American Oil Chemist's Society

43rd

FALL MEETING

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PROGRAM

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OCTOBER 5-8, 1969

Leamington Hotel

Minneapolis, Minnesota

OPENING PLENARY SESSION, 43RD AOCS FALL MEETING
MINNEAPOLIS, MINNESOTA
MONDAY MORNING, OCTOBER 6, 1969

9:00 A.M.-12:00 Noon

Call to Order.....George C. Cavanaugh, A.O.C.S. President

Announcements and Greetings.....D. H. Wheeler, General Chairman, 43rd AOCS Fall Meeting

Welcome .....Office of Mayor, City of Minneapolis

Response .....G. C. Cavanaugh

Business Session
Vote on Revised By-Laws, Presented by Ron Stillman
Other Business

Address .....George Grange, Chairman, U.S. Delegation of the Codex Alimentarius Commission

Presentation of Honored Student Awards
Ralph Holman, Chairman
Honored Students Sub-Committee of Education Com.

Presentation of Bond Award .....G. Feldman

Presentation of Award of Merit .....J. Harris

Presentation of Award in Lipid Chemistry...Leo Goldblatt

Address by Lipid Chemistry Awardee

MONDAY AFTERNOON—OCTOBER 6

2:00 P.M.—Chicago Philadelphia New York Rooms

SESSION A—SYMPOSIUM: MARGARINE CENTENNIAL

Chairman—**Stanley C. Miksta,** National Dairy Products Corp., Chicago, Illinois

2:00 **WELCOME**
S. F. Riepma, President, National Association of Margarine Manufacturers

2:05 **KEYNOTE — "MARGARINE — 100 YEARS OF TECHNOLOGICAL AND LEGAL PROGRESS"**
Stanley C. Miksta, National Dairy Products Corp.

2:30 **1. THE DIET-HEART QUESTION OR THE DOCTOR'S DILEMMA**
Edward H. Ahrens, Jr., The Rockefeller University

3:00 **2. MARGARINE FLAVORS OF THE FUTURE**
E. A. Day, International Flavors and Fragrances

3:30 **INTERMISSION**

3:40 **3. FUTURE CONSIDERATIONS IN MARGARINE FORTIFICATION**
B. Borenstein, R. H. Bunnell and G. W. Schutt, Hoffman-La Roche, Inc.

4:10 **4. PROBLEMS AND OUTLOOK IN EVOLVING FOOD REGULATION**
George M. Burditt, Chicago

MONDAY AFTERNOON—OCTOBER 6

2:00 P.M.—Lincoln Room

SESSION B-1—SYMPOSIUM: THE OCCURRENCE, METABOLISM AND BIOSYNTHESIS OF ETHER-LINKED NEUTRAL GLYCERIDES AND PHOSPHOGLYCERIDES

Chairman—**Randall Wood,** Oak Ridge Associated Universities, Oak Ridge, Tennessee

2:00 **INTRODUCTORY REMARKS**
Randall Wood, Oak Ridge Associated Universities

2:05 **5. THE CHEMICAL SYNTHESIS OF PLASMALOGENS**
Jill Gigg and Roy Gigg, National Institute for Medical Research, London, England

2:45 **6. RECENT STUDIES ON NEUTRAL ALKOXYLIPIDS**
F. Spencer, W. J. Baumann, H. H. O. Schmid and H. K. Mangold, The Hormel Institute

3:30 **INTERMISSION**

3:45 **7. INTER-RELATIONSHIPS OF GLYCEROL ETHERS**
M. L. Karnovsky and J. Ellingboe, Harvard Medical School

4:30 **8. THE METABOLISM OF ALKYL AND ALKENYL IN THE DOGFISH (Squalus acanthias)**
Donald C. Malins, Bureau of Commercial Fisheries

MONDAY AFTERNOON—OCTOBER 6

2:00 P.M.—Twin Cities Room

SESSION C—SURFACTANTS

Chairman—**Edmund N. Harvey, Jr.,** Inmont Corp., Clifton, New Jersey

2:00 **9. FOAMS AND FOAM INHIBITION**
T. F. O'Farrell, Drew Chemical Corp.

2:20 **10. HIGHER ALKYL POLYGLUCOSIDES**
Francis A. Hughes and Baak W. Lew, Atlas Chemical Ind.

2:40 **11. REDUCTION OF PHOSPHATE BUILDER IN TALLOW-BASED DETERGENT FORMULATIONS**
R. G. Bistline, Jr. and A. J. Stirton, Eastern Regional Research Lab.

3:00 **12. A SIMPLE AND RAPID SCREENING TECHNIQUE FOR DETERGENT EVALUATION**
P. N. Ramachandran and S. M. Barkin, Colgate-Palmolive Co.

3:20 **13. METHODS OF EVALUATING HARD SURFACE CLEANERS**
Theodore L. Treitler, FMC Corp.

3:40 **14. SYNTHESIS AND PROPERTIES OF SULFATED ALKANOLAMIDES**
J. K. Weil, N. Parris and A. J. Stirton, Eastern Regional Research Lab.

4:00 **15. SULFATION OF SYNTHETIC LINEAR PRIMARY ALCOHOLS WITH CHLOROSULFONIC ACID**
Paul Sosis and Leo J. Dringoli, Continental Oil Co.

4:20 **16. MEASUREMENT AND ASSESSMENT OF THE WHITENESS OF SPECIMENS TREATED WITH FLUORESCENT WHITENING AGENTS**
G. Anders and C. Daul, Ciba Corp., Basel, Switzerland

MONDAY AFTERNOON—OCTOBER 6

2:00 P.M.—Cleveland Detroit Milwaukee Rooms

SESSION D—SYMPOSIUM: BIOSYNTHESIS OF BRANCHED CHAIN FATTY ACIDS

Chairman—**Robert G. Ackman,** Fisheries Research Board of Canada, Halifax, Nova Scotia, Canada

2:00 **17. BIOSYNTHESIS OF BRANCHED CHAIN FATTY ACIDS**
Toshi Kaneda, Research Council of Alberta

2:30 **18. FATTY ACID COMPOSITION OF Listeria Monocytogenes**
K. K. Carroll, R. A. Tadayon and N. Kosaric, University of Western Ontario

3:00 **19. THE OCCURRENCE OF BRANCHED CHAIN FATTY ACIDS IN FUNGI**
David Tyrrell, Insect. Pathology Research Institute, Saulte Ste. Marie, Canada

3:30 **20. RUMEN MICROORGANISMS AND THEIR RELATION TO RUMINANT FATS**
Mark Keeney, University of Maryland

4:00 **21. THE BIOCHEMISTRY OF BRANCHED CHAIN FATTY ACIDS AND RELATED HYDROCARBONS**
Max Blumer, Woods Hole Oceanographic Institution

4:30 **22. BRANCHED CHAIN FATTY ACIDS IN TRIGLYCERIDES OF THE BELUGA (WHITE) WHALE**
R. G. Ackman and Carter Litchfield, Fisheries Research Board of Canada

MONDAY AFTERNOON—OCTOBER 6

2:00 P.M.—Taft Room

SESSION E—LIPID COMPONENTS AND COMPOSITIONS

Chairman—**Clarence G. Youngs,** National Research Council of Canada, Saskatoon, Saskatchewan

2:00 **23. UNUSUAL LIPIDS IN THE SEBACEOUS GLANDS OF RODENTS**
F. Spencer, H. K. Mangold, G. Sansone and J. G. Hamilton, Harbor General Hospital

2:20 **24. SOME MINOR LIPID CONSTITUENTS OF Brassica Oleracea LEAVES**
H. H. O. Schmid and P. C. Bandi, The Hormel Institute

2:40 **25. NEW NATURALLY OCCURRING LIPIDS: DIALKYL ETHER DERIVATIVES OF DIOLS FROM THE PORPOISE (Phocaena phocaena)**
Usha Varanasi and Donald C. Malins, Bureau of Commercial Fisheries

3:00 **26. CHARACTERIZATION OF THE SEX ODOR COMPONENTS IN PORCINE ADIPOSE TISSUE**
Kenneth E. Beery, John D. Sink, Stuart Patton and John H. Ziegler, Pennsylvania State University

3:20 **27. UNUSUAL FATTY ACIDS AND GLYCERIDES FROM Monnina Emarginata SEED OIL**
B. E. Phillips, C. R. Smith, Jr. and L. W. Tjarks, Northern Regional Research Lab.

3:40 **28. FATTY ACID PATTERNS IN TRIGLYCERIDES OF CORN (Zea mays L.)**
Ian A. de la Roche, Evelyn J. Weber and D. E. Alexander, University of Illinois

4:00 **29. STEROLS IN RICE BRAN OIL**
M. A. M. Kamal, S. I. El-Hinnawy and N. S. Erian, Ain Shams University, Cairo, U.A.R.

4:30 **30. FRACTIONATION OF RICE BRAN WAXES**
M. A. M. Kamal, S. I. El-Hinnawy and N. S. Erian, Ain Shams University, Cairo, U.A.R.

MONDAY AFTERNOON—OCTOBER 6

2:00 P.M.—Jefferson Room

SESSION F—ANALYTICAL AIDS TO PROCESSING

Chairman—**Gerald G. Wilson,** General Mills, Inc., Minneapolis, Minnesota

2:00 **31. NITROGEN DETERMINATION FOR RAPID QUALITY CONTROL OF OILSEED MEALS**
R. M. McCready, G. Fuller and Mona Gauger, Western Regional Research Lab.

2:20 **32. PRETREATING DELINTERED COTTONSEED TO INCREASE YIELD OF WHOLE KERNELS**
J. T. Lawhon, Oilseed Products Research Center

2:40 **33. ANALYSIS OF RESIDUAL SOLVENT IN OILSEED MARC EXTRACTED WITH AQUEOUS MIXED SOLVENTS**
William H. King, Southern Regional Research Lab.

3:00 **34. A WATER RECYCLE METHOD FOR WASHING ALKALI-REFINED SOYBEAN OIL**
R. A. Eisenhauer, R. E. Beal and E. L. Griffin, Jr., Northern Regional Research Lab.

3:20 **35. DETERMINATION OF RESIDUAL SOLVENT IN OILSEED MEALS AND FLOURS: II. VOLATILIZATION PROCEDURE**
H. P. Dupuy and Sara P. Fore, Southern Regional Research Lab.

TUESDAY MORNING—OCTOBER 7

9:00 A.M.—Chicago Philadelphia New York Rooms

SESSION G-1—SYMPOSIUM: WIDE-LINE NUCLEAR MAGNETIC RESONANCE (NMR)

Chairman—**W. A. Bosin,** Pillsbury Co., Minneapolis, Minn.

9:00 **INTRODUCTORY REMARKS**

9:05 **36. AN INTRODUCTION TO NUCLEAR MAGNETIC RESONANCE**
Warren G. Proctor, Varian Associates

9:30 **37. THE USE OF LOW RESOLUTION NMR FOR THE RAPID DETERMINATION OF SOLIDS CONTENT OF FAT BLENDS**
P. B. Mansfield, Newport Instruments Ltd., Buckinghamshire, England

9:55 **38. APPLICATIONS OF THE PAT-20, VARIAN'S NEW PROCESS ANALYZER**
Lars Olov Andersson, Varian Associates

10:20 **39. SOLID-LIQUID RATIO IN FATS**
A. J. Haighton, Unilever Research Lab., Vlaardingen, The Netherlands

10:45 **40. COMPARISON OF SFI, DSC AND NMR METHODS FOR DETERMINING SOLID-LIQUID RATIOS IN FATS**
R. C. Walker and W. A. Bosin, Anderson Clayton Foods

11:10 **41. DETERMINATION OF OIL IN AQUEOUS EMULSIONS BY WIDE-LINE NMR**
Sudhakar Shanbhag M. P. Steinberg and A. I. Nelson, University of Illinois

11:35 **42. A WIDE-LINE NMR R-F SATURATION METHOD TO MEASURE FAT IN MOIST SAMPLES OF DEFATTED CORN GERM**
Thomas F. Conway, GPC International

TUESDAY MORNING—OCTOBER 7

9:00 A.M.—Lincoln Room

SESSION B-2—SYMPOSIUM: THE OCCURRENCE, METABOLISM AND BIOSYNTHESIS OF ETHER-LINKED NEUTRAL GLYCERIDES AND PHOSPHOGLYCERIDES

Chairman—**Gordon B. Ansell,** The Medical School, Birmingham, England

9:00 **43. PLASMALOGEN METABOLISM IN THE BRAIN**
Gordon B. Ansell, R. F. Metcalfe and Sheila Spanner, Department of Experimental Neuropharmacology, The Medical School, Birmingham, England

9:45 **44. ON THE BIOSYNTHESIS OF ETHANOLAMINE PLASMALOGENS OF BRAIN DURING MYELINATION**
Hildegard Debuch, Alfred Etzrodt, Harald Friedeman and Jochen Muller, Physiological Chemistry Institute, Univ. of Cologne, Germany

10:30 **INTERMISSION**

10:45 **45. MAMMALIAN BRAIN ALK-1-ENYL ACYL AND ALKYL ACYL GLYCEROPHOSPHORYL ETHANOLAMINES (GPE)**
Lloyd A. Horrocks, Ohio State University

11:30 **46. INFLUENCE OF ETHER GROUPINGS ON PHOSPHOLIPID REACTIVITIES**
William E. M. Lands, Univ. of Michigan Medical School

TUESDAY MORNING—OCTOBER 7

9:00 A.M.—Twin Cities Room

SESSION H-1—SYMPOSIUM: SOLVENT EXTRACTION TECHNIQUES FOR SOYBEAN AND OTHER SEEDS

Chairman—**N. H. Witte,** Central Soya Co., Fort Wayne, Indiana

9:30 **47. MOISTURE EXTRACTION FROM SOYBEANS: CONCEPTS, DESIGN AND PRACTICE**
Julian W. Bunn, Jr., Aeroglide Corp.

9:55 **48. METHODS OF REMOVING HULLS FROM SOYBEANS AND THE EFFECT OF CRACKING ON HULL REMOVAL**
N. Hunt Moore, N. Hunt Moore and Associates

10:20 **49. FLAKING AND CONDITIONING OF SOYBEANS**
Ernie Micek, Cargill, Inc.

10:45 **INTERMISSION**

11:00 **50. EXTRACTION**
Gene C. Mason, Arkansas Grain Corp.

11:25 **51. DESOLVENTIZING AND TOASTING**
C. Louis Kingsbaker, Blaw-Knox Co.

11:50 **52. DISTILLATION AND SOLVENT RECOVERY FOR SOYBEAN AND OTHER OILSEEDS PLANTS**
Kenneth W. Becker, Blaw-Knox Co.

TUESDAY MORNING—OCTOBER 7

8:45 A.M.—Cleveland Detroit Milwaukee Room

SESSION I—SYMPOSIUM: TALL OIL

Chairman—**Jacob P. Krumbein,** Tenneco Chem., Inc., Pensacola, Florida

8:45 **53. TALL OIL: PAST, PRESENT AND FUTURE**
Ralph H. Potts, Armour Industrial Chemical Co.

9:05 **54. A CHROMATOGRAPHIC STUDY OF THE FATTY ACIDS FOUND IN CRUDE TALL OIL**
W. M. Hargrove, D. M. Nall and R. W. Johnson, Union Camp Corp.

9:25 **55. DISTILLATION OF CRUDE TALL OIL**
D. F. Bress, Foster Wheeler Corp.

10:05 **56. SHORT-TIME THIN FILM PROCESSING OF HEAT SENSITIVE ORGANICS**
James Donovan and Francis C. Brown, Artisan Industries, Inc.

10:25 **57. ECKEY HORIZONTAL FRACTIONATOR**
L. W. Nisbet, Jr., Vulcan Manufacturing Co.

10:45 **58. PERFORMANCE OF ALLOYS IN TALL OIL DISTILLATION SERVICE**
Harold C. Templeton, Walworth-Aloyco Div., Walworth Co.

11:05 **59. ETHYLENE AND PROPYLENE OXIDE ADDUCTS OF A NUMBER OF HYDROXYLATED TALL OIL FATTY ACIDS**
S. T. Bauer and T. L. Crosby, Crosby Chemicals, Inc.

11:25 **60. REACTION OF ETHYLENIMINE WITH FATTY ACIDS AND FATTY AMINES**
A. M. DeRoo, The Dow Chemical Co.

11:45 **61. POSSIBLE APPLICATIONS OF TALL OIL ACIDS REACTED WITH ETHYLENIMINE**
J. D. Camisa, Dow Chemical Co.

12:05 **62. TALL OIL PRECURSORS: APPROACHES TO THE ANALYSIS OF PINE WOOD EXTRACTIVES**
Duane F. Zinkel, U.S. Forest Products Laboratory

TUESDAY MORNING—OCTOBER 7

9:00 A.M.—Taft Room

SESSION J—SYMPOSIUM: STATISTICAL APPLICATIONS

Chairman—**Horace P. Andrews,** Rutgers University, New Brunswick, New Jersey

9:00 **63. HUMAN ERYTHROCYTE MEMBRANE AND PLASMA LIPID VARIATION, AN EXAMPLE OF STATISTICAL ANALYSIS OF COMPLEX LIPID MIXTURES IN TWO PHASES**
Joe C. Christian, Pao-Lo Yu, Ke Won Kang and James A. Norton, Indiana Univ. School of Medicine

9:30 **64. TECHNIQUES FOR THE ANALYSIS OF RESPONSE CURVE DATA**
Ronald D. Snee, E. I. du Pont de Nemours and Co.

10:00 **65. CHECK SAMPLE DATA ANALYSIS AND RANKING OF LABORATORIES**
Edwin M. Glocker, W. R. Grace and Co.

10:30 **66. DESIGNS FOR EXPERIMENTS TO STUDY FORMULATION AND PROCESSING VARIABLES SIMULTANEOUSLY AND EFFICIENTLY**
Horace P. Andrews and Jane C. Li, Rutgers University

TUESDAY MORNING—OCTOBER 7

9:00 A.M.—Jefferson Room

SESSION K—BIOCHEMISTRY AND NUTRITION

Chairman—**Forrest W. Quackenbush,** Purdue University, Lafayette, Indiana

9:00 **67. ESSENTIAL FATTY ACID NUTRITION—AN INTERACTION WITH DIELDRIN**
Ian J. Tinsley and Robert R. Lowry, Oregon State University

9:20 **68. EFFECT OF BOUND GOSSYPOL ON ENZYMATIC RELEASE OF FREE AMINO ACIDS AND PEPTIDES**
Carl M. Cater and Carl M. Lyman (deceased), Texas A & M University

9:40 **69. INCORPORATION OF 1-^{14}C-PALMITIC ACID BY THE ADULT RAT BRAIN**
G. A. Dhopeshwarkar and James F. Mead, Lab. of Nuclear Medicine and Radiation Biology

10:00 **70. EFFECT OF PRENATAL AND EARLY POSTNATAL DIETS CONTAINING CYCLOPROPENE FATTY ACIDS ON THE DEVELOPMENT OF THE STEAROYL DESATURASE IN RAT LIVER**
Nadine N. Sumpter, P. K. Raju and Raymond Reiser, Texas A & M University

10:20 **71. MUCOSAL LIPID VARIATIONS AFTER FEEDING DOUBLY LABELED TRIOLEIN AND TRILINOLEIN**
Margaret G. Morehouse, Phyllis Haines and Judy Schmidt, University of Southern California

10:40 **72. EFFECT OF HIGH AND LOW LEVELS OF DIETARY LINOLEATE ON THE FATTY ACID COMPOSITION OF PHOSPHOLIPIDS IN RAT TISSUES**
R. R. del Rosario, Agnes Wong and L. R. Dugan, Jr., Food Science Dept., Michigan State University

11:00 **73. NUTRITIONAL PROPERTIES OF FATS: THEIR INDIVIDUALITY**
Hans Kaunitz, Ruth E. Johnson and Lewis Pegus, Columbia University

11:20 **74. COCONUT AND SOYBEAN OILS IN MILK SUBSTITUTES FED TO MONKEYS**
Hans Kaunitz and Jaime Sanyer, Columbia University

TUESDAY AFTERNOON—OCTOBER 7

2:00 P.M.—Chicago Philadelphia New York Rooms

SESSION G-2—SYMPOSIUM: WIDE-LINE NUCLEAR MAGNETIC RESONANCE (NMR)

Chairman—**T. F. Conway,** CPC International, Inc., Argo, Illinois

2:00 **75. WIDE-LINE NMR FOR PRODUCT AND PROCESS CONTROL IN FAT INDUSTRIES**
Rune Wetterström, AB Karlshamns Oljefabriker, Karlshamns, Sweden

2:25 **76. PROCESS CONTROL APPLICATION OF WIDE-LINE NMR IN A CORN WET MILLING PLANT**
Joseph A. Palmer, Corn Industrial, Division of CPC International, Inc.

2:50 **77. ON-STREAM NMR MEASUREMENTS AND CONTROL**
William L. Rollwitz and Gilbert A. Persyn, Southwest Research Institute.

3:15 **78. TRANSIENT NMR QUANTITATIVE MEASUREMENTS**
Gilbert A. Persyn and William L. Rollwitz, Southwest Research Institute

3:40 **79. APPLICATION OF WIDE-LINE NMR SPECTROSCOPY TO PLANT BREEDING**
D. E. Alexander, University of Illinois

4:05 **80. NMR METHOD FOR RAPID NONDESTRUCTIVE OIL CONTENT DETERMINATION IN SEEDS**
R. Blinc, V. Erzen, J. Porok, S. Vrscaj, I. Zupancic and J. Dumanovic, Institute "J. Stefan," Ljubljana, Yugoslavia

4:30 **DISCUSSION**

TUESDAY AFTERNOON—OCTOBER 7

2:00 P.M.—Lincoln Room

SESSION B-3—SYMPOSIUM: THE OCCURRENCE, METABOLISM AND BIOSYNTHESIS OF ETHER-LINKED NEUTRAL GLYCERIDES AND PHOSPHOGLYCERIDES

Chairman—**Guy A. Thompson, Jr.,** University of Texas, Austin, Texas

2:00 **81. THE BIOSYNTHESIS OF GLYCERYL ETHERS BY CELL-FREE PREPARATION OF *Tetrahymena pyriformis***
Guy A. Thompson, Jr. and Vassilios M. Kapoulas, University of Texas

2:45 **82. SYNTHESIS OF GLYCERYL ETHERS IN A CELL-FREE SYSTEM FROM *Tetrahymena Pyriformis***
Samuel J. Friedberg and Ronald C. Greene, University of Texas Medical School

3:30 **INTERMISSION**

3:45 **83. STRUCTURE AND BIOSYNTHESIS OF PHYTANYL GLYCEROL ETHER CONTAINING LIPIDS IN EXTREMELY HALOPHILIC BACTERIA**
M. Kates, E. L. Pugh and M. K. Wassef, University of Ottawa, Canada

4:30 **84. PLASMALOGENS IN BACTERIA**
Howard Goldfine, University of Pennsylvania

TUESDAY AFTERNOON—OCTOBER 7

1:45 P.M.—Twin Cities Room

SESSION H-2—SYMPOSIUM: SOLVENT EXTRACTION TECHNIQUES FOR SOYBEAN AND OTHER SEEDS

Chairman—**C. Louis Kingbaker, Jr.,** Blaw-Knox Co., Pittsburgh, Pennsylvania

1:45 **85. THE ART OF OIL-SEED MEAL GRINDING**
George R. Thomas, Prater Pulverizer Co.

210 **86. SCREENING AND TAIL END DEHULLING**
J. F. Sullivan, Triple/S Dynamics

2:35 **87. DUST CONTROL**
C. R. Rockwell, Carter Day Co.

3:00 **88. SUNFLOWER PROCESSING TECHNIQUES**
Robert M. Pierce, Minnesota Linseed Oil Co.

3:25 **DISCUSSION**

TUESDAY AFTERNOON—OCTOBER 7

2:00 P.M.—Cleveland Detroit Milwaukee Rooms

SESSION L: PHOSPHOLIPIDS

Chairman—**Robert M. Burton,** Washington University School of Medicine, St. Louis, Missouri

2:00 **89. THE USE OF COUNTER-CURRENT DISTRIBUTION IN THE SEPARATION OF INDIVIDUAL MOLECULAR SPECIES OF PHOSPHOLIPIDS**
F. D. Collins and M. A. Trewhella, University of Melbourne, Victoria, Australia

2:20 **90. REACTION THIN LAYER CHROMATOGRAPHY IN THE ISOLATION AND CHARACTERIZATION OF SPHINGOLIPIDS**
C. V. Viswanathan, F. Phillips and W. O. Lundberg, The Hormel Institute

2:40 **91. PREPARATION AND CHARACTERIZATION OF MURINE PHOSPHOLIPASE**
Athos Ottolenghi, Duke University Medical Center

3:00 **92. PLATELET LIPIDS**
C. V. Viswanathan, F. Phillips, W. O. Lundberg, C. A. Owens, H. F. Taswell and E. J. W. Bowie, The Hormel Institute

3:20 **93. LIPID COMPOSITION OF BEEF AND HUMAN PITUITARY GLANDS**
H. Singh and K. K. Carroll, University of Western Ontario, London, Canada

3:40 **94. THE PHOSPHOLIPIDS OF MATURE BOVINE AND RABBIT RETINA**
Robert E. Anderson and Gerald L. Feldman, Baylor Medical College

4:00 **95. LIPID BROWNING REACTION: I. REACTION OF SATURATED ALDEHYDES WITH PHOSPHOLIPIDS**
G. Venkateswara Rao and L. R. Dugan, Jr., Michigan State University

4:20 **96. PHOSPHATIDES OF Chlamydia Psittaci, STRAINS MENINGOPNEUMONITIS AND 6BC**
H. M. Jenkin, Thomas Gerson, DeWayne Townsend and Robert Leif, The Hormel Institute

TUESDAY AFTERNOON—OCTOBER 7

2:00 P.M.—Taft Room

SESSION M—CHEMICAL REACTIONS

Chairman—**Glen Lichtenwalter,** Armour and Co.

2:00 **97. AN ADDITION COMPOUND OF TOCOPHEROL AND LINOLEIC ACID**
W. L. Porter, L. A. Levasseur and A. S. Henick, U.S. Army Natick Laboratories

2:20 **98. CYCLIZATION OF UNSATURATED FATTY ACIDS**
Harry Scharmann, Unilever Forschungslaboratorium, Hamburg, Germany

2:40 **99. CHEMICAL REACTIONS OF TRIOLEIN UNDER SIMULATED DEEP FAT FRYING CONDITIONS**
M. M. Paulose, Jan Pokorny and S. S. Chang, Rutgers University

3:00 **100. CONJUGATED NONADIENES FROM PYROLYSIS OF UNSATURATED ACETATES**
G. R. List, C. D. Evans, E. Selke and C. A. Glass, Northern Regional Research Lab.

320. **101. KINETIC STUDY OF ACID CATALYZED CONVERSION OF AFLATOXINS B_1 AND G_1 TO B_{2a} AND G_{2a}**
Walter A. Pons, Jr., Alva F. Cucullu, Louise S. Lee, Hermann J. Janssen and Leo A. Goldblatt, Southern Regional Research Lab.

3:40 **102. MRA MICROREACTIONS FOR LIPID ANALYSIS**
E. D. Bitner, Alan C. Lanser and H. J. Dutton, Northern Regional Research Lab.

TUESDAY AFTERNOON—OCTOBER 7

2:00 P.M.—Jefferson Room

SESSION N—BIOSYNTHESIS

Chairman—**Jacques R. Chipault,** The Hormel Institute, Austin, Minnesota

2:00 **103. THE BIOSYNTHESIS OF PLASMALOGENS IN MAMMALIAN TISSUES**
H. H. O. Schmid and T. Takahashi, The Hormel Institute

2:20 **104. BIOSYNTHESIS OF PHOSPHATIDATE AND NEUTRAL GLYCERIDES FROM TRIOSE PHOSPHATES BY RAT LIVER MICROSOMES**
Larry E. Puleo, G. Ananda Rao, M. F. Sorrels and Raymond Reiser, Texas A & M University

2:40 **105. THE NONCONVERSION OF 5,11,14-20:3 INTO 5,8,11,14-20:4**
H. Schlenk, J. Gellerman and D. Sand, The Hormel Institute

3:00 **106. BIOSYNTHESIS OF STEROLS AND STEROL ESTERS**
Ann M. Dnistrian and R. Cecil Jack, St. John's University

3:20 **107. BIOLOGICAL REDUCTION OF FATTY ACIDS TO ALCOHOLS IN FISH**
Donald M. Sand and Hermann Schlenk, The Hormel Institute

3:40 **108. THE TOTAL SYNTHESIS OF PHOSPHATIDES CONTAINING ACETYLENIC ACIDS AND THEIR ACTIVITY IN BLOOD CLOTTING**
D. L. Turner, M. J. Silver, R. R. Holburn, E. Baczynski, S. F. Herb and F. E. Luddy, Jefferson Medical College

4:00 **109. THE BIOSYNTHESIS OF ALKYL GLYCERYL ETHERS BY A MICROSOMAL ENZYME SYSTEM FROM EHRLICH ASCITES CELLS: KINETIC AND STRUCTURAL STUDIES**
Robert L. Wykle and Fred Snyder, Oak Ridge Associated Universities

WEDNESDAY MORNING—OCTOBER 8

9:00 A.M.—Chicago Philadelphia New York Rooms

SESSION O-1—SYMPOSIUM: ROLE OF COMPUTERS IN CHEMISTRY

Chairman—**Royden O. Butterfield,** Northern Regional Research Laboratory, Peoria, Illinois

9:00 **110. QUANTITATIVE MEASURE OF GEOMETRICAL ISOMERIZATION DURING THE PARTIAL HYDROGENATION OF TRIGLYCERIDE OILS**
Lyle F. Albright, R. R. Allen and M. C. Moore, Purdue University

9:30 **111. COMPUTER TREATMENT OF SPECIFIC HEAT DATA DETERMINED BY DIFFERENTIAL SCANNING CALORIMETRY**
H. L. Rothbart, J. W. Hampson, R. A. Barford and V. G. Martin, Eastern Regional Research Lab.

10:00 **112. GE TIME-SHARING—A VERSATILE TOOL FOR COMPUTER ANALYSIS OF ANALYTICAL CHEMISTRY DATA**
Max Tochner, General Electric Co.

10:30 **113. THE APPLICATION OF COMPUTER TECHNIQUES AND PHASE EQUILIBRIA DATA TO LIQUID-LIQUID EXTRACTION**
V. G. Martin, R. A. Barford, H. L. Rothbart and

C. R. Eddy, Eastern Regional Research Laboratory

11:00 114. **A COMPUTER PROGRAM FOR RATING THE PERFORMANCE OF LABORATORIES IN ANALYTICAL CHECK SAMPLES**
Carl W. Fritsch, General Mills, Inc.

WEDNESDAY MORNING—OCTOBER 8

9:00 A.M.—Lincoln Room

SESSION B-4—SYMPOSIUM: THE OCCURRENCE, METABOLISM AND BIOSYNTHESIS OF ETHER-LINKED NEUTRAL GLYCERIDES AND PHOSPHOGLYCERIDES

Chairman—**M. L. Karnovsky,** Harvard Medical School

9:00 115. **ENZYMIC PATHWAYS FOR THE BIOSYNTHESIS AND BIOCLEAVAGE OF ALKYL GLYCERYL ETHERS**
Fred Snyder, Oak Ridge Associated Universities

9:45 116. **METABOLIC RELATIONS DERIVED FROM STRUCTURAL ANALYSES OF NEUTRAL GLYCERIDES AND PHOSPHOGLYCERIDES**
Randall Wood and R. D. Harlow, Oak Ridge Associated Universities

10:30 **DISCUSSION**

WEDNESDAY MORNING—OCTOBER 8

9:00 A.M.—Twin Cities Room

SESSION P—ANALYTICAL SEPARATIONS

Chairman—**Lincoln D. Metcalfe,** Armor Industrial Chemical Co., McCook, Illinois

9:00 117. **DETERMINATION OF BROMINATED VEGETABLE OILS IN SOFT DRINKS BY GLC**
H. B. S. Conacher and M. R. Sahasrabudhe, Food and Drug Directorate, Ottawa, Canada

9:20 118. **HOW GOOD ARE ANALYSES OF OILS BY GLC?**
S. F. Herb and V. G. Martin, Eastern Regional Research Lab.

9:40 119. **THE ANALYSIS OF 1-EPOXY OLEFINS BY GAS LIQUID CHROMATOGRAPHY**
Clifford R. Glowacki, Peter J. Menardi and William E. Link, Ashland Chemical Co.

10:00 120. **AN AUTOMATIC SYSTEM FOR THE PURIFICATION OF LIPID EXTRACTS**
Gary J. Nelson, Lawrence Radiation Laboratory

10:20 121. **SIMULTANEOUS MULTIPLE AUTOMATED DETERMINATION OF THE ISOMER DISTRIBUTION OF POLYBROMINATED SALICYLANILIDES**
Neil P. Loeb, Lever Brothers Co.

10:40 122. **A MICRO OZONE GENERATOR AND ITS APPLICATION IN A NEW MICRO METHOD OF OZONOLYSIS FOR THE DETERMINATION OF THE STRUCTURE OF UNSATURATED FATTY ACIDS**
E. Christense Nickell and O. S. Privett, The Hormel Institute

WEDNESDAY MORNING—OCTOBER 8

9:00 A.M.—Cleveland Detroit Milwaukee Rooms

SESSION Q-1—SYMPOSIUM: BIOSYNTHESIS OF UNSATURATED AND OXYGENATED FATTY ACIDS

Chairman—**Lindsay J. Morris,** Unilever Research Laboratory, Sharnbrook, Bedford, England
Co-chairman—**Ralph T. Holman,** The Hormel Institute, Austin, Minnesota

9:00 123. **MODULATION OF END PRODUCTS IN FATTY ACID SYNTHESIS**
M. Sumper, D. Oesterhelt and F. Lynen, Max-Planck Institut für Zellchemie, Münich, Germany

9:30 124. **BIOSYNTHESIS OF MONOUNSATURATED FATTY ACIDS IN HIGHER PLANTS**
Eugene M. Stearns, Jr. and William Morton, The Hormel Institute

10:00 125. **CELL-FREE DESATURATION SYSTEMS FOR FATTY ACIDS**
F. W. Quackenbush, Purdue University

10:30 126. **OLEIC ACID SYNTHESIS IN DEVELOPING CASTOR OIL SEEDS**
D. T. Canvin, Queen's University, Kingston, Ontario, Canada

11:00 127. **BIOSYNTHESIS OF MONOENOIC ACIDS IN ANIMALS**
Raymond Reiser, P. K. Raju and L. J. Cook, Texas A & M University

11:30 128. **SOME SPECIFICITIES IN THE DESATURATIONS OF LONG CHAIN FATTY ACIDS**
Lindsay J. Morris, Unilever Research Laboratory, Sharnbrook, Bedford, England

WEDNESDAY MORNING—OCTOBER 8

9:00 A.M.—Taft Room

SESSION R—CHEMICAL SYNTHESIS

Chairman—**Marvin W. Formo,** Cargill, Inc., Minneapolis, Minnesota

9:00 129. **SYNTHESES AND MASS SPECTRAL CHARACTERISTICS OF SOME HIGHER BRANCHED CHAIN UNSATURATED FATTY ESTERS**
D. G. Chasin and E. G. Perkins, University of Illinois

9:20 130. **PREPARATION OF SUCROSE ESTERS BY INTERESTERIFICATION**
R. O. Feuge, H. J. Zeringue, Jr., T. J. Weiss and M. L. Brown, Southern Regional Research Lab.

9:40 131. **PROPERTIES OF 2-OLEODIPALMITIN, 2-ELAIDODIPALMITIN, AND SOME OF THEIR MIXTURES**
N. V. Lovegren, M. S. Gray and R. O. Feuge, Southern Regional Research Lab.

10:00 132. **ALKYL ESTERS OF DIEPOXYSTEARIC ACID AND CYCLIC DERIVATIVES AS PLASTICIZERS FOR PVC**
George R. Riser, Ronald E. Koos and Hogan B. Knight, Eastern Research Lab.

10:20 133. **PREPARATION AND REACTIONS OF ALPHA ANIONS OF CARBOXYLIC ACIDS IN HEXAMETHYLPHOSPHORAMIDE SOLUTIONS**
Philip E. Pfeffer and Leonard S. Silbert, Eastern Regional Research Lab.

10:40 134. **POTENTIAL JUVENILE HORMONES: PREPARATION OF FATTY β-METHYL CROTONYL AND 3,4-METHYLENEDIOXYPHENYL DERIVATIVES**
E. W. Bell, L. E. Gast, J. P. Friedrich and J. C. Cowan, Northern Regional Research Lab.

WEDNESDAY AFTERNOON—OCTOBER 8

2:00 P.M.—Chicago Philadelphia New York Rooms

SESSION O-2—SYMPOSIUM: ROLE OF COMPUTERS IN CHEMISTRY

Chairman—**Royden O. Butterfield,** Northern Regional Research Laboratory, Peoria, Illinois

2:00 135. **QUANTITATION AND AUTOMATION OF GAS CHROMATOGRAPHY**
Jack M. Gill and Frederick Baumann, Varian Aerograph

2:30 136. **STANDARDIZATION OF PROGRAMMED TEMPERATURE OPERATION**
Herbert J. Dutton, A. E. Johnston and J. A. Massa, Northern Regional Research Lab.

3:00 137. **A NEW, REMOTE, ON-LINE DATA ACQUISITION-PROCESSING SYSTEM FOR LOW RESOLUTION COMBINATION GAS CHROMATOGRAPH—MASS SPECTROGRAPH**
G. R. Waller, H-Y. Li, K. Kinneberg, R. Saunders, D. Simpson and L. Mills, Oklahoma State University

3:30 138. **COMPUTER RECORDING AND PROCESSING OF MASS SPECTRA**
Ronald A. Hites and K. Biemann, Northern Regional Research Lab.

4:00 138A. **AUTOMATED GENERATION OF MOLECULAR STRUCTURES FROM MASS SPECTROMETRY DATA**
Eli J. Gilbert, National Institutes of Health

WEDNESDAY AFTERNOON—OCTOBER 8
2:00 P.M.—Lincoln Room

SESSION S—BIOCHEMICAL REACTIONS AND ASSAYS

Chairman—**Helmut K. Mangold,** The Hormel Institute, Austin, Minnesota

2:00 139. THE OCCURRENCE OF FATTY ALCOHOLS IN NORMAL TISSUES AND NEOPLASMS
M. L. Blank and Fred Snyder, Oak Ridge Associated Universities

2:20 140. SPECIFICITY AND SPECIFIC ACTIVITY OF ACYL DESATURASE IN RAT LIVER MICROSOMES
John R. Paulsrud and Ralph T. Holman, The Hormel Institute

2:40 141. HEME COMPOUND CATALYSIS OF LINOLEATE EMULSION OXIDATION
Yoshio Hirano and Harold S. Olcott, University of California

3:00 142. RADIOCHEMICAL ASSAY OF LONG CHAIN FREE FATTY ACIDS
R. J. Ho and H. C. Meng, Vanderbilt University

3:20 143. FATTY ACID COMPOSITION AND STRUCTURAL STUDIES ON THE GLYCOLIPIDS AND PHOSPHOLIPIDS OF MATURING SOYBEANS
H. Singh and O. S. Privett, The Hormel Institute

3:40 144. CHANGES IN GLYCERIDE STRUCTURE OF SOYBEANS DURING MATURATION
Jeffrey N. Roehm and Orville S. Privett, The Hormel Institute

WEDNESDAY AFTERNOON—OCTOBER 8
2:00 P.M.—Twin Cities Room

SESSION T—ANALYTICAL—GENERAL

Chairman—**Peter J. Menardi,** Ashland Chemical Co., Minneapolis, Minnesota

2:00 145. POTENTIOMETRIC DETERMINATION OF MICROQUANTITIES OF LIPID PEROXIDES
M. Lindquist and T. Richardson, University of Wisconsin

2:20 146. ANALYSIS OF PEROXIDE TYPES IN OXIDIZED FATTY ESTER MIXTURES
K. G. Raghuveer and E. G. Hammond, Iowa State University

2:40 147. QUANTITATIVE ESTIMATION OF SUCROSE ESTERS OF PALMITIC ACID
T. J. Weiss, M. L. Brown, H. J. Zeringue, Jr., and R. O. Feuge, Southern Regional Research Lab.

3:00 148. A SENSITIVE METHOD FOR DETERMINATION OF CARBONYL COMPOUNDS
D. C. Johnson and E. G. Hammond, Iowa State University

3:20 149. EDIBLE OIL HEADSPACE GAS ANALYSIS BY MASS SPECTROMETRY
C. D. Evans and E. Selke, Northern Regional Research Lab.

3:40 150. DIRECT DETERMINATION OF SODIUM IN SOYBEAN OIL BY FLAME PHOTOMETRY
L. T. Black, Northern Regional Research Lab.

WEDNESDAY AFTERNOON—OCTOBER 8
2:00 P.M.—Cleveland Detroit Milwaukee Rooms

SESSION Q-2—SYMPOSIUM: BIOSYNTHESIS OF UNSATURATED AND OXYGENATED FATTY ACIDS

Chairman—**Lindsay J. Morris,** Unilever Research Laboratory Sharnbrook, Bedford, England

Co-chairman—**Ralph T. Holman,** The Hormel Institute, Austin, Minnesota

2:00 151. THE EFFECT OF STRUCTURE UPON THE METABOLISM OF UNSATURATED ACIDS
Ralph T. Holman, The Hormel Institute

2:30 152. RETROCONVERSION OF POLYUNSATURATED FATTY ACIDS
Hermann Schlenk, D. M. Sand and Joanne L. Gellerman, The Hormel Institute

3:00 153. MECHANISMS AND STEREO CHEMISTRY IN THE BIOGENESIS OF OXYGENATED FATTY ACIDS
Lindsay J. Morris, Unilever Research Laboratory, Sharnbrook, Bedford, England

3:30 154. THE BIOSYNTHESIS OF CIS-9,10-EPOXYOCTADECANOIC ACID
H. W. Knoche, University of Nebraska

4:00 155. METABOLISM OF THE 2-HYDROXY FATTY ACIDS OF BRAIN
Norman S. Radin, University of Michigan

WEDNESDAY AFTERNOON—OCTOBER 8
2:00 P.M.—Taft Room

SESSION U—FATTY CHEMICALS IN ORE FLOTATION

Chairman—**James A. Hartlage,** Ashland Chemical Co., Minneapolis, Minnesota

2:00 156. IRON ORE FLOTATION—1969
D. W. Frommer, U.S. Bureau of Mines

2:30 157. CATIONIC FLOTATION OF SILICA FROM MAGNETIC IRON ORE CONCENTRATES
Marlin C. Hedberg, General Mills, Inc.

3:00 158. ADSORPTION STUDIES OF ALKYLAMINES AT MERCURY-SOLUTION INTERFACE THROUGH DIFFERENTIAL CAPACITY MEASUREMENTS AND THEIR IMPLICATION IN FLOTATION
Shinnosuke Usui, University of Minnesota

3:30 159. MECHANISM OF ADSORPTION OF XANTHATE ESTERS AND THIONOCARBAMATES ON COPPER AND ZINC SULFIDES
W. L. Freyberger, J. E. Wennen and A. Ahmed, Michigan Technological University

ABSTRACTS OF PAPERS

1

THE DIET-HEART QUESTION, OR THE DOCTOR'S DILEMMA. E. H. AHRENS, JR., The Rockefeller University, New York, N.Y. 10021.

It is the purpose of this presentation to defend the conviction that there is still no clear answer on the question whether the ravages of arteriosclerosis in man can be reduced in number or deferred in time by instituting a major change in dietary habits; to present the arguments why it is still necessary to test the diet-heart question and to test in large-scale populations with double-blind diets; and to suggest how such studies can be designed for maximum effectiveness with least manpower and dollar cost. Until such studies have been completed, I would argue for an informed but open mind (among scientists, in government, in industry and in the public) and for a moratorium on advice-giving by official agencies in the health field.

2

MARGARINE FLAVORS OF THE FUTURE. E. A. DAY, International Flavors & Fragrances, Inc., Union Beach, N.J. 07735.

Advances in the flavoring of margarine over the past one hundred years have been due to technological developments in areas of fats and oils processing and research on butter flavor. Processes leading to margarine bases with desired rheological properties coupled with minimum inherent flavor and maximum storage stability have provided the more ideal medium for flavor application. Successful implementation of research findings on the chemistry of butter flavor also has contributed to the successful history of the industry. Advances in the flavoring of margarine in the future will continue to depend upon developments in the aforementioned areas that will allow greater fidelity and functionality of flavor. Factors affecting these developments will be discussed.

3

FUTURE CONSIDERATIONS IN MARGARINE FORTIFICATION. B. BORENSTEIN, R. H. BUNNELL and G. W. SCHUTT, Hoffmann-La Roche, Inc., Nutley, N.J. 07110.

The nutritional rationale for margarine fortification must be reviewed periodically as new nutrition findings are made and when compositional changes are made. The trend to increase the polyunsaturated fat content of margarine coupled with the newer knowledge of vitamin E requirements suggest that vitamin E fortification of margarine be considered, a practice common in Europe. The composition of current margarines will be discussed with respect to PUFA and vitamin E. The philosophy of food fortification in the U.S. is changing as we learn more about specific dietary deficiencies and about the nutritional effects of both affluence and poverty. Recent data indicate less than adequate serum vitamin A levels in 30% of the 0-9 age group in a population sample taken primarily from the lowest 25% income group. The vitamin A content, low cost, wide availability and high caloric value of margarine suggest a possible role in feeding the underpriviledged. Simultaneously, the vitamin A fortification level of margarine should be reviewed. Is the historical level of 15,000 U/lb nutritionally valid now? The possibility of fortification with other micronutrients will also be discussed.

4

PROBLEMS AND OUTLOOK IN EVOLVING FOOD REGULATION. GEORGE M. BURDITT, 135 S. La Salle St., Chicago, Ill. 60603.

Oil chemists and other food technologists are confronted by a rapidly changing food regulatory environment. New concepts of standards, procedures, tolerances, etc., are being reviewed amid the emergence of significant recent and foreseeable legislation. Designed foods such as margarine are significantly affected. Major changes are discussed. They involve new federal food regulatory organization different from the traditional FDA; problems of interrelationship of FDA and USDA controls and procedures; a mixed situation in state regulatory work where federal law, funding and leadership is strengthening in some sectors, but where other phases of enforcement may become more state-oriented. A definite new problem of uniformity and government intervention has emerged. Leadership personnel also is changing. Net, the responsibility of oils and food technologists is increasing. It is necessary to re-examine their relationships and goals in the regulatory field interest of continued development of food products and public acceptance of existing standards of preparation and handling.

5

THE CHEMICAL SYNTHESIS OF PLASMALOGENS. JILL GIGG and ROY GIGG. National Institute for Medical Research, London, N.W. 7, England.

The methods for the chemical synthesis of 1-*O*-alk-1′-enylglycerols reported by different research groups (Piantadosi, Craig, Preobrazhenskii, van Deenen, Gig) will be reviewed with emphasis on the introduction of the molecular architecture that has been shown to be present in the natural plasmalogens particularly the *cis*-configuration of the vinyl ether grouping and the correct absolute configuration of the glycerol moiety. Methods for the conversion of the synthetic 1-*O*-alk-1′-enylglycerols into plasmalogens will also be discussed.

6

RECENT STUDIES ON NEUTRAL ALKOXYLIPIDS. F. SPENER, W. J. BAUMANN, H. H. O. SCHMID and H. K. MANGOLD. The Hormel Institute, Austin, Minn. 55912.

Alkyl and alk-1-enyl ethers of glycerol and ethanediol, and their esters, were synthesized. Alkyl diglycerides and alk-1-enyl diglycerides were isolated from human perinephric fat, adipose tissue, heart and aorta, and from shark livers. Comparison of their IR and NMR spectra and optical rotations with those of synthetic compounds allowed configurational assignments of the naturally occurring neutral alkoxylipids. Comparative analyses of the alkyl, alk-1-enyl and acyl chains in these lipids, as well as of the alkyl and acyl moieties of wax esters from the same source were undertaken to assess metabolic relationships. Radioactively labeled trialkyl glycerol ethers, dialkyl glycerol ethers and alkyl glycerol ethers were used for absorption studies in rats. It was found that the intestinal absorption of these compounds increases with decreasing number of ether linkages per molecule. For example, the rat does not absorb dietary trioleyl glycerol ether.

7

INTER-RELATIONSHIPS OF GLYCEROL ETHERS. M. L. KARNOVSKY and J. ELLINGBOE, Harvard Medical School, Boston, Mass. 02167.

Possible inter-relationships between glycerol ethers, i.e., between glycerol-1-alkyl and -1-alkenyl ethers, and between phosphatide and neutral lipids of both of these types have been explored. Two main sets of experiments were performed. In the first, ^{14}C-acetate served as a lipid precursor and the distribution of radioactivity among 1-standing moieties of glycerolipids was determined. The data were considered as a function of chain length and unsaturation. In the second set, ^{14}C-labeled glycerol-1-alkyl ethers and glycerol-1(3)-alkenyl ethers were synthesized chemically. Their metabolic products were compared. Both sets of experiments were carried out in vitro with viable fragments of the hepato-pancreas of the starfish. In neither set was there evidence of significant interconversion of alkyl and alkenyl ethers. The data are consistent with information pointing to two quite separate pathways of biosynthesis of the alkyl and alkenyl ethers of glycerol.

8

THE METABOLISM OF ALKYL AND ALKENYL ETHERS IN THE DOGFISH *(Squalus acanthias)*. DONALD C. MALINS, Bureau of Commercial Fisheries, Food Science Pioneer Research Laboratory, Seattle, Wash. 98102.

Fatty acids are reductively incorporated into the alkyl and alkenyl ether chains of glycerolipids in dogfish *(Squalus acanthias)* liver. Although large amounts of diacyl glyceryl ethers (DAGE) are stored in specialized fat cells of this hydrostatic organ, enzymes are present which extensively oxidize the ether linkage. The active metabolism of the intracellular DAGE, and a number of other factors, clearly suggests that these compounds are synthesized and degraded primarily for the purpose of maintaining neutral buoyancy during vertical migrations. A wide spectrum of ethers are present throughout the body of the dogfish, including compounds that are not derivatives of glycerol. The metabolism of these compounds in the liver and spiral intestine will be discussed and compared with respect to both synthesis in vivo and exogenous demands.

9

FOAMS AND FOAM INHIBITION. T. F. O'FARRELL, Drew Chemical Corp., Boonton, N.J. 07005.

This paper will discuss the formation of foam, factors affecting foam stability and mechanisms of foam control and inhibition with application to the paint industry. The presence of surfactants in a gas-liquid system produces foam by concentrating at the gas-liquid interface. Most foam characteristics of aqueous colloidal systems, alcohols, organic acids and esters are usually not desirable when encountered in chemical industries. The foam stability of each system will vary according to factors of surface tension, viscosity, surface area, temperature, pH and concentrations. Stable foams are: (a) associated with a solution surface tension lower than that of the pure solvent; (b) characterized by elastic films whose area changes in response to surface tension changes $E = 2A(d\gamma/dA)$; (c) promoted when Marangoni effects, producing higher surface tension, counteract detrimental Laplace drainage effects; and (d) produced also by formation of gelatinous surface layers seen in fire fighting foams, through the synergistic use of nonionic and anionic surfactants. Mechanisms of foam control often include use of a co-solvent, mechanical shock, thermal stresses and chemical agents, extremely effective as both defoaming and anti-foaming agents, whose action depends upon insolubility and spreading at the gas-liquid interface, achieved by low surface tension and dewetting by the medium. Unwanted foams in industry are uneconomical, causing process slowdown and product deterioration. Defoamer technology must consider also the engineering and economic limitations encountered. The need for defoamer technology in the paint industry is a striking one. The processing of water-based paints produces much foam in the grind and let-down. To evaluate defoamer efficiency, shake tests and rollouts are common. Crater and fisheye formation, color compatibility and defoamer persistence tests are also run. Defoamer formulators utilize blends of alcohols, esters, oils, phosphates, sulfates and silicones.

10

HIGHER ALKYL POLYGLUCOSIDES. FRANCIS A. HUGHES and BAAK W. LEW, Atlas Chemical Industries, Inc., Wilmington, Del. 19899.

The higher alkyl polyglucosides are a new class of nonionic surfactants which can be formulated to give properties ranging from soft greases to hard glassy water-soluble solids melting from about 30 C to above 300 C and which are insoluble in common organic solvents. The aqueous solutions do not exhibit inverse solubility with temperature or concentration. They show low eye and skin irritation and a very low degree of toxicity (LD_{50} greater than 35 g/kg), have a bland taste and are biodegradable. They have shown good functionality in various applications.

11

REDUCTION OF PHOSPHATE BUILDER IN TALLOW-BASED DETERGENT FORMULATIONS. R. G. BISTLINE, JR. and A. J. STIRTON, E. Utiliz. Res. Dev. Div., ARS, USDA, Philadelphia, Pa. 19118.

Laboratory experiments were carried out, washing different types of standard soiled cotton in the Terg-O-Tometer, in soft and hard water. Most of the experiments were with hydrogenated tallow alcohol sulfate, sodium methyl α-sulfotallowate, linear sodium dodecylbenzene sulfonate and soap. With tallow alcohol sulfate

as the active ingredient, in hard water of 300 ppm, it was possible to reduce the conventional phosphate builder to one half the usual amount, without significant loss in detergency. Phosphate builder could be replaced wholly or in part by nitrilotriacetate, ethylenediamine tetraacetate or sodium citrate. Other builders which have been suggested may be useful with tallow-based detergents. Tallow alcohol sulfates could be partly replaced by alkylbenzenesulfonate or sodium methyl α-sulfotallowate without loss in detergency. These combinations were more soluble and had better foaming properties. Laboratory washing experiments with standard soiled cotton can be instructive and may suggest adventageous changes in detergent formulation, but they do not always apply directly to the rather different conditions encountered in household washing.

12

A SIMPLE AND RAPID SCREENING TECHNIQUE FOR DETERGENT EVALUATION.

P. N. RAMACHANDRAN and S. M. BARKIN, Colgate-Palmolive Co., Piscataway, N.J. 08854.

Detergency evaluation is generally carried out by Terg-O-Tometer washing tests on fabric swatches soiled with natural body sebum or one of the many available synthetic soils. Some laboratories employ radioactive tracer techniques using tagged soil ingredients. These tests are very time consuming and very expensive despite having their own merits. A new screening technique has been devised for rapid detergent evaluation. This technique involves the measurement of the rise of the liquid boundary of a test surfactant solution through a uniformly soiled fabric as a function of time. Either the height to which the liquid boundary rises through a soiled fabric strip in a given time or the time required for the liquid boundary to rise to a given height is measured. The results show that this method could be used as a rapid screening technique for detergent evaluation.

13

METHODS OF EVALUATING HARD SURFACE CLEANERS.

THEODORE L. TREITLER, FMC Corporation, Princeton, N.J. 08540.

A method has been developed for evaluating soil removal and redeposition performance of hard surface spray and wipe cleaners which are intended for full strength application to the substrate. An oil-soil emulsion is applied to vinyl tile or painted wood panels using a wide putty knife and a template having a rectangular opening (thereby soiling only the center portion of the substrate panel). Formulation variations of spray and wipe cleaners are performance tested on the dry baked panels under controlled conditions using a paper towel covered sponge mounted in a Gardner Washability machine. After rinsing, the dried panels are read with a Photovolt Reflectometer to measure not only the soil removal from the originally soiled areas but also the deposition of soil on the adjacent areas that were not originally covered with soil. Cleaning efficiencies of commercial products varied from 50-96% and soil deposition varied from 2-20%. Simulated natural soils were ultrasonically dispersed in solvent-oil mixtures and applied by the same procedure used for spray and wipe cleaners. An evaluation was made of several commercial and experimental concentrated powder and liquid floor and wall cleaners which are diluted with water prior to use. The effects of composition and use conditions on detergency performance and soil deposition was evaluated.

14

SYNTHESIS AND PROPERTIES OF SULFATED ALKANOLAMIDES.

J. K. WEIL, N. PARRIS and A. J. STIRTON, E. Utiliz. Res. Dev. Div., ARS, USDA, Philadelphia, Pa. 19118.

Fatty acid alkanolamides were prepared in good yield and purity by the sodium catalyzed reaction of methyl laurate, methyl palmitate and methyl stearate with enthanolamine, 2-hydroxypropylamine, 3-hydroxypropylamine and N-methyl-N-hydroxyethylamine. The alkanolamides were sulfated with chlorosulfonic acid and purified by crystallization from ethanol. Surface active properties of the purified sulfated alkanolamides were studied and related to chemical structure. The solubility of the sulfated alkanolamides was improved by methyl substitution at the nitrogen atom or at the carbon atom adjacent to the sulfate group. Critical micelle concentration was dependent upon the length of the hydrophobic chain and was only slightly influenced by structural changes in the amide portion of the molecule. Stability to acid and alkali were measured. Hydrolysis of sulfated N-methyl-N-hydroxyethyl stearamide was found to proceed rapidly in acid or base according to first order kinetics. Alkaline hydrolysis of sulfated hydroxyalkyl primary amides followed second order kinetics to cause sulfate ester hydrolysis, probably through a neighboring group effect. Stability to both acid and base was improved slightly by methyl substitution adjacent to the sulfate group and considerably improved by the presence of one more methylene group in the hydroxyalkylamine chain. Sulfated alkanolamides based on palmitic and stearic acids were found to be excellent lime soap dispersants and except for the less stable N-methyl compounds, they were good detergents.

15

SULFATION OF SYNTHETIC LINEAR PRIMARY ALCOHOLS WITH CHLOROSULFONIC ACID.

PAUL SOSIS and LEO J. DRINGOLI, Continental Oil Co., Teterboro, N.J. 07608.

This laboratory optimization program was undertaken to describe a method for sulfating linear primary synthetic alcohols with chlorosulfonic acid. Several alcohol blends containing carbon chain lengths from C_{12} to C_{16} were studied. These products find applications in cosmetic and shampoo formulations. A number of quality factors (color, odor, free unsulfated alcohol) demanded by this market are discussed and comparisons to industry wide standards are made. Some of the operating parameters detailed in this work are: mole ratio of alcohol to acid; rate of reaction; reaction temperature; post reaction sparge time; sparging conditions, and reaction time. It was shown that the color of a finished triethanolamine salt based on Alfol 1216 SP alcohol was significantly improved by proper sparging of the reaction mixture. Further, the color passed through a maximum during this final step. It was also demonstrated that dry air is functional in this quality improvement while nitrogen seems to be inert.

16

MEASUREMENT AND ASSESSMENT OF THE DEGREE OF WHITENESS OF SPECIMENS TREATED WITH FLUORESCENT WHITENING AGENTS.

G. ANDERS and C. DAUL, CIBA Aktiengesellschaft, Basel, 420/405 Switzerland.

To date there is no mandatory standard method of measuring the whiteness and fastness properties of specimens treated with fluorescent whitening agents. The main obstacle here has been the lack of a standard source for fluorescent specimens. Standardization by the International Commission on Illumination (CIE) of the new illuminant D 6500 having an emission spectrum resembling that of natural daylight provides a standard procedure for measuring the color of white fluorescent specimens. New tristimulus-filters were developed for a Zeiss tristimulus filter photometer. Standard illuminant D 6500 was imitated with a xenon lamp and a suitable conversion-filter. In principle the standard method for determining the color of whites also enables the degree of whiteness and the fastness properties of fluorescent white specimens to be ascertained. To check the quality of the formulae used for calculating degrees of whiteness, the formulae of Vaeck, Taube, Stensby, Berger, Croes and Hunter were used. Two convenient nomograms were developed which afford a speedy and reliable means of assessing the degree of whiteness and the hue of fluorescent white specimens. Nomogram 1 serves for the straightforward determination of the optimum degree of whiteness, given a known hue preference, and systematic allowance for brightness and saturation in the CIE color solid 1931. Nomogram 2 is used to determine the dominant wavelength and hence the hue. The nomograms are suitable for the values obtained from tristimulus filter photometers permitting virtually standard measurement with illuminant D 6500 for the CIE-System 1931 and 2°-observer. The smallest perceptible degree of whiteness was ascertained and statistically evaluated from 1,210 individual results provided by 22 experienced observers.

17

BIOSYNTHESIS OF BRANCHED CHAIN FATTY ACIDS.

TOSHI KANEDA, Research Council of Alberta, Edmonton 7, Alberta, Canada.

Branched chain fatty acids, iso and anteiso series, have recently been found in many organisms (lower and higher plants, animals, and even human skin). In particular, a number of grampositive microorganisms produce these fatty acids as the major components of total fatty acids. *Bacillus subtilis* produces iso and anteiso-fatty acids with 14 to 17 carbon atoms as the major portion of total fatty acids (≈80%). Valine, leucine and isoleucine or their related α-keto acids have been shown to be incorporated by the growing cells of *B. subtilis* into the terminal portions of these fatty acids. To study this incorporation further an active cell-free extract that incorporates U-^{14}C-α-ketoisovalerate into iso-fatty acids was prepared from *B. subtilis* by ultrasonic treatment. The incorporation was found to be dependent upon the presence of malonyl CoA and NADPH and was increased by the addition of dithioerythritol and NAD. The system could utilize U-^{14}C-isobutyryl CoA as substrate instead of U-^{14}C-α-ketoisovalerate and the former inhibited the incorporation of the latter into the fatty acids. The extract was fractionated into two protein components, one being heat sensitive and the other heat stable, both of which were essential for the incorporation. These results suggest that the incorporation involves the oxidative decarboxylation of α-keto acid substrate by an α-keto acid dehydrogenase to produce the related acyl CoA ester which elongates by repeated condensation of malonyl CoA to yield the fatty acids. The detailed mechanism for the incorporation will be compared with the well-established mechanism for palmitic acid synthesis by *E. coli* system. Metabolic and physiological significance of the synthesis of branched chain fatty acids in the organisms will be discussed.

18

FATTY ACID COMPOSITION OF *Listeria monocytogenes*.

K. K. CARROLL, R. A. TADAYON and N. KOSARIC, University of Western Ontario, London 72, Ontario, Canada.

Branched chain iso and anteiso fatty acids are frequently major components of the lipids of gram-positive bacteria and in such cases, unsaturated fatty acids are generally absent or present only in small amounts. The different lipid classes of the gram-positive bacterium *Listeria monocytogenes* all contain C_{15} and C_{17} anteiso fatty acids as major components, with lesser amounts of iso and straight chain saturated acids, ranging from C_{14} to C_{18}. The proportions vary somewhat from class to class and the ratio of C_{17} to C_{15} is higher in the glycolipid than in the phospholipids. Positional analysis of the fatty acids in the phosphatidylglycerols, which are the main phospholipid components, showed that the C_{15} acid was preferentially esterified to the β-position in each case. Different strains of *L. monocytogenes* showed small differences in fatty acid composition and the pattern was also influenced by the culture medium, the temperature of incubation and the age of the culture. The proportion of shorter chain fatty acids increased when the bacteria were grown at lower temperatures and they also tended to predominate to a greater extent in later stages of the growth curve. Changes due to environmental conditions were often greater than those due to strain differences. Although *L. monocytogenes* is classified with the Corynebacteria on the basis of morphology, its fatty acid pattern differs markedly from that of other members of the family.

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THE OCCURRENCE OF BRANCHED CHAIN FATTY ACIDS IN FUNGI.

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The occurrence of branched chain fatty acids in fungi appears to be very restricted, notwithstanding the somewhat limited nature of studies on fungal lipids. In most cases these acids do not amount to more than 1% or 2% of the total fatty acids. *Conidiobolus denaeosporus* Drechsl, and *C. heterosporus* Drechsl, are unique amongst fungi so far studied in that branched chain fatty acids comprise up to 50% of the total fatty acids of these fungi. Branched chain acids identified include iso tetradecanoic, iso hexadecanoic and anteiso pentadecanoic acids, together with small amounts of other homologues. No iso acids containing an odd number of carbon atoms were detected. Fractionation of the lipid revealed that the branched chain acids are located predominantly in the neutral fraction, with considerably lower proportions in the polar lipid. This evidence, together with the fact that the monounsaturated acids are much lower in these fungi than in other related Conidiobolus species, suggests that the branched chain acids are fulfilling the function normally carried out by the monounsaturates in other fungi. Biosynthesis of the branched chain acids in *C. denaeosporus* and *C. heterosporus* appears to follow a similar route to that found in bacterial and animal systems, valine being the branched precursor for the iso series and iso leucine the precursor of the anteiso series. As expected, leucine, precursor of the iso series with an odd number of carbon atoms, does not stimulate the synthesis of branched chain fatty acids in these fungi.

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RUMEN MICROORGANISMS AND THEIR RELATION TO RUMINANT FATS. MARK KEENEY, University of Maryland, College Park, Md. 20742.

Rumen microorganisms have unique direct effects upon the composition of ruminant fats. The fatty acid components of the lipids in several strains of rumen bacteria grown on chemically defined media have revealed the ability of these organisms to synthesize odd carbon chain length saturated and monounsaturated and branched chain fatty acids from carbohydrate and acetate carbon. These fatty acids are apparently assimilated by normal digestive processes of the host animal and are incorporated into milk and meat fat. The large number of trace component acids found in detailed studies of milk fat composition originates from rumen microbial synthesis. The major bacterial acids in ruminant fats are the iso- and anteiso-C_{15} fatty acids which account for approximately 2% of the fatty acid weight in many milk fats. The branched chain fatty acids in rumen microbes have been found to be concentrated in the 2 position of the cellular phospholipids where they may serve essential structural functions for membrane properties. Rumen microbes are rich sources of plasmalogens (approximately 20% of natural rumen bacterial phospholipid is plasmalogen). The major bacterial fatty aldehydes are palmitaldehyde and C_{18}, and odd and branched chain aldehydes. The patterns of carbon skeletons of the fatty aldehydes found in neutral plasmalogens of milk fat and in certain phospholipid fractions of ruminant organs are identical to the rumen bacterial patterns, again indicating a bacterial origin. Another important event of rumen microbial lipid metabolism is the hydrogenation of dietary unsaturated fatty acids to high yields of stearic acid and smaller yields of positional and geometric isomers of linoleic and oleic acids. These isomers are incorporated into ruminant fats and account for some of the unique flavor precursors in these fats.

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THE BIOGEOCHEMISTRY OF BRANCHED CHAIN FATTY ACIDS AND RELATED HYDROCARBONS. MAX BLUMER, Woods Hole Oceanographic Institution, Woods Hole, Mass. 02543.

Recent and ancient sediments and petroleum contain many acids and hydrocarbons that are structually—and by implication genetically—related to the branched acids of living organisms. In contrast to the recent sediments which contain only compounds also found in organisms, ancient sediments and crude oil contain a much wider range of structures, apparently formed from biogenic precursors in slow nonbiological transformation reactions at depth. Because of their complexity, ancient sedimentary materials present the analytical chemist with a greater challenge than the lipids of recent plants and animals; for the same reason, ancient sediments may provide the lipid chemist with unusual reference compounds which are not easily obtained from other sources. The paper will describe the inventory of branched acids and hydrocarbons in living organisms, in recent and in ancient geological material. The special analytical problems in the analysis of branched hydrocarbons and acids in sedimentary materials will be discussed.

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BRANCHED CHAIN FATTY ACIDS IN TRIGLYCERIDES OF THE BELUGA (WHITE) WHALE. R. G. ACKMAN and CARTER LITCHFIELD, Fisheries Research Board of Canada, Halifax, Nova Scotia, Canada.

The blubber (depot fat) of whales and related marine mammals may contain, in addition to triglycerides rich in the long chain or highly unsaturated fatty acids characteristic of marine oils, further novel features. In the sperm whales and certain bottlenosed (beaked) whales, the triglycerides are accompanied by wax esters. In many dolphins and porpoises the triglycerides are modified by inclusion of substantial proportions of isovaleric acid. modified by inclusion of substantial proportions of isovaleric acid. These animals are also noted for the presence of fat deposits in the jawbones, and also in forehead "melons," which are even richer (40 wt %, 62 mole % in beluga) in isovaleric acid, and contain substantial amounts (up to 20 wt %) of longer chain isoacids such as isopentadecanoic. The blubber and melon oils from beluga have been studied by direct GLC of the hydrogenated triglycerides. Three groups of peaks were apparent in the blubber triglycerides, corresponding to those with 2, 1 and 0 molecules of isovaleric acid. No triisovalerin could be detected. The three groups could be isolated effectively by TLC of the hydrogenated triglycerides, or by repeated gel chromatography of the unhydrogenated triglycerides. Monoacyl-diisovalerin constituted 86% of the melon oil. The relationship of this compound to the animal's ability to use reflected sound waves for underwater orientation will be discussed.

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UNUSUAL LIPIDS IN THE SEBACEOUS GLANDS OF RODENTS. F. SPENER, H. K. MANGOLD, G. SANSONE and J. G. HAMILTON, Harbor General Hospital, Torrance, Calif. 90509.

Preputial gland lipids of mouse and rat were investigated. These lipids consist mainly of wax esters, alk-1-enyl diglycerides, alkyl diglycerides and triglycerides. In addition, we have found several classes of compounds previously not known to occur in preputial glands or, as for the example reported, not known to occur in vertebrates. For example, in the preputial gland of the mouse, a lipid class was found which migrated on adsorption layers between wax esters and alk-1-enyl diglycerides. Its saponification, lithium aluminum hydride reduction or methanolysis led to long chain alcohols. The IR spectrum of the unknown fraction indicated the presence of an acetyl group. The major fraction of this material was isolated by gas chromatograyhy. Its mass spectrum agreed in all details with that of a synthetic preparation of *n*-hexadecyl-(1) acetate. Lithium aluminum hydride reduction of the unknown material followed by acetylation yielded a mixture whose composition was identical to that of the starting material. Thus, the unknown lipid fraction in the preputial gland of the mouse consists of alkyl acetates, the major compounds being hexadecyl acetate (75.2%), hexadecenyl acetate (9.6%) and octadecyl acetate (4.8%). Studies on the lipids of the preputial gland of the rat will be reported.

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SOME MINOR LIPID CONSTITUENTS OF *Brassica oleracea* LEAVES. H. H. O. SCHMID and P. C. BANDI, The Hormel Institute, Austin, Minn. 55912.

Several classes of lipids occurring in small amounts in the surface wax of *Brassica oleracea* leaves were isolated and their structures were determined. They were identified as long chain aldehydes, 4%, consisting mainly of *n*-octacosanal and *n*-triacontanal. Radioactivity from ^{14}C-acetate was readily incorporated into the aldehydes reaching up to 20% of the total radioactivity recovered from the extractable surface lipids. Another lipid class, <1%, exhibiting a very high specific activity was tentatively identified as a C_{29}-β-ketol. Derivatives of the ketol were prepared by reduction to the corresponding diol. The long chain diol was converted to the diacetate as well as to the isopropylidene derivative. Standards of long chain diols were synthesized by reduction of aldols prepared from fatty aldehydes. Spectroscopic and chromatographic properties of the natural ketol and its derivatives and of the synthetic standards are reported. The possible biosynthesis of the ketol as the product of a condensation reaction is discussed.

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NEW NATURALLY OCCURRING LIPIDS: DIALKYL ETHER DERIVATIVES OF DIOLS FROM THE PORPOISE *(Phocaena phocaena)*. USHA VARANASI and DONALD C. MALINS, Bureau of Commercial Fisheries, Food Science Pioneer Research Lab., Seattle, Wash. 98102.

We have demonstrated the presence of naturally occurring diol lipids containing alkyl ether chains in the jaw oil of the porpoise. Such compounds have not been previously reported in the literature. Small percentages of dialkyl ether derivatives of diols were isolated by preparative TLC and further purified by a series of separation-reaction-separation techniques. The diol ethers were characterized by infrared spectroscopy, nuclear magnetic resonance spectroscopy, and mass spectroscopy. GLC of the 1-iodo derivatives revealed a wide spectrum of alkyl chains. Techniques for the isolation and characterization of naturally occurring alkyl ether derivatives of diol lipids will be discussed.

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CHARACTERIZATION OF THE SEX ODOR COMPONENTS IN PORCINE ADIPOSE TISSUE. KENNETH E. BEERY, JOHN D. SINK, STUART PATTON and JOHN H. ZIEGLER, The Pennsylvania State University, University Park, Pa. 16802.

Samples from the inner and outer layers of *Panniculus adiposa* from adult male swine carcasses have been analyzed for the components responsible for the odoriferous perspiration-like sex odor. The nonsaponifiable fraction of the ethyl acetate extract from these issues has been chromatographed using both thin layer and gas liquid techniques with further analysis by gas liquid chromatography-mass spectrometry. Organoleptic evaluation of the heated column effluent from the gas liquid chromatograph has uncovered a series of the odoriferous components. The presence of 3-keto and 3-hydroxy steroids, as well as other unidentified components, has been shown to contribute to this sex odor.

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UNUSUAL FATTY ACIDS AND GLYCERIDES FROM *Monnina emarginata* SEED OIL. B. E. PHILLIPS, C. R. SMITH, JR. and L. W. TJARKS, No. Utiliz. Res. Dev. Div., ARS, USDA, Peoria, Ill. 61604.

Monnina emarginata (Polygalaceae) seed oil contains three oxygenated long chain acids, not previously described. Certain structural features of each acid were deduced from their ultraviolet, infrared and proton magnetic resonance spectra. The positions of olefinic unsaturation were determined by oxidation with a permanganate-periodate reagent or with ozone. Mass spectural analyses of the hydrogenated esters indicated that each of the oxygen functions was bound to C-13 of C_{18} acids. The three acids were: 13-L-hydroxy-*cis*-9,*trans*-11-octadecadienoic (26%), 13-oxo-*trans*-9,*trans*-11-octadecadienoic (0.9%), and 13-oxo-*trans*-9-octadecenoic (0.2%). Methyl 13-hydroxy-*cis*-9,*trans*-11-octadecadienoate and its hydrogenation product both displayed plain positive optical rotatory dispersion curves. Thus both hydroxy esters had the L-configuration. Sequential TLC separated the seed oil into four groups of glycerides and partial glycerides. The glycerides were grouped as follows: triglycerides of common fatty acids (20%); coriolate-containing triglycerides with the 13-hydroxyl group acylated with long chain acids, i.e., estolides (41%), monocoriolins with a free hydroxyl (25%), and tri- and tetra-acid glycerides containing keto-acyl groups (3%). Pancreatic lipase was used to obtain an acyl distribution pattern for each of the glyceride fractions. The acyl groups esterified to the coriolate were removed by dilute-acidic (0.2 M) methanolysis. More than 95% of the coriolate moieties in the glycerides were esterified to one of the α-positions. The β-positions were bound almost exclusively (>97%) to 18:1 (oleic) and 18.2 (linoleic) acids. No evidence suggesting penta-acid or larger glycerides was found.

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FATTY ACID PATTERNS IN TRIGLYCERIDES OF CORN (*Zea mays* L.). IAN A. DE LA ROCHE, EVELYN J. WEBER and D. E. ALEXANDER, University of Illinois, Urbana, Ill. 61801.

Fatty acid patterns of seed triglycerides from several strains of maize and their F_1 intercrosses were studied. In contrast to the commercially refined corn oil used in previous studies, these strains represent well-defined genotypes that exhibit a wide range of oil content (1-16%) and of fatty acid distribution (oleic acid, 20.3-43.2%; linoleic acid, 40.2-70.7%). The fatty acid composition at the 2 position of the triglycerides was determined by lipase hydrolysis. Linoleic acid was concentrated in the 2 position. However, this percentage varied. A significant inverse relationship existed between the percentage of linoleic acid in the total triglyceride and in the 2 position. The triglycerides of the various genotypes were also fractionated by silver nitrate TLC, and the molar concentrations of the major triglyceride classes were compared.

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STEROLS IN RICE BRAN OIL. M. A. M. KAMAL, S. I. EL-HINNAWY and N. S. ERIAN, Faculty of Agriculture, Ain Shams University, Shoubra El Khemah, Cairo, U.A.R.

The unsaponifiable matter in rice bran oil was fractionated by the alumina column chromatography technique and three sterol compounds corresponding 4.03%, 2.27% and 4.26% of the unsaponifiable matter were separated. The above three sterol compounds have maximum absorptions in their spectrographic analysis at 3140 A, 3280 A and 3220 A, respectively. This indicates clearly that the above separated sterol compounds were 7-dehydrositosterol, stigmasterol and sitosterol, respectively.

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FRACTIONATION OF RICE BRAN WAXES.

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Crude rice bran waxes were fractionated by toluene, due to polarity, into two main compounds in amounts of (a) 64.49% and (b) 35.25%, respectively, having the following properties: (a) mp 78.5C acid value 8.96, sap value 89.67, iodine value 18.50; and (b) mp 73.0C, acid value 20.00, sap value 116.97, iodine value 8.08. The differential thermal analysis of both fractions showed that the exothermic reactions were at 370 C for compound (a) and 342 C for compound (b). While the exothermic reaction of the original sample of rice bran wax was 356 C, which was the average of that of both compounds (a) and (b), this indicates clearly that the rice bran waxes contained only two compounds and pointed out clearly the efficiency of toluene to separate the components of crude rice bran waxes.

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NITROGEN DETERMINATION FOR RAPID QUALITY CONTROL OF OILSEED MEALS.

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The price of oilseed meals is determined primarily by the protein content of the meals, a quantity usually calculated by analysis of total nitrogen. The classic Kjeldahl procedure for nitrogen determination is accurate but it is overly time-consuming for quality control in plants handling large quantities of meal. This paper describes some attempts to decrease the time required for nitrogen analysis of safflower seed and safflower meal. A dye-binding method for undigested proteins using orange-G under acidic conditions was tested. This was not satisfactory because fiber content and processing conditions caused uncertain results. The phenol-hypochlorite colorimetric method of Berthelot on protein digests was tested and permitted no savings in time over the AOAC Kjeldahl procedure. A third series of tests were made to accelerate the digestion and titration procedures of the basic Kjeldahl method. Several digestion catalysts and variations on distillation procedures were examined. Conditions are described for reducing the digestion time to 15 min and distillation time to 10 min. Data comparing the standard and rapid procedures are reported for several samples of safflower seeds and meals.

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PRETREATING DELINTERED COTTONSEED TO INCREASE YIELD OF WHOLE KERNELS.

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The use of whole glandless cottonseed kernels to prepare a high-protein low-cost nut-like product (known as Tamunuts) for human food has proven to be highly satisfactory. Methods are needed to prevent breakage of whole kernels during the seed decortication process to increase the yield of whole kernels. Increased yields of whole kernels would make glandless cottonseed a far less expensive source of nut meats than peanuts and other conventional sources. Pretreatment of delintered glandless seed before decortication by (a) dry indirect heating, (b) heating directly with live steam, (c) heating directly with live steam followed by rapid cooling, (d) heating directly with live steam followed by hot air drying and (e) heating with superheated steam was investigated. The yields obtained from treated seed and untreated seed were compared and statistically analyzed. Also reported are analytical data which allow an assessment of any changes in protein quality resulting from the treatments applied and data from organoleptic evaluations of Tamunuts made from treated and untreated glandless seed kernels.

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ANALYSIS OF RESIDUAL SOLVENT IN OILSEED MARC EXTRACTED WITH AQUEOUS MIXED SOLVENTS.

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The amount and composition of residual solvent adhering to, or absorbed by, extracted oilseed meats is important to research on the design and control of mixed solvent extraction processes. A simple method for analysis of the extracted marc is described, requiring unsophisticated apparatus and instrumentation usually available in oilseed processing laboratories. The method consists of azeotropic distillation of the marc followed by centrifugation of the two-phase distillate in calibrated oil centrifuge tubes. The volume of the lower layer is read, the water content is obtained from this reading and a graph previously contructed by applying the method to known mixtures. Total volatile matter is determined by evaporation and oven drying. Equations are given for calculating the other components of the marc. Data are shown for the recovery and quantitative determination of certain mixed polar and nonpolar organic solvents and water in cottonseed marc extracted with the solvents.

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A WATER RECYCLE METHOD FOR WASHING ALKALI-REFINED SOYBEAN OIL.

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In a modified method for washing alkali-refined soybean oil, the wash water is passed through a cation exchange resin and reused continuously. Reuse eliminates the disposal problem associated with the method now used industrially. Batch tests were made in the laboratory with mixtures of water, soybean oil and cation exchange resin. The amount of sodium remaining in the treated soybean oil was reduced from 34 ppm to less than 0.5 ppm. In continuous tests conducted in the pilot plant with a centrifugal contractor, the sodium level of a commercially refined oil (not water-washed) was reduced from 34 ppm to less than 1.5. These results are equal to or better than those obtained by the conventional method of water-washing soybean oil.

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DETERMINATION OF RESIDUAL SOLVENT IN OILSEED MEALS AND FLOURS: II. VOLATILIZATION PROCEDURE.

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A relatively simple procedure was developed for the determination of residual hexane in oilseed meals or flours. The sample of meal or flour is weighed into a serum bottle. After the bottle has been sealed with a rubber septum and heated to volatilize the residual hexane, an aliquot of the gaseous material is analzed by GLC. This technique appears to be much simpler and more efficient than available extraction procedures. This procedure has also been found useful for the determination of other residual solvents such as acetone and isopropanol and for the determination of mesityl oxide and diacetone alcohol in oilseed meals and flours processed by a solvent system containing acetone.

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AN INTRODUCTION TO NUCLEAR MAGNETIC RESONANCE.

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Nuclear magnetic resonance is a physical method for exploring the magnetic and electric environment of the atomic nuclei of the atoms which compose the molecules under study. The substance is placed in a strong magnetic field and the nuclei take on an orientation with respect to this field. The reason for this is that the nuclei have angular momentum (spin) and, being charged, have magnetic moments like small compass needles. By subtle radio-frequency techniques the nuclei are simply made to reorient (resonate) in this field. The reorientation involves a change of energy, and the energy is supplied by a quantum, hv, the frequency of which is therefore proportional to the reorientation energy or hence, to the magnetic field in which the nucleus is found. As in other forms of spectroscopy, the absorption line has a certain width which comes from a variety of sources and thus provides useful information. In solid samples, a contribution is made to the line width because nearby nuclei have fixed lattice positions and each nucleus contributes some field to the others. A contribution is made also by the fact that due to thermal motion, quanta with the necessary energy for reorientation are naturally present in the sample materials so that nuclei relax. The lifetime in each quantized state of orientation is thus limited and the energy of that state thus uncertain or broadened. Some isotopes which are not perfectly round are sensitive to the presence of electric fields so that the line width also must include the change of electrical energy as the nucleus reorients or resonates. Nuclei which are found in chemically different positions in the molecule experience different shielding by the diamagnetic cyclotron motion of the electrons of the molecule and thus give resonances at distinctly different frequencies, an extremely useful phenomenon for the study of molecular structure. The apparatus for the experimentation of this kind must obviously involve a large electromagnet with a very homogeneous and stable magnetic field; a radio frequency transmitter and a receiver; an oscilloscope or chart recorder, as well as certain less obvious electronic instruments.

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THE USE OF LOW RESOLUTION NMR FOR THE RAPID DETERMINATION OF SOLIDS CONTENT OF FAT BLENDS.

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The paper reviews methods of using the Newport low resolution NMR Analyzer for the rapid determination of the solids content of fats and shortenings. Reproducible (within 1%) measurements of solids content at five different temperatures may be obtained within one hour of sampling the molten blend. Solid CO_2 and ice are compared as chilling media, and experimental methods of tempering the samples are described, including the use of ultrasonic agitation. A comparison is given of measurements made on a wide range of fat blends using NMR determination and dilatation. The relative merits of using pure oils or fat blends as calibrants for the NMR determinations are assessed.

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APPLICATIONS OF THE PAT-20, VARIAN'S NEW NMR PROCESS ANALYZER.

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Varian's earlier process analyzer, the PA-7, is now being replaced by a new solid-state instrument, the PAT-20, with improved reliability and performance and simplified operation. The instrument measures the NMR signal of the protons in the sample, integrating the narrow line to give a quick and accurate quantitative analysis of water or oil in a previously weighed sample. The result can be displayed on a recorder or on a digital readout. It can also be fed directly into a computer for on-line process regulation. In the present paper a short description of the construction of the instrument is given and the principles of operation are explained. Some applications are described, with examples from the first measurements in which the new instrument has been used.

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SOLID-LIQUID RATIO IN FATS.

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The use of NMR for process control in the fat industry is hampered by the high cost of the instruments and the skilled personnel required. Since approximately a year, a relatively inexpensive instrument has been on the market, namely the wide line NMR Quantity Analyzer manufactured by Newport Instruments. Both the melting range of the fats and the design of the instrument make a strict temperature control of coil and sample necessary. Hence a device producing a constant temperature airstream was constructed. Air of the same temperature as the sample flows between the magnets and prevents temperature changes in the sample and the coil. The dependency of the integrated signal on temperature and the number of protons, i.e., on the degree of unsaturation of the fat (iodine value) and the average acid chain length (saponification value) will be discussed. Using the derived formulas, the NMR measurements agree very well with those obtained by dilatometric procedures and with results from the Zobel dye dilution method. The main problem in comparing NMR, SFI, DSC and other methods for the determination of the solid-liquid ratio is that the fats should undergo exactly the same temperature treatment in all the methods used. It should also be emphasized that the AOCS-SFI is not the true solid fat content.

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COMPARISON OF SFI, DSC AND NMR METHODS FOR DETERMINING SOLID-LIQUID RATIOS IN FATS.

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Dilatometry (solid fat index) has gained wide acceptance for the characterization of solid-liquid contents of fats over approximately the past 15 years. Wide line nuclear magnetic resonance has in more recent times been used for this purpose. Still more recently, the differential scanning calorimetry (DSC) technique

has been used to determine solid-liquid contents. These three techniques were used to determine the properties of seven fats and oils which represent a cross-section of commercially available materials. These products were blended into 14 different compositions and the solid-liquid contents were determined by the three methods. A comparison is made on results obtained on the various samples by SFI, NMR and DSC techniques. The results of each procedure are compared according to fat composition.

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DETERMINATION OF OIL IN AQUEOUS EMULSIONS BY WIDE-LINE NMR. SUDHAKAR SHANBHAG, M. P. STEINBERG and A. I. NELSON, Department of Food Science, University of Illinois, Urbana, Ill. 61801.

Oil-water and water-oil emulsions that covered the range of 0-100% oil gave an NMR signal equivalent to the sum of signals from oil and water. When an inert substance (glass beads) was added to the emulsion, the signal remained quantitative for oil and water content. Commercial margarine gave a signal that was additive for both oil and water. Magnesium perchlorate was added to the system to convert the moisture to water of crystallization which does not give an NMR signal. This was not completely successful due to the masking of water by fat in the emulsion. Prior addition of carbon tetrachloride to the system broke the emulsion and liquified the fat. Determination of fat and water in margarine by taking NMR readings with only CCl_4 in the system and with both CCl_4 and $Mg(ClO_4)_2$ present was applied to both laboratory and commercial samples.

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A WIDE-LINE NMR R-F SATURATION METHOD TO MEASURE FAT IN MOIST SAMPLES OF DEFATTED CORN GERM. THOMAS F. CONWAY, Moffett Technical Center, Argo, Ill. 60502.

A wide-line NMR radio-frequency (r-f) saturation technique has been applied successfully to measure fat (1-6%) in defatted corn germ process samples containing significant amounts (4-11%) of moisture. NMR relaxation times for protons associated with the fat differ from those associated with the water, and it is possible to use these differences as a basis for discrimination. In process samples where these differences are marginal, they can often be enhanced by high-speed milling the moisture-containing sample in carbon tetrachloride to alter the relaxation times of the protons associated with the fat. The fat content is derived from NMR signals obtained at two r-f levels. At the lower r-f level, energy absorbed is proportional to the number of protons associated with both water and fat. At the higher r-f level, signals from fat are saturated preferentially. The reduction in signal intensity, due to r-f saturation, is proportional to the amount of fat in the sample and can be used as a quantitative measurement. Examples of this methodology to laboratory prepared and process samples are given. Experimental data for 40 random process samples indicate that the method is accurate to within 0.3% fat, absolute (95% confidence limits).

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PLASMALOGEN METABOLISM IN THE BRAIN. G. B. ANSELL, R. F. METCALFE and SHEILA SPANNER, Dept. of Experimental Neuropharmacology, The Medical School, Birmingham 15, England.

Current theories of the formation of plasmalogens include: (a) the direct conversion of the diacyl lipid to the plasmalogen by a conversion of the acyl group in the 1 position to an alkenyl group, (b) the introduction of a long chain aldehyde into the 1 position of 2-acyl-glycero-3-phosphorylethanolamine, and (c) the transfer of phosphorylethanolamine to 1-alkenyl-2-acyl glycerol (plasmalogenic diglyceride). Experiments in vivo with ^{32}P orthophosphate and 1,2-^{14}C-ethanolamine have demonstrated that in whole brain the phosphoryl-base moiety turns over significantly slower in the ethanolamine plasmalogen than in the phosphatidylethanolamine. This is also true for all the sub-cellular fractions examined. It is therefore highly unlikely that the plasmalogen can give rise to the diacyl lipid but the reverse reaction postulated in (a) is possible. Studies in vitro have shown that, while brain contains a phospholipase A and C active towards ethanolamine plasmalogen, the hydrolytic enzyme with the highest activity towards this lipid is a plasmalogenase. This yields a 2-acyl glycero-3-phosphorylethanolamine which could re-participate in plasmalogen formation as in (b). One current suggestion that the formation of the alkenyl ether linkage takes place at the glyceride stage would lend support to (c). Both diacylglycerol and plasmalogenic diglyceride are effective acceptors of phosphorylethanolamine from CDP-ethanolamine in the presence of a brain microsomal fraction optimally at pH 8.8. It is likely that the same ethanolamine phosphotransferase (EC. 2. 7. 8. 1) is responsible though the reaction with the two substrates exhibit some differences. Synthetic D-2-acyl-3-alkenylglycerol with the natural *cis* configuration was as active as a plasmalogenic diglyceride prepared from native plasmalogen, but the *trans* isomer had only 60% of this activity. L-2-acyl-3-alkenyl glycerol was inactive. Phosphotransferase activity was found to be highest during myelination when plasmalogens are deposited in the brain at the fastest rate. If the cytidine pathway is involved in plasmalogen synthesis one important rate-limiting reaction to be considered is the ethanolaminephosphate cytidyltransferase (EC. 2. 7. 7. 14) whose activity is low in brain. Any consideration of turnover of ethanolamine plasmalogen in brain must take into account the catabolic system. It is of some interest that the plasmalogenase is most active in the mitochondrial fraction of white matter.

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ON THE BIOSYNTHESIS OF ETHANOLAMINE PLASMALOGENS OF BRAIN DURING MYELINATION. HILDEGARD DEBUCH, ALFRED ETZRODT, HARALD FRIEDEMANN and JOCHEN MULLER, Physiol.-chem. Institute of the University of Cologne, Josef-Stelzmann-Str. 52, West Germany.

Using ^{14}C-acetate application into brains of young rats in vivo we studied the incorporation into the different acyl and enol-ether chains respectively of the ethanolamine containing glycerophospholipids to elucidate the relation of the metabolic turnover between the 1,2-diacyl-glycerophosphorylethanolamine and the corresponding 1-alkenyl-2-acyl derivative. Furthermore we investigated the biosynthesis of the plasmalogens of brain. With respect to the question whether the enolether linkage of plasmalogens is a result of the phospholipid metabolism, we administrated two of the possible precursors of this kind of lipid: the radioactive 1,2-diacyl-sn-glycerophosphorylethanolamine and the radioactive 1-alkenyl-2-acyl-sn-glycerophosphoryl-ethanolamine. After isolating the pure lipid fractions, the radioactivity of the aldehydes and fatty acids of the different chain lengths was investigated. The results will be discussed.

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MAMMALIAN BRAIN ALK-1-ENYL ACYL AND ALKYL ACYL GLYCEROPHOSPHORYLETHANOLAMINES (GPE). LLOYD A. HORROCKS, The Ohio State University, Columbus, Ohio 43210.

The alk-1-enyl acyl GPE (ethanolamine plasmalogen) of brain accounts for one fifth of the lipid phosphorus and most of the brain alk-1-enyl groups. The detailed composition of this lipid class will be described for human, bovine and murine brain, myelin, and other subcellular fractions. The alk-1-enyl acyl GPE (labeled in the ethanolamine moiety) has a slightly slower turnover rate than do the diacyl and alkyl acyl GPE in mouse brain. These experiments, together with experiments using labeled glycerol and palmitic acid, strongly suggest that neither glycerol-3-phosphate nor palmitoyl CoA are on the direct pathway for the biosynthesis of the alk-1-enyl acyl GPE and that the latter's immediate precursor is the alkyl acyl GPE.

46

INFLUENCE OF ETHER GROUPINGS ON PHOSPHOLIPID REACTIVITIES. W. E. M. LANDS, University of Michigan Medical School, Ann Arbor, Mich. 48104.

A review of the work on phospholipid metabolism as influenced by alkyl and alk-1-enyl ethers will be presented.

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MOISTURE EXTRACTION FROM SOYBEANS: CONCEPTS, DESIGN AND PRACTICE. JULIAN W. BRUNN, JR., Aeroglide Corporation, Raleigh, N.C. 27602.

Expanded markets for soybean products have dictated large increases in processing plant capacities. Larger and more sophisticated oil extraction plants are being put on stream by the industry. Lower moisture beans, and in larger volumes, are necessary for the production of high protein meal. Standard grain drier design criteria no longer suffice—a special soybean process drier-cooler has evolved. The resulting driers must have a large production capability while producing bean to bean uniformity with a high degree of reliability and safety. Consideration will be given to the physical and chemical characteristics of the bean, to drying concepts and to drier requirements. Rate of moisture migration, allowable air temperatures versus heat tolerance of the bean, air flow requirements for moisture removal and operational as well as safety controls will be discussed. Soybean process driers-coolers of today demand a new perspective of the engineer in predicting capacity requirements, in designing adequate feed and take-away equipment, and in the location in the processing plant. Fields are currently being explored to assure the processor of the bigger, better drier that will be required.

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METHODS OF REMOVING HULLS FROM SOYBEANS AND THE EFFECTS OF CRACKING ON HULL REMOVAL. N. HUNT MOORE, N. Hunt Moore and Associates, Memphis, Tenn. 38118.

Several systems of dehulling will be compared as to their efficiency, cost, utility consumption, etc. Typical flow sheets of various dehulling systems, the tempering time required for various types of dehulling systems, and the best specification of cracking beans for the best hull removal will be discussed.

49

FLAKING AND CONDITIONING OF SOYBEANS. ERNIE MICEK, Cargill, Inc., Minneapolis, Minn. 55402.

Conditioning and flaking are important steps in the preparation of soybeans for solvent extraction. Conditioning is done to temper the cracked beans for flaking, and some drying is normally realized in present conditioning practices. Temperature is an important factor in both ease of flaking and the extraction rate, which changes significantly with temperature change. Flake thickness controls the specific surface for extraction. The extraction rate decreases with increasing flake thickness and the increase in flake thickness increases the bound or unextractable oil. Large flakes will extract more rapidly than small flakes of the same thickness. It was found that the type of flake has an effect on the drainage experienced in the extractor.

50

EXTRACTION. GENE C. MASON, Arkansas Grain Corporation, Stuttgart, Ark. 72160.

This paper will discuss flaking roll aspiration and operation affecting the condition of raw flakes to the extractor and extraction efficiency; conveyance of raw material from preparation to extraction by conventional means as compared to possibly pumping a miscella-flake slurry direct to the extractor; hexane type and temperature changes affecting the extraction process—control of extractor vent and its effect on solvent loss; spent flake conveyor systems incorporating additional solvent wash and drainage time for increased plant efficiency; outline of present day extractor designs and mechanical operation—preventative maintenance schedule and safety precautions to insure minimum down time and safe plant operation; improvements required in extractor engineering and design to reduce unit size, minimize weight carried by moving parts and control of compartment filling and uniform flooding; and engineering and design information that should be investigated prior to purchasing a new extractor.

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DESOLVENTIZING AND TOASTING. C. L. KINGSBAKER, Blaw-Knox Chemical Plants, Inc., Pittsburgh, Pa. 15222.

Desolventizing and toasting of vegetable meals is done in the United States by one of three systems. The earliest was the Schnecken. It was followed by the Blaw-Knox vapor desolventizer-deodorizer-pressure toaster system and finally by the desolventizer-toaster patented by the Central Soya Company. Most animal food is processed in the desolventizer-toaster unit. However, if a higher water soluble protein animal feed is required, the vapor desolventizer-deodorizer system is used. In order to produce protein foods for human consumption, water soluble protein levels of 70% to 90% are required. Desolventizing is accomplished by using a vapor desolventizer and deodorizing under vacuum so that the meal temperature does not exceed 180 F to minimize protein denaturation.

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DISTILLATION AND SOLVENT RECOVERY FOR SOYBEAN AND OTHER OILSEEDS PLANTS. KENNETH W. BECKER, Blaw-Knox Chemical Plants, Inc., Pittsburgh, Pa. 15222.

Features which a modern, well designed distillation and solvent recovery system should contain in order to permit safe and profitable operation will be discussed. The technology has advanced rapidly during the past 10 years in the development of more efficient and profitable distillation and solvent recovery systems. These systems operate with less down-time and far more efficiency than they did 20 years ago. The application of good chemical engineering practice, together with a long background of plant operations, will permit continued improvements of these systems in the future. To permit continuous development in this area it is essential that design and operating companies have a two-way interchange of information.

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TALL OIL: PAST, PRESENT AND FUTURE. RALPH H. POTTS, Armour Industrial Chemical Co., McCook, Ill. 60010.

In a paper on Tall Oil, presented 11 years ago, the vigorous growth of an infant industry and a bright future was predicted for the decade ahead. In our present paper we will show that actual production records outperformed the estimates made at that time. A brief summary of the industry's present status will be given, followed by another gaze into the "crystal ball."

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A CHROMATOGRAPHIC STUDY OF THE FATTY ACIDS FOUND IN CRUDE TALL OIL. W. M. HARGROVE, D. M. NALL and R. W. JOHNSON, Union Camp Corp., Savannah, Ga. 31402.

Although a number of fatty acids have been reported as constituents of crude tall oil, no single investigation attempts to identify or characterize the entire fatty acid content. This investigation reports the fatty acid content found in a tall oil produced in southeast Georgia. The fatty acid fraction was separated from the resin acids by selective esterification. A semi-preparative gas chromatograph was used to separate the fatty acids into six cuts. The individual cuts were rechromatographed on two separate high resolution columns. Characterization was made by comparison to authentic standards. Hydrogenation followed by chromatographic analysis helped to substantiate the identifications. Our results show the presence of 34 different fatty acids in the above sample. These include both odd and even numbered acids from C_{12} through C_{24}. In addition, seven branched chained acids are indicated. Procedures, results and rough quantitative data will be given.

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DISTILLATION OF CRUDE TALL OIL. D. F. BRESS, Foster Wheeler Corp., Livingston, N.J. 07039.

This paper will briefly review the source and production of crude tall oil, its composition as given and as required for the design of a fractionation system. The products made by distillation will be given and the sequence of the distillation steps described for both blocked and continuous systems. The equipment used will be discussed and pollution problems encountered in tall oil fractionation described. A comparison will be made of the results obtained when distilling crude from the Southeast United States with those when distilling crude from Finland.

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SHORT-TIME THIN FILM PROCESSING OF HEAT SENSITIVE ORGANICS. JAMES DONOVAN and FRANCIS C. BROWN, Artisan Industries Inc., Waltham, Mass. 02154.

Concepts and experimental data for rising film-falling film and agitated thin film evaporative equipment will be presented. There will be process flow sheets.

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ECKEY HORIZONTAL FRACTIONATOR. L. W. NISBET, JR., Vulcan Manufacturing Company, Cincinnati, Ohio 45246.

The Eckey Horizontal Fractionator is a low liquid retention, low pressure drop, multi-stage, horizontal mass transfer column. It is a proprietary equipment item built and marketed by Vulcan Manufacturing Company, Cincinnati. It is ideally suited for multi-stage distillation applications in the pressure range of 1 to 100 mm of Hg absolute. The units consist of a horizontal shell with heads at each end, with a rotating shaft located below and parallel with the axis of the shell. Impellers are mounted on this shaft which is connected to an outside driver through a mechanical seal. During operation, liquid flows from one end to the other with vapor countercurrent. The impellers successfully spray the liquid, forming curtains through which the vapor must pass. These curtains form the actual distillation stages, and unique proprietary internals prevent vapor-liquid bypassing from stage to stage, improving stage efficiency. Conventional heat exchange equipment is used for condenser and reboiler. Feed is usually introduced in the center of the unit for normal fractionations. Because of extremely low pressure drop per theoretical stage, reboiler pressures are just slightly higher than the total pressure at the condenser, even with many theoretical stages for separation. Distillations normally done with stripping steam to reduce temperatures within other more conventional distillation equipment can be done dry in the Eckey column with consequent savings in utilities and equipment. Future applications include crude tall oil distilling. Also data has been obtained on removing residual marketable rosin from tall oil pitch and fractionation of tall oil heads.

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PERFORMANCE OF ALLOYS IN TALL OIL DISTILLATION SERVICE. HAROLD C. TEMPLETON, Walworth-Aloyco Div., Walworth Co., Linden, N.J. 07036.

A report will be presented on in-plant corrosion tests of various metals and alloys, the effect of alloy composition on corrosion resistance, and the effect of process stream composition on corrosion. Three variables: temperature, alloy composition and stream composition were correlated and can be a useful guide to material selection for the tall oil distillation plants. Molybdenum is the most important alloy addition to the austenitic stainless steel and increasing molybdenum content materially reduces corrosion attack. It was found that corrosion attack is normally from pitting and molybdenum improved pitting resistance. Process stream composition was an important factor in corrosion and streams high in fatty acid content were more corrosive than streams high in rosin acid content.

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ETHYLENE AND PROPYLENE OXIDE ADDUCTS OF A NUMBER OF HYDROXYLATED TALL OIL FATTY ACIDS. S. T. BAUER and T. L. CROSBY, Crosby Chemicals, Inc., Picayune, Miss. 39466.

Hydroxylation of pure tall oil fatty acids has been studied over a wide spectrum of reaction conditions using a variety of oxidation reagents. The hydroxylated derivatives of this mixture of oleic and linoleic acids have been further reacted with various quantities of ethylene and propylene oxides for the production of polyols suitable for use as components in automotive brake fluids or reactants in urethane foam. A description of some of these products and their evaluation in commercial applications will be presented.

60

REACTION OF ETHYLENIMINE WITH FATTY ACIDS AND FATTY AMINES. A. M. DEROO, The Dow Chemical Co., Midland, Mich. 48640.

Ethylenimine (EI) has been reacted with various fatty amines (such as dodecyl and octadecyl amines) and fatty acids (such as oleic and stearic acids) to produce multiple-aminoethylated products. Tall oil and tall oil-fatty acids were reacted with EI in a similar fashion to produce multiple-aminoethylated esters or multiple-aminoethylated hydroxyethylamides or a combination of these depending on conditions. General reactions of EI, specific reaction conditions to be employed, the various end products obtained, and a derivative of EI which was reacted with fatty acids and produced interesting fatty amino amides will be discussed.

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POSSIBLE APPLICATIONS OF TALL OIL ACIDS REACTED WITH ETHYLENIMINE. J. D. CAMISA, The Dow Chemical Company, Midland, Mich. 48640.

The use of tall oil acids reacted with ethylenimine (EI) as surfactants has been investigated. Data on surface tension, interfacial tension, foam height and stability, and wetting time has been compiled. In the area of textile softening products, these samples gave interesting results when compared to an industry standard. Rosin acids also showed surfactant and softening properties. Other work was carried out with rosin acids reacted with polyethylenimine. These compounds were looked at as paper sizing materials at both the wet and dry end.

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TALL OIL PRECURSORS: APPROACHES TO THE ANALYSIS OF PINE WOOD EXTRACTIVES. DUANE F. ZINKEL, U.S. Forest Products Laboratory, Madison, Wis. 53705.

A fundamental knowledge of the precursors in the living tree is necessary in order to understand the chemical changes that occur during wood handling and the kraft pulping process, and that affect the qualitative and quantitative composition as well as the yield of tall oil. The overall approach to the analysis of the fatty and resin acid fraction of pine wood extracts makes use of a combination of ion-exchange, gel-permeation, silver nitrate-pi complex and gas liquid chromatography. In the development of the methodology, particular attention has been given to maintaining the integrity of the readily isomerizable levopimaric acid. Applications of the chromatographic methods to various problems, including the purification and characterization of tall oil constituents, are given.

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HUMAN ERYTHROCYTE MEMBRANE AND PLASMA LIPID VARIATION. AN EXAMPLE OF STATISTICAL ANALYSIS OF COMPLEX LIPID MIXTURES IN TWO PHASES. JOE C. CHRISTIAN, PAO-LO YU, KE WON KANG and JAMES A. NORTON, Indiana University School of Medicine, Indianapolis, Ind. 46202.

Lipid chemists often are faced with the problem of measuring and analyzing complex mixtures of compounds in two or more phases such as the aqueous and fat phase of extracts, cultured cells and their media, mixtures of subcellular particles or blood cells and plasma. The present study measured plasma and erythrocyte ghost phospholipids and cholesterol to study the variation among and between plasma and ghost variables. The 15 variables measured were displayed graphically by a computerized polygonal plot and analysis of the variance of duplicate determination from six samples taken at two to three week intervals was significant within and between individual variation for cholesterol and phospholipids of both plasma and ghosts. The within individual variation was further studied by correlation, revealing positive correlations among the plasma lipids and among the ghost lipids, but generally negative correlations between the two groups of variables. Multiple regression, in a stepwise manner, was used to determine which plasma lipids were the most closely related to the variation in ghost lipids. This analysis was followed by canonical correlation (correlation of two sets of variables) which confirmed the stepwise regression and revealed even more complex relationships between plasma and ghost lipids. This sequence of analysis is proposed as a general means of analyzing multiple lipid components in two or more phases.

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TECHNIQUES FOR THE ANALYSIS OF RESPONSE CURVE DATA. RONALD D. SNEE, E. I duPont de Nemours & Company, Wilmington, Del.

Experimenters often make several observations on a given experimental unit. If these observations can be associated with some continuous variable, such as time or temperature, they collectively form a curve. In other situations the properties of the experimental unit are measured by an automatic analyzer whose output is a curve. Two procedures for the analysis of this type of data are discussed. In the first procedure a general regression model is fitted to each curve, and the coefficients in the model are analyzed to determine the effects of the experimental treatments on the curve. It may not be possible to find a model which will describe all curves; on the other hand, the model may contain many coefficients complicating the overall interpretation of the experiment. In these situations it is recommended that a procedure which combines analysis of variance and principal component analysis be used. An example is presented which illustrates the use of these procedures for the analysis and interpretation of response curve data.

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CHECK SAMPLE DATA ANALYSIS AND RANKING OF LABORATORIES. EDWIN M. GLOCKER, W. R. Grace & Co., Research Division, Clarksville, Md. 21029.

A system is described for measuring the performance of laboratories participating in check sample programs. Individual analytical results are treated to obtain normalized differences from the censored mean of comparable results from all participants. Laboratory performance in the use of a number of analytical methods is measured by calculating the quadratic mean of a laboratory's normalized differences, that is, its average total error, also referred to as an average accuracy index. Rank among laboratories is from smallest to largest average total error. Rank can be based on one or on several check samples. When the basis is several check samples, each analytical method which a laboratory uses on a current check sample is evaluated. The evaluation shows normalized bias, precision and accuracy over the time interval which the samples cover. Accuracy over the interval is the quadratic mean of bias and precision. The system also generates censored means, standard deviations and average ranges of duplicate analyses for all analytical methods; the effect of concentration on analytical precision; the magnitude of effects due to differences among samples or due to different compositions; a ranking of comparable analytical methods; and the effect of time on laboratory precision. A computer program which performs the calculations allows participants an unhampered choice concerning the kinds of analyses to be made and the number of different analytical methods to be used on a particular check sample.

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DESIGNS FOR EXPERIMENTS TO STUDY FORMULATION AND PROCESSING VARIABLES SIMULTANEOUSLY AND EFFICIENTLY. HORACE P. ANDREWS and JANE C. LI, Rutgers University, New Brunswick, N.J. 08901.

Statistical designs for experiments involving mixtures of multiple components or ingredients, where the percentage of all must equal 100, have been proposed by Scheffe and have been rather widely used in certain areas of formulation research. Similarly efficient designs (fractions of two level factorials) are widely used to investigate the effects of and interrelationships among independent variables, say "process" variables, i.e., temperature, pressure, mixing time, etc., upon some response criteria. The combined problem is prevalent, but the development of efficient experimental designs for such joint investigations has been slow. This paper incorporates some of the ideas of the mixture designs with the notions of fractional factorial experiments to develop efficient (minimum number of experimental treatment combinations) designs for investigating the interrelationships among process variables and varying composition of components or ingredients. These designs propose the simultaneous investigation of component and process variables in single experiments and provide methods of estimating the effects and testing their statistical significance.

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ESSENTIAL FATTY ACID NUTRITION—AN INTERACTION WITH DIELDRIN. IAN J. TINSLEY and ROBERT R. LOWRY, Oregon State University, Corvallis, Ore. 97331.

Dieldrin reduces the growth of female rats raised on a ration deficient in essential fatty acids. The growth of male rats raised on the same ration is not affected by the dieldrin; however, the 20:3,ω9/20:4,ω6 ratio in liver lipids is increased. These data indicate an interaction between the nutritional and toxic stresses since dieldrin did not produce comparable changes in control rats raised on a ration containing adequate levels of essential fatty acids. Investigation of the fatty acid composition of liver lipids demonstrated that dieldrin increased the level of stearate together with the level of polyunsaturated fatty acids—the ω6 series of fatty acids in the control animals and 20:3,ω9 in the deficient animals. Since dieldrin induces the activity of the mixed function oxidases through a proliferation of the endoplasmic reticulum, the changes in fatty acid composition could be attributed to an increase in the level of lecithin, the principal phospholipid of this membrane. A comparison of the fatty acid composition of total lipids with that of a microsomal fraction would substantiate this hypothesis. The increased demand for the ω6-fatty acids in the production of endoplasmic reticulum might account for the effect of dieldrin in essential fatty acid nutrition.

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EFFECT OF BOUND GOSSYPOL ON ENZYMATIC RELEASE OF FREE AMINO ACIDS AND PEPTIDES. CARL M. CATER and CARL M. LYMAN, (Deceased March 9, 1969), Oilseed Products Research Center, College Station, Texas 77843.

The nutritive value of cottonseed protein is lowered by the presence of bound gossypol. Samples of cottonseed protein containing from 0.003% to 1.02% bound gossypol were hydrolyzed enzymatically and the amounts of free amino acids released were determined. The amounts of amino acids contained in peptides not precipitated by 1% picric acid were also determined. The proportionate reduction in the release of free and peptide amino acids in the presence of bound gossypol was noted. Although the amount of lysine released is reduced in the presence of bound gossypol as expected, there is a markedly larger reduction in the release of a number of other amino acids.

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INCORPORATION OF 1-^{14}C-PALMITIC ACID BY THE ADULT RAT BRAIN. G. A. DHOPESHWARKAR and JAMES F. MEAD, Laboratory of Nuclear Medicine and Radiation Biology, Los Angeles, Calif. 90024.

The uptake of acetate 1-^{14}C in vivo, by developing rat brain was studied using animals of various ages ranging from 9 days to 60 days. It was observed that there was a steady increase in the lipid content of the brain accompanied by a marked decrease in the incorporation of radioactivity from 9 to 30 days. The incorporation of 1-^{14}C-acetate in the 13 day old rats was greater in the brain as compared to the liver whereas the opposite was true in adult animals. The labeling pattern in terms of distribution of radioactivity in the brain fatty acid of the adult animals showed that the radioactivity of palmitic acid was evenly distributed, giving 12.5% of the total radioactivity in the carboxyl carbon. These results were used to interpret the data on the incorporation of orally fed 1-^{14}C-palmitic acid into adult rat brain. It was observed that: (a) the radioactivity from palmitate was incorporated into brain lipids to the extent of 0.02% of the fed dose which was about the same as observed in the case of 1-^{14}C-acetate; (b) the observed radioactivity in the brain could not have been contributed by trapped blood, because the activity of the circulating blood was very low; (c) during the entire period of 1 to 24 hr. after feeding, the palmitic acid isolated from the brain had 85-87% of the total radioactivity in the carboxyl carbon—this clearly showed that palmitic acid was largely incorporated unchanged into the brain lipids rather than synthesized from acetate derived from its oxidation; (d) a low activity in the brain cholesterol showed that a small amount of the fed palmitate must have been degraded to give radioactive acetate—this also resulted in labeling of stearic acid by chain elongation; and (e) the radioactivity from orally fed 1-^{14}C-palmitic acid after rapid incorporation remained virtually unchanged up to 24 hrs. in the brain, when both the liver and blood radioactivity had decreased considerably—this unusual finding will be discussed.

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EFFECT OF PRENATAL AND EARLY POSTNATAL DIETS CONTAINING CYCLOPROPENE FATTY ACIDS ON THE DEVELOPMENT OF THE STEAROYL DESATURASE IN RAT LIVER. NADINE N. SUMPTER, P. K. RAJU and RAYMOND REISER, Texas A&M University, College Station, Texas 77843.

The object of this study was to determine the effect of binding liver stearoyl desaturase with cyclopropene fatty acids during embryonic and suckling periods on the activity of the enzyme in the adult animal. Mother rats were given 0.2% *Sterculia foetida* seed oil, equivalent to about 0.1% cyclopropene fatty acids, during their pregnancy and nursing periods (Group 1), or only while nursing (Group 2). A control group (Group 3) received Lab Chow only. The liver stearoyl desaturase activities of the young were determined at 22 days of age (weaning), and 36 days later, at which time some of them had been on a fat free diet for one week; otherwise, after weaning, the only regimen was Lab Chow. The activities of the enzymes in the treated mother were also determined at weaning and 36 days later. At weaning the animals in Group 1 had only 10% and Group 2 20%, of the desaturase activity of the controls. The mothers of each group had about twice the desaturase activities of the young. After 36 days on Lab Chow the desaturase of the control group was the same as at weaning while that of Group 1 increased 10 times, recovering to the full activity of the controls. The desaturase of Group 2 on the Lab Chow increased to levels 30% higher than Group 1 and the controls. Fat free diet ingested for only one week resulted in desaturase levels almost twice that of the Lab Chow diet in Groups 1 and 3, but only 25% greater in Group 2. At all stages the fatty acid compositions of the liver triglycerides and phospholipids reflected the stearoyl desaturase activities. *S. foetida* seed oil contains a high percentage of cyclopropene fatty acids, and it is believed that these cyclopropene fatty acids had a permanent effect on stearoyl desaturase development as demonstrated by the differences in enzyme activities among the three groups.

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MUCOSAL LIPID VARIATIONS AFTER FEEDING DOUBLY LABELED TRIOLEIN AND TRILINOLEIN. MARGARET G. MOREHOUSE, PHYLLIS HAINES and JUDY SCHMIDT, University of Southern California, Los Angeles, Calif. 90007.

Male rats of Sprague-Dawley strain were fed by oral intubation an aqueous suspension of sucrose, albumin, salts and triglycerides. The triolein and trilinolein were present at ca. 15% level and were differentially tagged with tritium or ^{14}C in the glycerol and fatty acid moieties. Controls were fed the same mixture except that the lipid portion was omitted. The animals were killed 1½-2 hr. subsequent to feeding and the lipids were extracted from the mucosa of the small intestine. Triglycerides, lecithin and phosphatidyl ethanolamine were isolated from these lipid fractions and were analyzed for fatty acid composition and site of attachment, and for radioactivity levels. Results indicated that, although the proportion of oleic acid in the triglyceride molecules increased from some 25-35% in these compounds from the control animals to about 85% in the glycerides from rats fed the triolein, the exogenous acid was handled in a manner similar to that of the endogenous acid, namely one third was attached to the secondary alcohol group with the remainder being present at the primary alcohol sites. In contrast, after the ingestion of isotopic trilinolein the proportion of the total triglyceride fatty acids contributed by linoleic acid rose from some 25% in these compounds from the controls to only 65% in the glyceride fed rats. In addition, 45% or more of the linoleic acid found in the mucosal triglycerides from the control rats was esterified to the secondary alcohol group but only some 25-30% was found at this locale after the trilinolein feeding. Thus the specificity for this binding site was lost either due to differences in the handling of the exogenous acid or to the increase in the amounts which must be handled. When the radioactivity levels were examined some 50% of the glyceride glycerol of the triglycerides was derived from the doubly tagged triolein fed while only 21-25% of these glycerol moieties were so derived after trilinolein ingestion. The isotopic levels of the mucosal lecithins showed an incorporation in the reverse manner, i.e., 23% of the glycerol portion had its origin in the isotopic trilinolein and only some 10% had originated from the tagged triolein. Comparable figures for the phosphatidyl ethanolamine were 10% and 4%, respectively. Thus the monoglyceride entering from the lumen appeared to be well used for phosphatid formation if it was monolinolein but less well used if monoolein. An alteration in the pathway of formation which was dependent upon the fatty acid absorbed could explain these data.

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EFFECT OF HIGH AND LOW LEVELS OF DIETARY LINOLEATE ON THE FATTY ACID COMPOSITION OF PHOSPHOLIPIDS IN RAT TISSUES. R. R. DEL ROSARIO, AGNES WONG and L. R. DUGAN, JR., Michigan State University, East Lansing, Mich. 48823.

Weanling rats were fed for seven weeks on diets containing linoleate as 0.0%, 0.5%, 4.0%, and 12% of calories in a diet containing 20% of total diet calories as lipid. Phospholipids of heart, liver and blood lipids were separated by thin layer chromatography, the acyl components converted to methyl esters, and the fatty acid composition determined by GLC. The phospholipids of linoleate deficient rats had levels of monoenoic fatty acids which generally were in inverse proportion to the amount of linoleate in the diet. The major polyunsaturated fatty acid in the phospholipids of these rats was C 20:3. This occurred in lesser quantity or was absent from phospholipids of rats receiving adequate amounts of linoleate in the diet. These results were observed in phosphatidylcholine, phosphatidylethanolamine, phosphatidylinositol and phosphatidylserine. The C 18:2 content and the C 20:4 content of the phospholipids was at increasingly higher

levels in rats receiving adequate amounts of linoleate. The cardiolipins responded markedly to amounts of linoleate in the diet and appeared to act as storage lipids for linoleate since no C 20:4 or C 20:3 was found in samples from rats on any of the diets.

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NUTRITIONAL PROPERTIES OF FATS: THEIR INDIVIDUALITY. HANS KAUNITZ, RUTH E. JOHNSON and LEWIS PEGUS, Columbia University, New York, N.Y. 10032.

In previous long term studies of the nutritional effects of various fresh and mildly oxidized fats and oils fed to male rats of the Columbia-Sherman strain in a marginally iodine-low diet, the fats were found to differ markedly in their effects on life span and pathology. A second, more extensive study has been under way since the fall of 1967 with Charles River COBS male rats. The following fats are being fed in an iodine sufficient diet; fresh and mildly oxidized cottonseed, olive, corn and soybean oils, beef and chicken fats, butter oil and lard. An additional group is being fed synthetic mixed triglycerides of saturated medium chain fatty acids (MCT). Thus far, the death rate of the groups fed beef fat has been lower than in most other groups ($P < .01$ in comparison with those fed either butter oil or cottonseed oil). Inasmuch as beef fat and butter oil have similar low linoleate contents whereas cottonseed oil has a high one, one can probably conclude that the linoleate content of natural fats has been overrated. Death rates and incidence of such diseases as cardiorenal disease, pulmonary infections and tumors did not correlate with any dietary fatty acid pattern. A possible exception may be the low death rate among the animals fed MCT with a low linoleate supplement. Altogether, natural fats have their own individuality, with the triglycerides being perhaps less important for differences in biological effects than are the non-triglyceride portions.

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COCONUT AND SOYBEAN OILS IN MILK SUBSTITUTES FED TO MONKEYS. HANS KAUNITZ and JAIME SANYER, Columbia University, New York, N.Y. 10032.

For 15 months, filled milks containing coconut oil hydrogenated to 0.6% linoleate or soybean oil have been fed to cynomolgus monkeys. The monkeys were placed in the experiment when they were 6 to 10 weeks of age. Groups of 2 to 4 monkeys are being given small amounts of solid food and free access to filled milk samples containing 96.75% skim milk plus 3.05% coconut oil or soybean oil and 0.2% emulsifier. Included in the study are other samples containing coconut oil plus 0.24% cottonseed oil with and without 0.81% buttermilk powder. The control milk is skim milk plus 3.25% of the cream portion of milk. Particular attention is being given to proper emulsification of the fat in the milks to a particle size of 1-5μ. Growth, appearance and stools have been equally good in all groups. Repeated stool cultures show no differences in the flora. Recently, an additional group of four young monkeys have been placed on an imitation milk containing 7.1% whey, 1.7% sodium caseinate and 3.0% coconut oil and having a protein content of 3.5%. So far, these animals have also been doing well.

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WIDE-LINE NMR FOR PRODUCT AND PROCESS CONTROL IN FAT INDUSTRIES. RUNE WETTSTRÖM, AB Karlshamns Oljefabriker, 292 00 Karlshamns, Sweden.

A modified method is described for determination of the content of solid phase in fats at various temperatures using a Varian PA-7 wide line NMR instrument with temperature accessory. To avoid variations of instrument sensivity a liquid soybean oil was used as a reference. Furthermore there will be no need for corrections depending on the iodine value of the fat or on the temperature. The optimal instrument settings have been determined and the importance of a standardized temperature conditioning of the sample is confirmed. With observance of proper conditions a relative standard deviation of 1.0% liquid phase has been obtained. With this method a great amount of samples can be examined with only a reasonable amount of work, but there is an increased demand for faster and more exact temperature conditioning of the samples, better stability and easier handling to fit more routine conditions. With these improvements the NMR method does offer some advantages for product control over solid fat index. However, for the time being the NMR method can not be used for process control of hydrogenation, because the necessity of conditioning the sample does not permit the determination of the results in less than 1 hr.

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PROCESS CONTROL APPLICATION OF WIDE-LINE NMR IN A CORN WET MILLING PLANT. JOSEPH A. PALMER, Corn Industrial, Division of CPC International, Inc., Argo, Ill. 60501.

Wide-line nuclear magnetic resonance (NMR) has been used as a routine quality control tool at the Argo, Illinois Plant of CPC International since 1957 for moisture analysis and since 1966 for fat analysis. During this time, both advantages and disadvantages have been demonstrated. Its use for moisture analysis of starches has provided improved uniformity and quality to customers; its use for fat analysis has aided in the daily control and optimization of process streams. Some of the topics covered in this paper are the various methods which have been developed, calibration procedures for reference standards and discussions of the different process areas in which the NMR has proven useful. Also discussed are disadvantages and problems which have occurred in this routine operation and measures taken to minimize their effect.

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ON-STREAM NMR MEASUREMENTS AND CONTROL. WILLIAM L. ROLLWITZ and GILBERT A. PERSYN, Southwest Research Institute, San Antonio, Texas 78228.

Nuclear magnetic resonance instrumentation in the steady state mode can be made to both lock onto the resonance absorption line from the nuclei to be measured by the first harmonic and also to indicate the quantity of the nuclei by the second harmonic. The measurement thus made is also sensitive to the changes in the relaxation times, T_1 and T_2, of the nuclei being measured. Therefore, to make the measurement independent of the relaxation times, the area under the absorption signal must be used rather than its peak value. These characteristics were constructed into two NMR devices which were used to measure the amount of aluminum and the amount of hydrogen in a thick mixture. The area under the absorption curve for hydrogen and the peak amplitude of the second harmonic of the aluminum signal were both recorded. At a flow rate of 100 lb/min through a 3 in. diameter process stream (the flows through the NMR devices were also through 3 in. pipes), the 3 σ error of the amounts of the measured values of aluminum was 0.7% of the amount. The 3 σ error for the amounts of the measured values of hydrogen was 0.2% of the amount. These values were taken for five 8 hr. runs at 100 lb/min.

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TRANSIENT NMR QUANTITATIVE MEASUREMENTS. GILBERT A. PERSYN and WILLIAM L. ROLLWITZ, Southwest Research Institute, San Antonio, Texas 78228.

Nuclear magnetic resonance in its transient mode not only provides a means for determining the values of the relaxation times of the nuclei being measured, but also provides a means of measuring the quantity of the nuclei with different values of relaxation times. The spin echo transient measurement can be used to determine the values of T_1 and T_2. For conditions of multiple values of T_1 and T_2, not only the different values of the relaxation times but also the number of nuclei with each of the values can be determined. When the values of T_2 are less than the equivalent relaxation time for the magnet inhomogeniety, then the amounts of the same nuclei with different values of T_2 can be measured from the free induction decay. The multiple values of relaxation times and their corresponding quantities have been measured in many hygroscopic materials using the hydrogen nuclei in the absorbant, the hydrogen nuclei in the absorbed water and the hydrogen nuclei in the oil present. The free induction decay has been used where the nuclei being measured has two values of T_2 that are favorably related such as occurs for low moisture values less than 1% in hygroscopic materials.

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APPLICATION OF WIDE-LINE NMR SPECTROSCOPY TO PLANT BREEDING. D. E. ALEXANDER, University of Illinois, Urbana, Ill. 61801.

Prior to October 4, 1960, breeding for oil content in corn was dependent upon and restricted by slow, expensive gravimetric analysis. Since that time the application of wide-line NMR has come to be accepted as a standard analytical procedure by many breeders of corn, soybeans, sunflower, safflower, rape, castors and several other species. The method is of particular advantage to breeders of oil crops in that it is nondestructive, precise, inexpensive and capable of estimating oil content on the basic unit of selection, the zygote itself. Selection for high oil content on an individual kernel basis in corn has been continuously conducted at Illinois since 1962. Oil content in Alexho Synthetic reached 10.2% in the 1968 crop. Results of similar selection experiments carried out with collaborators in Spain and Peru will be summarized. Performance trials suggest that hybrids possessing as much as 8% oil perform as well as commercial hybrids containing 4-4.5% oil. Exciting opportunities for ultra high intensity selection for oil content in certain species now exist because of the development of short scan time spectroscopes. One such experiment will be proposed.

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NMR METHOD FOR RAPID NONDESTRUCTIVE OIL CONTENT DETERMINATION IN SEEDS. R. BLINC, V. ERZEN, J. POROK, S. VRSCAJ, I. ZUPANCIC and J. DUMANOVIC, "J. Stefan" Nuclear Institute, Jamova 39, Ljubljana, Yugoslavia.

Nuclear magnetic resonance instrument for nondestructive oil content determination is described. The instrument is a modification of wide-line NMR spectrometer with possibilities to adjust for transient method the various parameters: r.f. power, modulation frequency and amplitude, sweep range and time. It is possible to suppress the water signal with respect to oil by 1:15 in corn seeds, providing the water content is less than 8%. The signal is automatically recovered in digital form. One measurement is finished in 10 sec. The method has been applied to the sunflower and rape seeds in order to measure the oil content per volume. Results are compared with the results of the chemical methods. An estimation of reliability and accuracy of the NMR method is given. In corn seed the oil content has been measured for genetical selection purposes.

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THE BIOSYNTHESIS OF GLYCERYL ETHERS BY CELL-FREE PREPARATIONS OF *Tetrahymena pyriformis*. GUY A. THOMPSON, JR. and VASSILIOS M. KAPOULAS, The University of Texas at Austin, Austin, Texas 78712.

The protozoan *Tetrahymena pyriformis* contains lipids rich in glyceryl ethers, principally chimyl alcohol. A cell-free enzyme system from *Tetrahymena* will catalyze the biosynthesis of glyceryl ethers from 1-^{14}C-palmitic acid or 1-^{14}C-cetyl alcohol. The latter compound is the more efficient precursor and there is evidence that ^{14}C-palmitate enters glyceryl ethers only after reduction to the alcohol. Incorporation of both compounds into ethers requires the presence of CoASH, ATP, Mg^{+2}, and reduced pyridine nucleotides. The glyceryl moiety is derived from glycerol-3-phosphate, or, more efficiently, glyceraldehyde-3-phosphate. Centrifugation studies have shown that the highest enzymatic activity resides in the 100,000 *g* supernatant. The activity is essentially unchanged after 24 hr dialysis at 4 C or storage for 2 weeks at -20 C. If this fraction is incubated with ^{14}C-cetyl alcohol in a complete system minus reduced pyridine nucleotides, little glyceryl ether formation occurs, but an unknown alkali-stable polar lipid accumulates. Addition of NADPH to the incubation mixture brings about the rapid formation of free glyceryl ethers. A similar pattern is observed in the 27,000 *g* supernatant except that the NADPH-induced glyceryl ethers are not released in free form but rather are incorporated into phospholipids and diacyl glyceryl ethers. The unknown alkali-stable compound can be isolated in relatively pure form. It yields another, less polar compound following acetolysis and saponification. Characterization of these possible glyceryl ether intermediates is now in progress.

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SYNTHESIS OF GLYCERYL ETHERS IN A CELL-FREE SYSTEM FROM *Tetrahymena pyriformis*. SAMUEL J. FRIEDBERG and RONALD C. GREENE, University of Texas Medical School at San Antonio, San Antonio, Texas 78229.

In the past year we have presented evidence that glyceryl ethers are synthesized from long chain alcohols and from a triose rather than from glycerol. This work was done in *Tetrahymena pyriformis*. The present report concerns the synthesis of glyceryl ethers in a cell-free system prepared from this organism. *Tetrahymena* were harvested by low-speed centrifugation and washed

once in ice-cold phosphate buffer pH 7.2 containing 0.25 M sucrose and 0.04 M sodium fluoride. The cells were resuspended in the same buffer and disrupted by sonication. The material was then spun at 8,000 *g* for 20 min and the supernatant saved. The enzyme system, containing both microsome and supernatant, could be stored in the frozen state, but the duration of the activity under these circumstances has not yet been determined. Incorporation of ^{14}C-cetyl alcohol into ether linkage was maximal with the addition of ATP, Coenzyme A, magnesium, ^{14}C-cetyl alcohol and glyceraldehyde-3-phosphate. Glyceryl ethers were liberated by treatment with lithium aluminum hydride and their identity established by gas liquid chromatography of their isopropylidene derivatives. ^{14}C labeled cetyl phosphate and pyrophosphate could not be substituted for cetyl alcohol and ATP in this system. Incorporation of activity from ^{32}ATP into a cetyl alcohol ^{14}C labeled compound could not be demonstrated. Several radioactive peaks derived from ^{14}C-cetyl alcohol were present on thin layer chromatograms. Although these might represent various postulated intermediates they have not yet been identified. The results reported here seem to be identical with those reported by Snyder et al. in mouse tumor.

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STRUCTURE AND BIOSYNTHESIS OF PHYTANYL GLYCEROL ETHER CONTAINING LIPIDS IN EXTREMELY HALOPHILIC BACTERIA.

M. KATES, E. L. PUGH and M. K. WASSEF, University of Ottawa, Ottawa 2, Canada.

The lipids of extremely halophilic bacteria are unusual in that they consist virtually exclusively of glycerol ether derivatives in which all the hydrocarbon chains are phytanyl (3, 7, 11, 15-tetramethylhexadecyl) groups. Both diether and monoether derivatives have been found. The diether derivatives consist mostly of di-*O*-phytanyl analogs of phosphatidyl glycerophosphate and phosphatidyl glycerol. The monoethers are derivatives of both *sn*-3-*O*- and 2-*O*-monophytanyl glycerol. Radioisotopic studies with various labeled precursors in whole-cell systems showed that the mevalonate pathway is utilized exclusively for biosynthesis of the phytanyl groups. Incorporation of glycerol into the diphytanyl glycerol ether probably occurs via a dehydrogenation step at C 2. Studies with cell-free systems indicate that incorporation of the phytanyl group into the glycerol ethers probably occurs via phytanyl pyrophosphate. Investigations on the nature of the glycerol-derived intermediate(s) involved in biosynthesis of the phytanyl glycerol ethers will be reported.

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PLASMALOGENS IN BACTERIA.

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Plasmalogens have been found in a number of gram-positive and gram-negative, anaerobic bacteria. The bulk of these alkenyl ether-containing lipids is usually associated with the phospholipid fraction. The chemistry of these bacterial plasmalogens and their contribution to the total cellular lipid will be outlined. Studies on the biosynthesis of plasmalogens in *Clostridium butyricium* will be described and possible biosynthetic routes will be evaluated. The question of whether studies on plasmalogen metabolism in bacteria can serve as a model for that in animal tissues will also be considered.

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THE ART OF OIL-SEED MEAL GRINDING.

GEORGE R. THOMAS, Prater Pulverizer Co., Chicago, Ill. 60650.

Meal grinding is an art, or a science, because one cannot just introduce meal to a hammermill without carefully planning for the quality of the finished product. There may be a slight difference of opinion as to the specifications of the finished grind but generally, they all closely agree on a narrow range of sieve analysis without excessive coarse or fine particles. To accomplish this, many features must be built into a meal grinder, and the meal grinder must be installed in the system properly. The original concept of solvent extracted soybean meal grinding was to use the two stage grinding system. However, the advent of front end hull removal equipment resulted in the development of the single stage grinding system, utilizing the grinders with just one sifter. This system lends itself well to grinding right on stream. Meal grinding installations must be carefully planned to accommodate all parameters such as desired consistency of finished product, dust control, conveyance systems, placement of all equipment in meal grinding system, and provisions for hot-meal or wet-meal grinding requirements. Ideas on all of the above, as well as on figuring capacities for required production on various similar oil-seed products, will be discussed.

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SCREENING AND TAIL END DEHULLING.

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In tail end dehulling operations, the three indispensable elements of the typical system are the hammermill, the screen and the specific gravity separator. On the proper selection of these elements depends the success that will be achieved in attaining the system's objective: the product of maximum yield of high-protein, low-fiber meal. The screening and separating equipment, their interactions with each other and with the hammermill, and the factors that influence their performance in terms of the system's objective will be discussed.

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DUST CONTROL.

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Good dust control in a solvent plant includes control at the grain receiving pits, the storage area, the grain drier preparation building and the meal handling area. The techniques and equipment required are fairly standardized. The four types of collectors available are the cyclone, wet scrubber, filter and electrostatic precipitator. Of these, the cyclone has been by far the most common because of its relatively low cost. The next most used collector has been the filter. The electrostatic precipitator is not suitable for grain collection because of the explosion possibility. The wet scrubber has not been used to any great degree in grain handling plants; however, the scrubber plus the filter, may find wider use in the future because of the new air pollution laws. Most State Air Pollution Codes are set up on the basis that a certain emission rate of dust into the atmosphere is allowed for a given amount of product being handled. In most cases collector efficiencies will have to be greater than 90% to meet the code and this makes the use of cyclones questionable. Filters will have to be used more frequently in the future to assure compliance with pollution codes. The wet scrubber may also be used more extensively, especially in the preparation area on such applications as flaking rolls where high humidity precludes the use of filters.

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SUNFLOWER PROCESSING TECHNIQUES.

ROBERT M. PIERCE, Minnesota Linseed Oil Co., Minneapolis, Minn. 55421.

A great deal of interest has recently been shown in sunflower seed as an oilseed crop. The introduction of new Russian seed varieties with higher oil content have helped to stimulate this interest, particularly in the flax and cottonseed growing areas. This paper will present background material on sunflower processing, including seed structure, oil and meal quality, and certain economic considerations. Processing techniques currently used, comparisons with the processing of other oil seeds, storage and handling of the seeds, meal and oil, extraction, and seed preparation and handling prior to extraction will be discussed. Sunflower seeds are nearly 30% hulls, high in crude fiber content. For this reason, dehulling and hull separation practices are important aspects of processing sunflowers. Expeller operating variables are also important where prepressing is part of the process. Direct solvent extraction and prepress-solvent extraction methods are currently being used successfully. Features of both methods and their applicability are discussed along with seed preparation needed for each method.

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THE USE OF COUNTER-CURRENT DISTRIBUTION IN THE SEPARATION OF INDIVIDUAL MOLECULAR SPECIES OF PHOSPHOLIPIDS.

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To measure the specific radioactivity of individual phosphatidyl cholines (diacyl GPC) and phosphatidyl ethanolamines (diacyl GPE) a two-step fractionation is necessary. Argentation thin layer chromatography yields fractions differing in degree of unsaturation, and counter-current distribution will separate these fractions further on the basis of both chain length and unsaturation. The former techniques will not seperate 1-palmitoyl-2-linoleoyl GPC from 1-stearoyl-2-linoleoyl GPC. Reversed phase thin layer chromatography can be used to separate on the basis of chain length but is only efficient at low concentrations. Compounds containing oleic or palmitoleic acids at the 1 position are not readily separated from the corresponding compounds with a saturated fatty acid at the 1 position by either silver nitrate or reversed phase chromatography. In these cases, where the separations are not complete, counter-current distribution provides a powerful tool. The use of this technique will be illustrated with both diacyl GPC and diacyl GPE. In the latter case the conversion of the native phospholipid to its methylated and dinitrophenylated derivative produces a nonpolar compound and improved resolution can be obtained with all the methods investigated. The analysis of the counter-current distribution of a mixture of several compounds can be facilitated by the use of a computer.

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REACTION THIN LAYER CHROMATOGRAPHY IN THE ISOLATION AND CHARACTERIZATION OF SPHINGOLIPIDS.

C. V. VISWANATHAN, F. PHILLIPS and W. O. LUNDBERG, The Hormel Institute, Austin, Minn. 55912.

After briefly surveying methods of reaction thin layer chromatography developed in this laboratory for the characterization of phosphatide plasmalogens, extension of these and similar methods in the isolation and characterization of brain sphingolipids such as sphingomyelins, cerebrosides, sulfatides and gangliosides will be described and discussed.

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PREPARATION AND CHARACTERIZATION OF MURINE PHOSPHOLIPASE.

ATHOS OTTOLENGHI, Duke University Medical Center, Durham, N.C. 27706.

A phospholipase which hydrolyzes lecithin, lysolecithin cephalin and phosphatidic acid with liberation of fatty acid and the corresponding glycerol-phosphoryl moiety has been isolated and partially purified from mouse intestine. Stable preparations of high specific activity have been obtained by fractionation with citrate and absorption on calcium phosphate gel. The enzyme is active on biological structures such as red blood cells of a variety of species and beef heart mitochondria. In the former, the enzyme action results in hemolysis; in the mitochondria, a progressive loss of NADH oxidase and succinate-cytochrome c reductase is observed. The succinate-cytochrome c reductase can be restored by addition of microdispersed mitochondrial lipids.

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PLATELET LIPIDS.

C. V. VISWANATHAN, F. PHILLIPS, W. O. LUNDBERG, C. A. OWENS, H. F. TASWELL and E. J. W. BOWIE, The Hormel Institute, Austin, Minn. 55912.

Characterization of lipids of blood platelets that are important in blood coagulation is still somewhat limited, largely because of limitations on the quantities of human blood samples that can be used for platelet lipid analysis, and the development of microtechniques therefore became necessary. Studies of human and animal platelet lipids contained in 50 to 100 ml of blood revealed two glycolipids and also glycerol ether choline phosphatides. These lipids were characterized chemically; also, fatty acid chains of alkenyl acyl and diacyl ethanolamine phosphatides were characterized separately. Comparatively detailed lipid analysis of a number of samples from normal and abnormal human platelets will be presented and discussed.

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LIPID COMPOSITION OF BEEF AND HUMAN PITUITARY GLANDS.

H. SINGH and K. K. CARROLL, University of Western Ontario, London, Canada.

The lipids of beef anterior and posterior pituitary and human pituitary as a whole were extracted with chloroform-methanol (2:1) and separated into neutral lipids and phospholipids by column chromatography. Beef pituitary lipid contained about 25% neutral lipids and 75% phospholipids whereas neutral lipid made up approximately 60% of the total in human pituitaries. The main neutral lipids in human pituitary were triglycerides, cholesterol, free fatty acids and an unidentified component in the triglyceride fraction. Cholesterol was the major neutral lipid component in freshly collected beef anterior and posterior pituitary but the amount of free fatty acids appear to increase during storage. Preliminary investigation of the unknown neutral lipid

in human pituitaries suggested that it was an unsaturated hydroxy compound with no carbonyl functions. Thin layer chromatography indicated that it was also present in smaller amounts in freshly collected beef pituitaries. The main phospholipids of beef anterior, posterior and human pituitary were phosphatidyl ethanolamine, phosphatidyl choline, phosphatidyl inositol, phosphatidyl serine and sphingomyelin. The fatty acid composition of total neutral lipids, free fatty acids, total phospholipids, phosphatidyl ethanolamine and phosphatidyl choline were determined by GLC. Mixtures of saturated and unsaturated fatty acids ranging from C_{12} to C_{22} were present but the main fatty acids were palmitic, stearic, oleic, linoleic and arachidonic.

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THE PHOSPHOLIPIDS OF MATURE BOVINE AND RABBIT RETINA.

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Phospholipids of mature bovine and rabbit retina have been studied. Two-dimensional TLC followed by phosphorus assay revealed that each specie has identical phospholipid class distributions. LPC was 2.6 ± 0.7 (mole % P + S.D.) in rabbit and 0.2 ± 0.2 in bovine; SPH, 4.4 ± 0.7 and 2.1 ± 0.0; PI, 4.3 ± 0.6 and 5.6 ± 0.8; PS, 7.4 ± 2.0 and 10. ± 1.1; PE, 34.7 ± 1.9 and 34.1 ± 2.0; PC, 43.9 ± 2.7 and 43.2 ± 0.9 in rabbit and bovine, respectively. In addition, GLC analysis of the fatty acids of the individual phospholipid classes revealed that the same classes from each species have characteristic and nearly identical fatty acid compositions. For example, the major fatty acids of PI from each species are 18:0 (41% and 36%, rabbit and bovine, resp.) and 20:4 (34% and 42%), while in PS, the major acids are 18:0 (43% and 34%) and 22:6 (20% and 24%). The PC from each specie contains 16:0 (42% and 41%), 18:0 (16% and 18%), and 18:1 (19% and 19%), and has only modest amounts of polyunsaturates. In contrast, the PE contains mostly 18:0 (27% and 32%) and 22:6 (25% and 30%). Our results suggest that a common retinal phospholipid pattern may exist between species. Retinas from other animals are now being examined to test this hypothesis.

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LIPID BROWNING REACTION: I. REACTION OF SATURATED ALDEHYDES WITH PHOSPHOLIPIDS.

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Saturated normal aliphatic aldehydes were permitted to react with hydrogenated and non-hydrogenated phospholipids from egg yolk in a model freeze-dried system. The system was prepared by freeze-drying a slurry of phospholipid, aldehyde and cellulose in borate buffer at pH 6.0. Rapid browning ensued on holding at 90 C for 2 hrs. The products of the reactions were extracted from the cellulose matrix by extraction first with 80% ethanol followed by extraction of the residue with chloroform. The extracts were further fractionated on columns of silicic acid. The alcohol extracts contained both nitrogen and phosphorus while the chloroform extract contained phosphorus but no nitrogen. Infrared spectra of the fractions containing nitrogen confirm the presence of $-\overset{|}{\underset{|}{C}}-\overset{|}{N}-H$, $-C=N-$ and $C\equiv N$ groups. Spectra of other fractions from this extract confirm the presence of a methyl phosphatidate. Saturated normal aliphatic aldehydes may react with phosphatidyl ethanolamine to form a Schiff base compound which, in turn, undergoes molecular rearrangement and fission to yield the observed products.

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PHOSPHATIDES OF *Chlamydia Psittaci*, STRAINS MENINGOPNEUMONITIS AND 6BC.

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Analyses of phosphatidyl choline (PC) and phosphatidyl ethanolamine (PE) extracted from *Chlamydia psittaci*, strains meningopneumonitis (MN) and 6BC, were made to determine characteristic structural differences between non-pathogenic (MN) and pathogenic (6BC) strain of psittacosis agents. Chlamydial agents are filterable (0.45 μ filter), obligate intracellular bacteria which contain 20-30% total lipid of which 60-80% is phospholipid. Organisms cultivated in the chick embryos were harvested from allantoic fluid, washed by repeated alternate high and low speed sedimentation. The lipids were extracted and analyzed using conventional techniques. PE and PC fractions constitute almost 80% of the total phospholipid. The ratio of PC/PE in the non-pathogen (MN) was 1:1 whereas in the pathogen (6BC) the ratio was 1:0.68. Branched fatty acids were found as components in both organisms but were not found in host tissue. The 15:0 anteiso branched chain fatty acid was present in higher concentration in the total lipid of MN (15%) than in 6BC (9%). Separation and analysis of the phosphatides and plasmalogens of PE and PC fractions after mild acid hydrolysis on thin layer chromatography and enzymatic deacylation revealed the presence of the 15:0 branched chain fatty acid exclusively in the beta position of PE (44%). This component was essentially absent in the PC fractions and the PE plasmalogen. Mass spectral data confirmed the structure of this compound. The plasmalogens constituted about 26% of the total PC and PE fraction. These data show that detailed structural lipid analysis may serve as a tool for differentiating microbial strains.

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AN ADDITION COMPOUND OF TOCOPHEROL AND LINOLEIC ACID.

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Evidence is presented for the formation of an addition compound of oxidized dl-alpha-tocopherol and linoleic acid. The compound is formed when the components are adsorbed in mixed monolayer on silica gel at a molecular ratio of 1:20, and subjected to heating in air at 80 C. A relatively nonpolar tocopheryl quinone is also formed in smaller amounts. These are the major tocopherol oxidation products isolated in this system and do not correspond to any known to the authors. The addition compound has about the same mobility as linoleic acid in most TLC and chromatographic systems, but can be isolated by successive chromatography on silica and gel filtration on Sephadex LH-20. It yields a single spot in TLC in several systems. The elemental analysis is reproducible and consistent with a simple addition compound of linoleic acid and bivalently oxidized tocopherol. The compound has a carboxyl group which can be esterified. The ester has about the same TLC mobility as methyl linoleate. The molecular weight of the ester is 723. The ultraviolet spectrum

$$\xrightarrow{\text{ETOH}}$$

shows a single peak, λ max = 3000 A°, E = 4.5. The infrared spectrum shows a strong chroman ether band at 9.14 μ, a strong methyl band at 7.24 μ and carboxyl but no hydroxyl absorption. The NMR spectrum shows, in contrast to that of tocopherol, a reduction in aromatic methyl protons, a carboxyl proton exchangeable with deuterium oxide, but no hydroxyl proton. The compound does not reduce Emmerie-Engel reagent prior to treatment with concentrated hydriodic acid, nor do the ether-extractable products after such treatment. The present data are consistent with an addition product whose bridging group is a new chroman ring.

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CYCLIZATION OF UNSATURATED FATTY ACIDS.

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The cyclization of linolenic, linolenelaidic and α-eleostearic acid has been studied in alkaline diethylene glycol solutions at 180-220 C. The nonconjugated linolenic acid undergoes allylic rearrangement by an alkali-induced ionic reaction. The conjugated acids exhibit *cis-trans* rearrangement and shifts of the triene-system. The *t,c,t*-triene formed by this reaction is cyclized in a thermal multicenter process to yield ω-(2-alkylcyclohexadienyl)-carboxylic acids. As a result of migration of the dien-systems, all conceivable cyclohexadienes and cyclohexenes having conjugated semi-cyclic double bonds are observed. Part of the cyclic dienes form *o*-alkyl substituted aromatic carboxylic acids by losing two hydrogen atoms. All the isomeric *o*-alkyl substituted aromatic carboxylic acids could be identified by IR, UV, gas chromatography, mass spectrometry and by comparison with synthetic compounds. Interpretation of the reaction mechanism is greatly facilitated by the nightly significant distribution of the alkyl and ester side chain length for each for the acids investigated. An alternative mechanism for the formation of aromatic acids is discussed. In a two-step reaction involving hydride transfer, alkyl-cyclohexadienyl carboxylic acids may give aromatic acids and alkyl-cyclohexenyl carboxylic acids. Bicyclic alkyl-indanyl carboxylic acids were found as a by-product of the aromatization reaction.

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CHEMICAL REACTIONS OF TRIOLEIN UNDER SIMULATED DEEP FAT FRYING CONDITIONS.

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Linoleic and oleic acids are the most common fatty acids present in fats used for deep fat frying. Changes of trilinolein were reported in previous papers. In the present paper changes of triolein are discussed. Triolein was heated under simulated deep fat frying conditions at 185 C for 24 hr. The thermally oxidized triolein was converted into methyl esters, and then fractionated by urea. The urea adduct-forming esters were found to be methyl oleate. The non-urea adduct-forming esters (10.8% in comparison with 26.3% in case of trilinolein) were further separated by silicic column chromatography into nine fractions with molecular weights ranging from 304 to 742, some of them containing oxygen atoms which could not be accounted for by ordinary functional group analyses. The nonpolar dimers, characterized after further purification by TLC and GLC by elemental and functional group analyses, IR and NMR spectrometry, consisted of equal amounts (1.36% each) of a noncyclic dimer and a noncyclic dimer containing a carbonyl group. No cyclic dimers were detected contrary to thermally oxidized trilinolein. The polar polymers (7.07% compared to 13.3% in case of trilinolein) were studied by depolymerization, TLC fractionation, and elemental and functional-group analyses. They consisted of 1.91% noncyclic dimers and trimers through carbon to carbon linkages, 1.07% of noncyclic trimers through carbon to carbon linkages, 3.06% noncyclic dimers and trimers through carbon to oxygen linkages and carbon to carbon linkages in the same molecules, and also dimers and trimers in which all the monomeric fragments were joined through carbon to oxygen linkages. As oxygen linkages were not reduced by hydrochloric acid and reduced by hydroiodic acid they are probably ether linkages.

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CONJUGATED NONADIENES FROM PYROLYSIS OF UNSATURATED ACETATES.

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Current studies on odor thresholds of hydrocarbons autoxidatively derived from fats required the preparation of 1,3- and 2,4-nonadienes. These conjugated diolefins are difficult to prepare and have been rarely reported in the literature. The pyrolysis of 3-acetoxy nonene-1 and 4-acetoxy nonene-2 was investigated as a route to 1,3- and 2,4-nonadienes, respectively. 1-Nonene-3-ol and 2-nonene-4-ol were prepared by the addition of acrolein and crotonaldehyde to the appropriate Grignard reagent. Their acetates were prepared by acetylation either with acetic anhydride or acetyl chloride in pyridine. Pyrolysis of the acetates was carried out over glass helices at 400 C. Distillation of the pyrolysates gave the dienes in approximately 75% yield based on titration of acetic acid liberated during pyrolysis. Two different side reactions were observed. Since allylic ester gave approximately a 50:50 mixture of the 1,3- and 2,4-isomers, an observation earlier was confirmed that allylic esters may rearrange before elimination. The vinyl ester gave 85% and 15% of the 1,3- and 2,4-isomers, respectively. The presence of the 2,4-isomer is presumably caused by thermal rearrangement and is contrary to literature reports. In pyrolysis, both the vinyl and allylic acetates gave conjugated products almost exclusively. Ultraviolet spectroscopy showed epsilon values in the range of 24,000 to 27,000. Although pyrolysis produces a mixture, the positional isomeric dienes are separated by preparative GLC. The preparation and characterization of 1,3- and 2,4-nonadienes from pyrolysis of unsaturated acetates will be described and limitations of the method discussed.

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KINETIC STUDY OF ACID CATALYZED CONVERSION OF AFLATOXINS B_1 AND G_1 TO B_{2a} AND G_{2a}.

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Adjusting aqueous alkaline solutions of aflatoxins B_1 and G_1 to pH values of 1, 2 and 3, and heating in the range of 40-100 C resulted in the conversion of B_1 to B_{2a}, and G_1 to G_{2a} as major products. The conversion products were identified by co-chromatography with authentic B_{2a}, G_{2a} and M_1 on silica gel coated thin layer plates, using four different development solvents. The

rate of conversion was followed by TLC of aliquots of the heated solutions, using fluorodensitometry to estimate residual B_1 and G_1. The rates of disappearance of B_1 and G_1, at constant temperature and pH, were first order with respect to each aflatoxin. The average relative increase in k (min^{-1}) per 10 C was 1.8 for B_1 and 2.0 for G_1. At a given temperature the reaction is strongly pH dependent, with the average relative increase in k per 10-fold increase in hydrogen ion concentration (1 pH unit) being 8.4 for B_1 and 10.2 for G_1.

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MRA MICROREACTIONS FOR LIPID ANALYSIS. E. D. BITNER, ALAN C. LANSER and H. J. DUTTON, Northern Regional Research Laboratory, Peoria, Ill. 61604.

Many types of reactions can be performed on a microscale with the microreactor apparatus (MRA) system which incorporates a modified soldering gun. Procedures and results of some typical reactions include bromination of olive methyl esters, hydrazine reduction of oleic acid, silylation of castor methyl esters, hydrogenation of soybean methyl esters, several methods of methyl ester preparation from soybean fatty acids, and saponification of soybean triglycerides followed by esterification. The reaction chamber of the MRA has been redesigned to increase its versatility and to reduce explosion hazards when diazomethane is used. Advantages of the MRA over other systems are less handling of sample, minimum hazards due to small sample size, and direct injection of products into analytical instruments, such as a gas chromatograph or mass spectrometer.

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THE BIOSYNTHESIS OF PLASMALOGENS IN MAMMALIAN TISSUES. H. H. O. SCHMID and T. TAKAHASHI, The Hormel Institute, Austin, Minn. 55912.

Labeled fatty acids were injected into various organs of rats and the radioactivity of the acyl and alk-1-enyl moieties of the glycerophosphatides were determined after 3, 6 and 22 hr. Minute amounts of free aldehydes having high specific activities were isolated. Total radioactivity was found to be incorporated into free aldehydes at about the same rate as into the alk-1-enyl moieties of the ethanolamine phosphatides, but the specific activities of the free aldehydes were several thousand times higher. Data are presented which suggest that fatty acids, administered to mammalian tissues, are reduced slowly to the corresponding aldehydes which are then incorporated into the alk-1-enyl moieties of plasmalogens.

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BIOSYNTHESIS OF PHOSPHATIDATE AND NEUTRAL GLYCERIDES FROM TRIOSE PHOSPHATES BY RAT LIVER MICROSOMES. LARRY E. PULEO, G. ANANDA RAO, M. F. SORRELS and RAYMOND REISER, Texas A&M University, College Station, Texas 77843.

It has been previously suggested that there are biosynthetic mechanisms for glyceride synthesis other than the glycerol 3-phosphate (GP) pathway. These alternate routes utilize dihydroxyacetone phosphate (DHAP) and glyceraldehyde 3-phosphate (GAP) as direct acyl acceptors. Present investigations show that rat liver microsomes, washed by suspension in sucrose (0.25 M) and centrifugation, can produce phosphatidate and neutral glycerides from DHAP or GAP and fatty acids. Cofactors required for this process are ATP, CoA, Mg^{++}, and either NADH or NADPH. NADH is twice as active as NADPH. L-GP:NAD oxidoreductase (EC 1.1.1.8) was absent in the washed microsomes, demonstrating that the synthesis of glycerides from either DHAP or GAP does not require a prior conversion to GP. Appreciable oxidation of NADH by microsomes was observed in the presence of GAP and L-GP:NAD oxidoreductase suggesting the presence of D-GAP ketol isomerase (EC 5.3.1.1) in this organelle. Hence the formation of DHAP from GAP may be necessary for glyceride synthesis.

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THE NONCONVERSION OF 5,11,14-20:3 INTO 5,8,11,14-20:4. H. SCHLENK, J. GELLERMAN and D. SAND, The Hormel Institute, Austin, Minn. 55912.

Uniformly ^{14}C-labeled 5,11,14-20:3 was administered to rats that had been on fat-free diet for 260 days. After 12 hr the animals were killed and the liver lipids investigated in particular for conversion of 5,11,14-20:3 into 5,8,11,14-20:4. Virtually all radioactivity was in phospholipids, and among their acids it was in those of chain length C_{20}. After fractionation by GLC, the ratio of ^{14}C in 5,11,14-20:3 and in 5,8,11,14-20:4 was about 100:1. However, with the former migrating closely ahead of the latter acid, some trailing is to be expected. The order of migration is changed in reversed polarity PC and after such separation the ratio of ^{14}C in the two acids was 100:0.3. In addition, ^{14}C-5,11,14-20:3 mixed with cold rat liver fatty esters was subjected to the same separation procedures with very similar results for the radioactivity found with, but not in 5,8,11,14-20:4. Apparently, 5,11,14-20:3 has not been converted into 5,8,11,14-20:4 by the rat under the conditions chosen here. Takagi reported in 1965 from experiments where cold 5,11,14-20:3 had been fed to rats that such conversion took place very efficiently. Different age, strain, condition of rats, time given for conversion, etc. may account for quantitative differences. These factors may deserve further investigation, but it seems unlikely that they can cause the opposite results.

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BIOSYNTHESIS OF STEROLS AND STEROL ESTERS. ANN M. DNISTRIAN and R. CECIL JACK, St. John's University, Jamaica, N.Y. 11432.

The biosynthesis of sterols and sterol esters was investigated in cultures of the fungus *Glomerella cingulata* at 1½, 2, 3, 4 and 5 days old. Synthesis was defined as the specific activity of the sterols and sterol esters isolated from cultures which were pulse labeled with 2-^{14}C-acetate or with 2-^{14}C-mevalonate for 30 min. With both precursors, the greatest synthesis of sterols occurred when the cultures were between 2 and 3 days old. This maximum synthesis declined rapidly within 24 hr. With both precursors, also, the peak of sterol ester synthesis was attained about 24 hr later than the peak of sterol synthesis; but, like sterol synthesis, the synthesis of sterol esters from the two precursors declined rapidly after maximum synthetic activity had been attained. Assay of the acyl and sterol moieties of the sterol esters for radioactivity revealed that acetate was incorporated into the acyl moieties to a greater extent than into the sterol moieties and that the peak of radioactivity in unesterified sterols preceded the peak of radioactivity in the sterols derived from sterol esters.

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BIOLOGICAL REDUCTION OF FATTY ACIDS TO ALCOHOLS IN FISH. DONALD M. SAND and HERMANN SCHLENK, The Hormel Institute, Austin, Minn. 55912.

Gourami *(Trichogaster)* fish, like mullet *(Mugil cephalus)*, have wax esters as major components (80%) of their egg lipids. The wax esters contain polyunsaturated alcohols and acids of identical double bond structures. The analytical evidence suggests close biosynthetic relationship between alcohols and acids, and this was verified by feeding labeled compounds to gouramis. Incorporation of ^{14}C into wax esters from uniformly labeled 16:0 acid and methyl ester, and 18:0 methyl ester was 20-30%. Most of that radioactivity (nearly 90%) was in the alcohol moiety as 16:0 and 18:0, respectively. Identical results were obtained from feeding [1-^{14}C] 16:0 methyl ester; 16:0 alcohol was incorporated into waxes at the same level as the acid or methyl ester, and the ratio of ^{14}C in alcohols-acids was again 9:1. Palmityl [1-^{14}C] acetate yielded more ^{14}C in alcohols than in acids of wax esters; 18:1, 18:2ω6, 18:3ω3, 20:4ω6, and 22:6ω3 were reduced to the corresponding alcohols but not to so great an extent. The experiments show that 16:0 acid is efficiently reduced; that unsaturated acids can also be reduced; that acid can arise from alcohol; and that alcohols involved in these reactions are readily incorporated into wax esters.

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THE TOTAL SYNTHESIS OF PHOSPHATIDES CONTAINING ACETYLENIC ACIDS AND THEIR ACTIVITY IN BLOOD CLOTTING. D. L. TURNER, M. J. SILVER, R. R. HOLBURN, E. BACZYNSKI, S. F. HERB and F. E. LUDDY, Jefferson Medical College, Philadelphia, Pa. 19107.

Phosphatides containing acetylenic acids are of special interest in blood coagulation studies because of the alleged resistance of acetylenic acids to autoxidation. DL-1-(2'-tetrahydropyranyl)-glycerol was treated with the acid chloride of stearolic acid to make the DL-1,2-dioctadecynoyl-3-(2'-tetrahydropyranyl)-glycerol, from which the tetrahydropyranyl group was removed to give the diglyceride. A diglyceride was also made from DL-2-stearoyl glycerol with stearolic acid chloride. The two diglycerides were purified by silicic acid chromatography. They were used in phosphatide synthesis by combination with phosphorus oxychloride and either *tert*-butyloxycarbonylaminoethanol or the phthalimidomethyl ester of anisyloxycarbonyl-L-serine. This gave the four protected phosphatides. The *tert*-butyloxycarbonyl group and the anisyloxycarbonyl group were removed with formic acid at room temperature while the phthalimidomethyl group was removed with hydrazine. Thus, dioctadecynoylphosphatidylethanolamine, dioctadecynoylphosphatidylserine, stearoyl, octadecynoyl PE and stearoyl, octadecynoyl PS were obtained. These were purified by chromatography on DEAE cellulose acetate and silicic acid and their fatty acids were analyzed by GLC, showing duplication of the composition of the fatty acids used for their preparation. The phosphatides were tested after solubilization with sodium desoxycholate or albumin, using the Hicks-Pitney test and the antithromboplastin test. The dioctadecynoyl PS had about the same anticoagulant activity as beef brain PS in the antithromboplastin and Hicks-Pitney tests. The dioctadecynoyl PE was an accelerator in the Hicks-Pitney test. The Phosphatidyl-Ethanolamine with only one acetylenic acid was not well solubilized and had considerably less activity than the dioctadecynoyl phosphatide.

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THE BIOSYNTHESIS OF ALKYL GLYCERYL ETHERS BY A MICROSOMAL ENZYME SYSTEM FROM EHRLICH ASCITES CELLS: KINETIC AND STRUCTURAL STUDIES. ROBERT L. WYKLE and FRED SNYDER, Oak Ridge Associated Universities, Oak Ridge, Tenn. 37830.

A new metabolic pathway by which a microsomal enzyme system from mouse preputial gland tumor synthesizes alkyl glyceryl ethers from glyceraldehyde-3-PO_4 and long chain alcohols in the presence of ATP, CoA, and Mg^{++} has been recently described. Using a microsomal enzyme system and the conditions described for the preputial gland tumor system, the same pathway is demonstrated in Ehrlich ascites cells. The Ehrlich ascites cell system has proven to be more suitable for kinetic studies, since wax formation is essentially absent. Products and intermediates were characterized by chromatography of organic derivatives. Isopropylidene derivatives, products of $LiAlH_4$ reduction, and periodate oxidation products indicate that alkyl dihydroxyacetone phosphate and alkyl dihydroxyacetone are intermediates in this system.

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QUANTITATIVE MEASURE OF GEOMETRICAL ISOMERIZATION DURING THE PARTIAL HYDROGENATION OF TRIGLYCERIDE OILS. LYLE F. ALBRIGHT, ROBERT R. ALLEN and M. C. MOORE, Purdue University, School of Chemical Engineering, Lafayette, Ind. 47907.

A mathematical model has been developed using a digital computer for the calculation of the isomerization index for a partially hydrogenated oil, such as cottonseed, soybean, peanut or corn oil. This model is an expansion of the one presented earlier by Albright for determining the selectivity ratio of hydrogenated oils. The isomerization index is defined as the ratio of the rate of geometrical isomerization of an unsaturated group to the rate of hydrogenation. The assumptions required in the development of the isomerization model are explained and justified. Isomerization indices from about 0.3 to 11 were found to occur for hydrogenations using commercial nickel catalysts. Calculation of both an isomerization index and a selectivity ratio will be useful methods of quantitatively characterizing the partial hydrogenation of triglyceride oils or the type of hydrogenation which can be obtained by various catalysts.

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COMPUTER TREATMENT OF SPECIFIC HEAT DATA DETERMINED BY DIFFERENTIAL SCANNING CALORIMETRY. H. L. ROTHBART, J. W. HAMPSON, R. A. BARFORD and V. G. MARTIN, E. Utiliz. Res. Dev. Div., ARS, USDA, Philadelphia, Pa. 19118.

Differential Scanning Calorimetry may be used for the determination of specific heats of polymorphic lipids. Sapphire is used as a reference material. Difficulties in processing the large volume of data are overcome by use of the IBM 1130 computer. The data is manually punched on cards. A computer program has been developed to determine: the specific heat as a function of temperature; the lowest-order polynomial which adequately

fits the data; and predictive and mean confidence limits for the polynomial. The curve and confidence limits are automatically drawn on a plotter after a tabulation of specific heat at various temperatures, and the equation of the curve has been printed out. Studies of benzoic acid and the three polymorphic forms of tristearin, tripalmitin, trimyristin and trilaurin have been made from -90 to +100 C. The results compare well with literature values.

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GE TIME-SHARING—A VERSATILE TOOL FOR COMPUTER ANALYSIS OF ANALYTICAL CHEMISTRY DATA. MAX TOCHNER, General Electric Co., Silicone Products Dept., Waterford, N.Y. 12188.

The General Electric Time-Sharing Computer System can be effectively utilized for the rapid analysis of analytical chemistry data. The speed and simplicity with which a user can gain access to the system facilitates its application to problems not normally analyzed by computer. Computer programs have been implemented for a wide variety of analytical techniques. Some of the routine applications include the following: absorption spectroscopy, gas chromatography, polymer characterization, potentiometric titration, surface chemistry and thermogravimetric analysis. Specific examples of the user's interaction with the time-sharing computer from a teletype terminal are presented to illustrate the nature of the particular input information required and the associated output generated by the computer. The availability of a very simple computer language called Basic enables the analytical chemist to write programs by himself with a minimal amount of programming experience. An analytical chemist with some experience can write a program, gain access to the system, debug the program, and solve the problem in an equivalent amount of time to that required to solve the same problem by desk calculator. Evaluation of these types of applications for routine and non-routine calculations demonstrates that the time-sharing computer is faster, more accurate and even cheaper than using a desk calculator.

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THE APPLICATION OF COMPUTER TECHNIQUES AND PHASE EQUILIBRIA DATA TO LIQUID-LIQUID EXTRACTION. V. G. MARTIN, R. A. BARFORD, H. L. ROTHBART and C. R. EDDY, E. Utiliz. Res. Dev. Div., ARS, USDA, Philadelphia, Pa. 19118.

An IBM 1130 computer was employed to simulate countercurrent distributions using phase equilibria data for a three-component system. For this purpose, the solubility curves were described by empirical equations which were determined by the method of least squares utilizing the computer. Tie lines were described by their slopes and Y intercepts. Data specific to a given system is isolated in subroutines, so the main programs need not be recompiled for each separate system. The steps involved in the simulation are as follows: (a) Initial conditions within the distribution and feed profiles are stated. (b) The weight and weight fraction of each component in each tube are determined. (c) The point describing the system is located on the ternary diagram and it is determined whether or not this point lies within the immescible region and below the isopycnic tie line, (d) The weight fractions of all components in each phase are determined. (e) Densities, masses and volumes of both phases are determined. (f) All material above the cut-off arm is transferred to the next tube. This process is repeated for as many transfers as are desired. Since the computation may be lengthy for a large number of transfers, the program is interruptible. Phase volumes and compositions in all tubes at any point in the distribution may be printed out. Effluent information is printed out at the end of a run. Any feed profile and initial tube condition, as well as many types of phase diagrams, may be used. Applications will be given and compared with experimental evidence.

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A COMPUTER PROGRAM FOR RATING THE PERFORMANCE OF LABORATORIES IN ANALYTICAL CHECK SAMPLES. CARL W. FRITSCH, General Mills, Inc., Minneapolis, Minn. 55427.

The computer program described is the one used for calculating the normalized means, interlaboratory standard deviations and laboratory ratings of the AOCS Smalley Edible Fats Check Series. The program was written in Fortran and run on a CDC 3200 computer. The statistics used were those described by C. H. Perrin and E. M. Glucker (1968). It is hoped that this paper will provide collaborating laboratories with an understanding of the computation of their results and aid those who wish to write a program for other analytical check series.

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ENZYMIC PATHWAYS FOR THE BIOSYNTHESIS AND BIOCLEAVAGE OF ALKYL GLYCERYL ETHERS. FRED SNYDER, Oak Ridge Associated Universities, Oak Ridge, Tenn. 37830.

Our laboratory has recently determined the enzymic synthesis of alkyl glyceryl ethers in a number of neoplastic cells, normal cells grown in tissue culture, dogfish liver and the digestive gland or gonads of starfish. The reaction, which occurs predominantly in microsomes (on the basis of specific activities of organelles and activity in fractions collected by zonal centrifugation), uses glyceraldehyde-3-phosphate and fatty alcohols as substrates and ATP, CoA, and Mg^{++} as cofactors. At one stage NADPH is required for reduction of what we believe is an O-alkyl dihydroxyacetone-PO_4 intermediate. Recent findings of a pteridine-requiring enzyme that cleaves the O-alkyl linkage in liver cells will be summarized as related to the cleavage products formed in this reaction (fatty aldehydes, fatty acids and fatty alcohols). The activity of the cleavage enzyme system is lacking or diminished in cells rich in alkyl glyceryl ethers.

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METABOLIC RELATIONS DERIVED FROM STRUCTURAL ANALYSES OF NEUTRAL GLYCERIDES AND PHOSPHOGLYCERIDES. RANDALL WOOD and R. D. HARLOW, Oak Ridge Associated Universities, Oak Ridge, Tenn. 37830.

The distribution of fatty acids esterified at the 1 and 2 positions of phosphatidyl choline, phosphatidyl ethanolamine, phosphatidyl serine, phosphatidyl inositol and diphosphatidyl glycerol derived from rat liver and Ehrlich ascites cells was determined. Triglycerides were subjected to stereospecific analysis and GLC analysis of the intact glycerides. Diglyceride acetates derived from each of the phosphoglyceride classes were also analyzed intact by GLC. Glyceryl ether diesters and alkyl and alk-1-enyl ether-linked phosphoglycerides of the Ehrlich ascites cell lipids were subjected to analyses similar to those described for the acyl lipids. Comparison of the data revealed several quantitative and qualitative differences in the structure of glycerides and phosphoglycerides between normal and neoplastic tissue. The structure of rat liver diglycerides derived from each phosphoglyceride class was different and none resembled 1,2-diglycerides of the triglycerides: these results differed from that obtained for Ehrlich ascites cell glycerides and phosphoglycerides. The data also indicate a relation between alkyl and alk-1-enyl ethers, demonstrate that the ether-linked lipids are not derived from the corresponding acyl lipids, and give rise to a proposed metabolic pathway for the biosynthesis of ether-linked lipids.

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DETERMINATION OF BROMINATED VEGETABLE OILS IN SOFT DRINKS BY GLC. H. B. S. CONACHER and M. R. SAHASRABUDHE, Food and Drug Directorate, Tunney's Pasture, Ottawa 3, Canada.

A gas liquid chromatographic method has been developed for the quantitative determination and identification of brominated vegetable oils in soft drinks. The method involves treatment of the brominated oil with sodium methoxide followed by GLC analysis of the resulting methyl esters using methyl pentadecanoate as internal standard. Recoveries of brominated olive, sesame, cottonseed and corn oils were in the range 94-104%. Application of the technique to several commercial soft drinks has revealed brominated oil contents of 10-45 mg/10 oz of drink.

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HOW GOOD ARE ANALYSES OF OILS BY GLC? S. F. HERB and V. G. MARTIN, E. Utiliz. Res. Dev. Div., Philadelphia, Pa. 19118.

A statistical treatment was given to the results of analyses of the fatty acid composition of two methyl ester mixtures and four oils. These results, obtained by about 30 collaborators from the 1968-69 Smalley Gas Chromatography Check Program, are compared with results obtained by this group in previous years. The statistical data may be interpreted to indicate groups of analysts who made an excellent, statisfactory or unsatisfactory analysis. The data will also indicate the relative degree of difficulty of analyzing one oil compared to a different oil.

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THE ANALYSIS OF 1-EPOXY OLEFINS BY GAS LIQUID CHROMATOGRAPHY. CLIFFORD R. GLOWACKI, PETER J. MENARDI and WILLIAM E. LINK, Ashland Chemical Co., Bloomington, Minn. 55420.

The analysis of 1-epoxy olefins may be performed on an "as-is" basis using GLC, if an all-glass system and on-column injection are used. The reaction of 1-epoxy olefins with BF_3-methanol solution produces two isomeric hydroxy methyl ethers of known structure which are separable on a FFAP column. The proposed method, using this derivative, was compared with the conventional method and with a procedure in which the 1-epoxy olefins were reduced to alcohols with lithium aluminum hydride. It does not require the special instrumentation of the usual method and is simpler and more rapid than the lithium aluminum hydride procedure. A statistical analysis was performed on experimental data obtained from two known mixtures. Results of this analysis demonstrated the superior accuracy and precision of the proposed method compared to the other methods investigated.

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AN AUTOMATIC SYSTEM FOR THE PURIFICATION OF LIPID EXTRACTS. GARY J. NELSON, Lawrence Radiation Laboratory, Livermore, Calif. 94550.

The removal of nonlipid substances from lipid extracts of various tissues is a persistent problem. Recently dextran-gel, partition chromatography has provided a method which appears to be superior to previous procedures, such as aqueous washing. However, the chromatographic procedure is relatively time consuming particularly when many samples are being analyzed. This presentation will describe an automatic chromatographic system which can operate untended, once the sample has been introduced, thereby relieving the operator from many of the inconveniences of the manual chromatographic procedure. The apparatus carries out the entire elution sequence for the purification of the extract as well as separating any gangliosides present in the original sample. The system consists of four solvent reservoirs, a constant volume, non-pulsating pump, adjustable program timers, and automatic solenoid valves. The column is all glass and teflon, fitted with flow adaptors for either ascending or descending chromatography, and will withstand pressures to 500 psi. The sample and solvents contact only organic-solvent resisting plastics and glass. The pressure in the system is monitored continuously and an automatic cutoff is provided if the pressure exceeds an arbitrary limit set by the operator at the start of the run. Details of the design and construction of the system will be described. The operating parameters and results obtained during use for about one year will be presented. While the system was designed primarily for dextran-gel, chromatographic purification of lipid extracts, it should be useful for a wide variety of chromatographic procedures where precise control of flow, temperature and pressure are advantageous.

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SIMULTANEOUS MULTIPLE AUTOMATED DETERMINATION OF THE ISOMER DISTRIBUTION OF POLYBROMINATED SALICYLANILIDES. NEIL P. LOEB, Lever Brothers Co., Edgewater, N.J. 07020.

Polybrominated salicylanilides are used extensively in the soap and detergent industry as germicides. Ion exchange and TLC are the methods most widely used for their analysis, with ion exchange generally accepted as the reference procedure. However, the long elution time normally required to resolve the isomers makes this procedure unsuitable for routine control work. This paper describes a relatively rapid ion exchange technique for the simultaneous analysis of a mixture of two, three or four polybrominated salicylanilides. The method resolves up to 10 isomers within a normal working day. Quantitation is achieved by calculating the areas under the peaks produced by each eluting component. The heart of the analytical system is a high quality multiple sample analyzer with a linear ultraviolet absorbance output. The ion exchange effluents are scanned sequentially for a predetermined time period and the resulting absorbances recorded. The samples are distinguished on the recorder by an

offset control which gives each sample a different baseline. The linear absorbance feature removes the need to collect fractions, as all the components can be calculated directly from the recorder chart. The instrumentation, the elution technique and the accuracy and reproducibility of the method will be discussed. The problems encountered when setting up the system and their solutions will also be presented.

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A MICRO OZONE GENERATOR AND ITS APPLICATION IN A NEW MICRO METHOD OF OZONOLYSIS FOR THE DETERMINATIONS OF THE STRUCTURE OF UNSATURATED FATTY ACIDS.

E. CHRISTENSE NICKELL and O. S. PRIVETT, The Hormel Institute, Austin, Minn. 55912.

Construction of a simple micro ozone generator of the Bonner type is described. Also described is a new micro method of ozonolysis for the determination of the structure of unsaturated fatty acids. The method is based on the catalytic reduction of ozonides to alcoholic fragments and analysis by GLC. The reduction is carried out with palladium on charcoal in the absence of solvent. Polyunsaturated methyl esters give a simple primary alcohol from the terminal end of the molecule, a diol(s) from the internal double bonds and a half-ester half-alcohol from the proximal end of the molecule. The fragments are stable and may be isolated by TLC. GLC analysis may be carried out directly on the alcohols or after derivitization. The method facilitates the analysis of mixtures of isomers, detection of impurities in minor constituents in preparations of unsaturated fatty acids, and is demonstrated on a variety of highly purified long chain unsaturated methyl esters.

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MODULATION OF END PRODUCTS IN FATTY ACID SYNTHESIS.

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The purified multienzyme complex, fatty acid synthetase of yeast, under standard conditions, with adequate NADPH, and a 1:2 ratio of acetyl CoA and malonyl CoA produces palmityl CoA and stearyl CoA in equal amounts. Based on the known enzymatic properties of fatty acid synthetase a model which rationalizes the chain termination at the level of C_{16} and C_{18}-acid is proposed. The model is based on two assumptions, supported by experimental evidence: (a) The probability of any covalently enzyme-bound saturated acyl residue forming a product by transfer to CoA is determined by the relative velocities of the condensing and transferring reactions. (b) The growing alkan chain interacts with the enzyme protein only after a chain length of 13 C-atoms has been attained; this interaction changes the relative velocities in favor of product formation by an energy increment of –0,9 kcal for each additional methylene group beyond the 13th. To calculate the probability of product release at a particular chain length, an equation was derived from the model describing quantitatively the observed product distribution. The model also explains the formation of β-ketoacyl-CoA- and α,β-unsaturated acyl CoA derivatives or short chain fatty acids as the predominant end products of fatty acid synthesis under certain experimental conditions. The physiological importance of the modulation of end products in fatty acid synthesis is discussed.

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BIOSYNTHESIS OF MONOUNSATURATED FATTY ACIDS IN HIGHER PLANTS.

EUGENE M. STEARNS, JR. and WILLIAM T. MORTON, The Hormel Institute, Austin, Minn. 55912.

Biosynthesis of saturated, dienoic and trienoic fatty acids in higher plants occurs by generally well accepted and easily demonstrated pathways. Studies of the origin of monoenoic acids on the other hand have produced data supporting conflicting views. Incorporation of radioactivity of labeled carbon dioxide, acetic acid and other simple precursors into oleic acid precedes and exceeds that into stearic acid in various plant tissues. Intermediate chain length fatty acids have given rise to oleic acid, while under the same conditions long chain acids have failed to do so. These findings are in sharp contrast with recent reports in which the direct desaturation of palmitic and stearic acids has been demonstrated. Evidence is reviewed and recent results in this laboratory are presented for the purpose of reaching a statement of the current situation regarding the formation of monounsaturated fatty acids in higher plants.

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CELL-FREE DESATURATION SYSTEMS FOR FATTY ACIDS.

F. W. QUACKENBUSH, Purdue University, Lafayette, Ind. 47907.

Cell-free systems which desaturate fatty acids have been prepared from rat liver, soybean cotyledons and *Penicillium chrysogenum* mycelia. From rat liver, a microsomal fraction contains two desaturases which are distinct with respect to substrate and which are inducible in response to different nutritional factors. The 9-desaturase, which acts upon stearate, is sharply reduced by fasting. The 6-desaturase, which acts upon linolenate, is not affected by fasting. Dietary carbohydrate or saturated fat increases 9-desaturase activity; dietary protein increases 6-desaturase activity. Induction of both desaturase systems is prevented by DL-ethionine or actinomycin D. From soybean cotyledons a soluble (105,000 × *g* supernatant) fraction has been obtained which readily effects 9-desaturation in stearate, palmitate and myristate. This fraction also effects 12-desaturation and 15-desaturation. These desaturative functions are also performed by similar supernatant fractions from the mycelium of *P. chrysogenum*. However, the fungus does not utilize myristate appreciably when added as a substrate in the medium. The studies suggest that 9-desaturation of stearate and palmitate represents a normal pathway to unsaturated acids which is common to these organisms and that further desaturation to specific polyunsaturated acids as a discrete function of the organism based on specific enzyme systems.

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OLEIC ACID SYNTHESIS IN DEVELOPING CASTOR OIL SEEDS.

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Oleic acid is the first detectable fatty acid labeled from ^{14}C-acetate in endosperm tissue from the developing castor oil seed. It is the direct precursor of ricinoleic acid and the kinetics of ^{14}C-acetate incorporation indicates that it exists in a nonenzyme-bound form prior to its conversion. Since the total unsaturated acids constitute 98% of the total fatty acids in this oil it follows that the oleic acid synthesizing system must synthesize at least 98% oleic acid as its product. If we are to make progress in determining the biochemical mechanism by which the fatty acid composition of seeds is regulated it is important to have an in vitro system that reflects the in vivo situation. With this rationale in mind, a sub-cellular particulate system has been isolated that synthesizes over 90% oleic acid from either acetyl CoA or malonyl CoA. The particles sedimenting between 500 × *g* and 36,000 × *g* synthesize oleic acid under aerobic conditions and in the presence of ATP, HCO_3^-, Mn^{++}, NADH and NADPH. Synthesis of oleic acid from malonyl CoA requires aerobic conditions and NADH, NADPH and acetyl CoA. Under anaerobic conditions or in the absence of NADPH stearic acid is the major product. NADH is the major reducing cofactor required. A fatty acid synthesizing system can also be detected in the soluble and microsomal fractions but here the products are primarily saturated fatty acids, and it is presently believed that these systems arise from the breakdown of the larger particles. There is, however, no definitive evidence that would rule out the existence in these seeds of two systems, a particulate and a soluble. The 500 × *g* to 36,000 × *g* particles have been separated by linear sucrose density gradient centrifugation into four protein bands and each of these has been visualized by electron microscopy. Particulate fatty acid synthetase activity was associated with a major protein band of density 1.21 g/cc. Although palmitic acid now contained 55% of the radioactivity incorporated from 1-^{14}C-acetyl-CoA, oleic acid still constituted 40% of the total fatty acids synthesized. Electron microscopy revealed that the proplastid or a closely related organelle were the sub-cellular sites of particulate oleate synthesis. Proplastids were shown to be abundantly present in intact seeds.

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BIOSYNTHESIS OF MONOENOIC ACIDS IN ANIMALS.

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Aerobic desaturation is the major pathway for the biosynthesis of oleic acids in animal systems. However, liver desaturase(s) activity varies with species: chicken>rat>pigs>sheep. It also varies with the chain length, myristic, palmitic and stearic acids being desaturated to their corresponding *cis*-9-monoenes by rats in the order of 18:0>16:0>14:0. Desaturase activity also increases under conditions of increased lipogenesis such as fat free diets and lactation. The distribution between triglycerides and phospholipids of oleic acid produced by desaturation of stearic acid varies with the animal. In rats this oleic acid is predominantly incorporated into triglycerides, whereas in chickens it is distributed equally between triglycerides and phospholipids. This may be related to the fact that in rats there is an alternative pathway for the biosynthesis of oleic acid, probably via β,γ desaturation of laurate which provides oleic acid for phospholipid synthesis, whereas in chickens under normal conditions there is no alternate pathway.

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SOME SPECIFICITIES IN THE DESATURATIONS OF LONG CHAIN FATTY ACIDS.

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The basic pathways of biosynthesis of the common unsaturated fatty acids in both plant and animal systems are now well established. Only recently, however, have more detailed aspects of desaturation of fatty acids begun to be examined, such as positional specificities, stereospecificities, nature of the substrate and its association with the enzyme, control mechanisms, and so on. For example, studies with homologous ^{14}C-labeled saturated fatty acids, in both plant and animal systems, have shown that the position of the first double bond introduced into the chain is strictly controlled and is mediated by the distance from the carboxyl group. The introduction of the second double bond by plant systems, however, is not quite so rigidly controlled so that, although methylene-interrupted dienes are always formed, these can be, for example, 8,11– or 10,13–dienes instead of the more usual 9,12–dienes. Again, all the desaturations so far examined have been completely stereospecific, hydrogen atoms in the *cis*–relative and D–absolute configuration being removed. From the kinetic isotope effects observed with the tritiated and deuterated substrates used in such stereochemical studies, some conclusions can be drawn as to the detailed mechanisms of these desaturations. Various other aspects of fatty acid desaturations in plant and animal systems will also be discussed.

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SYNTHESES AND MASS SPECTRAL CHARACTERISTICS OF SOME HIGHER BRANCHED CHAIN UNSATURATED FATTY ESTERS.

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The Wittig reaction between eight alkylidene triphenylphosphoranes $R—CH=P(C_6H_5)_3$ (R varied from H to n—$C_{11}H_{35}$) and methyl 12-oxooctadecanoate in DMF has been employed in the synthesis of a partial homologous series of alkenyl branched chain fatty acid esters in high yields. Purification was readily accomplished by chromatography on a column of silver nitrate impregnated silicic acid-celite mixture. More like the mass spectra of α,β-unsaturated esters, and in contrast to normal chain unsaturated esters, the fragmentation pattern allows location of the double bond at the branch point. A fragment ion $[C_nH_{2n}]^+$ resulting from two proposed allylic cleavages and McLafferty transfers of γ-hydrogen atoms is present in 51-100% relative abundances and allows unambiguous determination of the length of the alkenyl branch. The phosphonoacetate carbonyl olefination reaction has been used for the synthesis of several α-branched-α,β-unsaturated long chain mono- and dicarboxylic acid esters. The NMR and mass spectral characteristics of both the phosphonoacetates and the unsaturated esters will be discussed.

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PREPARATION OF SUCROSE ESTERS BY INTERESTERIFICATION.

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Reactions between sucrose and esters of the long chain fatty acids customarily have been conducted in a mutual solvent such as dimethylformamide. The solvent-free interesterification of molten sucrose and fatty acid esters at temperatures between 170-187 C has now been performed with the aid of lithium, sodium and potassium soaps, which functioned as catalysts and solubilizers. When the reactants were heated rapidly and then subjected to reduced pressure, the interesterifications could be

brought to equilibrium in 12 min or less, including the time necessary to melt the sucrose. The several soaps and combinations of soaps employed differed markedly in their performance in the interesterification. No sucrose esters were obtained with lithium palmitate. The yield with lithium oleate was among the best, but consisted of over 90% tetra and higher esters of sucrose. Lower esters were best produced with combinations of lithium oleate and sodium or potassium oleate employed at a level of about 25% total soaps, based on the weight of sucrose. The type of fatty acid ester employed also markedly affected the yield of sucrose esters. Among the esters tested, methyl carbitol palmitate (which could be formed in situ), monopalmitin, distearin and technical grade diglycerides (48% diglycerides), prepared from completely hydrogenated cottonseed oil, interesterified readily with sucrose.

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PROPERTIES OF 2-OLEODIPALMITIN, 2-ELAIDODIPALMITIN, AND SOME OF THEIR MIXTURES.

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The glycerides 2-oleodipalmitin (POP) and 2-elaidodipalmitin (PEP) were synthesized and their melting behavior and dilatometric properties were determined. These glycerides are components of some confectionary fats and POP is a major component of solvent-winterized cottonseed oil stearin. Partial or total elaidinization of POP will produce PEP with a significant increase in melting point. Three mixtures of POP with PEP were examined. At least five polymorphs of POP and four of PEP were identified by x-ray diffraction patterns. The rates of transformation of the lower melting to higher melting polymorphs were in general quite rapid at temperatures just below their melting points. Transformation of POP to its highest melting form was slow and required several days at a temperature just below its melting point. The coefficient of expansion was determined for the highest melting polymorph and the liquid form of each glyceride. Melting dilation was determined for the highest melting polymorph. Mixtures of POP with PEP exhibit different melting ranges depending on the tempering procedures used, but even quickly solidified mixtures of these glycerides all tempered without melting to the form with the highest melting range as they were slowly heated over a period of 2 hr. Slow cooling from the melt essentially segregates the components.

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ALKYL ESTERS OF DIEPOXYSTEARIC ACID AND CYCLIC DERIVATIVES AS PLASTICIZERS FOR PVC.

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A series of alkyl esters of diepoxystearic acid was prepared and studied as plasticizers of PVC. From the esters a second series of plasticizers was made by cyclization and acetylation to esterify the undesirable hydroxyl functions generated. The resulting cyclic diacetoxy compounds were then evaluated as potential plasticizers of PVC. The diepoxy esters were all found to have good compatibility with PVC. They are more efficient than DOP and greatly increase the heat stability. The cyclic diacetoxy derivatives showed varying degrees of compatibility and they are less efficient than DOP.

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PREPARATION AND REACTIONS OF ALPHA ANIONS OF CARBOXYLIC ACIDS IN HEXAMETHYLPHOSPHORAMIDE SOLUTIONS.

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A superior method of preparing dianions of a straight chain saturated or unsaturated aliphatic carboxylic acid (RCHLiCOOLi) has been developed. In this procedure the fatty acid is metalated with lithium diisopropylamide in the mixed solvent system tetrahydrofuran-hexane-hexamethylphosphoramide (HMPA). Quantitative conversion of straight chain fatty acid to α-anion in homogeneous solution permits nucleophilic reactions on a variety of reagents to produce α-substituted derivatives in high yields. Reaction of the dianion with alkyl halide is demonstrated to be a highly successful application for preparing α-branched fatty acids in yields exceeding 90%. In contrast, α-alkylation on the dianion of α-branched acids in HMPA solution yields α,α,α-trialkyl acetic acid derivatives in poor yields (~10–15%) owing to elimination of HBr from alkyl bromide. A few additional synthetic applications are briefly presented to show the versatility of metalated straight chain fatty acids. These include α-anion reactions with CO_2, O_2, ethyl formate and alkyl nitrate to yield derivatives of malonic acid, α-hydroxy acid, aldehyde and nitroalkane, respectively.

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POTENTIAL JUVENILE HORMONES: PREPARATION OF FATTY β-METHYL CROTONYL AND 3,4-METHYLENEDIOXYPHENYL DERIVATIVES.

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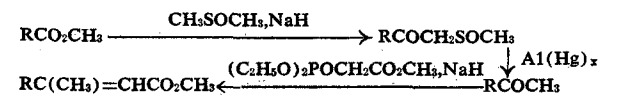
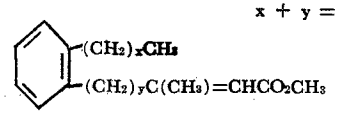
Certain compounds with β-methyl crotonyl and 3,4-methylenedioxyphenyl groups are known to be active juvenile hormones because they keep insects from maturing and procreating. A number of compounds containing these groups have been prepared from fatty acids and their derivatives and their activities as juvenile hormones have been determined. Among the potential insect hormones are fatty methyl crotonyl derivatives synthesized according to the scheme:



Fatty 3,4-methylenedioxyphenyl derivatives were prepared by the condensation of piperonal with fatty aldehydes and by esterification of piperonyl alcohol with fatty acid derivatives. A number of these chemicals showed juvenile hormone activity at 10-100 μg per insect in the Tenebrio test. Of the compounds tested to date the greatest activity (10 μg) was shown by an isomeric mixture of β-methylacrylates (I) prepared from C_{18}-aromatic cyclic acids.

$$x + y = 10$$



(I)

Structural studies on the C_{18}-aromatic cyclic acids have shown that the predominant isomer is methyl 11-(*o*-*n*-propylphenyl)-3-methyl-2-undecenoate when x = 2 and y = 8.

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QUANTITATION AND AUTOMATION OF GAS CHROMATOGRAPHY.

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Quantitative gas chromatography consists of three fundamental steps: generation of the analog signal (chromatography), analog to digital conversion (integration), and relating digital data to composition (calculation). The capabilities, limitations, accuracy and precision of today's gas chromatograph designs will be discussed. A comparison of the accuracy and precision of the commonly employed techniques for peak integration including strip chart methods, digital integrators and digital computer systems will be reviewed. Techniques for the standardization and calibration of gas chromatograph systems, including the use of sampling devices, response factors, internal and external standards, identification of peaks by retention indices, and other methods will be discussed. On-line computer systems are being installed in gas chromatograph laboratories at a rapid rate. The types of systems now in operation will be compared and contrasted, including large time-shared computer systems and small dedicated computer systems in various configurations. Hardware requirements for interfacing computers to multiple gas chromatographs including multiplexers, A/A converters and related equipment will be reviewed. The present state of the art in programming will be discussed with respect to routines for data smoothing, peak detection, baseline correction, integration, fused peak resolution and calculation. Some practical guides and considerations for those interested in evaluating means of laboratory automation will be given. Important considerations include operational flexibility required, econometric considerations, capability of upgrading system and the burden placed on the operator in terms of computer and programming knowledge required. The differing needs of research and control laboratories will be discussed.

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STANDARDIZATION OF PROGRAMMED TEMPERATURE OPERATION.

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Retention time data for identification purposes have been less reliable in temperature-programmed gas chromatography (TPGC) than in isothermal operation because initial starting temperatures cannot be reproduced. In one approach to standardizing TPGC, unsaturated fatty acids labeled with tritium in high specific activity were synthesized. These materials were used as internal standards for locating double bonds in partially hydrogenated fats by the microozonization-pyrolysis procedure. In another approach, relative *elution temperature* was used. Its independence of initial temperature, program rate, liquid substrates and loading has been shown by others and it is incongruous that in a temperature-programmed operation one should use time, the analog of temperature, rather than temperature itself. In our system, temperature is sensed by a thermocouple, converted from voltage to frequency and recorded on a magnetic tape along with the appropriate chromatographic elution curve. At the tape playback station, elution temperature is displayed in degrees Kelvin, printed on a paper tape and punched into a perforated paper tape along with the corresponding areas under the curve. The perforated tape serves as *input to a digital computer*. After the data have been introduced, the computer first calculates the relative elution temperatures by dividing the elution temperature for a standard compound into that for the other components; then compares these relative elution temperatures to those for known compounds; and, finally, prints out the identification and the analysis. Application of these two systems to fatty acid analyses and to location of unsaturation in fatty acids by ozonization-pyrolysis is described.

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A NEW, REMOTE ON-LINE DATA ACQUISITION-PROCESSING SYSTEM FOR LOW RESOLUTION COMBINATION GAS CHROMATOGRAPH-MASS SPECTROMETER.

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A new, remote data acquisition-processing system has been put in operation for the LKB-9000 single-focusing fast-scanning low-resolution combination gas chromatograph-mass spectrometer. An IBM-360/50 is used to process the data. The system uses two private analog lines to transmit the ion-intensity signal and the Hall generator signal (mass marker) via two pairs of line isolation differential amplifiers to an IBM-1827 analog-digital control unit situated one half mile from the mass spectrometer. The digitized signals are stored temporarily in a 60 K-byte buffer which is composed of 30,000 alternating half words of mass spectrometer and mass marker data. Digitized and reduced intensity-mass value pairs (up to 1,500 mass values) along with spectra labels are stored in the disk. The processed data (i.e., normalized by subtracting background) may be listed on the printer, punched on cards, stored on magnetic tape or plotted as a bar graph on a CalComp 565 digital incremental plotter upon request by the mass spectrometer operator. The plotter and an IBM-2741 Remote Communications Terminal are situated near the mass spectrometer. A digital line is provided to handle the two-way communication from and to the IBM-2741 and to send the plotting signal from the IBM-360/50 to the plotter. The digital signals from the IBM-360 reach the mass spectrometry lab via an IBM-2701 data adapter, a Western Electric 103F data set, and a CalComp 211 data interface control unit. Results obtained from this system will be discussed.

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COMPUTER RECORDING AND PROCESSING OF MASS SPECTRA.

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A digital recording technique has been developed for low-resolution mass spectra in which are used a medium-sized on-line digital computer and a magnetic scanning mass spectrometer. The speed with which data are taken and the large storage capacity of the system make it particularly suited for recording mass spectra of gas chromatographic effluents. Some features include: (a) spectra are recorded continuously during the gas chromatogram regardless of the emergence of fractions, (b) peak center and intensity calculations proceed while each spectrum is being scanned, (c) the computer controls the scanning function of the mass spectrometer, (d) peak positions in time units are converted to

masses according to an external mass standard, and (e) spectra are correlated with the gas chromatogram by a plot of the total mass spectrometer ionization current (calculated by the computer) vs. spectrum index number. To relieve the chemist from the tedious task of manually interpreting the large number of spectra obtained from a gas chromatographic run, an automatic mass spectral library searching technique has been developed that compares the spectrum of the unknown compound to a large file of reference spectra. Both the unknown and reference spectra are abbreviated, before comparison, by selecting the two largest peaks in each 14 mass unit interval throughout the entire spectrum. For each comparison, a similarity index is calculated, based on a weighted average ratio of the two spectra. This index is an absolute measure of the degree of match between the unknown and a particular reference spectrum. Other techniques have also been developed to present this large volume of data in chemically useful terms. The application of this system has been demonstrated for problems pertaining to lipid chemistry.

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AUTOMATED GENERATION OF MOLECULAR STRUCTURES FROM MASS SPECTROMETRY DATA.

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Two sources of information are employed to develop programs for the automated solving of chemical structure problems. The first of these is a fragmentation grammar that identifies forbidden, acceptable and preferred fragmentation steps. The second is a metastable ion mass spectrum. The fragmentation grammer function begins with an edited and unambiguous list of formulas, one for every relevant peak in the spectrum. The metastable information is currently obtained manually, but a device for scanning defocused metastable peaks exhaustively and automatically is being implemented. The device will operate on an A.E.I. MS-9 high resolution mass spectrometer, and is a computer controlled version of a device described by Jennings. The syntactic and metastable ion information are combined to produce a proposed fragmentation pathway. This is a graph that identifies necessary and sufficient fragmentation reactions. The pathway, while available to provide a picture of the molecular fragmentation, is most useful as the starting point for the structure building algorithm. A computer program, working in Lederberg's Dendral notation, runs back up the pathway, building larger ions from smaller ones. The pathway information directs the reconstruction process. Because of the large number of possible solutions to any particular empirical formula, the program had to be designed to examine only restricted sets of solutions. Two types of heuristics were used for this purpose: logical or general-purpose heuristics that removed duplicity and required that sets of solutions intersect, and chemical heuristics that, for example, prefer stable structures to unstable ones. Provision is made for the incorporation of additional chemical information. Application of the method to several simple acyclic molecules will be discussed.

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THE OCCURRENCE OF FATTY ALCOHOLS IN NORMAL TISSUES AND NEOPLASMS.

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Three neoplastic tissues, analyzed for fatty alcohols, contained small amounts $\simeq$ 0.3% of the total neutral lipids) in both the free and wax form. The major chain lengths of the alcohols consisted of 16:0, 18:0 and 18:1; only traces of longer chain polyunsaturated alcohols were found. The chain length distribution was similar to that observed in the O-alkyl glyceryl ether moieties of these tissues. Three normal tissues were found to contain lower levels of fatty alcohols than the neoplasms ($<$ 0.1% of the total neutral lipids) and precluded any accurate determination of their chain lengths. These results lend support to our in vitro studies that show fatty alcohols to be precursors of the O-alkyl ether side chain of glycerol.

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SPECIFICITY AND SPECIFIC ACTIVITY OF ACYL DESATURASE IN RAT LIVER MICROSOMES.

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A convenient method for the assay of acyl desaturase involving the use of silica gel and silver nitrate impregnated glass fiber sheets has been developed. With this method, studies of the specificity of acyl desaturase with regard to chain length and unsaturation have been performed. Desaturation rates for the saturated fatty acids 15:0 to 19:0 increase with carbon number in linear fashion from 15:0 to 18:0. The rate for nonadecanoic acid drops sharply to a level of only 1/9 that of 18:0 and 1/3 that of 15:0. Similar rate comparisons of mono-and diunsaturated acids will be discussed. Large differences were found in the specific activities of microsomal desaturase preparations from normal Vitamin E deficient and essential fatty acid (EFA) deficient rats. Animals fed lab chow have only 1/10 to 1/5 the desaturase activity found in the other two groups. The time course of the enzyme induction in EFA deficiency and its repression by linoleic and linolenic acids will be presented.

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HEME COMPOUND CATALYSIS OF LINOLEATE EMULSION OXIDATION.

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Heme compounds have long been recognized to be effective catalysts for lipid peroxidation in vitro. However, Banks et al. (1961) reported that high concentrations of cytochrome c were less effective than low concentrations as pro-oxidant catalysts for linoleic acid, and Lewis and Wills (1963) observed similar effects with hemoglobin. We have restudied the effects of some myoglobin, hemoglobin and hemin preparations on the rates of oxidation of linoleate (in the range, pH 3.5-9.0) or of trilinolein emulsions with Tween 20; a polarographic oxygen analyzer was used to estimate the free oxygen content of the system. The results show that (a) the concentrated heme compounds were less effective catalysts than the more dilute ones, (b) an increase in the apparent oxygen content after an initial absorbtion by linoleate suggested that the higher heme concentrations of compounds were catalyzing the decomposition of peroxides with liberation of oxygen, (c) the magnitude of the above effects was modified by temperature and pH, and (d) changes in Tween concentration sufficient to modify the turbidity of the emulsions did not change the shape of the oxygen consumption curves, indicating that the size of the micelles was not a controlling factor.

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RADIOCHEMICAL ASSAY OF LONG CHAIN FREE FATTY ACIDS.

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A radiochemical assay for the quantitative determination of long chain FFA as ^{60}Co-FA complex is developed. The radioactivity of ^{60}Co in Co-FA complex in the upper organic phase is counted. It is sensitive to a low as 0.08 nmoles of FFA, and the standard curve is linear up to 200 nmoles. The sensitivity of this method in measuring FFA less than 0.08 or higher than 200 nmoles per assay can be maintained by increasing or decreasing the specific activity of $^{60}Co(NO_3)_2$ used. The accuracy of this method is comparable with other methods. The molar ration of FFA to Co in Co-FA complex was found to be 2.03 with standard deviation of $\pm$ 0.16. Therefore, it is a cobaltous salt of fatty acid. This factor of 2 can be used directly for the calculation of the FFA content in the unknown sample. The standard deviation of the mean is approximately 8% of the mean, therefore, it reflects the reliability of this method. This method appears to be specific, more sensitive and simpler than previous methods.

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FATTY ACID COMPOSITION AND STRUCTURAL STUDIES ON THE GLYCOLIPIDS AND PHOSPHOLIPIDS OF MATURING SOYBEANS.

H. SINGH and O. S. PRIVETT, The Hormel Institute, Austin, Minn. 55912.

Soybeans undergo virtually a complete transformation in composition of the lipids during maturation. Described here are studies on fatty acid composition and characterization of glycolipids and phospholipids of immature soybeans. Soybeans were picked at intervals between 13 and 97 days after flowering and extracted with chloroform-methanol. After removal of the water soluble components, the lipids were fractionated into four fractions by column chromatography with acid treated florisil. Fraction 1 was eluted with chloroform and consisted of neutral lipids, mainly fatty acids, triglycerides, diglycerides and sterols; Fraction 2 and 3 eluted with chloroform-acetone (1:1) and acetone, respectively, consisted mainly of glycolipids. Phospholipids (Fraction 4) were eluted with methanol. The glycolipids and phospholipids were characterized by two-dimensional TLC. The individual components were isolated by preparative TLC, and their structures studied by spectral and chemical degradative methods of analysis. Fatty acid composition was also determined by GLC after interesterification with methanol. Among the glycolipids isolated and characterized were esterified sterol glycoside, sterol glycoside, digalactosyl diglyceride and a component tentatively identified as sulfolipid. A number of other glycolipids were detected but were not characterized. The main phospholipids of immature soybeans were phosphatidyl inositol and an unidentified component that decreased in concentration as the beans matured. No phosphatidyl choline or phosphatidyl ethanolamine, which together with phosphatidyl inositol were the main phospholipids of mature soybeans, were detected in the immature bean until the later stages of maturation.

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CHANGES IN GLYCERIDE STRUCTURE OF SOYBEAN DURING MATURATION.

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Soybeans of the Hawkeye variety were picked at five periods from 35 to 91 days after flowering, and the lipid was extracted with chloroform-methanol. The triglyceride fraction from each picking was isolated by silicic acid TLC and species composition determined by a combination of argentation TLC and lipase hydrolysis techniques. The triglyceride content of the total lipid increased from 6.5% at 30 days after flower to 83% in the mature bean. The greatest change in the composition of the triglycerides occurred approximately in the first 52 days after flowering. During this period the percentage of linolenic acid decreased from 34.2 to 7.6; the percentages of linoleic and oleic increased, stearic remained fairly constant and palmitic decreased slightly. Some 18 species of triglycerides were detected in the immature bean exclusive of positional isomers. During maturation all species containing linolenic acid decreased and some, notably trilinolenin, were absent in the mature bean. Although each species changed considerably in percentage and amount during maturation, the positional arrangement of the fatty acids, isomer composition, remained virtually constant. Linolenic acid was distributed fairly uniformly between the inner and outer positions, linoleate favored the 2 position and oleate the outer position slightly. Most of the stearic and palmitic acids were esterified in the outer positions. Phosphatidyl choline and phosphatidyl ethanolamine synthesis did not occur concurrently with that of triglycerides in the early stages of maturation, indicating differences in the relationship of the synthesis of these compounds in plants and animals.

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POTENTIOMETRIC DETERMINATION OF MICROQUANTITIES OF LIPID PEROXIDES.

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The thioglycolate method of Holman and Dahle for the measurement of micro amounts of lipid peroxides has been modified to permit potentiometric determination of the end point in highly colored lipid extracts. Analyses of *t*-butyl hydroperoxide and dilauroyl peroxide solutions of known concentration yielded recoveries varying from 96-101% of their theoretical value over the range 1.0-12.0 μmoles. Fresh total lipid extracts from spinach leaves and avocados had no measurable peroxide content. Fresh total spinach lipid extracts, when incubated in the dark with peroxide alone, contained a factor or factors that destroyed or consumed peroxides added to them. Freshly prepared solutions of β-carotene exhibited similar behavior in the presence of added peroxides. In the absence of sodium iodide, oxidation of this glycolate by known peroxides and peroxidized lipid extracts was too small to be accurately measured. In the presence of β-carotene, however, this glycolate was consumed in a detectable amount in these same peroxide solutions.

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ANALYSIS OF PEROXIDE TYPES IN OXIDIZED FATTY ESTER MIXTURES.

K. G. RAGHUVEER and E. G. HAMMOND, Iowa State University, Ames, Iowa 50010.

The autoxidation of natural fats can yield peroxides of different fatty acids, and each of these can be a mixture of two or more isomers. A method was devised to give a quantitative analysis of these peroxide types. The method is applicable to fats with peroxide values as low as 1. The peroxides are reduced to the corresponding alcohols with aqueous potassium iodide, converted to methyl esters, and the methyl esters of the hydroxy fatty acids are acetylated with acetic anhydride. The mass of unoxidized

methyl esters are removed from the acetylated esters by precipitation from methanol as urea complexes. The final purification and determination of the acetylated esters is accomplished by TLC on silica gel and silica gel impregnated with silver nitrate. The spots are detected by charring and measured by densitometer. *Pure methyl oleate, linoleate* and linolenate were autoxidized and samples recovered at various peroxide values. The recovery of acetylated ester accounted for 97% to 98% of the peroxide value. An additional 3% to 4% of unknown material more polar than the acetylated esters was recovered. Methyl oleate yielded two acetylated esters representing the *cis* and *trans* forms. The methyl linoleate and methyl linolenate yielded only one spot by TLC. Further information about the peroxide types may be obtained by ozonolysis of the acetylated esters and analysis of the fragments by gas chromatography. The method was applied to soybean and olive oil.

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QUANTITATIVE ESTIMATION OF SUCROSE ESTERS OF PALMITIC ACID. T. J. WEISS, M. L. BROWN, H. J. ZERINGUE, JR. and R. O. FEUGE, So. Utiliz. Res. Dev. Div., ARS, USDA, New Orleans, La. 70119.

Thin layer chromatography was adapted for direct quantitative estimation of sucrose esters of palmitic acid. Urea-phosphoric acid spray was used to detect the sucrose moiety of the various esters. It was observed that the photometrically determined density of each spot on the TLC plate was proportional to its sucrose content. Ester content was then obtained by multiplying sucrose by the factor (molecular weight ester/molecular weight sucrose). Ester mixtures were prepared by reacting sucrose with various proportions of methyl palmitate in dimethyl formamide solvent. Positional isomers were observed at all levels of substitution but could not be adequately separated from each other for quantitative evaluation.

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A SENSITIVE METHOD FOR DETERMINATION OF CARBONYL COMPOUNDS. D. C. JOHNSON and E. G. HAMMOND, Iowa State University, Ames, Iowa 50010.

Many of the compounds responsible for flavors in autoxidized fats and oils are detectable organoleptically at 0.1 ppb. More sensitive methods are needed to determine these compounds so that samples in the kilogram range or samples that are autoxidized excessively may be avoided. 2,4,6-Trichlorophenylhydrazine forms derivatives of carbonyl compounds which are volatile enough for convenient gas chromatography, and by using an electron capture detector, nanogram quantities of these derivatives may be measured. The derivatives are conveniently formed by passing a petroleum ether solution of the carbonyl compounds through a celite column impregnated with a solution of 2,4,6-trichlorophenylhydrazine in 1 N hydrochloric acid. In this way derivatives of series of aliphatic normal aldehydes, methyl ketones, 2-enals, 2,4-dienals and 2,3-diketones were prepared. Only acetone and formaldehyde and the diketones formed crystalline derivatives. The rest were viscous liquids. The derivatives were separated by chain length by gas chromatography. This was accomplished in glass columns using DC 200 silicone oil as a stationary phase. A weakly alkaline support such as freeze dried mixtures of sodium silicate, sodium phosphate and sodium sulfate (Tide) gave the best separations. TLC on alumina plates using 2% ether in petroleum ether as a developing solvent separated the aldehyde from the ketone derivatives. Alumina plates impregnated with silver nitrate gave separations according to the degree of unsaturation.

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EDIBLE OIL HEADSPACE GAS ANALYSIS BY MASS SPECTROMETRY. C. D. EVANS and E. SELKE, Northern Regional Research Laboratory, Peoria, Ill. 61604.

A mass spectrometer was used to analyze the content of hydrogen, nitrogen, oxygen, carbon dioxide and argon in the headspace gas of commercially packaged edible oils. A low level of oxygen is required to assure long-term stability and levels of 0.1% can be measured by this method of analysis. A leak-proof sampling system was designed to avoid air contamination and to obtain a representative sample of headspace gas. It is essential that the bottom of the screw cap be thoroughly sealed with a soft wax to the neck of the container to ensure a vacuum-tight system. Correct sampling is not possible without sealing the base of the screw cap. Each sampling was ascertained to be leak-free before rupture of the seal by holding the entire system under full vacuum for 2 min. Mass spectrometry has an advantage over other methods in detecting small air leaks because all gaseous components are determined, and it is possible to detect a slight amount of air leakage by comparing the ratios of the various components. In analysis where oxygen alone is determined only gross errors in oxygen levels become obvious. Results indicate that some edible oils are packaged under pure nitrogen, and other samples showed various amounts of oxygen in the headspace gas. The presence or absence of argon in the headspace gas indicates that some oils are packaged with pure nitrogen and others with nitrogen obtained by burning air. Since hydrogen was found in some samples where argon was also present, catalytic purifiers presumably were used to remove the last traces of oxygen and to obtain nitrogen for packaging oils. The decrease in headspace oxygen of oils bottled in air was followed during storage at room and elevated temperatures.

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DIRECT DETERMINATION OF SODIUM IN SOYBEAN OIL BY FLAME PHOTOMETRY. L. T. BLACK, No. Utiliz. Res. Dev. Div., ARS, USDA, Peoria, Ill. 61604.

A method was developed to aspirate a soybean oil-solvent solution directly into the flame of an emission spectrophotometer. The intensity of the sodium flame emission produced from the oil solution was compared with that of oil standards containing known amounts of sodium soaps. To prepare standards, sodium oleate was dissolved in ethylene glycol followed by the addition of a solvent and sodium-free soybean oil. This solution aspirated at a rapid and constant rate. This method is capable of determining sodium at a low limit of 0.01 μg/ml with good precision. The values obtained by the method compare well with other methods of sodium soap analysis.

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THE EFFECT OF STRUCTURE UPON THE METABOLISM OF UNSATURATED ACIDS. RALPH T. HOLMAN, The Hormel Institute, Austin, Minn. 55912.

The position of double bonds has been shown to have a profound effect upon the rates of several enzymatic reactions involving polyunsaturated acids. Acyl transfer, elongation by two carbon atoms, desaturation, and incorporation of acyl groups into various lipids by liver microsomes all show specificities favoring certain positions of double bonds in the isomeric series of octadecadienoic acids. The effects of chain length will also be discussed. The utilization of isomeric octadecenoic acids by a bacterium and by monkey kidney cells in tissue culture also indicates preference for certain structures. Soybean lipoxidase has a preference for acids which have double bonds ω6 and 9. Formation of prostaglandins shows specificity for certain chain length and double bond positions. These phenomena will be illustrated and discussed.

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RETROCONVERSION OF POLYUNSATURATED FATTY ACIDS. H. SCHLENK, D. M. SAND and J. L. GELLERMAN, The Hormel Institute, Austin, Minn. 55912.

The retroconversion of fatty acids signifies the metabolism where lower fatty acids arise from higher fatty acids. From many examples it is known that shorter chain acids can be formed by partial degradation from longer chain acids and can enter the regular pool of fatty acids in the rat. Retroconversion of polyunsaturated fatty acids to shorter chain and more saturated acids was first observed with 4,7,10,13,16-22:5. When this acid was fed to EFA deficient rats it gave rise to 5,8,11,14-20:4. Such retroconversion may proceed, as Klenk had suggested (1955, 1960), by partial degradation to C_{18} or shorter polyenoic acids from which 20:4 is resynthesized; or it may proceed more directly by hydrogenation of the first double bond in the chain which is not degraded farther than to C_{20}. Experiments with ^{14}C-22:5 decided in favor of the latter possibility but an intermediate was not isolated so that the course, 22:5 → 20:5 → 20:4 or 22:5 → 22:4 → 20:4 remained undecided. When uniformly ^{14}C-labeled 4,7,10,13,16,19-22:6 was given to normal rats, radioactive 7,10,13,16,19-22:5 and 5,8,11,14,17-20:5 were found. This may suggest that first hydrogenation and then β-oxidation takes place. However, radioactivity in the carboxyl group of 22:5 was only about 25% of that calculated for even distribution of ^{14}C in the chain whereas radioactivity in the carboxyl groups of 22:6 and 20:5 were as calculated for even distribution. Therefore, at least 75% of 22:5 must have been reconstituted from a C_{20} chain. The course 22:6 → 20:6 (not isolated) → 20:5 → 22:5 appears the most likely one. Normal rats retroconverted 22:6 to a much greater extent than EFA deficient rats. Retroconversion may contribute to establishing a desirable equilibrium of essential fatty acids.

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MECHANISMS AND STEREOCHEMISTRY IN THE BIOGENESIS OF OXYGENATED FATTY ACIDS. L. J. MORRIS, Unilever Research Laboratory, Colworth House, Sharnbrook, Bedford, England.

Many oxygenated fatty acids are produced in nature, almost always as one pure optically active form. The α-hydroxy acids in plant leaves are biosynthesized stereospecifically by a direct hydroxylation reaction, with retention of configuration at the site of substitution. The same type of mechanism is responsible for the formation of ω and (ω-1)-hydroxy acids by a *Torulopsis* yeast and of ricinoleic acid in the castor bean. The ricinoleic acid in ergot, however, is produced by a hydration-type of mechanism, and another simpler example of the stereospecific hydration of a double bond is provided by the production of D-10-hydroxystearic acid and related acids by strains of Pseudomonas. Lipoxidase produces hydroperoxy acids by a rather more complex mechanism but again in a completely stereospecific manner. Dihydroxy acids are produced by stereospecific hydration of epoxy acids in a number of systems and, by a combination of direct biochemical experimentation and the elucidation of the absolute optical configurations of substrates and products, the detailed mechanism of reaction of these hydratase enzymes can be established.

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THE BIOSYNTHESIS OF *CIS*-9,10-EPOXYOCTADECANOIC ACID. H. W. KNOCHE, The University of Nebraska, Lincoln, Neb. 68503.

For investigations on the biosynthesis of the epoxide function in fatty acids, wheat plants infected with the obligately parasitic fungus, *Puccinia graminis* (Pers.) f. Sp. *tritici* are an excellent source of biological tissue. The acid, *cis*-9,10-epoxyoctadecanoic acid, represents 20% of the fatty acids in uredospores of this fungus as shown by Tulloch and Ledingham (1960). Tissue slices of infected wheat plants have been shown to convert acetic acid, stearic acid and more directly oleic acid to *cis*-9,10-epoxyoctadecanoic acid. Light does not alter the biosynthetic rate significantly and aerobic incubation conditions are required for biosynthesis when either acetic acid or oleic acid are used as substrates. The probable synthetic sequence for *cis*-9,10-epoxyoctadecanoic acid is: acetic acid → stearic acid → oleic acid → *cis*-9,10-epoxyoctadecanoic acid. Investigations of this sequence, have been primarily directed towards the elucidation of biochemical reactions which take place in the conversion of oleic acid to the epoxy acid. The involvement of atmospheric oxygen and the role of possible oxygenated intermediates will be discussed.

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METABOLISM OF THE 2-HYDROXY FATTY ACIDS OF BRAIN. NORMAN S. RADIN, University of Michigan, Ann Arbor, Mich. 48104.

Evidence will be presented, based on the metabolic conversions of labeled acetate, propionate, stearate, lignocerate and their derivatives, to show that the hydroxy fatty acids (HFA) of brain are made by a hydroxylating conversion of the corresponding nonhydroxy fatty acids (NFA). The HFA appear to undergo degradation by oxidation to the ketone, then oxidative decarboxylation to the NFA containing one less C atom. The latter oxidation, in vitro, requires Mg, ascorbate, NAD and ATP, and is carried out by microsomal and mitochondrial preparations. This sequence of steps may explain why odd-numbered NFA and HFA are so prevalent in brain white matter lipids. The odd-numbered acids are also made by chain elongation of propionate. The HFA of brain occur primarily in HFA cerebrosides, which are made by a microsomal enzyme from HFA acyl sphingosines (HFA ceramides). The enzyme transfers galactose from UDP-galactose but will not use NFA ceramides as lipoidal acceptor. A lysosomal galactosidase acts to hydrolyze the HFA cerebrosides; it requires a low pH and a bile salt for activity.

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IRON ORE FLOTATION—1969. D. W. FROMMER, Bureau of Mines, Twin Cities, Minn. 55111.

Current flotation practice in the iron ore industry is reviewed with particular attention given to gains made since the 1966 AOCS meeting. Known applications are described with estimates of tonnage treated, the degree of beneficiation achieved, and the quantity and types of reagents used. Apparent trends and prospects for new applications of flotation in the iron ore industry are discussed.

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CATIONIC FLOTATION OF SILICA FROM MAGNETIC IRON ORE CONCENTRATES. MARLIN C. HEDBERG, General Mills, Inc., Minneapolis, Minn. 55413.

Normal alkyl primary amine acetates, N-alkyl-1,3-propylene diamine acetates and trimethyl alkyl ammonium chloride compounds with alkyl groups derived from lauryl, coco and tallow fatty acids have been tested as collectors in laboratory-scale rougher flotation of silica from magnetic iron ore concentrates. Five samples of magnetic concentrate from the Great Lakes region were used in the test program. Coco diamine and lauryl primary amine were the strongest silica collectors followed by coco primary amine and then tallow primary amine and the diamines containing tallow and oleyl alkyl. The trimethyl alkyl ammonium chloride compounds were somewhat less efficient than primary amines and diamines. Chain length effects were less pronounced in this latter group of compounds than with the amines and diamines. Finely ground (90% less than 325 mesh or finer) magnetic concentrates with iron and silica almost completely liberated were highly responsive to upgrading. Concentrates of the same fine mesh size but containing unliberated iron-silicate were less responsive.

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ADSORPTION STUDIES OF ALKYLAMINES AT MERCURY-SOLUTION INTERFACE THROUGH DIFFERENTIAL CAPACITY MEASUREMENTS AND THEIR IMPLICATION IN FLOTATION. SHINNOSUKE USUI, University of Minnesota, Minneapolis, Minn. 55455.

Differential capacities at mercury-electrolyte interfaces in the presence of dodecylammonium acetate (DAA) were determined as a function of the applied potential, the ionic strength (KF), and the solution pH. The differential capacity curves were found to be quite complex depending on the ionic strength and the DAA concentration. In the near neutral region the curves show, in general, two desorption peaks, one in the anodic and another in the cathodic branch, and the differential capacity between the two peaks was markedly depressed due to the adsorption of DAA. Each of the desorption peaks at 10^{-4}M DAA in 0.1 M potassium fluoride solution split into two peaks as the solution pH was raised, and the newly-appeared peaks increased their heights with increasing pH. From these results the adsorbed species were inferred to be in the ionic form in the low pH region, and in the form of free amine molecules in the high pH region with a possibility of coadsorption of the two species in different proportions in the moderately alkaline region. Together with additional measurements showing the effects of chain lengths and of quarternary amines, the results will be correlated with the published information on the use of alkylamines in the flotation process.

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MECHANISM OF ADSORPTION OF XANTHATE ESTERS AND THIONOCARBAMATES ON COPPER AND ZINC SULFIDES. W. L. FREYBERGER, J. E. WENNEN and A. AHMED, Michigan Technological University, Houghton, Mich. 49931.

The mechanisms of adsorption of alkoxy xanthates, ROC(S)SC(O)OR′, allyl xanthates, ROC(S)SCC=C, and thionocarbamates, RNHC(S)SR′, have been studied using infrared spectroscopy. Adsorption of the compounds from aqueous emulsions was studied as a function of pH with fine precipitates of cuprous and cupric sulfides and copper-activated zinc sulfide. Results showed that the alkoxy xanthate molecule is split during the adsorption reaction. A xanthate group, ROC(S)S–, is formed which is adsorbed by the solid. The ultimate fate of the remainder of the original molecule has not been clearly established, although it is known that this portion appears in the aqueous solution. Allyl xanthates were found to adsorb as the molecule, and could easily be removed from the solid surface. The results also indicated that the thionocarbamates adsorb through the formation of a surface chelate compound. Hydrolysis of aqueous emulsions of alkoxy and allyl xanthates and dixanthogen was studied as a function of pH. These results were interpreted in terms of the molecular structure. On the basis of the hydrolysis and adsorption reactions, it was concluded that cleavage of the alkoxy xanthate molecule is catalyzed by the solid.