}C NMR spectroscopy in the rapid, definitive evaluation of relative rates of reaction of the various model amines will be demonstrated. Comparative reaction rate data obtained from the study of these models will be presented and used to explain differences seen in the conversion of commercial faty dimethyl tertiary amines to their benzyl quats.

A4

Studies on the Preservative Kathon CG In Various Surfactant Based Systems. Donald J. Ferm, U.S. Borax Research Corporation, 412 Crescent Way, Anaheim, CA 92801, and T. Scott Griffin, U.S. Borax Research Corporation.

Kathon CG (Rohm & Haas) with 1.15% 5-chloro-2-methyl-4-isothiazolin-3-one and 0.35% 2-methyl-4-isothiazolin-3-one as active ingredients has been found to be a highly efficient antimicrobial preservative for formulated products. However, its use has been contraindicated for certain anionic surfactants, especially AOS, because of presence of residual bisulfite ion in many of these materials. This bisulfite is added as a finishing step to the hydrogen peroxide bleaching process to remove excess peroxide. It has been found that conventional analytical methods for bisulfite are not accurate in AOS systems. Alternative analytical methods are discussed. Bisulfite levels in various AOS raw materials were determined, as well as the effect of the formulation process on residual bisulfite present. A new HPLC method for determination of Kathon CG level in formulated products has been developed. By this method one can easily monitor the effect of various bisulfite levels on level of the Kathon active ingredient in the finished product.

A5

Ethoxylated Alcohols and Acids. Drs. Murphy and Seitz, Dial, Inc., 15101 N. Scottsdale, Rd., Scottsdale, AZ 85254.

Abstract not available at press time.

A6

Human Safety and Environmental Acceptability of Some Anionic Surfactants. Andrew Sivak, Arthur D. Little, Inc., Chemical and Life Sciences Section, Cambridge, MA 02140, and Marie Bonfiglia, Patricia Capomaccio and Murial Goyer, Arthur D. Little, Inc.

Linear alkylbenzene sulfonates (LAS), alkyl sulfates (AS) and alkyl ethoxy sulfates (AES) are surfactants that have found wide use in industrial and domestic detergent

formulations over the past two decades. Their continued use results from their facile degradation and their low order of toxicity to environmental organisms as well as humans. LAS, AS and AES are all rapidly biodegraded in both shake flask and activated sludge systems. Times to 90% biodegradation in shake flask cultures are LAS-7 days, AS and AES-2 to 5 days. In activated sludge reactors, the times to 90% biodegradation are LAS-10 to 20 days, AS and AES-approximately 5 days. Fish toxicity studies with fathead minnows and bluegills reveal acute toxicity concentrations in the range of 3 to 20 mg/l for LAS and AS. The acute toxicity for these two species for AES is at concentrations of 10 to 80 mg/l. Data on the fish toxicity of biodegraded surfactants, available only for LAS show a 90% reduction in toxicity for the substances that are the products of the biodegradation process. A similar pattern of toxicity is evident for the invertebrate, Daphnia, with acute toxicity concentrations for LAS and AS of 3 to 6 mg/l, and for AES, 5-40 mg/l. The acute oral toxicity for all three types of surfactants is in the mg per kg range, thus they would appear to be substances of low acute toxicity for humans. Investigations to determine the carcinogenicity and the reproductive toxicity of the surfactants in laboratory animals has demonstrated no positive responses, except for a single set of unconfirmed reports of a reproductive effect about ten years ago. These reports are contrary to a large body of experimental data showing no effect subsequent to that report. These surfactants are irritants for human skin at concentrations of 10 to 25% but have no effect at concentrations of normal consumer use (1%). Thus, the data on environmental and animal toxicity and the long history of safe use by humans support the view that the continued use of these materials does not pose a threat to environmental quality or human safety.

A7

Purification of Higher Alcohols and Amines—Via Pellet Bed/Charge Pot Addition of Venpure Sodium Borohydride Products. Richard J. Colby, Morton Thiokol/Ventron Products, 150 Andover Street, Danvers, MA 01923, and Richard A. Mikulski, Morton Thiokol/Ventron Products.

This presentation reviews recent advances in the use of pellet bed/charge pot systems to purify higher alcohols and amines with VenPure® sodium borohydride. Sodium borohydride effectively removes trace levels of carbonyl, organic peroxides and metal impurities from these materials which can result in color and odor problems for a manufacturer or end user. VenPure pellet beds/charge pots provide a large surface area of sodium borohydride and provide good contact between the process stream and the pellets. The pellets and pellet bed design make it possible to control the rate of addition of sodium borohydride, yielding carbonyl reductions of 90% or more and color reductions of 50% or more at cost efficient treatment levels. Successful purifications have been conducted on C-8 through C-20 alcohols, alkanolamines and ethoxylates. The important engineering aspects of these systems will be discussed along with the experimental procedures and the results and estimates of treatment.

Session B Monday morning

Pharmacological Effects of Lipids I: Introduction and Dietary Lipids and Tumor Development

B1

Cancer Development and Its Natural History. Emmanuel Farber, Dept. of Pathology and Biochemistry, University of Toronto, Toronto, ONT M5S 1A8, Canada.

Most cancers develop stepwise over a long period of time with non-malignant precursor lesions that only slowly evolve toward cancer. With many chemicals and some radiaitons, as well as some viruses (DNA and some retroviruses), cancer development can be divided into 3 major stages or periods, initiation, promotion and progression. Initiation is frequently associated with a more or less permanent change in the phenotype of a rare target cell, presumably due to a change in base composition in DNA or to gene rearrangements. During promotion, these rare cells expand by proliferation to generate focal proliferations that resemble benign neoplasms. These in turn exercise at least one of two options, regression to normal appearing tissue or slow evolution to cancer. Progression is self-generating but can be modulated by dietary manipulations or by other drugs or xenobiotics. The prolonged nature of the promotion-progression stages in most tissues and its modulability indicate that these stages are vulnerable sites for the development of dietary and other ways to prevent the progression to cancer. This overall pattern is known to occur in the liver, skin and urinary bladder and is probable in several other tissues or organs including the colon, breast and pancreas. What we know about the human suggests that the patterns may be very similar for cancer development in many sites. The best worked out is melanoma. The phenotypic pattern of the precursor lesions in the experimental animals are remarkably similar in any single organ. For example, the hepatocyte nodules are very similar to each other with many different carcinogens and promoting environments even though the ultimate cancers are quite heterogeneous and diverse. The diversity of heterogeneity appears to be an acquisition that is quite late in the step-by-step development of cancer. Although its exact step has not been delineated as yet, it appears to be acquired as malignancy is. Unlike the cancers, the commonality or homogeneity in the precursor lesions offers many opportunities for interrupting the process and thus in preventing cancer. The experience to date in experimental systems with some hormones, drugs and dietary manipulations indicates that inhibition of the development of cancer may be most readily achieved by effects on the promotion and progression sequences in carcinogenesis.

B2

Can Modulation of the Malignant Phenotype By an Endogenous Inhibitor Lead to Tumor Regression *in Vivo*. G. Lipkin, New York University School of Medicine, Department of Dermatology, New York, NY 10016, and M. Rosenberg and E. Fass, New York University School of Medicine.

Current approaches to treatment of malignancy are hampered by tumor cell heterogeneity and progressive clonal evolution fueled by genetic instability and selective pressures of therapy and host resistance. Modulation or partial reversion of the malignant phenotype by differentiation agents or endogenous inhibitors could favorably alter the tumor/host relationship by stabilizing phenotypes and reducing heterogeneity. We examined this hypothesis in a model of malignant melanoma, employing an endogenous contact inhibitory factor (CIF), obtained from conditioned media of cultures of a revertant line of hamster melanoma cells. CIF reversibly restores density-, anchorage-, and serum-dependent growth to hamster, mouse and human melanoma cells, promotes early G1 growth arrest, elevation of cyclic adenosine monophosphate, restoration of vitiligo-related pigment cell differentiation antigens and enhanced expression of several melanoma-related antigens. It also decreases susceptibility to lysis by natural killer (NK) cells but increases vulnerability to cytotoxic T cells. Contact inhibitory effects are non-toxic and transcend both species and tissue barriers. Further studies of a CIF-treated rat hepatoma line disclosed selective changes in cytoskeletal organization and proteins accompanying phenotypic reversion, including reduced levels of an actin-binding protein receptor. *In vivo (in situ)* treatment of subcutaneously transplanted hamster melanomas with either aqueous or liposome-entrapped, partially purified CIF preparations for 30 days led to retardation of tumor growth in both treated groups, with complete tumor regression and 100% survival in the liposome-CIF group compared to 100% mortality in controls. In a parallel experiment, *in situ* administration of an aqueous suspension of CIF daily for 10 days to C57BL/6J mice with established subcutaneously implanted Lewis lung carcinomas led to regression of 75% of tumors, compared to none in control animals. Endogenous inhibitors like CIF, or other agents which can modulate or reverse the malignant phenotype, may favorably shift the biologic balance between tumor and host by reducing heterogeneity, restoring sensitivity to normal environmental signals governing growth, and inducing expression of surface markers which alert and facilitate host response.

B3

Are Messenger Molecules In Microbes the Ancestors of Vertebrate Hormones and Tissue Factorsdisplay Memory. Derek LeRoith, National Institutes of Health, Bethesda, MD 20814.

Traditionally, intercellular communication in mam-

mals and other vertebrates was considered to be the unique property of two distinct systems; the nervous system with its rapid electrical response and the endocrine system with its slower response using hormones as signal messenger molecules. More recently it has become clear that these two systems overlap; using common signal messenger molecules and common receptor-effector systems on target cells. Furthermore, numerous other systems of intercellular communication including the immune system, the paracrine and autocrine systems share common messenger molecules, receptor-effector-type mechanisms with the nervous and endocrine systems. Phylogenetic studies have shed new insights into many aspects of the overlaps between these systems. Typical vertebrate-type peptide hormones such as insulin, ACTH and somatostatin are found in most species of multicellular non-vertebrates as well as unicellular organisms. In addition to these vertebrate-type hormonal peptides, multicellular non-vertebrates and unicellular organisms contain substances that bind hormones and are very similar to typical vertebrate receptors. These include the insulin receptors of Drosophila and the receptor of alpha mating factor in brewer's yeast (Saccharomyces). Furthermore, systems of intercellular communication between microbes are also well described including mating of Saccharomyces. Furthermore, systems of intercellular communication between microbes are also well described including mating of Saccharomyces, the steroid sex pheromones of the unicellular water mold achlya and the small Mr peptide mating pheromone of Streptococcus fecalis. Extending these studies we have also demonstrated the presence of insulin and somatostatin in higher plants. These findings lead us to postulate that the biochemical elements of the systems of intercellular communication of vertebrates have common early evolutionary origins. These common origins may help to explain the overlaps between these various systems. For example, in classic paracrine or autocrine systems, the messenger molecules are typical peptide hormones or growth factors. In addition our hypothesis suggests that hormone production is not unique to endocrine glands but all tissues produce these hormones. Thus malignancy associated with excess hormone production may reflect alterations in normal hormonal synthesis and/or release.

B4

Role of Dietary Fat In Carcinogenesis. K.K. Carroll, University of Western Ontario, Department of Biochemistry, London, ONT N6A 5C1, Canada

The level of fat in the diets of different countries shows a strong positive correlation with cancer incidence and mortality at sites such as the breast, colon, prostate and pancreas. This evidence of an association between dietary fat and carcinogenesis is supported by observations that animals fed high-fat diets develop tumors at these sites more readily than animals fed low-fat diets. Attempts to relate dietary fat to cancer by studies within countries have been less successful. Possible reasons for this include the smaller variations in dietary fat within countries compared to those between countries; the limited time of observation; and the smaller population size of within country studies. In case-control studies, genetic variation may be a confounding variable since cases are more likely to be genetically susceptible to cancer than

controls. The results of experiments on animals indicate that high-fat diets act primarily at the promotional stage of carcinogenesis to produce tumors more quickly and in larger numbers. It appears that a longer time is required to demonstrate this effect when a lower dose of carcinogen is used. Since the levels of carcinogens to which humans are normally exposed are probably much lower than those commonly used for animal experiments, a relatively long period of observation may be required to detect differences in human cancer incidence and mortality related to dietary fat.

B5

Influence of Dietary Fat on Normal Mammary Gland Developmental Processes. Clifford W. Welsch, Michigan State University, Department of Anatomy, East Lansing, MI 48824.

It is now well known that marked enhancement of mammary tumorigenesis in experimental animals can be achieved by increasing and/or altering the fat composition of the diet. In contrast, very little information is available as to whether or not the fat composition of the diet can affect the developmental growth processes of the normal mammary gland. In this communication, I will present evidence that the amount and type of dietary fat (vegetable fats rich in polyunsaturated fatty acids, animal fats rich in saturated fatty acids and fish oils rich in omega-3 fatty acids) can indeed affect mammary gland development in laboratory animals (mice). In addition, I will present a mechanism by which dietary fat may influence normal and neoplastic mammary gland development, i.e., the fat content of the diet may affect this process by modifying hormone induced mammae growth responsiveness.

B6

Supression of *In Vitro* Activation of Tumoricidal Function In Peritoneal Macrophages from Fish Oil Fed Mice. R.S. Chapkin, University of California, Dept. of Human Anatomy, Medical School, Davis, CA 95616, and S.D. Somers, K.L. Erickson (speaker), University of California, Davis.

Although dietary oils containing γ-linolenic acid (18:3n-6) and eicosapentaenoic acid (20:5n-3) have been used in the management of inflammatory/immune disorders, the mechanism of their efficacious effect remains unknown. Because the macrophage plays a central role in the immune system, we evaluated the effects of feeding borage oil (BO), containing 18:2n-6 and 18:3n-6, and fish oil (MO) containing 20:5n-3 and 22:6n-3, on the activation of tumoricidal function in peritoneal macrophages. C57BL/6 mice were fed either 10% (wt) safflower oil (SO), BO, MO or hydrogenated coconut oil (HO) for 4 weeks, and injected 3 days prior to sacrifice with sterile fluid thioglycollate medium. There was no difference between the diets with respect to numbers or relative proportions of resultant inflammatory exudate populations. The n-3 fatty acids, 20:5n-3 and 22:6n-3, were readily incorporated into macrophage phospholipids in MO animals. Interestingly, 18:3n-6 was not detected in BO macrophages which contrasted with liver phospholipids, where 18:3n-6 levels were significantly elevated ($P<0.05$), although the macrophage dihomogammalinolenic acid (20:3n-6)/arachidonic acid (20:4n-6) ratio was significantly elevated ($P<0.05$) relative to CO, SO and MO fed mice. Macrophages from mice fed MO when activated *in vitro* with recombinant γ interferon (2.5 U/ml) plus bacterial lipopolysaccharide (LPS, 1 ng/ml), had significantly lower cytolytic capacity for the P815 mastocytoma targets than did macrophages from animals fed the other diets. Alternative methods for tumoricidal activation, either with pharmacologic agents (calcium ionophore A23187 and phorbol myristate acetate) or higher concentrations of LPS (100 ng/ml) rendered macrophages from all diets equally competent for tumoricidal function, suggesting that macrophages from MO mice have a relative deficit in the response to γ interferon. Additionally, macrophages from MO and CO mice secreted less prostaglandin E relative to BO and SO, while SO macrophages secreted greater amounts of hydrogen peroxide stimulated by zymosan than did macrophages from the other diets. These data indicate that MO feeding is capable of suppressing the activation of tumoricidal capability *in vitro* and may play a regulatory role in host protection against neoplastic and infections diseases.

Session C Monday morning

Flavor Chemistry of Lipid Foods I, Symposium in honor of Stephen S. Chang

Introduction to Symposium. Thomas H. Smouse, 563 Winding Trail Lane, Des Peres, MO 63131.

The definition of flavor by Webster is the blend of taste and smell sensations evoked by a substance in the mouth. However, Brozek states in 1947 that flavor is a complex sensation with taste, aroma and feeling as the three categories of components. Amerine, et al. in their 1965 publication of "Principles of Sensory Evaluation of Food" say flavor is a mingled but unitary experience which includes sensations of taste, smell, pressure, and other cutaneous sensations such as warmth, cold and pain. The best definition that is brief and complete was given by Bailey and has not been published: "Flavor is a psychological interpretation of a physiological response to a physical stimulus." In other words, flavor involves three branches of science, namely psychology or sensory, physiology/neurology or the detection and-transportation of the signal to the brain and chemistry or the composition, structure and properties of the flavor substance. This symposium is in honor of Stephen S. Chang and his contributions to the Flavor Chemistry of Lipid Foods. For this reason we have developed a technical program to address Flavor Chemistry mostly with a minor emphasis on sensory evaluation. We have not directed any attention to physiology or neurology aspects of flavor although for a complete understanding, all three aspects are important. The program includes outstanding and well known speakers from around the world and includes many of the subject areas that Professor Chang and his graduate students have researched over the past 35 years.

C1

Contribution of Flavor Chemistry to the Food Industry—Overview. D. Richard Ensor, Firmenich, S.A., Flavor Division, Case Postale 239, Geneva 8, CH-1211, Switzerland.

In a brief historical review the author links flavor uses and perceptions of our primative ancestors (who were already experimenting with a wide range of tastes available to them in the wild) to the highly sophisticated and varied contributions made available by the flavor industry for the food manufacturers and ultimately the pleasure of today's consumers. He introduces the various phases involved in the study of both natural products and processed flavor targets, stressing the close and indispensible collaboration between chemist, spectroscopist, specialist in organic synthesis, flavorist and sensory analyst. Examples of the major breakthroughs in flavor chemistry plus the indispensable role of the food technologist are reviewed with discussion on recent developments in analysis during the past two decades, current trends and the short to mid-term outlook. In summary the author focuses upon the flavor industry's partnership role with the food industry, academia and the consumer through the sophisticated and disciplined sciences of chemical and sensory analysis. "There is nobody but eats and drinks. But they are few who can distinguish flavors." -TZE-SZE (5th Century B.C.) Grandson of Confucius.

C2

Development of Methodology for Flavor Chemistry—Past, Present and Future. Roy Teranishi, Western Regional Research Center, USDA, ARS, 800 Buchanan Street, Albany, CA 94710.

In recent years, there has been a remarkable advancement in methods of chemical and sensory identifications. Modern instrumental methods—such as gas chromatography, nuclear magnetic resonance, infrared and mass spectrometry—make it possible to identify compounds in much smaller amounts and in much shorter time than with old classical methods. Also, a methodical procedure has been developed to assess odor contributions. This method utilizes odor thresholds to find the significant components which contribute to the main characteristic odor. A brief history, some applications of methods developed and what might be future developments will be discussed.

C3

Isolation of Flavors. Gary Reineccius, University of Minnesota, Dept. Food Science and Nutrition, St. Paul, MN 55108.

Obtaining representative flavor isolates from foods is complicated due to the low levels found in foods, their diversity in physical and chemical properties, their potential interaction with major food constituents and the possibility of artifact formation. These considerations have resulted in the development of numerous techniques for the isolation of flavor compounds from foods. Each method has its own strengths and weaknesses thereby limiting its application to a particular problem. This presentation will provide an overview of methods currently being used to obtain flavor isolates for further analysis. While traditional methods will be discusses, emphasis will be placed on newer techniques for flavor isolation. These would include, for example, the use of a partial vacuum to enhance flavor recovery during dynamic headspace trapping, nontraditional headspace concentration methods (e.g. cryotrapping and charcoal/microwave desorption systems), supercritical solvents for flavor extraction and solid phase chromatography for concentration of dilute aqueous essences.

C4

Gas Chromatography and Gas Chromatography—Mass Spectrometry of Flavor and Odor Products From Fats and Oil. Edward G. Perkins, University of Illinois, Department of Food Science, 1208 W. Pennsylvania Avenue, Urbana, IL 61801.

Lipid derived compounds contribute both desirable and undesirable flavors and odors to fats, oils and fatty foods. The isolation and determination of such components is usually complicated by the fact that they are complex mixtures of organic compounds. Further complications arise since one must exercise caution such that labile compounds are not converted to other structural types as a result of interaction with components of the

isolation/preparation/analytical system/and detector system. Thus one cannot separate the steps listed above. For system optimization they must all be considered as part of an integrated system. The various chromatographic and mass spectrometric variables which must be controlled for optimum results will be discussed.

Session D Monday morning
HPLC of Lipids and Proteins

D1

HPLC of Lipids Employing A Silver Ion Column. William W. Christie, The Hannah Research Institute, Ayr, KA6 5HL, Scotland.

An HPLC column containing a microparticulate silica with bonded sulphonic acid groups was loaded with silver ions simply by injecting silver nitrate into an aqueous mobile phase via a rheodyne injector. The resulting column could be used with gradients of acetonitrile into methanol with mass detection to separate cleanly methyl ester derivatives of fatty acids with zero to six double bonds. The resulting fractions were then analyzed comprehensively by gas chromatography-mass spectrometry in the form of the picolinyl ester derivatives. Applications to samples of marine origin are described. With mobile phases containing aprotic solvents, phenacyl derivatives of fatty acids and uv detection, the silver ion column can be used to separate and quantify *cis*- and *trans*-isomers. Under similar conditions, molecular species of triacylglycerols can be separated. The column has been used continuously for a year with no obvious loss of resolution.

D2

High Performance Liquid Chromatography of Unconventional Oils. S. Nielsen, Aarhus Oliefabrik A/S, Analytical R & D Laboratories, P.O. Box 50, Aarhus C, DK-8100 Denmark, and Vijai K.S. Shukla, Aarhus Oliefabrik A/S.

We have successfully employed high performance liquid chromatography of triglycerides as one of the major techniques for the evaluation of unconventional oils from the whole world. Several examples of this technique as applied to oils from Asia and South America will be presented. An extension of the technique for analyzing essential fatty acid oils, so-called premium oils, will be discussed.

D3

HPLC Analysis of Phospholipids In Crude Oil for Evaluation of Soybean Deterioration. A.M. Nash, Northern Regional Research Center, ARS/USDA, 1815 North University Street, Peoria, IL 61604, and T.L. Mounts (speaker), Northern Regional Research Center.

Phospholipids in crude soybean oil extracted from distressed soybeans have been analyzed by gradient high-performance liquid chromatography. Crude oil was fractionated using a mini-column procedure on Sep-Pak silica cartridges by sequential elution for recovery of phosphatides. High-performance liquid chromatography of the concentrated phospholipids was accomplished on a Lichrosorb Si-60 10μ column, 250 × 4.6 mm with ultraviolet detection at 206 nm. A 20-minute solvent gradient of 2-propanol:hexane:water (42:56:2; 51:38:11) gave profiles of phospholipid distribution (major subclasses) that changed with impact of stress applied to plant or seed. Soybeans stored at high moisture levels (16% and 20% moisture) for up to 28 days yielded oils with phosphorus contents that decreased in direct relationship to days of storage. Distribution profiles were unusable for fractions isolated from oils with phosphorus contents below 50 ppm. Data show that during progressive damage, the content of phosphatidyl choline and phosphatidyl inositol decreases while the phosphatidic acid content increased.

D4

HPLC Of Ether Lipids. Thomas Foglia, USDA, Eastern Regional Research Center, 600 East Mermaid Lane, Philadelphia, PA 19118.

Ether lipids can serve as useful substrates in defining the positional selectivity of lipases. Additionally, such compounds also have ultility in studies on transport properties of lipids, i.e., intestinal fat absorption. Several synthesis of mixed alkyl-acyl-glycerols have been described, but such methods often lead to isomeric mixtures which are difficult to separate. Moreover, in the past, the quantitation of such mixtures was difficult at best because of the lack of a universal detector for various lipid subclasses. With the recent advances in high performance liquid chromatography (HPLC) column technology and availability of universal detectors, e.g., flame ionization, many of the separation and quantitation problems previously encountered have been overcome. In this paper we will present data on the normal and reverse phase separation of series of isomeric alkyl-acyl-glycerols as well as the quantitative determination of these and other lipid type materials.

Session E Monday Morning
Effects of Dietary Omega-3 Fatty Acids I

E1

PUFA Of Rat Liver Phospholipids In Starvation and Short-Term Switch Feeding Of Corn Oil and Menhaden Oil Diets. Ralph T. Holman, The Hormel Institute, University of Minnesota, 801 16th Avenue NE, Austin, MN 55912, and Susan B. Johnson, The Hormel Institute, Bruce A. Svingen, Winona State University and Frank B. Cerra, University of Minnesota Hospitals.

Weanling male Sprague-Dawley rats were randomly divided into two dietary groups fed 10% corn oil (CO) or 10% menhaden oil (MO) (w/w). After four months of feeding, the groups were sub-divided into three subgroups. The first subgroup was continued on the previous diets. The second subgroup was switched to the opposite diet (10% CO to 10% MO and vice versa). The third subgroup was given free access to H_2O but not feed. At the end of 5 days, animals were anesthetized and sacrificed by exsanguination. Livers were quickly removed, retrogradively

flushed with ice-cold 0.9% NaCl (w/w) and frozen until analysis. Liver total lipids were extracted by the method of Folch et al. The phospholipid fraction was isolated by TLC, and methyl esters were prepared and analyzed by capillary gas chromatography. The results indicate that 20:5ω3 is quickly incorporated into the liver phospholipids, even if previously fed a great excess of ω6 fatty acids. In the liver phospholipids, 20:5ω3 does not stoichiometrically replace 20:4ω6. In fact, the reduction in 20:4ω6 is greater than the amount of 20:5ω3 incorporated. The data indicate that 20:5ω3 is very quickly lost from liver phospholipids when the diet is switched from 10% MO to 10% CO or when the animals are starved. The data are illustrative of phenomena of stress.

E2

Human Epidermis Transforms Eicosapentaenoic Acid To 15-Hydroxy 5,8,11,13,17-Eicosapentaenoic Acid: A Potent Inhibitor Of 5-Lipoxygenase. Craig C. Miller, University of California, Department of Dermatology, T.B. 192, Davis, CA 95616, and Vincent A. Ziboh, University of California.

Although fish oil has been used in the management of hyperproliferative, inflammatory skin disorders such as psoriasis, the mechanism of its effect remains unknown. In psoriatics given dietary supplements of fish oil, clinical improvement was linked to elevated epidermal levels of eicosapentaenoic acid (EPA; 20:5n3), a major constituent of marine oils. Prompted by this finding, we investigated the fate of EPA in the epidermis. We incubated human epidermal cytosolic enzyme preparations with ^{3}H-20:5n3. Radiometabolites were separated by high performance liquid chromatography (HPLC) and identified by comigration with known standards. Results showed that the major metabolite of EPA in the epidermis cochromatographed with the hydroxy fatty acid 15-hydroxy-5,8,11,13,17-eicosapentaenoic acid (15-OH 20:5). Identification of the product as 15-OH 20:5 was confirmed by gas chromatography/mass spectrometry (GC/MS). Since 15-hydroxy fatty acids are reported to inhibit 5-lipoxygenase activity, an enzyme whose products are known to play a role in the pathogenesis of psoriasis, we tested varying concentrations (0-50μM) of 15-OH 20:5 on 5-lipoxygenase activity from rat basophilic leukemia cells (RBL-1). Analysis showed that 15-OH 20:5 is a potent inhibitor of 5-lipoxygenase activity ($1C_{50} \cong 20\mu M$). These results suggest that the ameliorative effects of fish oil on hyperproliferative, inflammatory skin disorders may be due in part for the inhibitory effect of 15-OH 20:5 on 5-lipoxygenase activity. (Honored Student presentation.)

E3

Human Absorption Of Fish Oil Eicosapentaenoic Acid (EPA) and Docosahexaenoic Acid (DHA) As Triacylglycerols, Free Acids or Ethyl Esters. Larry D. Lawson, Murdock Pharmaceuticals, Inc., 10 Mountain Springs Parkway, Springville, UT 84663, and Bronwyn G. Hughes, Murdock Pharmaceuticals, Inc.

The short-term rise in plasma triacylglycerol fatty acids after ingestion of single doses of fish oil as triacylglycerols (TG), free acids (FA) or ethyl esters was used to estimate the absorption of EPA (1.0 g/dose) and DHA (0.7 g/dose). Linseed oil TG, containing 1.1 g/dose of alpha-linolenic acid (ALA), was given simultaneously as a standard for complete absorption. Blood samples were taken hourly for 8 hours after ingestion, the plasma TG isolated and the fatty acids quantitated by gas chromatography using an internal standard. Maximum concentrations of EPA, DHA, and ALA in plasma TG were usually achieved 5 hours after ingestion. When the fish oil was administered as free acids, EPA and DHA were absorbed equally as well as ALA. As triacylglycerols, however, EPA and DHA were absorbed only 71 ± 13%(S.D.) and 60 ± 11% as well as ALA-TG or as EPA-FA and DHA-FA ($P<0.001, n=8$). EPA-TG was absorbed somewhat better than DHA-TG ($p<0.05$). The ethyl esters of EPA and DHA were only absorbed 22 ± 6% and 25 ± 13% as well as ALA-TG or as EPA-FA and DHA-FA ($P<0.001, n=6$). These results agree with the in vitro pancreatic lipase studies which have shown that triacylglycerols containing fatty acids with a double bond near the carboxyl-end are poor substrates. The first double bonds for EPA and DHA are at positions 5 and 4, respectively. In summary, EPA and DHA were completely absorbed only as FA, moderately absorbed as TG and poorly absorbed as ethyl esters.

E4

Some EPA Artifacts In Heated Oils. R.C. Wijesundera, Canadian Institute of Fisheries Tech., Technical University of Nova Scotia, P.O. Box 1000, Halifax, NS B3J 2X4, Canada, and W.M.N. Ratnayake (speaker) and R.G. Ackman, Canadian Institute of Fisheries Tech.

It is sometime now since it was shown that the Greenland Eskimos have a low incidence of cardiovascular disease although they eat a diet that is high in fat and animal protein. This apparent anomaly has been explained in terms of the marine nature of their diet, with EPA as the beneficial component. Nowadays, increased consumption of EPA, in the form of fish and shellfish in the diet or fish oil capsules, is being actively promoted. Either way, the EOA is subjected to some degree of heat treatment before consumption. This study was addressed to the effect of heat on EPA. Heating EPA at 220 C for 5 hrs under nitrogen resulted in the formation of several new products (15÷17%). They were isolated by silver ion chromatography and identified by a combination of chemical and physical techniques as a complex mixture of *cis/trans* isomers of EPA. No evidence was found for any positional isomerization.

E5

The Lipids Of The Greenland Eskimo Mummies, Or Five Hundred Years In The Freezer. Ralph T. Holman, The Hormel Institute, University of Minnesota, 801 16th Avenue NE, Austin, MN 55912, and Susan B. Johnson, Fred Phillips and Fred J. Pusch, The Hormel Institute, and J.P. Hart Hanson, Gentafte Hospital.

Lipids from adipose tissue from the desiccated and frozen remains of four mummies found at Qilakitsoq in Northwestern Greenland, dating from 1460 AD ± 50 years, were subjected to analysis for lipids and for fatty acid composition. Total lipids were extracted and separated into lipid groups by this layer chromatography for subsequent analysis of their fatty acids. Other aliquots were

used for quantified lipid analysis by HPLC. The total lipid extract was also converted to methyl esters for separation into saturated, monounsaturated and polyunsaturated acids. The monoenoic asters were separated by chain length HPLC and each fraction was subjected to ozonolysis to measure the proportions of isomers present. The composition of lipids and fatty acids indicates extensive degradation of the original lipids.

Session F Monday morning

Physical Chemistry of Fats and Oils I

F1

Fat Crystal Networks—Structure and Rheological Properties. J.M. deMan, University of Guelph, Department of Food Science, Guelph, ONT N1G 2W1, Canada.

The solid character of plastic fats is the result of the presence of a certain percentage of crystallized fat. Although methods are now available for the measurement of solid/liquid ratios, there is no conclusive theory which will relate crystal size and shape, solid fat content and rheological properties. It is generally assumed that plastic fats contain a three-dimensional network of fat crystals, held together by primary (non-reversible) and secondary (reversible) bonds. The exact nature of these bonds is not well known and several theories have been put forward. Newer methods, especially electron microscopy, show a more complex network than was postulated before. It has now become possible to count absolute numbers of crystals in a fat as well as determining size distribution. Examples of laser based techniques will be given.

F2

Polymorphic Behavior Of Palm Oil and Palm Oil Products. V.F. D'Souza, University of Guelph, Department of Food Science, Guelph, ONT N1G 2W1, Canada, and J. deMan, University of Guelph.

Palm oil, hydrogenated palm oil and palm stearin were stored at 5 C for 0, 3, 7, 14, 28 and 56 days respectively. The melting and crystallization behavior was examined by Differential Scanning Calorimetry. Shifting of major transition peaks were observed in palm stearin and palm oil. Palm stearin exhibited two melting peaks at 53.0 and 61.0 C. This indicates the formationof higher melting crystals due to polymorphic transition. Hydrogenated palm oil exhibited identical melting behavior suggesting highest polymorphic stability. Polymorphic transition was measured by X-ray diffraction patterns and crystal growth by polarized light microscopy. X-ray diffraction bands were quantified by using a laser scanning densitometer. The crystal structure of the samples remained mostly in the beta prime form up to 56 days of storage. The beta prime content increased with time. Samples were also subjected to temperature cycling between 5 C and 25 C. Repeated cycling caused no change in the melting profile. (Honored Student presentation.)

F3

Effect Of Addition Of Palm Oil On The Polymorphic Stability Of Hydrogenated Canola Oil. J.M. deMan, University of Guelph, Department of Food Sciences, Guelph, ONT N1G 2W1, Canada, and Peck Hong Yap, University of Guelph.

Palm oil was added to canola oil before and after hydrogenation and polymorphic stability determined by X-ray diffraction analysis and crystal size estimated by polarized light microscopy. Palm oil added at the 10% level before hydrogenation and 15% after hydrogenation was effective in increasing polymorphic stability in nonselectively hydrogenated canola oil. The beta prime stabilization effect of palm oil is most likely caused by increased diglyceride content and by decrease in the fatty acid homogeneity of the hydrogenated oil.

F4

Polymorphism Of POP. K. Sato, Hiroshima University, Faculty of Applied Biological Science, 2-17, Midori-cho, Fukuyama 720, Japan, and T. Arishima, Hiroshima University, K. Ojima, N. Sagi and H. Mori, Fuji Oil Co.

The polymorphic modifications of POP were identified with X-ray diffraction (XRD), DSC and optical microscope by using the pure samples (>99%). Six polymorphs; α, γ, pseudo-β'_2, pseudo-β'_1, β_2 and β_1 were obtained. In addition, the 99.2% sample crystallized another form, δ, but the 99.9% sample did not. The four polymorphs, α, γ, β_2 and β_1, revealed the XRD and DSC patterns quite similar to the four forms of SOS nomenclated by the same symbols. Peculiarity of POP was partly revealed in the two intermediate forms of pseudo-β'_2 and pseudo-β'_1 which have the XRD short spacing patterns similar to pseudo-β' of SOS. However, their XRD long spacing data looked to be fitted to double chain length structure like α of SOS and POP, although γ, β_2, β_1 of SOS and POP and Pseudo-β' of SOS are triple chain length. The melting points of pseudo-β'_2 and pseudo-β'_1 differed by 3.2 C. As for the more stable forms, β_2 and β_1, the identification was also supported by observation of the single crystal of each form crystallized from solution. β_2 are irregular needle shape, whereas β_1 was well-defined crystal shape. The polymorphic transformation monotropically underwent from α to β_1, although the conversion involving pseudo-β'_2 and pseudo-β'_1 was complicated. Another peculiarity of POP was revealed in enthalpy value of the melt crystallization of α: $\Delta H_c(\alpha)$ = 68.1 kJ/mol. This value was quite larger than those of SOS (47.7 kJ/mol, 99.0%) and AOA (C_{20} acid, 60.2 kJ/mol, 94.5%). Hence, it is concluded that the double chain length structure in the α form of POP is of more stable packing than the others. The change in the subcell structures during the transformation processes seemed to occur independently in the oleic and saturated acid lamellae when the triple chain length structure was attained.

F5

Rystallization Of Polymorphs Of POP and SOS. T. Koyano, Feiji Seika Co., Food R & D Laboratories, 580, Horikawa-cho, Saiwai-ku, Kawasaki 210, Japan, and I. Hachiya, Meiji Seika Co., H. Mori, Fuji Oil Co., T. Arishima and K. Sato, Hiroshima University.

The melt crystallization of the polymorphs of SOS: α, γ, pseudo-β',β_2 and POP: α, γ, pseudo-β'_1, β_2 and $\beta<_1$

was examined using pure samples (>99%). Induction time τ for newly occurring crystals in the melt phase was measured with polarizing microscope equipped with a temperature-controlled growth cell. τ-1, a measure for the crystallization rate, was obtained for each polymorph of every substance whose identification was done with X-ray diffraction and DSC simultaneously. Two methods of crystallization, melt-cooling and melt-mediated, were applied; the latter is the recrystallization of the more stable forms from the melt which was formed by rapidly raising the temperature of the less stable polymorphs just above their melting points, e.g., α-melt or γ-melt mediated crystallization. Both crystallizations presented common results for SOS and POP: the rates of crystallization were always higher in the less stable forms than the more stable ones, and conversely β_2 only crystallized via γ-melt mediated. β_1 did not crystallize in the present study. The rate of melt-mediated crystallization was alway higher than the melt-cooling, when the crystallization was examined at the same range of temperature in which either forms occurred exclusively, was clearly defined by the two crystallization methods. Conclusively, the present study gave another proof for existence of at least five (SOS) and six (POP) polymorphs which were first detected by the polymorphic transformation in a crystalline state. The crystallization behavior of mixtured system of POP and SOS will also be presented.

F6

Kinetics Of Crystallization In Simple Triglycerides. Allen E. Blaurock, Kraft Inc., Technology Center, 801 Waukegan Road, Glenview, IL 60025, and Frank J. Sasevich and Thomas M. Eads, Kraft Inc.

The kinetics of crystallization of the simple triglycerides tri-laurin, -palmitin, -stearin and -olein have been studied as a function of temperature (T), using the PE DSC-7. Crystallization occurred during cooling scans and/or isothermal scans of the supercooled liquid. Melting scans were done to measure the amounts of beta prime and beta polymorphs that had formed at various times; the amount of alpha could not be determined reliably in this way. As expected, crystallization is very rapid at or below T_a, the melting T of the alpha polymorph. Both alpha and beta prime crystals form at temperatures only slightly below T_a is while alpha crystals alone are found after cooling rapidly to $T \ll T_a$. In isothermal scans where $T_b, > T > T_a$ the delay in onset of crystallization of the supercooled liquid varies strongly and non-linearly with T. The melting endotherms show formation of beta prime, which increases to a maximum and then drops to zero, and beta, which increases to a maximum and remains there. Nucleation is limiting for $T_b, < T < T_b$ and onset of crystallization is a random event and can be delayed for many hours. The kinetics of crystallization were found to depend strongly on chain length and degree of unsaturation as well as on T.

Session G Monday morning

Oilseed Outlook

G1

USDA'S 1988 Oilseed Production and Consumption Outlook. Philip Mackie, Foreign Agricultural Service, U.S. Department of Agriculture, Room 5646 South Building, Washington, DC 20250-1000.

Changing worldwide production and consumption patterns for oilseeds as well as fats and oils affect supplies of raw materials and their cost in the United States. The speaker will review the latest data on the 1988 southern hemisphere harvests, the outlook for 1988 harvests in the northern hemisphere, and the current forecast for 1988 worldwide and domestic demand.

G2

1988 Oilseed Futures Outlook. Mario P. Baletto, Merrill Lynch Capital Markets, Merrill Lynch World Headquarters, North Tower, World Financial Center, New York, NY 10281-1216.

Production, demand, weather, monetary fluctuations and many other factors affect the the rise or fall of oilseed commodity prices. The speaker will look at the current status of many of these factors and how these might affect oilseed prices, with particular emphasis on the soybean complex, during the rest of 1988.

G3

World Situation and Outlook For Major Oils & Fats. Thomas Mielke, Oil World, ISTA Mielke GmbH, P.O. Box 90 08 03, 2100 Hamburg 90, West Germany.

The author will briefly outline the effects of the substantial boost in EEC oilseed production during the past couple of years on net imports of oilseeds as well as on the imports, eports and the composition of disappearance of oils and fats. The boost of 3 mill.T in EEC oilseed production this season has not created another surplus of oils and meals on the world market. Crop failures in India, the USSR and some other countries plus another increase in world demand of oils as well as of oilmeals will cause the stocks/usage ratio of oilseeds to decline in the second consecutive year. The Soviet soybean meal import policy will hold a major key this season concerning the volume of crush, the extent of the decline in oilseed stocks as well as concerning the development of world production and inventories of major oils and fats. Thomas Mielke will speak on the features of the new Oil World supply and demand projections. What is the medium-term price outlook? Will world stocks of vegetable oils decline and the oil prices gain relative to meals in April/Sept. 1988? The development of world inventories of vegetable oils in April/Sept. 1988 will depend on a) the world demand for oilmeals (particularly of the USSR), b) production of palm, palmkernel and coconut oils as well as c) on the world demand for oils. What lies ahead? The writer will give a very tentative view on propective EEC area, yields and production of oilseeds for 88/89.

G4

1988 Outlook For Specialty Crops and Oils. Joseph Smith, Oilseeds International Ltd., 855 Sansome St., Suite 100, San Francisco, CA 94111.

While specialty crops and oils are affected by many of the same factors that influence market-dominating

oilseeds and oils, the specialty crops production, consumption and prices are affected by other factors unique to their markets. The speaker will look at the current situation, then outline potential results for the rest of 1988 for specialty crops such as safflower.

G5

Annual Surveys Of Regional Patterns In Soybean Protein and Oil Content. Charles R. Hurburgh, Jr., Iowa State University, 219C Davidson Hall, Ames, IA 50011, and R.A. Hartwig and T.J. Brumm, Iowa State University.

Annual protein and oil content data on a regional basis are not currently available in the public domain. Iowa State University conducted surveys of the U.S. soybean crop in 1986 and 1987, using two sample-collection methodologies. In 1986, we received samples mailed by growers; in 1987 we tested grower samples and samples used by USDA to estimate national production. All analyses were done by near-infrared reflectance. There were economically significant regional patterns in soybean protein and content. Statistical differentiation could be done by region (group of states), individual states and in some states, crop reporting district within a state. The USDA-sample method was more efficient and statistically equivalent to the mailed-sample method. The survey will be continued on an annual basis.

Session H Monday afternoon

Surfactants and Detergents II: Specialty Surfactants

H1

Properties Of Alkane Sulfonates. Khalid Rasheed, Witco Corporation, Organics Division, 3200 Brookfield Street, Houston, TX 77045, and Robert Herke, Witco Corporation.

A series of alkane sulfonates (C_8-C_{14}) have been prepared. The properties of these materials will be presented. This will include foaming, wetting, emulsification and stability to bleach. Solubility in different solvent systems and stability in the presence of acids and bases as well as data on surface tension and interfacial tensions will be discussed.

H2

Dynamic Surface Tension Behavior Of Aqueous Silicone Surfactants. Alan Zombeck, Dow Corning Corporation, Technical Service and Development, 2200 W. Salzburg Road, Midland, MI 48684-0994, and Lenin J. Petroff, Dow Corning Corporation.

A differential bubble pressure technique was used to assess the ability of various surfactants to reduce surface tension. Significant differences were observed among common surfactants in their abilities to reduce surface energies in dynamic systems. Comparing common hydrocarbon, fluorocarbon and silicone surfactants, the silicone surfactants were the most effective at lowering dynamic surface tensions under a variety of dynamic conditions. All dynamic surface tension data were obtained utilizing a computer interfaced differential bubble pressure surface tensiometer. The computer interfacing allows for accurate rampings of bubble pressures, temperature, pH control and data analysis in a timely fashion.

H3

Sodium Alkyl Polyether Sulfonates: Properties, Characteristics, and Applications. William A. Williams, PPG-Mazer, P.O. Box 31, Barberton, OH 44203, and Louis J. Nehmsmann, PPG-Mazer.

Sodium alkyl polyether sulfonates are a novel class of anionic surfactants which exhibit a unique combination of properties and characteristics. The chemistry of these materials is discussed from the viewpoint of their utility in various applications which take advantage of their special combination of properties. Their stability in the presence of oxidative materials and over a wide range of pH is shown. Low critical micelle concentrations, good Ca and Mg tolerance, good emulsification properties, surfactant interactions and sheeting actions are all illustrated in apprpriate formulations and applications. Hard surface cleaning—including glass, metal and liquid dishwashing (ADL)—is highlighted. The effectiveness of these structures in various types of emulsion polymerizations, including high acid systems, will be discussed.

H4

Phosphate Esters: Solubility Factors That Influence Detergency. Joseph A. Komor, Mona Industries, Inc., 76 East 24th Street, Paterson, NJ 07544.

Hard surface detergency properties of anionic phosphate ester type surfactants are controlled by their solubility and solution properties. Soil removal efficiency is primarily dependent upon the critical micelle concentration of the surfactant in the test solution. A relationship between the spreading coefficient and wetting with detergency can be observed. Each of these dynamic properties can be related to the structural compositions of these surfactants. The relative importance in selecting the proper nonionic intermediates, and the control of mono- and diester ratios and residual nonionics in these surfactants in regards to detergency and solubility will be discussed as well as the selective use of phosphate esters as hydrotropes to enhance the detergency process.

H5

Properties of Detergent Builder Solutions Containing Various Alkylated Diphenyloxide Disulfonates. T.J. Loughney, Dow Chemical Company, Secialty Chemicals, 2040 Dow Center, Midland, MI 48674.

Physical properties of common detergent builder solutions as affected by level and molecular weight of alkylated diphenyloxide disulfonates have been measured. Solubility phase diagrams, foam height, wetting times, surface tension and contact angle measurements are reported. The builder solutions include TSPP, TKPP, Sodium Citrate, NTA and Sodium Meta Silicate. This data is useful when formulating concentrated products.

H6

Surface Active Polyether Amines. Carter G. Naylor, Texaco Chemical Company, P.O. Box 15730, Austin, TX 78761.

Ethoxylates of fatty alcohols and alkylphenols are converted to primary amines by a two-step process. Solubility and surfactant properties of the amines are dependent on pH and oxyethylene chain length. They and their ammonium salts have advantages over fatty amines, such as solubility in water and high ionic strength brines, low odor and compatibility with anionic surfactants. At pH values below their pKa the amines have cationic surfactant behavior.

H7

Some Synergistic Properties of N-Alkylpyrrolidones, A New Class Of Surfactants. Zhen Huo Zhu, Brooklyn College, Surfactant Research Institute, City University of New York, Brooklyn, NY 11210, and Harun Ayanzen and Milton J. Rosen, Brooklyn College.

N-Alkylpyrrolidones, a new class of commercial surfactants, interact synergistically with anionic surfactants. Mixtures of the N-2-ethylhexyl-(C2,6P), N-octyl-(C8P), N-decyl-(C10P) and N-dodecyl-(C12P) pyrrolidones with commercial linear sodium alkylbenzenesulfonate (LAS) were investigated. Measurement of the molecular interaction parameter, $\beta°$, for mixed monolayer formation in these mixtures indicated that they show synergism in surface tension reduction effectiveness. The N-alkylpyrrolidone-LAS mixtures also show synergism in Ross-Miles foaming and in Draves (skein) wetting.

H8

Oilfield Applications Of A Novel Amine. F.W. Valone, Texaco, Bellaire, Texas.

Many oilfield corrosion inhibitors consist of salts prepared by reacting a tall oil fatty acid with an amine such as coco amine or tallow amine. A novel, cost-effective series of corrosion inhibitors have recently been prepared utilizing the amine, MNPA-750. This primary amine is prepared by alkoxylation of nonylphenol, followed by amination. This paper will present comparative laboratory corrosion test data for MNPA-750 formulated inhibitors versus those prepared from tallow amines and alkoxylated tallow amines. In addition, results from field tests with one MNPA-750 formulated inhibitor will be included.

Session I Monday afternoon

Pharmacological Effects of Lipids II: Dietary Lipids and Tumor Development

I1

Prostaglandins and Tumor Growth and Dissemination. Silvio Garattini, Istituto di Ricerche Farmacologiche, "Mario Negri", Via Eritrea 62, Milano 20157, Italy, and Roberto Fanelli and Chiara Chiabrando, Istituto di Ricerche Farmacologiche.

Arachidonic acid (AA) metabolites produced through the cyclooxygenated pathway (prostaglandins and thromboxane, PG) have been proposed as modulators of a number of biological events involved in cancer growth and dissemination. The large number of data on this topic can be summarized as follows: (a) Neoplastic tissues can synthesize higher amounts of PG than normal tissues; (b)The synthetic potential for selected PG of some experimental tumors is highly increased during tumor growth; (c) Different PG have been shown to positively or negatively affect tumor growth or metastasis when administered *in vivo* or *in vitro*; (d) A different synthesis capacity for specific AA metabolites has been demonstrated in highly metastatic as compared to poorly metastatic tumor cell lines; and (e) Administration of non-steroidal anti-inflammatory drugs (PG synthesis inhibitors) or thromboxane synthetase inhibitors to tumor bearing animals resulted in conflicting evidence about the capacity of these drugs to reduce tumor growth and spread. Despite the large body of evidence suggesting a role for PG in tumor growth and dissemination, the precise relationship between arachidonic acid metabolism and malignancy has not been conclusively defined. A number of critical issues regarding the data available so far should be considered for future studies: (a) Although different tumors can synthesize different AA metabolites, probably according to their cellular origin, most authors focused on a single PG as an index of global PG synthesis. Since it has been demonstrated that different PG can exert diverse and often opposite effects on tumor biology, the description of complete AA metabolic profiles in the different tumors studied should be preferred to the study of selected products; (b) Many authors have measured PG by immunological methods (RIA) without sample purification and validation by chemico-physical methods such as mass spectrometry. The specificity of RIA has often proven to be insufficient especially in the field of prostanoid analysis; (c) Most data on PG synthesis by tumors describe the potential capacity of neoplastic cells to synthesize prostanoids. Although this approach might be useful for describing differences among various tumors and tissues in different experimental conditions, the results might reflect only a different composition of membrane lipids or enzyme endowment but not necessarily the metabolic profile changes induced by these drugs (e.g. AA metabolic diversion toward other Pg after selective inhibition of thromboxane synthetase) were rarely documented. Moreover, it has been recently shown that the *in vivo* relevance of *ex vivo* documented PG inhibition should be carefully evaluated, since doses of aspirin or dazmegrel (athromboxane synthetase inhibitors) which almost completely block the capacity of platelets to form thromboxane *ex vivo* only slightly inhibited its *in vivo* synthesis. Therefore, new approaches taking into account all these critical issues should be developed for studying the relationship between AA metabolism and malignancy. In particular, more specific methods of detection and a more direct evaluation of the *in vivo* PG synthesis (e.g. by non-invasive measurement of urinary AA metabolites) should be used for future studies.

I2

Prostaglandin A and J—Antiproliferative, Antiviral Activities and The Mode Of Action. Masanori Fukushima,

Aichi Cancer Center, Department of Internal Medicine, Chikusa-ku, Nagoya, 464 Japan.

In the past two decades numerous reports showed antiproliferative effect of prostaglandin(PG)s of E, D, A and J. Recently we have clarified that in the presence of serum, PGE2 and PGD2 are enzymatically dehydrated to PGA2 and Δ^{12}PGJ2, respectively. Several lines of evidences indicate that actual antiproliferative activity is exerted by such ultimate metabolites and PGE2 or PGD2 serves only as a precursor of the active compounds. Therby, active α, β-unsaturated ketone in the cyclopentenone ring of PG is the active moiety to excert antiproliferative activity i.e. cytotoxicity. The cytotoxicity of Δ^7PGA1 which is several times more potent than PGA1 is found to be potentiated further 10 fold by the introduction of both 10-Cl- and 12-OH-. At a non-cytotoxic dose such PGs induce cell growth inhibition by blocking the cell cycle at G1/S. The concentrations of these PGs required for cell cycle block are paralleled with those for cytotoxic activity suggesting that active α, β-unsaturated ketone is also responsible for the reaction leading to cell cycle block. We recently have demonstrated that such PGS, A and J are actively incorporated into the cells, and they are transferred to the nuclei, and covalently bound to nucleoproteins. At the concentration evoke antiproliferative activity, these PGS inhibit cellular uptake of precursors such as thymidine, amino acids and glucose, and eventually DNA polymerase β was found to decrease. Recently, such PGs are found to suppress viral replication at noncytotoxic doses. All of the above facts indicate that PGA and J constitute a unique PG category awaiting further investigations.

I3

Dietary Fat and Colon Cancer: Effect Of Type and Amount Of Fat. Bandaru S. Reddy, American Health Foundation, Division of Nutrition and Endocrinology, Valhalla, NY 10595.

Since Wynder and Shigematsu in 1967 first suggested that high dietary fat is a risk factor in colon cancer, there have been numerous human epidemiologic and laboratory animal model studies to test this hypothesis. Several studies using laboratory animal models suggest that not only the amount of fat but also types of fat differing in fatty acid composition are important factors in colon tumor development. Chemically-induced colon tumor incidence was increased in rats fed semipurified diets containing 23% corn oil, safflower oil, lard or beef tallow compared to those fed 5% corn oil, safflower oil, lard, or beef tallow diets. Diets containing 23% coconut oil, olive oil or fish oil, or high fat diets containing varying levels of trans fat had no colon tumor enhancing effects compared to their respective lowfat diets. The stage of carcinogenesis at which the effect of dietary fat is exerted appears to be mostly during the post-initiation phase of colon carcinogenesis, rather than during the initiation phase. Although the mechanisms by which various dietary fats increase the colon carcinogenesis are not fully understood; in most instances, however, the high fat diet appears to enhance colon carcinogenesis through its elevation of agents such as secondary bile acids that act as promoters of tumor development. Lack of colon tumor promotion by dietary fish oil and *trans* fat appears to be mediated through their effect on mucosal ornithine decarboxylase activity and colonic secondary bile acids.

I4

Effects Of Dietary Fat On Pancreatic Carcinogenesis In The Syrian Hamster. Diane F. Birt, University of Nebraska Medical Center, Eppley Inst. for Research in Cancer, 42nd and Dewey Avenues, Omaha, NE 68105.

Pancreatic cancer induced by N-nitrosobis(2-oxopropyl)amine (BOP) in the Syrian hamster is of a ductular morphology and thus this system provides an excellent model for human pancreatic cancer. This model was used to assess the influence of low (4.5 gm/385 kcal), medium (9.0 gm/385 kcal), and high (18.0 gm/385 kcal) corn oil diets fed with low (9 gm/385 kcal), medium (18 gm/385 kcal) and high 36 gm/385 kcal) casein levels on pancreatic carcinogenesis by 10 mg BOP/kg body weight given in a single injection. When fed with the low protein level following carcinogen treatment, the different dietary fat levels had no influence on pancreatic carcinogenesis. However, when fed with the medium or high protein diets, a 5- to 6-fold increase was observed in the yield of pancreatic cancer in hamsters fed the high fat diet in comparison with the low fat diet. In this initial investigation hamsters were allowed to consume diet *ad libitum* and animals fed the high fat diets consumed more calories. In more recent studies, the effects of low and high corn oil diets at a control protein level were compared in animals fed in a controlled manner and in animals fed *ad libitum*. The controlled feeding regimen allowed low and high fat animals to consume equivalent calorie allotments. Carcinoma yield was elevated 3 to 5 times in hamsters fed high fat diet in comparison with low fat diet irrespective of the method of diet feeding. Ongoing studies are determining the influence of low and high levels of a more saturated fat (beef tallow) on pancreatic carcinogenesis.

I5

Comparative Effects Of Butter, Margarine, Safflower Oil, and Dextrin On Mammary Tumorigeneses In Mice and Rats. Susumu Yanangi, Dept. of Biochemistry, Nara Medical College, Shijo-cho Kashihara, Nara, 634 Japan, and Mariko Yamashita, Mitsuaki Sakamoto, Kyoko Kumazawa and Shunsuke Imai, Nara Medical College.

The purpose of this study was to determine whether butter and margarine exert different influences on mammary tumorigenesis. In the first experiment 4-week-old femal DD/Tbr mice were divided into 5 dietary treatment groups and fed *ad libitum* one of the following diets: a basal diet (N) and the same basal diet enriched with 20% dextrin (D), 20% butter (B), 20% margarine (M), and 20% safflower oil (S), respectively. Spontaneous development of mammary tumors was observed without any other experimental treatment than the diets for 105 weeks until all the mice died out. No significant differences in body weights were observed among the experimental groups. Percent incidences of mammary tumors were significantly lower in B and D groups than in N, M and S groups (7.1 and 21.1 vs. 47.1, 42.9 and 44.4%, respectively). To confirm the lower incidences in D and B groups 6-week old female Sprague-Dawley rats were divided into 5 groups and each group was fed *ad libitum* one of the above experi-

mental diets. All the rats were given a single dose of 5.0 mg DMBA ig at 7 weeks of age. In the 20th week after the DMBA administration the body weight of D group was significantly lower than those of the high fat groups. The percent incidence of mammary tumors in B group was also significantly lower than those of N and M groups (40.0 vs. 56.5 and 66.7%, respectively), however, the incidence in D group (52.0%) was not so low as in the mice. Tumor sizes and tumor numbers per tumor-bearing rat in S group were higher than in any other groups, although the incidences of the tumor were lower in S group (46.2) than in N and M groups. The results suggest that butter has a protecting effect on the incidence of mammary tumor.

I6

Medium Chain Triglycerides and Experimental Mammary Carcinogenesis. L.A. Cohen, American Health Foundation, Division Nutri. and Tech., Dana Road, Valhalla, NY 10595.

The N-nitrosomethylurea-induced rat mammary tumor model was used to assess the tumor-promoting effects of a high-fat (HF) diet containing a 3:1 mixture of medium chain triglycerides (MCT) and corn oil, with that of a HF (23% wt/wt) and low-fat (LF) corn oil (5% wt/wt) diet. Serum and tumor lipid content and fatty acyl (FA) group composition were also determined in the three dietary groups. Rats fed MCT exhibited significantly decreased tumor incidence and increased latency when compared to rats fed a HF corn oil diet (tumor incdence, 87%, 63:, and 60% respectively for HF corn, LF corn and MCT groups). Total serum cholesterol was markedly depressed in the HF corn group compared to the LF corn and MCT groups. In general, serum FA profiles reflected that of the diet particularly with regard to the essential fatty acid, linoleate (LA) which comprised 56% of total corn oil FA. The serum of the HF corn group exhibited 2X more LA than the other 2 treatment groups (28% vs. 13%). Tumor neutral lipid profiles were similar to serum with the exception that LA made up a greater proportion of the total (43% vs. 28% and 19% for HF corn, LF corn and MCT respectively). Tumor phospholipid (PL) profiles were also reflective of serum and dietary LA levels (11% vs. 4% and 5% respectively). Tumor PL arachidonic acid levels, on the other hand, did not differ among the 3 treatment groups indicating that incorporation into membranes of this key metabolite of dietary LA is resistant to variations in dietary fat intake. Medium chain length FA -C10:0, C12:0 - were found only in the tumor neutral lipid fraction in very small amounts (<1%). These results are consistent with the hypothesis that tumor promotion by dietary fat is more a function of the type than the amount of fat consumed. In addition, they suggest that MCT, due at least in part to their unique physical and chemical properties (i.e., not transported in lymph or chylomicrons, not incorporated into membranes, rapidly oxidized), exert markedly different effects on mammary tumor development than conventional long chain saturated and unsaturated FA.

I7

Selective Antineoplastic Effects Of Polyunsaturated Fatty Acids. M.E. Begin, Efamol Research Institute, P.O. Box 818, Kentville, NS B4N 4H8, Canada.

A variety of human cell lines were killed following exposure to n-3 and n-6 polyunsaturated fatty acids (PUFA) in vitro whereas the same treatment was not lethal to a variety of normal cell lines. Selectivity of killing was also demonstrated by challenging tumor cells in the presence of normal cells. The cytotoxic effects were time and dose-dependent. All PUFA do not have the same ability to kill cancer cells. The cytotoxic potential was dependent on but not directly proportional to the number of double bonds in the carbon chain. The most extensive cytotoxic effects were obtained with n-6 PUFA containing 3 and 4 double bonds and with n-3 PUFA containing 5 double bonds. Gammalinolenic acid was the cytotoxic PUFA showing the greatest selectivity. Transition metals accelerated the rate of cancer cell destruction whereas the same combination was not lethal to normal cells. Inhibitors of endoperoxide formation failed to block cell death. In contrast, antioxidants inhibited the cytotoxic effect dose-dependently. Since the presence of PUFA in cell membranes makes cells susceptible to damage by lipid peroxidation, the contribuiton of lipid peroxidation in the killing of established human breast cancer cells by GLA was examined. Its effect was also compared with the effect of PUFA of lesser cytotoxic potential on cancer and normal cells. We showed that the killing of cancer cells was fatty acid specific and that the potency of a given PUFA correlated with its extent of intracellular peroxidation but was independent of its ability to synthesize eicosanoids. As nonspecific indicators of lipid peroxidation, we measured the content of superoxide anion and the loss of fatty acid unsaturation in the pohspholipids of PUFA-supplemented cells together with the amounts of oxidized PUFA degradation products as determined by the thiobarbituric acid test. In similar experiments, the extent of peroxidation in supplemented normal cells varied depending on the fatty acid used but was 2-6 times less than the levels found in supplemented tumor cells. There was no correlation between PUFA supplementation, extent of lipid peroxidation and cell death in the normal cells. The results show that PUFA addition induces a greater stimulation of intracellular lipid peroxidation in the cancer cells than in the normal cells resulting in the death of the tumor cells selectively. We suggest that cancer cells are killed as a result of an elevation of toxic peroxidation products generated by the PUFA in the cells. These results imply that exposure of tumor cells to adequate amounts of the right PUFA may constitute a safe and general mean of eliminating cancer cells selectively.

I8

Toxic and Ecological Effects Of Fatty Acids On Microorganisms and Animals. Miyoshi Ikawa, University of New Hampshire, Department of Biochemistry, Durham, NH 03824.

A review is presented where the natural occurrence of fatty acids has been implicated in having toxic and ecological effects on various organisms. Short and medium chain fatty acids can exhibit toxic, repellant and attractive effects. They occur as sexual attractants in insects and primates, serve as insect trail pheromones, and cause insect aggregation. On the toxic and inhibitory side, they occur in the defensive sprays of insects, as

territorial markers in mammals, and as antifungal agents in insects. Longer chain fatty acids, especially unsaturated, have attractive properties for certain insects, but most of the effects reported are toxic. They are present in the "diarrhetic shellfish poison" of scallops, the ichthyotoxin of algae, the hemolytic factor in many tissues, and antifungal agents in certain fungus-infected plants. Evidence suggests that they may also be produced by algae to inhibit the growth of other algae. Studies on the inhibitory effects of unsaturated fatty acids on the growth of the green algae Chlorella suggest that this may be true and have some ecological significance. Arachidonic acid and the eicosanoids occur in a diversity of organisms and exhibit various toxic and other effects. They cause algal toxicity to mammals, are toxic components of marine cone snail venoms and are defensive agents against predators in corals and nudibranches.

I9

Biological Activity Of Synthetic Glycerophospholipids. S. Kluge, Department of Life Sciences, Karl Marx University, Leipzig, G.D.R.

Glycerophospholipids stand out for their extraordinary wide range of biological activity. They occur in small quantities in organisms and play an important role as mediators in physiological processes. Synthetic glycerophospholipids used as xenobiotics demonstrate various effects on erythrocytes, plant protoplasts, bacteria and viruses. Erythrocytes aggregation was triggered by addition of very small amounts of glycerophospholipids. Some of the analogs show a remarkable concentration-dependent effect. The concentration of the most effective compound for triggering platelet aggregation is about tenfold higher than that of PAF-acether. Plant protoplasts isolated from different plant material can be fused by incubation with glycerophospholipids. The fusion rate is high and dependent on the enzymes used for the isolation of protoplasts. Spin label studies suggest changes in the protoplast membrane. Bacteria (*E. coli, Pseudomonas aeruginosa, Rhizobium trifolii*) are influenced by a few glycerophospholipids in a concentration of 0.1 M. Density of bacteria around the holes in agar diffusion test declined as compared with the control. In some cases the formation of radial lysis rays was observed in connection with phages. In low concentrations the compounds reduced the virus content in plant protoplasts without changing the number of infected protoplasts detected by staining with fluorescent antibodies. An antiviral effect could also be found in the virus multiplication in whole plants and in human viruses.

I10

Influence Of Dietary Fat On The Synthesis Of Prostanoids By Colonic Tumors. N. Robblee, Ludwig Institute for Cancer Research, 9 Earl Street, Toronto, ONT M4Y 1M4, Canada, and R.P. Bird (speaker), Ludwig Institute for Cancer Research.

Various studies suggest that prostanoids influence tumor development and effect of dietary fat on tumor growth may be mediated via altered production of certain prostanoids. Previously, we have reported that high fat diets (known to promote colon tumor development) do not alter prostanoid synthesis by normal colons. In the present study F344 female rats were given weekly injections of a colon carcinogen, azoxymethane (15 mg/kg) for two weeks, one week later the animals (25 test and 10 controls/group) were randomly allocated to low or high beef tallow diets. They were killed 32 weeks later. Synthesis of prostaglandin E_2 (PGE_2), prostacyclin and thromboxane A_2 by adenomas, (n=5,—4mm) belonging to low or high fat groups, was measured as their stable metabolites, bicyclic PGE_2, $PGF_{1\alpha}$ and $T \times B_2$ respectively. The level (ng/g tissue/30 min) of PGE_2 was elevated in adenomas compared to the control mucosa and this effect was statistically significant ($P \leq 0.05$) in the high fat groups (3580 ± 878 vs 1717 ± 267). The level of $PGF1\alpha$:$T \times B_2$ was significantly lower than the corresponding control value (i.e. 3.4 vs 12.3 for the high fat group). The present study demonstrates that colonic tumors synthesize altered levels of prostanoids and that the synthesis of PGE2 in the tumors but not in the normal mucosa was influenced by a high fat diet.

Session J Monday afternoon

Flavor Chemistry of Lipid Foods II in honor of Stephen S. Chang

J1

Singlet Oxygen Oxidation In Vegetable Oils. David B. Min, The Ohio State University, Dept. Food Science and Nutrition, 2121 Fyffe Rd., Room 122, Vivian Hall, Columbus, OH 43210-1097.

One of the interesting and important research areas in lipid oxidation of foods is to study the origin of radicals that initiate the autooxidation chain reaction. The initiation of free radicals in vegetable oils may be due to singlet oxygen formed by photosensitizers in foods. The single oxygen initiates the autooxidation of vegetable oils by addition to carbon-carbon double bonds and then abstracts hydrogen from alpha-carbon to double bonds to start free radical autooxidation chain reaction. The singlet oxygen lipid oxidation can be also minimized by natural quenchers in vegetable oils. The kinetics and mechanisms of natural initiator and quenchers in singlet oxygen soybean oil oxidation have been studied by measuring headspace volatile compound formation and oxygen depletion using gas chromatography and peroxide value. Chlorophyll acted as a photosensitizer for singlet oxygen formation. Singlet oxygen was responsible for the initial oxidation of oil in the presence of chlorophyll and light. Free radical oxidation was the main chemical reaction after the chlorophyll was destroyed. The chlorophyll had disappeared within 24 hrs. of storage under light. Interaction effects of chlorophyll and beta-carotene showed that beta-carotene minimized the oxidation of oil by the combination of light filtering and singlet oxygen-quenching effects. The experiment of 3 levels of chlorophyll, 4 levels of beta-carotene and 4 levels of tocopherol showed that tocopherol minimized singlet oxygen oxidation by quenching singlet only. It did not quench excited triplet sensitizer of chlorophyll. Chlorophyll, beta-carotene and tocopherol showed synergistic effects on the minimization of singlet

oxygen oxidation of soybean oil containing 8ppm chlorophyll.

J2

Oxidation Of Lipids By Enzymes. H.W. Gardner, Northern Regional Research Center, USDA, ARS, 1815 North University Street, Peoria, IL 61604.

The enzymic oxidation of lipids by reactions which cause certain characteristic flavors in foods of plant origin will be reviewed. The flavors are produced by a cascade of events involving conversion of linoleic and linolenic acids into volatile aldehydes by sequential action of lipoxygenase and hydroperoxide lyase isoenzymes. The type of flavor aldehydes produced is dependent upon a number of factors; the most important of which is the specificity of isoenzymes involved. Depending on specificity, flavors can range from grassy/beany to cucumber/melon. These flavor considerations will be discussed, including recent research in our laboratory concerning lipoxygenase and hydroperoxide lyase in soybeans. In addition to flavor volatiles, the enzymic oxidation of lipids sometimes causes the formation of compounds that elicit bitter tastes, particularly in cereals. The reaction sequence responsible for bitterness is a lipoxygenase/hydroperoxide isomerase reaction leading to trihydroxy fatty acids. The possible mechanisms of this isomerase will be discussed.

J3

Flavor Chemistry Of Deep-Fat Frying Of Oil. Jan Pokorny, Prague Institute of Chemical Technology, Department of Food Science, Prague CS-166 28, Czechoslovakia.

Under conditions of deep fat frying, oil is exposed to air at high temperatures of 150–180 C. Volatile oxidation products of linoleic are the most important flavor compounds of fried food, articularly dienals, alkenals, lactones, hydrocarbons and various cyclic compounds. Oxidation products of linolenic acids, such as trienals, when present in small amounts, contribute to the fried flavor so that food fried in soybean oil has particularly rich flavor. Oxidation products of oleic acid are of lesser importance. Hydrogenated fats contain isomeric polyenoic acids which may give rise to off-flavors if present in higher amounts. The typical fried flavor is produced only at low access of oxygen, and disagreeable off-flavor compounds are formed if the oxygen level is high; on contrary, only weak and poor flavor is obtained by frying in inert gas. Non-lipidic components of fried foods contribute to the fried flavor, such as amino acids, sugars and essential oils. Degradation products of sulfur-containing amino acids, especially methionine are important, and pyrolytic reactions accompanying the Maillard reaction which give rise to nitrogen, sulfur and oxygen-containing heterocyclic compounds. Fried-flavor compounds are sensitive to oxidation so that the fried flavor is rapidly lost on prolonged storage of fried foods before the consumption.

J4

Rapid Test For The Deterioration Of Frying Oil. Michael M. Blumenthal, Libra Laboratories, Inc., 44 Stelton Road, Piscataway, NJ 08854.

Health inspectors, food processors and foodservice chains require rapid testing of used frying oils for quality control purposes and to determine the proper discard time for the oil. Older quick tests and devices have not been widely applicable for field testing oils in a variety of frying situations. A newly patented colorimetric quick test has been developed which correlates with the performance characteristics of frying oils with regulatory limits and with the major collaborated laboratory test specified by many countries. The new colorimetric quick test performs in minutes, does not require an instrument and is not influenced by type of fryer, frying oil or food fried. The quick test monitors the cumulative changes in an oil as it is heated, with or without food being fried. The test also spots the presence of soluble contaminants in an oil which are contributed by excessive ingredient levels in the fried food. Official laboratory evaluation and extensive use have shown its potential as a screening tool for submitting suspect samples to regulatory or quality control laboratories. Examples of use and supporting chemical data are presented.

J5

Importance Of Lipid-Derived Volatiles To Vegetable Flavor. Ron G. Buttery, Western Regional Research Center, USDA, ARS, 800 Buchanan Street, Albany, CA 94710.

Vegetables usually contain only minute concentrations of lipid, however, many of the most important vegetable flavor components result from oxidative lipid breakdown. The particular types of enzyme systems and the particular chemical make up of the vegetable seem to influence the specific types of lipid (unsaturated fatty acid) breakdown products that predominate. Characteristic lipid derived vegetable aroma compounds include (Z)-3-hexenal (tomato aroma), (E,Z)-2,6-nonadienal (cucumber aroma), (Z)-6-nonenal (watermelon aroma) and 1-octen-3-ol (mushroom aroma). More unusual lipid breakdown products such as 1-nonen-4-one (cooked bell pepper), 1-hexen-3-one (artichoke) and (Z)-4-hepten-2-one (corn) also contribute to vegetable aroma. The importance of lipid derived volatiles to vegetable aroma and their probable origins will be discussed.

Session K Monday afternoon

Protein Symposium I: Effect of Protein Modification on Functionality

K1

Sturcutre—Functional Relationships In Food Proteins: Some Effects Of Modification On Surface Properties. J.E. Kinsella, Cornell University, Dept. Food Science, 106 Stocking Hall, Ithaca, NY 14853, and L. Phillips and Doug Rector, Cornell University.

The functional attributes of proteins are diverse and reflect the structure and physical properties of the protein(s) per se, their interactions with other molecules in the system as these are affected by prevailing environmental conditions. Elucidation of mechanisms responsible for functional properties can be facilitated by the ra-

tional modification of proteins or manipulating environmental factors and monitoring the resultant changes. Modification of the net charge on proteins by altering pH, ionic strength or chemical derivatization, e.g. succinylation, markedly alters functional behavior i.e. solubility, soagulation vs gelation, emulsion stabilization etc. Alteration of molecular "flexibility" by cleavage of disulfide bonds can be useful in improving emulsifying activity. In this presentation the effects of modification of some food proteins (glycinin, serum albumin, β-lactoglobulin) by chemical, (succinylation) enzymatic (transglutaminase) and environmental manipulation (pH, ions) will be reviewed in the context of understanding relationships between structure and functional properties with emphasis on surface properties and protein:protein interactions.

K2

Genetic Modification Of Milk Proteins. Tom Richardson, University of California, Dept. of Food Science & Technology, Davis, CA 95616, and Rafael Jimenez-Flores (speaker), University of California.

The structure-function relationships of many enzymes and other proteins have been studied in a systematic and detailed way by genetic engineering methods. The substitution of a single amino acid in a protein is possible. Substitutions have increased the affinity of an enzyme for its substrate, have made proteins more resistant to oxidation or have enhanced their heat stability. In a broader sense, food protein functionality can also be studied in a systematic way by means of a range of modifications of their primary zmino acid sequence, and their correlation with functionality. Milk proteins constitute a very good model system in which to study food protein functionality given the extensive background information on these proteins and the detailed characterization of their functionality. This paper will focus on the technology involved in the isolation of the cDNAs coding for the major milk proteins, the design of various modifications in the primary structure of such proteins and the possible ways of producing the proteins for their study.

K3

Effects Of Medium Composition and Chemical Modifications Upon Thermal Behavior Of Food Protein. V.R. Harwalker, Agriculture Canada, C.E. Farm, Building No. 55, Ottawa, ONT K1A 0C6, Canada, and C.-Y. Ma, Agriculture Canada.

Effects of medium composition, preheating and chemical modification upon thermal behavior of oat globulin (OG) and β-lactoglobulin (Lg) were studied by differential scanning calorimetry (DSC). High or low pH reduced denaturation temperature (Td), enthalpy ΔH) and cooperativity indicated by increase in width at half height Δ-$T_{1/2}$. The effect of salts was related to their position in the lyotropic series and suggests involvement of hydrophobic interactions in thermal stability of the proteins. Additives such as polyols, ethylene glycol, urea, SDS and reducing agents have profound influence on DSC characteristics. The data indicate that disulfide bonds do not contribute to thermal stability of these proteins. Preheating OG below its Td caused progressive decrease in ΔH and a marked increase in Td and decrease in $\Delta T_{1/2}$ suggesting aggregation of OG to form a more compact structure with high thermal stability and cooperativity. Preheating also caused pronounced increase in activation energy and preexponential factor. Succinylation and carboxyl modification raised Td and broadened endothermic peaks for Lg. The role of different physico-chemical forces contributing to the stability of modified protein will be discussed.

K4

Film Properties Of Modified Proteins. Damodaran Srinivasan, University of Wisconsin - Madison, Department of Food Science, 1605 Linden Drive, Madison, WI 53706.

The differences in the surfactive properties of food proteins are related to variations in the ionic, hydrophobic and conformational characteristics. To elucidate the role of protein conformation on the kinetics of adsorption at interfaces, seven structural intermediates of bovine serum albumin were prepared and their adsorption at the air-water interface was studied. Molecular area calculations indicated two distinct processes, viz., initial anchoring of the molecule at the interface and subsequent reorientation and rearrangement of the adsorbed molecules. While the molecular area cleared for anchoring of the molecule was independent of the conformational state, the area cleared during the reorientation and rearrangement process was dependent on protein conformation. Calculation of diffusion coefficients indicated that greater the unfolded state of the albumin intermediate, greater was the diffusion coefficient. It is shown that the simple diffusion theory is inadequate to explain the kinetics of protein adsorption. Several evidences suggest that in addition to thermal energy and the energy barrier at the interface, the potential energy of the molecule in the subphase, which is related to conformation, may play a controlling role in protein adsorption at interfaces.

K5

Glycosylation Of Beta-Lactoglobulin and Surface Active Properties. Ralph D. Waniska, Texas A&M University, College Station, TX 77843-2474.

The chemical, structural and functional properties of beta-lactoglobulin (bLG) and chemically glycosylated derivatives of bLG were studied to elucidate relationships between their physicochemical characteristics and functional properties. Carbohydrates were coupled to bLG using the cyclic carbonate and carbodiimide methods. The carbohydrates moieties increased the hydrophilicity and decreased the hydrophobicity of bLG. The glycoprotein derivatives had an increased viscosity, positive UV difference spectra, decreased intrinsic fluorescence, and more unordered secondary conformations. The rate of proteolysis increased but the extent of proteolysis decreased after glycosylation. The surface pressure, rates of adsorption and rearrangement and surface viscosity of bLG decreased after glycosylation. Glycosylated derivatives formed foams that retained more liquid and that were stronger than those of bLG. Emulsifying activity of glycosylated proteins were slightly improved. The conformation of glycosylated derivatives of bLG was unfolded slightly. Interfacial films of glycosylated proteins were more stable even though classical surface activity properties decreased. In summary, a protein that contains many hydrophilic and

hydrophobic groups and that denatures at the interface should possess good foaming and emulsifying properties.

K6

Nutritional Aspects Of Dietary Textured Soy Protein—An Overview. George Liepa, Texas Woman's University, P.O. Box 24134, TWU Station, Denton, TX 76204, and Annemarie Richmond, Texas Woman's University.

The processing of vegetable proteins into food products with meat-like characteristics may be considered one of the great food inventions of all time. With increased recognition of the nutritional and economical importance of vegetable protein foods in the past twenty-five years, the food industry has accomplished significant advances in the manufacturing of textured vegetable protein (TVP) products of superior quality. Undesirable antinutritional factors can be removed effectively while nutritional attributes and functional properties can be enhanced. TVP may be processed from amorphous defatted plant protein flours (i.e. soy, cottonseed), which are an important byproduct of the vegetable oil industry. Several texturization processes are available now to produce the basic two types of textured meat-like products: meat extenders and meat analogs. TVPs have found extensive use as extenders of fresh and processed meat products and as meat-like ingredients in many convenience foods. TVP products contain well-balanced essential amino acids and provide an important source of protein nutriture. Substitution of meat with TVP is cost and energy efficient, carries important health benefits (i.e. decreased serum lipids and biliary lipids) and increases the protein food supply while decreasing environmental stress.

K7

Optimization Of Cottonseed Flour Substitution In Food Products. C. Clay King, Texas Woman's University, Dept. of Nutrition and Food Sciences, P.O. Box 24134, Denton, TX 76204, and Mary Ellen Camire, Seyed Emam and Shih Hsiang, Texas Woman's University.

Regression analysis has been used to maximize and optimize the substitution of cottonseed flour for wheat flour in various products. The successful substitution of cottonseed requires the minimization of the adverse effects but at the same time emphasizing the positive effects on quality. Therefore four products and their formulations were chosen. Various levels of cottonseed flour substitution ranging from 0 to 50% by weight were made in brownies, fried meat patties, pie crust, and spinach pasta. The effect on color was measured by the Hunterlab D25 color meter. The Baker compressimeter, Bailey shortometer, and weight loss were other objective measurements made on certain products. An 8-member semi-trained panel evaluated the intensity and acceptability of color, flavor, chewiness and other characteristics. The nutrient composition of the foods was calculated to indicate changes in the nutritional quality due to substitution. Both functional and nutritional values were used in regression analysis to determine the maximum and optimal levels of cottonseed flour substitution. These levels varied for each product but overall ranged from 20–25%, except for meat patties, with a range of 5–10%.

K8

Enhancing The Utility Of Hydrolyzed Vegetable Proteins By Membrane Processing. S.S. Koseoglu, Texas A&M University, Food Protein R & D Center, F.M. Box 183, College Station, TX 77843-2476, and K.C. Rhee and E.W. Lusas, Texas A & M University.

Membrane processing offers several advantages over extraction, evaporation and other separations. These include low capital cost, potential for large savings of energy, production of high quality products (since no heat treatment is required), and the practical abilities to recover desirable compounds or to remove unwanted components from mixtures. In the work reported, 15 membranes [one ultrafiltration (UF) membrane and 14 reverse osmosis (RO) membranes] made from various materials were tested for their abilities to desalinate hydrolyzed vegetable proteins (HVPs). Nine membranes desalinated HVPs with reasonable flow rates ranging from 5.83 l/m2/hr to 57.56 l/m2/hr. Six of these membranes had salt removal capacities above 78.5%, although one membrane removed only 39.3% of the salt. Two membranes yielded almost colorless permeates, indicating retention of most of the HVP in the retentate fraction. Protein and ash analyses of permeates and retentates indicated that about 93% of HVPs were retained in the retentate fractions, while most of the salt passed into permeates. These results document that the salt content of HVP can be reduced by about 75% by using UF and/or RO systems.

Session L Monday afternoon

Physical Chemistry of Fats and Oils II

L1

Polymorphism Of 1,2-Diacyl-SN-Glycerols. Dharma R. Kodali, Boston University School of Medicine, Biophysics Inst., Housman Med. Res. Ctr., 80 East Concord Street, Boston, MA 02118, and David A. Fahey and Donald M. Small, Boston University School of Medicine.

The molecular packing in different polymorphic forms of optically active saturated monoacid 1,2-diacyl-*sn*-glycerols (1,2-DGs) with acyl chain length of 12,16,18,22 and 24 were studied by DSC, x-ray diffraction and vibrational spectroscopy and compared to 1,3 analogues. For all the 1,2-DGs the solvent-crystallized form melted with a single sharp endotherm. The solid phase is β' with orthorhombic perpendicular chain packing (wide angle diffraction 4.3Å^{-1}, 4.0Å^{-1}, and 3.8Å^{-1}; Raman 1421 Cm^{-1} and infrared 729 and 720 Cm^{-1}). The strong sharp infra-red O-H stretching at 3507 Cm^{-1} along with dual C=O absorptions (1730 Cm^{-1}, 1707 Cm^{-1}) of this phase indicated a specific intermolecular hydrogen bonding. On rapid cooling from the isotropic liquid the C_{12}, C_{16} and C_{18} formed a hexagonally packed (4.1Å^{-1}) α-phase which converts to β'-phase after α-phase melting. On quenching C_{22} and C_{24}, a pseudohexagonal (4.1Å^{-1} and 3.8Å^{-1}) bilayered sub α-phase is formed. This phase converts to an α-phase before melting to an isotropic liquid. The bilayer periodicity in both α- and β'-forms of these compounds increased linearly with chain length. The corresponding saturated monoacid 1,3-diacylglycerols do not form α- or β'-phases.

Rather they form solvent crystallized $\beta 1$- and melt crystallized $\beta 2$ forms. Both are triclinic parallel with acyl chain tilts of 79° and 68° and glycerol region thichness of (approximately) 7.5Å. In contrast the 1,2-DGs in the α and β' forms have chain tilts and glycerol thickness of 90° and 66°, 9Å and 7Å respectively. Thus the 1,2-DGs have quite different crystal structures and polymorphism compared to their 1,3 isomers.

L2

Polymorphic Behaviors Of Petroselinic Acid. K. Sato, Hiroshima University, Faculty of Applied Biological Science, 2-17, Midori-cho, Fukuyama, 720 Japan, and N. Yoshimoto, Hiroshima University, F. Kaneko and M. Kobayashi, Osaka University, and M. Suzuki, Nippon Oil and Fats Co.

Two polymorphs of petroselinic acid (C_{18};1ω12) were found to be remarkably different from those of other one *cis*-double bonded acids. High and low temperature forms melt at 30.5 C and 28.5 C, respectively. The two forms always occurred concurrently from the melt phase; the relative ratio of the high-temperature form increased with increasing temperature. The solid-state transformation was irreversible, the low-temperature form converted slowly to the high-temperature form above 25 C, but the opposite case did not occur. The solubility measurement for each polymorph in acetonitrile proved that crystal Gibbs energies of the two forms have the same value at 18.7 C. Hence the transformation in crystal is influenced by steric hindrance due to different molecular structures. The X-ray diffraction patterns of the two forms have no similarity to three polymorphs of oleic acid (C_{18};1ω9), but, instead, the short spacing pattern of the low temperature form is almost the same as that of β form of stearic acid. To support this, the crystal habit of the low temperature form grown from acetonitrile was identical to stearic acid B. More convincingly, infrared absorption spectra showed that the low-temperature form is packed according to O-like stearic acid B. The O-packing in the *cis*-unsaturated acid is exclusively observed in this form. The high-temperature form assumes parallel packing. Accordingly, the conformation of the olefin group was deformed from those in oleic, erucic and palmitoleic acids, so that the perpendicular arrangement of the aliphatic chain is realized.

L3

On The Polymorphism Of Principal *Cis*-Mono-Unsaturated Fatty Acids. K. Sato, Hiroshima University, Faculty of Applied Biological Science, 2-17, Midori-cho, Fukuyama, 720 Japan, and M. Suzuki, Nippon Oil and Fats Co., and M. Kobayashi, Osaka University.

Some characteristic remarks in polymorphism of principal *cis*-mono-unsaturated fatty acids; oleic (C_{18}:ω9), petroselinic (C_{18}:ω12), ascrepic (C_{18}:ω7), palmitoleic (C_{16}:ω7) and erucic (C_{22}:ω9) acids, will be presented. A total number of independent polymorphs, their molecular structures and transformation features for each acid are collectedly discussed, being based on DSC, X-ray and vibrational spectroscopic studies. 1) The polymorphism differs from one acid to others, indicating sensitive influence of the relative position of the double bond in the aliphatic chain. This is most manifest in three C_{18}-acids: the thermal behaviors and molecular structures of the polymorphs of oleic acid (three), petroselinic acid (two) and ascrepic acid (three) are quite different. 2) Order-disorder transformation has been discovered, being characterized by conformational disordering in the chain between the double bond and CH_3 end group. This transformation occurs in oleic acid, erucic acid and palmitoleic acid, but interestigly not in petroselinic and ascrepic acids. 3) The subcell structures (not examined in ascrepic acid) are of parallel chain packing in all polymorphs of oleic, erucic, palmitoleic acids, and high-temperature form of petroselinic acid. However, low-temperature form of petroselinic acid is packed according to a perpendicular chain arrangement. Including this chain packing, overall features of this low-temperature form exhibit close similarity to the B-form of even-numbered saturated acids. 4) Basic conformations of the olefin group are *skew-cis-skew'* in γ of oleic, erucic and palmitoleic acids, and *skew-cis-skew* in β of oleic acid and α_1 of erucic acid. Another conformation may be revealed in the low-temperature form of petroselinic acid, so that the perpendicular chain packing is arranged.

L4

Some Physical Properties Of Shortenings And Margarines. L. deMan, DeMan Food Technology Services Inc., 58 Applewood Crescent, Guelph, ONT N1H 6B5, Canada, and J.M. deMan, University of Guelph.

The solid-liquid ratio in four commercial shortenings and two canola-based margarines was determined directly with the Bruker Minispec pulsed NMR. These values were compared with the solid fat contents determined on the isolated fats, and using different cooling and tempering methods. The solid fat content of the melted shortenings then tempered at 0 C followed the same trend as that of the actual shortenings. The solid fat content of the melted margarine fats was more closely related to that of the actual products when no tempering of the fats took place. Dropping points of the fats and softening points of the products were also compared as were the major melting peaks determined by DSC. No large differences were observed. Penetration values of the products differed widely. Compression tests of cylindrical samples showed characteristics related to different crystal networks.

L5

Rheological Properties Of Shortenings As Affected By Temperature Cycling. P. Chawla, University of Guelph, Department of Food Sciences, Guelph, ONT N1G 2W1, Canada, and J.M. deMan, University of Guelph.

The effect of supercooling followed by temperature cycling at 23 C and 5 C on the rheological properties of various shortenings were studied. With temperature cycling, the solid-liquid ratio as determined by NMR was found to decrease. Similar trends were seen with values on hardness index measured by cone penetrometry and firmness as determined by the penetration of a punch attached to the Instron. The temperature cycled samples showed a decrease in viscoelastic parameters—instantaneous elasticity, retarded elassticity and viscous flow as revealed by creep measurement. X-ray diffraction studies showed that beta crystallinity was produced as a result

of the temperature cycling. Polarized light microscopy showed an increase in the size of the fat crystals as the cycling proceeded. The study revealed that not only the size, shape and form of the crystals was an important determinant of the rheological properties, but also the solid-liquid ratio.

L6

Composition Of Seed Crystals Isolated From Cocoa Butter. Paul S. Dimick, Penn State University, 116 Borland Laboratory, University Park, PA 16802, and Thomas R. Davis, Penn State University.

The seeding of molten chocolate with pre-formed fat crystals is important for achieving the desired temper in chocolate. Proper tempering insures that the cocoa fat present in a confectionery product solidifies in the desired crystalline form, and this form dictates surface gloss, mouth feel, melting point, contractibility and bloom resistance. The objective of this study was to investigate the early stages of cocoa butter solidification; namely, seed crystal formation. Seed crystals were grown statically from melts at 26.5 C. The resulting seed crystals displayed melting points greater than 60 C in contrast to tempered cocoa butter crystals with melt at approximately 31 C. A procedure to separate the high-melting seed crystals from the liquid mass was developed. Compositional analysis revealed elevated phospho- and glycolipid concentrations for the seed crystals in comparison to the cocoa butter from which the seeds were grown. Moreover, the seed crystals had a significantly higher degree of saturated fatty acids as compared to pure cocoa butter, 91.2% vs. 63.2%. Conversely, a decrease in unsaturated fatty acids was observed. The increase in saturation was most highly reflected in the triglyceride composition of the seed crystals. The saturated glycerides, PPS, PSS, and SSS of the seed crystals amounted to 67% while less than 5% of the glycerides of cocoa butter were trisaturated. The elevated melting point of the seed crystals was attributed to the presence of the phospho- and glycolipids in addition to the abundance of saturated glycerides.

L7

The Development Of Empirical Energy Parameters For Triglycerides. Richard H. Lee, Kraft Inc., Technology Center, 801 Waukegan Road, Glenview, IL 60025.

Theoretical chemical studies of triglycerides require a suitable mathematical model to describe the behavior of the molecules in a crystal environment. Because of the large number of atoms in a typical triglyceride molecule, only empirical energy methods can be employed. Here a strategy is presented for the development of such energy parameters for these compounds. The intermolecular interactions seen in a crystalline environment were simulated by using an algorithm employing periodic boundary conditions. The values of the parameters were adjusted iteratively until the minimum energy conformation of the beta form of trilaurin closely resembled that seen by single crystal X-ray diffraction. The resulting parameter set was tested by comparing the predicted minimum energy conformations of 11-bromoundecanoic mono- and diglycerides with their X-ray crystal forms.

L8

Polymorphic Behavior In Mixtures Of Saturated Triglycerides: Effect Of Sorbitan Esters. Nissim Garti, The Hebrew University of Jerusalem, Casali Institute of Applied Chemistry, Jerusalem 91904, Israel, and Judith Aronhime and Sara Sarig, The Hebrew University of Jerusalem.

It is known by our recent results on polymorphic behavior of fats that the presence of solid surfactants affects the kinetics of transformations in tristearin and inhibits the crystallization of the form during heating in the DSC. It was found that the addition of a saturated triglyceride with different chain length has also a kinetic effect on the transformation, different from that of the emulsifier. It is known in the literature that in mixtures of triglycerides with different chain length the orthorhombic form is stabilized. This statement is confirmed by the present work, in which mixtures of tristearin and tripalmitin at different ratios were prepared in the absence and in the presence of solid emulsifiers. During polymorphic transformation in the DSC, a strong effect on the stabilization of β' form was shown in the mixtures. The further addition of the emulsifier inhibited both transformations. Although the β' form was kinetically stabilized, it was not yet stable enough to be isolated during aging. Both tripalmitin and emulsifier had a kinetic effect on the transformation of tristearin. But their effect is different. The presence of tripalmitin stabilizing the intermediate form which does not appear during the transformation in pure tristearin. On the other hand, the presence of the emulsifier merely affects the extent of transformation. The effect of tripalmitin is a structural effect, although not thermodynamic. The effect of the emulsifier is not structural, but rather the emulsifier's presence affects the transformation step, without interferring with the molecular packing that is formed. The stabilization of β'-form is probably due to the discontinuity in the methyl and groups plane. The distinct difference between the effects of emulsifier and tripalmitin on the polymorphic behavior of tristearin may explain how different additives affect the polymorphism of complex fats and stresses the significance of emulsifier's effect as dynamic controller of polymorphic transformations.

L9

Polymorphic Behavior Of POP and SOS In The Presence Of Sorbitan Monostearate, Studied By DSC. Nissim Garti, The Hebrew University of Jerusalem, Casali Institute of Applied Chemistry, Jerusalem 91904, Israel, and Judith Aronhime and Sara Sarig, The Hebrew University of Jerusalem.

Dipalmito-2-olein (POP) is the main component of cocoa butter (15%) together with distearo-2-olein (SOS) (30%) and palmito-oleo-stearin (40%). In the literature it is shown that POP and SOS do not form a solid solution; furthermore, their polymorphic behavior is slightly different. The polymorphic transformations of POP and SOS were followed individually in the DSC in the absence and in the presence of sorbitan monostearate at low percentages. The presence of the emulsifier clearly affects the kinetics of each transformation. It was found that the same conclusions drawn on the effect of the emulsifier on the polymorphic transformations in monoacid saturated triglycerides are valid also in the case of complex triglycerides

in which the polymorphism is more complicated. It has been shown that the presence of the emulsifier interferes with the mechanism and extent of the transformations but does not interfere with the thermodynamic properties of the polymorphs. A mechanism of emulsifier incorporation and performance is suggested.

Session M Monday afternoon

HPLC of Lipids and Proteins II

M1

High Performance Liquid Chromatographic Determination Of Amino Acids In Leguminous Proteins. Vibeke Axelsen, Aarhus Oliefabrik A/S, Analytical R & D Laboratories, P.O. Box 50, Aarhus C DK-8100, Denmark, and Vijai K.S. Shukla, Aarhus Oliefabrik A/S.

Proteins are one of the most versatile of food components. The protein quality is estimated as the capacity of a protein to meet animal or human nutritional requirements for non-essential nitrogen and essential amino acids. Thus the determination of amino acid composition of proteins is of great importance for establishing the quality of the proteins. High performance liquid chromatography (HPLC) has been extensively employed for the determination of amino acids during the last decade. The chief disadvantages of these methods are that they are tedious and time consuming and are not sufficiently reproducible for routine analysis. During our studies, we have investigated the critical parameters for the development of a reproducible, efficient HPLC method for the quantitative evaluation of leguminous proteins such as soybean and rapeseed. The details of this development together with the critical evaluation of the existing HPLC methods will be presented.

M2

High Speed HPLC-Analysis Of Interesterification and Hydrolysis Products Of Fats and Oils. Friedrich Spener, University of Münster, Department of Biochemistry, Wilhelm-Klemm-Str. 2, Münster D-4400, West Germany, and Susanne Eick, University of Münster.

Solid animal fats and liquid plant oils were interesterified with medium-chain fatty acids as well as unusual fatty acids. In addition, the hydrolysis of castor oil was investigated. Using high performance liquid chromatography, we elaborated an analytical control to monitor the time dependent progress of synthesis and hydrolysis. A commercially available HPLC apparatus was used, equipped with thermostated columns and RI-detector; mobile phases applied were mixtures of acetonitrile and tetrahydrofuran. Baseline separation of reaction products by high speed HPLC-analysis was eventually achieved by using especially prepared RP-18 columns. The time required for one analytical run was lowered from 40 min to below 20 min.

M3

HPLC Of Lipid Oxidation Products. Nancy J. Moriarity, Eastern Regional Research Center, USDA/ARS, 600 E. Mermaid Lane, Philadelphia, PA 19118, and F.A. Kummerow, University of Illinois.

The physiological effects of various lipid oxidation products are due to their structures and chemical natures. The utilization of HPLC for the separation and purification of oxidized lipids is becoming an increasingly important analytical tool. Recent advances in the HPLC of oxidation products of cholesterol, phospholipids, and free fatty acids (including the prostaglandins) as well as their methyl esters will be presented. The use of specialized columns and applications involving precisely defined solvent systems will be covered. New detection methods for specific types of compounds and recent improvements in detector sensitivity will also be examined. The discussion will include the application of methods used in our laboratory for the separation of geometrical and positional isomers of fatty acid hydroperoxides.

M4

Identity and Purity Of Vegetable Oils By HPLC. B.G. Herslöf, University of Stockholm, Analytical Chemistry, Stockholm, Sweden.

The use of fats and oils in modern society has many applications of which the use in food is by far the most important. In accordance with this the most used analyses are the ones accepted as quality parameters for edible oils. However, in other types of applications the identity or relative purity of oils might be required. These concepts are of general interest also to the food industry. In the presentation possible ways to determine the identity of an oil and its relative purity is discussed. This may have relevance for instance as a complement to the accepted pharmacopoeial descriptions. The use of HPLC as a tool for this purpose will be discussed and experimental results from different approaches will be presented and evaluated as possible routine procedures.

M5

Determination Of Reesterified Olive Oils By HPLC Analysis. Richard Flor, U.S. Customs Service, Office of Technical Services, 1301 Constitution Ave., N.W., Washington, DC 20229, and Aimee Taylor, Augusta College.

We have previously reported a study of 100 olive oils wherein HPLC analysis of the triglycerides allows a determination of grade among extra virgin and virgin, pure, refined or adluterated. The ratio of the four largest triglycerides when plotted as LOO/LOP vs. OOO/POO establishes two distinctly separated lines. Of the unadluterated olive oils, 66 fell on one line, Line A, and 13 fell on another, line B. Lines A and B are nearly parallel but are separated by ca. 0.60 on the LOO/LOP axis and ca. 0.37 on the OOO/POO axis. We have treated nine representative olive oils with base or acid to effect randomization of the triglyceride positions. Both acids and base smoothly shift all 9 olive oils from Line A to Line B. In accord with usual expectations of relative catalytic effectiveness for such randomization, the base (NaOMe) catalyzed reaction is far faster than acid catalysis. In these reaction systems, the catalyst was added to the olive oil, sealed under N_2, and heated for varying periods of time. The demonstration that a position on Line B is achieved by randomi-

zation of an originally Line A olive oil is proof that Line B oils are randomized. Such olive oils would be produced by reesterification—whether from glycerol and partially hydrolyzed olive oils, or glycerol and the free fatty acids obtained by refining of olive oils, or simple treatment of partially hydrolyzed oils. In any of these cases, the acid catalysts will randomize the triglyceride positions as well as reesterify the oil. Consequently, we have shown that the use of an HPLC analysis immediately identifies pure reesterified olive oils.

M6

Determination OF Chlorophyll Pigments In Crude and Degummed Canola Oils By HPLC and Spectrophotometry. J.K. Daun, Canadian Grain Commission, Grain Research Laboratory, 1404-303 Main Street, Winnipeg, MB R3C 3G8, Canada, and C.T., Thorstesin, Canadian Grain Commission.

Chlorophyll pigments in crude and degummed canola oils were analyzed by spectrophotometry using a modified AOCS Method and by reversed phase HPLC. HPLC showed that crude canola oils contained very little chlorophyll a or b, these pigments having been converted to pheophytins and other pigments with similar spectral properties. As the AOCS Method for determining oil chlorophyll was calibrated using pure chlorophyll, the use of this method on crude canola oil gave a significant error. Recalibration of the spectrophotometric procedure with pheophytin resulted in good agreement with the HPLC method.

M7

Separations Of Alkane-1,2-Diols and Monoacylmonoalkylglycerol Enantiomers By High Performance Liquid Chromatography On A Chiral Phase. Toru Takagi, Hokkaido University, Department of Chemistry, Minatocho, Hakodate, Japan, and Yutaka Itabashi, Hokkaido University.

Rapid and practical separations of alkane-1,2-diol and monoacylmonoalkylglycerol enantiomers as their 3,5-dinitrophenylurethane derivatives were carried out by normal phase high performance liquid chromatography on a chiral stationary phase, N-(R)-1-(α)-naphthyl-ethylaminocarbonyl-(S)-valine chemically bonded to γ-aminopropyl silanized silica and others. Complete separations of the racemates into enantiomers were achieved for hexadecane-1,2-diol and 2-hexadecanoyl-1-octadecylglycerol within 20 min by an isocratic elution with a mixture of hexane/ethylene dichloride/ethanol as a mobile phase. Satisfactory separation of the racemate of 3-hexadecanoyl-1-octadecylglycerol was also obtained under the similar conditions on the chiral column. The identification of the peaks to the enantiomers was carried out using some pure specimens synthesized in our laboratory. The formations of hydrogen bonding and charge transfer complex between the urethane derivatives and stationary phase may contribute to the enantiomer separations.

Session N Monday afternoon

New Frontiers of Plant Lipid Research

N1

Sites, Substrates and Regulation Of Fatty Acid Desaturation. Judith B. St. John, USDA, ARS, WSL, Bldg. 001, Rm. 234, BARC-West, Beltsville, MD 20705, and Helen A. Norman, USDA, ARS, WSL.

Galactolipids and phospholipids are mixtures of lipid classes that can be further resolved by recently developed HPLC techniques into individual molecular species based on the *sn*-1 and *sn*-2 positional specificity of the fatty acids occurring together within the same galacto-and phospholipid molecule. Chloroplast membranes always contain high amounts of galactolipid molecular species enriched in linolenic acid (18:3) or in some plants a combination of 18:3 and hexadecatrienoic acid (16:3). We have used the wild type and a mutant of *Arabidopsis thaliana* (L.) Heynh deficient in 18:3 and 16:3, a pyridazinone inhibitor of fatty acid desaturation, and the protein synthesis inhibitors chloramphenicol and cycloheximide to obtain details of the desaturation reactions leading to the formation of these trienoic fatty acids. Our studies (a) confirm chloroplastic and cytoplasmic sites for fatty acid desaturation to form 18:3; (b) show that desaturation reactions forming 18:3 on phosphatidylcholine (PC) in the cytoplasm and 18:3 on monogalactosyldiacylglycerol (MGDG) in the chloroplast are under different controls; (c) identify the specific MGDG and PC molecular species that serve as the complex lipid substrates for desaturations in the *sn*-1 and *sn*-2 positions; and (d) indicate that the desaturase enzyme(s) operative in the chloroplast to form 16:3 is under both cytoplasmic and chloroplastic control.

N2

Acyl Specificity Of Acyl Transferases In Maturing Seed and Lipases and β-Oxidation Enzymes In Germinating Seeds. Anthony H.C. Huang, University of South Carolina, Biology Department, Columbia, SC 29208.

It may soon be technically feasible to genetically engineer the mechanism of fatty acid synthesis in oilseeds, such that the chain length of the synthesized fatty acid can be manipulated artificially. However, whether the seed acyl transferases for triacylglycerol synthesis can utilize the altered fatty acids is unknown. Also uncertain is whether the lipase and β-oxidation enzymes in the seedlings can act on the altered glycerides and fatty acids; these enzymes are involved in gluconeogenesis from lipids and thus their activities are linked to seed vigor and vitality. Answers to these problems are directly related to the success of genetic engineering programs for modifying seed fatty acids. I will report results of experiments which are designed to provide the answers.

N3

Acetyl-CoA Carboxylase In Plants. Basil J. Nikolau, NPI, 417 Wakara Way, Salt Lake City, UT 84108, and Eve Syrkin Wurtele, NPI.

Acetyl-CoA carboxylase catalyzes the initial committed reaction of *de novo* fatty acid biosynthesis, namely the ATP-dependent carboxylation of acetyl-CoA to form malonyl-CoA. There is considerable evidence that in bacteria, yeasts and animals, the reaction catalyzed by this enzyme is rate-limiting for fatty acid biosynthesis. The molecular organization of this biotin-containing enzyme is fairly well characterized from *Escherichia coli*, yeasts and animals. Comparison of these structures indicate interesting functional changes during evolution. Acetyl-CoA carboxylase in plants has a number of metabolic functions, supplying malonyl-CoA for the biosynthesis of at least six groups of phytochemicals. The major fate of malonyl-CoA is for the biosynthesis of fatty acids. Consistent with its function in supplying malonyl-CoA for fatty acid biosynthesis, acetyl-CoA carboxylase is located in plastids, the sole site of fatty acid biosynthesis in plant cells. The kinetic properties of purified plant acetyl-CoA carboxylase suggest that this enzyme has a role in regulating fatty acid biosynthesis in photosynthetic tissues during day-night and night-day transitions. Furthermore, during the development of leaves, and embryos *in vivo* and *in vitro*, acetyl-CoA carboxylase accumulation changes in parallel with fatty acid accumulation. Plant acetyl-CoA carboxylase(s) is being characterized in order to gain insight into its molecular structure and the mechanisms regulating its biosynthesis.

N4

Developmental Biology of Oil Synthesis in Seeds. Vic Knauf, Calgene Inc.

Abstract not available at press time.

Session O Tuesday morning

Surfactants and Detergents III: A Panel Discussion—Detergency Testing

O1

Terg-O-Tometer Testing. W.S. Gilman, United States Testing Co., Inc., Chemical Services Division, 1415 Park Avenue, Hoboken, NJ 07030.

The Terg-O-Tometer is one of the most basic laboratory instruments for the evaluation of a laundry detergent product in conjunction with standard laboratory soil cloths. The Terg-O-Tometer is a laboratory-scaled, multistage machine, which simulates the action of an agitator-type home washing machine. Utilizing this machine, it is possible to determine the soil removal and redeposition properties of the detergent products at various water hardnesses, temperatures and detergent concentrations. The paper will describe typical conditions of use, features, reproducibility, operation, specifications and new applications developed.

O2

Detergency Testing With Launder-O-Meter. J.L. Berna, Petresa, Calle de Oriense, 68, Madrid 28020, Spain.

For a number of years the detergency testing operations have been usually done using the Launder-o-meter equipment. This is a standard laboratory washing machine provided with two important parts: (a) control cabinet, and (b) rotor and container holding device with temperature control. The standard soiled fabrics used for detergency testing have been manufactured by EMPA (Laboratoire Federal D'essai des Materiaux et Institut de Recherches, Unterstrasse 11, Case Postale 977, Ch-9001 St. Gall, Switzerland), and in particular the following ones are the most frequently used: (a) Empa 101, cotton soiled with carbon black-olive oil (1/1), (b) Empa 102, wool fabric with same soil, (c) Empa 103, Polyester/cotton, same soil, and (d) Empa 116, cotton with blood/milk/carbon black. Reflectance increments of the soiled fabrics are read before and after washing using a reflectometer. We have noticed that a difference of two or even three reflectance units can be easily found for the same soiled fabric after a number of replicates. A reproducibility comparison with other detergency testing methods will be shown based on using a typical European low foaming heavy duty powder.

O3

Radiotracer Detergency Method. Nelson Prieto, Shell Development Company, Westhollow Research Center, P.O. Box 1380, Houston, TX 77251.

Shell Radiotracer Detergency Method provides a quantitative means of evaluating detergency performance utilizing radiolabeled soils. The method can be used, for example, to determine absolute soil removal, soil redeposition and enzyme efficacy. Its results usually parallel those obtained using reflectance with somewhat greater precision. An overview of the methodology involved will be presented, including a comparison with the reflectance method.

O4

Soiled Test Cloths. George Feighner, Scientific Services.

Abstract not available at press time.

O5

Bundle Testing. Jay R. Brummer, FMC Corporation, Chemical Products Group, Box 8, Princeton, NJ 08543.

The bundle test is a test method that allows a formulator to compare the cleaning and brightening performance of any two home laundry detergents or home laundry procedures. The method uses naturally soiled paired clothing and linens that are given to "typical" families and subsequently washed and visually evaluated under controlled laboratory conditions for a specified number of wash cycles. This discussion will review the development of the bundle test method, objectives of the test, mechanics, test variables and the significance of the results.

O6

A Laboratory Method For the Prediction Of Bundle Test Visual Preference. P.K. Riccobono, Colgate-Palmolive Co., 909 River Road, Piscataway, NJ 08854.

A mathematical model has been developed that will

predict the visually preferred product in a Bundle Test by utilizing data generated in a relatively rapid laboratory procedure. The Visual Preference Ratio (VPR) generated by this method has been tested against a number of Bundle Tests not used in the data base for the model. The results show that the extent and direction of the Bundle Test preference ratio can be predicted with a high degree of confidence. Use of the VPR as a measure of ultimate product performance should enhance formulating programs by providing information regarding visual acceptability under "real world" conditions in a few days that would otherwise take six to eight weeks to obtain.

O7

In-Home Testing. Kenneth Mills, Lever Brothers.
Abstract not available at press time.

O8

On-Site Institutional Laundry. Linda Marquardt, Ecolab Inc., Institutional Division, St. Paul, MN 55102.

Detergency testing in the institutional laundry market involves a stepwise progression from either tergotometer or launderometer testing, to laboratory washwheel testing, and then field testing in Ecolab accounts. In the initial tergotometer testing, selected fabrics are artificially soiled and used to screen the performance of various detergent components. Once this is completed, the conclusions reached are retested vs. in-house or competitive standards in an institutional washer under a range of conditions. At the completion of this phase, the product is manufactured in larger volumes and placed in test accounts which have previously been surveyed by a field test engineer. The product is evaluated by the field test engineer in the account for approximately two to three months before expanding to market test and eventual national expansion.

O9

Large Industrial Laundry. John Birckbichler, Ecolab Inc., Textile Care Division, 840 Sibley Memorial Highway, St. Paul, MN 55118.

This presentation is designed to give an overview of the procedures and techniques that are used to develop an industrial detergency system for the large industrial laundry segment. Information will be provided as to raw material evaluation and choice, complementation of components, cost evaluation, and test procedures used from inception through field test. Particular attention will be paid to wash quality and efficiency of the product developed.

Session P Tuesday morning

Pharmacological Effects of Lipids III: Sterol and Carcinogenesis and Lipid Peroxides and Carcinogenesis

P1

Effect Of Cholesterol Binding On Enzyme Activity and Fluidity Of Biomembranes. Studies On the Consequences Of Cholesterol Interaction With Normal and Leukemia Cells. George Deliconstantinos, University of Athens, Dept. of Experimental Physiology, Medical School, Athens, Greece, and Gregory Skalkeas, University of Athens, and Gerhard R.F. Krueger, University of Cologne.

The binding of cholesterol (up to 5 μM) into dog brain synaptosomal plasma membranes (SPM) used as model biomembranes in these studies, follows an exponential curve described by the general formula $y=a \times e^{bx}$. Newer studies showed that this binding which represents the total binding (specific and non-specific) in the presence of cholesterol glucoside (100 μM), acquires sigmoid character with a Hill coefficient h-2.98 $\pm$ 0.18. The Hill plot in combination with the biphasic nature of the curve to obtain the equilibrium constant, showed a moderate degree of positive cooperativity in the binding of cholesterol into SPM. Arrhenius plot of $(Na^+ + K^+)$ATPase activity exhibited a break point at 23.2 $\pm$ 1.1° in control SPM which was abolished in SPM treated with cholesterol (5 μM), suggesting differences in the interaction of $(Na^+ + K^+)$ATPase with its annular lipids between cholesterol treated and untreated SPM, the allosteric properties of the SPM-bound $(NA^+ + K^+)$ATPase by fluoride ions (F^-) and Ca^{2+}-ATPase by Na^+ (as reflected by changes in the Hill coefficient) were modulated by cholesterol. The apparent cooperativity of both enzymes decreased in SPM treated with cholesterol, suggesting that the physical state of the $(Na^+ + K^+)$ATPase and Ca^{2+}-ATPase lipid annulus changed from a gel phase to a liquid-crystalline phase. Cholesterol carried by albumin isolated from human or rat serum are capable of evoking structural and functional changes in biomembranes. Serum albumin-cholesterol fraction acts in a similar manner to free non-esterified cholesterol, or its hydroxylated derivatives in diluted aqueous solutions, on their evoked effects on the SPM-bound $(Na^+ + K^+)$ATPase and Ca^{2+}-ATPase and also on the ecto-ATPase of human normal and CLL lymphocytes. Situation where serum cholesterol levels may be elevated, for example cancer or nutritional disorders, may increase the level of albumin-cholesterol fraction with detrimental effects on cell metabolism. Rotational mobility measured by the fluorescence polarization of 1,6-diphenyl-1,3,5-hexatriene (DPH) decreased with cholesterol or its derivatives binding into SPM and increased in parallel to cholesterol removal. CLL lymphocytes have a more fluid lipid bilayer in their plasma membrane than normal lymphocytes. Treatment of both groups of lymphocytes with cholesterol hemisuccinate resulted in rigidification of cell membranes. A lipid thermotropic transition temperature was observed at 23.6 $\pm$ 1.1° in normal lymphocytes and at 16.3 $\pm$ 1.0° in CLL lymphocytes, which rose to 32.3 $\pm$ 1.3° in normal and was abolished in CLL lymphocytes after treatment with cholesterol hemisuccinate. Similar results were obtained using mouse spleen cells, where a thermotropic transition temperature was observed at 23.8 $\pm$ 1.2° which rose to 30.5 $\pm$ 1.7° in cholesterol treated cells. Membrane fluidity may have a role in the metastatic spread of leukemic lymphocytes and also a bioregulatory role on the lymphocyte proliferation. The present studies concerning cholesterol or its derivatives and albumin-cholesterol complex, their behavior

and their role in the structure and function of biomembranes, provide important new clues to the role of this fascinating molecule in normal and pathological conditions.

P2

Sterol Carrier and Lipid Transfer Proteins. Terence J. Scallen.

Abstract not available at press time.

P3

Roles Of Isoprenoid Compounds In Cell Replication. James W. Doyle, The Jackson Laboratory, Bar Harbor, ME 04609, and Bruce D. Kabakoff and Andrew A. Kandutsch (speaker), The Jackson Laboratory.

Increased synthesis of isoprenoid compounds appears to be essential prior to S phase of the cell cycle. To investigate this requirement DNA synthesis was examined in cultured Chinese hamster ovary (CHO) cells in which the synthesis of mevalonate was blocked by mevinolin, a competitive inhibitor of HMG-CoA reductase, alone or in combination with 25-hydroxy cholesterol, a repressor of reductase synthesis. Blocking mevalonate biosynthesis by either procedure leads to a decline in DNA synthesis and a reduction in the S phase cell population with a comparable increase in cells found in the G1 or G0 phase of the cell cycle. When mevinolin is removed from cultures arrested with this inhibitor alone, synchronous DNA synthesis begins after a lag of 8 hours. The addition of mevalonate, cholesterol or dolichol and ubiquinone did not decrease the the lag-time or increase the extent of DNA synthesis recovery although cell viability was increased by exogenous cholesterol when mevalonate synthesis was inhibited for more than 24 h. The insensitivity of this recovery to exogenous mevalonate is probably due to an elevated synthesis of mevalonate by the reductase, which was induced 4-fold by mevinolin. In cultures treated with mevinolin and 25-hydroxycholesterol there was no induction of the enzyme and recovery of DNA synthesis was dependent upon added mevalonate. Exogenous dolichol and ubiquinone or isopentenyl adenine had no effect on the arrest or recovery of DNA synthesis; however, cholesterol was required during the arrest incubation. Optimal recovery of DNA synthesis was obtained with 200 μg/ml mevalonate following an 8 hour lag whereas a progressively longer lag-time was found with lower concentrations of mevalonate. The recovery of DNA synthesis by 200 μg/ml mevalonate, which was maximal 14–16 hours after the addition of mevalonate, only required that the mevalonate be present for the first 4 hours whereas more than an 8 hour incubation was required for maximal recovery with 25 μg/ml mevalonate. Maximal recovery at either concentration of mevalonate was achieved after approximately 400 fmol mevalonate /μg protein was incorporated into nonsaponifiable lipids. Following the addition of mevalonate there is an almost immediate rise in the synthesis of total protein and glycoprotein, reaching maximum steady levels by four hours. These changes in protein synthesis are not correlated with concentrations of dolichol and coenzyme Q which increase much more slowly. Our results so far indicate that a quantitatively minor product(s) of mevalonate metabolism is required during the first 4 hours following release of the block before other cellular events necessary for entry into S phase can occur.

P4

The Effect Of Oxygenated Sterols On Cellular Properties. Ross P. Holmes, Bowman Gray School of Medicine, Urology Section, Winston-Salem, NC 27103.

At low concentrations oxygenated sterols influence a number of cellular properties including cell shape, sterol synthesis, DNA synthesis, membrane permeability and endocytosis. The mechanism by which they exert these pleiotropic effects is not known. Many cells possess a carrier protein which has a high affinity for a number of oxygenated sterols. However, the function of this carrier protein and which sterols it transports within the cell are not known. Because of their amphipathic properties, oxygenated sterols can intercalate in membranes and influence their properties. Their orientation in membranes appears to be similar to that of cholesterol. In contrast to cholesterol, sterols oxygenated either in the B ring or in the isoprenoid side chain do not increase the molecular order in fluid, synthetic membranes. Furthermore they increase rather than decrease membrane permeability to ions and small, uncharged molecules. Their effects on lipid interactions in membranes is reflected in phase transitions, either changes in liquid-crystalline to gel or lamellar to hexagonal $H1^1$ transitions. These results indicate that oxygenated sterols are potent effectors of many membrane-related functions in cells. An important change in cells exposed to oxygenated sterols, may be a change in their membrane permeability to Ca^{2+}. We have observed that hydroxysterols increase the Ca^{2+} permeability of synthetic membranes. We have also observed that hydroxysterols can influence biological membranes as noted by a change in Ca^{2+} homeostasis in platelets. We have observed that incubation of platelets with concentrations of 26-hydroxycholesterol as low as 250 /ml can significantly increase the cytoplasmic concentration of Ca^{2+}. The observed effects of oxygenated sterols on cells and membranes suggest that membrane perturbations have to be considered in determining their mechanism of action.

P5

Cholesterol Synthesis, IL-2 Production and the Effects Of Dexamethasone In Glucocorticoid-Sensitive and Glucocorticoid Resistant Human Lymphoid Cells Of Neoplastic Derivation. G. Melnykovych.

Two cell lines derived from acute lymphoblastic leukemia were used in this study. Although both cell lines contain specific glucocorticoid receptors, one line (CEM-C7) is glucocorticoid sensitive whereas the other line (CEM-C1) is glucocorticoid resistant. The latter shows no evidence of cytolysis or growth inhibition at concentrations of dexamethasone (DEX) as high as 5×10^{-6}M. In both lines synthesis of cholesterol is repressed by exogenous sources of cholesterol but the cells use mainly de novo cholesterologenic pathway for their membrane cholesterol. Cholesterol esters taken up by the CEM-C7 cells from LDL are stored in the cellular cholesterol ester compartment and virtually all newly synthesized free cholesterol

may be shown to be derived from acetate. The CEM-7 line is extremely sensitive to mevinolin ($ID_{50} \cong 0.1$ μg per ml). In this line DEX reduces the activity of HMG CoA synthase but has no effect on HMG CoA reductase. No effect of DEX on either HMG CoA reductase or HMG CoA synthase can be shown in the resistant CEM-C1 line. Experiments using cells synchronized by thymidine/colcemid method demonstrate inhibition of cholesterol synthesis in the G_1 phase of the growth cycle, preceding the inhibition of protein synthesis and the delay in the cell cycle traverse. Both cell lines studied produce interleukin-2 (IL-2) which they appear to utilize in an autocrine manner. The production and/or release of IL-2 into the culture medium is inhibited by DEX in CEM-C7 cells but not in the CEM C-1 cells. Although IL-2 can partially reverse the inhibition of DNA synthesis by mevinolin, it alone is clearly not sufficient to reverse the growth inhibitory effect by either mevinolin or DEX. In contrast, the inhibition of both DNA synthesis and cell growth is partially reversible by mevalonate added to the cultures of CEM-C7 cell together with cholesterol/phosphatidycholine sonic dispersions. Whether another mevalonate product, in addition to cholesterol, is involved in these apparently complicated relationships between DEX, IL-2 and cholesterol remains to be seen.

P6

Effects of Steroid Hormones (Eddysteroids) On Adult Development In Manduca Sexta. James A. Svoboda, USDA, BARC, Building 467, Beltsville, MD 20705.

The effects of various ecdysteroids (molting hormones) and analogs on adult emergence and ovarian development when injected into pupae of the tobacco hornworm, *Manduca sexta*, were examined in structure-activity relationship studies. Ecdysteroids having both nuclear and sidechain modifications were tested. Ovarian development and/or adult emergence were severely inhibited following injection of 20-hydroxyecdysone, whereas, no adverse effects were noted when ecdysone was injected. Effects on both ovarian and adult development of all ecdysteriods tested were associated with the presence of a hydroxyl group at C-20. Significance of these findings in light of our knowledge of the normal ecdysteroid profile during this period of development and the fact that acdysone is a precursor of 20-hydroxyecdysone will be discussed.

P7

Antitumoral and Immunosuppressive Activities Of Oxygenated Sterols In Mice. Bang Luu, CNRS, Lab. de Chimie des Substances Naturelles, 5 rue Blaise Pascal, Strasbourg Cedex 67084, France.

Our previous studies have shown that oxygenated sterols are selectively cytotoxic to tumor cells cultured *in vitro*. We have also shown that some of these oxygenated sterols markedly inhibit lymphocyte activation. For *in vivo* studies, the main difficulty in administration of these lipophilic compounds to animals resides in their weak solubility in usual hydrophilic medium. Previously, we have overcome this difficulty by using a water soluble derivative, the the sodium salt of bishemisuccinate of 7-hydroxycholesterol. Injected intraperitoneally to mice bearing Krebs II carcinoma, they lead, in about 30% of the cases, to a fast and complete disappearance of tumor and in the remaining 70% to a highly significant life prolongation. Similar positive results on mice bearing S-180 sarcoma have also been obtained. However, with the same experimental conditions, negative results were obtained on other tumor strains cited in the protocol of National Cancer Institute. We now carry *per os* administration of triol or tetrol (for example the 7β, 25 dihydroxycholesterol) dissolved in olive oil, to mice bearing RDM-4 lymphoma and obtain significant life prolongation on treated mice. This result has to be compared with the one obtained by a Norwegian group. They have reported the inhibitory effect of 7, 22R dihydroxycholesterol on the induction and progression of DMBA-induced mammary carcinoma in the rat, the sterol being dissolved in drinking water. We have also shown that by an appropriate *per os* administration of the above-cited triols or tetrols, the ability of spleen cells from treated mice to stimulate *in vitro* the lymphocyte in response to mitogen and alloantigen is markedly depressed. The effect shows several analogies to that of cyclosporin A. In the cases we have studied, *per os* administrations seem to give the most interesting results.

P8

Lipid Peroxides and Arachidonate Metabolism In Mitogenesis and Viability. H. Zhang, The Ohio State University, Departments of Physiological Chemistry, Anatomy and Internal Medicine, Columbus, OH 43210, and K.H. Jones, R.V. Panganamala, W.B. Davis and D.G. Cornwell (speaker), The Ohio State University.

Endogenous lipid peroxides generated by intracellular polyunsaturated fatty acid (PUFA) metabolism and exogenous lipid peroxides provided to the cell by naturally occurring molecular complexes such as plasma lipoproteins have very different effects on mitogenesis and viability of smooth muscle cells (SMC) in tissue culture. These effects may be related to the differences in arachidonic acid (AA) metabolism that are observed when SMC are challenged with endogenous or exogenous lipid peroxides. SMC were treated with increasing amounts of PUFA and intracellular lipid peroxides were generated by this process. Studies with various antioxidants showed that these lipid peroxides had little effect on the synthesis of prostanoids and other AA metabolites. Exogenous lipid peroxides supplied to the cell as components of low density lipoproteins greatly diminished prostanoid metabolism and at the same time stimulated the formation of a number of new AA metabolites that were not products of cyclooxygenase or co-oxidation reactions. The effects of exogenous lipid peroxides were influenced more by the degree of lipid peroxidation in the lipoprotein than the total amount of lipid peroxide supplied to the cell. Exogenous lipid peroxides had much greater effects than endogenous lipid peroxides on mitogenesis and viability. These studies show that lipid peroxides have different cellular effects which depend on their source, concentration, the degree of lipid peroxidation and their location within the cell.

P9

Molecular Mechanisms For the Involvement Of Lipid Per-

oxide and Prostaglandins In the Initiation and Promotion Stages of Carcinogenesis. Peter J. O'Brien, University of Toronto, Faculty of Pharmacy, Ontario, Canada.

Lipid peroxidation and prostaglandin synthesis can enhance several stages of carcinogenesis. Thus a wide variety of arylamines, phenols, aminophenols, biphenols, benzidines, etc. are oxidized to products that readily bind covalently or noncovalently to critical macromolecules including nucleic acids. Similar changes occur in intact cells treated with these products and can result in DNA strand breakage. These changes can cause genotoxicity as micronuclei formation and sister chromatid exchange occur in daughter cells. It is therefore likely that lipid peroxidation and prostaglandin synthesis can initiate carcinogenesis. Inhibition of prostaglandin synthesis by antiinflamatory agents prevent these effects. Hydroperoxides formed by lipid peroxidation and prostaglandin synthetase can also induce ornithine decarboxylase and stimulate DNA synthesis in tissues; components of cell proliferation and tumor promotion. Hydroperoxides at noncytotoxic concentrations cause DNA single strand breaks, increase cytosotic calcium and increase the synthesis of "defensive" proteins in intact cells.

P10

The Role Of Dietary Lipids In Photocarcinogenesis. Homer S. Black, Baylor College of Medicine, Veterans Administration Medical Center, Department of Dermatology, Houston, TX 77030.

The potential role of dietary lipid in carcinogenesis has provoked much interest since the initial study of Watson and Mellanby in 1930 in which dietary fat was observed to enhance coal-tar induced skin tumors. For the most part, subsequent studies have dealt with chemical-induced cancers in which it has been shown that diets high in fat content enhance carcinogenesis. This response has been most frequently observed for the intestine, mammae, and skin. A similar effect has been demonstrated in photocarcinogenesis where induction of skin cancer is not subject to the dietarily potentiated vagaries of carcinogen metabolism inherent in chemical carcinogenesis models. Nevertheless, the homolgy of dietary lipid effects upon chemical and ultraviolet radiation induced cancers suggests a fundamental role for lipids in the underlying mechanism(s) of cancer expression and validates the utility of a UV-carcinogenesis/nutritional model. In such a model, it has been shown that tumor expression is enhanced when animals are fed high levels of an unsaturated lipid (corn oil) that is rich in linoleic acid. Antioxidants added to diets containing high levels of corn oil inhibited tumor expression almost equally to the degree of exacerbation caused by the lipid and to the same degree as that which occurred in diets providing the minimal requirement of the essential fatty acid. Lipid peroxidation of epidermal homogenates was also found to be directly related to level of dietary lipid intake and to be inhibited by antioxidants. On this basis it was suggested that lipid peroxidation played an important role in photocarcinogenic expression. This supposition was supported by the fact that diets containing hydrogenated corn oil modified tumor expresion to about the same degreeas antioxidants. Nevertheless, recent studies with diets containing menhaden oil, an unsaturated lipid source rich in omega-3 fatty acid and poor in linoleic acid, show that this oil, when compared to similar levels of corn oil, retards tumor expression. Peroxidation levels of epidermal homogenates from animals fed either source did not differ, however. In addition, menhaden oil inhibits inflammatory responses, i.e., erythema and edema, in UV radiated skin. Others have shown that omega-3 fatty acid inhibits prostaglandin (E-series) synthesis and evidence exists that some prostaglandins affect tumor promotion. Thus the effects observed in the photocarcinogenesis model indicate that the role of lipids in tumor expression is more complex than that reflected in lipid peroxidation, alone and suggest the involvement of prostanoid metabolism.

P11

Free Radical Dietary Antioxidants and Mechanisms In Cancer Prevention. Carmia Borek, Columbia University, Radiological Res Lab & Dept of Pathology, College of Physicians and Surgeons, New York, NY 10032.

A growing body of data now provides compelling evidence that reactive oxygen species produced by radiation and some chemicals including tumor promoters play a role in the process of carcinogenesis *in vivo* and *in vitro*. Agents that catalytically scavenge intermediates of oxygen reduction and serve as antioxidants have been shown to inhibit various steps in neoplastic transformation and defend the cells in a manner that may vary among species and tissues. For example, superoxide dismutase, catalase, vitamin A analogs and the food additive bisulfite have been shown to suppress cell transformation and, in some cases, inhibit the action of tumor promoters. The identification of nutritional antioxidants, which act alone or in concert to inhibit carcinogenesis, is of public concern because of their potential role in cancer prevention. Selenium, vitamin E and vitamin C represent ubiquitous dietary antioxidants whose role in carcinogenesis has been of interest for some time. An initiating event in many free radical reactions may be the production of superoxides (O_2), which are formed naturally in cellular metabolic processes and are enhanced in living cells by the action of radiation and a variety of chemicals. Superoxides dismutate to form hydrogen peroxides that can react with reduced metals (Fenton reactions) to produce the more toxic reactive hydroxyl radicals. Hydroxyl radicals react with biologically important molecules such as lipids and DNA to produce additional chain reactions with oxygen. The results are a variety of products such as aldehydes, which cross-link cellular macromolecules including DNA and may play a role in the carcinogenic process. While x-ray action directly leads to oxygen radicals that play a role in initiation and promotion, procarcinogens like benzo(a)pyrene or pyrolysates produce free radicals but also employ oxygen radicals for their activation via the P-450 system. Our finding indicate that vitamin E and selenium and vitamin C alone or in various combinations act to suppress cell transformation *in vitro* by radiation, benzo(a)pyrene and tryptophan pyrolysate. We find that selenium acts by enhancing the levels of cellular scavenging systems including catalase, glutathione and glutathione peroxidase and by doubling peroxide breakdown. We find that vitamin E which also suppresses ozone induced transformation acts by influencing lipid peroxidation processes in the cell and by modifying quinone levels. Discussion will focus on the experiments described above and on ongoing work related to the effects of lipids on transformation.

P12

A Role For Free Radicals In the Process Of Tumor Promotion. Bonita G. Taffe, Johns Hopkins Medical Institutions, Baltimore, Maryland, and Thomas W. Kensler, Johns Hopkins Medical Institutions.

Although the molecular mechanisms involved in carcinogenesis are incompletely understood at this time, intermediary events in the development of cancer have been described through the selective actions of discrete chemical agents. These processes have been studied in various model systems and have been termed initiation, promotion and progression. Initiation appears to involve the modification of cellular DNA, resulting in genotypically altered cells, while promotion encompasses a continuum of events allowing for the selection and clonal expansion of the initiated cells. Finally, progression completes the conversion of premalignant cells to malignant cells. Substantial evidence supports the involvement of free radical species, especially those derived from molecular oxygen in multiple aspects of these processes. Five major lines of experimental evidence indicate a role of free radicals in tumor promotion. Briefly, (a) potential free radical generating compounds such as organic hydroperoxides are tumor promoters; (b) some tumor promoters stimulate the production of reactive oxygen species from endogenous sources in a variety of cell types; (c) reactive oxygen species can mimic the biochemical actions of tumor promoters; (d) tumor promoters modulate antioxidant defense systems; and (e) free radical scavengers and detoxifiers inhibit tumor promotion. One approach to difining the role of free radicals in the process of tumor promotion involves both the demonstration and identification of the radical species generated by the promoting agent and the identification of the molecular targets of these reactive species. A variety of organic peroxides and hydroperoxides function as tumor promoters and progressors in mouse skin previously treated with an initiating agent such as 7,12-dimethylbenzanthracene. While the activities of these promoters are ascribed to the ability of these compounds to generate free radicals, peroxides are generally quite stable to uncatalyzed unimolecular homolysis at body temperature. Utilizing spin trapping and electron spin resonance techniques, it has been possible to demonstrate the formation of alkoxyl and/or alkyl radicals in primary cultures of murine keratinocytes treated with *tert*-butyl hydroperoxide, cumene hydroperoxide, dicumyl peroxide, the hydroperoxide of butylated hydroxytoluene, and benzoyl peroxide. Subcellular fractionation studies demonstrate that the formation of these radicals is dependent on a heat-liable factor which is predominantly localized to the cytosol of the epidermal cell. The generation of radicals from the hydroperoxides is presumed to require the redox cycling of an iron-centered protein and may generate both peroxyl and alkoxyl radicals. A tertiary alkoxyl radical thus formed is not stable and undergoes fragmentation through β-scission to form alkyl radicals such as the methyl radical. However, the significance of any of the radicals that have been detected in these spin trapping studies to tumor promotion or progression is unknown. Alkyl radicals can participate in hydrogen abstraction, substitution, or alkylation reactions. Methylation of cellular proteins through enzymatic pathways is an established mechanism of post-translational modification of proteins while phospholipid methylation alters membrane composition and physical characteristics such as membrane fluidity and could serve as a mechanism by which alkyl radicals modify signal transduction cascades. The peroxide promoters are also weak mutagens and can cause DNA strand breaks in epidermal cells. However, since the cytosolic compartment of the keratinocyte appears to be the principal site of peroxide activation, the relative importance in tumor promotion of modification of cellular phenotype by the actions of radicals at non-genetic versus genetic sites remains to be determined.

Session Q Tuesday morning

Flavor Chemistry of Lipid Foods III in honor of Stephen S. Chang

Q1

Chemistry of Meat Flavor. Ki Soon Rhee, Texas A & M University, Dept. of Animal Science, Meats & Muscle Biology Section, College Station, TX, 77843.

Meat is a highly desirable food, and flavor is one of the attributes contributing the most to its desirability. The flavor of meat develops upon cooking through many chemical reactions. The flavor of normal cooked meat generally is due to a mixture of volatiles, nonvolatiles and potentiators and synergists. However, much is still unknown about the components that contribute to meat aroma. Flavor/aroma differences exist among meats of different animal species, resulting from quantitative and/or qualitative differences in flavor/aroma precursors and meat volatiles. Some species-associated flavors (e.g., lamb and mutton flavor) are unacceptable to many people, and the components causing the undesirable aspects of these species-specific flavors have remained elusive. The most common cause of undesirable meat flavor is the oxidation of lipids that occurs during storage or holding. Cooked meat is much more susceptible to lipid oxidation than uncooked meat, and the development of oxidized off-flavors due to lipid oxidation is the most serious quality deterioration problem for precooked convenience meat products. Thus, the mechanisms of, and factors affecting, lipid oxidation in meat and meat products have been investigated with renewed interest in recent years. In this presentation, some of the important recent developments in the meat flavor chemistry will be reviewed with special emphasis on catalysis of lipid oxidation and the development of oxidized off-flavors.

Q2

Chemistry of Fish Flavor. Robert C. Lindsay, University of Wisconsin, Department of Food Science, Madison, WI 53606.

Very fresh fish and other seafoods are characterized by very delicate aromas and flavors that lack the pronounced fishiness encountered in less fresh products. Much of the characteristic aroma and flavor of fresh fish is provided by volatile 6-, 8-, and 9-carbon alcohols and carbonyls that are derived by endogenous lipoxygenase action on long-chain polyunsaturated omega-3 and omega-6 fatty acids. Differences in aromas between marine and freshwater fish as well as species result from varying

occurrences of individual alcohols and carbonyls. Pronounced fishiness-type aromas and flavors develop when certain products of autoxidation of polyunsaturated fatty acids accumulate, and these flavors are often enhanced by the presence of trimethylamine and related compounds. Many of the changes in the quality of seafood flavors encountered in packaging, processing, and cooking can be explained by chemical transformations involving the volatile alcohols and carbonyls. However, the chemical definition of some key fish and seafood flavors remains to be accomplished.

Q3

The Flavor Chemistry of Dairy Products. Earl G. Hammond, Iowa State University, Department of Food Technology, Ames, IA, 50011.

Dairy products owe many of their unique flavors to unusual fatty acids that they contain. These include short chain fatty acids, 2-keto fatty acids, and 4- and 5-hydroxy fatty acids. These fatty acids can give rise to both desirable and undesirable flavors. Dairy products also are susceptible to the development of flavors caused by autoxidation of unsaturated fatty acids. The dominant flavor note in oxidized milk fat is that of vinylamyl ketone which presumably arises from the oxidation of n-6 polyunsaturated fatty acids. In fermented dairy products the flavors produced by various degrees of fat hydrolysis are blended with those produced by degradation of milk protein and the reaction of amino acids with carbonyls produced by microorganisms.

Q4

Volatile Flavor Compounds Developed During Hydrogenation of Soybean Oil. R.R. Allen, consultant, Rt. 9 - Box 137, Mc Kinney, TX 75069, and C.M. Wu and S.M. Chang, Food Industry R & D Institute.

Flavor compounds developed during hydrogenation of soybean oils are shown to be derived from the hydrogenation of volatile aldehydes and ketones formed by the thermal decomposition of hydroperoxides of linoleic and linolenic esters. Since 2,4 decadienals are the major aldehydes formed from the linoleic hydroperoxides, decanol is the major component and causes the odor associated with hydrogenation of vegetable oils. Also, the typical "sweet" flavor of hydrogenated oils may be caused by the in-situ formation of decanol and subsequent flavor persistence.

Q5

Flavor Chemistry of Phospholipids. Bernard F. Szuhaj, Central Soya Co., Inc., P.O. Box 1400, Ft. Wayne, IN 46801.

Review of the role of phospholipids in the flavor development of lipid-containing foods, including the chemistry involved as a result of hydrolytic and oxidative rancidity and interaction of flavor compounds with various reactive sites in the food matrix. Organoleptic problems in specific foods, such as meats, fish, cereals and legumes, and assessment of lipid-induced flavors in common food systems are addressed. The biogenesis of phospholipid-generated flavors are examined in terms of autoxidation, membrane lipid peroxidation, water activity, etc. Particular emphasis is given to the role of phospholipids in the flavor profile of soybean products by discussing the chemical and physical basis for organoleptic attributes in these products. Measures for eliminating off-flavors caused by lipid materials in soybean processing are highlighted.

Q6

The Effect of Phospholipids Upon the Flavor of Lipid Foods. Alice Nasner, Lucas Meyer GmbH & Company, Ausschlager Elbdeich 62, 2000 Hamburg 28, Federal Republic of Germany.

Phospholipids are a very important ingredient in the manufacture of foods. Phospholipids obtained from plant sources became more important than synthetic emulsifiers in food processing. But the function of phospholipids as food additive must not be reduced only to their emulsifying properties. Phospholipids influence the distribution of different phases, the viscosity, the texture, the appearance and mouth-feel of foods. The simultaneous sensation of taste in the mouth and odor in the back of the nose is flavor. Phospholipids can influence flavor in different foods, i.e., margarine, bakery goods, chocolate, instant products. A review of usage of phospholipids in different foods will be given. The relation between the processing of phospholipids, their selection and their eventual purification and the task of foods will be discussed in particular.

Session R Tuesday morning

Protein Symposium II: Structure and Molecular Modeling

R1

Protein Secondary Structure. George Rose, Pennsylvania State University, Dept. Biological Chemistry, Hershey Medical Center, Hershey, PA 17033, and Leonard G. Presta, Pennsylvania State University.

Recent efforts in protein engineering have focused on changing the specificity or enhancing the stability of natural proteins as well as designing elements of secondary structure or even entire proteins de novo. We have been analyzing segments of secondary structure in X-ray elucidated molecules in order to extract general principles that can be used in protein design. Elements of secondary structure can be classified as repetitive and non-repetitive. Both helix and sheet are repetitive structures because their residues have repeating mainchain torsion angles, (phi, psi), and their backbone N-H and C=O groups are arranged in a periodic pattern of hydrogen bonding. Non-repetitive regions, those with non-repeating mainchain angles, include reverse turns and omega-loops. Turns are sites where the polypeptide chain changes its overall direction, and their frequent occurrence is responsible for the globularity of globular proteins. Loops are chain segments that trace a "loop-shaped" path in space, with small end-to-end distance between their segment termini. The segment mainchain of an idealized loop resembles a Greek omega. Useful generalizations from both repetitive

and non-repetitive categories will be discussed, with particular emphasis on alpha-helices and omega-loops.

R2

Comparative Modeling of Proteins In the Complement Pathway. Jonathan Greer, Abbott Labs, D-47E Abbott Labs, Abbott Park, North Chicago, Il 60064.

The anaphylatoxins are a family of proteins produced during the course of complement activation. These proteins are involved in a variety of biological functions, including inflammation. Three proteins of this family have been studied: C3a, C5a and C4a. The three-dimensional structure of the central portion of C5a, corresponding to residues 11 through 76 of C3a, was modeled directly from the published C3a crystal structure by comparative modeling techniques. The internal core residues of the C5a structure are completely conserved, while almost all the external residues are different from C3a. Through the N-terminal 12 residues of C3a are disordered into the crystal, the N-terminal sequence of C5a was proposed to be an amphipathic helix that docks onto a nicely complementary, hydrophobic contact. Similar modeling studies were performed on C4a and the N-terminus of C3a. The resulting three structures are compared in detail. The model structure proposed for human C5a will be compared to the solution structure of human C5a recently determined by NMR methods in our laboratory.

R3

Numerical Modelling of Peptides: Technical Capabilities. Ray Hagstrom, Argonne National Laboratory, 9700 S. Cass Avenue, Argonne, IL 60439.

Numerical modelling and design of proteins and smaller peptide structures is a rapidly expanding scientific tool. As these techniques progress toward applied usability, it is important to identify the classes of problems for which true predictive capability is to be expected. This difficult task of assessing predictive capability at present centers upon reasoning from published treatments of "analogous cases". Limitations to predictive capability arise from several quarters including: (a) economics of computer hardware; (b) inaccuracies in interatomic forcefields; (c) limitations of common algorithms; and (d) unavailability of approximate starting structures. Predictive capability in any given case is limited by some combination of the above effects together with the less quantifiable notion of how sensitive the desired structure is.

R4

The Role of Dynamics and Solvation In Protein Structure and Function. John W. Brady, Cornell University, Department of Food Science, Ithaca, NY 14853.

Molecular mechanics calculations, which make use of empirical energy functions to numerically simulate the conformational properties of biopolymer systems, can be a particularly powerful tool in the investigation of structure-function relationships. Physical properties are actually determined by free energies, however, which in some cases can differ substantially from the relative conformational potential energy and can include significant contributions from dynamical fluctuations and from the solvent. One molecular mechanics technique, molecular dynamics simulations, attempts to model the dynamical behavior of chemical systems by numerical integration of Newton's equations of motion and has been particularly useful in examing such contributions to the free energy of protein systems. Molecular dynamics simulations are able to produce time-averaged structures which explicitly include the effects of fluctuations about low energy conformations and the transitions between different conformers, as well as the shifts in conformational preferences which may result from the presence of solvent, as has been found for alanine dipeptide, a frequently used model of protein behavior. Such effects will need to be considered in the practical manipulation of protein functional properties and the rational design of novel proteins and polypeptides.

R5

The Structure of Protein In Non-Crystalline Environments. Irwin Kuntz, University of California, San Francisco, California.

Abstract not available at press time.

Protein Symposium IV: Importance of Sulfhydryl Group and Thermal Effects on Protein Structure and Function in Food

R6

Relationship of SH Groups To Functionality of Ovalbumin. Etsushiro Doi, Kyoto University, Research Institute for Food Science, Uji, Kyoto, 611 Japan, and Naofumi Kitabatake, Kyoto University, Hajime Hatta, Taiyo Kagaku Co., Ltd., and Taihei Koseki, Kyoto University.

Ovalbumin which has the molecular weight of 45,000 contains one disulfide bond and four free sulfhydryl groups per molecule. These sulfhydryls have different reactivities with different reagents and do not react with DTNB. Two of the sulfhydryl groups become reactive with DTNB when denatured by heat or being frozen. Denatured ovalbumin contains two disulfides. Usually, an ovalbumin solution gives a turbid gel when heated. We found that a transparent solution, transparent gel, turbid gel, or turbid solution was obtained with heating depending on conditions of the medium such as pH and ionic strength. Hardness was greatest with the conditions that gave a transparent or slightly turbid gel. The gel was solubilized with 1% SDS. The solution obtained by SDS treatment contained polymers that were octamers or shorter, which showed that the intramolecular disulfide bonds had little effect on the formation of the gel network. The clear solution obtained by the heating of ovalbumin solutions at low ionic strength and at a pH far from the pI (4.7) contained linear polymers. The molecular weight of the linear polymers were from 1,000,000 to 8,000,000. The presence of N-ethylmaleimide did not inhibit the formation of these linear polymers.

R7

Effects of Molecular Changes (SH Groups and Hydrophobicity) of Food Proteins on Their Functionality. Eunice Li-Chan, Univeristy of British Columbia, Department of Food Science, 248-2357 Main Hall, Vancouver, BC V6T 2A2, Canada, and Shuryo Nakai, University of British Columbia.

Hydrophobic, electral and steric parameters are important in elucidating structure-functionality relationships of proteins. For example, protein solubility has been correlated with low hydrophobicity and high charge frequency in addition to molecular size, while good emulsification properties are attributed to amphiphilic proteins with high solubility and surface hydrophobicity. Since it is surface and not total hydrophobicity which is the key parameter which influences functionality, structural factors that affect the degree of exposure of hydrophobic regions must also be considered. Molecular flexibility is important to allow protein unfolding. The hydrophobicity of unfolded proteins and sulfhydryl group content were correlated with thermal functional properties, e.g. thickening, coagulation and gelation. Proteins such as lysozyme which are held in a stable rigid, globular conformation by intramolecular disulfide bonds may be made more flexible by heating in the presence of reducing agents. Whereas native lysozyme has low surface hydrophobicity as measured by fluorescent probes, partially reduced lysozyme shows increased surface hydrophobicity and flexibility, as well as improved heat gelation properties. Similarly, thiol-induced gelation of conalbumen is preceded by a lag during which concomitant increases in free sulfhydryl groups and surface hydrophobicity occur. The effects of these molecular changes on protein structure and function are discussed.

R8

Use of Radiolabelled Protein As Tracers To Study Thermally-Induced Thiol-Disulfide Exchange Reaction In Milk Systems. Tom Richardson, University of California, Department of Food Scient & Technology, Davis, CA 95616, and Bongsoo Noh, University of California.

Heat induced complexes between milk proteins are of considerable importance in determining the heat stability and rennin clottability of milk products. Thioldisulfide interchange reactions have been suggested as the principal reaction mechanism for complex formation. Studies to date have not adequately established the mechanism and stoichiometry of complex formation *in situ* in total milk system. Tracer amounts of $_{14}C$ β-lactoglobulin were added to skim milk, which was heated under various conditions. After clotting with rennet, radioactivity retained in the curd was counted to estimate extent of interaction of β-lactoglobulin with casein. Also, milk containing $_{3}H$ k-casein and $_{14}C$ β-lactoglobulin was subjected to various heat treatments and protein complexes containing $_{3}H$ and $_{14}C$ were separated on Sephacryl S-300 eluted with 6M Gu HCl (pH 6.58). Further separations of protein complexes were obtained using controlled pore glass chromatography in the presence of 6M Gu HCl (pH 6.58). Ratios of radioactivities in protein complex peaks suggested various stoichiometries of β-lactoglobulin and k-casein in complexes possible as a function of heat treatment.

R9

Functional Roles of Heat Induces Protein Gelation In Processed Meat. James C. Acton, Clemson University, Department of Food Science, 219 Poole Agricultural Center, Clemson, SC 29634-0371, and Rhoda L. Dick, Clemson University.

Stabilization of comminuted meat matrices involves three principal physio-chemical events that occur in the protein fraction during heat processing. Functionally these events are (1) protein-water interaction, (2) protein-fat interaction and (3) protein-protein interaction. The responses of the meat tissue's myofibrillar proteins, primarily myosin and actomyosin, determine the ultimate development of the internal gel structure in heat processed products. The functional roles of myosin and actomyosin in water binding and fat stabilization are dependent on the protein sol-to-gel transformation during the continuous input of thermal energy associated with cooking. In the 30 C to 70 C temperature zone, molecular transition temperatures of myofibrillar proteins provide valuable evidence for the sequence of events in protein-protein interactions and gel matrix formation.

Session S Tuesday morning

Effects of Dietary Omega-3 Fatty Acids II

S1

Effects Of Vegetable and Marine Oils On Platelet Aggregation At Rest and During Stress. David E. Mills, University of Waterloo, Department of Health Studies, Waterloo, ONT N2L 3G1, Canada, and K.M. Prkachin, K. Harvey, R. Ward and Y.S. Huang, University of Waterloo.

The present study examined the effects of 1) acute psychological stress on platelet aggregation and 2) n-6 and n-3 fatty acid-rich dietary supplements on platelet aggregation at rest and following stress. Thirty men, randomized into 3 groups, received 9 capsules/day of olive oil (placebo), borage oil (Boracelle), or fish oil (Maxepa) for 30 days. One day prior to initiation of the supplementation, and on day 30 blood samples were drawn prior to and following a 25 minute battery of psychological stressors (mental arithmetic, Stroop test, and favorable impression interview). In vitro responses of PRP were measured to 2 doses of ADP, epinephrine, and collagen on a Payton aggregometer. Stress did not significantly alter aggregation parameters in the pre-diet condition, although there were consistent trends toward reductions in platelet count, aggregation rate in response to ADP and collagen, latency of aggregation in response to collagen, and disaggregation following ADP. Rate of aggregation tended to increase in response to epinephrine. Neither olive or borage oil altered platelet responses before or following stress. Fish oil decreased the pre-stress rate of aggregation in response to epinephrine and ADP, and extent of aggregation following epinephrine. These effects were abolished following stress. Rate of aggregation in response to collagen, however, was reduced following stress. Thus, with the exception of collagen-induced aggregation, the anti-aggregatory effects of fish oil were reversed by stress.

S2

Dietary Menhaden Oil Effects On Rabbit Lipid Metabolism. John E. Bauer, University of Florida, Depart. of Physiological Sciences, Box J-144, JHMHC, Gainesville, FL 32610, and C. Henry Beauchamp and Patricia A. Schenck, University of Florida.

The effect of fats containing n-6 and n-3 fatty acids in semi-purified diets on rabbit lipid metabolism were investigated. Diets containing either safflower (SAF) or menhaden (MHO) oil were used (14% w/w) in conjunction with a known atherogenic casein/wheat starch basal diet. Increased lipoprotein cholesterol was observed in all low density lipoprotein fractions of rabbits fed the MHO diet ($d < 1.063$ g/ml), with a major increase (5-6 fold) in the $1.022 < d < 1.063$ g/ml (LDL) fraction. Differences in the polyunsaturated to saturated fat ratio of these 2 oils may help explain this difference. Compositional analysis revealed significant elevations of serum (CE) and phospholipid (PL) and of liver CE and free cholesterol in the MHO group. In liver microsomes, acyl-CoA acyl transferase (ACAT) activities of rabbits fed both the SAF and MHO diets were 2X higher than chow fed controls but no differences between the semi-purified diet groups were found. The HMG-CoA reductase activities were 2X lower in the SAF and MHO groups compared to chow feeding. It appears that dietary casein resulted in increased hepatic cholesterol esterification and decreased de novo cholesterol synthesis. The presence of safflower or menhaden oils did not differentially modulate this effect. In intestinal mucosal cell microsomes, ACAT activities were 2X higher but HMG CoA reductase was unchanged compared to chow fed rabbits. No differences due to fat type were observed. Liver microsomes of the MHO group contained increased total PL relative to protein and a trend toward increased amounts of CE. Intestinal mucosal microsomes showed no differences in PL content but a decrease in triglyceride along with the slight trend toward increased CE. This finding suggests that differential re-esterification rates of dietary fatty acids by the intestinal mucosal cells may occur when fish oils are fed due to increased ACAT activities.

S3

Structured Lipids—Preferred Fats and Oils For Nutritional Acceptability and Health. Vigen K. Babayan, New England Deaconess Hospital, Cancer Research Institute, 194 Pilgrim Road, Boston, MA 02215.

Fats and oils have come under a great deal of attention in recent years. Both the advantages and disadvantages of the different lipids have been the subject of symposiums and workshops. Structuring lipids to tailor make glycerides that demonstrate the nutritional advantages and benefits have been prepared and animal studies carried out to validate their benefits. It remains for the publications of the clinical studies on humans to prove beyond any reservation their preferability. Structured lipids of several types are described and their benefits are demonstrated. The need for recognition of subclasses in the classification of fatty acids is proposed based upon the adsorption and metabolic patterns of such fatty acids and glycerides.

S4

Developmental Changes In Thermotrophic Properties Of Synaptosomal Acetylcholinesterase are Altered By Diet-Induced Depletion of Long Chain N-3 Polyenoic Fatty Acids. N. Hrboticky, University of British Columbia, Department of Paediatrics, 950 W. 28th Avenue, Vancouver, BC V5Z 4H4, Canada, and S.M. Innis, University of British Columbia.

Long chain (≥20c) n-3 polyenoic fatty acids (n-3 LCP) are essential to the structural integrity and function of biological membranes. In the early neonatal period, rapid accretion of membrane n-3 LCP occurs in tissues such as the brain, where this coincides with post-natal neuronal maturation. It has been suggested that exclusive feeding of currently available infant formulae which, unlike breast milk, contain no n-3 LCP may compromise membrane n-3 LCP deposition and thus development of the neonatal brain. Our study compared the developmental changes in synaptosomal membrane fatty acid composition and the temperature dependent behavior of membrane-bound synaptosomal acetylcholinesterase (ACHase) in formula fed (FF: n-3 LCP-0, 18:2n-6=33% total fatty acids) and sow milk fed (SMF: n-3 LCP-0.7%, 18:2n-6=12%) piglets (age 0, 5, 10, 15 and 25 post partum). Transition temperatures (TT) of ACHase declined with age in the SMF piglets, suggesting a developmental increase in synaptosomal membrane "fluidity". TT of the FF group were higher at all ages and did not decrease until day 25 post partum. In contrast to the SMF piglets, FF animals demonstrated an age related decrease in synaptosomal n-3 LCP content. These findings suggest that neonatal feeding of diets devoid in n-3 and enriched in 18:2n-6 results in a derangement of normal developmental n-3 LCP accretion. The concomitant alterations in membrane-bound enzyme thermotropic properties suggest functional changes related to the membrane phospholipid fatty acids. These studies support the concept that the fatty acid composition of infant formula is a determinant of neonatal brain development.

S5

The Influence Of Various Dietary Fats On Serum Cholesterol, Triglycerides and Lipoprotein Distributions In Rabbits: Menhaden Oil Is Hypercholesterolemic. Gary J. Nelson, Western Human Nutrition Research Center, ARS, USDA, P.O. Box 29997, San Francisco, CA 94129, and Darshan S. Kelley, Perla C. Schmidt and Claire M. Serrato, Western Human Nutrition Research Center, and Frank T. Lindgren, University of California.

There is considerable recent interest in the physiological effects of dietary n-3 fatty acids from marine oils. This study compared the effects of dietary fats containing saturated, n-6 and n-3 (of both terrestrial and marine origin) polyunsaturated fatty acids on blood lipids and lipoproteins in rabbits. Four groups of New Zealand White rabbits (n=7) were fed semi-synthetic diets containing 7.6% fat (w/w) for 5 months. The fats were: 1. hydrogenated soybean oil (HSO), 80% stearic acid, 18:0, with 2% safflower oil (SO), 2. safflower oil, 78% linoleic acid, 18:2(n-6), 3. linseed oil (LO), 54% linolenic acid, 18:3(n-3), and 4. menhaden oil (MO), 21% palmitic acid, 16:0, 13% EPA, 20:5(n-3) and 8% DHA, 22:6(n-3). The diets contained 14.2% protein, 40.8% carbohydrate, and 30.0% fiber by weight

(20% of calories were from protein, 56% from carbohydrate, and 24% from fat) and 1100 IU/g of tocopherol, 0.2 ppm Se and the recommended amounts of other vitamins and minerals for rabbits. The MO diet also contained 0.06% cholesterol while the other diets were cholesterol free. Blood was taken at 0,1,2,3,4 mo. and at the end of the study. Cholesterol and triglyceride concentrations were determined using an enzymatic method on fresh serum. Lipoprotein distributions were obtained by analytical ultracentrifugation on pooled samples from each diet group drawn after the animals consumed the diets for 1, 3 and 4 months. At the age of three months, before assignment to experimental diets, the animals had serum cholesterol values of 62.1 ± 20.3 mg/dl and triglyceride concentration of 40.3 ± 14.3 mg/dl (Values are the mean ± S.D.). After 1 mo. on the diets, the cholesterol values in the four groups were: HSO, 70.9 ± 21.2 mg/dl; SO 59.1 ± 15.9 mg/dl; LO 65.1 ± 50.7 mg/dl; and MO 141.7 ± 67.2 mg/dl. Only the MO value differed significantly from the pre-experimental diet value (P=0.01). The triglyceride concentration had not increased significantly in any group by this time. For the remainder of the study serum cholesterol values in the SO, LO, and MO groups did not change significantly while in the HSO group, the cholesterol and triglycerides concentration rose significantly to 127.8 ± 82.2 mg/d., and 130.6 ± 60.3 mg/dl, respectively, at the end of the study (P 0.05). The MO group's serum triglycerides exhibited a tendency toward higher values but the elevated (P 0.01) in the HSO and MO groups when compared to the SO and LO groups. The MO diet cholesterol and LDL levels after 1 mo. while the LO diet, which contained over 50% n-3 fatty acids, primarily linolenic acid, but no cholesterol, did not produce a corresponding hypercholesterolemia. Whether the twenty and twenty-two carbon n-3 fatty acids in menhaden oil, EPA, 20:5(n-3) and DHA, 22:6(n-3), are hypercholesterolemic in rabbits in the absence of dietary cholesterol remains to be determined. The data suggest, however, that refined menhaden oil which contains 0.8% cholesterol is a potent hypercholesterolemic agent for rabbits.

S6

Effect Of N-6 Fatty Acid (FA) Depletion On The Distribution Of 20-Carbon Polyunsaturated Fatty Acids (PUFA) In Rat Kidney Phospholipids (PL). Yung-Sheng Huang, University of Waterloo, Department of Health Studies, Waterloo, ONT N2L 3G1, Canada, and David Horrobin, Efamol Research Institute.

Effects of prolonged n-6 FA depletion on the distribution of C-20 PUFA in kidney PL fractions were examined in growing rats. Weanling male SD rats were maintained for 2-wk on a diet with 10% (wt) of 18:2n-6 rich-safflower oil and were then fed with either 10% hydrogenated coconut oil (HCO, containing no n-6 FA) or 10% fish oil (FO, rich in n-3 FA). Animals (n=5) were killed after 2, 4, 8, and 12 weeks on their respective diet. Kidney lipids were extracted and FA distribution in PL fractions were examined. HCO-feeding rapidly increased the levels of 20:3n-9 in the first 2 weeks, but less rapidly in the next 10 weeks, whereas FO-feeding increased the levels of 20:5n-3 after 2-wk feeding and remained constant thereafter. On either diet, the proportions of 20:4n-6 were significantly reduced after 2-wk, but were not thereafter, indicating that a constant proportion of 20:4n-6 is retained, despite a prolonged n-6 FA depletion. The replacements of 20:4n-6 by 20:3n-9 in HCO and by 20:5n-3 in FO groups were not equal in various PL fractions, suggesting that the relative size of the replaceable 20:4n-6 pool may be related to their locations in the membrane.

S7

Fatty Acid Composition Of Some Tissues From Ringed Seals (*Phoca Hispida*) From The Canadian Arctic. M. Yurkowski, Fisheries and Oceans Canada, 501 University Crescent, Winnipeg, MB R3T 2N6, Canada.

Lipid and moisture content (% wet weight range in brackets) and fatty acid composition in blubber (87.7 - 93.6; 4.4 - 9.6; n = 9), liver (3.5 - 4.9; 68.5 - 73.7), muscle (0.9 - 1.9; 69.9 - 73.2), kidney (2.7 - 3.4; 75.2 -78.8) and stomach content (3.6; 82.7; n = 1) of ringed seals (*Phoca hispida*) from Sachs Harbour, N.W.T., Canada. Blubber had higher levels of 16:1ω9 and 16:1ω6 and lower levels of 16:0 than the other tissues. The blubber and stomach content had higher levels of 14:0, 14:1 and 16:1ω7 and lower levels of 18:0 and 20:0. The blubber, muscle and stomach content had higher levels of 20:1ω11, 20:1ω9, 22:1ω11 and 22:1ω9. The liver had lower levels of 18:1ω9 and higher levels of 18:1ω7. The liver, muscle and kidney retained higher levels of 20:4ω6 (more than 5 times) and 18:2W6 than the blubber and stomach content. The blubber had highest levels of W3 acids (18:3; 18:4; 20:4; 22:5; 22:6) and stomach content had highest level of 20:5ω3. Large variations occurred in the levels of most major tissue fatty acids among these ringed seals, suggesting that individuals in the population had different diets or were in different physiological states.

S8

Synthesis of Fish Oil Omega-3 Triglycerides. Virginia F. Stout, Northwest & Alaska Fisheries Center, US Dept of Commerce, Utilization Res Ctr, 2725 Montlake Blvd. East, Seattle, WA 98112, and Fuad M. Teeny, Northwest & Alaska Fisheries Center.

Triglycerides containing three omega-3 polyunsaturated fatty acid chains were synthesized by a new technique suitable for preparing large quantities for physiological evaluation. Their structures were studied indirectly by gas-liquid chromatography of their methyl ester derivatives, and directly by thin layer (TLC) and high performance liquid chromatography (HPLC). A reverse phase HPLC procedure on 3μ ODS columns with acetonitrile/absolute ethanol as the mobile phase was developed with whole fish oil as the reference triglyceride mixture. The complexity of fish oil was reflected by the more than 100 triglyceride peaks distinguishable by this procedure. Ethyl esters and glycerol were reacted in the presence of a sodium-dispersion catalyst to give mono-, di-, and mainly triglycerides. The reaction mixture was separated by preparative TLC. The effectiveness of the synthetic method for triglycerides containing predominantly C:16, C:18, C:20, C:20+21+22, or C:22 omega-3 moieties was determined. These chain-length fractionated esters were prepared by supercritical fluid carbon dioxide extraction of urea-complexed fish oil esters. Triglycerides containing specific chain lengths were compared by HPLC to the more heterogeneous triglycerides present in whole fish oil and

omega-3 enriched triglycerides now available as nutritional supplements.

S9

The Effect Of Deodorization Time and Temperature On The Chemical, Physical and Sensory Characteristics Of Menhaden Oil. Timothy J. Pelura, KabiVitrum Inc., 1311 Harbor Bay Parkway, Alameda, CA 94501, and Stephen S. Chang, Rutgers University.

Recent studies have indicated possible beneficial effects ensuing from the consumption of fish oils containing ω3 fatty acids, of which menhaden is a prime source. However, menhaden oil is not considered acceptable for human consumption due to problems associated with odor, flavor, color, minor impurities, and poor oxidative stability. Deodorization is used by commercial manufacturers of edible oils to improve the sensory, color, and stability characteristics of the final products. However, high temperature processing of highly unsaturated oils, such as menhaden oil, may consequently produce a product with poor chemical and physical properties in addition to reduced nutritional efficacy. In the present study, menhaden oil was vacuum-steam deodorized for various times and temperatures and subsequently subjected to various chemical, physical and sensory analyses. It was found that temperatures below 200 C were able to produce a quality, bland product, whereas higher temperatures resulted in dramatic quality losses in terms of ω3 fatty acid content, isomerization and polymerization. Also, analysis of the volatiles distilled at the extremes of deodorization temperatures revealed major qualitative as well as quantitative differences. Optimum deodorization conditions are proposed and various antioxidants of natural and synthetic origin are evaluated in the deodorized oils.

Session T Tuesday morning
General Analytical I

T1

The Fractionation Of Phosphatidylcholine and Other Phospholipids By Silver Resin Chromatography. R.O. Adlof, Northern Regional Research Center, ARS-USDA, 1815 North University Street, Peoria, IL 61604, and W.J. DeJarlais, Northern Regional Research Center.

Rohm and Haas XN 1010 resin (a sulfonated, polystyrene-divinylbenzene macroreticular copolymer) was ground in a burr mill, and a fraction of ca. 35 microns was isolated by air elutriation. After silver ion incorporation, several methods of column packing were investigated, and a 4.6 × 25 cm stainless steel column was packed with silver ion-saturated resin. Samples (10 microliter) of various phospholipid mixtures (10% in methanol or chloroform) were fractionated by utilizing an acetonitrile in methanol solvent system. Egg (frozen and fresh) and soybean phosphatidylcholine were analyzed as well as samples of phosphatidylethenolamine and phosphatidylserine. The phospholipids were fractionated based on the number of double bonds. The fractionation of crude phospholipids and the development of this system for larger scale separations of phospholipids was also investigated.

T2

Densitometry of Lipids With Iodine Staining On HPTLC. U. Olsson, University of Stockholm, Analytical Chemistry, Stockholm, Sweden, and P. Kaufmann and B.G. Herslöf, University of Stockholm.

The new generation of scanning densitometers using the flying spot or meander principle of measurement has improved the accuracy of *in situ* quantitation of spots on thin layer plates. With the use of this technique, studies were performed on the uptake of iodine vapors from various lipid classes, such as phospholipids and glycerides. For the separation of complex lipid samples containing slow or non-eluting metrix components the open column, i.e. HPTLC, is generally to be preferred before HPLC. It is essential to obtain a precise and accurate quantitation, and to that aim the factors affecting the uptake of iodine vapor were explored. The results will be presented in this paper.

T3

Characterization of Solute-Solvent Interactions In Soybean Oil By Inverse Gas Chromatography. Jerry W. King, Northern Regional Research Center, ARS/USDA, 1815 N. University Street, Peoria, IL 61604, and Gary R. List (speaker) and John P. Friedrich, Northern Regional Research Center.

Inverse gas chromatography (IGC) has seen wide application in the characterization of fibers, proteins, molten polymers, and other materials in the past fifteen years. In this presentation, we shall describe a relatively simple IGC technique for evaluating solute-solvent interactions with a refined soybean oil as the solvent. Utilizing solvent loadings of 5–20% by weight, we have determined a number of thermodynamic solution parameters for 22 solutes in the temperature range of 55–125 C. Weight and mole fraction activity coefficients, along with interaction parameters, will be presented for soybean oil-solute systems at infinite dilution for six solute classes including n-alkanes, n-alkanols, and chlorinated hydrocarbons. In general, mole fraction activity coefficients and interaction parameters increase with carbon number for n-alkanes, alkyl-substituted benzenes, and n-alkanoic acids at all temperatures investigated, while the inverse is found for the n-alkanols. The above activity coefficient data as well as the interaction parameters indicate that aromatic solutes, chlorinated hydrocarbons, ketones, and cyclohexane are readily miscible with the oil phase. Calculated heats of mixing for n-alkanols were found to be positive (to 2.84 kcal/mole) while recorded enthalpic interactions were weak for aromatic solutes, lower alkanes, and chlorinated hydrocarbons. From measurements of interaction parameters for solutes of varying solubility parameters, the stationary phase solubility parameter was determined to range from 7.89 to 6.95 cal 1/2 /cm 3/2 in the above temperature interval. The relevance of the data to such problems as oil dissolution, solvent devolatization, and entrainer selection in supercritical fluid extraction will be discussed.

T4

Influence of Fatty Acid Composition on The Wavelength Selection For The Estimation of Oil Content In Oilseeds

by NIR Spectroscopy. J.A. Panford, Canadian Grain Commission, Grain Research Laboratory, 1404-303 Main Street, Winnipeg, MB R3C 3G8, Canada, and J.M. deMan, University of Guelph, and P.C. Williams, Canadian Grain Commission.

The oil content of eight different types of oilseeds has been determined by NIR spectroscopy. A Northstar computer was used to select the wavelengths that best describe the oil content in these seeds. Selected wavelengths were often in the same area of the spectrum but differed with respect to the number of wavelength points required and their order of selection. Wavelength assignments for typical functional groups in fatty acids are discussed. The fatty acid composition and the predominant fatty acid component appeared to influence significantly the wavelengths used for the estimation of oil content in each seed type.

T5

Measurement of Total Unsaturation Contents In Vegetable OIls Using NIR Procedures. R.B. Roy, Bran+Luebbe, Technicon Industrial Systems Corp., 511 Benedict Avenue, Tarrytown, NY 10591, and L. McDermott, Bran+Luebbe.

Vegetable oils are mixtures of mixed triglycerides and contain different, mostly straight chain, saturated and unsaturated fatty acids. The common unsaturated fatty acids are oleic, linoleic and linolenic acids that contain 1,2 and 3 double bonds respectively. Unsaturated fatty acids affect the stability of vegetable oils for both storage and during frying operations. Partially hydrogenated vegetable oils contain reduced numbers of unsaturated carbon-carbon double bonds and are relatively stable. A rapid measurement of total unsaturation contents in vegetable oils is desireable for partial hydrogenation control and quality specifications. AOAC recommended Wijs method for the measurement of unsaturation of fatty acids is slow and time-consuming. In addition, Wijs reagent is unstable and often reacts with compounds containing no double bonds. In the NIR procedure developed, several commercial vegetable oils were spiked with known amounts of unsaturated fatty acids and analyzed for the total unsaturation contents. Excellent correlation between manual and predicted values were obtained. NIR scans of several unsaturated fatty acids will be discussed.

T6

Quantitation of *trans* Unsaturation In Fatty Acid Methyl Esters By Fourier Transform Infrared Spectroscopy. A.C. Lanser, Northern Regional Research Center, USDA/ARS, 1815 North University Street, Peoria, IL 61604, and E.A. Emken, Northern Regional Research Center.

A computer-assisted method has been developed for estimation of isolated *trans* unsaturation by means of the peak area of the *trans* absorbance band at 966 cm^{-1} from FTIR spectra of fatty acid methyl esters. Peak areas were used to determine the *trans* content of weighed standards containing from 3 to 51% methyl elaidate and of hydrogenated soybean oil samples. These data for percent *trans* by FTIR were compared to corresponding data obtained by capillary gas chromatography and the AOCS Official Method 14-61. Determination of isolated *trans* composition in oils by using peak areas gave values with the smallest standard deviation for weighed standards and values within 2% of those obtained by capillary gas chromatography and the AOCS Official Method for hydrogenated samples.

T7

Rapid Analysis of Cholesterol In Beef Lipids. Myung Joo Han, University of Tennessee, Food Technology and Science, P.O. Box 1071, Knoxville, TN 37901, and Sharon L. Melton, University of Tennessee.

A procedure for extraction of free cholesterol from beef and a rapid method for the separation and quantitation of free cholesterol in the total lipids were developed. Total lipids containing the free chlolesterol were extracted from beef longissimus muscle by a chloroform-methanol procedure at room temperature. The free cholesterol was separated from the total lipids by elution from a disposable Bond-Elut (Analytichem) silica column by the following procedure. A 90-mg sample of the total lipids was separated into 3 fractions by elution from the column. The first fraction containing saturated and unsaturated hydrocarbons was eluted with 20-ml of hexane, the second fraction containing triglycerides was eluted with 20 ml of hexane:diethyl ether, 92:8, v/v, and the third fraction containing the free cholesterol was eluted with 20-ml of hexane:diethyl ether, 20:80, v/v. The more polar phospholipids remained on the column but could have been eluted with pure methanol as a fourth fraction. Other compounds such as free fatty acids and mono- and diglycerides also eluted with the free cholesterol; however, derivitization of the cholesterol to a silyl ether followed by gas chromatographic analysis resulted in separation and quantitation of the free cholesterol. Excellent recovery (>90%) was obtained for free cholesterol from 90-mg total lipid samples spiked with 1-mg of free cholesterol using this procedure. Efforts are underway to develop a rapid procedure for the separation of cholesterol esters from the total lipids followed by quantitative measurement. Results of these efforts will also be reported.

Session U Tuesday morning

Processing I: Corrosion and Materials of Construction

U1

Choosing Proper Stainless Steel. John C. Tverberg, Trent Tube Division.

Abstract not available at press time.

U2

Proper Selection of Materials and Welding techniques for Process Equipment. Kenneth F. Krysiak, Hercules Incorporated, 1313 Market Street, Wilmington, DE 19894.

This paper suggests that the proper selection of materials is keyed to first understanding the environmental conditions to which these materials will be exposed. Over 60% of equipment failures have been shown to be caused

by some form of preferential corrosion, usually associated with the weld. Suggestions are made on how to avoid failures of stainless and carbon steels with special consideration given to corrosion factors, weldment design, joint preparation, selection of the welding process, choice of filler metal, welding techniques, finishing, cleaning and testing the weld.

U3

Material Selection for High Temperature Oil Processing. Donald M. Godell, Wurster & Sanger, Inc.

Abstract not available at press time.

U4

Concern About Corrosion In Computer Controls. Ewa Bardasz, Union Camp Corporation.

Abstract not available at press time.

U5

Corrosion In Heating Coils. James R. Smith, Armstrong-Hunt Inc., 5902 Clarendon Court, Hanover Park, IL 60103, and Douglas Bloss, Armstrong-Hunt, Inc.

The subject paper addresses the need to consider "internal" as well as "external" factors related to premature failure of Process Heating Coils in the soybean, sunflower seed and related industries. Reasons for causes are discussed, including problems with feedwater, CO_2, O_2 affects and sub-cooling of condensate within the finned area of the coils.

U6

Choosing Correct Material For Plate Heat Exchangers. James A. Carlson, APV Crepace, Inc.

Abstract not available at press time.

U7

Special Consideration For Corrosion In Corn Germ Processing. Phil Bolheimer, Bolheimer & Associates.

Abstract not available at press time.

Session V Tuesday afternoon

Surfactants and Detergents IV: Surface Chemistry of Mixed Active Systems

V1

Physical Phenomena Important In The Application Of Mixed Actives. John F. Scamehorn, University of Oklahoma.

Abstract not available at press time.

V2

Interaction Of Cationic Surfactants With Anionic And Nonionic Surfactants. Dewey L. Smith, Vista Chemical Company, P.O. Box 500, Ponca City, OK 74601, and Michael F. Cox, Vista Chemical Company, and Phillip M. Lacke, Sherex Chemical Company.

Model studies were performed to examine the interactions of cationic surfactants with anionic and nonionic surfactants and with anionic/nonionic surfactant blends. The relationships among surfactant solubility, soil removal (detergency), and surfactant deposition (fabric softening) are discussed. Conditions for optimizing both detergency and softening are also examined.

V3

The Effects Of Electrolytes, Nonionic Amphiphiles and Ionic Surfactants On The Clouding (Upper Consolute Temperature) Of A Zwitterionic Surfactant. G.J.T. Tiddy, Unilever Research.

Abstract not available at press time.

V4

Solvent-Free High Active Matter Alcohol Ethoxysulfate/Alcohol Ethoxylate Blends: Preparation and Effect Of Surfactant Structure On Rheological Properties. L. Kravetz, Shell Development Co.

Abstract not available at press time.

V5

An Alkylbenzene Sulfonate/Alcohol Ethoxysulfate Mixed Active System For Laundry Detergent Powders. Isaac I. Secemski, Lever Brothers Company, 45 River Road, Edgewater, NJ 07020, and Jesse L. Lynn, Jr., Lever Brothers Company.

Linear alkylbenzene sulfonate (LAS) is widely used as a surfactant in laundry detergent powders. It is cost effective and a good foamer, and powders containing LAS are readily processible and have good flow and storage properties. The major drawback of LAS is that it is hardness-sensitive and performance drops off in under-built conditions as hardness ions, particularly calcium ions, precipitate free LAS monomers. One method of making LAS less hardness-sensitive is to add a co-active that forms a mixed micelle with LAS at a lower CMC, thus reducing the LAS monomer concentration. An alcohol ethoxysulfate derived from an alcohol ethoxylate with C_{12-14} hydrophobe and containing 60–70% by weight of ethylene oxide has been identified as a particularly good co-active for LAS in both phosphate and nonphosphate powders. This ethoxysulfate delivers excellent hardness protection for LAS at LAS/ethoxysulfate ratios of 3.5:1 to 1.5:1, and powders containing this active mix are more readily processible and have better flow properties than a comparable performing powder based on LAS/alcohol ethoxylate.

V6

Synergisms In Binary Surfactant Mixtures. M.J. Schwuger, Henkel KGaA, Postfach 11 00, 4000 Düsseldorf 13, Federal Republic of Germany, and F. Jost and H. Leiter, Henkel KGaA.

Significant correlations become apparent between synergisms of the micelle formation in surfactant mixtures, that are considered as deviations from the ideal mixture model, and a series of physicochemical properties and characteristics of application. Examples are the emulsifying, dispersing, wetting, flotation, washing and cleaning ability. The experimental work to determine the critical micelle concentration can be strongly reduced in accordance with the phase separation model. As a result, the effect of a co-surfactant with respect to problems of application can be predicted by only a few surface tension measurements.

Session W Tuesday afternoon

Pharmacological Effects of Lipids IV: Protein Kinase C and Carcinogenesis

W1

Modulation Of Cellular Immunity By Arachidonic Acid Metabolites. Kam H. Leung, E.I. DuPont de Nemours & Co., Medical Products Department, Glenolden, Pennsylvania.

Arachidonic acid (AA) metabolites play a central role in modulating a variety of immune cell functions. Various cells of the immune system and tumor cells are sources of AA metabolites. We have shown that prostaglandins (PG) inhibit development of cell-mediated immunity in cultures by mouse spleen cells in response to P815 allogeneic tumor cells. PGE_2 exerts its effect on the early time period of the antigen stimulation. Inhibition of cyclooxygenase enhances the response while inhibition of lipoxygenase inhibits the response. PGE_2 also has the ability to inhibit the cytolytic activity of the effector cells generated in mice. Since a large number of studies suggested that natural killer (NK) cells play a role in host resistance to tumor cells and their metastases, we have investigated the effect of AA metabolites on NK activity. We have shown that PGE_2 inhibits NK activity but has no effect on NK activation induced by interferons (INF) and interleukin-2 (IL-2). Activation of NK cells by IFN and IL-2 induces a partial resistance to suppression by PGE_2. Using various lipoxygenase inhibitors we have shown that lipozygenase activity plays an important role in NK cell function and activation. In summary, our data suggest an important role of AA metabolites in regulating cell-mediated immunity.

W2

Examining The Role Of Membrane Lipids In The Regulation Of Tumorigenicity and Immune Recognition. David S. Roos, Stanford University, Department of Biological Sciences, Stanford, CA 94305.

Characterization of a graded series of mouse fibroblast cell lines originally selected for resistance to the fusogenic effects of polyethylene glycol has shown that these cells are altered with respect to a wide variety of other membrane-associated phenomena as well. Susceptibility to chemically-induced fusion can be correlated with alterations in spontaneous cell hybridization, vesicular pinocytosis, virus-induced fusion and pathogenesis, bacterial invasion, immune recognition, and tumorigenicity and metastatic spread in vivo. Mutant cells produce tumors in mice at 1000-fold lower threshold doses than observed for the parental line, and these tumors are in every way more malignant regressing infrequently, invading muscle and bone, and readily metastasizing to lung tissue. Studies with isolated spleen cells and beige mouse mutants indicate that the variation in tumorigenicity observed in these closely related cell lines can be explained by their ability to evade recognition and lysis by "natural killer" cells. Detailed biochemical analysis of these cells has revealed striking alterations in their lipid composition, including highly increased saturation of fatty acyl chains and >30-fold elevated concentrations of neutral ether-linked lipids (1-O-alkyl, 2,3-diacylglycerols). Through the use of defined lipid supplements, it has been possible to completely control the various forms of cell fusion in a predictable manner, rendering fusion-resistant cells fusible, and vice-versa. These studies demonstrate a direct relationship between lipid composition and biological phenotype; extension along similar lines may also elucidate the role of lipids in regulating tumorigenicity and immune recognition.

W3

Regulatory Functions of Fatty Acids On Blood Platelets. Shuji Kitagawa, University of Tokushima, Faculty of Pharmaceutical Sciences, Tokushima, Japan.

Long-chain fatty acids have been suggested to modulate various cellular functions and cellular growth by modification of membrane physical properties. Long-chain *cis*-unsaturated fatty acids with different alkyl chain lengths and different numbers of double bonds inhibited both human and bovine platelet aggregation induced by ADP, thrombin and collagen. In accordance with the inhibitory effects of the *cis*-unsaturated fatty acids, they increased membrane fluidity of the platelets. On the other hand, the saturated fatty acids and *trans*-unsaturated fatty acid tested for comparison had much lower or no effects on aggregation and membrane fluidity. The inhibitory effects of mono *cis*-unsaturated fatty acids increased with increase of their alkyl chain length. *cis*-Unsaturated fatty acids with two or more double bonds had more inhibitory effects than mono-unsaturated fatty acids. The position of the double bonds had less influence than the number of double bonds. We also examined the effects of *cis*-unsaturated fatty acids on membrane fluidity with diphenylhexatriene and anthroyloxy derivatives of fatty acids as probes and observed increased fluidity to be considerable depths in the membrane lipid layer. Moreover, similar effects on aggregation and membrane fluidity were commonly observed for long-chain *cis*-unsaturated compounds such as unsaturated alkyl alcohols. These results suggest that the inhibition of platelet aggregation by *cis*-unsaturated fatty acids is due to perturbation of the lipid layer.

W4

Role of Oncogenes, Chemical Tumor Promoters and Growth Factors In The Modulation of Intercellular Communica-

tion During Carcinogenesis. J.E. Trosko, Michigan State University, Dept. of Pediatrics/Human Development, E. Lansing, MI 48824.

Gap junctional intercellular communication has been linked to the regulation of cell proliferation and differentiation. Since most normal mammalian cells have functional gap junctions while most malignant cells do not, it has been hypothesized that the carcinogenic process involves the inhibition of this important biological process. Using several in vitro assays (metabolic cooperation; Fluorescent Recovery After Photobleaching or "FRAP"; scrape-loading/dye transfer; and the cell-mat assay), we have examined the effects of various oncogenes, chemical tumor promoters and growth factors on gap junction function. Natural products (phorbol esters, teleocidin), drugs (phenobarbital), food additives (saccharin), solvents (heptanol), pollutants (PCB's, PBB's), pesticides and herbicides (DDT, 2,3,5-T), nutritional factors (unsaturated fatty acids), growth factors (EGF, GF-B), metabolic by-products (H_2O_2, cholesterol epoxides), oncogenes (src, ras), cigarette tar condensates, heavy metals (mercuric chloride), neurotoxins (dieldrin), and neurotransmitters (acetylcholine) have been shown to modulate gap junctional communication. These observations suggest a possible integrative hypothesis linking oncogenes, which act as growth factors, with chemical tumor promoters which act as growth factors, and with growth factors which act as tumor promoters; namely via their common effect and inhibition of gap junctional communication.

W5

The Role Of Lipids In Permeability Changes Induced By Toxins, Complement and Other Cytolytic Agents. C.A. Pasternak, St. George's Hospital Medical School, Department of Biochemistry, Cranmer Terrace, London SW17 0RE, England.

Membrane-mediated cell damage induced by cytotoxic agents occurs in three types of situation: first, exogenously-derived toxins such as the bee venom protein melittin or the α toxin secreted by infections *Staphylococcus aureus*, exert pathogenicity by increasing non-specific permeability across the plasma membrane of susceptible cells. Second, endogenously-derived proteins, such as the membrane attack complex of complement (C5b-9) or the cytolysins secreted by cytotoxic lymphocytes, exert protection by killing virus-infected host cells, certain invading bacteria or certain viruses themselves by a similar mechanism. Third, synthetically-constructed immunotoxins such as hybrids between monoclonal antibodies and certain toxins, or chimeric antibodies, exert therapeutic potential against tumor cells, again by inflicting membrane damage on such cells. Evidence from this laboratory has led to the view that in each situation, cytotoxicity is often the result of a similar type of permeability change: namely one in which leakage (of intracellular ions, of low molecular weight metabolites, or even of cytoplasmic proteins, depending on the conditions) can be prevented by H^+ or by divalent cations such as Ca^{2+} or Zn^{2+}. Divalent cations are therefore able to modulate—to the advantage or disadvantage of the host—such permeability changes. Because the site at which divalent cations act appears to involve the membrane lipids of susceptible cells—as shown by studies with pure lipid films—and because lipophilic drugs potentiate the action of cytolytic agents, the relationship between lipid composition and the cytotoxic action of certain toxins, complement, cytolysins and other agents is of importance in the understanding of basic mechanisms as well as for the design of novel anticancer drugs.

W6

Effects of Phorbol Esters On Multiplication and Differentiation of Mammary Cells. Louis Maria Houdebine, Institut National de la Recherche Agron., Lab. de Physiologie de la Lactation, Jouy-en-Josas 78350, and Paule Martel, Michele Ollivier-Bousquet and Eve Devinoy, Inst. National de la Recherche Agronom.

The onset of lactation results from multiple processes including mammary epithelial cell multiplication and differentiation. Cell multiplication and differentiation can be obtained in vitro using isolated cells cultured on floating collagen or explants cultured in a synthetic well-defined medium. Several hormones are involved in these processes. In the rabbit, prolacting alone can trigger the expression of casein genes (the major milk proteins). Its effects are markedly and independently amplified by insulin at supraphysiological concentration and cortisol which are both inactive alone. Cell multiplication in cultured explants, estimated by the incorporation of labelled thymidine into DNA is stimulated independently by insulin, EGF and prolactin associated with insulin and cortisol. Prolactin also stimulates transiently the secretion of milk proteins and lipids when added to mammary fragments explanted from a lactating animal. Thus, prolactin delivers multiple and possibly independent signals to the mammary cell. Phorbol 12,13-dibutyrate (PDB) at the concentration of 100 ng/ml totally prevented the induction of casein accumulation by prolacting in mammary explants cultured for 24 hours. Phorbol 12,13-diacetate (PDA) was inhibitory only at 1000 ng/ml. PDB alone or associated with the Ca^{++} ionophore A23187 was not able over a period of 8 hours to mimic prolactin action on the induction of β-casein mRNA accumulation on the contrary it almost totally prevented the hormonal effect. None of the phorbol esters was capable of stimulating the incorporation of ^{14}C thymidine into DNA. PDB at the concentration of 100 ng/ml strongly inhibited the stimulatory effects of insulin, EGF and prolactin whereas PDA was active only at 1000 ng/ml. None of the phorbol esters were cytotoxic in the range of concentration used since they did not reduce basal ^{14}C thymidine incorporation. PDB did not prevent prolactin binding to its receptors and it did not alter the down-regulation of the receptor. PDB at the concentration of 100 ng/ml stimulated casein secretion whereas remained inactive up to 1000 ng/ml.

W7

Regulation of Protein Kinase C. Curtis L. Ashendel, Purdue University, Dept. of Med. Chemistry & Pharmacognosy, School of Pharmacy & Pharmacal Sciences, West Lafayette, IN 47907.

The significance of protein kinase C (PKC) in signal and ultimately in tumor promotion and the control of cellular phenotype has underscored the need for identifying the critical phosphate-accepting substrates of PKC and events in signal transduction subsequent to PKC.

One approach to this challenge lies in understanding in detail the regulation of PKC. Several avenues of investigation of the regulation of PKC have been pursued, including activation, mechanism of subcellular localization, mechanism of down-regulation, transcription and translation of isozymes, differences in isozymic function, and effect on PKC of alterations by oncogenes in signal transduction. Studies of the mechanism of activation and down-modulation of PKC have led to new knowledge of the differential interactions of PKC with diacylglycerols and phorbol esters. Comparison of the isozymic forms of PKC isolated from rat brain indicate subtle differences in their regulation by phorbol esters. The use of recombinant DNA has allowed the effects on cells of over-expression and under-expression of the PKC isozymes to be evaluated. When these components of PKC regulation were examined in cells expressing active oncogenes, such as *ras* and *src*, the levels of PKC were found to be altered. Additionally PKC negatively regulates certain growth factor receptors and GTP-dependent coupling proteins, possibly including certain oncogene products. Clearly, signal transduction includes several complex interdependent processes. The use of cells modified by expression of transfected genes offers the promise of understanding these processes and their part in carcinogenesis.

W8

The Role Of Membrane Lipid Dynamics and Translocation of Protein Kinase C In the Induction of Differentiation In Human Promelocytic Leukemic Cells. Paul B. Fisher, Columbia University, Dept. of Pathology and Urology, Cancer Center/Institute of Cancer Res., New York, NY 10032, and David Schachter, Columbia University, and Eliezer Huberman, Argonne National Laboratory.

Diterpene phorbol ester tumor promoters such as TPA are potent modulators of differentiation in diverse target cells. In a number of cell types, TPA can inhibit cellular proliferation and induce differentiation. The ability to study the mechanism by which these agents modify differentiation has been facilitated by the isolation of stable variants which are resistant to TPA-induced differentiation. In the case of TPA-resistant human HL-60 promyelocytic leukemia cells, resistant variants differ from susceptible parental cells in a number of biochemical and physical parameters including down-regulation of specific binding of phorbol esters, membrane lipid fluidity, TPA-dependent protein phosphorylation and translocation of protein kinase C from the cytosol to the plasma membrane. By employing a series of membrane-impermeant fluorophores (stachyose derivatives of anthroyloxystearate and pyrenebutyryl hydrazide) and the membrane-permeant fluorophore [1,6-diphenyl-1,3,5-hexatriene(DPH)], we have demonstrated that the ability of HL-60 cells to respond to TPA may be affected by the physical state of the plasma membrane lipids and that the resistant phenotype is associated with decreased fluidity of either the inner leaflet of the plasma membrane and/or of the cytosolic organellar membranes. When exposed to TPA, TPA-resistant HL-60 cells display an increased phosphorylation of nuclear proteins, which approach that observed in untreated HL-60 cells but are less than observed in TPA-sensitive HL-60 cells treated with phorbol ester tumor promoters. In addition, TPA induces the redistribution of protein kinase C from the cytosolic to the membrane fraction in TPA-sensitive HL-60 cells, whereas no such translocation of protein kinase C occurs in resistant variants. These observations support the hypothesis that the inability of TPA-resistant HL-60 cells to be induced to differentiate when exposed to phorbol esters could involve a defect in the ability of these cells to transmit the appropriate transmembrane signal, possibly involving the phosphorylation of specific nuclear proteins(s), following the binding of TPA to its receptor (protein kinase C).

W9

Inhibition of Gap Junction-Mediated Intercellular Communication By Unsaturated Lipids: Potential Involvement In The Promotion of Cancer. Charles A. Aylsworth, Michigan State University, Department of Anatomy, East Lansing, MI 48824-1101.

Dietary lipids, expecially those which contain unsaturated fatty acids, have repeatedly been demonstrated to promote the development of many types of experimentally-induced tumors and have been implicated in the etiology of certain human cancers. Additionally, certain unsaturated fatty acids have been shown to stimulate the proliferation of various cell types in vitro. Inhibition of gap junctional communication is an effect that has been demonstrated with many types of tumor promoting compounds and has been implicated mechanistically in the promotional phase of carcinogenesis. In an attempt to explore the mechanism(s) involved in the tumor promoting effects of unsaturated lipids, the effects of such lipids on gap junctional communication has been investigated. By using an in vitro assay to measure metabolic cooperation between V79 Chinese hamster cells, it has been demonstrated that many unsaturated lipids inhibit gap junctional communication, whereas saturated lipids are unable to do so. In this presentation the effects of lipids on gap junctional communication will be reviewed and the potential involvement of inhibition of gap junctional communication in the tumor promoting effects of unsaturated lipids will be addressed. In addition, potential mechanisms that might be involved in the inhibition of gap junctional communication by unsaturated lipids, especially the activation of protein kinase C, will be discussed.

Session X Tuesday afternoon

Flavor Chemistry of Lipid Foods IV in honor of Stephen S. Chang

X1

Natural Antioxidants. J. Loliger, Nestec Ltd., Nestle Research Centre, Vers-chez-les-Blanc, Lausanne 26, CH-1000, Switzerland.

There is an ever increasing interest in natural antioxidants, and hence in their mechanisms of action and their utilization as ingredients to stabilize foods. Recent results obtained in studies of radical exchange reactions between autoxidizing polyunsaturated lipids and vitamins E and C have contributed to the basic understanding of radical scavenger mechanisms of chain breaking antioxidants for the protection of polyunsaturated lipids. This

molecular level understanding leads to a number of different concepts for the utilization of natural antioxidants to stabilize polyunsaturated oils. The antioxidant protection efficiency of various plant extracts has been evaluated in various food applications (dried, moist and emulsions). The protection efficiency is assessed using chemical analysis techniques closely correlating with organoleptically perceived degradation. The various aspects of this work, including legislative problems and consumer concern will be discussed.

X2

Recovery of Flavor Compounds During The Processing Of Foods. Stanley Kazeniac, Journal of Food Science, 107A Hampden Avenue, Narberth, PA 19072.

Recovery of volatile flavor compounds by distillation processes will be reviewed. Essence is now recovered in the processing of fruits, e.g. citrus, apples, grapes and berries, into juices and beverages, though the processes could be used to collect vegetable volatiles if desired. Recovery of desirable volatile flavors during the processing of meats and fish by distillation methods is difficult because of the chemical activity of some of the compounds. Membrane separations appear promising for the recovery of non-volatile compounds. This technology has been used to recover flavor compounds from blanch and wash waters, e.g. mushrooms and fish, and should be applicable to thaw and chill waters, e.g. poultry. There are also potential advantages for membrane separations in the recovery of volatile flavors of all foods with advantages over the distillation methods since heat can produce artifacts that can alter the natural flavors. Other methods such as dense gas or super-critical extractions and thermostable binding of flavor compounds will also be discussed. Biotechnology, e.g. pectic anzyme treatments, is also being developed to improve the quality and recovery of food flavors.

X3

Plant Cell Culture Systems for Flavor Production. Susan K. Harlander, University of Minnesota, Dept. of Food Science & Nutrition, St. Paul, MN 55108.

Plant cell tissue cultures are potentially rich sources of valuable biochemicals, including pharmaceuticals, fragrances, essential oils and natural food colors and flavors. Efforts to commercially exploit plant cell culture systems for flavor production have been thwarted by the fact that very few cultures synthesize these secondary metabolites over extended periods in amounts comparable to those found in the whole plant. Regulation of secondary metabolism in cell culture systems is poorly understood but appears to be influenced by nutritional factors, phytohormone levels, light, temperature, pH and aeration conditions. This presentation will focus on what we know about the biogenesis of flavor compounds in cultured plant cells, the potential use of elicitors to induce secondary metabolite production and the challenges associated with large scale cultivation of plant cells and down-stream processing of flavor compounds. Examples of compounds currently produced by commercial plant cell culture processes will be discussed.

X4

Generation of Flavor and Aroma Components by Microbial Fermentation and Enzyme Engineering Technology. Helmut Grueb, Haarmann & Reimer Corp. GmbH, Holzminden 3450, West Germany.

The flavor and aroma of many foodstuffs are formed as a result of the action of enzymes and microorganisms. This knowledge can be exploited to obtain both complex flavor mixtures and individual flavor compounds via microbial fermentation and/or enzyme technology. Many different classes of compound can be obtained this way including esters, lactones, aldehydes, ketones and acids.

X5

Flavor Binding By Food Components, Particularly Proteins. J.E. Kinsella, Cornell University, Institute of Food Science, Ithaca, NY 14853.

The identification of major components of food flavors has been successful, and progress has been made in the synthesis and formulation of desirable food flavors. Progress in these two areas has dramatized a major remaining problem i.e. flavor binding and release by food components. This problem has become accentuated recently because the demand for natural flavors has increased cost and made users more conscious of the problems of flavor binding. There are limited data concerning the manner and mechanisms by which individual flavors of a blend interact with food components. Different flavors adsorb or bind to various food components in a differential manner. Binding of flavors tend to suppress their impact and/or perception and frequently result in an imbalance. The flavor impact as perceived by the consumer is important in determining the acceptability of foods, hence, knowledge of the interactions of flavor compounds with food components is of practical interest. Such data are needed to facilitate the development of appropriate flavor blends and for products fabrication, formulation and optimization of processing. Excessive binding of flavors by food components, of flavors during processing and storage and the preferential or uneven release of flavor components of a blend during food consumption are major problems particularly in fabricated foods. Because the perceived flavor is ultimately important in determining acceptability of food, more information concerning the phenomena of flavor binding and release is needed. Because they are important functional components in formulated foods, the binding of flavors by proteins is of interest. The binding behavior of food proteins vary immensely depending upon the nature of the flavor ligand, the nature of the surface of the protein molecules, (i.e. topographical features and available hydrophoblic surface patches), conformational state of the protein and several environmental factors. Information is needed concerning the flavor binding capacities of different food proteins. In this presentation, flavor binding behavior of a number of proteins namely β-lactoglobulin, bovine serum albumin and glycinin for volatile 2-alkanones will be reported. On an equivalent molecular mass basis, β-Lg has the highest affinity for these compounds using equilibrium dialysis. A simple microgravimetric method for determining flavor sorption/desorption isotherms will be described.

X6

Correlation of Instrumental and Sensory Analysis of Lipid Foods. Glen A. Jacobson, Campbell Soup Company, Campbell Place, Camden, NJ 08101, and Denise M. Horsley and J.A. Ford, Campbell Soup Company.

The perceived quality of many foods can be greatly affected by lipid-derived flavor components of these foods. Flavor evaluation by sensory methods remains very important in determining consumer acceptance, but instrumental measurement of the key flavor components is needed for more accurate, non-biased estimations of the relative levels of the components. Instrumental analysis also can provide valuable insight into the origin and conditions favoring the development of these key flavorants. Workers from several laboratories have shown that gas chromatographic and sensory measurements correlate well for estimating the quality of vegetable oil flavor. Similarly, we will report on correlative tests involving bakery products, marine lipids, fried foods and other lipid-containing ingredients or foods. The effects of certain environmental factors such as water activity, temperature, oxygen and light exposure, etc. on the generation of lipid-derived flavorants will also be reported.

X7

Use of Multivariate Statistical Methods To Extract Information In Flavor-Analysis Results. John J. Powers, University of Georgia, Department of Food Science, Athens, GA, 30602.

The integration of statistics with flavor analysis is not new. Bengtsson (1943) very ably did that when he originated the triangular method. However, the need for integration is far more pressing today. No longer does mere evaluation of a difference suffice. Data today often encompass quantitative assessment of 10 or more flavor attributes, 100s of chromatographic peaks, separate analysis of subfractions of the sample and interrelations among these data species. Univariate and multivariate statistical analyses applied jointly enable the maximum amount of information to be extracted from such data sets. The functions, applications, limitations and benefits of the various methods will be illustrated relative to flavor analysis.

Session Y Tuesday afternoon

Protein Symposium III:- Molecular Properties of Proteins Important for Emulsification, Foaming and Gelation

Y1

Molecular Properties Of Food Proteins and Their Measurement. Damodaran, Srinivasan, University of Wisconsin, Department of Food Science, 1605 Linden Drive, Madison, WI 53706.

The functional properties of food proteins in fabricated foods, such as foam, emulsion and gel type products are fundamentally related to their molecular properties such as molecular weight, charge, hydrophobic/hydrophilic residue balance, amino acid sequence and composition and secondary, tertiary conformations. Under processing conditions some of these physical properties, especially the surface hydrophobicity/hydrophilicity and the conformation undergo changes and affect the behavior of proteins. To predict and to improve the functional properties of novel food proteins, it is fundamentally important to define how each of these molecular parameters, individually as well as in combination, affect their behavior in a given food system. An overview of the various methods that are used to elucidate and understand the physicochemical properties of food proteins and the influence of various molecular parameters on foaming, emulsifying and gelling properties of foods proteins are described.

Y2

Molecular Properties and Functionality of Proteins In Food Emulsions: Meat Products. J.M. Regenstein, Cornell University, Poultry & Avian Sciences Dept., 112 Rice Hall, Ithaca, NY 14853.

Are meat batters really emulsions? Traditional efforts to measure the process involved in forming comminuted meats are based on assumption that they are true emulsions, i.e., the bind value is based on the emulsion capacity of soluble muscle protein. Recent data, using the method of timed emulsification and the stability of the timed emulsification cream layer has led us to question this assumption. Research by others also supports the idea that the meat batter may actually depend more on the gelation properties of the aqueous matrix than on the surface properties at the oil-water interface. In addition to learning more about the meat batter process, these newer methods may permit us to evaluate the effect of non-meat ingredients on meat batter systems and to incorporate an evaluation of both meat and non-meat ingredients in processed meats that is compatible with modern least cost formulation methodology.

Y3

Molecular Properties and Functionality of Proteins In Food Emulsions: Liquid Food Systems. M.E. Mangino, The Ohio State University, 2121 Fyffe Road, Columbus, OH 43210-1097.

Emulsions are themodynamically unstable dispersions of immiscible liquids. If work is applied the systems may be dispersed. The increased surface energy will cause the phases to rapidly coalesce unless an energy barrier is established. The emulsion can be stabilized to coalescence by the addition of molecules that are partially soluble in both phases. In foods a number of small molecules can serve this function. Proteins that can unfold at the interface can also function as emulsifiers. The protein will coat the lipid droplet and may provide an energy barrier to both particle association (creaming) and to phase separation. In order to function well as an emulsifier the protein molecule must be flexible, impart a rigid structure to the interface and contain enough hydrophobic groups to interact with the oil phase. In general proteins that contain large numbers of sulfhydryl groups do not function well as emulsifiers while those with high effective hydrophobi-

cities tend to form more stable emulsions. Phase separation is unusual in food emulsions, but creaming upon prolonged storage is a common problem. Proteins that contain residual structure may stabilize the emulsion towards creaming by sterically hindering the aggregation of lipid droplets.

Y4

Molecular Properties and Functionality of Proteins In Food Foams. B. German, University of California, Food Science and Technology, 1480 Chemistry Annex, Davis, CA 95616, and Lance Phillips, Cornell University.

Foams are thermodynamically unstable colloidal systems in which gas is maintained as a distinct dispersed phase by a kinetic barrier typically provided by a layer of protein surrounding the bubble structure. The goal in understanding the role of protein structure in this functionality is determining how the forces enjoined on the protein during a dynamic interfacial exposure period alter its structure leading to novel molecular and macromolecular interactions which then resist collapse. The ability to associate in a denaturing environment, i.e. an interface, and yet retain some residual conformation appears to be important to the formation of a stable film. Thus, typically pure proteins foam less well than mixtures; proteins foam optimally near their isoelectric point; and fully denatured proteins foam poorly. Soy 11 s, a poorly foaming protein, resists unfolding due to the presence of intramolecular disulfide linkages. Cleavage of these linkages does not in itself dissociate the protein but significantly reduces the stability. Reduction of the intramolecular disulfide linkages enhances foam and film strength. The foaming properties of egg white proteins have been ascribed to electrostatic interactions between the globular egg proteins and lysozyme. Lysozyme similarly enhances the foaming of other negatively charged globular proteins illustrating optimized attractive and repulsive forces. Repulsive electrostatic interactions are emphasized in colloidal stability theory but excessive electrostatic repulsion between proteins during the period of film formation can prevent development of intermolecular associations. Thus at pH 7 the presence of salt as neutralizing counter ion is necessary for the formation of a stable film of reduced 11 s protein. The many variables which impact on foam and film structure emphasize the necessity of adopting standardized or at least comparable methodologies for foam measurement.

Y5

Molecular Properties and Functionality of Proteins In Food Gels. E. Allen Foegeding, North Carolina State University, Department of Food Science, Box 7624, Raleigh, NC 27695-7624.

Food gels are solid materials, consisting of a small concentration of polymer matrix entrapping an aqueous suspension. The polymer matrix and aqueous suspension contribute to the texture, water-binding and appearance of food gels. By varying the polymer matrix and composition of the aqueous suspension, a wide spectrum of textures can be obtained. Proteins can function as the gel matrix and as suspended particles. The functional properties of proteins related to the matrix are: 1) the lowest protein concentration for gelation; 2) the change in protein structure required for polymerization and 3) the bonding, geometry and resultant physical properties of the gel matrix. Food proteins, such as whey and muscle, form gels during heating due to denaturation driven association. Therefore, the unfolding process, intermediate unfolded states and association (aggregation) of denatured molecules will determine matrix-forming functional properties. Suspended proteins which are not interacting with the matrix funciton by binding water and fat. By contrast to matrix function properties, maintaining water and fat binding ability over a wide range of temperature and ionic conditions, generally requires a stable protein which does not associate. This review will address the relationship between protein structure and gelation.

Y6

Lipid-Protein-Surfactant-Water Interactions In Whippable Emulsions. N.M. Barfod, Grindsted Products, 38 Edwin Rahr's Vej, Brabrand DK-8220, Denmark, and N. Krog, Grindsted Products, and W. Buchheim, Milk Research Institute.

In spray-dried whippable emulsions (toppings) the fat phase of the emulsion droplet is in a supercooled state due to strong lipid-protein interactions which can be measured by pNMR. During reconstitution in temperate water, the emulsion is stabilized by protein adsorption at the fat-water interface. Upon cooling of the emulsion, the lipid surfactant (propylene glycol monostearate) present in the fat phase becomes very surface-active and displaces the protein from the fat-water interface. The surfactant multilayers in the fat phase absorb water as seen by X-ray diffraction. This latter reaction accelerates protein desorption from the fat-water interface. The deproteinated fat surface lacks stability resulting in coalescence and crystallization of supercooled fat which can be followed by pNMR-SFC measurements. The spontaneous crystallization is important for the texture of the whipped emulsion which is stabilized by fat crystals adsorbed at the air-water interface. The concentration of surfactant in the fat phase controls the rate and degree of emulsion destabilization.

Session Z Tuesday afternoon

Effects of Dietary Omega-3 Fatty Acids III

Z1

Metabolism of Deuterium-Labeled Linolenic Acid In Humans. E.A. Emken, Northern Regional Research Center, ARS-USDA, 1815 North University Street, Peoria, IL 61604, and R.O. Adlof, H. Rakoff and W.K. Rohwedder, Northern Regional Research Center.

Two adult male subjects were fed mixtures of triglycerides containing deuterium-labeled octadecanoic acid (18:0), *cis*-9-octadecenoic acid (18:1ω9), *cis*-9,*cis*-12-octadecadienoic acid (18:2ω6) and *cis*-9,*cis*-12,*cis*-15-octadecatrienoic acid (18:3ω3). Blood lipid fractions were collected over a 8-hr period and analyzed by gas chromatography-mass spectrometry. Comparison of the metabolism of the deuterium-labeled 18:3ω3 to the other labeled fatty acids showed the

following: (A) 18:3ω3 was not absorbed as well as 18:1ω9 or 18:2ω6, but better than 18:0; (B) esterification of cholesterol with 18:3ω3 was the same as for 18:1ω9, but ca. 7 times lower than for 18:2ω6; (C) 18:3ω3 incorporation into phosphatidylcholine (PC) was much lower (5 to 10 times) than for 18:0 and 18:2ω6, due to selective incorporation of 18:0 at the 1-acyl PC position and 18:2ω6 at the 2-acyl PC position; and (D) conversion of 18:3ω3 to 20:5ω3 was not detected. These results show that relative to 18:2ω6, 18:3ω3 is a poor substrate for phosphatidylcholine acyltransferase and lecithin:cholesteryl ester acyltransferase. These preliminary data indicate that fatty acid composition is tightly controlled, and that desaturase and elongase activities are low in man. Thus, one reason that 18:3ω3 elicits a smaller physiological response in man than that observed in studies involving fish oil supplementation may be because of the low conversion of 18:3ω3 to the physiologically more active 20:5ω3.

Z2

Reduced Growth and Metastasis of A Transplantable Syngeneic Mammary Tumor (410.4) By Dietary Alpha-Linolenic Acid (18:3N-3). Kevin L. Fritsche, University of Illinois, 1208 W. Pennsylvania Avenue, Urbana, IL 61801, and Patricia V. Johnston, University of Illinois.

Weanling female BALB/c mice were fed a purified diet containing 10% by weight corn oil (CO) or linseed oil (LO), which provided a ratio of 18:2n-6 to 18:3n-3 of 50:1 and 1:2, respectively. After 8 weeks on diets mice received s.c. injections of the highly metastatic mammary tumor cell line (410.4). Upon reaching a minimum of 10 mm in width the primary tumor was surgically removed. Three weeks later, or upon death, lungs were removed and metastatic foci enumberated. Tumors grew more slowly in LO compared to CO-fed mice. Surgical removal of 1° tumors averaged 9 days later for LO vs. CO mice. Furthermore, tumors from CO mice weighed significantly more ($P<0.005$) than from LO mice (0.45 ± 0.5 vs. 0.24 ± 0.4 g) for CO vs. LO, respectively. Survival post-surgery averaged 5 day longer for LO vs. CO fed mice and metastasis to the lungs was 3-fold greater in CO vs. LO-fed mice. Similar results were obtained in a follow-up study in which diets were fed for only 3 weeks prior to tumor cell injection. Interestingly, in this study a third diet group fed fish (menhaden) oil responded more like the CO than the LO-fed mice. In the 2nd study tumor fatty acid composition and PG synthesis was determined. PGE synthesis by tumor homogenates was 22 and 56% lower in LO and FO-fed mice, respectively, compared to CO-fed mice. While there have been several reports of reduced growth of transplantable mammary tumors upon feeding diets rich in the long-chain n-3 fatty acids this is the first report of such an effect by dietary 18:3n-3, the parent of the n-3 family of fatty acids.

Z3

Alteration of Blood Platelet Reactivity and Phospholipid Composition By A Fish Oil Concentrate In Human Subjects. Bruce J. Holub, University of Guelph, Department of Nutritional Sciences, Guelph, ONT N1G 2W1, Canada.

The consumption of fish oils containing eicosapentaenoic acid (EPA) has been found to have the potential to favorably influence several risk factors for cardiovascular disease even without a concomitant lowering of total blood cholesterol levels. In this regard, we have focused upon the effect of EPA on blood platelet phospholipid compositions and reactivity since platelet aggregation is intimately associated with arterial thrombosis. Using low concentrations of collagen or other agonists (eg., PAF), aggregation in washed platelet suspensions was significantly reduced *ex vivo* when human volunteers ingested a fish oil concentrate (MaxEPA) providing 3.6 g EPA/day (approx. 1% of caloric intake) over several weeks. Lipid analyses revealed that the incorporated EPA selectivity replaced arachidonic acid (AA) in some phospholipid pools [choline phospholipid (PC) and ethanolamine phospholipid (PE)] more than in others (inositol- and serine-phospholipid). Interestingly, the ether-containing phospholipid, 1-alkenyl 2-eicosapentaenoyl PE, was found to be a predominant reservoir of EPA in the platelets of human subjects consuming the fish oil concentrate. Furthermore, the relative contributions of different phospholipid reservoirs to releasable eicosanoid precursor were markedly different for EPA versus AA upon agonist exposure (eg., thrombin).

Z4

Dietary Omega-3 Fatty Acid Supplementation In Type II Diabetic: Diverse Effects On Glucose and Lipoprotein Metabolism. John W. Ensinck, University of Washington, Department of Medicine, RC-14, Seattle, WA 98195.

Fish oil capsules containing omega-3 fatty acids (ω3FA) have become popular as a means to decrease very low density lipoprotein (VLDL) cholesterol and triglycerides (TG). Since hypertriglyceridemia is frequent in Type II diabetes and ω3FA might perturb both insulin secretion and insulin resistance favorably in these patients, we examined the effects of ω3FA on lipoproteins and glucose homeostasis in Type II diabetic men. Their diet was supplemented with 8g of omega-3 FA daily for 8 weeks. Before and after ω3FA supplementation, the following were measured: plasma lipoproteins and RBC fatty acids, plasma glucose, insulin, glucagon, and somatostatin levels before and after a mixed meal. After ω3FA supplementation, RBC membrance composition increased five-fold, whereas VLDL and TG fell by 51% and 33% respectively. In contrast, fasting plasma glucose levels increased by 29% and post-prandial glucose assimilation decreased associated with diminished circulating glucose-regulatory peptides. We conclude that in Type II diabetics, omega-3 FA supplements, while improving hypertriglyceridemia, leads to an impairment in glucose homeostasis.

Session AA Tuesday afternoon

Capillary Column Chromatography

AA1

Capillary Columns—They Have Finally Arrived! R.G. Ackman, Canadian Institute of Fisheries Tech., Technical University of Nova Scotia, P.O. Box 1000, Halifax, NS B3J 2X4, Canada.

Capillary columns are almost as old as GLC itself. One can pass quickly from 1959 to 1979 with brief consideration of both home-made glass and Perkin-Elmer stainless steel capillary columns en route. The astounding success of the "flexible fused silica" wall-coated open-tubular gas-liquid chromatography columns in the last decade is not that they are that much better, or that much easier to use, and certainly not because they are cheaper, but represents a step in the normal scientific development process. By 1975 packed GLC columns had developed about as far as they could go. The need for a technological advance was apparent, and the solution, once presented, was seized upon and brilliantly developed by Hewlett-Packard. This development has not been without its problems. Nevertheless the application of ffs-wcot columns to the C_{14}-C_{22} fatty acids common to fish oils and their concentrates on the one hand, and to human or other animal body organ lipids on the other hand, is another remarkable coincidence of the tool being developed in time to answer the need and will be the focus of this presentation.

AA2

Measurement of *cis-cis* & *trans* Values In Fatty Acid Methyl Esters From Vegetable Oils By Capillary Gas Chromatography. R.A. DePalma, The Procter and Gamble Company, Winton Hill Technical Center, 6071 Center Hill Road, Cincinnati, OH 45224.

The cyano-propyl stationary phases have the ability to separate fatty acid methyl esters (FAME) by double bond geometry in addition to chain length and degree of unsaturation. With this separation ability, two additional properties of an oil can be determined from an analysis of the FAME: the level of *trans* and *cis-cis* components in the sample. A 60 meter capillary column which is coated with SP-2340 has been used to separate FAME and measure the fatty acid composition, iodine value, *trans* value and *cis-cis* value from a single gas chromatographic analysis. This separation works well for a variety of oils, and there is good agreement between the *trans* and *cis-cis* values by gas chromatography and the traditional methods: infrared for *trans* and lipoxygenase for *cis-cis*. This method is now undergoing a collaborative study, and preliminary results from the study will be discussed.

AA3

Status Of The AOAC Collaborative GLC Study. Jeanne D. Joseph, National Marine Fisheries Service, Charleston Laboratory, P.O. Box 12607, Charleston, SC 29412.

Since almost all marine oils contain 60-80 different fatty acids, they cannot be analyzed by current official methods which employ packed GLC columns. However, wall-coated open-tubular columns provide excellent resolution of most of the fatty acids commonly encountered in marine oils. Experience in a number of laboratories over the past few years suggests that columns made of flexible fused silica and coated with a bonded polyglycol give excellent separations and quantitative results and have a long life when protected from oxygen. A collaborative study of such columns has been developed to examine inter- and intra-laboratory reproducibility in the analysis of marine oils. Samples consisted of four different marine oils, plus one blind duplicate, and an omega-3 ethyl ester concentrate, all in soft gelation capsules. Methyl and ethyl esters of 23:0 were provided for use as internal standards. Collaborators were asked to report data from a single analysis of each sample, carried out on a 25–50 meter column coated with a bonded polyglycol such as Carbowax-20M, Supelcowax-10 or equivalent liquid phase. The status of the study will be reviewed.

AA4

Wide Bore Capillary Columns for Fatty Acide Analysis. Nicholas Pelick, Supelco, Inc., Supelco Park, Bellefonte, PA 16823-0048, and Leonard M. Sidisky, Supelco, Inc.

Analyses of fatty acids, both as free acids and methyl ester derivatives, are recognized as among the most important areas in gas chromatography. Numerous papers have been published on analyses of fatty acids, using a variety of packed and narrow bore capillary columns. Recently a new group of columns—wide bore capillary columns—has received considerable attention. These columns, 0.53 and 0.75 mm ID, offer the advantages of better resolution, greater inertness, wider application range, and faster analysis times than packed columns, and simpler operation and higher sample capacity than narrow bore capillary columns. These advantages make wide bore capillary columns very important analytical tools. We will present performance data demonstrating some of the advantages of wide bore capillary columns over other column types. The utility of wide bore columns for analyses of both free fatty acids and fatty acid methyl esters from a variety of matrices will be presented.

AA5

Quantitative Esterification of Fatty Acids. R.G. Einig, Warner Lamber Co., Consumer Products Research & Development, 170 Tabor Road, Morris Plains, NJ 07950, and C.A. Georgiades, Warner Lamber Co.

Interest in the absolute concentration of individual fatty acids (f.a.) from mixed triglycerides has been intensified by recent nutritional considerations, and has focused attention on the quantitative aspects of f.a. analytical methodology. In AOCS Method Ce2-66 is described the procedure for preparing esters of f.a. for further analysis by gas chromatography. When fish oil triglycerides and free f.a. were methylated according to this procedure, it was found that the rates of reaction were dependent on the f.a. species. Quantitative recovery was not obtained for all species under these reaction conditions. Various methylating agents were used and time and temperature parameters were changed to achieve complete reaction.

AA6

Quantitation of FAME—Response Factors and Injection Technique. J.D. Craske, consultant, 20 Woodford St., Longueville, NSW 2066, Australia, and C.D., Bannon.

It has been shown by Craske and Bannon that, to ensure that FAME results shall be accurate, there are eight factors that need to be addressed. While all are important and must be carefully optimized, this paper will deal with two only, viz. theoretical response factors and injection technique. Results will be presented to show

that, for both saturated and unsaturated FAME, the theoretical response factors, as first proposed by Ackman, are valid. A proof of validity for unsaturated FAME will be discussed. An approach to the optimization of splitting injectors will be outlined. Points of particular importance are elimination of needle discrimination, rapid sample vaporization and complete homogenization of sampled and carrier gas stream. If these factors are optimized, others that may influence accuracy are of little importance. In spite of the high accuracy of results that can be obtained by careful optimization of the injection system, injection remains a difficult factor in the total analysis and there is still opportunity to develop systems of greater reliability and ease of use.

AA7

Analysis of Vegetable Oil Volatiles by Multiple Headspace Extraction. J.M. Snyder, Northern Regional Research Center, ARS/USDA, 1815 North University Street, Peoria, IL 61604, and T.L. Mounts, Northern Regional Research Center.

Quantitative determination of the volatiles produced from oxidized vegetable oils has become an important indicator of oil quality. Five vegetable oils, low-erucic acid rapeseed, corn, soybean, sunflower, and high oleic sunflower, were stored at 60 C for four and eight days to yield oils with several levels of oxidation. Peroxide values of the fresh oils ranged from 0.6 to 1.8 while those of the oxidized oils were from 1.6 to 42. Volatile analyses by the multiple headspace extraction (MHE) technique, which includes a pressure and time-controlled injection onto the GC-column (a chemically bonded capillary column), was compared with those obtained by static headspace gas chromatography (SHS-GC). Several volatile compounds, indicative of the oxidation of polyunsaturated fatty acids from the vegetable oils, were identified and measured by MHE; pure compounds of twelve major volatiles were also measured by MHE, and peak areas were determined. Multiple extractions of the oil headspace provided a more accurate correlation of GC peak area to volatile concentration than was obtained by SHS-GC. Concentrations of all volatiles increased with increased oxidation, as measured by peroxide value of the oil.

AA8

Determination of Trace Levels of Linoleic Acid and Its Esters By Argentation Solid Phase Extraction and Gas Chromatography. William L. Grady, Union Camp Corporation, Chemical Products Division, P.O. Box 2668, Savannah, GA 31402.

Trace levels of linoleates and linoleic acid in substrates in contact with food is believed to cause alterations of taste quality. Resource intensive GC/MS is currently the method of choice for measuring linoleates (or linoleic acid). The paper will describe a method whereby the sample is saponified and esterified and the resulting methyl linoleate concentrated by solid phase extraction on a silver nitrate impregnated alumina column. Concentration factors greater than 200 are obtainable. The linoleate concentrate is analyzed by capillary gas chromatography with flame ionization detection. Detection limits based on the original sample are below 10 ppm. Results from several substrates and comparisons to GC/MS will be presented.

Session BB Tuesday afternoon

Processing II: Preparation/ Prepress/Extraction and Chemical and Physical Refining

BB1

Fluidbed Soybean Preparation System—Experience After 5 Years of Operation. Jack G. Moore, Hunt Moore & Associates, Inc., 3951 Senator Street, Memphis, TN 38118.

Fluidbed preparation of soybeans is discussed giving the history of development and evolution after 5 years of operational experience. Slides will cover basic operation and operational data including energy performance.

BB2

Trends and Developments In Oilseed Screw Pressing. Martin A. Stainsby, Simon-Rosedowns Ltd., Mechanical Development Manager, Cannon Street, Hull HU2 0AD, England.

This paper firstly discusses the problems that can be encountered when running a screw press with regard to maintenance and obtaining optimum performance. It then goes on to describe how the problems are being tackled and the advantages that this will bring to the oilseed processor. General trends in screw press development are discussed and so too are likely future developments.

BB3

Update on Desolventizing and Predesolventizing. Jerry Fawbush, Central Soya Inc., P.O. Box 1400, Ft. Wayne Bank Building, Ft. Wayne, IN 46801.

This article will cover advances in desolventizing and predesolventizing soybean meal. Summaries will be given on operational advantages and energy requirements for the different arrangements.

BB4

Nonelectrolyte Partitioning By UF/RO Membranes—An Application To Cottonseed Extraction. M.S. Kuk, Southern Regional Research Center, USDA, ARS, P.O. Box 19687, New Orleans, LA 70179, and R.J. Hron, Sr., Southern Regional Research Center.

Although hexane is the most popular solvent for extracting oil from oilseeds, short-chained aliphatic alcohols have been considered as potential alternative solvents. Aqueous and pure ethanol have been studied for extracting oil and other components from cottonseed. One of the most important process prerequisite for the ethanolic solvent is that the residual oil content in the extracted meal be equal to that achieved by hexane, namely ca. 1 wt.%. Miscella regeneration, which has been routinely performed in the conventional extraction by evaporators and scrubbers, becomes very critical in the ethanol extraction. A rigorous regeneration of the solvent is essential not only because of the process economics constraint but also the equilibrium requisite. In an effort to search for a new

technical alternative to the conventional solvent regeneration method, which may not be the most economical route sometime in the future, polymeric membranes used in reverse osmosis (RO) or ultrafiltration (UF) were examined for regenerating the miscella. Chromatographic analysis of the miscella and the permeate products indicates that not only triglycerides but also polysaccharides present in the miscella were effectively removed by UF or RO membranes. The principal rectifying mechanisms are discussed based upon the chromatographic analysis and thermodynamics.

BB5

Phospholipid Analysis of Canola Oil. R. Przybylski, University of Manitoba, Department of Foods and Nutrition, Winnipeg, MB R3T 2N2, Canada, and N.A.M. Eskin, University of Manitoba.

Phospholipid analyses were conducted on canola oil samples obtained from several crushing plants after pressing, extraction and degumming. Phospholipids were isolated by modified silica and separated by thin layer chromatography. Individual phospholipids were further separated on chromarods and quantitatively evaluated with a flame ionization detector. Standard phospholipids were used to evaluate this procedure in which the recoveries of phosphatidylcholine (PC), phosphatidylinositol (PI), phosphatidylethanolamine (PE) and phosphatidylserine (PS) were all found to be greater than 90%. Using this procedure to characterize phospholipids in canola oil, significant differences were observed between producers and stages of processing. A 50% reduction in total phospholipids was found for the expelled oil compared to the solvent extracted oil. Differences were also observed in the distribution of the individual phospholipids with hydratable phosphoplipids being much lower in the expelled oil compared to the solvent extracted oil. Non-hydratable phospholipids, however, accounted for the majority of phospholipids in both expelled and solvent extracted canola oil samples.

BB6

Continuous Ultrasonic Degumming of Crude Soybean Oil. K.J. Moulton, Sr., Northern Regional Research Center, USDA/ARS, 1815 North University Street, Peoria, IL 61604.

The replacement of chemical refining with a physical refining process for purification of soybean oil is a likely response of the food oils industry to increasing energy costs and growing sensitivity to environmental problems. Implementation of a combined of deacidification-deodorization process is depends on efficient pretreatment for removal of phospholipids. Early attempts to apply this technology with soybean oil failed due to inconsistent quality of the crude oil and inadequate pretreatment to overcome these inconsistencies. We have investigated the application of ultrasonic energy to continuous degumming for the efficient removal of phospholipids from crude soybean oil. The crude oil and water (2.0% by weight) were pumped through an ultrasonic processing cell, oil and hydrated gums were separated by centrifugation, and the recovered oil was vacuum bleached. The degummed and bleached oil had a residual phosphorus content of less than 10 ppm and was subsequently deacidified-deodorized in all-glass laboratory deodorization equipment. Odor and flavor evaluation indicated that the salad oil produced by the process of ultrasonic degumming/deodorization-deacidification was equivalent in quality and stability to a conventionally processed salad oil.

BB7

The Effect of Acid Pretreatment of Phospholipid Removal. James M. Bogdanor, W.R. Grace & Co., Davison Chemical Division, 7379 Route 32, Columbia, MD 21044.

Acid pretreatment of crude oils containing significant levels of phospholipids is widely practiced on a commercial scale to remove nonhydratable phosphatides. Data comparing the efficacy of both phosphoric acid and citric acid pretreatment are presented. Experimental results show that insufficient acid treatment in both physical and caustic refining results in poor phospholipid removal in degumming and subsequent adsorptive bleaching. Over-addition of acid is costly and, in the case of phosphoric acid, can result in residual P that is often mistakenly assumed to be associated with phospholipids. Formulae for acid pretreatment levels based on crude oil Ca and Mg levels are given. Trace metal analyses for Ca and Mg are used to discriminate between P from phosphoric acid and phospholipid in downstream processes. In addition, the effects of water addition in degumming and moisture content of oil entering bleaching on phospholipid removal are discussed.

BB8

Preconditioning, Degumming and Acid Treatment Practices Before Physical Refining. Peter Kalustian, Peter Kalustian Associates, Inc., 239 Reserve Street, Boonton, NJ 07005.

There is continued worldwide interest for more physical refining of fats and oils for such obvious reasons as simpler and more uniform processing, waste water pollution abatement, higher yield and overall cost reduction. It is essential that the quality of the fully refined oil be at least comparable to that available from chemical refining. The industry practices vary widely in the mills and in the refining plants depending on the established processes and the type of oilseed or crude oil. The proper preconditioning and various mill practices will be described as they can contribute materially to insure the necessary quality. Adequate degumming and specific acid treatment are essential. Such practices will be described including the equipment required and the specific acids that can be used. Adequate laboratory control is required to insure adherence to the quality standards. These limits will be suggested. Those who have the foresight to adopt proper practices will profit by greater acceptance of these products.

BB9

Operating Parameters for Miscella Processing Various Types of OIls. George C. Cavanagh, Cavanagh Associates, 1752A West Calimyrna Ave., Fresno, CA 93711.

Miscella refining has been an industrial unit process

in oilseed solvent extraction plants for at least 40 years. This paper addresses the decision-making processes for determining the operating parameters for miscella refining direct extracted oils and prepressed-solvent extracted oils. Data is presented on solvent fractional crystallization and on solvent dewaxing various oilseeds. Properly practiced miscella refining results in lower refined and deodorized oil colors and lower refining losses than oil conventionally refined. Fractional crystallization in solvent is accomplished in approximately 30 minutes with separation of phases done centrifugally. Solvent dewaxing requires lower temperature and a fraction of the time required for conventional dewaxing.

BB10

Winterizing of Vegetable Oil In Conjunction With Alkali Refining. K.P. Eickhoff, Westfalia Separator AG, and K.W. Klein (speaker), Centrico, Inc.

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

BB11

Optimization of Heat Recovery In Multi Stockchange Deodorizer. Anthony John Harper, Simon-Rosedowns Limited, Cannon Street, Hull, North Humberside HU2 0AD, England.

Experience has shown that to produce the best quality deodorized products, the oils and fats should be steam sparged at all stages during the deodorization process. This statement may be better defined by applying some temperature limits but essentially it means that ideally the dried, deaerated feedstock fed to the deodorizer should be under steam sparging during the heating, heat recovery and cooling sequences of the operation. The relatively poor heat transfer characteristics of oils and fats and the pursuance of high recovery figures has required the use of large heat transfer surface areas. To satisfy this latter requirement the process designer has felt the need to use external heat exchangers. It is difficult to sparge the oil in an external heat exchanger and problems with complete drainage leads to unacceptable interstock contamination. This paper illustrates a deodorizer design which optimizes the heat recovery system within the deodorizer vessel, permits frequent feedstock change but still keeps interstock contamination to a minimum.

Session CC Wednesday morning
Surfactants and Detergents V: Performance and Evaluation

CC1

Precipitation In Mixtures of Anionic and Cataionic Surfactants. Joel C. Amante, University of Oklahoma, Institute for Applied Surfactant Res., Norman, OK 73019, and John F. Scamehorn (speaker) and Jeffrey H. Harwell, University of Oklahoma.

It is increasingly desirable to include both anionic and cationic surfactants in a number of consumer products. An example is the desire to both clean and fabric soften clothing in the wash cycle. The topic of this presentation is the precipitation of anionic and cationic surfactants from water. The effect of temperature, salinity, pH and surfactant structure on the equilibrium phase boundaries will be discussed. These phase boundaries can be described by using a theory involving solubility products of monomeric surfactant and regular solution theory to describe monomer-micelle equilibrium. Consequences for practical application of anionic/cationic mixtures will be outlined.

CC2

Effect of Molecular Composition on the Physical Properties and Performance of Linear Alcohol Ether Sulfates. Michael F. Cox, Vista Chemical Company, P.O. Box 500, Ponca City, OK 74602.

The effects of alcohol carbon chain length and ethylene oxide content on the physical properties and performance of linear alcohol ether sulfates were examined. Physical properties include solubility and viscosity. Performance properties include surface activity (critical micelle concentration, surface tension reduction and surface excess adsorption), foaming, wetting and detergency. The effect of ethylene oxide distribution (e.g., ether sulfates made from peaked distribution ethoxylates) is also examined.

CC3

Liquid Detergent Based On A Blend of Cationic, Anionic and Nonionic Surfactants. Adsorption, Detergency and Antistatic Properties. K.M.E. Hellsten, Berol Kemi AB, Stenungsund S-44401, Sweden, and A.W. Klingberg and B.T.G. Karlsson, Berol Kemi AB.

The adsorption from a mixture of cationic (c) and anionic (a) surfactants on cellulose fibers is highly dependent on the ratio a/c with a maximum at a/c = 0.9. When a/c is > 1.1 the adsorption is negligible. The presence of nonionic surfactants in the solution impairs the adsorption of the ionic species and this effect is stronger for nonionic surfactants with long alkyl and polyglycolether chains. The detergency—measured on WFK cotton cloth—is highest when a/c > 1 and decreases sharply when a/c goes below 0.8. The antistatic effect for a formulated liquid detergent based on these principles was compared to two commercial detergents plus a commercial softener in the rinse and was found to be 5, 7 and 23 times higher for polyamide, polyester and polyacrylonitrile fabrics respectively. Terry towel cloth was also softened by the liquid detergent—but this effect was smaller than for the commercial softener. The removal of pigment and fatty soil at 40 C was comparable to the commercial detergents.

CC4

Synthetic Background Soil for Laundry Product Perform-

ance Evaluations. Paul Anderson, Clorox Technical Center, P.O. Box 493, Pleasanton, CA 94566.

It is desirable to conduct laundry product performance evaluations in the presence of naturally soiled ballast to simulate actual consumer laundering conditions. Since securing naturally soiled items is often impractical and the level of soil varies widely even when it can be obtained, we have developed a synthetic background soil that approximates natural consumer soil. This soil was developed based on known components of natural soil and is comprised mainly of particulate clay, oils, urea and water hardness. The soil is easy to prepare and is introduced to a washload on a single pillowcase. Our testing shows that the synthetic soil models the wash water pH drops, suspended soil levels, and hypochlorite degradation profiles seen in washes containing consumer soil. Testing results for stain removal, soil removal, and whitening performance versus natural soil will also be discussed.

CC5

Influence Of L.A.S. Counterion and L.A.B. Characteristics on The Physicochemical Properties of Linear Alkylbenzene Sulfonate. L. Cohen, Petroquimica Espanola, S.A., Orense, 68, Madrid 28020, Spain, and J.L. Berna and A. Moreno, Petroquimica Espanola, S.A.

Linear alkylbenzene sulfonate or L.A.S. is produced as a salt by neutralization either with an inorganic cation or with an organic radical as the counterion. The nature of this "counterion" has an important influence on the physicochemical properties of the final sulfonate. The following ones will be considered: solubility, viscosity, surface tension, critical micelle concentration and detergency performance. The neutralizing ions have been: Inorganic—Li^+, Na^+, K^+, NH_4^+; and Organic—Monoethanotalamine (MEA), Diethanolamine (DEA) and Triethanolamine (TEA). The study was carried out using three alkylbenzenes. Two of them were obtained using the HF alkylation process and the third one was obtained through the $AlCl_3$ process. It was concluded that a) the counterion hydration radius of the corresponding commercial L.A.S. has great influence on the following parameters: solubility, viscosity, surface tension and critical micelle concentration; b) the L.A.S. counterion has no influence on the detergency performance of the finished formulation; and c) the alkyl chain length and the presence of tetralines have an important influence on solubility, viscosity and surface tension.

CC6

Role of Free Surfactant In Destabilizing Oil-In-Water Emulsions. Michael Aronson, Lever Research Inc., 45 River Road, Edgewater, NJ 07020.

Emulsion formulations of practical interest usually contain appreciable surfactants, polymers and other functional ingredients. It is useful to understand how such additives affect emulsion stability particularly creaming. Recently, it was reported that nonionic surfactants when present at some critical concentration in excess of that required to saturate the interfaces, destabilized emulsions to cause rapid creaming. The work reported here was undertaken to better understand this process and how it depends on surfactant structure. A series of paraffin oil in water emulsions were prepared using a technique which produces a uniform emulsion of a controlled droplet size in the range of 0.2 to 1.5 microns and a narrow distribution. The stability and rheological characteristics of these emulsions were determined as a function of surfactant concentration for a variety of surfactant structures. Rheological measurements (shear thinning behavior) and direct observation indicate that the creaming which takes place above a critical concentration of free surfactant results from rapid flocculation. The process seems to be general and is observed for a variety of charged and uncharged water soluble surfactants. The critical concentration was found to decrease with increasing droplet size and in some cases depended on temperature. A preliminary theory has been developed which is based on the concept of an osmotic compression contribution to the interaction energy. This arises from micelles that are excluded from between the droplets that flocculate into a secondary minimum. The process is similar to that observed for the flocculation of colloids by excess free polymer. The role of deformation in the contact zone in the case of emulsions is also considered.

CC7

A Practical Approach To The Development of Microemulsions. Barbara H. Munk, Stepan Company, 22 W. Frontage Road, Northfield, IL 60093.

A practical and simple three phase approach to the formulation of microemulsions has been developed. This approach was originally used to develop pesticide microemulsions but has been demonstrated to be useful in the formulation of products in other areas. In Phase I, the emulsification and solubility properties of the hydrophobic or "oil" phase with a variety of surfactants and solvents are defined. Promising surfactants and solvents are blended in Phase 2 to identify emulsifier systems which provide the desired physical properties at fixed water and "oil" levels. These emulsifier systems are optimized in Phase 3 to produce the final formulation. Ternary phase diagrams are used in Phases 2 and 3 as a tool for quickly evaluating the ability of an emulsifier system to produce a microemulsion of a specified "oil phase." An example of the use of this approach to develop a cosmetic microemulsion will be discussed.

CC8

Dimer Acid Vesicles. G.R. Shore, Unichema Chemie B.V., P.O. Box 2, Gouda 2800 AA, The Netherlands.

Vesicle structures are formed by certain surfactants in aqueous media. They comprise spherical shells of surfactant bilayers, which can be mono or multilamellar. Some products, notably fabric softeners, are supplied in vesicular form. In this case a multilamellar dispersion of a quaternary ammonium compound such as the quaternary ammonium salt of di-hardened tallow is often used. There is much interest currently in the use of vesicle structure as carriers for active materials. The enclosed aqueous phase, or phases, provide a protective environment for water soluble molecules. Similarly the nonpolar alkyl center of the bilayer(s) has encapsulation potential for water insoluble molecules. The key problem has been in maintaining the stability of vesicular systems against aggregation,

especially in the presence of a surfactant. Unichema's PRIPOL dimer acids have been shown to form vesicles from aqueous dispersion in the presence of low concentrations of "spacer" molecules. They are also capable of spontaneously forming vesicles on dilution of non-vesicular gels. The stability of these vesicles is also very high. These properties, together with the fact that dimer acid vesicles offer a carboxylic acid covered surface can result in applications such as targetting drugs or the encapsulation and delivery of active ingredients from personal product or detergent formulations.

CC9

Application of d-Limonene In Cleaning Compounds. Dilip D. Desai, Stepan Company, 22 W. Frontage Road, Northfield, IL 60093, and Joseph C. Drozd, Stepan Company.

Limonene, a by-product of the citrus industry, derived from the rinds or peels of citrus fruits, is an effective and relatively safe cleaning and degreasing solvent. Formulation of this water immiscible solvent using surface active agents to obtain aqueous household and industrial cleaners and microemulsion technique will be discussed.

Session DD Wednesday morning

Pharmacological Effects of Lipids V: O-Alkyl Ethers in Experimental Cancer Therapy

DD1

Antineoplastic Activity of Ether Lipids and Derivatives Related To Platelet Activating Factor (PAF). W.E. Berdel, Div. of Hematology/Oncology, Dept. of Medicine I, Ismaningerst. 22, 8000 Münich 80, Federal Republic of Germany.

Various 1-O-alkyl-lysophospholipid-derivatives (ALP) show therapeutic activity in mouse transplantation tumor model systems and in metastatic 3-Lewis lung carcinoma in vivo. However, certain autochthonous mouse leukemias and radiation-induced lymphomas are resistant to ALP treatment. The therapeutic effects of these compounds are partially due to the activation of cytotoxic macrophages and direct cytotoxicity. Approximately 20 ether lipids and derivatives were tested for direct cytotoxicity in cells from human solid tumors and leukemias using [^{3}H]-thymidine uptake, trypan blue dye exclusion, human tumor clonogenic assays (HTCA) and cell morphology as assay systems. Certain ALP, thioether-lysophospholipid-derivatives (TLP), ether-linked lipoidal amines, sn-2 analogs of PAF and conjugates of etherlipids and cytosine arabinoside were found cytotoxic in a dose- and time-dependent fashion. Cytotoxicity of some of the ether lipids tested is based on destruction of cell membranes. Comparative studies with normal bone marrow cells and leukemic blasts from humans revealed selective antileukemic properties of three ether lipids. Interestingly one of the most cytotoxic derivatives, the lipoidal amine CP-46,665 did not reveal selective antileukemic cytotoxicity after >/= 24 hours of incubation and furthermore was therapeutically inactive in vivo. Studies concerning the mechanisms leading to accumulation and cytotoxicity of these compounds so far remained inconclusive. Structure-activity studies did not lead to minimum requirements within the molecule for cytotoxicity. The importance of an O-alkyl-cleavage enzyme present in normal tissues and absent from some neoplastic tissues is contradictory and there seems to be no correlation of cytotoxicity and binding of some of those compounds to PAF-specific binding sites as being present on human platelets. After completion of clinical phase I pilot trials with the reference compound ET-18-OCH_3, we have performed a multi-institutional phase I trial with the TLP BM 41.440 given orally. An update will be presented on the results of this study.

DD2

Resistance To Invasion of Heart Tissue Pretreated With Racemic-1-O-Octadecyl-2-O-Methylglycero 3-Phosphocholine (ET-18-OCH^3). E.A. Bruyneel, Vrije Universiteit, Cancer Research Unit, Oncology Center, Brussels, Belgium, and G.A. Storme (speaker), University Hospital, D.C. Schallier, Vrije Universiteit, J.G. Bolscher, The Netherlands Cancer Institute, and M.M. Mareel, University Hospital.

Invasion of cells from continuous cell lines was tested in a three-dimensional organ culture assay. Confrontations between malignant mouse MO4 cells and precultured embryonic chick heart fragments (PHF) in presence of ET-18-OCH_3 (10 μg/ml) showed complete inhibition of invasion with minor effects on growth or directional migration of the MO4 cells. ET-18-OCH_3 (5 μg/ml) also inhibited invasion of malignant baby rat kidney cells (12 RIC-RK), whereas a highly metastatic Lewis lung carcinoma (LLC-H61) was found to be resistant to treatment with 30 μg/ml ET-18-OCH_3. Pretreatment of the PHF with 10 μg/ml ET-18-OCH_3 for 48 hours made it resistant to invasion by MO4 cells as tested in absence of ET-18-OCH_3. Gel filtration of cell surface glycopeptides from chick heart cells metabolically labeled with $_3$H-fucose showed that treatment with ET-18-OCH_3 lead to an increase of the apparent molecular weight of the heart cell glycopeptides. This effect of ET-18-OCH_3 on heart cell glycopeptides remained present 4 days after removal of the drug from the culture medium. We report here on experiments to evaluate the reversibility of invasion resistance induced in PHF by pretreatment with ET-18-OCH_3. PHF were treated with ET-18-OCH_3 (10 μg/ml) during 48 hours, followed by washing (4 × 5 minutes) in fresh culture medium and further incubation on Gyrotory® shaker for 4 and 7 days. Then, PHF were confronted with MO4 cell aggregates during 7 to 14 days. In these cultures, invasion was absent, in contrast with control confrontations between MO4 cells and untreated PHF where invasion invariably was observed after 4 days. Explantation (on tissue culture plastic substrate) of confronting pairs after a 4-day pretreatment showed migration and proliferation of both heart cells and MO4 cells, indicating that lack of invasion was not due to cytotoxicity. We currently examine if ET-18-OCH_3 induced alterations of cell surface glycopeptides are responsible for the resistance of PHF to invasion.

DD3

Effects Of Alkyl-Lysophospholipids On Phosphati-

dylcholine Biosynthesis In Leukemic Cell Lines. W.R. Vogler, Emory University, Atlanta, Georgia, and A.C. Olson, Z. Kiss, M. Shoji and J.F. Kuo, Emory University.

Alkyl-lysophospholipid derivatives are a newly described family of compounds which have selective cytotoxicity to neoplastic cells. The mechanism of action of these compounds is unclear but appears to be a membrane effect. Using leukemic cell lines, we have investigated the effects of 1-O-octadecyl-2-O-methyl-rac-glycero-3-phosphocholine (ET-18-OCH_3) on cytotoxicity, biosynthesis of phospholipids, phorbol ester induced stimulation of phospholipid biosynthesis, and activity of protein kinase C. The cell lines were HL60, a sensitive cell line, and K562, a resistant cell line. Cytotoxicity was assessed by trypan blue dye exclusion, tritiated thymidine incorporation and clonogenicity in soft agar. We found a dose-and time-dependent effect of ET-18-OCH_3 on phosphatidylcholine (PC) biosynthesis in HL60 cells and little effect in K562 cells using radiolabeled choline (^3H), methionine (^3H) and lysophosphatidylcholine ($_{14}C$) (LPC). Without ET-18-OCH_3, incorporation of these precursors into PC by intact cells was similar in the 2 cell lines. However, in the presence of ET-18-OCH_3, a dose-dependent inhibition of choline and LPC incorporation into PC was observed in HL60 cells, but not in K562 cells. LPC acyltransferase activity was inhibited in HL60 cells, but not in K562 cells using intact cells. However, when ET-18-OCH_3 was added to cell homogenates, LPC acyltransferase activity was inhibited in both cell lines. The phorbol ester, 12-O-tetradecanoylphorbol-13-acetate (TPA) significantly increased the uptake of ^3H choline into PC in both HL60 and K562 cell lines, but to a greater extent in HL60 cells. ET-18-OCH_3 inhibited TPA stimulated protein kinase C activity in both cell lines as measured by phosphorylation of endogenous substrate proteins. Furthermore, it inhibited TPA induced down-regulation of protein kinase C and differentiation in HL60 cells. These, and other investigations, localize the major sites of action of ET-18-OCH_3 to the cell membrane. The precise mechanisms leading to cell death and selectivity for neoplastic cells remain to be elucidated.

DD4

Protein Kinase C Inhibition By Anti-Neoplastic Ether Lipids. Larry W. Daniel, Wake Forest University, Bowman Gray School of Medicine, Department of Biochemistry, Winston-Salem, NC 27103.

Ether-linked phospholipids exhibit selective cytotoxicity toward neoplastic cells by an unknown mechanism. It has been suggested that the cytotoxicity may be due in part to the inhibition of cellular enzymes. The prototype anti-neoplastic ether lipid, 1-*O*-octadecyl-2-*O*-methyl-*rac*-glycero-3-phosphocholine (ET-18-OCH_3), has been shown to inhibit protein kinase C (PKC); thus the inhibition of PKC by the ether lipids may contribute to their biological activities. Tumor promoting phorbol diesters (TPA) stimulate PKC, therefore TPA and ET-18-OCH_3 may have opposing effects on cellular events regulated by PKC. TPA stimulates prostaglandin E_2 synthesis, phosphatidylcholine turnover and phosphorylation of specific proteins in MDCK cells and we find that ET-18-OCH_3 inhibits all these effects. In addition, the antineoplastic 1-thio analogs of the ether lipids have been found to inhibit PKC in in vitro assays and to inhibit the effects of TPA in intact cells. These results indicate that PKC inhibition may be important in the biological effects of the ether lipid analogs and indicate that these analogs may be useful tools in identifying cellular activities that are regulated by protein kinase C.

DD5

Pharmacological Effects and Anticancer Activity of New Ether Phospholipid Analogs. E.J. Modest, Wake Forest University, Bowman Gray School of Medicine, Department of Biochemistry, Winston Salem, NC 27103, and M.E. Berens, University of California-San Francisco, A. Noseda, Wake Forest University and C. Piantadosi, University of North Carolina-Chapel Hill.

Ether phospholipid (EL) analogs of platelet activatingfactor(1-octadecyl-2-acetyl-*sn*-glycero-3-phosphocholine, PAF) have proved to be a class of biologically very active compounds. Among these activities, they possess the capability to inhibit neoplastic cell growth in vitro and in vivo. For this reason, we have undertaken a collaborative effort involving our different institutions on the design, synthesis and pharmacological evaluation of new EL active against neoplastic cells in order to identify analogs of possible clinical interest. We have already conducted the evaluation of different classes of EL: dialkyl glycero-3-phosphocholine analogs, their thio and amido derivatives, dialkyl glycero-3-phosphoinositol analogs and dialkyl glycerols. In particular we are now focusing our attention on the thioether and the amido alkyl derivatives, two classes of analogs which have shown the most promising inhibitory activities against leukemic cells (HL60, K562) and solid tumors (gynecological and brain neoplasias) in vitro. In vivo administration of these compounds resulted in no toxicity in normal mice when given subcutaneously by continuous infusion for 21 days up to 40 mg/kg/day. This prompted us to start in vivo studies using mouse leukemias and rat brain tumors, as well as human gynecological tumor xenografts in nude mice. These experiments are currently in progress. Our group has also developed the concept of the employment of EL, believed to be membrane-interactive agents, with classical DNA-interactive chemotherapeutic agents. Thas has led to increased antineoplastic effects. Results of various combinations in vitro and in vivo experiments will be discussed. The mechanism of action of this novel group of agents is not yet fully understood, but evidence indicates that they act at the membrane level. We are trying to characterize the importance of their membrane-interaction using model membranes and calorimetric techniques. EL were found to interact easily with model membranes, changing their physical properties. This may reflect a phenomenon occurring in vivo, and data obtained so far seem to indicate some relationship between EL affinity for membranes and cytotoxicity. These pharmacological evaluations of new and original EL are conducted in parallel with biochemical studies performed by the group of Dr. Larry W. Daniel at our institution.

DD6

Alkyllysophospholipids As Antitumor and Anticarcinogenic Agents. P.G. Munder, Max-Planck Institut für Immunbiologie, Freiburg, West Germany.

Alkylphospholipids and in particular alkyllysophospholipids were synthesized 20 years ago as possible immunomodulating compounds of the natural physiological compound 2-lysophosphatidylcholine (2-LPC) which had been found to increase the immune response. 2-LPC is, however, rapidly turned over by at least three enzymes. Therefore, slowly metabolizable alkyllysophospholipids were synthesized. These synthetic compounds had indeed a greater impact on the immunological response in vivo. But more important was the observation that these compounds will inhibit rather specifically tumor cell growth in vitro and in vivo. More than 95% of all tumor cells, established or freshly explanted, will be destroyed within 24 to 48 hours after the addition of certain alkyllysophospholipids. Chemical structure and biological activity are closely related. Moreover, the finding that the compounds will be taken up from the gastro-intestinal tract allowed us to study the development of chemical induced tumors in vivo under continuous oral treatment of these animals with alkyllysophospholipids after the implantation of a carcinogen. These compounds (50 μg/mouse) were applied twice weekly until all of the animals in the control group had tumors greater than one cm in diameter. All of the untreated animals died finally after about 120 to 150 days. Animals in the groups treated with alkyllysophospholipids also developed tumors during the first four to six weeks which, however, regressed completely in about 70% to 80% of the treated animals.

DD7

Alkylphosphocholines: A New Class of Antitumor Drugs. H. Eibl, Max-Planck-Institut für Biophys. Chemie, Göttingen D-3400, West Germany.

The classical treatment of malignant alterations in human tissue by irradiation or operation is often not curative, since frequently tumor cells and normal cells are closely connected and the infiltrations of neoplastic cells into normal tissue cannot be localized exactly. Even more complex and not controlled by macroscopic methods is the problem of metastasis; neoplastic cells generated by the primary tumor are distributed over the organism via body fluids and may settle in different organs and tissues far away from the induction of the tumor. Theoretically these complex events can be controlled only by chemotherapy, which works on a cellular level and may include the advantage of a selective therapy. In practice, the clinically applied antineoplastic agents are strong toxins and their administration is limited in concentration and time. Expecially the strong suppression of immune response will restrict continuous application over extended time periods. The main goal of our work, therefore, is to improve the selectivity of antitumor drugs. This can be achieved by different methods. For instance, the drug can be directed by carrier molecules, like liposomes, selectively to organs by altering the surface charge of the carrier or specifically to tumors by using target molecules in the surface of the liposomes. In experiments with N-methylnitrosourea-induced mammary carcinomas we have demonstrated a specific antitumor effect with lysolecithin analogs at concentrations that were not toxic. The new compounds are alkylphospholipids. They lack glycerol and per definition they are not phospholipid molecules.

Session EE Wednesday morning

Castor Oil I

EE1

Agronomy of Castor Seed-1988 Update.

Abstract not available at press time.

EE2

Deallergenation of Castor Meal: 1988 Update. Khee Choon Rhee, Texas A&M University, Food Protein Research and Development, Faculty Mail Box 183, College Station, TX 77843-2476, and Byong Ki Kim, Texas A&M University.

The Food Protein Research and Development Center at Texas A&M University reported last year that toxins and allergens present in defatted castor meals can effectively be destroyed by treating the meals with selected chemicals using Wenger extruders as high temperature short time chemical reactors. Since that time, the Center has expanded its testings to include a considerable less expensive chemical, quicklime (construction grade calcium hydroxide), and extruders such as an Anderson International expander and an Insta-Pro extruder. This paper summarizes the results of these additional testings to update the status of process development for production of toxin and allergen free castor meal feed supplements. The construction grade calcium hydroxide has been proven very effective in destroying CB-1A even at 0.5% concentration when Wenger X-20 extruder was used. Neither the Anderson International Expander nor the Insta-Pro Extruder was as effective as the Wenger X-20 Extruder in CB-1A destruction. However, the results show that both machines can be used as high temperature short time reactors but at a somewhat high chemical concentration for certain chemicals, i.e. 2.5% quicklime, to accomplish the same objective.

EE3

The Use of An Anderson Expander for Deallergenation of Castor Bean Meal. Jerry Horton, Anderson International Corporation, 6200 Harvard Avenue, Cleveland, OH 44105, and Maurice A. Williams, Anderson International Corp.

This paper discusses how an Anderson Expander can be used to implement the process for deallergenation of castor bean meal developed by Dr. Khee C. Rhee and his colleagues at Texas A&M University. The Anderson expander is a high temperature, short residence time, cooking extruder that generates frictional heat as it compresses and propels material within the barrel and out through the extrusion dies. Adjustment of water and steam input flow rates allows for selection of moisture levels of cook; selection of die size and number of openings allows for adjustment of temperature of cook. An important part of the process is the mixing, blending and absorption of chemical additives into intimate contact with the castor bean meal prior to entry into the extruder. Various methods for doing this are discussed, and a brief overview of what kind of equipment might be incorporated into a deallergenation process line is presented.

EE4

Pilot Scale Refining of Castor Oil Via Steam High Vacuum Distillation. Frank V. Lee-Poy, The Cambrian Engineering Group Limited, 2200 Argentia Road, Mississauga, ONT L5N 2K7, Canada, and P.W. Sleggs, T. Kaji and R.I. Matanic, The Cambrian Engineering Group Ltd., and R.L. Vignolo.

Oil extracted from the castor bean is unique from other fats and oils due to its high content of the hydroxy acid, ricinoleic acid. Hydroxy acids have been reported in other fats but none of them are commercially available. Since the importance of castor oil is derived from the content of ricinoleic acid, a major consideration in processing the oil is the preservation of this acid. A discussion of castor oil processing should therefore start with a review of the structure and properties of ricinoleic acid, together with some of the commercial uses of the acid. This background information was used to develop a process scheme, based on steam high vacuum distillation in the campro deodorizer/physical refiner. The process scheme was divided into two main parts: pretreatment and physical refining. Pretreatment included all processing of the oil in preparation for physical refining. Steam refining involved distillation of volatile components from the oil with steam under high vacuum conditions. Preliminary tests were performed in the laboratory under batch conditions. These were followed by pilot plant runs on the Campro 10 metric tons/day continuous unit. The results for both laboratory scale and pilot plant test will be presented, together with recommendations for the commercial process.

EE5

Literautre Review and Update on Genetic Engineering and Recombinant Techniques for Oleochemicals. Roger L. Logan, OCA Corporation, 20 Oxbow Lane, Newfoundland, NJ 07435.

A review and update of developments in genetic engineering and recombinant techniques with potential to alter oleochemical feed stocks. Particular emphasis on hydroxylated oils and potential new derivatives from altered feed stocks. A projection of how new techniques may affect the oleochemical industry in the 90's and beyond.

EE6

Bleaching of Castor Oil. Werner Zschau, Sued-Chemie AG, Munich, West Germany.

Ricinoleic acid undergoes a dehydration in the presence of acid catalysts. As bleaching earth can be regarded as an acid catalyst, we studied the effect of various bleaching clays on castor oil. The paper will discuss the results of our tests.

Session FF Wednesday morning

Protein Symposium III: Toxic Compounds in Vegetable Proteins

FF1

Inactivation and Analysis of Soybean Inhibitors of Digestive Enzymes. Mendel Friedman, Western Regional Research Center, Agricultural Research Service, USDA, 800 Buchanan Street, Albany, CA 94710, and Michael R. Gumbmann and David L. Brandon, Western Regional Research Center.

Inhibitors of digestive enzymes appear in many foods. Feeding soybeans containing trypsin and chymotrypsin inhibitors to rats depresses growth in comparison with feeding inhibitor-free soybeans. Growth inhibition and the accompanying pancreatic hypertrophy are presumably partly or fully due to the inhibitors of digestive enzymes. For these reasons, extensive efforts have been made to devise processing conditions that inactivate or remove the inhibitors from legumes. These approaches are based largely on heat treatments. However, heat does not inactivate all of the inhibitors present. The possible adverse effects of residual inhibitors in food are largely unknown. In addition, conditions used to inactivate inhibitors may destroy important amino acids including sulfur amino acids, arginine and lysine. An unsolved problem is that enzyme assays of inhibitors (a) often give inaccurate results with processed foods such as infant formulas having low residual inhibitory activity and (b) do not specifically differentiate among the major types of inhibitors, Kunitz and Bowman-Birk and their respective isoforms. In this presentation, we will (a) review various approaches that have been proposed to inactivate or remove inhibitors from soybeans, including possible strategies for complete inactivation; (b) describe studies designed to develop immunoassays (ELISA) for specific soybean inhibitors; and (c) compare the results from immunoassays to those from enzyme assays.

FF2

The Nutritional Significance of Lectins. Irvin E. Liener, University of Minnesota, Biochemistry Department, 1479 Gortner Avenue, St. Paul, MN 55108.

Lectins are widely distributed in foods of plant origin and are responsible, at least in part, for the poor nutritional quality of inadequately processed vegetable proteins, particularly the legumes. The toxic effects induced in animals by dietary sources of lectins include retarded growth, diarrhea and ultimate death. All of these effects appear to be the culmination of a series of events initiated by the ability of the lectins to bind to specific glycoprotein receptor sites located on the surface of the epithelial cells lining the small intestine. The precise mechanism whereby this lectin-gut interaction causes a toxic response has been ascribed to one or more of the following: (a) morphological damage to the integrity of the brush border of the small intestine, which in turn results in an impairment in the absorption of essential nutrients, (b) colonization of the small intestine by coliform bacteria, (c) systemic effects of lectins or bacterial toxins which cross the gut mucosal barrier, and (d) inhibition of brush border hydrolases. The relevance of these observations to the nutritional significance of lectins in the human diet will be discussed.

FF3

Properties of α-Amylase Inhibitors of Common Beans (*Phaseolus vulgaris*). John R. Whitaker, University of

California, Dept. of Food Science and Technology, 1480 Chemistry Annex, Davis, CA 95616.

Many varieties of the common bean (*Phaseolus vulgaris*) contain a protein that inhibits α-amylases of insects and animals but not of plants and microorganisms. The α-amylase inhibitor of red kidney beans (Linden cultivar), is about 5% of the total protein, a glycoprotein of ~50,000D, contains four subunits and forms a slow, tight binding complex with porcine pancreatic α-amylase by a two-step pathway. The complex is more hydrophobic than the inhibitor or the enzyme. The glyco groups of the inhibitor do not appear to be important for recognition and binding with α-amylase. The inhibitor does not bind at the active of α-amylase; a tryptophan residue of the inhibitor appears to be involved in binding. The black bean α-amylase inhibitor is about 10% larger in molecular weight than the red kidney bean inhibitor, has three (or four) subunits, and a single sulfhydryl group (red kidney bean inhibitor has four). The sulfhydryl group is buried and not involved in binding to α-amylase. The two sulfhydryl groups of porcine pancreatic α-amylase are not involved in complex formation, nor is the Ca^{2+} required for binding. Chloride ions are not required for α-amylase to bind with inhibitor at pH 5.4 but they are at pH 6.9. Complex formation does not involve ionic interaction but rather hydrophobic interaction between the two molecules. Evidence for the properties above and the mechanism of recognition and complex formation between the two proteins will be presented.

FF4

Toxic Compounds In Vegetable Proteins—Cyanogens. Jonathan E. Poulton, University of Iowa, Department of Botany, Iowa City, IA 52242.

Cyanogenesis, the release of hydrogen cyanide (HCN) by biological organisms, has been demonstrated in over 2,000 species of higher plants distributed throughout 110 different families of ferns, gymnosperms and angiosperms. HCN production results from the hydrolysis of cyanogenic glycosides or cyanolipids by endogenous hydrolases following tissue disruption either by crushing, food processing, mastication or fungal injury. Many plants used as food sources by humans and domestic animals may be markedly cyanogenic and have caused numerous cases of acute and chronic cyanide poisoning. For example, the ingestion of cassava in certain areas of the world has been linked with neuropathological syndromes such as tropical ataxic neuropathy and with endemic goiter and cretinism. The potential toxicity of several cyanogenic species has been reduced by selective breeding (e.g. almonds, lima beans, sorghum) and by food processing techniques which serve to remove cyanogens and/or inactivate endogenous hydrolases.

FF5

New Perspectives on the Antinutritional Effects of Tannins. Larry Butler, Purdue University, West Lafayette, IN 47907.

The diminished weight gains and feed efficiencies of experimental animals and livestock on diets containing tannin and structurally similar polyphenols have usually been attributed to inhibition of protein digestion by tannins. Studies of the specificity of protein binding by tannins and of the physiological effects of tannin consumption lead to several new perspectives. Inhibition of protein digestion in rats by dietary tannin is much less nutritionally significant than is inhibition of the post-digestion metabolism of digested and absorbed nutrients. In sorghum particularly, some polyphenol component(s) associated with high tannin content may be absorbed from the digestive tract and serve as a metabolic poison. Many animals (including humans) which normally consume tannin-containing plant materials protect themselves by producing specialized proline-rich salivary proteins that strongly bind dietary tannins and ameliorate their effects, which would otherwise be much more severe. Because of the strong specificity for tannin binding by fibrous, open-structured proteins (e.g. collagen) which are often deficient in essential amino acids, the nutritional loss due to dietary tannin is less than it would be if tannins were nonspecific protein binding agents.

FF6

Nutritional and Physiological Effects of Phytic Acid. Lilian U. Thompson, University of Toronto, Dept. of Nutritional Sciences, 150 College St., Toronto, ONT M5S 1A8, Canada.

Phytic acid (PA), an antinutrient commonly found in legumes, cereals and oilseeds, is highly negatively charged and can bind with positively charged groups such as cations and proteins. The formation of insoluble complexes from its reactions has both adverse and beneficial nutritional and physiological implications. For example, high intake of PA can cause mineral deficiency, especially zinc, but this depends on the PA × calcium/zinc molar ratio in the diet. Although the in vitro digestibility of the proteins is affected by PA, the in vivo digestibility does not appear to be. However, PA can change the pattern of release of amino acids from the proteins. The rate of starch digestion and blood glucose response to carbohydrate foods is lowered by PA; this may be beneficial especially to diabetic and hyperlipidemic individuals. PA may also have some potential health benefits in the colon but the mechanism of its effect is not yet established. The PA concentration which provides health benefits with negligible adverse effects needs to be determined.

FF7

Effect of Dietary Casein and Cottonseed Protein on Serum and Biliary Constituents and On Gallstone Formation and Regression In The Hamster. Glenda Johnson, Texas Christian University, Department of Nutrition and Dietetics, Box 32869, Ft. Worth, TX 76129, and Mary Anne Gorman (speaker), Jim Johnson, Jane Anderson and George U. Liepa, Texas Woman's University.

This research examined the effects of dietary casein and cottonseed proteins on the serum cholesterol concentration and concentrations of biliary constituents which play a role in gallstone formation and regression in the hamster. Sixty-four male hamsters were fed a diet containing 20 percent casein for 14 days to induce the formation of gallstones. Confirmation of gallstone formation was determined when 5 animals were sacrificed on Day 15, and 60 percent of the animals exhibited gallstone formation. An experimental diet containing 20 percent

cottonseed protein was fed for the remainder of the study. When the cottonseed protein-containing diet replaced the casein diet, 89 percent of the hamsters produced observable gallstones after 4 weeks on the regression (cottonseed protein) diet. Three weeks later, 95 percent of the cottonseed protein-fed hamsters exhibited gallstones. After an additional three weeks on the regression diet, 71 percent of the hamsters exhibited gallstones. The serum cholesterol concentration in hamsters during the casein-feeding period was significantly higher than at any time during the regression phase ($p<0.05$). Hamsters fed casein-containing diets were significantly lower in relative bile acid concentration and higher in relative concentrations of biliary phospholipids and cholesterol than animals fed cottonseed protein-containing diets for 7 and 10 weeks ($p<0.05$). Gallstone incidence was reduced from 75 percent to 71 percent after ten weeks on the cottonseed protein-containing regression diet.

FF8

A Study of Gossypol Reduction In Cottonseed Flour by Choline and Ethanolamine. O. Akomas, University of Manitoba, Department of Foods and Nutrition, Winnipeg, MB R3T 2N2, Canada, and N.A.M. Eskin, University of Manitoba.

A cottonseed flour:gossypol model system was established in which the time, temperature and level of gossypol was adjusted to obtain a 33-38% decrease in available lysine. A model system composed of cottonseed:gossypol (16:1) heated to 90 C for 30 minutes under alkaline conditions (pH 8.0) resulted in a reduction of available lysine from 21-22 to 12-14 mMoles/100g protein. Different levels of choline and ethanolamine were added to the cottonseed flour model system (0.4, 0.8 and 1.6×10^{-1}M) to study the ability to compete with lysine for gossypol. Based on the measurement of available lysine by the dye-binding method, a significant (p 0.05) increase in available lysine was observed when 0.8 and 1.6×10^{-1}M solutions of choline or ethanolamine were added to the model system. Ethanolamine proved to be approximately twice as effective as choline in restoring the level of available lysine to 19.1 mMoles/100g protein. This study demonstrates the potential of these bases, particularly ethanolamine, for reducing the toxicity of gossypol while at the same time protecting the available lysine.

Session GG Wednesday morning
Frying Fats and Oils

GG1

Markets and Trends. G. Farmer, ACF.

Abstract not available at press time.

GG2

Distribution of Edible Oil Products to the Food Service Industry. Jack Davis, Wilsey Foods, Inc., 14840 E. Don Julian Road, City of Industry, CA 91746.

The raw material source for food service edible oils is dominately USA produced vegetable oils, meat fats and imported palm and coconut oil. These oils are processed by refiners who may or may not be crude producers. These refined oils are packaged by manufacturers who may or may not be refiners. Edible oils are packaged into a wide range of products and package sizes under the manufacturer's brand as well as private labels. These food service products include margarine, shortening, salad oil, mayonnaise, salad dressing, snack foods and dairy substitutes. The packager delivers to a food service distributor, chain account distribution system or an industrial user who does further processing. These various distribution systems deliver the final products to a restaurant, coffee shop, fast food chain, hospital, industrial feeder or caterer, who in turn uses these as ingredients in their offerings to the final consumer.

GG3

Food Service Oils. James J. Jasko, Durkee Industrial and Foodservice Corp., 16651 Sprague Road, Strongsville, OH 44136.

The utilization of processed fats and oils in the foodservice industry as both a cooking medium and a food source will be discussed via a published literature review format. Particular attention will be directed to applications for frying, pan and griddle, salad oil, and other identified foodservice fat and oil uses. Beneficial attributes of type and source of various oils and their impact on functionality will be explored and presented.

GG4

The Analysis of Frying Fats and Oils. Edward G. Perkins, University of Illinois, Department of Food Science, 1208 W. Pennsylvania Avenue, Urbana, IL 61801.

Fats and oils used for frying are subjected to a variety of conditions which contribute to their chemical and nutritional deterioration. There is a complex relationship between the quality of a frying oil and that of foods fried in them. Triglycerides provide an ideal medium for oxidative deteriorative reactions in the presence of heat, water, and atmospheric oxygen. Literally hundreds of chemical reactions take place at this time which lead to the formation of volatile and non-volatile oxidation products and frying fat deterioration. Both chemical and instrumental methods are now available for the determination of many of these materials. Changes in the physical characteristics of used frying oils also take place. The purpose of this presentation is to present an overview of the methodology for the analysis of frying fats, their performance and deterioration.

GG5

Comparisons of Vegetable Oils for Frying Stability. K. Warner, Northern Regional Research Center, ARS-USDA, 1815 North University Street, Peoria, IL 61604, and T.L. Mounts, Northern Regional Research Center.

Samples of laboratory deodorized soybean, sunflower, high oleic sunflower, cottonseed, and low erucic acid rapeseed (LEAR) oils were evaluated for performance in deep-fat frying tests. Oils were heated at 190 C with periodic frying of bread cubes. The extent of oil deterioration was

measured by room odor, flavor quality of fried food, free fatty acids, and foaming of oil. Results of the initial room odor evaluations showed that soybean oil had significantly stronger odor intensity than cottonseed, sunflower and high oleic sunflower oils. However, no significant differences in odor scores were noted between soybean and LEAR oils. The predominant odor description for all oils was fried food. Both soybean oil and LEAR oil were described as fishy. All other oils had slight off-odors with both cottonseed and high oleic sunflower oil being described as waxy and plastic. Bread cubes fried in the initial oils showed no differences in flavor quality scores either before or after aging at 60 C. However, breads fried in deteriorated oils and aged for 4 days at 60 C had significantly lower flavor quality scores than bread cubes fried in fresh oil and aged under the same conditions. Storage stability tests of the fried food proved to be a more sensitive measurement of oil deterioration than did room odor.

GG6

Cottonseed Oil and Its Uses: A Review. C. Clay King, Texas Woman's University, Dept. of Nutrition and Food Sciences, P.O. Box 24134, Denton, TX 76204, and Lynn Jones, National Cottonseed Products Assoc., Inc, Frank Orthoefer, Nabisco Brands, Inc., and Kristan Frerck, Texas Woman's University.

A comprehensive and timely review of cottonseed oil and its uses has been compiled. The review includes: (1) chemical and physical characteristics of cottonseed oil in comparison with other vegetable oils; (2) the impact of the functional properties of cottonseed oil on its use in shortenings, frying oils, salad oils, margarines, mayonnaise, and salad dressings and other uses; (3) health aspects of cottonseed oil with emphasis on unsaturated fatty acids and essential nutrients; and (4) use of cottonseed oil in practical applications for the preparation of foods. Historically, cottonseed oil is one of the most widely used in the food oil industry. With the advent of new or improved types of oil, the prominence of cottonseed oil has diminished, despite its high quality. This review of the literature indicates that cottonseed oil should continue to play an important role in the future of the food industry.

GG7

Frying Dynamics of Two Oils In Commercial Applications. Roger D. Sinram, A.E. Staley Manufacturing Co., R&D, 2200 E. Eldorado Street, 63 Building, Decatur, IL 62525.

An extensive study was done to evaluate the performance of two frying shortenings over several frying cycles in a commercial environment. Batter-breaded chicken pieces were deep fried in a partially-hydrogenated vegetable oil blend, and french fried potatoes were cooked in a blend of beef tallow and vegetable oil. Oil samples were collected daily, and selected samples were investigated for their breakdown characteristics, including the following: buildup of free fatty acid; change in smoke point; and development of color intensity. Size exclusion liquid chromatography was utilized to determine trends in dimer and trimer formation and decomposition of triglycerides to mono- and di-glycerides. Gas chromatography was used to monitor changes in fatty acid distribution and the formation of flavor volatiles over several frying cycles. Rheological aspects, including changes in viscosity, shear stress, and surface tension, exhibited definite trends over each frying cycle. The effect of the frying fat's total usage was determined for each fried food's flavor, texture, and mouthfeel by consumer panels. The paper includes highlights of data collected in the study and interpretation of inter-relationships of certain phenomena observed. From this, a general model indicating the dynamic nature of deep-frying will be presented.

GG8

Deterioration of Frying Fat During Restaurant Frying and Flavor of Fish Fried In New and Discarded Frying Fat. Sharon L. Melton, University of Tennessee, Dept. of Food Technology & Science, P.O. Box 1071, Knoxville, TN 37901, and Danielle Sykes, University of Tennessee.

The objectives of this experiment were to investigate the deterioration of frying fat with rapid measurement methods (RM) during actual restaurant frying, to determine the relationship among the RM and level of % total polar components (TPC) and free fatty acids (FFA), and to analyze the flavor of fish fried in new and discarded fat by sensory evaluation. Frying fat (beef tallow-soybean oil) samples were collected from 8 fryers in a local seafood restaurant at 2, 5, 8, 14, 17, 23, 29, 35, 44 and 69 (discard) hours of use over a 7-day period which represented a single replication (88 samples). Three reps were collected. All samples were measured by the Food Oil Sensor (FOS), Shortening Monitor Strips (SMS) and color change (ΔE). Fifty samples from fresh to discarded were also analyzed for %TPC and FFA. For each fryer, significant differences existed between sampling times with discarded fat samples having FOS values of 2.5 to 3.0, No. 4 SMS and ΔE of 40 to 50. Highest γ-values were of % TPC with FFA (0.92), FOS (0.90) and ΔE (0.84) and between FOS and ΔE (0.88). The O-level SMS samples had an average of 5.7% TPC, 0.18% FFA, ΔE of 5.8 and FOS of 0.7, and the No. 4 SMS samples had 23.9% TPC, 4.95% FFA, ΔE of 45 and FOS of 3.0. For the whole panel of 79 judges, no significant differences were found for the flavor of codfish fried in new and discarded fat. However, 39 judges liked the flavor of fish fried in new fat (6.8) more than in discarded fat (5.4), 24 judges reversed this trend by liking the flavor of fish fried in the new fat (4.7) less than that fried in discarded fat (6.4), and 24 panelists could not tell any difference in the flavor of the fish fried in the two fats ($P<0.05$).

GG9

High Monounsaturated Oils For Food Service. Ilija Gawrilow, SVO Enterprises, 1550 Old Henderson Road, Columbus, OH 43220.

The latest advances in genetic engineering of oilseed crops has provided the food service operator and processor several new oils for their utilization. Excellent flavor characteristics of the high monounsaturated oils along with the inherent oxidative stability without antioxidants and/or hydrogenation qualify them as premium oils for deep fat frying, salad dressing oils, and a wide variety of formulated foods which require extended shelf life. A low saturate level, the absence of transisomers, and the poten-

tial improved health by lowering plasma cholesterol offer unique nutritional advantages in products marketed by food service establishments. A review of these natural high monounsaturated oils in terms of performance characteristics and applications is presented along with suggested nutritional implications in the human diet.

GG10

Nutritional Recommendations for Dietary Fat. Laura E. Granger, Kaiser Permanente, 3033 Bunker Hill Street, San Diego, CA 92109.

Government sponsored education efforts such as the National Cholesterol Education Program (NCEP) and the National Cancer Institute's Dietary Recommendations to Reduce Cancer Risk will continue to have an impact on consumer preferences for fats and fat-containing foods. This impact will increase as a result of the NCEP's newly defined standards for desirable blood cholesterol levels which place an estimated 50% of the adult population in a risk category indicating the need for significant change in dietary habits. In addition, the anticipated elimination of FDA regulations prohibiting health and disease claims on food labels may influence food manufacturer's choice of oils for their products. This presentation will review the nutritional properties of commonly used fats and oils, and the latest recommendations for their intake as they relate to heart disease and cancer risk reduction.

GG11

Customer Service for Frying Fats in the Food Service Industry. Michael D. Erickson, Interstate Foods Corp., 3800 South Morgan Street, Chicago, IL, 60609.

As a result of the growing public demand for quality in fast foods, the need for a comprehensive customer service program exists. This includes an extensive quality control system, the ability to assist customers in identifying and correcting frying problems (troubleshooting), and educating them on proper frying practices. An effective quality control system consists of determining acceptability of raw materials, adequate process control and finished product monitoring. Troubleshooting results from customer complaints concerning such problems as premature foaming, smoking and undesirable odors and flavors. A key to effective customer relations is to educate them on matters pertaining to practices that lead to maximizing fry life.

GG12

Frying Operations and QC. R. Regutti, consultant.

Abstract not available at press time.

Session HH Wednesday morning
Biochemistry I

HH1

Effect of Dietary Isomeric Monounsaturated Fatty Acids on The Lipid Metabolism of Various Tissues. Randall Wood, Texas A&M University, Dept. of Biochemistry and Biophysics, College Station, TX 77843, and Roberta Crook, Texas A&M University.

Male weaning rats (75 to 85 g) were placed in groups of three on a semisynthetic fat-free diet fortified with 1.5% linoleic acid and supplemented with 10% of one of the following fatty acids: *cis* 18:1Δ9; *cis* 18:1Δ12; *cis* 18:1Δ14; *trans* 18:1Δ9; *trans* 18:1Δ10; *trans* 18:1Δ12; and *trans* 18:1Δ14. A group of animals fed only the basic diet was also included. After 14 days on the diets the animals were killed, tissues collected, frozen in liquid nitrogen and stored at -76 C. Lipids were extracted from adipose, liver, heart and muscle by the Bligh and Dyer procedure, the triglycerides (TG), phosphatidylcholines (PC) and phosphatidylethanolamines (PE) lipid classes were isolated by thin-layer-chromatography, methyl esters were prepared and analyzed by gas-liquid chromatography. By using polar and nonpolar capillary columns all of isomeric fatty acids were resolved from the isomeric monoenoic fatty acids normally present. Using this approach we have been able to determine the effects of various dietary geometrical and positional octadecenoate isomers on the fatty acid profiles of various tissue lipid classes. A multitude of changes in profiles were observed. Generally, the triglyceride profiles were affected by the configuration, position, and the nature of the unsaturation. Some *cis* and *trans* isomers caused an elevation of 18:1 percentages in both PC and PE while others had no effect, indicating both configuration and position of unsaturation affect the degree of incorporation into tissue phosphoglycerides as well as fatty acid biosynthesis. The lipid class fatty acid profiles also indicate that some of the geometrical and positional isomers were metabolized into shorter and longer chain unsaturated fatty acids.

HH2

Fatty Acyl CoA Interacts with Multiple Protein Factors During Vesicular Transport In A Cell-Free System. Benjamin S. Glick, Stanford University, Biochemistry Department, Medical Center, Stanford, CA 94305, and Paul Melancon, Marc Block and James E. Rothman, Stanford University.

The movement of proteins between subcellular compartments is mediated by transport vesicles. We reported earlier that fatty acyl coenzyme A (CoA) acts as cofactor to a protein termed NSF, which is required for vesicular traffic between cisternae of the Golgi apparatus in a cell-free system. These data suggest that activated fatty acids form part of the transport machinery, but the details remain unknown. We have addressed this question by further investigating the conditions under which acyl CoA promotes transport. Acyl CoA stimulates when NSF is present in limiting amounts; we recently found that acyl CoA also boosts transport when the levels of soluble cytosolic factors are reduced. This stimulation requires the presence of reducing agents, which implies that an oxidation-sensitive protein is involved--perhaps NSF once again. In other experiments, we have attempted to deplete acyl CoA from the reaction mix. One approach is simply to add bovine serum albumin (BSA), which binds acyl CoA. BSA strongly inhibits transport, even at low concentrations, but this inhibition is never complete. Our results are integrated into the working hypothesis that that transport requires an acylated form of NSF. (Honored student presentation.)

HH3

The Generation of Fatty Acid Analogs To Investigate the Role Of Covalently Bound Lipids In Protein Function: Potential Anti-Viral and Anti-Neoplastic Agents. Robert O. Heuckeroth, Washington University, School of Nutrition, 660 S. Euclid Ave., Box 8094, St. Louis, MO 63110, and David A. Rudnick, Washington Univ. School of Medicine, Steve P. Adams, Monsanto Company, Jeffrey I. Gordon, Washington Univ. School of Medicine.

The covalent attachment of fatty acids to proteins has been demonstrated to be critical for the function of several biologically important acylproteins. Blocking the attachment of myristate (C 14:0) to $p60^{v\text{-}src}$ prevents src-mediated cell transformation and the association of src with membranes. Inhibition of myristate attachment to the gag (internal core) proteins of two retroviruses (including Type D retroviruses of which the AIDS virus is a member) blocks either virus assembly or budding from cells. The enzyme which transfers myristic acid to proteins (N-myristoyl transferase (NMT)) is highly specific for both the fatty acid and protein substrates. The reason for this specificity, which has been conserved through evolution, is unknown. To evaluate the role of myristate in protein function, we have chemically synthesized several fatty acid analogs which are less hydrophobic than myristic acid. These analogs have been characterized chemically (by ^{1}H, and ^{13}C NMR as well as mass spectroscopy) and enzymatically. Their utility as substrates for NMT was examined using enzyme purified from yeast, wheat germ and human placenta. The kinetic analysis indicated that these analogs are substrates for both acyl CoA ligase and NMT. The analog 11-(ethylthio)-undecanoic acid is at least as good a substrate for NMT as myristate, yet behaves on C-18 reserve phase HPLC as a 11-12 carbon fatty acid. The ether analog 11-(methoxy)undecanoic acid also acts as an NMT substrate, but behaves on reverse phase HPLC as a C8 to C10 fatty acid. Attachment of these analogs to myristoyl proteins in place of myristic acid may dramatically effect protein folding, protein-protein, or protein-membrane interactions. We believe that a series of fatty acid analogs will be useful probes for the role of myristate in acyl protein processing, targeting and function. They are also potential anti-viral and anti-neoplastic agents. (Ralph G. Potts Memorial Fellowship presentation.)

HH4

Daily Prostaglandin E Turnover In Adult Men. Its Determination By Sim Mass Spectrometry. Aldo Ferretti, Lipid Nutrition Laboratory, BHNRC, ARS/USDA, Beltsville, MD 20705, and Vincent P. Flanagan and Valerie B. Reeves, Lipid Nutrition Laboratory, BHNRC, USDA.

Urine was collected over 24 hours during three consecutive days by 24 healthy, male subjects, age 24 to 54 (mean 36.1 + 1.7), who had not been taking anti-inflammatory drugs during the previous ten days. Two percent portions of each 24-h collection from the same subject were pooled. A 20-ml aliquot of the resulting mixture was analyzed to assess the mean daily turnover of prostaglanding (PG)E in vivo during the 72-h period. This was done by measuring the terminal catabolite PGE-M. The mean urinary excretion rate of PGE-M was 13.86 + 1.46 (SE) μg/24 h (N=24), and the range was 4.0 to 36.5 μg/24 h. These values are in good agreement with those found by previous investigators. We used an assay system—recently developed by us—consisting of solid phase extraction, multidimensional chromatography and selected ion monitoring mass spectrometry with a ^{13}C-labeled internal standard. A relative stadard deviation of 0.8% (N=4) was associated with the overall procedure, while the intra-assay coefficient of variation ranged from 0.9 to 1.7% (N=4). The recovery curve, developed by unweighted least-squares linear regression analysis from three separate experiments with urine from three donors followed the equation $y = 1.05x - 5.84$ (R=0.998).

HH5

Incorporation Of Deuterium-Labeled *trans*-8- and *cis*-8-Octadecenoic Acid Isomers vs. *cis*-9-Octadecenoic Acid In Human Plasma and Lipoprotein Lipids. E.A. Emken, Northern Regional Research Center, ARS-USDA, 1815 North University Street, Peoria, IL 61604, and R.O. Adlof and W.K. Rohwedder, USDA Northern Regional Research Center, R.M. Gulley, St. Francis Medical Center.

Two adult male subjects were fed mixtures of triglycerides (TG) containing deuterium-labeled *trans*-8-, *cis*-9-octadecenoic acids (8t-18:1, 8c-18:1, 9c-18:1). Sequential blood samples were collected over a 48-hr period. Plasma and lipoprotein lipids were separated by thin-layer chromatography and analyzed by gas chromatography-mass spectrometry. Results indicate that (A) the 8t- and 8c-18:1 isomer were well absorbed, (B) the 8t-18:1 isomer was cleared ca. 35% faster than 9c-18:1 from plasma TG, (c) esterification of cholesterol ester samples contained 10 times less 8t-18:1 than 9c-18:1, (D) selective incorporation at the 1-acyl PC position was higher for 8t-18:1 and 8c-18:1 (3.9 and 2.8 times) than for 9c-18:1, and (E) discrimination at the 2-acyl PC position was 5.5-fold for 8t-18:1 and 2.3-fold for 8c-18:1 compared to 9c-18:1. Discrimination against uptake of the delta 8 isomers in both neutral and phospholipid classes suggests that both 8t- and 8c-18:1 are preferentially oxidized relative to 9c-18:1. Except for the TG data, the plasma and lipoprotein lipid class data were similar, which indicate that the lipoprotein class had a minor role in the uptake and turnover of the deuterated fats. The maximum isotopic enrichment detected in the chylomicron TG fractions was 60% which indicates a substantial amount of endogenous TG was mobilized during absorption of the deuterated fats. In general, the double bond at the 8 position in these 18:1 isomers does not impart metabolic characteristics which are substantially different from other trans and cis 18:1 positional isomers. Based on the comparison of the metabolism of the 8t- and 8c-18:1 isomers to 9c-18:1, there is no obvious biochemical basis for suggesting the 8t- and 8c-18:1 isomers have a special impact on health problems associated with dietary fats.

HH6

Essential Fatty Acid (EFA) Metabolism In Premenstrual Syndrome (PMS). D.F. Horrobin, Efamol Research Institute, P.O. Box 818, Annapolis Valley Industrial Park, Kentville, NS B4N 4H8, Canada, and M.S. Manku (speaker), Efamol Research Institute.

No consistent hormone abnormalities have been found in PMS suggesting that the problem may lie in abnormal responses to normal or near normal hormone concentrations. EFAs and the derived eicosanoids including prostaglandins (PGs) are known to play a role in modulating responses to prolactin, for example, may act both as 2nd messengers and feed back to limit the responses to prolactin. We propose that in PMS there are abnormal responses to normal levels of ovarian and pituitary hormones due to abnormal levels of EFAs in membranes and/or to abnormal PG formation from those EFAs. Defects could occur in intake of linoleic acid (LA), in conversion of LA via gamma-linolenic (GLA) to the PG precursors, or in conversion of the PG precursors to PGs. We have obtained evidence for the last two mechanisms. Women with PMS have normal blood concentrations of LA but reduced levels of metabolites. Such a pattern could result from impaired 6-desaturation of LA to GLA as a result of atopy, excesses of alcohol or catecholamines, thyroid deficiency, or undue amounts of *trans* fatty acids and simple sugars in the diet. EFA depletion in pregnancy or lactation could exacerbate this situation. The hypothesis of defective 6-desaturation has been tested by double blind, placebo-controlled trials of the administration of GLA as evening primrose oil. Several such trials have given positive results. We will present fatty acid profiles from these clinical trials. Women who respond to GLA show evidence of efficient onward conversion of EFAs to eicosanoids, while non-responders do not metabolize the EFAs efficiently.

HH7

Molecular Species of Glycerophospholipids (GPL) Of Human Erythrocytes. J.J. Myher, University of Toronto, Charles H. Best Institute, 112 College Street, Toronto, ONT M5G 1L6, Canada, and S. Pind and A. Kuksis, University of Toronto.

Demonstration of specific metabolic roles for individual or small groups of molecular species of GPL has rekindled interest in detailed lipid composition of cell membranes and lipoproteins. This study reports application of modern methods of molecular species analysis to determination of the structure of both major and minor GPL of human erythrocytes. Individual GPL classes were resolved from total lipid extracts by TLC. Diradylglycerols were released by phospholipase C (*B. cereus*), converted into TMS ethers, and separated into alkenylacyl-, alkylacyl- and diacylglycerols by normal phase HPLC. Molecular species of diradylglycerols were quantitated according to carbon and double bond number by GLC using a 15 m × 0.32 mm ID fused silica capillary column wall-coated with bondedRTx-2330. The phosphatidylcholines contained 93.0% diacyl, 4.6% alkylacyl and 2.5% alkenylacyl, while the phosphatidylethanolamines were made up of 49.0% diacyl, 47.0% alkenylacyl and 4.1% alkylacyl subclasses. Serine and inositol phosphatides contained only the diacyl subclass. The molecular species of individual GPL subclasses were qualitatively made up of combinations of fatty chains expected from fatty acid and glyceryl ether analyses. However, the long-chain polyunsaturated acids were preferentially combined with the C_{16}, except 20:4ω6, which was preferentially combined with C_{18}, saturated fatty chains. In addition to the C_{16} and C_{18} alkyland alkenyl, the ether fractions also contained significant proportions of C_{20}, C_{22} and C_{24} chains. Over 200 molecular species were identified and quantitated in a representative sample of human red blood cells.

Session II Wednesday morning

Processing III: Bleaching and Hydrogenation

II1

Effects Of Bleaching On Oil Oxidative Properties. Charles B. Ungermann, Harshaw/Filtrol Partnership, c/o Kaiser Aluminum & Chemical Corp., P.O. Box 877, Pleasanton, CA 94566, and Dennis R. Taylor, Harshaw/Filtrol Partnership.

The oxidation of edible oils initially results in the formation of hydroperoxides. Later, these (hydro)peroxides decompose to a variety of secondary oxidation products. The decomposition products, if present in sufficient quantities, will impart unpleasant flavor and odor properties to the oil. Hence, one object of oil refining is to reduce their levels. The present study examines the effects of bleaching and bleaching clay activity on the levels of peroxides and secondary oxidation products in bleached and bleached-deodorized soybean oil. Although it is known that bleaching clays reduce peroxides (as measured by peroxide value, PV) through catalytic decomposition to aldehydes (as measured by anisidine value, AV) and other products, it will be shown that the relationship between PV and AV in bleached oil is quite complex. In fact, one outcome of the present study is the conclusion that neither PV nor AV, alone, can be utilized to predict finished (deodorized) oil quality. It will be argued that the TOTOX value (2 × PV + AV) is, however, useful in this regard. Furthermore, although it is known that peroxides can be decomposed thermally (and removed via distillation) during the deodorization step, the lowest levels of residual (secondary) oxidation products in a finished oil are obtained only when the decomposition has been accomplished catalytically (during the bleach step).

II2

The Synergistic Effect Of Neutral Bleaching Earth and Citric Acid: Metals Removal. G.R. Goss, Oil-Dri Corporation of America, 520 N. Michigan Avenue, Chicago, IL 60611, and D. Brooks, W. Moll, S. Brophy and D. Pietroske, Oil-Dri Corporation of America.

The ability to remove metals during bleaching is important. The presence of metals can cause premature oxidation of the oil or catalyst poisoning during hydrogenation. A recently developed unique neutral bleaching clay has been found to be superior in metals removal. Freundlich adsorption isotherms characterize the clay as having a lower n and higher k than acid activated clays. Use of citric acid with this neutral clay further enhances its ability to remove metals. Once refined soybean oil was obtained from a commercial refinery. Bleaches were conducted under vacuum (50 mm Hg) at 120 C for 30 minutes in the laboratory. Clay was used at 0.25, 0.50 and 1.0% of the oil weight. Citric acid was used at 200 ppm and 400 ppm. Sodium, calcium, phosphorous and iron levels were determined by direct coupled plasma emission spectros-

copy. The addition of citric acid during bleaching greatly enhances metals removal. Raising the level of citric acid from 200 ppm to 400 ppm improved metals removal but not proportional to the concentration increase. Adding citric acid as an aqueous solution was found beneficial. Little or no carryover of citric acid in the bleached oil was observed.

II3

The Synergistics Effect of Neutral Bleaching Clay and Citric Acid: Chlorophyll Removal. D.D. Brooks, Oil-Dri Corporation of America, 520 N. Michigan Ave., Chicago, IL 60611, and G.R. Goss, S. Brophy, D. Pietroske and J. Stein, Oil-Dri Corporation of America.

Abstract not available at press time.

II4

Scale-Up Of Fluid Mixers In Hydrogenation Process. James Oldshue, Mixing Equipment Company.

Abstract not available at press time.

II5

Advanced Techniques for Effective Oxygen Removal From Oleochemicals. Alan T.Y. Cheng, Linde Div.-Union Carbide Corp., Tarrytown Technical Center, Old Saw Mill River Road, Tarrytown, NY 10591.

Removal of dissolved oxygen from fatty oils and oil chemicals is an important step in improving refined product qualities. Present stripping techniques are often slow and inefficient. Furthermore, the solubility of free oxygen (other than chemically bonded) is seldomly known. In this experimental study, oxygen was stripped from several vegetable oils and fatty acids using nitrogen gas. Optimum stripping conditions were determined for various stripping devices. A co-current in-line stripping system was found to be ten times more efficient than a batch stripper while a high efficiency counter-current stripping column achieved more than a 50 to 1 reduction ratio of oxygen in a single pass. True solubility constants of oxygen in oil were also determined. It was found that the stripping rate is effected strongly by the physical properties of the oil such as viscosity and surface tension. Linde's stripping systems which have been field tested at several oil and fat manufacturing facilities will be discussed.

II6

Ultrasonic vs. Non-Ultrasonic Hydrogenation In A Batch Reactor. Jesse E. Covey, 1404 Avenue R, Plano, TX, 75074, and Mukana wa Muanda, University of Kinshasa, and Peter J. Wan, Anderson Clayton Foods.

Refined and bleached soybean oil was hydrogenated with and without the presence of ultrasonic energy in a batch system. Reactions were carried out at 170 C with 0.02% nickel catalyst. Hydrogen pressure was varied from 15 to 90 psi. After 20 minutes the average reaction rate was about 5 times faster in the presence of ultrasonic energy. However, samples run at various pressure levels indicate various reaction rates with ultrasonic energy.

II7

Natural Carotene from Palm Oil. Masayoshi Nakamura, Lion Corporation, No. 2-1, 7 Chome, Hirai, Edogawaku, Tokyo, Japan, and Ryozo Iwasaki and Toshiaki Ohgoshi, Lion Corporation.

Crude palm oil contains about 600 ppm of carotene which is provitamin A. Carotene extraction from crude palm oil has been investigated since 1940, using various methods. However, their industrialization has never been commercially successful. We developed new technology to extract carotene from crude palm ester efficiently, using phase equilibrium of palm ester, hydrophilic organic solvent and water. Palm carotene consists of 30% α-carotene, 60% β-carotene, and 10% other carotenoids. These component percentages for palm carotene are almost the same as those for carrot carotene. Applications of palm carotene include its use as a Vitamin A supplement, health food additive, and natural coloring agent in such food as butter or margarine. We also confirmed new applications of palm carotene such as for color improvement of prawns and to enhance the bright attractive color of black tea. Furthermore, the physiological activity of palm carotene is superior to that of synthetic β-carotene, and possible new applications as pharmaceutical agents are considerable.

II8

Hydrogenation of Corn Oil Using Nickel Catalysts. V. Abraham, Carson Foods, 8 Carson Crt., Brampton, ONT L6T 4P8, Canada, and R. Parisi, Carson Foods, and J.M. deMan, University of Guelph.

Refined and bleached corn oil was hydrogenated under selective (200 C and 8 psi) and nonselective conditions (160 C and 44 psi). Samples were taken at 15 min intervals and rate of hydrogenation, fatty acid profile, solid fat content and dropping points were determined. The rate of hydrogenation was higher at nonselective conditions than selective conditions. Nonselective conditions also resulted in higher solid content and 18:0 content than selective conditions. There was direct relationship between refractive index and iodine value. Linear regression of refractive index with iodine value (IV) by Wijs method provided a correlation coefficient of 1.

II9

Advances In The Hydrogenation of Oleochemicals. Mark K. Weise, Union Carbide Corporations, Old Saw Mill River Road, Tarrytown, NY 10591, and Wayne I. Rowell and Del Young, Sherex Chemical Co.

The hydrogenation of oleochemicals greatly depends upon the mass transfer rates both from the gas to the liquid and between the liquid and catalyst surface. Aside from the physical conditions of the system, such as temperature and pressure, mixing plays the most important role. Advanced mixing technology developed and commercialized by the Linde Division of Union Carbide has demonstrated catalyst savings and increased productivity. Pilot test results presented compare this new technology with conventional mixers in the hydrogenation of fatty acids and fatty amines. Hydrogen purity effects upon mass transfer and catalyst activity are also discussed.

II10

Hydrogen Supply Options and Issues. K.A. Kuberka, Union Carbide Corporation, Linde Division, Tarrytown Technical Center, Saw Mill River Road, Rte. 100C, Tarrytown, NY 10591, and C.A. Messina, Union Carbide Corporation, Danbury, CT, 06817, and M.K. Weise, Union Carbide Corporation, Tarrytown, New York.

Methods of hydrogen gas production for hydrogenation are discussed: steam reforming of natural gas, electrolysis, by-product clean-up by PSA (pressure swing adsorption) or scrubbing, and other. Hydrogen can be obtained from a customer-owned hydrogen plant or as merchant product, supplied by an industrial gas supplier. The merchant product can be delivered in trailers as gas or liquid—high (up to 2,200 psig) or low pressure (up to 130 psig), or supplied over the fence from a pipeline or hydrogen generating plant. Several factors must be considered in selecting an optimum supply including availability and cost of capital and of operating labor, use patterns, average demand, instantaneous demand, use pressure, growth projections, and purity requirements. Hydrogen gas purity and its effect of processing (with experimental results) will be reviewed.

II11

A Technical Audit Program for Refineries. K.G. Berger, PORIM, Brickendonbury Hertford, Hertfordshire SG13 8NL, England, and M. McLellan and T. Thiagarajan, PORIM.

Malaysian refineries process 4 1/2 million tons of palm oil annually. Of 36 refineries the largest is handling up to 2,000 tons/day. As part of the quality assurance system, the Palm Oil Research Institute of Malaysia carries out an independent technical audit. The scheme is voluntary, the evaluations are based on an agreed itemized mark sheet. Every refinery receives a confidential report detailing points of weakness. Those obtaining sufficient marks are awarded a certificate with one year's validity. The audit is carried out by two officers under 6 headings, viz. General Appearance, Quality Control, Laboratory/Factory Interaction, Operations, Product Handling and Maintenance. The results over 5 years operation will be presented and discussed.

Session JJ Wednesday afternoon

Surfactants and Detergents VI: Additives, Builders and Analysis

JJ1

Modifying Soluble Silicate Properties with Anionic Functional Siliconates. Jeffrey A. Kosal, Dow Corning Corporation, 3901 S. Saginaw Road, Mail Stop #528, Midland, MI 48640.

The complex chemistry of soluble silicates has limited their use in many applications. A family of anionic functional siliconate materials has been discovered which modifies the physical and solution properties of soluble silicates. Modification is accomplished through surface interactions between the anionic siliconate and the dissolved silicate. These siliconate modifications create unique silicates that are soluble and stable at neutral pH and are also resistant to cation induced condensation. Dried films of modified silicates also exhibit greater resolubilization properties. The degree of modification is dependent upon the concentration, and to a lesser extent, functionality of the anionic siliconate added. Enhancing the physical and solution properties of soluble silicates will allow silicates to be utilized in products and processes not deemed possible in the past. The future role of soluble silicates will now be determined by the creativity of the developmental chemist.

JJ2

The Effect of Sodium Silicate on Phosphate Heavy Duty Laundry Powder Crutcher Slurries. Mitchell T. Holtzer, PQ Corporation, P.O. Box 840, Valley Forge, PA 19482, and Richard T. Coffey, PQ Corporation.

Sodium silicate is included in heavy duty laundry powders for its contribution to both cleaning efficacy, and spray dry processing. Silicate adds buffered alkalinity to the wash liquor, aids in the sequestration of iron and manganese, acts as a soil anti-redeposition agent, and helps to neutralize acidic soils. As a process aid, soluble silicates increase particle crispness and resistance to package attrition, and add surface area for surfactant absorbance as well. The properties of the crutcher slurry, however, are rarely considered. Silicate is known to behave as a slurry thinner, and as a phosphate reversion inhibitor. This paper will quantify the effect that various silicate loadings have on phosphate speciation, and demonstrate the viscosity versus solids profile for a typical household laundry powder formulation. It will be demonstrated that judicious choice of silicate level can lower the cost of detergent manufacture in two ways. Optimizing the phosphate speciation in a crutcher slurry can reduce the initial quantity of STPP required to achieve desired cleaning properties. Reducing the slurry viscosity allows the detergent manufacturer to increase slurry solids, and reduce energy requirements associated with evaporating the water of solution.

JJ3

Quantitative Characterization of Mixtures of Inorganic Phosphates and Organophosphate Esters using NMR Spectroscopy. G. Steve Caravajal, The Procter & Gamble Company, Ivorydale Technical Center, 5299 Spring Grove Avenue, Cincinnati, OH 45217, and Gary L. Pennington, The Procter & Gamble Company.

The determination of the composition of mixtures of tripolyphosphate, pyrophosphate, orthophosphate and trimetaphosphate can be performed simultaneously, rapidly and quantitatively using P-31 NMR. This type of analysis can be applied to both raw materials and complex detergent matrices. P-31 NMR can also be applied to multicomponent characterization of organophosphate esters. Organophosphate esters are important in a wide variety of applications. Commercially available organophosphate esters usually contain monoesters, diesters, inorganic phosphates and unreacted alcohol. P-31 NMR can provide quan-

titative information about the types and amounts of esters and inorganic phosphates present. In addition to P-31 NMR, C-13 and H-1 NMR are useful for identifying the structural nature of the alcohol (e.g., branched or straight-chain, average chain length, average number of ethoxylate groups if present) and for providing complementary information about the types and amounts of organophosphate esters present. Examples illustrating the use and advantages of NMR for determination of the composition of commercially available organophosphate esters and mixtures of inorganic phosphates will be presented.

JJ4

Performance of Non-Cellulosic Antiredeposition Agents. Edward J. Parker, BASF Corporation, 1419 Biddle Avenue, Wyandotte, MI 48192-3736, and Richard J. Holland, BASF Corporation.

Once soil has been removed from clothing, it is important that the soil be prevented from redepositing on any cloth. Traditionally, cellulosic derivatives have been added to laundry detergents to achieve this goal. However, cellulosics are not the only structures that can effectively prevent soil redeposition. During our search for laundry performance additives, we have found systems which provide effective antiredeposition. In this paper, we will examine the performance of these non-cellulosic antiredeposition agents. Their utility will be defined by soil and substrate. We will also examine the possible mechanisms of action.

JJ5

Computer Optimization of Detergent Formulations Replacing Phosphates with Zeolites. A. Bobland, The PQ Corporation, and R.J. Coffey, The PQ Corporation.

Abstract not available at press time.

JJ6

Amorphous Water Measurements on Granular Solids Using ^{1}H-NMR Spectroscopy. T. Michael Rothgeb, The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217, and Elizabeth R. Jacobs, The Procter & Gamble Company.

The amorphous water levels in granular solids such as detergent products impact importantly on the solids' physical properties. As important as these levels are, their measurement is difficult to effect. Broad-line ^{1}H-NMR is the preferred spectroscopic technique for determining amorphous water. However, the ability to use ^{1}H-NMR in a truly quantitative sense has disappeared with the advent of pulsed instruments replacing continuous wave instruments. Several experimental criteria must be met before quantitative broad-line spectra can be recorded in a pulsed mode. These criteria are generally not met especially on high resolution instruments. Yet they can be effectively overcome by recording a series of spectra using a very simple single pulse sequence and fitting the intensity data to a function describing the intensity decay. This experimental procedure when implemented on a high resolution spectrometer is capable of determining both the types and levels of amorphous water on granular solids.

JJ7

Protein-Engineering of the Detergent Protease, Maxacal. L.J.S.M. Mulleners, Gist-Brocades N.V., Wateringseweg 1 - 2600 MA, Box 1, Delft, Netherlands, and R.A. Cuperus, Gist-Brocades N.V., and J.H. van Ee and M.C. Crossin, General Bio-Synthetics.

Tremendous progress has been made in recent years towards the understanding of the structure/function relationship in enzymes. "Protein-engineering" techniques now exist that enable specific amino acids in an enzyme to be replaced by other amino acids. One of these techniques, known as site directed mutagenisis, is an extremely powerful tool to tailor on enzymes' properties to a specific application by a targeted modification of the enzyme's structure. We have constructed a protein-engineered derivative of our high alkaline detergent protease, Maxacal, which possesses temperature activity characteristics, different from those of the native enzyme. The mutant's physical and chemical properties will be discussed in comparison to the native, Maxacal enzyme.

JJ8

Choosing Surfactants for Hypochlorite Containing Detergents. Terri Germain, Stepan Company, 22 W. Frontage Road, Northfield, IL 60093, and Joseph C. Drozd, Stepan Company.

This paper will discuss how one chooses surfactants for systems that contain hypochlorite bleach. The degradation of hypochlorite by various surfactants will be evaluated in bleach/surfactant systems and fully formulated products. Examples of bleach stable surfactants and bleach containing formulations will be given.

JJ9

Purification of Amides, Ethoxylated Amines, and Imidazolines with VenPure Borohydride Products. Michael M. Cook, Morton Thiokol/Ventron Products, 150 Andovers Street, Danvers, MA 01923, and Mark J. Eugenio, Robert M. Gelinas, Richard A. Mikulski and P. Nga Trinh, Morton Thiokol/Ventron Products.

This presentation reviews the use of VenPure borohydride products for purification of various types of surfactants, specifically: fatty amides, ethoxylated fatty amines and imidazolines. Several methods were employed to produce the various surfactants. For example, fatty amides were prepared from both triglycerides and methyl esters of fatty acids with diethanolamine (one equivalent of amine per carboxylate group). Generally, addition of sodium borohydride to the alkanolamine precursor resulted in significantly lighter colored amides. Conversely, postpurification of the fatty alkanolamide with sodium borohydride was much less effective. In the case of ethoxylated amines, a series of fatty primary amine ethoxylates were prepared. Comparison of amine prepurification (with either sodium or potassium borohydride) to purification during ethoxylation and/or postpurification will be presented. Imidazolines were prepared from coconut and tallow triglycerides, fatty acid methyl esters, or fatty acids with 2-(2'-aminoethyl)aminoethylamine or 2-(2'-aminoethyl)aminnoethanol using standard conditions. In the cases studied to date, prepurification of the triamine or

alkanolamine with sodium borohydride resulted in a lighter colored imidazoline. This technology offers surfactant producers a convenient, cost-effective method of improving the color of these amine based products. The color reduction realized may not only improve general product quality, but also allow the use of less costly starting materials.

Session KK Wednesday afternoon

Oxidative Stability of Fats and Oils

KK1

Autoxidation of Trilinolein and Trilinolenin. W.E. Neff, Northern Regional Research Center, USDA/ARS, 1815 North University Street, Peoria, IL 61604, and E.N. Frankel, Northern Regional Research Center.

The hydroperoxides and secondary products from the autoxidation of model triglycerides were isolated to clarify their contribution to flavor deterioration of vegetable oils. The products identified spectrometrically from trilinolein included the 9- and 13-mono hydroperoxides. The products from trilinolenin included 9-, 12-, 13-, and 16-monohydroperoxides, 9- and 16-hydroperoxy epidioxides and 9- and 16-hydroperoxy bicyclic endoperoxides and 9,12-; 13,16-; 9,16-dihydroperoxides. In trilinolein and trilinolenin the formation of bis- and tris-monohydroperoxides was observed at peroxide values exceeding 50. Analytical HPLC studies showed that during autoxidation, the mono-, bis- and tris-hydroperoxides formed consecutively. Monohydroperoxides of linoleate and linolenate triglycerides may be the most important precursors of volatile compounds contributing to flavor deterioration of vegetable oils.

KK2

Prooxidant Chemical Mechanisms of Mono- and Di-Glycerides and Fatty Acids in Soybean Oil. Behroze S. Mistry, Ohio State University, Room 122 VH, 2121 Fyffe Road, Columbus, OH 43210, and David B. Min, Ohio State University.

Minor components were isolated from soybean oil be silicic acid column chromatography. The minor components were separated into subfractions by gradient elution chromatography and low-temperature fractional crystallization. They were then identified and chracterized by IR, mass and NMR spectrometries. Effects of the minor componenets on oxidative stability of purified soybean oil were determined by measuring peroxide values, and headspace oxygen contents and volatile compounds by gas chromatography. Fatty acids, monoglycerides and diglycerides acted as prooxidants. Fatty acids showed least prooxidant activity, followed by diglycerides, and monoglycerides showed greatest prooxidant activity. Among the different fatty acids, there was no significant difference at $\alpha=0.05$ in prooxidant activities. The chemical mechanisms of the prooxidant activities of fatty acids, mono-and di-glycerides in soybean oil were studied using radio-isotope tracer techniques. Experimental data show that fatty acids, mono- and di-glycerides may concentrate at the oil surface and accelerate the solubility of surface oxygen into the oil which in turn will decrease oxidative stability of the oil. (Honored Student presentation.)

KK3

Elucidation of the Structures of Cyclic Fatty Acid Monomers Isolated from Heated Vegetable Oils. J.L. Le Quere, I.N.R.A., Laboratoire des Aromes, 17 rue Sully, BV 1540, Dijon Cedex 21034, France, and J.L. Sebedio and E. Semon, I.N.R.A. Laboratoire des Aromes.

Cyclic fatty acid monomers (CFAM) were isolated from heated linseed and sunflower oils. The structures of the major mono- and di-unsaturated CFAM were elucidated by a combination of various on-line and derivatization techniques. Gas-liquid chromatography coupled with mass spectrometry (GC-MS) studies of the unsaturated and of the on-line hydrogenated components gave the number of ethylenic bonds and the size of the rings (5 or 6 carbon membered rings). This was confirmed by syntheses of some of the hydrogenated compounds. Gas-liquid chromatography coupled with Fourier transform infrared spectrometry (GC-FTIR) studies revealed the geometry of the ethylenic bonds and, finally, the positional isomers were elucidated by a combination of ozonolysis, derivatization methods and chemical ionization GC-MS studies.

KK4

High-Temperature Stabilities of Low-Linolenate, High-Stearate and Common Soybean Oils. Lynne A. Miller, Iowa State University, Food and Nutrition Department, 111 Mackay Hall, Ames, IA 50011, and Pamela J. White, Iowa State University.

Four soybean oils (SBO) with different fatty acid (FA) compositions were tested for stability during intermittent heating and frying of bread cubes. None of the oils was hydrogenated or contained any additives. Two of the oils were from common commercial varieties. The other two oils were from seed developed in a mutation breeding program and included the line, A5, which contained 3.5% linolenate, and the line, A6, which contained 20% stearate. Each oil (450 g) was heated to 185 C in a minifryer. Bread cubes were fried at the beginning of heating, and half were stored at -10 C to preserve freshness. The second half was stored at 60 C for 14 days. Heating was continued for 10 h/day for 4 days. After 40 h of heating, an additional 30 g of bread cubes were fried. According to sensory evaluations of the fried bread cubes, peroxide values of oil extracted from the cubes and conjugated diene values of the oils, A5 and A6 oils were more stable than those from the commercial varieties. Small differences occurred in the flavor and oxidative stability of the cubes fried after 40 h of heating the oils. Large differences between A5 and A6 and the commercial varieties occurred after storage of bread cubes for 14 d.

KK5

The Flavor and Oxidative Stability of Canola Oil Blends. S. Durance-Tod, University of Manitoba, Department of Foods & Nutrition, Winnipeg, MB R3T 2N2, Canada, and R. Przybylski (Speaker), N.A.M. Eskin and M. Vaisey-Genser, University of Manitoba.

The relative flavor and oxidative stabilities of canola/sunflower and canola/cottonseed oil blends were investigated using the Schaal Oven Test at 65 C for 12 days or exposure to fluorescent light (250 ft.c.) for 4 days at 40 C. Progress of lipid oxidation was monitored by measuring peroxide value, hydroperoxide value, TBA number, total volatile carbonyls and dienals as well as volatiles by gas chromatography. Sensory evaluation of these oil blends included odor intensity and acceptability. Blending canola with sunflower or cottonseed oils improved its stability to heat-accelerated oxidation. In the case of light exposure, however, canola/cottonseed oil blends developed "light struck" flavor.

KK6

Effect of Ascorbyl Palmitate on the Accleerated Storage Stability of Canola Oil. Lynn M. McMullen, The University of Alberta, Department of Foods and Nutrition, 308 Home Economics Building, Edmonton, AB T6G 2M8, Canada, and Zenia J. Hawrysh (speaker), University of Alberta.

The effects of various levels of ascorbyl palmitate (AP) and of butylated hydroxyanisole/toluene (BHA/BHT) on the accelerated storage stability of canola oils were determined by sensory and chemical evaluations. In Schaal oven test, chemical and trained panel data indicated that 200 ppm AP was effective in retarding autoxidative changes in the oils. The addition of BHA/BHT, at 100 ppm each, to canola oil, did not improve storage stability. In fluorescent light tests (7500 lux), chemical data for oil samples indicated that 200 ppm AP was effective in retarding photooxidative changes; however, BHA/BHT was not. Data from trained panelists showed that the addition of 200 ppm AP to canola oils improved the odor characteristics but not the flavor characteristics of samples exposed to fluorescent light.

KK7

Frying Performance of Partially Hydrogenated Soybean Oil Versus Palm Olein During Laboratory Frying and Their Effect on the Flavor of Fried Potatoes. Sharon L. Melton, University of Tennessee, Department of Food Technology & Science, P.O. Box 1071, Knoxville, TN 37901, and Sajida Jafar (speaker) and Kaye Trigiano, University of Tennessee.

The objectives of this experiment were to measure the deterioration of partially hydrogenated soybean oil (PHSO) vs. palm olein (PO) under controlled laboratory conditions and to assess the effect of the oils on the flavor of fried potatoes by sensory evaluation and GCMS. Two PHSO samples and one PO were used to fry potatoes. A 400-g sample of parfried potatoes was fried every hour for 8-hours a day for 4 days in each oil. This represented a single rep, and two reps were run. Oil samples were taken at the end of each day for analysis by the Food Oil Sensor (FOS), Shortening Monitor Strip (SMS), and for color (L, a, b and ΔE), % total polar components (TPC) and % free fatty acids (FFA). The first sample of potatoes fried in each oil at the beginning of the first day and the next to last sample each day were sensory evaluated by a panel of 35 judges. The last potato sample at the end of each day was stored at -38 C for flavor volatile analysis by GCMS. Across frying time, PO developed the highest level of FFA (0.74%) and TPC (10.8%) compared with PHSO which had an ave. of 0.59% FFA and 7.9% TPC. Compared with PHSO, PO also became darker (L of 89.7 vs 92.3), more yellow (a of 7.9 vs 6.4) and redder (18.6 vs 16.4). Across frying time no significant difference in FOS was found between PO and PHSO. With increasing frying time, L decreased and a, b, %FFA and FOS increased. A panel of 35 judges couldn't tell a difference ($P<.05$) in the flavor of potatoes fried in the three oils. However, 18 judges liked the flavor of potatoes fried in PO (3.4) less than those fried in PHSO (4.5), and 17 judges liked the flavor of potatoes fried in PO (4.9) more than those fried in PHSO (4.2). GCMS analyses are underway and will be reported.

KK8

Behavior of Pre-Fried Frozen French Fries During the Final Frying Process. A. Bonpunt, I.N.R.A.-Station de Recherches sur la Qualite des Aliments de l'Homme, 17 rue Sully, BV 1540, Dijon Cedex 21034, France, and J.L. Sebedio (speaker), J. Prevost and A. Grandgirard, I.N.R.A.

Samples of pre-fried french fries were fried in both peanut and soybean oils. The purpose of the study was to determine the lipid exchanges during the second deep fat frying process between the french fries and the oil bath as a function of the number of frying operations and the type of oil used. 200 g of frozen french fries were fried in the oil bath at 180 C for 5 min. Thirty frying operations were affected. The amount of lipid was determined using the method of Folch et al., and the amount of polar components was determined using Silica cartridges. The polymers were analyzed by gel permeation chromatography. The 18:1 positional and geometrical isomers were studied by a combination of silver nitrate thin layer chromatography, high performance liquid chromatography and ozonolysis in BF3-MeOH. The cyclic fatty acid monomers were isolated using urea adduct fractionation and studied by GC-MS after total hydrogenation. The study of the nature of *trans* 18:1 acids of the oils and the lipids of the french fries showed exchanges between the pre-fried french potatoes and the oil bath. The study of the components formed after frying showed that at 180 C, one should not do more than 15 frying operations at this temperature.

KK9

Automated Determination of Peroxide Value. Melinda Guzman-Harty, Ross Laboratories, Analytical R & D Technical Center, 625 Cleveland Avenue, Columbus, OH 43216, and Madeleine Dautartas, Ross Laboratories.

An automated procedure which uses the same iodometric chemistry as the manual method for peroxide value (A.O.C.S. Method No. Cd 8-53) was developed. This method can measure low peroxide values ranging from 0.09 to 13 with 3.5% relative standard deviation or better. Its improved sensitivity and precision is attributed to the automated potentiometric endpoint determination which replaced the manual iodine-starch endpoint detection. With the use of a computer-aided autotitrator interfaced with a balance and printer, an oil sample analysis from initial weighing to the final calculation of peroxide value can be completed in less than 10 minutes. Comparison of the

precision and accuracy of the automated method with that of the manual method using different types of oil will be presented. The parameters which may affect the accuracy and reproducibility of the automated method (solvent composition, sample size, deoxygenation and subdued light conditions, reaction time) were investigated.

KK10

Deficiencies in the Active Oxygen Method. Mark Matlock, Archer Daniel Midland Company, Lakeview Technical Center, 1001 Brush College Road, Decatur, IL 62525.

Since first described by King in 1933, the use of peroxide value to monitor accelerated oxidation of vegetable oils has been this industry's primary tool for the measurement of oil stability. This methodology is embodied in the Active Oxygen Method (AOM AOCS Cd 12-57). This technique, while capable of producing reliable data, has numerous deficiencies which are compounded from common quality control laboratory modifications. This paper will discuss errors introduced by several of these common modifications, as well as subtle errors inadvertantly introduced.

KK11

Improvements in a Procedure for Quality Control: The Oil Stability Index (OSI). Mark Matlock, Archer Daniel Midland Co., Lakeview Technical Center, 1001 Brush College Road, Decatur, IL 62525.

An instrumental procedure far superior to the AOM was studied. For the reasons outlined in this paper, it is a strong candidate for total replacement of AOM. An instrument designed in our laboratory and previously described, determines oil stability by measurement of evolved volatile organic acids by conductance. Computerized data acquisition with mathematical end point determination by a second derivative algorithm improves precision. With this instrument the effects of various parameters on oil stability were studied. A single model equation accurately predicted oil stability index values from 85 C to 140 C for soy oil. This is of major benefit to the quality control laboratory, since it enables faster analysis and prediction of product stability. An excellent correlation of OSI values with AOM data was obtained over a range of 20 to 450 hours. In order to obtain accurate data for the AOM, it was necessary to rigorously run the procedure as described in Part I of this series of papers. This correlation would allow this automated method to directly replace the use of AOM.

Session LL Wednesday afternoon
Castor Oil II

LL1

Review and Critique on Hydrolytic and Enzymatic Splitting of Castor Oil. N.O.V. Sonntag, consultant, 306 Shadowwood Trail, Red Oak, TX 75154.

Castor oil undergoes several undesired reactions when subjected to conventional splitting conditions: dehydration, conjugation and/or polymerization and both internal and external (esterlide) esterification. These competitive reactions have essentially prevented the application of conventional fat splitting methods, like the Colgate-Emery process, for the production of castor oil fatty acids. Although castor oil was one of the very first vegetable oils to be split enzymatically, the batch splitting method has never been a satisfactory process for commercial production. This paper reviews and summarizes optimum conditions for production of fatty acids and methyl esters from castor oil.

LL2

The Role of Ricinoleate Products in Coatings. J. Chu, CasChem Inc., 40 Avenue A, Bayonne, NJ 07002, and M. Brauer and F. Naughton, CasChem Inc.

Castor oil and its derivatives have been used to formulate alkyd, epoxy, acrylic, melamine and urethane coatings. Typically castor oil itself and various value added derivatives of castor oil such as: ricinoleic acid, dehydrated castor oil, linoleic acid and ricinoleic and linoleic esters have been used in conventional coatings with volatile organic contents in the range of 5–7 pounds per gallon. The ricinoleate derivatives impart hydrophobicity and flexibility to the cured coating and also provide good flow characteristics due to excellent pigment wetting characteristics. More recently, there has been a demand for coatings with much lower volatile organic contents. In order to satisfy this need, new ricinoleate polyols have been developed. These polyols are relatively low in viscosity, and they exhibit excellent compatibilities with higher viscosity, acrylic, polyester and polybutadiene polyols. By blending these concentional polyols with the new ricinoleate polyols, coatings with VOC's as low as 2.6 have been marketed by various coating companies. Moreover, these coatings have retained the excellent rheology, flexibility and hydrophobicity of the products based upon the older ricinoleate technology. This paper will illustrate the use of ricinoleate chemistry in both the traditional and low VOC coatings applications.

LL3

The Use of Ricinoleate Polyols in Automotive Polyurethane Elastomers. W.J. Downey, Cas Chem Inc., 40 Avenue A, Bayonne, NJ 07002, and M. Brauer and F. Naughton, CasChem Inc.

For many years polyurethane foams have been used by the automotive industry in the passenger and storage compartments. Non-cellular polyurethanes were then used in mechanically functioning parts and now have found their way into large exterior automotive parts. However, polyurethanes are only beginning to be examined in under-the-hood applications. With ever increasing technology in control and sensing devices there is an expanding need for low stress insulating elastomers. Polyurethanes will need to be resistant to automotive fluids, be electrically insulating and provide a wide range of physical properties. Polyurethane elastomers based on ricinoleate chemistry provide these qualities. Due to numerous ricinoleate derivatives, properties can be easily altered. In comparison to polybutadiene and silicone polyol based polyurethanes the ricinoleates will give a better balance of chemical resistance and physical performance. They will also

out perform polyether polyol based formulations. Comparisons of physical properties, electrical properties and chemical resistance will be presented. Also, the influence of molecular weights per crosslink will be illustrated.

LL4

The Use of Ricinoleate Polyols as Polybutadine-Urethane Modifiers. M. Brauer, CasChem Inc., 40 Avenue A, Bayonne, NJ 07002, and W.J. Downey and F. Naughton.

Hydroxyl terminated polybutadiene (HTBD) oligomers have found use in a variety of applications such as solid propellant binders, elastomeric coatings, sealants and potting compounds. The oligomers are cured by reacting the hydroxyl group with a multifunctional isocyanate. The resulting polyurethanes exhibit desirable properties such as low moisture absorption, low water permeability, high extensibility, good dielectrics and low glass transition temperatures. However, the HTBD polyols exhibit some undesirable properties such as high viscosity, low functionality and very poor compatibility with other polyols. These characteristics have limited the utility of HTBD based castable urethane systems. It has been found, however, that multifunctional ricinoleate polyols are highly compatible with the HTBD. Consequently, it is now possible to achieve low viscosity, castable urethanes based upon true solutions of HTBD and ricinoleate polyols. Moreover, important properties such as hydrophobicity, dielectrics, glass transition temperatures and extensibility remain essentially uncompromised. Furthermore, it will be shown that HTBD based urethane obtained by blending the oligomers with ricinoleate polyols exhibit, for many applications, improved physical properties.

LL5

Use of Castor Oil and Its Derivatives in Cosmetic Applications. W. Woods, CasChem Inc., 40 Avenue A, Bayonne, NJ 07002, and M. Brauer and F. Naughton.

Castor oil plays two prominent roles in cosmetics. First, as a raw material in itself, castor oil has been formulated into numerous cosmetic formulations. Castor oil's unique chemical and physical properties are responsible for its wide cosmetic use. Castor oil also serves as a feedstock for its derivatives, which is another prominent role. Castor oil's unique chemical and physical properties are retained by its derivatives and are imparted to formulations. This paper will relate castor oil's molecular structure with its function and property. Emolliency, mildness and non-comedogenicity are a few of castor oil's more attractive properties which will be highlighted in this paper.

LL6

Oleochemicals From Castor Oil.

Abstract not available at press time.

Session MM Wednesday afternoon Biochemistry II

MM1

Altered Membrane Structure After Lipid Peroxidation Activates Phospholipase A_2. Alex Sevanian, University of Southern California, 1985 Zonal Avenue, Los Angeles, CA 90033, and Laurie McLeod, Mary Lou Wratten and Eunjoo Kim, University of Southern California.

The ability of phospholipase A_2 (PLA_2) to degrade oxidized phospholipids (PL) is associated with membrane structural changes imposed by lipid peroxidation (LP). Membrane fluidity was significantly decreased after peroxidation of liposomes prepared from liver PL. Minor levels of LP are needed to alter thermotropic characteristics of artificial membranes. For example, a similar decrease in fluidity was achieved by peroxidation of ~5% of the liposome PL as by increasing the proportion of phosphatidylethanolamine in phosphatidylcholine liposomes by 20%. Peroxidized membranes were hydrolyzed by PLA_2 at rates three times greater than unoxidized membranes which exhibited greater fluidity with lower and more distinct phase transition temperatures (Tc). Although there was considerable hydrolysis of oxidized fatty acids, substantial amounts of unoxidized fatty acids were also released. PLA_2 activity appeared to be self-limiting since hydrolysis ceased well before all PL were degraded. The limited action of PLA_2 may be due to imposed structural alterations rather than product inhibition. Membrane instability following LP was evidenced by enhanced fusion of unilamellar vesicles forming larger mixed vesicles. Enhanced PLA_2 activity is generally seen when oxidized PL shift the Tc of membranes and when the Tc approaches ambient temperatures of the assay. These results indicate that PLA_2 is activated by structural imperfections created in peroxidized microenvironments. Oxidized and intact fatty acids entrapped in these microenvironments are in turn released.

MM2

Effect of Methyl Arachidonate Hydroperoxide Postitional Isomers on Liposomal Calcium Ion Uptake. Nancy J. Moriarity, Eastern Regional Research Center, USDA, ARS, 600 E. Mermaid Lane, Philadelphia, PA 19118, and Fred A. Kummerow, University of Illinois.

Lipid peroxidation has been shown to occur *in vitro* and *in vivo*. One of the basic functions of the lipid bilayer membrane is its ability to restrict random ion penetration due to its highly hydrophobic interior. Many cellular processes and enzyme activities are affected by intracellular Ca^{2+} concentration. In this study, hydroperoxides were synthesized by methylene blue-generated singlet oxygen catalysis. Normal and reverse phase HPLC were utilized to separate various positional isomers. Products were identified by GC-MS and quantitated by liquid scintillation counting. Hydroperoxides were incorporated into DPPC:DPPG large unilamellar vesicles at levels that were not uniform but were quantitated. Trends indicated that increased vesicle content of methyl arachidonate or its hydroperoxides resulted in decreased Ca^{2+} uptake. Vesicles containing neither methyl arachidonate nor its hydroperoxides exhibited the greatest Ca^{2+} uptake. Several positional isomers displayed effects which were exceptions to the overall trends. The 5-hydroperoxide did not decrease Ca^{2+} uptake of vesicles to the extent that all other compounds did. Additionally, 6-, and 14-hydroperoxymethyl arachidonate (the non-conjugated isomers) appeared to decrease Ca^{2+} uptake even more than methyl arachidonate controls. When cholesterol was a vesicle component,

Ca^{2+} uptake data were different. In this case, methyl arachidonate incorporation at low levels resulted in dramatic decreases in vesicle Ca^{2+} uptake. However, 15-hydroperoxy-methyl arachidonate incorporation barely effected Ca^{2+} uptake.

MM3

Identification of Phospholipase B as a "Stalked" Membrane Protein of the Intestinal Brush Border. A. Kuksis, C.H. Best Institute, Banting and Best Dept. of Medical Res., 112 College Street, Toronto, ONT M5G 1L6, Canada, and S. Pind (speaker), C.H. Best Institute.

The intestinal brush-border membrane contains a number of intrinsic proteins which catalyze the final stages of digestion, prior to absorption of nutrients from the gut. Many of these enzymes are 'stalked' membrane proteins in that most of their mass, including their active site, projects in to the intestinal lumen; they are anchored in the membrane by a small hydrophobic segment and connected to the main protein mass by a polypeptide stalk. We now report that the phospholipase A_2 previously identified in rat jejunal brush-border membranes is actually a phospholipase B, with phospholipase A_2 and lysophospholipase activities, conforming with the model of a stalked protein. Both enzyme activities were renatured following non-reducing sodium dodecyl sulphate polyacrylamide gel electrophoresis (SDS-PAGE) of the membrane proteins, and were shown to co-migrate with a protein band having a relative molecular mass of 170 kDa. This band accounted for approximately 0.1-1% of the total membrane protein. Both activities were liberated, in an active form, from the membranes by a proteolytic treatment with papain, resulting in a reduction of the protein's relative mass to approximately 165 kDa by SDS-PAGE. This active fragment was now water soluble and eluted as a single peak during gel filtration on a Sephacryl S-300 column. This enzyme hydrolyzes choline and ethanolamine phosphatides and may play a role in phospholipid digestion and absorption.

MM4

Regulation of Sterol Biosynthesis in Cultured Plant and Animal Cells by 24(*RS*), 25-Epiminolanosterol. W. David Nes, U.S. Department of Agriculture, Richard B. Russell Research Center, P.O. Box 5677, Athens, GA 30613, and Beni Tal, U.S. Department of Agriculture, George Popjak and Aniko Meenan, U.C.L.A. School of Medicine, and Edward J. Parish, Auburn University.

In our efforts to determine whether cells of plant and animal origin utilize sterols in multiple roles analogous to the fungal systems studied, we cultured sunflower and rat hepatoma (H4) cells in chemically defined media with an N-steroid-24(*RS*), 25-epiminolanosterol (EL.) that selectively interferes with the metabolism of the sterol side chain δ^{24}-bond. A direct correlation between increasing levels of EL., cessation of end product formation and growth inhibition was observed for both cell cultures. EL. is toxic at 2.5 ppm in the plant cultures and 20.0 ppm in the animal cultures. Even though sterol biosynthesis continues in the EL.-treated cultures viz., producing cycloartenol in sunflower and zymosterol in H4 cells, and the natural end product(s) is supplied in the media the cells fail to recover from the drug's inhibitory effect. The results are consistent with the concept (Popjak-Nes) that a vitamin level of endogenously formed sterol (which must be localized in the nucleus) is required together with a bulk sterol (that can be acquired from the media) in aerobically grown cells to mediate the cell cycle events that govern cell proliferation.

MM5

The Cytotoxicity and Antiproliferative Effects of Lysophosphatidylcholine and Alkyl Lysophospholipids are Modulated by Cholesterol. Barbara Malewicz, The Hormel Institute, University of Minnesota, 801 16th Avenue NE, Austin, MN 55912, and Wolfgang J. Baumann, The Hormel Institute.

The effect of lysophospholipids on cell growth and cell viability was studied in Novikoff rat hepatoma cells as a function of cell cholesterol. Novikoff cells adapted to serum-free conditions particularly lend themselves to these studies, because cholesterol levels can be modulated by growing the cells in cholesterol-supplemented medium. We were able to increase free cell cholesterol more than 6-fold in cells grown in high cholesterol medium (80 nmol/ml); yet, cell growth, protein synthesis, nucleic acid synthesis, and phospholipid content were not affected. We found that 1-*O*-hexadecanoyl-*sn*-glycero-3-phosphocholine (lysoPC) or 1-*O*-octadecyl-2-*O*-methyl-*sn*-glycero-3-phosphocholine (dietherGPC) at low micromolar concentration inhibited cell growth as judged by the rate of [^{14}C]thymidine incorporation. Growth inhibition by lysoPC and dietherGPC was dose-dependent and was significantly lower in high cholesterol cells. Furthermore, the resistance of the cells to cytotoxic attack by lysoPC and dietherGPC, as measured by $^{15}Cr^{3+}$ release, increased with increasing cell cholesterol levels. Apparent loss of the agents' effective cytotoxicity was proportional to the amount of free cell cholesterol. Inhibition of cell growth and cytotoxicity induced by lysoPC or dietherGPC over longer growth periods (24 hrs) responded differently to cell cholesterol.

MM6

Characterization and Quantification of Three Plasma Lp(a) Lipoprotein Subclasses. Frank T. Lindgren, Lawrence Berkeley Laboratory, Donner Laboratory, Room 315, 1 Cyclotron Road, Berkeley, CA 94720, and Virgie G. Shore, Lawrence Livermore National Laboratory, Gerald L. Adamson and Laura A. Glines, Lawrence Berkeley Laboratory.

One of the least characterized atherogenic human plasma lipoproteins is lipoprotein (a) or Lp(a). It exists in the density range of 1.05-1.08 g/ml and has a molecular weight ranging from 5-9 million Daltons. In normal adult males, it is either absent or in the form of 1-3 subfractions of density (d) d_1<1.063 g/ml, d_2=1.063 g/ml, and/or 1.063 g/ml<d=^{3}<1.08 g/ml. Analysis was by 2-16% (Pharmacia) gradient gel electrophoresis (GGE) with a -70 C frozen standard of total low density lipoproteins (LDL). All GGE runs, stained with Coomassie Blue-R250, were made on the above density fractions isolated by preparative ultracentrifugation and the standard (calibrated by analytic ultracentrifugation) was included in each gel run. Quantification of Lp(a), when present, was by appropri-

ately relating the peak heights of the standard with the peak heights of each fraction by densitometry at 555 nm. The d_1 and d_2 diameters were both in the 295-305Å range, whereas the denser d_3 fraction included a larger range of approximately 305-340Å. The order of abundance was $d_1 > d_3 > d_2$ and the total mean and standard deviation was 33 ± 41 mg/100 ml. Verification of the presence of the Lp(a) antigen was made by western immunoblotting on cellulose acetate. When present, the Lp(a) co-blotted with apolipoprotein B-100 and apolipoprotein E. Faint co-blotting was also observed with the antigen, plasminogen. Correlations were made of the Lp(a) concentrations with analytic ultracentrifugation in a middle-aged male population (n=26). Lp(a) concentrations correlated positively and significantly only with S_f 0-3 and S_f 20-30 lipoproteins.

Session NN Wednesday afternoon General Synthesis

NN1

Synthesis and Characterization of Linoleate- and Linolenate-Containing Triglycerides in Vegetable Oils for Autoxidation Studies. R.A. Awl, Northern Regional Research Center, ARS-USDA, 1815 North University Street, Peoria, IL 61604, and D. Weisleder and E.N. Frankel, USDA Northern Regional Research Center.

Major unsaturated triglycerides found in vegetable oils were synthesized to determine the effect of fatty acid position on their relative oxidative stabilities. The triglycerides LLLn, LLnL, LnLnL, LnLLn, PPL, PLP, PPLn, PLnP, PLL, LPL, PLnLn, and LnPLn (where P = palmitic, L = linoleic and Ln = linolenic acids) were synthesized in gram quantities and purified by dry column chromatography. Triglyceride purity was monitored by thin-layer and gas liquid chromatography of the methyl esters, by lipase hydrolysis, and by ^{13}C nuclear magnetic resonance (NMR). Quantitative ^{13}C NMR of the unsaturated triglycerides proved useful for identifying the isomeric structures, and it complemented lipase hydrolysis as a method of determining isomeric composition. The synthetic triglycerides are valuable models to elucidate the interrelationship of unsaturated fatty acids on their oxidative stability in vegetable oils.

NN2

Microbiological Syntheses of Triglycerides and Wax Esters. S. Koritala, Northern Regional Research Center, USDA/ARS, 1815 North University Street, Peoria, IL 61604.

Aspergillus flavus (NRRL 1957) grown on soybean oil fatty acids as the sole carbon source produced triglycerides. Most of these triglycerides were intracellular, although considerable amounts were also found extracellularly. The content of polyunsaturated acids in these triglycerides was greater than expected from the added substrate. *Euglena gracilis* (ATCC 12716) grown on yeast-malt extract medium synthesized wax esters. Tetradecanoic acid and tetradecanyl alcohol were the predominant components of the wax esters. Only saturated even-numbered acids and alcohols (C_{12} to C_{18}) were found with traces of odd-numbered fatty acids and alcohols. Tetradecanyl tetradecanoate was the predominant component in the wax esters.

NN3

The Acid-Catalyzed Addition of Alkoxyl Groups to the Olefinic Double Bonds of Soybean Oil. R.V. Madrigal, Northern Regional Research Center, USDA/ARS, 1815 North University Street, Peoria, IL 61604, and M.O. Bagby, USDA Northern Regional Research Center, and E.H. Pryde (Deceased).

The acid-catalyzed reaction of soybean oil with the homologous series of straight-chain alcohols: methyl, ethyl, n-propyl, n-butyl, n-hexyl and n-octyl in a pressurized system yields completely transesterified products and 17-28% substituted alkyl ethers. Mass spectrometry of the hydrogenated methyl ester derivatives of these ethers showed that the addition reaction occurred mainly at one of three double bonds of the unsaturated fatty acids. Reactions with secondary alcohols yielded only 0.1-2.5% substituted alkyl ethers. The alkoxyl group alters the hydrocarbon chain linearity thus altering viscosity. The alkyl ether products should have decreased reactivity with oxygen and be less subject to oxidative polymerization and cross-linking at high temperatures. Such products from unsaturated fatty materials might have enhanced properties with regard to alternative fuels, fuel additives, cosmetics and similar products.

NN4

Preparation of Deuterated Methyl 6,9,12-Octadecatrienoates and Methyl 6,9,12,15-Octadecatetraenoates. H. Rakoff, Northern Regional Research Center, ARS-USDA, 1815 North University Street, Peoria, IL 61604.

Methyl 6,9,12-octadecatrienoate-15,15,16,16-d_4 was obtained from Wittig coupling between 3-nonenyl-6,6,7,7-d_4-triphenylphosphonium iodide, 1, and methyl 9-oxo-6-nonenoate, 2. For the preparation of compound 2, methyl 6-oxohexanoate, obtained from the ozonolysis of cyclohexene, was coupled in a Wittig reaction with [2-(1,3-dioxan-2-yl)ethyl]triphenylphosphonium bromide to give methyl 8-dioxanyl-6-octenoate. This compound was transacetalized to methyl 9,9-dimethoxy-6-nonenoate which was then hydrolyzed to 2. For the preparation of compound 1, 2-pentynol was converted to the tetrahydropyranyl ether and deuterated with deuterium gas and tris(triphenylphosphine)rhodium (I) chloride. Reaction of the tetradeuterated tetrahydropyranyl ether with triphenylphosphine dibromide in methylene chloride yielded 1-bromopentane-2,2,3,3-d_4 which was coupled with 3-butynol with lithium amide in liquid ammonia to give 3-nonynol-6,6,7,7-d_4. Lindlar reduction converted the deuterated alkynol to 3-nonenol-6,6,7,7-d_4. This deuterated alkenol was converted to the bromide with triphenylphosphine dibromide, then to the iodide with sodium iodide in acetone and finally to 1 with triphenylphosphine in acetonitrile. Methyl 6,9,12,15-octadecatetraenoate-15,16-d_2 was prepared in a similar manner with the only difference being the conversion of the tetrahydropyranyl ether of 2-pentynol to the tetrahydropyranyl ether of 2-pentenol-2,3-d_2 with deuterium gas and Lindlar's cata-

lyst. Mixtures of geometric isomers formed were separated by silver resin chromatography.

NN5

1,2- and 1,3-Dialkylglycerol Ethers: Synthesis and Configuration Analysis. Philip E. Sonnet, Agricultural Research Service, USDA, 600 E. Mermaid Lane, Philadelphia, PA 19118.

The preparation of a series 1,2- and 1,3-(unsymmetrically substituted) dialkylglycerol ethers is described. These compounds are projected as model substrates by which to judge lipase reactivity. The absolute configurations of these compounds and their configurational purity can be determined by conversion to diastereomeric derivatives, the chromatographic properties of which are reported here. The elution orders of the diastereomeric derivatives are discussed with reference to existing conceptual models for related separations.

NN6

Stereospecific Alkene Formation via Peterson Olefination. John Flygare, Northwestern University, Evanston, IL 60208, and A.G.M. Barrett, Northwestern University.

Simple alkene units occur in numerous natural products including a wide range of unsaturated fatty acids and oils. The critical step in their synthesis is the condensation of two carbon fragments to form the alkene. Existing methods of generating alkenes are not convenient to produce either the E or Z alkene from a common intermediate. Our research centers on the Peterson olefination, the stereochemical outcome of which depends on the diastereospecific construction of erythro or threo β-hydroxy silanes. We have synthesized novel silyl reagents that will lead to predominately one β-hydroxy silane. Acidic work up at this point will lead to one alkene, while basic work up will lead to the other. The procedure is applicable to internal, nonfunctionalized alkenes, for the reagent inducing the selectivity is not a part of the substrate. This modification of the Peterson olefination, allowing versatile means to either alkene, should prove invaluable to the synthesis of unsaturated fatty acids and oils. (Ralph Potts Award presentation.

NN7

Synthesis and Properties of 2,2'-Oxirane and Epithio Fatty Acid Esters. Marcel S.F. Lie Ken Jie, University of Hong Kong, Department of Chemistry, Pokfulam Road, Hong Kong.

Keto fatty acid esters were readily converted to the corresponding 2,2'-oxirane derivatives by two-phase methylene transfer reaction. Treatment of such oxirane derivatives with dimethylthioformamide gave the epithio derivatives. The physical properties of these two classes of novel fatty acid derivatives are described. Boron trifluoride catalyzed cyclization of a dimethylene interrupted bi-2,2'-oxirane C_{18} fatty ester gave substituted tetrahydropyranyl and bicyclo oxygeterocyclic derivatives.

Session OO Wednesday afternoon
General Analytical II

OO1

Determination of Oil Content in Canola Seed by a Modified Regrind Procedure—Comparison with Grinding with Diatomaceous Earth. J.K. Daun, Canadian Grain Commission, Grain Research Laboratory, 1404-303 Main Street, Winnipeg, MB R3C 3G8, Canada, and H.K. Howard, Canadian Grain Commission.

Regrinding partially extracted oilseed meals in the presence of solvent using stainless steel tubes and ball bearings was compared with the currently recommended AOCS Method AI 3-76 which specifies a single grind in the presence of diatomaceous earth. The regrind procedure is essentially the same as the recently adopted FOSFA Method except for the sample size and the type of ball mill employed. Results from the regrind procedure were consistently higher than results from the AOCS Method by 0.5% to 1.7% depending on the sample analyzed. Although somewhat more labor intensive than the AOCS method, the regrind method can be completed within 7.5 hours.

OO2

Development of a Rapid Equilibrium Method for Analysis of Total Oil in Soybeans. Patricia Clark, University of Arkansas, Department of Food Science, Route 11, Fayetteville, AR 72703, and Harry E. Snyder, University of Arkansas.

Previous work has shown that finely ground and sieved soybean tissue can be analyzed for total oil by equilibration with solvent instead of by exhaustive extraction. We have further studied this equilibrium method and have determined procedures needed to improve the accuracy. Factors studied were the temperature of the solvent, preheating of soybeans before equilibration, storage time of the ground tissue before equilibration, moisture of the flour and evaporation of solvent. Also, we have compared the rapid equilibrium method with a traditional Goldfisch extraction. The Goldfisch method usually gives 0.5 to 1.5% more lipid than the equilibrium method, and the reason for this difference has been studied in terms of phospholipid extracted. The Goldfisch and equilibrium methods have been applied to 13 varieties of soybeans over 3 growing seasons, and results of these analyses will be presented. (Honored Student presentation.)

OO3

Determination of Total Sulfur Contents in Fats and Oils and Identification of Some Sulfur-Bearing Fatty Acids in Canola Oil. R.C. Wijesundera, Canadian Institute of Fisheries Tech., Technical University of Nova Scotia, P.O. Box 1000, Halifax, NS B3J 2X4, Canada, and R.G. Ackman (speaker), Canadian Institute of Fisheries Tech.

A simple and reliable method has been developed for the determination of ppm levels of sulfur in fats and oils. The method involves the combustion of a sample in an oxygen bomb and subsequent quantitative determination of the resultant sulphate ions by ion chromatography with indirect UV photometric detection. It is shown that

sulfur is not limited to the *Cruciferae* family, but is in many vegetable oils, albeit often at a low level. To identify the sulfur compounds in canola oil, its methyl esters were fractionated by urea complexation. The non-urea complexing fraction, which contained most of the sulfur was further fractionated by preparative TLC and the fractions were analyzed by GC/MS. By this means, the isomeric 9,12;8,11; and 7,10 epithio stearic acids were identified as minor constituents of canola oil.

OO4

Analysis of Oil and Meal From *Lesquerella fendleri* Seed. Kenneth D. Carlson, Northern Regional Research Center, ARS, USDA, 1815 North University Street, Peoria, IL 61604, and Alka Chaudhry and Marvin O. Bagby, USDA Northern Regional Research Center.

Attention is being focused on *Lesquerella* species as a source of hydroxy acids to replace imported castor oil. Genetic and agronomic improvement and utilization of the seed oil and meal are being studied. We have conducted laboratory experiments to extract oil from *L. fendleri* seed in preparation for extracting large quantities of seed. *L. fendleri* is a member of the *Cruciferae* family, and when seeds are crushed glucosinolates release isothiocyanates by the action of a thioglucosidase enzyme system. Therefore, our experiments included moist heat treatment of whole seeds to inactivate this enzyme. The seed was then flaked in a Wolf mill, and the flakes were exhaustively extracted with hexane. The oil was degummed and bleached, and then analyzed for hydroxyl (103), saponification (174), and iodine values (107), and for unsaponifiables (1.5%), FFA (1.13%) and P (10 ppm) contents. Hydroxy fatty acids, 55% lesquerolic (14-hydroxy-*cis*-11-eicosenoic) and 3% auricolic (14-hydroxy-*cis*-11, *cis*-17-eicosadienoic), and total fatty acid distribution were determined by GC of the methyl esters. The defatted meal was analyzed for residual oil (1%), protein (29.8%), non-protein nitrogen (0.7%), ash (6.45%), crude fiber (12.9%), and for distribution of amino acids. Defatted *L. fendleri* meal has an excellent distribution of amino acids, including higher levels of lysine and methionine, and of valine, histidine, alanine, glycine, arginine, and threonine than soybean meal.

OO5

Mucilage in Canola Seeds. N.A.M. Eskin, University of Manitoba, Department of Foods and Nutrition, Winnipeg, MB R3T 2N2, Canada, and S. Sharafabadhi, University of Manitoba.

Six canola varieties were grown at five different locations in Western Canada and examined for their mucilage content. These varieties included two *Bassica campestris*, Tobin and Candle and four *Brassica napus*, Andor, Regent, Triton and Westar grown in Alberta, Saskatchewan and Manitoba. The seeds were preheated prior to cold water extraction followed by precipitation with ethanol. This paper will discuss some chemical and physical properties of mucilage obtained from these canola varieties.

OO6

Variation in the Fatty Acid Composition of Lecithins. P. Kaufmann, University of Stockholm, Analytical Chemistry, Stockholm, Sweden, and U. Olsson and B.G. Herslöf, University of Stockholm.

The variation in the fatty acid composition of phospholipid classes in different batches of lecithins was studied. The classes were separated by gradient column extraction and preparative TLC. The resulting fractions were transesterified to methyl esters and analyzed by capillary GC. The obtained data were treated by univariate statistics, ANOVA, and multivariate statistics, SIMCA. The results show that there is a significant difference in the fatty acid composition between batches of similar origin and class distribution. Multivariate statistics were applied in an effort to correlate the fatty acid composition with the physical chemical behavior of the class.

OO7

Correlation of Heats of Combustion with Empirical Formulas for Fatty Alcohols. Bernard Freedman, Northern Regional Research Center, ARS/USDA, 1815 N. University Street, Peoria, IL 61604, and M.O. Bagby, USDA Northern Regional Research Center.

Multiple regression analysis (MULREG) was used to correlate gross heats of combustion (Hg) of fatty alcohols with selected physical constants related to the empirical formula. The Hg for the homologous series of fatty alcohols C_{10}-C_{22} were measured in a Parr adiabatic calorimeter, and ranged from 1582.4 to 3452.9 kg-cal/mole. MU-

LREG input consisted of the dependent variable-measured Hg-and 29 combinations of independent variables involving carbon number (CN), electron number (EN), molecular weight (MW) and their squares. The output consisted of statistical data including multiple correlation (MC), standard error, and F value. Statistical evaluation of the combination EN+MW led to its selection as the best variable combination to correlate the dependent and independent variables. The program determined a calculated Hg according to the following equation associated with this selection: Hg = -72.36663 + 12.96461 EN + 5.49736 MW. Comparison of the measured and calculated Hg values showed very close agreement. For example, the measured and calculated Hg for stearyl alcohol were 2825.70 and 2827.05 kg-cal/mole. Furthermore, a plot of measured vs. calculated Hg for C_{10}-C_{22} alcohols showed a linear relationship with a correlation coefficient of 1.0000. A plot of measured Hg vs. chain length for these alcohols also showed a perfect linear relationship. Thus, knowing chain length of an unknown fatty alcohol, its Hg could be accurately predicted.

OO8

Squalene, a Natural Inhibitor of Chilling Injury in Stored Grapefruit. Harold E. Nordby, U.S. Department of Agriculture-ARS, Horticultural Research Laboratory, 2120 Camden Road, Orlando, FL 32803.

During shipment overseas, grapefruit kept at temperatures near 40 F tend to be subject to pitting or brown staining of the flavedo (rind) called chilling injury, CI. This CI can be diminished to a certain extent if the fruit is conditioned by storing at 60 F for 7 days prior to shipment. The mechanisms of CI and this conditioning are largely unknown, although there is some evidence that lipid biomembranes are involved. In a TLC comparison of the flavedo lipids from conditioned and nonconditioned grapefruit, a major concentration difference occurred in the hydrocarbon area of the plate. Isolation of the epicuticular wax, separation of the hydrocarbons from the waxes, other components, and GLC analyses revealed the level of squalene to be 12 times greater in the conditioned fruit. Both non- and conditioned grapefruit stored monthly during the September-April 86-87 season were examined for CI and squalene levels. An inverse correlation occurred between squalene level and the CI index during the season. Confirmation of squalene as a natural CI inhibitor is being obtained with ongoing squalene-application studies.

Session PP Wednesday afternoon

Environmental Control: Extraction and Disposal of Spent Bleaching Clays—A Round Table Discussion

Session RR Tuesday afternoon

Poster Presentations

RR1

The Lipids of Bovine Teat Canal Keratin. Joel Bitman, Milk Secretion and Mastitis Laboratory, U.S. Department of Agriculture, Building 173, Beltsville, MD 20705, and D.L. Wood, S.A. Bright and R.H. Miller, Milk Secretion and Mastitis Laboratory.

Keratin (K), the soft, waxy material in the bovine teat canal, is presumed to be a natural physical and antimicrobial barrier to mastitis. Teat canals from 12 lactating (LACT) and 12 dry (DRY) cows were scraped to obtain K. Lipids were extracted from K with 2:1 chloroform-methanol. Neutral lipids and fatty acids (FA) were determined by thin-layer and capillary gas-liquid chromatography. Mean wet wt of K from DRY was 2X that of LACT cows. Water content was 60% and lipid content was 4% of K wet wt. Triglycerides were higher in K from LACT cows, 58% vs 28%, whereas cholesterol was lower in K from LACT cows, 19% vs 38%. Short and medium-chain FA were 3X higher in LACT than in DRY; 18:2 and polyunsaturated FA were 2X lower in LACT than in DRY K. Phospholipids constituted only 3-5% of the neutral lipids. No differences were apparent between the distribution of phospholipid classes of K from LACT and DRY cows. Neutral lipids of K from LACT and DRY cows were very different from neutral lipids of milk, where triglycerides constitute 98% of total lipids and cholesterol is a very minor component. Results indicated major differences between the neutral lipid composition of keratin from DRY and LACT dairy cows.

RR2

Analysis of Cereal Products by Dynamic Headspace/Gas Chromatography. Brian D. Kirk, Tekmar Company, P.O. Box 371856, 10 Knollcrest Drive, Cincinnati, OH 45222-1856.

Dynamic Headspace/Gas Chromatography (DH/GC) has gained popularity as an effective and sensitive technique for the analysis of volatile organic compounds in cereal products. The increased popularity of DH/GC over other available techniques is due primarily to the superior sensitivity obtainable. A larger quantity of volatile compounds are actually injected into the gas chromatograph. This allows a greater number of individual volatiles to be characterized. DH/GC has also gained acceptance based on the mechanism by which the sample molecules are extracted. The cereal sample is swept with an inert gas in order to encourage the volatile analytes to leave the solid matrix in favor of the gas phase, thus emulating the sampling process utilized in the human sense of smell. This similarity to the human olfactory process makes it possible to relate and compare the results obtained for DH/GC analysis directly to those obtained from human test panels. The results obtained from DH/GC are quantitatively more reproducible than those of the human nose. However, reproducibility is probably its major shortcoming. The difficulties associated with obtaining reproducible results stem from the lack of homogeneity of the sample matrix. Volatile compounds located near the surface of a solid particle are more easily removed than compounds more deeply entrained. This paper will illustrate several methods to overcome these matrix effects and optimize reproducibility, thus enhancing quantitation. Data will be presented showing statistical variance of cereal samples prepared and purged in a variety of configurations.

RR3

Impact of Adsorbent Bleaching on Oxygenated Compounds and Stability. James M. Bogdanor, W.R. Grace & Co., Davison Chemical Division, 7379 Route 32, Columbia, MD 21044.

The presence of oxygenated compounds, as indicated by the peroxide and anisidine values (PV and AV), is of great concern to refiners. A high level of oxygenated products is an indication of damaged oil and can result in poor oil stability. Data are presented which explore the impact of adsorbent type, PV and AV before and after bleaching, bleaching temperature and bleaching vacuum on deodorized oil stability. In particular, the relationship between PV and AV at various processing stages is addressed in order to discern the impact of the parameters investigated on the total concentration of oxygenated products. Oils examined include soybean, sunflower and palm.

RR4

New High Purity Dimer Fatty Acids and Their Application. K.D. Haasc, Unichema Chemie B.V., Buurtje 1, Gouda 2802 BE, The Netherlands.

The highest quality of industrial available dimer fatty acid still contains such a high proportion of mono- and trifunctional groups that polycondensates with high molecular weight cannot be produced. New developments allow the production of waterwhite, oxidation-stable dimer fatty acids with 99% difunctionality on industrial scale. Depending on the raw materials used, the reaction conditions as well as the purification steps, different ratios of isomers (aromatic, cycloaliphatic, aliphatic) can be achieved. These extremely pure dimer fatty acids allow the production of high molecular weight polyamides and polyesters with extreme flexibility, impact strength and hydrolytic resistance.

RR5

Results from the Danish Food Monitoring System for Nutrients with Special Emphasis on the Variation of Vitamin A in Milk and in the Fatty Acid Pattern of Herrings. Torben Leth, National Food Agency, Central Laboratory Division, 19, Morkhoj Bygade, Soborg DK-2860, Denmark.

A food monitoring system for nutrients has been established in Denmark in 1984 with the purpose of following the intake of nutrients in the Danish population, making it possible to detect and deal with any major changes. Each year a group of foods (fruit and vegetables, bread and cereals, dairy products, meat, fish) are analyzed for a long range of nutrients and proximate constituents. The first cycle has now been completed, and the second cycle starts in 1988 with fruit and vegetables making it possible to compare with the 4 year earlier investigation. Some interesting results have already been found for Vitamin A in dairy products, where a significant 10-20% variation between regions in Denmark can be demonstrated, and for the fatty acid pattern of herrings, which shows an enormous variation especially for C22:1, C20:1, C18:1 and C18:2 between herrings caught in the North Sea and in the Baltic Sea.

RR6

Causes of Turbidity in Canola Oil. J.K. Daun, Canadian Grain Commission, Grain Research Lab, 1404-303 Main Street, Winnipeg, MB R3C 3G8, Canada, and L.E. Jeffery, Canola Council of Canada.

Bottles of canola salad oil which had become cloudy during storage were filtered at four degrees Celsius to remove a high-melting point fraction (0.3% to 0.5% of oil) which was responsible for the turbidity. Thin layer chromatography showed that the fraction consisted mainly of triglyceride with lesser amounts of wax esters and polar material. Fatty acids in the triglyceride fraction were found to be mainly stearic (36%), oleic (24%) and palmitic (23%). Filtration of the cloudy oil at room temperature (ca. 20 C) resulted in a lower recovery of the sediment (0.1%) which was found to consist of triglyceride with somewhat more wax ester fraction. Oil filtered at room temperature became cloudy on refrigeration at 4 C. Gas chromatography showed the wax fraction to consist of esters with equivalent carbon numbers of 40 to 56.

RR7

The Effect of Dietary Linoleate on Energy Metabolism, Lipid Composition and Function of Liver Mitochondria.

Remi De Schrijver, University of Leuven, Kardinaal Mercierlaan 92, Leuven 3030, Belgium.

In 10 week-feeding experiments, rats (58-62g) were fed semi-synthetic diets containing 10% fat and different linoleic acid amounts, corresponding with 0%, 1.5%, 3%, 6% and 19% of the dietary metabolizable energy. The less efficient utilization of metabolizable energy by the linoleic acid-deficient animals was related to impaired coupling of oxidative phosphorylation in the liver mitochondria as measured in vitro. The major changes induced by the linoleic acid deficiency were the higher saturation of the total phospholipid fraction, the lower content of diphosphatidylglycerol, the lower linoleic acid content of diphosphatidylglycerol and the elevated cholesterol and free fatty acid levels in the liver mitochondria. With the diets providing 6 and 19% of the energy as linoleic acid, decreased weight gains and lower efficiencies of both food conversion and metabolizable energy utilization were observed. The rats fed the 19 energy % linoleic acid-diet showed significantly depressed ADP/O ratios and elevated activities of the respiratory enzymes in the liver. Mitochondrial lipid composition of the 19 energy % linoleate group was characterized by increased contents of free fatty acids and high linoleic acid levels of diphosphatidylglycerol. It could be hypothesized that inhibition of mitochondrial energy conversion might be related to elevated levels of free fatty acids (due to stimulated phospholipase A2 activity) and to exceeding critical concentrations of diphosphatidylglycerol and of its linoleic acid content.

RR8

The Influence of Different Dietary Sources of Gamma-Linolenic Acid (GLA) From Evening Primrose Oil, Blackcurrant Oil, Borage Oil and Fungal Oil on Free Fatty Acid Production by the Rat Mesenteric Vasculature. M.S. Manku, Efamol Research Institute, P.O. Box 818, Kentville, NS B4N 4H8, Canada, and D.K. Jenkins, J. Shay and D.F. Horrobin, Efamol Research Institute.

It is now widely known that there are four main sources of GLA: blackcurrant seed oil (14%GLA), primrose oil (9%GLA), borage oil (25%GLA) and fungal oil (14%GLA). Each of these oils has varying proportions of other fatty acids. Primrose oil is the richest in linoleic acid and is the most widely used dietary supplement in the world. We have shown in our previous studies that the rat mesenteric vascular bed continuously releases large amounts and varying proportions of prostaglandins (PGs) and free fatty acids (FFAs). We also demonstrated that the fatty acid composition of FFAs can be altered by changing the dietary ratios of n-6 and n-3 fatty acids. The aim of this investigation was to determine whether the outflow of FFAs in this preparation can be altered when the rats are fed oils containing GLA. Thirty Sprague-Dawley rats (150-200 g) were divided into 5 groups and fed for 5 weeks a fat-free semi-synthetic diet supplemented with equal amounts of GLA from each source. After 6 weeks the animals were anesthetized with ether, the superior mesenteric artery cannulated and perfused using buffer containing 1 mg/ml fatty acid free bovine serum albumin to trap the free fatty acid released in the effluent. The animals in the EPO group released the highest amounts of 20:3n-6 followed by borage, blackcurrant and fungal oil. Generally EPO was the most effective in releasing longer chain n-6 free fatty acids. A complete comparative data will be presented. These results suggest that the GLA in different forms is metabolized differently by the tissues. This may be due to different triglyceride configurations of each of the oils.

RR9

The Effects of Diet on the Triaglycerol Structure of Human Milk. Robert G. Jensen, University of Connecticut, Department of Nutritional Sciences, 3624 Horsebarn Road Ext., Storrs, CT 06268, and G.C. Del Savio, A.M. Ferris, C.J. Lammi-Keefe, T.R. Omara-Alwala and C. Stewart, University of Connecticut.

In order to determine the effects of diet on the triacylglycerol (TG) structure of human milk, mature milk samples were obtained from 3 women who were consuming mixed (M) diets; 4 lacto-ovo (LO) diets; and, 4 vegan (V) diets. Milk, milk products, and eggs were the only source of animal proteins in the LO regimens. There were no animal products in the V diets. The identity of the fatty acids in each of the TG positions was determined by stereospecific analysis. As the amount of animal products in the diets decreased (M > LO > V, data will be presented in this sequence) the quantities (M%) of 18:2 in milk TG increased (14.7, 26.5, 36.5) and 16:0 dropped (21.4, 17.2, 13.1). There were alterations in the TG structure, with 16:0 partially displaced by 18:2 as the predominant *sn*-2 ester; (61.2, 48.2, 40.5). Lauric acid was not detected at the *sn*-1 position, while 18:1 was lower (42.2, 39.0, 21.2) and 18:2 higher (12.5, 18.9, 20.1). At the *sn*-3 position, 12:0, 14:0 and 16:0 dropped, while 18:2 rose (22.6, 32.9, 48.2). These changes could influence intestinal absorption of the fatty acids because the efficient absorption of human milk TG has been attributed in part to the preponderance of 16:0 at the *sn*-2 position.

RR10

Comparative Study of Molecular Species of Glycerophospholipids (GPL) of Human Plasma and Erythrocytes. A. Kuksis, University of Toronto, Charles H. Best Institute, 112 College Street, Toronto, ONT M5G 1L6, Canada, and S. Pind and J.J. Myher, University of Toronto.

In addition to phosphatidylcholine (PC) human plasma also contains small amounts of other GPL, which may have special metabolic function. The structure and origin of these minor plasma lipids has not been determined. Knowledge of the detailed composition of the GPL of red cells permits evaluation of one of the possible sources. For this purpose lipid extracts of plasma and erythrocytes obtained from same blood were analyzed by HPLC and GLC as outlined by Myher, Pind and Kuksis. The proportions of the GPL classes in plasma and erythrocytes were similar to published values, including the essential absence of serine phosphatides from plasma. Plasma PC contained 93.6% diacyl, 5.2% alkylacyl and 2.6% alkenylacyl, while the phosphatidylethanolamine (PE) consisted of 68.5% alkenylacyl, 23.9% diacyl and 8.0% alkyl acyl subclasses. The inositol phosphatide was 100% diacyl. The content of the minor subclasses of plasma PC is similar to that of the red cells, but the ether content of PE is higher in plasma than in cells. The ether subclasses of plasma GPL also contain a higher proportion of the

C_{20}, C_{22} and C_{24} alkyl and alkenyl chains than those of the cells. Furthermore, the C_{16} and C_{18}-containing species in the PE subclasses vary with the nature of the polyunsaturated acid, while in PC subclasses the polyunsaturated acids are combined with the C_{16} and C_{18} acids in equal proportions. The striking differences in composition of molecular species of the minor GPL of plasma and red cells would appear to exclude any direct transfer or equilibration between them.

RR11

Preparative Chromatographic Isolation of Hydroxy Acids from *Lesquerella fendleri* and *L. gordonii* Seed Oils. K.D. Carlson, Northern Regional Research Center, USDA/ARS, 1815 North University Street, Peoria, IL 61604, and A. Chaudhry and R.E. Peterson, Northern Regional Research Center.

To conduct product development research on *Lesquerella* seed oils, we explored methods to obtain 100-g quantities of lesquerolic (14-hydroxy-*cis*-11-eicosenoic) acid. Open-column silica gel chromatography of *L. fendleri* oil gave 3 triglyceride (TG) fractions. The first (10%) contained non-hydroxy 16- (13%) and 18-carbon acids (65% 18:1,2,3). The second fraction (15%) contained monolesquerolins (39% lesquerolic acid). The major TG fraction (73%) was mainly dilesquerolins (66% lesquerolic acid). Thus, an hydroxy acid-enriched TG oil was obtained. Silica gel chromatography of *L. fendleri* fatty acid methyl esters (FAME) provided an hydroxy-free ester fraction (40-44%) that is an uncommon mix of unsaturated FAME (92%) consisting largely of 18:1 (39%), 18:2 (19%), and 18:3 (31%), and an hydroxy ester fraction (56-60%) that is largely lesquerolate (94%) with small amounts of auricolate (5%) (14-hydroxy-*cis*-11, *cis*-17-eicosadienoate) and traces of 18-carbon hydroxy esters. The process for isolating the hydroxy FAME of *L. gordonii* oil was scaled up 15 to 100 fold by high-performance preparative liquid chromatography, using 15 to 50 g of *L. gordonii* FAME and hexane/ethyl acetate eluants. Quantities of methyl lesquerolate were obtained with purities from 92-99%, the contaminants being methyl auricolate (1-3%) and methyl ricinoleate (t-3%).

RR12

Aflatoxin in Arizona Cottonseed: A Paired Study of Insect Damaged Bolls with Non-Damaged Bolls. Louise S. Lee, Southern Regional Research Center, USDA, ARS, P.O. Box 19687, New Orleans, LA 70179, and Peter J. Cotty, Southern Regional Research Center.

Insect damage, particularly by pink boll worm (PBW), is indirectly associated with aflatoxin contamination of cottonseed because reduction in toxin levels has been demonstrated with improved PBW control. The current study questioned: (a) What proportion of PBW damaged bolls typically become contaminated? (b) Is contamination localized in insect damaged locks or distributed throughout the boll? and (c) What proportion of bolls not damaged by PBW become contaminated? Carpel walls of fully open cotton bolls in the Yuma Valley in Arizona were randomly examined for PBW exit holes. Bolls with exit holes were harvested along with non-damaged bolls occurring at similar positions on the same plants. All bolls had at least one fully fluffed lock. Damaged and non-damaged locks of the bolls with exit holes were separated. Seeds from each of the three categories [non-damaged bolls (NDB), insect damaged locks (IDL) and non-damaged locks from insect damaged bolls (NDL/IDB)] were ginned and assayed for aflatoxin. Toxins were detected in 60% of IDL; toxin levels ranged from above 20000 ng/g to less than 20 ng/g. Trace amounts accurred in 8% of both NDB and NDL/IDB. These results indicate that, in this particular field, insect damage accounted for most of the aflatoxin contamination. The spread of *Aspergillus flavus* from insect damaged locks to non-damaged locks was slow and did not account for a substantial proportion of the contamination.

RR13

Aflatoxin in Arizona Cottonseed: The Nucellus as a Potential Barrier to Invasion of the Embryo by *Aspergillus flavus*. Louise S. Lee, Southern Regional Research Center, USDA, ARS, P.O. Box 19687, New Orleans, LA 70179, and Wilton R. Goynes and Peter J. Cotty, Southern Regional Research Center.

Aflatoxin in cottonseed results from invasion of cotton bolls by *Aspergillus flavus*. Toxin does not form on the lint or hulls; it forms only after the fungus penetrates

the embryo. Microscopic examination of sections of infected seed show fungal hyphae restricted within the chalazal cap above the highly nutritive endosperm. The endosperm is surrounded by the perisperm (nucellus). The nucellus appears as a contiguous thick envelope of spongy cells in immature seeds that dissipates as seeds mature. It is not known how fungal contamination affects this dissipation nor has the effect of this physical barrier on fungal growth and/or toxin formation been investigated. Bolls, 20 and 30 days post anthesis, on cotton plants grown in a controlled environment that simulated field conditions in Arizona were inoculated through natural injury sites in carpel walls. After 7 days, bolls were harvested at 2-day intervals until boll opening. Aflatoxin assays and electron microscopical examinations indicated: (1) a relationship of nucellus thickness and toxin formation; and (2) an effect of inoculation on seed maturation and nucellus shrinkage. This information will help define the seed maturation stages at which host defenses may occur; information that could be exploited to interrupt both *A. flavus* penetration and the resultant aflatoxin formation.

RR14

Composition of Human Adipose Tissue Lipids. Daniel P. Schwartz, Eastern Regional Research Center, USDA/ARS, 600 E. Mermaid Lane, Philadelphia, PA 19118.

In conjunction with a study of fat-soluble drug residues in the unsaponifiable matter of animal fats, human adipose tissue lipids obtained from the lower abdominal wall of a living subject were analyzed by conventional, improved and new methodology. The lipids were extracted from the tissue by homogenization in purified cyclohexane followed by centrifugation. The following classes and components were then quantitatively determined: total unsaponifiable matter and its content of cholesterol and squalene; total unesterified alcohols; the fatty acid, keto fatty acid, and hydroxy fatty acid composition of the glycerides; the individual unesterified fatty acids; the peroxide value. Appropriate experimental details and results of the analyses will be given.

RR15

Phospholipid Distribution and Headgroup Motion in Phosphatidylcholine Liposomes. A Phosphorus 31 NMR Study. Wolfgang J. Baumann, The Hormel Institute, University of Minnesota, 801 16th Avenue NE, Austin, MN 55912, and V.V. Kumar, The Hormel Institute.

Phosphatidylcholine liposomes of different size were prepared by sonication or extrusion. 1-Palmitoyl-2-oleoyl-*sn*-glycero-3-phosphocholine (0.15 mmol) was hydrated in 2.5 ml buffer (150 mM NaCl, 20 mM Tris or Hepes, pH 7.4, in D_2O). The dispersions were repeatedly frozen and thawed before passing through polycarbonate membranes (Lipex Biomembranes Extruder, 800 psi). The liposomes were characterized by freeze-fracture electron microscopy. Both sonication and extrusion through filters of up to 100 nm produced unilamellar vesicles. Vesicle diameter ranged from 22 × 3 nm for sonicated vesicles to 80 × 18 nm obtained by extrusion through 100-nm filters. With the smaller size filters (30 and 50 nm), the vesicles were somewhat larger than the respective pore size; with the larger filters (80 and 100 nm), the opposite was observed. Liposomes extruded through 200-nm filters also contained some multilamellar structures. Phosphorus-31 NMR (32.2 MHz) in the presence of Pr^{3+} (3mM) showed that the ratio of POPC in the outer versus the inner vesicle leaflet ($R_{o/i}$) decreased from 1.9 for 22-nm vesicles to 1.0 for 80-nm liposomes. Ion leakage did not occur. While 22-nm vesicles gave rise to a sharp phosphorus signal near 40 ppm ($\nu_{1/2}$ 8.5 Hz), half-height linewidth significantly increased with increasing vesicle size ($\nu_{1/2}$ 43 Hz for 80-nm liposomes). The decrease in observed T_2* values indicates a considerable decrease in headgroup motion, which can be attributed to a decrease in vesicle rotational motion due to an increase in vesicle size.

RR16

Prediction of Induction Period of Soybean Oil by Initial Peroxide Value. Ana Rauen-Miguel, Unicamp, Cx. Postal 6091, Campinas SP, Brasil, and Walter Esteves, Unicamp.

The induction period (IP) is an important parameter related with the oxidative stability of fats and oils. It can be measured by methods that use ambient temperatures or by accelerated tests at higher temperatures. The ambient methods are slow (weeks or months) and the high temperature ones normally require special equipment. These disadvantages limit the use of both types of methods in industries for quality control of fats and oils. The objective of this research was to determine the correlation existing between the initial peroxide value (PV) and the induction period (IP) for soybean oils, as determined by the Metrohm Rancimat 617. The induction period for 126 samples of refined soybean oil with the initial peroxide values between 0.27 and 46.78 was determined with the Rancimat under the following conditions: temperature = 110 C; air flow = 10L/h; sample weight = 2.5 g. Linear regression analysis showed an inverse correlation between PV (meq/kg) and IP (h) according to the equation: $1/IP = 0.00774PV + 0.158$ with $r = 0.984$ and standard error of 5%. The induction period for soybean oils would be estimated by this equation from a simple, inexpensive and rapid determination of peroxide value.

RR17

Acid Water Resource Recovery, an Environmental Treatment Alternative. Ralph S. Daniels, Daniels Fertilizer Company, 80 Old Faith Road, Shrewsbury, MA 01545.

The trend of environmental legislation is causing the disposition of acid water waste to become increasingly more difficult and costly. The Daniels Process, by converting this waste product into commercially viable fertilizer by-products, eliminates environmental compliance concerns while creating a low cost product of use. A zero discharge system, this process allows the refining of vegetable oils to become a closed loop agricultural process system.

RR18

Vacuum Bleaching Soybean Oil in the Laboratory: An Evaluation of the Variables Involved. S. Brophy, Oil-Dri Corporation, 520 N. Michigan Avenue, Chicago, IL 60611, and D.D. Brooks, Oil-Dri Corporation of America.

The bleaching process of soybean oil over the last 40

years has slowly evolved from atmospheric batch bleaching to continuous vacuum bleaching. This evolution in the plant has not been transposed to the laboratory. Currently, the only bleaching method officially recognized by the American Oil Chemists' Society is an atmospheric method. We therefore suggest a vacuum bleaching apparatus and have evaluated the many variables involved (such as time, temperature, warm up time, rpm's of the stirring mechanism and the volume of oil/clay slurry) to determine which would have the greatest effect on the final bleached oil. Color, chlorophyll concentrations, peroxide values and free fatty acid values were monitored to aid in our evaluations.

RR18a

A Comparative Evaluation of Bleaching Clay of Various PH for Color and Chlorophyll In Once Refined Soybean Oil. D.D. Brooks, Oil-Dri Corporation of America, 520 N. Michigan Avenue, Chicago, IL 60611, and S. Brophy and J. Stein, Oil-Dri Corporation of America.

Over the past 40 years, researchers have evaluated the adsorptive qualities of bleaching clays of various pH and have found that acid activated clays have a higher bleaching efficiency than neutral clays. We have developed a neutral bleaching clay which demonstrates unique bleaching efficiencies. Data presented represents a comparison of this unique neutral clay to acid activated clays at three levels of clay dosages (0.25, 0.5 and 1.0 %) in two once refined soybean oils. Data shows that this unique neutral clay has better color reduction than most of the clays evaluated and comparable chlorophyll reduction to the acid activated clays.

RR19

Solvent-Free Enzymatic Synthesis of Glycerides. Francoise Ergan, National Research Council Canada, Biotechnology Research Institute, 6100 Royalmount Avenue, Montreal Quebec H4P 2R2, Canada, and Michael Trani and Gerald André, National Research Council Canada.

The first objective and result of this work was to produce an immobilized lipase able to work toward the synthesis of mono-, di- and triglycerides. A glutaraldehyde crosslinked albumin matrix has been selected to immobilize the lipase. A new way of dehydrating gently the support has been devised in order to work in nonaqueous environment without damaging the enzyme. The enzyme support is dry, strong, cheap and easy to produce. It has been possible to use this support in pure nonmiscible substrates (oleic acid and glycerol) mixed in stroechiometric amounts, without adding any organic solvent. The lipases from *Candida cylindracea, Mucor miehei, Rhizopus arrhizus* and *Rhizopus delemar* have been successfully immobilized. The carrier has been reused in following cycles of two weeks each. Increased activity has been observed with the number of cycles up to the fourth cycle. Research is going on to improve the rate of the reaction and the yield of product formation.

RR20

Volatile Compounds Formed During Simulated Deep-Fat Frying of Rice Bran Oil. Lucy Sun Hwang, National Taiwan University, Graduate Inst. of Food Science & Tech., 59, Lane 144, Keelung Rd., Sec. 4, Taipei, Taiwan, Republic of China, and Shyong-En Tsai and Lung-Bin Hau, National Taiwan University, and George Huang and Chi-Tang Ho, Rutgers University.

Rice bran oil is one of the major edible oils produced in Taiwan. The objective of this study was to investigate the volatile decomposition products formed during deep-fat frying. Rice bran oil was heated at 190 C and a fixed amount of steam was bubbled through the oil at 30 min intervals. The volatiles were collected in cold traps, called smoke condensate. Both the smoke condensate and the volatiles dissolved in the fried oil were analyzed. The smoke condensate was separated into acidic and nonacidic fractions. Seventy-two compounds were identified in the nonacidic fraction including hydrocarbons, alcohols, aldehydes, ketones, furans, esters and alkyl benzenes. Eighteen compounds were identified in the acidic fraction. In the dissolved volatiles fourty-four compounds were identified including hydrocarbons, alcohols, aldehydes, ketones, esters, lactones, aromatics and furans . It was interesting to note that 2,4-dienals could undergo retro-aldolization to yield 2-enals and acetaldehyde during the simulated deep-fat frying condition.

RR21

Effect of Oral Contraceptive on Lipids during the Menstrual Cycle. Eric Sing, IIT Research Institute, % H.J. O'Neill, Ph.D., 10 West 35th Street, Chicago, IL 60616.

Oral contraception is widely used by young healthy menstruating women (ages 20-25) who expect their physicians to prescribe safe pills which will not harm their health. Blood samples are collected in EDTA after an overnight fast during the follicular, ovulatory, and luteal phases of the menstrual cycle with and without oral contraceptive (OVRAL). The analysis of lipid fractions during the menstrual cycle without contraceptive, reveal no significant differences in total plasma cholesterol levels in the three phases of the cycle. The total cholesterol is estimated after saponification. The total cholesterol valuues of the follicular, ovulatory and luteal phases are 4.53 + 0.12, 4.68 + 0.07 and 4.54 + 0.09 mmol/L without oral contraceptives, and 4.34 + 0.10, 4.40 + 0.08, 4.32 + 0.07 mmol/L respectively with contraceptives. Data are averages of 2 to 3 samples. The ovulatory phase (without contraceptive) is associated with slight elevations of total cholesterol and correlated with the elevation at estradiol and estrone in plasma. There is a reduction in plasma total cholesterol during oral contraceptive use, but it is not significant. It may be possible for significant reduction in total cholesterol, more potent-sex steroids are needed or some other pills. The heart attacks occur mainly in women with additional risk factors—increasing age, smoking, hypertension, diabetes, and high level of cholesterol. Oral contraceptive preparations have changed recently and breast tumors may develop more often in later life, when oral contraceptives are no longer used.

RR22

Quantitative Analysis of High Molecular Weight Ethoxylated Alcohols by Supercritical fluid Chromatography.

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Several references for the use of Supercritical Fluid Chromatography (SFC) to analyze ethoxylated alcohols have been published, but to our knowledge none discuss quantitative procedures. Using single isomer ethoxylate standards containing from one to eight ethylene oxide (EO) units per alcohol, we have been able to generate a response factor correlation for the SFC's flame ionization detector that enables us to extrapolate from ethoxylates with less than eight EO units to those with higher EO units. SFC separation of the ethoxylates is accomplished using a density programmed carbon dioxide mobile phase with a five meter methyl polysiloxane coated open tubular column at temperatures below 125 C. The validity and accuracy of this SFC analysis was demonstrated by comparing its results for % unreacted alcohol, average EO/alcohol ration, and weight of sample injected relative to an internal standard in both single isomer and mixed carbon number alcohol ethoxylates with values measured independently by standard methods. These methods include internal standard gas chromatography for weight percent unreacted alcohol and wet chemical hydroxyl number and NMR for average EO/alcohol determinations. In addition, SFC determined EO distributions are in excellent agreement with theoretical Weibull-Nycander distributions for these ethoxylates.

RR23

Guerbet Alcohol, a Versatile Hydrophobe. Joseph J. Fanelli, Alkaril Chemicals Inc., P.O. Box 1010, Winder, GA 30680.

Guerbet alcohols have been known since the 1890's when Marcel Guerbet first synthesized the compound. The reaction sequence that bears his name is essentially a combined aldol condensation followed by subsequent hydrogenation. This results in a high molecular weight branched saturated alcohol of essentially twice the molecular weight of the starting alcohol. Because of the unique structure of guerbet alcohols several advantages are immediately recognized, such as very low pour points, low volatility, lquid at ambient temperatures and good lubricating properties. Some of the areas of use involve suntan lotion components, anticracking agents for soap bars and superfatting shampoo additives. Since guerbet alcohols are primary alcohols, many types of derivatives can be synthesized as would be expected from primaryalcohols. These include ethoxylates, propoxylates, esters, sulfates, amphoterics and so forth. This presents a very interesting and unique set of surfactant and specialty chemicals. Guerbet esters have unique properties of combining excellent lubricating properties with desirable low pour point and fluidity characteristics and used in a variety of lubrication applications. Guerbet ethoxylated sulfates are used in shampoo applications where low irritation can be obtained with negligible effects on product viscosity. Guerbet ethoxylated esters have the combined properties of excellent lubrication along with water dispersibility or solubility depending on the molecule's HLB value. In summary, guerbet alcohols offer the potential benefits of high molecular weight, branching, liquidity and the ability to be used in derivatives as very hydrophobic raw materials. Additionally because both the hydrophobe as well as the type and amount of derivatization (example--ethoxylation) can be varied, an endless number of guerbet based products can be developed to meet today's ever-changing needs and challenges.

RR24

Dietary Fatty Acids, and More Particularly $\omega 3$ Polyunsaturated Fatty Acids, Have a Direct Influence on Cerebral Membranes, and Hence on Their Function. J.M. Bourre, INSERM U26, Hop. F. Widal, 200 rue du Fg Sain-Denis, Paris 75010, France, and M. Francois, C. Weidner, O. Dumont, M. Piciotti, G. Pascal and G. Durand, INSERM U26.

Rats were fed through generations with diet containing either sunflower (or peanut) or soya oil (or rapeseed). Feeding animals with oils that have a low $\omega 3$ acid content results in serious anomalies in the composition of brain membranes in all brain cells and organelles. Reduced amount of 22:6$\omega 3$ is compensated by increase in 22:5$\omega 6$. The speed at which it recuperates from these anomalies is extremely slow. Compared to other systems, the nervous system is not very protected against deficiency nor has it priority in the satisfaction of its needs. Essential fatty acids for the brain could be those with very long chains. They are probably synthesized in the liver from linolenic acids. They can also be supplied directly by food. During the period of cerebral development there is a linear relation between the w3 acid content of the brain and that of food until linolenic acid represents 150 mg per 100 g of food (for 1100 mg linoleic acid). Beyond that point there is a plateau in brain 22:6$\omega 3$, which is the same although the linolenic acid requirement increase with the dietary content of linoleic acid. A decrease in acids of the linolenic series in the membranes results in a 40% reduction of Na-K-ATPase in nerve terminals and a 20% reduction in 5'-nucleotidase. A diet low in linolenic acid leads to anomalies in the electroretinogram which partially disappear with age. The presence of linolenci acid in the diet confers a greater resistance to certain neurotoxic agents (triethyltin, for example). Deficiency in linolenic acid has little effect on motor activity, but it seriously affects learning tasks.