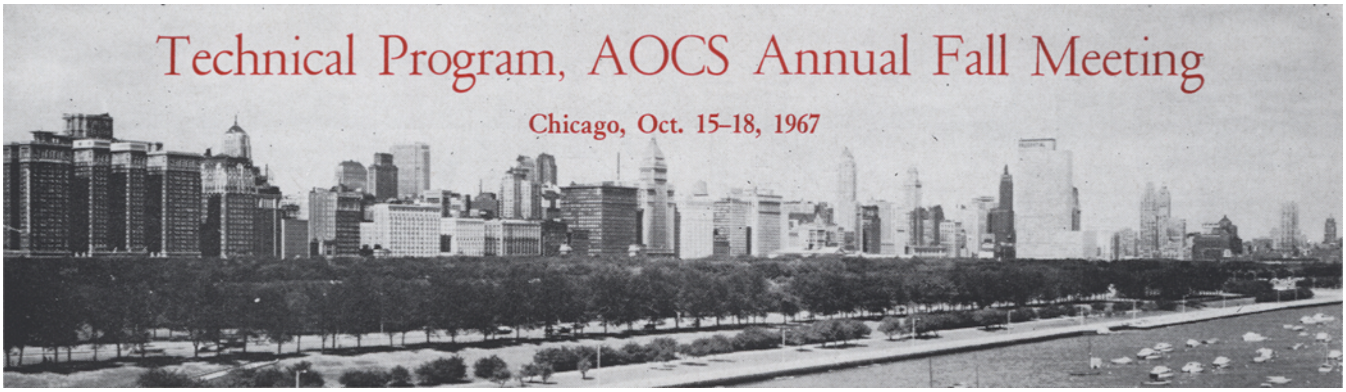
Technical Program, AOCS Annual Fall Meeting

Chicago, Oct. 15–18, 1967



MONDAY MORNING, OCTOBER 16, 1967

SESSION A—AVENUE WEST

SYMPOSIUM: OIL PROCESSING

Chairman: D. P. Arndtsen, DeLaval Separator Company

Introductory remarks 10:20

1. **Modern Soybean Dehulling** 10:30
James Sullivan,* Overstrom & Sons, Dallas, Texas

2. **Mineral Oil Adsorption** 11:00
Kenneth Becker, Blaw-Knox Company, Pittsburgh, Pa.

3. **Mechanically Aided, Thin-Film Drying of Lecithin Gums** 11:30
A. R. Gudheim, Kontro Company, Inc., Petersham, Mass.

MONDAY MORNING, OCTOBER 16, 1967

SESSION B—GREAT HALL

SYMPOSIUM: COMPUTERS AND AUTOMATION

Chairman: H. J. Dutton, USDA, Northern Regional Research Laboratory

Introductory Remarks 10:20
H. J. Dutton

6. **Laboratory Automation** 10:30
E. W. Roland, International Business Machines, Inc.

7. **Computer Analysis of Kinetic Data from Hydrogenations** 10:50
R. O. Butterfield, USDA, Northern Regional Research Laboratory

8. **Integrated System for Microreactor Gas Chromatography** 11:10
E. D. Bitner, V. L. Davison and H. J. Dutton, USDA, Northern Regional Research Laboratory

9. **Micro Vapor-Phase Hydrogenation Monitored with Tandem Chromatography-Radioactivity. III. Isomeric Monoenes** 11:30
T. L. Mounts, R. O. Butterfield, C. R. Scholfield and H. J. Dutton, USDA, Northern Regional Research Laboratory

10. **Calculation of the Rates of Isomerization and Hydrogenation of Triglycerides** 11:50
R. R. Allen, D. C. Stone, M. C. Moore and L. F. Albright, Anderson, Clayton & Co. Foods Division and Purdue University

MONDAY MORNING, OCTOBER 16, 1967

SESSION C—PLAZA ROOM

SYMPOSIUM: ROLE OF LIPIDS IN ENZYMES

Chairman: J. J. Kabara, University of Detroit

11. **Effect of Various Physical States on Brain Isozymes** 10:20
J. J. Kabara, University of Detroit, and Daria Konich, Wayne State University

12. **Effects of Various Physical States on Enzyme Catalysis: Some Physiological Implications** 10:40
Steven Price, Medical College of Virginia

13. **Nonpolar Interactions in the Binding of Pyridine Nucleotides to Dehydrogenases** 11:00
B. M. Anderson, University of Tennessee

15. **The Role of Lipids in Membrane Transport in Mycoplasma laidlawaii** 11:40
P. F. Smith, University of South Dakota

MONDAY MORNING, OCTOBER 16, 1967

SESSION D—FLORENTINE ROOM

DETERGENTS

Chairman: M. E. Ginn, Armour Grocery Products

16. **Measurement of Machine and Detergent Efficiency in Drycleaning** 10:20
W. H. Smith, Manfred Wentz and A. R. Martin, National Institute of Drycleaning

17. **Improvements in Detergency Precision with Radioactive Soil** 10:40
W. T. Shebs and *B. E. Gordon*, Shell Development Company

18. **Analysis for Sulfate Ion in the Biodegradation of Anionic Detergent** 11:00
T. C. Cordon, E. W. Maurer, O. Panasiuk and A. J. Stirton, USDA, Eastern Regional Research Laboratory

19. **Effect of Tallow/Coconut Fatty Acid Ratios on Properties of Bar Soaps** 11:20
M. E. Ginn, R. C. Steinhauer, I. Liebman and Eric Jungermann, Armour Grocery Products Co.

20. **Measuring Soil Dispersion Power of Detergents by Filtration** 11:40
W. H. Smith, Manfred Wentz, Nancy McCullough and *A. R. Martin*, National Institute of Drycleaning

MONDAY AFTERNOON, OCTOBER 16, 1967

SESSION E—GREAT HALL

SYMPOSIUM: GAS-LIQUID CHROMATOGRAPHY

Chairman: Lincoln Metcalfe, Armour & Co.

21. **Selection and Evaluation of Columns for Analysis of Lipids** 2:00
W. R. Supina and Nicholas Pelick, Supelco, Inc.

22. **Silicic Acid Column Chromatography: Parameters for a Binary Solvent** 2:20
D. G. McConnell, R. L. Hoffmann, G. J. Elman and C. D. Evans, USDA, Northern Regional Research Laboratory

23. **Silicic Acid Column Chromatography: Adsorption Mechanism and Solvent Systems** 2:40
R. L. Hoffmann, *D. G. McConnell* and C. D. Evans, USDA, Northern Regional Research Laboratory

24. **Thermally Stable Polyester Sorbents for High-Temperature Gas Chromatography** 3:00
D. J. Moore and V. L. Davison, USDA, Northern Regional Research Laboratory

25. **The Gas Chromatographic Separation of Long Chain Aldehyde Dimethyl Hydrazones** 3:20
C. B. Johnson, A. M. Pearson and L. R. Dugan, Michigan State University

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* Speakers' names shown in italics.

26. A Rapid Microozonolysis-GLC Procedure for Locating Unsaturation in Olenic Acids, Including Trienes and Tetraenes 3:40
R. Kleiman, G. F. Spencer and F. R. Earles, USDA, Northern Regional Research Laboratory

27. Identification and Estimation of Complex Fatty Derivatives by Gas-Liquid Chromatography—Partial Glycerides 4:00
A. E. Thomas, III, and *R. G. Manning*, Durkee Famous Foods

28. Hydrocarbons of Marine and Human Lipids 4:20
L. L. Gershbein and E. J. Singh, Northwest Institute for Medical Research

29. Selective Hydrogenation of the Methyl Ester of 7,9-Octadecadiynoic Acid 4:40
S. G. Morris, Paul Magidman, S. F. Herb and F. E. Luddy, USDA, Eastern Regional Research Laboratory

MONDAY AFTERNOON, OCTOBER 16, 1967

SESSION F—PLAZA ROOM

SYMPOSIUM: ROLE OF LIPIDS IN ENZYMES

Chairman: J. J. Kabara, University of Detroit

32. Lecithin-Protein Interaction in a GTP-Dependent Acyl-CoA Synthetase 2:00
Lauro Galzigna, Lodovico Sartorelli, C. R. Rossi, University of Padova, Italy; and D. M. Gibson, Indiana University Medical College

34. The Role of Lipid in Glucose 6-Phosphatase 3:20
W. L. Byrne and *Sue M. Duttera*, Duke University Medical Center

35. Activation of Phosphoryl Choline-Cytidyl Transferase of Phospholipids 3:40
W. G. Fiscus, Oklahoma University Hospitals, and W. C. Schneider, National Cancer Institute

36. Interactions of Heart Succinate Dehydrogenase with Phospholipids 4:00
P. Cerletti, M. G. Giordano, M. A. Giovenco, G. Magni and G. Testolin, University of Camerino, Italy

38. The Role of Lipid on Heme Synthesis 4:40
Yoshimasa Yoneyama, Hideo Sawada, Masazumi Takeshita and Yoshiki Sugita, Kanazawa University, Japan

MONDAY AFTERNOON, OCTOBER 16, 1967

SESSION G—FLORENTINE ROOM

DETERGENTS

Chairman: J. K. Weil, USDA, Eastern Regional Research Laboratory

39. Surface-Active Brassylic Acid-Ethylene Oxide Adducts: Preparation and Evaluation 2:00
T. K. Miwa, *R. V. Madrigal*, W. H. Tallent and I. A. Wolff, USDA, Northern Regional Research Laboratory

40. Foam Performance Tests in Dishwashing 2:20
F. C. Davis, G. R. Edwards, J. E. Woodrow and T. B. Albin, Shell Development Co.

41. Protein Soil Defoaming in Machine Dishwashers 2:40
I. R. Schmolka and *T. M. Kaneko*, Wyandotte Chemicals Corporation

42. The Use of Optical Brighteners for Synthetic Fibers in Detergents 3:00
R. Anliker, H. Hefti and K. Kasperl, CIBA Limited Basle Division, Technical Application Products, Switzerland

43. Enzymes as Additives to Laundry Compositions 3:20
J. C. Hoogerheide, Royal Netherlands Fermentation Industries, Ltd., Delft, Holland

44. Surface Activity of Sodium Salts of α-Sulfo Fatty Esters: The Oil/Water Interface 3:40
V. V. Subba Rao, R. J. Fix and *A. C. Zettlemoyer*, Lehigh University

MONDAY AFTERNOON, OCTOBER 16, 1967

SESSION G-1—AVENUE WEST ROOM

OIL PROCESSING

Chairman: D. P. Arndtsen, DeLaval Separator Co.

44A. Fatty Oil Processing—Conventional vs. Miscella 2:00
Frank Sullivan, Arthur McKee and Company, San Francisco

44B. Modern Techniques of Continuous Bleaching of Vegetable Oil 3:00
Hans Mueller, Mannedorf, Zurich, Switzerland

44C. Centrifugal Separation of Partially Hydrogenated Soybean Oil 3:30
D. Horton, American Tool and Machine Co., Hyde Park, Mass.

Discussion 4:00

TUESDAY MORNING, OCTOBER 17, 1967

SESSION H—AVENUE WEST

SYMPOSIUM: SURFACTANTS IN COSMETICS

Chairman: I. R. Schmolka, Wyandotte Chemicals Corp.

Introduction 9:00
Donald Laiderman, The Toni Company

45. Amphoteric Surface-Active Agents in Cosmetics 9:25
H. S. Mannheimer, Miranol Chemical Co.

46. Fatty Amido-Amine Derivatives 9:50
T. Muzyczko, S. Shore and J. Loboda, The Richardson Company

47. Effect of Structure of Amine Oxides in Foaming Properties of Shampoos 10:15
R. N. Goodell, Onyx Chemical Co.

48. Alcohol Ether Sulfates in Shampoos 10:40
Henry Watanabe and *W. L. Groves*, Continental Oil Company

49. A New Quaternary Ammonium Compound Hair Conditioning Agent 11:05
R. R. Egan and B. J. Hoffman, Archer-Daniels-Midland Co.

TUESDAY MORNING, OCTOBER 17, 1967

SESSION I—PLAZA ROOM

SYMPOSIUM: MASS SPECTROGRAPH

Co-Chairmen: R. T. Holman, Hormel Institute; and W. K. Rohwedder, USDA, Northern Regional Research Laboratory

50. Mass Spectra of Polyhydroxy Extranes 9:00
S. G. Levine, North Carolina State University; C. Cordes, *G. E. Van Lear* and K. L. Rinehart, Jr., University of Illinois

51. Molecular-Weight Determination of Long-Chain Methyl Esters by Field-Ion Mass Spectroscopy 9:20
W. K. Rohwedder, USDA, Northern Regional Research Laboratory

52. Elimination Reactions in the Mass Spectra of Long Chain Esters 9:40
R. E. Wolff, M. Greff, R. N. Stilwell, A. M. Lawson and J. A. McCloskey, Institute de Chimie (CNRS), Strasbourg, France, and Baylor University College of Medicine, Houston, Texas

53. A Study of Pyrolysis of Fatty Acid Esters Using Pyrolysis-Gas Chromatography-Mass Spectrometry 10:00
K. K. Sun, H. W. Hayes and *R. T. Holman*, The Hormel Institute

54. Digital Readout System for Mass Spectrometry 10:20
Don Oliver and M. C. Simmons

55. The Mass Spectra of Retinol (Vitamin A) and Related Compounds 10:40
G. R. Waller, R. L. Lin, K. S. Yang, E. D. Mitchell and E. C. Nelson, Oklahoma State University; and R. D. Grigsby, Continental Oil Company

(Continued on page 348A)

• *Local Section News*

Northeast Section

Award to Dr. Melnick at September Meeting

Daniel Melnick

The September 19th Meeting of the Northeast Section of AOCS will be held at Whyte's Restaurant in New York City.

The speaker will be Daniel Melnick, Director of Research and Quality Control of Corn Products Co. (Bayonne and Associated Laboratories). Dr. Melnick is the 1967 Lipid Award Winner. The title of his talk will be, "Essential Fatty Acids or Polyunsaturates—That Is the Question." The talk will deal with natural and unnatural (man-made) polyunsaturates, methodology and biological responses.

Dr. Melnick will receive the Lipid Award for his "Research in Industry," primarily for his research in the absence of aflatoxins from refined vegetable oils.

Background and Research Activities Noted

Dr. Melnick received his Bachelor's degree, with a major in Chemistry, and the PhD degree, with a major in biochemistry, from Yale University. Following four years of postdoctorate research at both Yale and at the University of Michigan, he entered industry as Chief Chemist and Supervisor of Research at Food Research Laboratories, New York. Ten years were spent in serving all segments of the food industry, at the latter consulting laboratory and then as Chief of the Food Development Division of the Quartermaster Food and Container Institute for the Armed Forces. During the past eighteen years, he has been with The Best Foods Division of Corn Products Company, first as Chief Technologist and then as Director of Research.

Dr. Melnick is a member of the American Chemical Society, American Society of Biological Chemists, American Institute of Nutrition, Institute of Food Technologists, American Association of Cereal Chemists, and, of course, of the American Oil Chemists' Society.

He is certified as a Specialist in Human Nutrition by the American Board of Nutrition, is a member of the honor societies of Sigma Xi and Phi Tau Sigma, is a member of the National Research Council Committee servicing the U.S. Army Natick Laboratories on Oil and Fat Product Developments, and is a member of the Council on Basic Science of the American Heart Association. He was Chairman of the Food and Nutrition Section of the Gordon Research Conferences sponsored by the American Association for the Advancement of Science, Associate Editor of the journal "Food Research," President of the New York Institute of Food Technologists and a National Councilor for this Chapter.

June Meeting Draws Record Attendance!

The final spring meeting of the Northeast Section of the AOCS was held at Whyte's Restaurant, and overflowed with the largest turnout in the history of the Section.

Reason—Karl Zilch, of Emery Industries (Cincinnati) was the guest speaker and his subject, "Synthetic Fatty Acids" (derived from petroleum factions).

Dr. Zilch's talk dealt with the possible methods that could be used to produce the desired results. He pointed out that the present products now available suffer from purity, odor and taste problems (where these can be objectionable); however, uses for even the crude material now being produced have met with acceptance. He pointed out that, given time and an upward turn in the cost of the "natural origin," the synthetics "will be in."

As a result of tremendous attendance at this meeting, the Northeast Section is planning a "follow-up" in June of 1968 with its supper meeting dealing with the actual manufacturing of the synthetics.

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(Continued from page 346A)

TUESDAY MORNING, OCTOBER 17, 1967

SESSION J—AVENUE WEST ROOM

SYMPOSIUM: SAFETY IN SOLVENT EXTRACTION

Chairman: N. H. Witte, Central Soya, Inc.

56. History of AOCS Safety and Engineering Committee **10:00**
N. H. Witte

57. Hazards in Solvent Extraction as Seen from a Property Insurance Point of View **10:30**
W. Meinhardt, Factory Mutual Insurance Company

58. Methods and Results of Purging Extractors **11:00**
L. Kingsbaker, Blaw-Knox Company

59. Some Specific Extraction Plant Safety Problems and Suggestions for Control **11:30**
N. W. Myers, Archer-Daniels-Midland Co.

TUESDAY MORNING, OCTOBER 17, 1967

SESSION K—FLORENTINE ROOM

REACTIONS AND COMPOSITION

Chairman: E. C. Leonard, National Dairy Products Corp.

61. Improved Synthesis of Long-Chain Polyhydric Alcohols **9:00**
D. J. Moore and E. H. Pryde, USDA, Northern Regional Research Laboratory

62. Preparation of Alcohols by Ozonolysis of Unsaturated Fatty Esters **9:20**
E. H. Pryde, C. M. Thierfelder and J. C. Cowan, USDA, Northern Regional Research Laboratory

63. Hydrocarbons Derived from Autoxidized Vegetable Oils Through Thermal Splitting **9:40**
C. D. Evans, R. L. Hoffmann, G. R. List and E. Selke, USDA, Northern Regional Research Laboratory

64. 9-Aminonanamide, a Polyamide Intermediate from Soybean Oil **10:00**
W. L. Kohlhase, E. H. Pryde and J. C. Cowan, USDA, Northern Regional Research Laboratory

65. Search for New Industrial Oils. XVI. Seed Oils of the Umbelliflorae **10:20**
F. R. Earle, G. F. Spencer, R. Kleiman and I. A. Wolff, USDA, Northern Regional Research Laboratory

66. Industrial Uses for High-Oleic Safflower Oil **10:40**
M. J. Diamond and *G. Fuller*, USDA, Western Regional Research Laboratory

67. Isomeric Phenylstearic Acids and Related Compounds. Composition and Partial Separation **11:00**
F. D. Smith and A. J. Stirton, USDA, Eastern Regional Research Laboratory

68. Correlation of Fatty Acid Structure with Preferential Order of Urea Complex Formation **11:20**
J. L. Iverson and R. W. Weik, Department of Health, Education and Welfare, FDA

68.A. Fatty Acid Composition of Cod Liver Oil Determined by Urea Fractionation and Modified PTGC **11:30**
J. L. Iverson, Department of Health, Education and Welfare, FDA

69. Molecular Sieves as Catalysts for Cyclic Fatty Acid Formation **11:40**
R. A. Eisenhauer and R. E. Beal, USDA, Northern Regional Research Laboratory

TUESDAY AFTERNOON, OCTOBER 17, 1967

SESSION L—PLAZA ROOM

BIOCHEMISTRY

Chairman: E. E. Rice, Swift & Co.

70. Studies on the Autoxidation of Human Serum Lipoproteins Using Ultraviolet Spectrophotometry **2:00**
W. L. Robinson and *G. J. Nelson*, University of California

71. Quantitative Determination of Glyceryl Alk-l-enyl and Aklyl-Alkenyl Ethers in Neutral and Phospholipids **2:20**
Randall Wood and Fred Snyder, Oak Ridge Institute of Nuclear Studies

72. The Subcellular Distribution and Metabolism of Glyceryl Ether Diesters in Ehrlich Ascites Cells 2:40
Fred Snyder and Randall Wood, Oak Ridge Institute of Nuclear Studies

73. An Improved Method for the Preparation of Cyclic Acetal Derivatives from Plasmalogens 3:00
Grace Y. Sun and L. A. Horrocks, Cleveland Psychiatric Institute

74. Characterization of Sialylgalactosylceramide (SGC) from Human Brain 3:20
Bader Siddiqui and R. H. McCluer, The Ohio State University

75. Lipids of the Preputial Gland of the Mouse 3:40
Gail Sansone and J. G. Hamilton, Tulane Medical School

76. Some Effects on Fatty Acids Induced by Exercise 4:00
J. B. Saddler, University of Washington; and H. M. Krueger, I. J. Tinsely and R. R. Lowry, Oregon State University

77. Acetoacetate Metabolism in Rats on "Ketogenic" Diets 4:40
Li Hsin Chung and *Jacqueline Dupont*, Colorado State University

TUESDAY AFTERNOON, OCTOBER 17, 1967

SESSION M—GREAT HALL

SYMPOSIUM: SURFACTANTS IN COSMETICS

Chairman: I. R. Schmolka, Wyandotte Chemicals Corp.

Introduction 2:00
Marshall Sorkin, The Alberto-Culver Co.

79. The Influence of Various Surfactants on the Antimicrobial Activity of Bromsalans and Other Ring-Halogenated Substances 2:25
N. M. Molnar, Fine Organics, Inc.

80. New Tertiary Amine-Based Surface-Active Polymers 2:50
R. R. Egan and B. J. Hoffman, Archer-Daniels-Midland Co.

81. Methyl Glucoside Esters in Cosmetics 3:15
O. E. Libman and Howard Packer, Hodag Chemical Corporation

82. Fatty Glycols and Isostearyl Alcohol as Lipstick Components 3:40
R. R. Egan and B. J. Hoffman, Archer-Daniels-Midland Co.

83. Reduced Lanolins: The Synthesis, Properties and Cosmetic Applications 4:05
F. P. Siegel, Theodore Kritchevsky and S. T. Goode, RITA Chemical Corporation

84. Proteins—Some New Studies 4:30
R. R. Risso, Stepan Chemical Co.

TUESDAY AFTERNOON, OCTOBER 17, 1967

SESSION N—AVENUE WEST

SYMPOSIUM: SAFETY IN SOLVENT EXTRACTION

84A. Latest Developments on the NFPA Standard for Solvent Extraction Plants 2:00
N. H. Moore, N. Hunt Moore and Assoc.

85. Some Special Safety Problems in Plants Outside the US 2:30
Les Watkins, Anderson Clayton Co.

86. Safety Problems in Operating DT Machines 3:00
H. James, Ralston Purina

87. A Review of Operating Rules Relating to Extraction Plant Safety 3:30
W. Pearson, Lauhoff Grain

Round Table Discussion 4:00

TUESDAY AFTERNOON, OCTOBER 17, 1967

SESSION O—FLORENTINE ROOM

EDIBLE FATS AND OILS

Chairman: Joseph Endrea, Armour & Co.

88. Selective Hydrogenation of Cyclopropenoids in Cottonseed Oil 2:00
J. P. Hutchins, A. Z. Ullman and L. H. Going, Procter & Gamble Company

89. Autoxidation of Monolayers of Linolenic Acid on Silica Gel 2:20
W. L. Porter, A. S. Henick, S. R. Cunnold, M. A. Sharkey and S. Warrington, US Army Natick Laboratories

90. The Color Problem in Experimental Varieties of Safflower 2:40
H. J. Burkhardt, USDA, Western Regional Research Laboratory

91. Phospholipid Oxidation in Emulsions 3:00
G. A. Corliss and L. R. Dugan, Michigan State University

92. High "Oleic" Oils by Selective Hydrogenation of Soybean Oil 3:20
H. J. Dutton, O. Popescu and S. Koritala, USDA, Northern Regional Research Laboratory

93. Selective Hydrogenation of Soybean Oil. III. Copper-Exchanged Molecular Sieve and Other Copper Catalysts 3:40
Sambasivarao Koritala, USDA, Northern Regional Research Laboratory

94. Artifact Formation in the Fractional Distillation of Long-Chain Polyunsaturated Methyl Esters 4:00
O. S. Privett, E. C. Nickell, J. D. Nadenicek and F. J. Pusch, The Hormel Institute

95. Distillation and Thermal Decomposition of Fatty Ozonides 4:20
E. M. Stearns, Jr., and *O. S. Privett*, The Hormel Institute

96. Removal of Copper from Hydrogenated Soybean Oil 4:40
R. E. Beal, K. J. Moulton and L. T. Black, USDA, Northern Regional Research Laboratory

WEDNESDAY MORNING, OCTOBER 18, 1967

SESSION P—AVENUE WEST

BIOCHEMISTRY

Chairman: F. W. Quackenbush, Purdue University

97. Uptake and Metabolism of Free Fatty Acid by Isolated Peritoneal Mast Cells of Rats 9:00
M. S. Cabut, R. J. Ho and H. C. Meng, Vanderbilt University

98. Inhibition of Lipolytic Enzymes by Organophosphates and Carbamates 9:20
R. G. Jensen and *Dorothy L. Carpenter*, University of Connecticut

99. Role of Lipids in CA^{++} Uptake and Mg-ATPase Activity of Rat Skeletal Muscle Sarcoplasmic Reticulum 9:40
B. P. Yu, E. J. Masoro and F. D. DeMartinis, Woman's Medical College

100. Chain Elongation of Polyunsaturated Fatty Acids by Microsomes in vitro 10:00
Kirsten Christiansen, Hans Mohrhauer, Yves Marcel, Minerva Gan and R. T. Holman, The Hormel Institute

101. Lipoxidase Deactivation to Improve Stability, Odor and Flavor of Full-Fat Soy Flours 10:20
G. C. Mustakas, W. J. Albrecht, J. E. McGhee, L. T. Black, G. N. Bookwalter and E. L. Griffin, USDA, Northern Regional Research Laboratory

102. Differences in Triglyceride Structure After Refeeding with Medium Chain Methyl Esters and Triglycerides 10:40
Hans Kaunitz, Ruth E. Johnson and Cynthia Belton, Columbia University

103. The Endogenous Triglycerides of the Pig 11:00
R. E. Anderson, N. R. Bottino and Raymond Reiser, Texas A&M University

(Continued on page 357A)

(Continued from page 350A)

104. Epoxides in Rat Lipids 11:20
J. A. Fioriti and R. J. Sims, General Foods Corp.

104A. Absorption of Labeled Nonvolatile Oxidation Products of Randomized Corn Oil 11:40
E. G. Perkins and S. M. Vachha, University of Illinois

WEDNESDAY MORNING, OCTOBER 18, 1967

SESSION Q—GREAT HALL

MODIFICATION OF OILSEEDS THROUGH PLANT BREEDING

Chairman: C. G. Youngs, National Research Council, Canada

Introductory Remarks 10:20
C. G. Youngs

105. Breeding Rapeseed for Oil and Seed Quality 10:30
R. K. Downey, Canadian Agricultural Research Station, Saskatoon; B. M. Craig and C. G. Youngs, Prairie Regional Laboratory of the National Research Council, Saskatoon

106. Altering the Gossypol Content of Cottonseed Through Breeding 10:50
J. A. Lee, North Carolina State University

107. Variation in Composition of Sunflower Oil from Composite Samples and Single Seeds of Varieties and Inbred Lines 11:10
E. D. Putt, Research Station, CDA, Morden, Manitoba; B. M. Craig and R. B. Carson, Research Branch, CDA, Ottawa

107A. Modification of Quantity and Quality of Safflower Oil Through Plant Breeding 11:30
P. F. Knowles, University of California, Davis

107B. Breeding for Oil Quality and Quantity in Flaxseed 11:50
D. M. Yermanos, University of California, Riverside

WEDNESDAY MORNING, OCTOBER 18, 1967

SESSION R—PLAZA ROOM

GENERAL ANALYTICAL

Chairman: W. D. Pohle, Swift & Co.

109. The Complete Characterization of Unsaturated n-Aldehyde Dinitrophenylhydrazones by Thin-Layer Chromatography 9:00
P. W. Meijboom, Unilever Research Laboratories, The Netherlands

110. Triglyceride Analysis by Consecutive Liquid-Liquid Partition and Gas-Liquid Chromatography. Ephedra nevadensis Seed Fat 9:20
Carter Litchfield, Texas Agricultural Experiment Station

111. Fractionation of Natural Mixtures of Diacyl Phosphatides Containing Alk-l-enyl Acyl Phosphatides 9:40
C. V. Viswanathan, S. P. Hoevet and W. O. Lundberg, The Hormel Institute

112. Chromatographic Separation of Plasmalogens, Alkyl-Acyl Phosphatides and Diacyl Phosphatides 10:00
Ossi Renkonen, University of Helsinki

113. Copper Determination of Edible Soybean Oils 10:20
Gary List and C. D. Evans, USDA, Northern Regional Research Laboratory

114. Titration of Cyclopropene Esters with Hydrogen Bromide 10:40
R. O. Feuge, Zigrida Zarins, J. L. White and R. L. Holmes, USDA, Southern Regional Research Laboratory

115. A Bromothymol Blue Dye-Binding Procedure for Evaluating Heat Processing of Soybean Meals 11:00
J. E. McGhee, G. C. Mustakas and W. J. Albrecht, USDA, Northern Regional Research Laboratory

116. An Improved Procedure for Quantitative Analysis of Lipid Classes via TLC by Charring and Densitometry 11:20
L. J. Nutter and O. S. Privett, The Hormel Institute

WEDNESDAY MORNING, OCTOBER 18, 1967

SESSION S—FLORENTINE ROOM

REACTIONS AND COMPOSITION

Chairman: E. C. Leonard, National Dairy Products Corp.

117. The Structure of Dimeric Fatty Acids and the Mechanism of Dimerization 9:00
Achintya K. Sen Gupta, Unilever Forschungslaboratorium Hamburg, Germany

118. Nonvolatile α-Branched Chain Fatty Esters. III. Addition of Acid Chlorides and Anhydrides to Terminal Olefins 9:20
T. Perlstein, A. Eisner, W. C. Ault, P. A. DeHaven, USDA, Eastern Regional Research Laboratory

119. A Structural Basis for the Development of Functional Defects in Isomerized Linolenates 9:40
J. P. Kass, Milwaukee, Wis.

120. Methylation of Fatty Acids in Lipids by Low-Temperature Base Catalysis 10:00
Barbara Zook and L. R. Dugan, Michigan State University

121. Properties of Wax Esters 10:20
R. T. Iyengar and H. Schlenk, The Hormel Institute

122. Synthesis of -Methyl Branched Fatty Acids via the Favorshky Reaction 10:40
T. Gerson and H. Schlenk, The Hormel Institute

123. High-Yield Preparation of Methyl Stearolate 11:00
R. O. Butterfield and H. J. Dutton, USDA, Northern Regional Research Laboratory

124. Relative Reduction Rates of Fatty Acid Isomers by Hydrazine 11:20
C. R. Scholfield, R. O. Butterfield and H. J. Dutton, USDA, Northern Regional Research Laboratory

125. Synthesis of Unsaturated Aldehydes 11:40
Henry Rakoff, USDA, Northern Regional Research Laboratory

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ABSTRACTS OF PAPERS 41ST FALL MEETING CHICAGO, ILLINOIS

— 1 —

MODERN SOYBEAN DEHULLING

J. Sullivan

— 2 —

MINERAL OIL ABSORPTION

K. Becker

— 3 —

MECHANICALLY AIDED, THIN-FILM DRYING OF LECITHIN GUMS

A. R. Gudheim

— 6 —

LABORATORY AUTOMATION

E. W. Roland

This paper describes a computer system configuration and program which automates the acquisition and reduction of data from analytical laboratory instruments such as gas chromatographs and low resolution mass spectrometers. The unique characteristics of these laboratory instruments and their effect on the computer system and configuration are discussed. Some of the problems of the laboratory instrument-computer interface are also discussed.

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COMPUTER ANALYSIS OF KINETIC DATA FROM HYDROGENATIONS

R. O. Butterfield

The use of digital computers to determine reaction rate constants from kinetic equations for hydrogenation is described. Rapid calculation of catalyst selectivities based upon consecutive order reactions is contrasted to the longer search for a set of rate constants which give a minimum least square fit for the linolenate reduction scheme of Mounts and Dutton. Characteristics of a kinetic error surface are shown for the simple model $A \rightarrow B$, $B \rightarrow C$ and $A \rightarrow C$. This three-dimensional system was used to determine which search routines would efficiently find rate constants for a least square error fit of a ten-dimensional linolenate reduction scheme.

— 8 —

INTEGRATED SYSTEM FOR MICROREACTOR GAS CHROMATOGRAPHY

E. D. Bitner, V. L. Davison and H. J. Dutton

A compact unit has been constructed to aid in using the microreactor apparatus recently described for location of double bonds and transesterification. Features are an ozone generator; gas flow rotameters; solenoid-operated, 6-way, gas valve; and a combination temperature and ozone meter. The meter provides a visual indication of ozone concentration during reactions and, by means of a built-in relay, controls and monitors reaction temperature. Basic electronic circuits and common laboratory items simplify construction of the unit.

Some microreactions possible with this integrated system are ozonization-pyrolysis, esterification, transesterification, saponification, reduction, and halogenation. Its applicability is illustrated by ozonization-pyrolysis and transesterification reactions.

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MICRO VAPOR-PHASE HYDROGENATION MONITORED WITH TANDEM CHROMATOGRAPHY-RADIOACTIVITY. III. ISOMERIC MONOENES

T. L. Mounts, R. O. Butterfield, C. R. Scholfield and H. J. Dutton

Micro vapor-phase hydrogenation (MVPH) techniques have been utilized to investigate the effect of geometric and positional isomerism on the rate of hydrogenation of monoene fatty esters. Methyl oleate-1-^{14}C (*cis*-Δ9 unsaturation) was added in tracer amounts to unlabeled isomeric monoenes. Reaction rates relative to the rate for hydrogenation of the radioactive methyl oleate have been determined for *cis* and *trans* unsaturation located in positions Δ6 through Δ12.

This MVPH technique provides simultaneous monitoring of both hydrogenation of essentially pure isomeric monoene by thermal conductivity and of methyl oleate by radioactivity. The two hydrogenations proceed simultaneously and have identical parameters of temperature, flow rate and catalyst activity. Hydrogenations were made with nickel, palladium, platinum and cobalt catalysts. The experimental data are plotted, relative reaction rates are calculated and theoretical curves are drawn by a digital computer-plotter system. Experiments with nickel catalysts indicate that methyl oleate hydrogenates faster than other isomeric monoenes studied. This result suggests that among the compounds with unsaturation Δ6 through Δ12 a *cis*-configuration with the double bond equidistant from the carboxyl and hydrocarbon ends of the molecule is the most susceptible to hydrogenation.

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CALCULATION OF THE RATES OF ISOMERIZATION AND HYDROGENATION OF TRIGLYCERIDES

R. R. Allen, D. C. Stone, M. C. Moore and L. F. Albright

A model for the reaction sequence of the hydrogenation of the tri, di and monounsaturated esters in fats has been developed. This model also includes the cis-trans isomerization of the monounsaturated esters since this isomerization is an integral part of the hydrogenation reaction and has a considerable effect on the consistency of the hydrogenated product.

The first order differential equations of the model have been integrated and used to calculate the relative composition of a hydrogenating system.

A digital computer program has been developed to numerically estimate the reaction rate constants of the model equations using data obtained from laboratory and plant hydrogenations.

These reaction rate constants are a numerical description of the isomerization and hydrogenation characteristics of a catalyst or set of hydrogenation conditions and thus can be used as a numerical isomerization and hydrogenation index.

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EFFECT OF VARIOUS PHYSICAL STATES ON BRAIN ISOZYMES

J. J. Kabara and Daria Konich

Attempts were made to find optimum extraction procedure for isolating brain lactic dehydrogenase and esterase activity. During these manipulative procedures, the effects of salt and alcohol were studied. These studies suggested that a lipoprotein was under investigation.

The differential effects of sodium and calcium salts have been interpreted on the basis of forming hydrophilic and hydrophobic sols.

Lipids extracted from mouse liver offered protection against the inactivating effects of calcium-butanol solvent systems.

Lipid extraction of purified LDH_1 and LDH_5 isozymes resulted in the appearance of unidentified lipids from both preparations. The usual amount of lipids in LDH_5 as opposed to LDH_1 may account for the increased stability of LDH_5 isozymes.

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EFFECTS OF VARIOUS PHYSICAL STATES ON ENZYME CATALYSIS: SOME PHYSIOLOGICAL IMPLICATIONS

Steven Price

Dilute aqueous solution is the usual state in which in vitro studies of enzyme catalysis are conducted. In the cell organelles, in which many enzymes are found in vivo, the conditions probably include hydrophobic media, high concentrations of polyelectrolytes, and lipid-water interfaces. This presentation reviews what little is known of the in vitro behavior of enzymes under comparable conditions. In hydrophobic media, in which enzymes are generally insoluble, catalytic activities are reduced relative to aqueous solutions, but are still substantial. Although effects of concentrated polyelectrolytes have received little attention, enzymes covalently bonded to polyelectrolytes have been studied. Such modified enzymes show altered pH-activity relations, often retain most of the catalytic activities, and may be more stable than native enzymes. Most proteins denature at lipid-water interfaces, although some enzymes are highly active at such interfaces.

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NONPOLAR INTERACTIONS IN THE BINDING OF PYRIDINE NUCLEOTIDES TO DEHYDROGENASES

B. M. Anderson

N^1-Alkylnicotinamide chlorides, varying in the alkyl substituent from the N^1-methyl to the N^1-dodecyl derivative, have been studied as inhibitors of dehydrogenase-catalyzed reactions. The functioning of these compounds as inhibitors appears related to various properties of the dehydrogenase involved. For example, these compounds effectively inhibit the yeast alcohol dehydrogenase-catalyzed oxidation of ethanol and up to a certain chain length of inhibitor, the inhibition observed was competitive with respect to the coenzyme, NAD. Through the application of multiple inhibition kinetics, employing combinations of adenine and with dimethyl sulfoxide and sodium bicarbonate. In studying the Rosenmund reduction of acid chlorides to aldehydes, White, Sulya and Cain [J. Lipid Res. *8*, 158 (1966)] found that while this method worked well for the preparation of saturated aldehydes, the reduction of oleoyl chloride gave stearaldehyde as well as olealdehyde. Moreover, the olealdehyde contained 26% *trans* bonds and the double bonds were scattered from C_6 through C_{14} with less than half remaining at C_9.

Since a noncatalytic method might give reduction without bond migration or isomerization, the reduction of unsaturated acid chlorides with lithium tri-*t*-butoxyaluminohydride [J. Am. Chem. Soc. *80*, 5377 (1958)] was studied. Infrared analyses of olealdehyde, linolealdehyde and stearolaldehyde prepared from the corresponding acid chlorides revealed no *trans* isomers. Ozonization-reduction of the ethylenic aldehydes or ozonization-hydrolysis-esterification of the acetylenic aldehyde followed by gas-liquid chromatographic analysis of the fragments showed that essentially no bond migration had occurred (at most 3–5%). Ultraviolet analysis of linolealdehyde showed the absence of conjugation. Therefore, lithium tri-*t*-butoxyaluminohydride can be used to reduce monoethylenic, diethylenic and monoacetylenic acid chlorides to the corresponding aldehydes with essentially no bond migration or isomerization.

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Flavor Chemists Elect Merwin President

E. L. Merwin has been elected to a one-year term as President of the Society of Flavor Chemists, Inc., at its Annual Meeting in New York City.

Other officers elected were: Vice President, Anthony Clemente of Fritsche Bros.; Secretary, Eugene Buday of Polak Frutal Works; Treasurer, A. V. Saldarini of Norda.

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Applications Now Being Accepted for Polymeric Materials Program

Applications for the graduate program in Polymer Chemistry and Technology at Polytechnic Institute of Brooklyn are now being accepted by the Office of Admissions, 333 Jay St., Brooklyn, N. Y. 11201.

Registration will be held Sept. 18–21, 1967. Classes begin Sept. 25. Research fellowships are available for the program, announced Prof. James Conti, Head of the Chemical Engineering Department. Interested students may write to Prof. Conti or call him at (212)643-2852 or 643-2962.

The program, leading to a master's degree in Polymeric Materials, can be pursued full-time in the day or part-time in the evening. A full-time student can complete the program in one calendar year.

Requirements for the program are a B.S. degree in Chemistry or Chemical Engineering or the equivalent from an approved college. Total semester hour credits required for the degree are 30. Of this total, 20 are elective credits.

Planned to make possible specialization in polymer science or engineering or to obtain a diversified training in both *polymer chemistry and technology,* the program conforms fully with the recommendations of the Education Committee of the Society of Plastics Engineers.

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(Continued from page 360A)

Synergistic sequestering agent. J. S. Pierce. *U.S. 3,294,689.* A synergistic sequestering composition of matter of wide utility is claimed which, when dissolved in water, consists essentially of an aqueous solution of $(HOCH_2)_3CNHCH_2CHOHCH_2NHC(CH_2OH)_3$ and citric acid, in which the molar ratio of polyhydroxyamine to citric acid has limits of 4/1 to 1/4.

Shaving cream containing polysiloxanes. J. L. Bishop, Jr. and C. W. Todd (Dow Corning Corp.). *U.S. 3,298,919.* A shaving cream composition consists of 0.5-9% stearic acid, 0.5-3% lauric acid, 1-15% glycerine, 1-7% triethanolamine, 40-80% water, 2-12% of a propellant and 0.1-5% of a silicone fluid.

Lime soap dispersants. R. R. Irani and K. Moedritzer (Monsanto Co.). *U.S. 3,298,956.* A soap composition is claimed, consisting essentially of soap and at least one per cent by weight of an organo-amino polymethylphosphonic compound of the formula $(R_1)(R_2)N{-}C(Y)(Y'){-}PO(OX)_2$, where X is a cation selected from the group consisting of hydrogen, alkali metal ion, ammonium ion and lower molecular weight alkyl, alkylene and alkanol amine ions; Y and Y′ are either hydrogen or lower alkyl groups containing 1-4 atoms; R_1 is either hydrogen, an aliphatic group containing 1 to 30 C atoms or $-C(Y)(Y'){-}PO(OX)_2$; R_2 is selected from the class consisting of hydrogen, aliphatic groups containing 1 to 30 C atoms, $-C(Y)(Y'){-}PO(OX)_2$ and $-[C(Y)(Y')]_n{-}N(Z')(Z)$, where n is an integer from 1 to 30; Z is a member selected from the class consisting of hydrogen and $-C(Y)(Y'){-}PO(OX)_2$ and Z′ is a member selected from the class consisting of hydrogen, $-C(Y)(Y'){-}PO(OX_2)$ and $-[C(Y)(Y')NZ]_m{-}C(Y)(Y'){-}PO(OX)_2$, where m is an integer from 1 to 30; with at least one of the groups represented by R_1 and R_2 containing at least one $-C(Y)(Y'){-}PO(OX)_2$ group.

Detergent breaker composition. J. S. Frank. *U.S. 3,298,963.* A synthetic detergent breaker composition consists essentially of 2-60% by wt. dialkylpolysiloxane having the general formula $(RSiO)_n$ where n is a positive integer from 2 to 100 and the R radicals are alkyl groups with, at the chain ends, from 1 to 6 C atoms; 2-70% alkylsiloxymetallic complex having the general formula $(RSiO)_3M$, where M is the metallic ion selected from the group consisting of Al, Fe^{2+}, Fe^{3+} and Co and the R consists of alkyl groups from C_1 to C_6; 10-70% metallic sulfate, the metal being Al, Fe^{2+}, Fe^{3+} or Co.; 0.5-20% silica gel; and 0.2-0.5% of a pH controlling material selected from the group consisting of sulfuric acid, sulfurous acid and ascorbic acid.

Alkylene oxide polymer composition flexibilized with salts of carboxylic acids. R. D. Lundberg and R. W. Callard (Union Carbide Corp.). *U.S. 3,298,980.* An homogeneous composition is claimed, comprising a polyethylene oxide having a reduced viscosity of at least 1 and from about 20 to 40% by wt., based on the weight of the polymer, of a salt containing 4-22 C atoms selected from the group consisting of ammonium or alkali metal salts of aliphatic carboxylic acids or aromatic carboxylic acids.

Method of selecting emulsions intended for the preparation of cosmetics and skin products. R. R. Aron-Brunetiere and C. F. Aron (Paris, France). *U.S. 3,300,386.* A method is described for testing emulsions as to their suitability in the treatment of dry and greasy skins. The method involves effecting a biopsy of an untreated portion of the shaven skin of an animal, applying the emulsion to be tested on another portion of the shaven skin at spaced intervals for a predetermined interval and effecting biopsies of the treated portion to determine the effect of the treatment. Emulsions for treating dry skins are expected to cause hyperplasia of the sebaceous glands and emulsions for treating greasy skins should fail to cause such an effect.

Pressed powder antiperspirant and method of preparation. R. L. Kole (Kolmar Laboratories, Inc.). *U.S. 3,300,387.* A topically applied product for human use consists of a dry pressed powder cosmetic base having dispersed in itself divided particles of a hygroscopic antiperspirant coated with a water-soluble wax-like material selected from one of the following: polyethylene glycols with an average molecular weight of 1000 to 6000; polypropylene glycols with an average molecular weight of 140 to 600; methoxy propylene glycols with an average molecular weight of 350 to 750; lanolin extracts; ethoxylated lanolin; fatty acid esters of polyalcohols containing C_8 to C_{20} fatty acids; ethoxylated fatty acids containing

(Continued on page 392A)

The feature beginning on page 298A of this issue, "Air Pollution Regulation of Nonvehicular, Organic-Solvent Emissions by Los Angeles Rule 66," by G. R. Maher, is a continuation of the series in publication from the AOCS Fats and Oils Processing Short Course held in East Lansing, Aug. 29–Sept. 1, 1966. Additional papers will appear in subsequent issues of the Journal.

• *New Products*

SUPELCO, INC., Bellefonte, Pa. has a new dimethylpolysiloxane stationary phase OV-1 for gas chromatography, designed for use at exceptionally high temperatures. It can be substituted for the commonly used nonpolar silicones without the need for recalibration since separation characteristics are identical.

VARIAN AEROGRAPH, Walnut Creek, Calif., has announced its new preparative gas chromatograph, Model 713, with a time pressure injector that allows automatic, reproducible introduction of a wide range of sample sizes up to 30 ml.

Also available from the company is a fully-automated gas chromatography integrator, Model 475, which can be used with all gas chromatography detectors. The compact, all-transistor model accepts an input signal range from 0 to 1400 mv and permits accuracy of better than 0.1%.

FISHER SCIENTIFIC CO., Pittsburgh Pa., has developed a new version of their potentiometric titralyzer. Called the photometric titralyzer, it fully automates routine colorimetric analysis, using optical-electronic detection of endpoints. It presents answers on paper tape; recycles itself to its initial condition; indexes the next sample into position; and proceeds with the next analysis. Capacity: 15 samples.

STEPAN CHEMICAL COMPANY, Northfield, Ill., has begun commercial production of alpha olefin sulfonates under the name Bio-Terge. They are said to offer complete and rapid biodegradability. Stevens says their nonhygroscopic surfactants offer good solubility and stability for hard water, acids, alkalis and heat, and are more compatible with soap than linear alkyl sulfonates.

SUPELCO, INC., Bellefonte, Pa., now has available 1,2 dimyristin, 1,2 dipalmitin, and 1,2 diolein. Each is offered as a 99% pure isomer and should be of value as calibration standards for those working with natural products or studying animal metabolism.

PHARMACIA FINE CHEMICALS, INC., Piscataway, N.J., has a new Sephadex laboratory column K 50 for analytical and preparative, as well as semi-industrial scale applications in gel filtration and ion exchange chromatography. Adjustable flow adaptors and a cooling jacket allow the column to be operated with aqueous systems at a constant temperature as part of an automatic or semiautomatic system.

BRINKMANN INSTRUMENTS, Westbury, N.Y., has announced a new line of homogenizers (dispersers, emulsifiers) for inducing physical or chemical change on samples with a kinematic high-frequency sonic and/or ultrasonic system. The latest version of Ultra Turrax homogenizers, they are most effective with highly concentrated samples.

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• *Obituaries*

FRANK WOODSON (1928), member emeritus of AOCS, died April 12 in Memphis, Tenn.

C. F. RASCHKE (1940), Manager, Brookside Division, Safeway Stores, Inc., Oakland, Calif., died June 27, 1967.

Word has been received of the death in June of MRS. J. R. MAYS, wife of J. R. Mays (1916) retired president of Barrow-Agee Labs, Inc.

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(Continued from page 388A)

C_8 to C_{20} fatty acids; and ethoxylated fatty alcohols containing C_8 to C_{20} fatty alcohols.

SURFACE ACTIVE COMPOSITIONS CONTAINING MIXTURES OF MONO- AND DI-ALKYLOXY-METHYL ETHERS OF SUGAR. G. R. Ames (U.S. Sec'y of Agr.). *U.S. 3,300,413.* A surface active composition is claimed, consisting essentially of about equal parts by weight of: (I) a mono-(alkyloxymethyl) ether of a sugar and (II) a di-(alkyloxymethyl) ether of a sugar. The sugar in both I and II is either glucose or sucrose and the alkyl groups contain 6 to 12 C atoms.

PROCESS FOR THE SULFONATION OF PEROXIDIZED, DEPEROXIDIZED UNSATURATED FATTY ACID ESTERS AND PRODUCT. J. Plapper and H. J. Krause (Bohme Fettchemie G.m.b.H., Dusseldorf, Germany). *U.S. 3,300,525.* A process for the production of sulfonated fatting agents from unsaturated, hydroxy-free fatty materials, such as either natural or synthetic fats and oils, comprises the steps of: (a) peroxidizing the fatty materials by treatment with oxygen containing gases at 65–100C; (b) deperoxidizing by heat treatment at 110–160C; (c) sulfonating by reaction with 5 to 15% of sulfur trioxide at 0–20C; (d) bleaching the sulfonated products with hydrogen peroxide, and (e) neutralizing the bleached, sulfonated product.

WATER SOLUBLE ESTERS OF HYDROXYL-CONTAINING, MICELLE FORMING SURFACE ACTIVE COMPOUNDS. F. E. Woodward and R. A. Grifo (General Aniline & Film Corp.). *U.S. 3,301,829.* A composition is claimed comprising a water-soluble partial ester of: (1) an hydroxyl-containing micelle-forming surface active agent selected from the group consisting of anionic surfactants, alkylene oxide condensation products, alkylolamine condensation products with fatty acids or with fatty esters, and glycol and polyesters of fatty acids, and (2) an alkali-soluble interpolymer of an ethylenically unsaturated carboxylic acid anhydride with a terminal unsaturated monomer selected from the group consisting of vinyl ethers, vinyl esters and alpha olefins; the said partial ester containing not more than about 5% of the carboxyl groups present as ester groups.

DETERGENT PROCESSES AND COMPOSITIONS THEREFOR. C. Y. Shen and J. S. Metcalf (Monsanto Co.). *U.S. 3,303,134.* A process for manufacturing a heat-dried composition containing hydrated penta alkali metal tripolyphosphate comprises the steps of preparing an aqueous slurry containing at least about 10% by wt., based on the total slurry weight, of water, at least about 5%, based on the total slurry weight, of an alkali metal trimetaphosphate, and an alkali metal base. The alkali metal base should have a pH of at least 10.2 at 25C at a 1% by wt. concentration in water and should be present in the aqueous detergent slurry in an amount sufficient to convert at least one third of the alkali metal trimetaphosphate to hydrated penta alkali metal tripolyphosphate. Lastly, the aqueous detergent slurry is heat-dried.

METHOD OF PREPARING CLEANSING COMPOSITIONS. S. Goldwasser (Lever Bros. Co.). *U.S. 3,303,135.* An improvement is claimed in the preparation of a heat-dried nonionic detergent composition consisting essentially of (a) at least one nonionic surface active agent having detergent properties, (b) a phosphate builder such as an alkali metal pyrophosphate or tripolyphosphate, (c) sodium carboxymethylcellulose and (d) sodium silicate in an amount effective to inhibit corrosion. The composition is prepared by blending the ingredients with water to prepare a slurry and subsequently heat-drying the resultant slurry. The improvement consists in combining the carboxymethylcellulose, water and sodium silicate with alpha; beta-di-5-methyl-benzoxazoyl-(2)-ethylene as a brightening agent, and agitating the mixture for at least three minutes to affix the brightening agent to the carboxymethylcellulose, the amount of carboxymethylcellulose being sufficient to adsorb the brightening dye and to maintain it in an active state. The other ingredients are then added and the resultant slurry is heat-dried.

DETERGENT COMPOSITIONS. W. M. Bright (Lever Bros. Co.). *U.S. 3,303,136.* A detergent composition is claimed, consisting essentially of about 40–85% of a condensed, inorganic polyphosphate and of about 15–60% of a water-soluble arylsulfonate selected from the group consisting of benzenesulfonate, *o*-xylene sulfonate, *m*-xylenesulfonate, *p*-xylenesulfonate, toluene sulfonate, ethylbenzenesulfonate, *n*-propylbenzenesulfonate, isopropylbenzenesulfonate and mixtures thereof, the composition providing an alkaline reaction in aqueous solution.

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nicotinamide derivatives, the N^1-alkylnicotinamide chlorides were demonstrated to be bound at a "pyridinium ring" region of the NAD binding site of the yeast enzyme. A linear chain length effect was observed in the binding of these inhibitors indicating that nonpolar interactions play a significant role in the functioning of these compounds. From these and related studies with other nitrogen bases, it was suggested that the "pyridinium ring" region of the NAD binding site of yeast alcohol dehydrogenase lies in a hydrophobic area of the protein.

Inhibition by N^1-alkylnicotinamide chlorides has been used as an experimental tool for locating hydrophobic regions of importance in the binding processes of other dehydrogenases. For example, in the case of horse liver alcohol dehydrogenase, the alcohol dehydrogenase, the nicotinamide derivatives appear to interact with the substrate binding site. With bovine liver glutamic dehydrogenase, the inhibitors are bound at an effector site presumably involved in the stabilization of one of the monomeric conformers of the enzyme. Beef heart and rabbit muscle lactic dehydrogenases, on the other hand, are not inhibited by N^1-alkylnicotinamide chlorides except at very high concentrations where extensive denaturation occurs. Studies are currently underway to investigate the importance of these nonpolar regions in the catalytic processes involved.

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THE ROLE OF LIPIDS IN MEMBRANE TRANSPORT IN MYCOPLASMA LAIDLAWII

P. F. Smith, PhD

Essentially all of the lipids of *Mycoplasma laidlawii* are located in the cytoplasmic membrane, the only integument enclosing the organism. These lipids consist of neurosporene; a dihydroxycarotenol; the acetate ester and the β-D-glucoside of this carotenol; phosphatidyl glycerol; phosphatidyl glucose, which yields upon deacylation α-glycerophosphoryl-1-(α,β)-D glucose; monoglucosyl diglyceride which yields upon deacylation 0-α-D-glucopyranosyl-(1$\rightarrow$1) D-glycerol; diglucosyl diglyceride, the deacylation product of which is 0-α-D-glucopyranosyl-(1$\rightarrow$2)-0-α-D-glucopyranosyl-(1$\rightarrow$1)-D-glycerol.

Enzymes involved in the degradation of the carotenyl acetate and the carotenyl-β-D-glucoside likewise are membrane-associated. Incomplete evidence suggests that all the enzymes involved in synthesis and degradation of the carotenyl ester and glucoside and phosphatidyl glucose are membrane associated. *M. laidlawii* is capable of glucose degradation to acetate by virtue of intracellular enzymes.

Pulse labeling of glucose metabolizing organisms with ^{14}C-glucose results in the incorporation and subsequent loss of radioactivity in carotenyl glucoside, carotenyl ester and phosphatidyl glucose. The same result is noted with phosphatidyl glucose when inorganic ^{32}P is used with unlabeled glucose. None of the other lipids become labeled except diglycosyl diglyceride which fails to lose the label following removal of exogenous ^{14}C glucose. The rate of C^{14}O$_2$ evolution generally is equivalent to the rate of disappearance of ^{14}C from the total lipids. Inhibition of β-glucosidase activity inhibits glucose turnover in the lipids and inhibits glucose metabolism.

These and other data suggest a role for the glucosyl lipids, the carotenyl ester and the enzymes involved in their synthesis and degradation in the transport of glucose into the cell and the transport of the end product of glucose metabolism, acetate, out of the cell. A schematic model of the cell membrane has been constructed which is compatible with current knowledge about the structure of the membrane and its function in selective permeability.

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MEASUREMENT OF MACHINE AND DETERGENT EFFICIENCY IN DRYCLEANING

W. H. Smith, Manfred Wentz and A. R. Martin

In a continuous flow system of drycleaning the concentration of insoluble soil suspended in the solvent in a washer cylinder increases from zero to a maximum and then decreases with time. The soil concentration approaches zero if a sufficient number of solvent changes occur to pump out the washer. The decrease in concentration from the maximum follows the mass transport law while the increase to the maximum depends on the detergency of the solvent-detergent solution. Data for the concentration-time curve can be obtained by removing samples from the washer at various time intervals and determining the quantity of soil in suspension by millipore filtration. The total quantity of soil removed from the load can be computed by integrating the curve graphically, and comparing the area with that of curves obtained with known quantities of soil.

If a known quantity of insoluble soil is placed on a load the percentage of soil removal can be computed. By this means the effectiveness of various detergents in releasing insoluble soil can be compared. The method is more accurate than reflectance methods for measuring removal of insoluble soil because it is direct and gravimetric. Assessment of percentage removal of solids from fabrics by reflectance involves assumptions that are not always valid in drycleaning systems.

Examples illustrating this technique are given using various detergents and soils. The method permits the evaluation of the washing efficiency of different machines and machine cycles. Examples illustrating this are also described.

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IMPROVEMENTS IN DETERGENCY PRECISION WITH RADIOACTIVE SOIL

W. T. Shebs and B. E. Gordon

With the development of precise and accurate radiochemical methods for the analyses of doubly labeled artificial soil left on washed fabric has come the need to improve the precision and accuracy of the laundering step. Using the Tergetometer as the laundering instrument a systematic study was carried out to determine the causes of low precision and accuracy and the elimination, or at least the reduction, of these sources of error.

The sine qua non of this study has been that of closure; i.e., the soil found in the wash water plus that remaining on the washed fabric had to equal the amount present on the unwashed fabric. The results have shown that it is now possible to more closely approach the precision and accuracy inherent in the analytical method by simply analyzing the wash water, an analysis which would be very difficult by conventional methods but is straightforward by radiochemical methods.

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ANALYSIS FOR SULFATE ION IN THE BIODEGRADATION OF ANIONIC DETERGENTS

T. C. Cordon, E. W. Maurer, O. Panasiuk and A. J. Stirton

An analytical method for sulfate ion would be useful to follow the course of biodegradation of organic sulfates and sulfonates and, in

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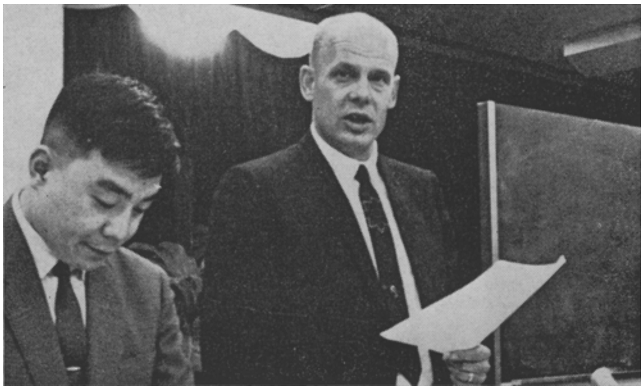
NRA Sponsors Seminars on Soap Marketing



Jack Northrup addresses seminar.

Jack Northrup, Vice President of Hunt-Wesson Foods and former Vice President of Purex Corporation recently conducted a series of Seminars on the marketing and distribution of soap in the Far East under the sponsorship of the National Renderers Association.

The original program scheduled four sessions in Osaka, four in Tokyo, and two in Taiwan. Because of the enthusiastic response of his audiences, however, additional seminars were scheduled and his entire lecture was videotaped so that other interested audiences might benefit from the sessions after his return to the U.S.

Northrup spoke to groups made up of soap manufacturers, margarine and shortening manufacturers, wholesalers, and distributors.

The National Renderers Association maintains a Far East office and Staff headquartered in Tokyo. International Headquarters are located at 3150 Des Plaines Avenue, Des Plaines, Illinois 60018.

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conjunction with Chemical Oxidation Demand and Methylene Blue Active Substance analyses, could help to establish the mechanism of detergent degradation.

Attempts to apply available turbidimetric methods were unsuccessful for two reasons: 1) barium chloride and detergent alone, in the absence of sulfate ion, caused turbidity; 2) the presence of detergent inhibited the precipitation of barium sulfate. These defects were remedied by the addition of gelatin to sequester detergent anions, and the addition of ethanol to destroy the micellar state responsible for solubilization. Gelatin served also to regulate the particle size and to stabilize the barium sulfate precipitate.

A procedure that incorporates these principles is described for following the formation of sulfate during the Esso test. The reagent used to precipitate sulfate, containing 2% $BaCl_2$ and 0.5% gelatin in 50% ethanol, was added to the detergent samples at a predetermined rate with constant, uniform, stirring. Absorbance was read against a blank at 420 mμ using 5 cm cells. Correction was made for turbidity before adding the reagent, and ppm SO_4^{--} were read from a standard curve.

In a preliminary test it was found that with sodium oleyl sulfate most of the inorganic sulfate appeared 2 days from the start of the test; with sodium octadecyloxyethyl sulfate 4–6 days; and with linear alkylbenzenesulfonate 10 days.

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EFFECT OF TALLOW/COCONUT FATTY ACID RATIOS ON PROPERTIES OF BAR SOAPS

M. E. Ginn, R. C. Steinhauer, I. Liebman and Eric Jungermann

Blends of tallow and coconut fatty acids were prepared at ratios from 95/5 to 75/25. These blends were converted to sodium soaps, then processed into soap bars through conventional milling and pressing techniques. Other minor ingredients were included in the bar to protect against rancidity and to provide color. The resulting bars were tested for lather, solubility, penetration, swell, slushing tendency, moisture and cracking. According to one mechanical method, the 85/15 tallow/coconut fatty acid blend yields optimum lather quickness. This does not agree with lather preference by an expert panel. The panel preferred bars with increasing sodium cocoate content or with increasing levels of sodium laurate. Foam volume and foam stability against water-hardness also increased as the sodium cocoate content was raised. Coincident with these effects was an increase in aqueous solubility. However, certain deleterious effects were observed with increase of sodium cocoate, namely: increased slushing, higher erosion rate and slower rate of rehardening. Considering all aspects, the 85/15 to 80/20 ratios appear to be optimum.

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MEASURING SOIL DISPERSION POWER OF DETERGENTS BY FILTRATION

W. H. Smith, Manfred Wentz, Nancy McCullough and A. R. Martin

The fundamental Poiseille-Darcy equation governing filtration states that:

$$\frac{\Delta P}{Q} = \frac{\mu a}{A} \cdot W$$

Where, ΔP = pressure drop across the filter
Q = quantity of liquid passing filter per unit time
W = quantity of residue per unit area of filter surface
μ = viscosity of liquid
A = surface area of filter
a = a constant that depends on the permeability of the residue, which in turn is governed by the particle size and compressibility of the residue.

For a given liquid, filter and solid residue μ, A and a are constants, so a plot of $\frac{\Delta P}{Q}$ vs W gives a straight line with a slope of $\frac{\mu a}{A}$. Since μ and A are fixed by the experimental conditions the value of a can be computed. Any change in the system that lowers the particle size in the slurry being filtered will increase the value of a. Thus a is a measure of the degree of dispersion of a solid suspension in a liquid. Its value is readily computed from simple pressure drop and flow rate measurements.

Solid particles that quickly aggregate and settle out of a slurry to form an incompressible residue exhibit an a value of zero. The presence of a detergent or other dispersant in the liquid leads to positive values of a that depend on the composition of the dispersant as well as its concentration.

Data illustrating the above statements are given using various model soil materials (e.g., carbon black, "Arizona Road Dust," etc.) and various drycleaning detergents in perchlorethylene.

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SELECTION AND EVALUATION OF COLUMNS FOR ANALYSIS OF LIPIDS

W. R. Supina and Nicholas Pelick

A wide variety of stationary phases are available for preparation of gas chromatograph columns. Unfortunately, many newly introduced phases are duplicates of or very similar to phases which have been in use for some time. When a new stationary phase is first made available, data for only a few applications are usually given. Consequently, many potential users neglect the new developments because of the difficulty of relating the data to their application. A method for classifying the stationary phases will be discussed which will aid in selection of the appropriate column for a given separation. In addition, several new stationary phases for lipid analysis will be described, and will be included in the overall classification of phases.

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SILICIC ACID COLUMN CHROMATOGRAPHY: PARAMETERS FOR A BINARY SOLVENT SYSTEM

D. G. McConnell, R. L. Hoffmann, G. J. Elman and C. D. Evans

The elution characteristics of polar and nonpolar fatty methyl esters were determined for methanol-benzene solvent systems by liquid chromatography on silicic acid. A series of curves were obtained that show the relationship between the elution volume for each component and the methanol concentration of the stationary phase. The resulting graphs serve as a basis to predict elution conditions for separating other compounds of different polarities. Adsorption isotherms of methanol-benzene systems on silicic acid were plotted from equilibrium studies in which the concentration of methanol in the various effluents was determined by its refractive index. An abrupt concentration change occurs in methanol content of the effluent when the mobile solvent is either richer or poorer in methanol than the equilibrated solvent. Elution position of this abrupt change depends upon the concentration of methanol in both mobile and stationary phases.

The method is highly reproducible since only one eluting solvent is used. Nonpolar triglycerides, diglycerides, monoglycerides and methyl esters of hydroxy fatty acids can be easily separated on one column. Also, isomeric α- and β-monoglycerides can be separated, and the chromatographic system is ideally suited for lipase hydrolysis studies.

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SILICIC-ACID COLUMN CHROMATOGRAPHY: ADSORPTION MECHANISM AND SOLVENT SYSTEMS

R. L. Hoffmann, D. G. McConnell and C. D. Evans

Investigations have been carried out on the relationship between chromatographic characteristics of silicic-acid columns and the electrophilicity-geometry of their adsorbed solvent. The associative bond that joins solute to absorbent is formed between a silanol hydrogen atom and an unshared pair of electrons in the solute molecule. Adsorption is influenced by the extent to which these electrons are inductively and sterically available for participation in a hydrogen bond. Data show that on the basis of electron distribution and molecular geometry of the adsorbed solvent it is possible to prepare columns of almost identical separation characteristics from a variety of dissimilar solvents.

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THERMALLY STABLE POLYESTER SORBENTS FOR HIGH-TEMPERATURE GAS CHROMATOGRAPHY

D. J. Moore and V. L. Davison

A novel polymeric sorbent system was developed for use in high-temperature chromatography. The polymers are poly(ester-acetals) having a spiro structure that is capable of undergoing a crosslinking reaction with the column substrate, as well as with themselves. We believe crosslinking takes place as a result of breaking and reforming acetal bonds and that silanol groups of the substrate participate in the reaction. After curing, the resulting crosslinked poly(ester-acetals) are thermally stable above 300C. Benefits of this system include a stable baseline for fatty esters of more than an 18-carbon chain, freedom from extraneous substances when gas chromatographs are used in conjunction with mass spectrometers and the possibility of producing sorbents of varying polarities by the use of different glycols and diabasic esters in the polymer preparation.

Thermogravimetric analysis was used to determine sorbent loading on the substrate both before and after curing and to establish the relative thermal stability of the various poly(ester-acetals).

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THE GAS CHROMATOGRAPHIC SEPARATION OF LONG CHAIN ALDEHYDE DIMETHYL HYDRAZONES

C. B. Johnson, A. M. Pearson and L. R. Dugan

The gas chromatographic separation of long chain aldehydes as their dimethyl hydrazones was investigated. The carbonyls (and fatty acids) were dissolved in dimethyl hydrazine and the mixture refluxed for one hour. Ice cold dilute sodium hydroxide solution was added at the end of the reaction period and the hydrazones were extracted with diethyl ether. Acidification followed by solvent extraction of the aqueous layer yielded the fatty acids. The hydrazones were chromatographed on columns of different polarity. To increase the certainty of aldehyde identification, the hydrazones were converted into the corresponding dimethyl acetals by refluxing with methanolic HCl or methanolic BF_3. The method has been applied and shown to be useful for the analysis of mixtures of aldehydes and acids. It is presently being tested for analysis of the plasmalogen aldehydes in beef heart and brain.

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A RAPID MICROÖZONOLYSIS-GLC PROCEDURE FOR LOCATING UNSATURATION IN OLEFINIC ACIDS, INCLUDING TRIENES AND TETRAENES

R. Kleiman, G. F. Spencer and F. R. Earle

Increased versatility has been achieved in the identification of unknown olefinic fatty acids by ozonolysis. The method has been applied to purified methyl esters containing up to four double bonds. Aldehydic fragments, obtained from esters by the Beroza-Bierl procedure [Anal. Chem. *38*, 1976–1977 (1966)], were analyzed by gas chromatography on two columns of different polarity. Equivalent chain lengths of each fragment on the two columns provide definite identification with few exceptions. For monoenoic esters the location of the double bond is clearly indicated by the aldehyde and aldehyde-ester fragments. Dienes are identified by the aldehyde and aldehyde-ester fragments when the original chain length of the ester is known; the dialdehyde fragment provides confirmatory evidence. Trienes and tetraenes are analyzed by interrupting the ozonolysis at various times, thereby producing unsaturated, as well as saturated, aldehydes and aldehyde-esters. Unsaturated fragments locate the central or interior double bonds. For example, products of the complete ozonolysis of an unusual C_{20} ester are: C_5 aldehyde-ester, C_6 dialdehyde, C_3 dialdehyde (presumed) and C_6 aldehyde. Since interrupted ozonolysis also produced a C_{11} unsaturated aldehyde-ester and a C_9 unsaturated aldehyde. the unusual ester must be 5,11,14-eicosatrienoate rather than a 5,8,14-isomer.

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IDENTIFICATION AND ESTIMATION OF COMPLEX FATTY DERIVATIVES BY GAS-LIQUID CHROMATOGRAPHY. PARTIAL GLYCERIDES

A. E. Thomas, III, and R. G. Manning

Previous work has shown that programmed temperature gas-liquid chromatographic techniques are applicable to the identification and estimation of complex fatty derivatives. Identifications are greatly simplified when basic principles of homology are employed. These techniques were utilized to identify and estimate the components of commercial partial glycerides. Results are compared to data obtained by other analytical methods.

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HYDROCARBONS OF MARINE AND HUMAN LIPIDS

L. L. Gershbein and E. J. Singh

Raw liver oils from the basking shark, Norway dogfish and cod have been submitted to TLC separation over silica gel G and the hydrocarbons isolated from the pertinent cuts as well as to hydrolysis with alkali and the unsaponifiable portion chromatographed over alumina. With the latter, column chromatography over silica gel allowed for concentration of the saturated hydrocarbons. Such mixtures were analyzed by temperature programmed gas chromatography to 275C (hydrocarbon flame detector; packing, 3% SE-30 on 80–100 mesh Gas-Chrom P; carrier gas, He at 12 lb pressure). The paraffinic hydrocarbons of basking shark liver oil displayed over 40 peaks and ranged up to C_{38}; the most prominent component was pristane and to a lesser but significant extent, the n-C_{19}. Numerous peaks were also obtained with the saturated hydrocarbon mixtures from the cod and dogfish liver oils in the ranges of $C_{17.5}$-C_{33} and $C_{11.5}$–C_{36}, respectively. By similar techniques of fractionation, saturated hydrocarbons from human ovarian dermoid cyst lipids and vernix caseosa were analyzed by GC and peaks obtained up to C_{44}; these findings were compared with those for the marine lipids as well as with the data for human hair and scalp lipids reported by this laboratory.

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SELECTIVE HYDROGENATION OF THE METHYL ESTER OF 7,9-OCTADECADIYNOIC ACID

S. G. Morris, Paul Magidman, S. F. Herb and F. E. Luddy

The diynoic acid was selectively reduced. Gas-liquid chromatography indicated that all the starting material had been reduced and that 80–85% of the reduced sample had a retention time similar to that of a conjugated diene. Gas-liquid and thin-layer chromatography confirmed the absence of monoenoic and saturated acids. Ultraviolet studies indicated the presence of conjugated dienoic acids and infrared spectra showed the absence of *trans* isomers. The molecular weight of the methyl ester, a major portion of the reduced product, was 294 as determined by mass spectrometry. These data are consistent with the properties of *cis,cis*-methyl octadecadienoate.

This method should be useful for the preparation of conjugated *cis,cis*-dienes.

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LECITHIN-PROTEIN INTERACTION IN A GTP-DEPENDENT ACYL-CoA SYNTHETASE

Lauro Galzigna, Lodovico Sartorelli, C. R. Rossi and D. M. Gibson

The enzymatic activity of a GTP-dependent acyl-CoA synthetase, recently isolated from rat liver mitochondria, is influenced by removal and addition of lecithin. In fact, purified preparations of the enzyme are rich in lecithin.

In a preceding study the type of interaction which takes place between protein and lecithin was not clarified thoroughly. In the present communication an attempt to understand the nature of such an interaction is made. From binding measurements performed at different temperatures it is possible to postulate what type of secondary bonds is holding together protein and lecithin.

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THE ROLE OF LIPID IN GLUCOSE 6-PHOSPHATASE

W. L. Byrne and Sue M. Duttera

Treatment of liver microsomes from fasted (48 hr) rats with phospholipase C (PLC) has been used to study the interrelation of phospholipid (PL) and the microsomal enzyme glucose 6-phosphatase (G6Pase). Enzyme activity was reduced to 15–20% of the original untreated activity concomitantly with product release from the action of the phospholipase. Approximately 70% of the microsomal PL is modified under the conditions used. An apparent concentration dependent PL requirement for G6Pase activity was observed when PL was added to the PLC treated preparation. Removal of soluble products (phosphorylchlorine and phosphorylethanolamine) of the PLC reaction resulted in no change in observed activity loss or reactivation on addition of PL. The insoluble diglyceride products also had no effect on activity loss or PL reactivation as indicated by partial removal of the diglyceride products and separate experiments where excess products were added. The PLC treated preparation has been used to study the effectiveness of a variety of lipids, individually and in mixtures, in reactivating G6Pase. The most effective single PL studied was phosphatidylethanolamine (PE) and the most effective mixture was microsomal PL (neutral lipid removed), as far as maximum reactivation was concerned. One hundred and twenty per cent of the original, untreated activity was observed with either microsomal or commercial PE and 160% with microsomal PL. Lysolecithin was the most effective lipid studied at low concentrations of added lipid. As the proportion of lecithin was increased in mixtures of lysolecithin and lecithin, the maximum activity regained was increased and the inhibition usually seen at high concentrations of lysolecithin was reduced. If the effectiveness of lysolecithin in the mixture was compared with lysolecithin alone, the equivalent reactivation was observed, up to approximately the 80% level of reactivation. It would appear that lysolecithin, presumably present as a mixed micelle, was acting as an individual PL.

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ACTIVATION OF PHOSPHORYL CHOLINE-CYTIDYL TRANSFERASE BY PHOSPHOLIPIDS

W. G. Fiscus and W. C. Schneider

PC-cytidyl transferase is known to catalyze the rate-limiting reaction in the biosynthesis of lecithin. We reported that the enzyme is activated by "altered" phospholipids such as lysolecithin, lysophosphatidyl ethanolamine and oxidized phospholipids (Federation Proc. *24*: 476, 1965). Lecithin activates the enzyme only slightly, if at all, whether in emulsion or micellar form. Further work has shown that certain combinations of phospholipids produce a synergistic activation of the enzyme. In addition, phospholipid-activated PC-cytidyl transferase in a rat liver supernatant fraction was found to sediment more rapidly (approximately two-fold) than the unactivated enzyme in a 5–20% sucrose density gradient. Chromatography of the enzyme on a column of polyacrylamide (P-300) gel in the presence of 6*M* urea indicates that it can be dissociated into sub units. Degraded phospholipids, therefore, appear to meditate a positive feedback regulation of PC-cytidyl transferase by producing an association of subunits.

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INTERACTIONS OF HEART SUCCINATE DEHYDROGENASE WITH PHOSPHOLIPIDS

P. Cerletti, M. G. Giordano, M. A. Giovenco, G. Magni and G. Testolin

Beef heart succinate dehydrogenase (SD) has been solubilized after extraction of phospholipids. (For details and previous work see P. Cerletti in E. C. Slater, ed., *Flavins and Flavoproteins*, B.B.A. Library Vol. 8, Elsevier, 1966, p 204). Such preparations exhibit lower turnover number (TN) and stability as compared to particulate preparations. The effect of added phosphatides depends on whether the flavoprotein is solubilized in the presence or absence of succinate. When solubilization is carried out in the presence of succinate addition of micellar phospholipids restores a higher TN and improves stability. Only acidic phospholipids are effective. If succinate is not present during solubilization, stimulation of activity and stabilization do not occur. However, added phospholipids remove the inhibition of succinate oxidation by oxaloacetate or by fumarate. Conversely, phosphatides inhibit the hydrogenation of fumarate by $FMNH_2$, i.e., the reverse reaction catalyzed by the flavoprotein. The mechanism of these latter effects probably differs from that of stimulation of succinate oxidation. The effect of succinate on the interaction of SD with lipids (and with the respiratory particle) is not based only on producing a proper redox state in the enzyme. Indeed preincubation with succinate of enzyme previously solubilized in the absence of succinate does not permit stimulation by lipids. It is suggested that during solubilization the conformational state of the native flavoprotein is favored by the presence of succinate. In the presence of phosphatides soluble SD is inhibited by the iron chelator 2-thenoyltrifluoroacetone (TTA). The features of this inhibition suggest that a part of the iron in the flavoprotein is involved in binding the lipids and may be distinguished from the iron having a catalytic role. The interaction and binding of soluble SD with phospholipids appear therefore in many respects to be similar to those of the flavoprotein with the respiratory particle. Interactions between endogenous phosphatides and particulate SD were investigated using phospholipases. Phospholipase C severely inhibits SD activity in particles. Purified SD solubilized after treatment of particles with phospholipase C, still exhibits a severe decrease of TN. Treatment with phospholipase C has no effect on soluble SD. Phosphorylcholine and diglycerides, the products of phospholipase C reaction, produce a moderate noncompetitive inhibition of soluble SD. It is suggested that the effect of phospholipase is to damage the particulate flavoprotein by disruption of phospholipid structure.

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THE ROLE OF LIPID ON HEME SYNTHESIS

Yoshimasa Yoneyama, Hideo Sawada, Masazumi Takeshita and Yoshiki Sugita

The activating effect of purified lipids, especially phospholipids, on the iron chelating enzyme to form heme from iron and protoporphyrin was investigated. The enzyme was extracted from the acetone powder of chicken erythrocytes stroma with 1% sodium cholate or 0.4*M* KCl. The enzyme activity of 0.4*M* KCl extract was stimulated severalfold by lipids but the activity of sodium cholate extract was not affected.

Phosphatidylethanolamine from egg yolk and cardiolipin from pig heart were effective in activating the reaction, while phosphatidyl-

choline from egg yolk was stimulative only in the presence of sodium cholate. Sodium cholate itself was effective in heme formation but its presence inhibited activating effects of phosphatidylethanolamine and cardiolipin. Sodium palmitate, lysophosphatidylcholine and hydrogenated phosphatidylcholine were also effective. Tween 40, nonionic detergent, and tripalmitin were ineffective.

It was shown that heme synthesis was stimulated by lipids but not by a single specific lipid. The relationship between the structure of lipids and their effectiveness will be discussed.

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SURFACE-ACTIVE BRASSYLIC ACID-ETHYLENE OXIDE ADDUCTS: PREPARATION AND EVALUATION

T. K. Miwa, R. V. Madrigal, W. H. Tallent and I. A. Wolff

Both liquid and solid ethylene oxide adducts of brassylic (tridecanedioic) acid were prepared by potassium hydroxide-catalyzed addition of ethylene oxide gas to the molten acid. The number-average molecular weights ($\overline{MW}_n$) of the adducts ranged from 500 to 3,000. These adducts cover a wide span in the ratios of hydrophilic to lipophilic portions of the molecule. They have the unique feature of hydrophilic end groups sandwiching a rather long chain of lipophilic methylene units. Treatment of some adducts with hot saturated aqueous sodium chloride induced transesterification and produced hydroxyl-terminated, multibrassylic, poly(ethylene glycol) esters (I) of $\overline{MW}_n$ 1,000 to 4,000, all of which

$$\mathrm{HO(CH_2CH_2O\cdot)_n\left[CO\underset{\mathrm{I}}{(CH_2)_{11}}COO(CH_2CH_2O\cdot)_n\right]_x H}$$

were efficient surface-active agents. Average degrees of polymerization (n) of the poly(ethylene oxide) chains were determined by (a) functional group analysis, (b) weight increase and (c) methanolysis of the products followed by gas chromatographic analysis of the isolated poly(ethylene glycol) fraction. Surface tension, critical micelle concentration, emulsion stability and efficiency as emulsifying agent in the aqueous polymerization of vinyl acetate were measured to evaluate surfactant properties of products in which DP of the poly(ethylene oxide) chains ranged from 1.4 to 44.

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FOAM PERFORMANCE TESTS IN DISHWASHING

F. C. Davis, G. R. Edwards, J. E. Woodrow and T. B. Albin

Foam stability in manual dishwashing is a key quality in judging light duty liquid detergents. Washing of naturally soiled plates is generally considered to afford the most reliable estimates of performance, provided that tests are replicated many times. This is arduous and expensive, however, and demands a daily source of a large number of soiled dishes, such as would be obtained from a cafeteria. Over the years numerous faster and cheaper laboratory procedures using artificial soils have been proposed. None of these procedures has however been widely accepted chiefly because capability for predicting performance under realistic use conditions has never been demonstrated.

One such screening test ("Shell SM-1 Method"), first described about three years ago, consists of manually washing dishes soiled with a fat-egg-water emulsion. This procedure has been continuously employed in our laboratory to provide rapid assessments of dishwashing formulations. As a consequence we have been able to accumulate extensive comparisons with some other dishwashing methods. Of main interest, a reasonably good correlation with a test using cafeteria soiled dishes has been established for a broad spectrum of detergent formulations, over a range of water hardness and detergent concentration. Reproducibility and precision are good enough to detect small foam stability changes caused by modest alterations in detergent composition. Thus, the method has proved to be very useful in guiding our development of detergent formulations.

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PROTEIN SOIL DEFOAMING IN MACHINE DISHWASHERS

I. R. Schmolka and T. M. Kaneko

The machine washing of dishes that are heavily loaded with proteinaceous soil has been a problem facing consumers and the surfactant industry alike for many years. The rapid growth in the machine dishwasher market and the trend toward the use of lower water temperatures have tended to aggravate the resulting foaming problem for both the household and the industrial consumer of machine dishwashing detergents. Although many surfactants have been recommended for use in defoaming protein soils, a product for defoaming protein soils over a temperature range of 100–180F has never been offered commercially.

A systematic study undertaken with the primary objective of defoaming egg and milk soils in machine dishwashers over wide temperature ranges has led to the development of an effective patented protein defoaming system. This consists of monostearyl ester of phosphoric acid blended with special nonionic surfactants, in a mixture of alkaline builders. It provides excellent control of protein foam from 100–180F. Studies have been undertaken to show the effects of variations in monoalkyl ester concentration, in types of surfactant, in soil load, in water temperature, in water hardness, and in builder systems.

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THE USE OF OPTICAL BRIGHTENERS FOR SYNTHETIC FIBERS IN DETERGENTS

R. Anliker, H. Hefti and H. Kasperl

The strong increase of the part of synthetic fibers in the washload creates new problems for the application of optical brighteners in detergents. In the field of white textile goods today only optically prebrightened textiles are coming on the market. Due to the fact that the behavior of synthetic fibers in the wash bath is more strongly influenced by the method chosen for prebrightening them than that of cotton, it was of interest to investigate these correlations with the help of a few examples, especially on polyamide and polyester.

It is shown that the choice of the right optical brightening agent for use in the dope or for topic-brightening in the textile-mill has a big influence on the ability of the fiber to be further brightened in the wash-bath, on the light-fastness and the wash-fastness of the white—and very often also on the colored—washload. The investigation also deals with the mutual influence of brighteners applied during the production of the fiber or the fabric and those used in the detergents.

As an interesting conclusion of this work ways will be shown to overcome undesired changes in the hues of pastel shades. Finally some aspects of the visual assessment and measurement of whitening effects are discussed.

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ENZYMES AS ADDITIVES TO LAUNDRY COMPOSITIONS

J. C. Hoogerheide

Laundry detergents with proteolytic and amylolytic enzyme additives made their appearance on the European markets some two years ago and have met with remarkable success.

Enzymes suitable as additives must be fully compatible with the usual ingredients used for laundry detergents such as TPF, different types of anionics and nonionics, soaps, CMC, etc. The enzyme systems should not only be stable under the usual marketing conditions but they also should exert their actions under conditions as close as possible to those under which household detergents usually are applied. The main function of the enzymes is to break down the protein and starchy components of the stains into particles of much smaller size, thus destroying their function as binding agent of dirt to the fibers of the fabric. Detergency then completes the removal of the dirt particles. Whereas either the enzyme of the detergent alone may have little effect on removal of protein stains, the combination of both exert a marked synergistic cleaning effect. Commercial compositions are designed in such a way that full advantage of this synergism is taken.

The properties of one of such enzymes suitable for combination with laundry detergents will be described as well as the technique to develop suitable biological laundry compounds with such an enzyme, using artificially soiled cloths as test objects. Advantages as well as still existing shortcomings of such biological cleaning compounds will be discussed.

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SURFACE ACTIVITY OF SODIUM SALTS OF α-SULFO FATTY ESTERS THE OIL/WATER INTERFACE

V. V. Subba Rao, R. J. Fix and A. C. Zettlemoyer

Adsorption studies at heptane/water and benzene/water interfaces have been carried out for the following four esters: sodium hexyl α-sulfopelargonate (C_7H_{15} CH (SO_3Na) COO C_6H_{13}), sodium heptyl α-sulfopelargonate (C_7H_{15}CH (So_3Na) COO C_7H_{15}), sodium methyl α-sulfomyristate ($C_{12}H_{25}$ CH (SO_3Na) COO CH_3) and sodium methyl α-sulfopalmitate ($C_{14}H_{29}$ CH (SO_3Na) COO CH_3). The results obtained were compared with those at the Air/Water (A/W) interface (E. A. Boucher, T. M. Grinchuk and A. C. Zettlemoyer, AOCS Meeting, New Orleans, May 1967).

Surfactant solutions with constant counter-ion concentrations 0.01 and 0.04 N Na^+ were used in case of the heptane/water interface and 0.01 N Na^+ in case of benzene/water interface. Interfacial tensions were determined by using the drop volume method. The Gibbs equation in the form

$$d\gamma = -RT\,\Gamma'\,d\ln C$$

(where α is the interfacial tension, Γ′ is the amount of surfactant adsorbed and C is the molar concentration of the surfactant ion and the rest have their usual meaning) was used to evaluate the Γ′ values and the co-areas were calculated.

The increase in the counter-ion concentration from 0.01 to 0.04 N Na^+ resulted in a decrease in the critical micelle concentration (CMC) and also for a given surfactant concentration, the interfacial tension values were lowered by about 7.5 dynes/cm. Further, the co-areas of the molecules decreased slightly (5–10%) indicating that the increase in ionic strength slightly increases the degree of packing at the interface.

The CMC values were lower in the presence of heptane than at the A/W interface; the effect was much more in the presence of benzene. The lowering in the CMC was related to the water solubility of the hydrocarbon, the larger the water solubility the greater the decrease in the CMC.

The co-areas were larger than at the A/W interface by about 10% in presence of heptane and by about 30% in presence of benzene indicating that the surface films at the Oil/Water interface are more expanded.

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FATTY OIL PROCESSING—CONVENTIONAL VS. MISCELLA

F. Sullivan

— 44B —

MODERN TECHNIQUES OF CONTINUOUS BLEACHING OF VEGETABLE OIL

H. Mueller

— 44C —

CENTRIFUGAL SEPARATION OF PARTIALLY HYDROGENATED SOYBEAN OIL

D. Horton

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AMPHOTERIC SURFACE ACTIVE AGENTS IN COSMETICS

H. S. Mannheimer

Amphoteric Surface Active Agents serve many diverse purposes in the cosmetic industry. Some of these are the formulation of completely non-eye-irritating and non-eye-stinging shampoos and facial cleansers, shampoos and cleansers of reduced irritation; reduction or elimination (de-toxification) of substances other than surface active agents; hair conditioning and improvement of combability, formulation of color shampoos, nonstripping shampoos and those that improve color acceptance. This recitation is by no means complete. Most of these applications are well known and have been well described for the most part.

A simple titrimetric method is described which when transposed into two curves, serves as positive identification, a distinctive fingerprint as it were of every amphoteric surface active agent, even if chemical differences are only slight. It positively identifies their isoelectric point, allows conclusions as to their utility for planned cosmetic products, can show the presence of unreacted cationic surface active agents and the admixture of anionics. It can show the presence of amphotetrics in mixtures of anionics, cationics and nonionics even if the concentration of the amphoteric surface active agent is very low.

The method offers very distinctive advantages over such well-known methods as infrared or ultraviolet spectroscopy and magnetic resonance, not the least of which is its utter simplicity. All that is required is a burette or two, Normal solutions of NaOH and HCl, an electric pH meter, a notbook and graph paper.

No special preparation of samples to be tested is necessary. Furthermore conclusions in regard to utility of the tested samples are not available from spectroscopy or magnetic resonance, nor is their application particularly useful in surface active agent mixtures.

The method is demonstrated with measurement determinations and resulting graphs. The conclusions to be drawn from them are explained.

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FATTY AMIDO-AMINE DERIVATIVES

T. Muzycko, S. Shore and Jo Loboda

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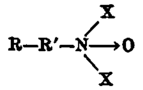
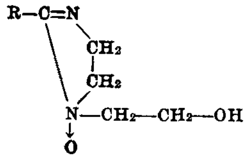
THE EFFECT OF STRUCTURAL DIFFERENCES OF AMINE OXIDES ON THE FOAMING PROPERTIES OF SIMPLE SHAMPOO FORMULATIONS

R. N. Goodell

The foaming properties of a simple two component shampoo formulation are examined with respect to varying amine oxide structures. No solubilizers, pH effects have been examined.

In the general formulae:





R varies from C_9–C_{18} saturated and unsaturated.
R′ may be absent, hydroxy propyl ether, or a branched alkyl group.
X may be methyl or $(C_2H_4—O)$ NH

The performance of the C_{16} C_{18} straight chain amine oxide may be enhanced by preparing the corresponding imidazoline oxides or by increasing the ethoxylation on the tertiary nitrogen of the amine oxide.

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ALCOHOL ETHER SULFATES IN SHAMPOOS

Henry Watanabe and W. L. Groves

Mono-, di- and triethanolamine sulfates of several different molecular weight alcohol ether sulfates were formulated into shampoos. The ethylene oxide content of the alcohol ethoxylates varied from about 20 to 60%, although 40% was usual. The shampoo formulation was 20% active ether sulfate and 5% foam stabilizer. Lauric diethanolamide, amine oxides and betaines were used as foam stabilizers.

The shampoos were tested for quality and quantity of foam, viscosity and cloud point. Although no "hair effects" tests were run, a limited home use test was made.

Alcohol ether sulfate shampoos are equal or superior to several popular commercial products on the basis of a lab foam test. They are comparable in foam to alcohol sulfates in similar formulations. Cloud points of these shampoos were generally good. Amine oxide foam stabilizers reduced the cloud point more than the amide or betaine. Viscosities of the shampoos were readily controllable. Although the choice of alkanolamine, alcohol molecular weight and degree of ethoxylation had some effect on these properties, none were highly critical; this allows considerable leeway in their selection. The home use tests assured us that these shampoos were not obviously deficient in the desired "hair effect" properties. The literature records that alcohol ether sulfates are preferred to alcohol sulfates for low skin and eye irritation.

By varying the free oil (unsulfated ethoxylate) content and making the proper choice of ether sulfate and foam stabilizer, bright and clear liquid shampoos with viscosities from about 10 centipoise to over 50,000 centipoise were made The latter are essentially gels. Paste shampoos were also made from these ether sulfates.

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A NEW QUATERNARY AMMONIUM COMPOUND HAIR CONDITIONING AGENT

R. R. Egan and B. J. Hoffman

Stearyl dimethyl benzyl ammonium chloride has long been the only quaternary ammonium compound used in hair rinses. The dialkyl dimethyl ammonium chlorides, because of their poor dispersibility in water at low temperature, could not be used, even though they are more highly substantive to the hair surface.

Adogen 432-CG is a dialkyl dimethyl ammonium chloride which readily forms dispersions in cold water. Creme rinses prepared from this material give long-lasting hair conditioning with good wet combthrough and manageability properties. An outstanding characteristic is the lack of a "greasy feel" as given by steryl dimethyl benzyl ammonium chloride.

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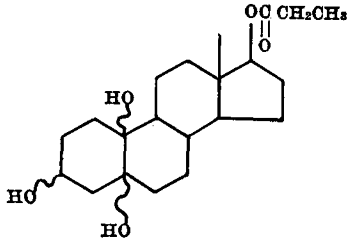
MASS SPECTRA OF POLYHYDROXY ESTRANES

S. G. Levine, C. Cordes, G. E. Van Lear and K. L. Rinehart, Jr.

Although the mass spectral fragmentation behavior of monohydroxy steroids has been reported in detail in the chemical literature, similar studies of polyhydroxy steroids have not appeared, presumably because of thermal decomposition during indirect sample introduction. However, direct inlet mass spectrometry allows one to investigate the fragmentation behavior of these important compounds while decreasing the chance of thermal decomposition.

We have obtained the mass spectra of a number of stereoisomers of the 17-propionate ester of estrane-3,5,10,17-tetrol (I), of their 3-acetates, and of related 5,10-epoxy estranes. In the discussion, the fragmentation behavior of the various stereoisomers of the tetrols and their acetates are compared, as well as salient features in the spectra of the epoxide derivatives.



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(Continued on page 366A)

Society of Cosmetic Chemists' Annual Seminar

The Society of Cosmetic Chemists holds its annual seminar at the Ambassador Hotel, 1300 N. State Parkway, Chicago, Ill., Sept. 21–22, 1967. Hyman Henkin of Curtis Industries, Inc., Seminar Program Committee Chairman, has announced the theme of the program, Color in Cosmetics.

To be considered at this meeting are the topics, "Physical and Chemical Aspects of Color," "Hair Color, Formulation and Evaluation," "Colored Products—General—Formulation and Evaluation," "Medical, Legal, Safety Aspects of Color."

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• *Industry Items*

The San Francisco Bay area sales office of Emery Industries, Inc., has been moved to 360 Pine St., San Francisco, Calif. 14104. The office, formerly located in Oakland, Calif., serves customers of the company's Fatty Acid and Organic Chemicals Divisions.

New address of the Society for Analytical Chemistry, *The Analyst, Analytical Abstracts* and Analytical Methods Committee will be: 9/10 Saville Row, London, W.1.

The Bendix Corporation will consolidate its expanding activities in the fields of sonic cleaning, vacuum technology and scientific instruments at its Scientific Instruments Division in Cincinnati. The move will immediately transfer the Vacuum Division formerly in Rochester, N. Y., and the Instruments and Life Support Division in Davenport, Iowa.

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MOLECULAR-WEIGHT DETERMINATION OF LONG-CHAIN METHYL ESTERS BY FIELD-ION MASS SPECTROSCOPY

W. K. Rohwedder

Extract molecular weights of long-chain fatty methyl esters can be determined readily in a mass spectrometer equipped with a field-ion source. Spectra from a field-ion source have the parent peak as the major peak, in an otherwise simple spectrum, rather than the extensive fragmentation found in normal mass spectra. Saturated esters gave the parent peak almost exclusively; unsaturated esters recorded parent peaks plus metastable peaks; whereas hydroxy esters had good parent, parent minus 18 and metastable peaks.

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ELIMINATION REACTIONS IN THE MASS SPECTRA LONG CHAIN ESTERS

R. E. Wolff, M. Greff, R. N. Stillwell, A. M. Lawson and J. A. McCloskey

Knowledge of the occurrence and mechanisms of elimination reactions in the mass spectra of long chain compounds is essential for a fundamental understanding of these processes, and subsequent applications to the structure determination of unknowns. An extensive investigation of elimination reactions, principally of CH_3OH, in the mass spectra of long chain methyl esters and related compounds bearing functional groups in the chain has been undertaken for this purpose, with the aid of deuterium labeling and high resolution mass spectrometry. Conclusive evidence has been obtained for the occurrence of large-membered transition states in the *elimination* process, implicating coiled conformations of long chain molecules in the vapor phase. Comparison of results from a number of different types of compounds and the resulting influence on the interpretation of their mass spectra will be presented.

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A STUDY OF PYROLYSIS OF FATTY ACID ESTERS USING PYROLYSIS—GAS CHROMATOGRAPHY—MASS SPECTROMETRY

K. K. Sun, H. W. Hayes and R. T. Holman

The identity of the products of pyrolysis of fatty acid esters has been studied by a pyrolysis-chromatograph directly coupled to a mass spectrometer. The compounds studied included a series of esters of lauric acid and methyl esters of selected fatty acids. The methyl esters pyrolyze to form a homologous series of olefins and a series of oxygen-containing substances. The latter appear to be methyl esters of olefinic fatty acids or the equivalents of ketenes. The relative proportions of products of pyrolysis change with temperature. Ethyl esters and esters of longer chain alcohols give more complex pyrolograms than do the methyl esters. Mehtyl 9,10-dideuterostearate pyrolyzed to yield products whose deuterium content clearly revealed the locations of the deuterium atoms, and thus the position of the double bond in the oleic acid from which it was prepared.

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DIGITAL READOUT SYSTEM FOR MASS SPECTROMETRY

Don Oliver and M. C. Simmons

An automatic digital readout system has been developed for the common types of general-purpose mass spectrometers. It is specifically designed for use with mass spectrometers which employ either acceleration voltage or magnet current scanning. By use of convenient scaling controls acceleration voltage can be read inversely as mass number.

Maximum ion currents on "peak heights" are determined by a digital "sample and compare" technique requiring the signal decreases after the peak by a selectable percentage before a readout is made. The system can handle peaks at rates up to 40 per second. Digital readout is five digits of "mass number" and five digits of "peak height." Results are normally printed out by a digital printer, but they also can be fed in digital form to computer compatible output devices, e.g., paper tape punch, or magnetic tape recorder.

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THE MASS SPECTRA OF RETINOL (VITAMIN A) AND RELATED COMPOUNDS

G. R. Waller, R. L. Lin, K. S. Yang, E. D. Mitchell, E. C. Nelson and R. D. Grigsby

Although many biologically active compounds have been examined by mass spectrometry, very little information has been reported on retinol (vitamin A) and related molecules. Research in progress on the metabolism of vitamin A has provided the impetus for a study using mass spectrometry as a method of identification of its metabolites. The mass spectra of all-*trans*-retinol, retinyl acetate, retinal, retionic acid and β-carotene were investigated using the direct inlet of a combination gas chromatograph—mass spectrometer. Upon electron impact each compound gave its molecular ion, $m/e = M^+$, and certain characteristic peaks representing the loss of their functional groups, thereby providing a quick method of identification. The hydrocarbon part of each spectrum was similar. The observed metastable ions were related to the appropriate decomposition transitions.

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SYMPOSIUM: SAFETY IN SOLVENT EXTRACTION

N. H. Witte, W. Meinhardt, L. Kingsbaker, N. W. Myers and N. H. Moore

The safety Symposium organized by the Technical and Engineering Committee will be devoted to up-dating information on safety in solvent extraction plants. Some of the safety problems which have occurred in the industry in recent years will be discussed and suggestions given for control of particular hazards.

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IMPROVED SYNTHESIS OF LONG-CHAIN POLYHYDRIC ALCOHOLS

D. J. Moore and E. H. Pryde

The reaction of aldehydes with formaldehyde in an alkaline medium to give polyhydric alcohols is well known. However, yields fall off considerably as the carbon chain of the aldehyde increases. For example, the yield of polydydric alcohol from acetaldehyde is 96%, but from decanal, 47%. To determine the cause for lower yields with higher aldehydes, we investigated the reaction for hexanal and nonanal, products of the reductive ozonolysis of soybean esters. Our investigations were facilitated by gas-liquid chromatographic analyses of the silylated derivatives of the reaction products. Extractions from neutral or acidic solution, the most commonly used procedures, gave a complex mixture including the 2,2-bis(hydroxymethyl)alkanal, the 1,1,1-tris(hydroxymethyl)alkane and the formate esters of these products. Extraction from alkaline reaction mixture, without neutralization of catalyst, gave only the two hydroxymethyl compounds but in high yield. Hydrogenation of the reaction product then resulted in the desired 1,1,1-tris(hydroxymethyl)alkane in overall yields of 85-90%. These polyhydric alcohols were characterized by infrared spectra and differential thermal analysis.

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PREPARATION OF ALCOHOLS BY OZONOLYSIS OF UNSATURATED FATTY ESTERS

E. H. Pryde, C. M. Thierfelder and J. C. Cowan

Methyl 9-hydroxynonanoate was produced in essentially quantitative yield by ozonolysis of soybean methyl esters in a mixed alcohol:acid solvent system followed by hydrogenation with a platinum catalyst. 1-Hexanol, 1-nonanol and 1,3-propanediol were also produced but in somewhat lower yields. With alcohol alone as solvent, hydrogenation with nickel gave an azelate ester as the major by-product. Nickel also formed complexes difficult to remove, and these complexes catalyzed polycondensation of methyl 9-hydroxynonanoate during distillation.

The benefits of participating solvents in the ozonolysis of unsaturated fatty esters, previously demonstrated for preparation of aldehydic compounds, are equally applicable to hydroxylic compounds. They include: (a) moderate temperatures for both ozonolysis and hydrogenation, (b) no degradation of carbon chains and (c) high yields.

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HYDROCARBONS DERIVED FROM AUTOXIDIZED VEGETABLE OILS THROUGH THERMAL SPLITTING

C. D. Evans, R. L. Hoffmann, G. R. List and E. Selke

Specific composition and type of hydrocarbon indicate the presence of many isomeric hydroperoxides in autoxidized oils. Easily recognizable hydrocarbon patterns are obtained from each species of vegetable oil. The distributions of the hydrocarbons are in agreement with reported literature values of the corresponding aldehydes (of 1-carbon atom greater chain length) from autoxidation of either specific oils or their methyl esters. Hydrocarbon gas chromatograms from different autoxidized vegetable oils and pure methyl esters will be presented, and the origin of saturated and unsaturated hydrocarbons discussed on the basis of structure of the precursor of fatty acid.

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9-AMINONONANAMIDE, A POLYAMIDE INTERMEDIATE FROM SOYBEAN OIL

W. L. Kohlhase, E. H. Pryde and J. C. Cowan

Although several ω-aminoalkanamides reportedly polymerize to polyamides, 9-aminononanamide has not been. By three different reaction sequences we synthesized this new amino amide from soybean oil. One sequence involved ammonolysis of the oil to fatty amides, reductive ozonolysis of the amides to 8-formyloctanamide, and then reductive amination of the formyl compound to the amino amide. Another sequence involved reductive ozonolysis of the oil to glyceryl azelaaldehydates, followed by conversion to the amino amide by reductive amination and simultaneous ammonolysis. The third comprised transesterification of the oil to lower alkyl esters, reductive ozonolysis of the esters to alkyl azelaaldehydates, and then reductive amination with ammonolysis (either simultaneously or separately). The third route gave a bifunctional intermediate (the alkyl azelaaldehydate) that was more easily purified than any of the others. Although optimization of reaction variables was not carried out, the maximum overall yield from soybean oil was about 40% of theory. All three sequences appear capable of significant yield improvement.

9-Aminononanamide is a strongly basic, water-soluble, waxy solid having a broad melting range, due in part to facile absorption of carbon dioxide and to oligomer formation. The amino amide can be polymerized; a preliminary experiment gave a polyamide with a molecular weight of 5700. Acid hydrolysis of the amino amide gave 9-aminonanoic acid, a more readily purified compound and a known monomer for fiber grade nylon-9.

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SEARCH FOR NEW INDUSTRIAL OILS. XVI. SEED OILS OF THE UMBELLIFLORAE

F. R. Earle, G. F. Spencer, R. Kleiman and I. A. Wolff

Seed oils of the order Umbelliflorae, including 75 samples from the family Umbelliferae and 5 samples from the Araliaceae, were analyzed for fatty acid composition by gas-liquid chromatography (GLC) of their methyl esters. The characteristic fatty acid of the order, petroselinic acid, occurred in the Umbelliferae in amounts ranging from 33 to 85% with the exception of one that contained none. In the Araliaceae, the content was from 62 to 79%. The other major acids were palmitic, oleic and linoleic acids, with small amounts of hexadecenoic, stearic, linolenic and, in some cases, C_{20} acids. Petroselinic acid was determined by micro-scale ozonolysis of the C_{18} monenoic esters and subsequent GLC of the ozonolysis products. Many of the Umbelliferae seed lipids contained large amounts of essential oils, but the data reported here pertain only to the fatty acid esters that eluted from the gas chromatograph. The high proportion of petroselinic acid *in* some oils suggests their continued consideration as industrial materials.

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INDUSTRIAL USES FOR HIGH-OLEIC SAFFLOWER OIL

M. J. Diamond and G. Fuller

High-oleic safflower (UC-1), recently developed by Knowles, produces an oil containing approximately 80% oleic acid and 12% linoleic acid. The oil is a potential source of industrial oleic acid, and fatty acids from the oil may be used without further separation in some applications where technical oleic acid is now used. Oxidation of this oil with hydrogen peroxide yields an epoxidized oil in which conversion is high and the product is less colored than other epoxy oils. Reaction with ozone followed by reductive cleavage yields a light-colored to colorless aldehyde oil. Ozone consumption for this

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oil prices above world levels so as to keep meal from going too high. This situation also provides an indirect support for other fats and oil prices.

Under these circumstances it is possible to show a correlation between soybean meal production and price (Fig. 4). The June edition of JAOCS carried this analysis. As price goes up so does production. And of course production is geared to demand because meal can be stored for only a short time. But when more meal is produced we also get more oil, and oil can be stored. For this reason it is important that users of oil should be keenly aware of what's going on in the meal market.

In April and May soybean meal prices were sagging badly and many people were expecting them to go considerably lower, while soybean oil prices were high and expected to go higher. We reasoned that, based on Charts C and D, meal would go higher and oil would go down. This, as you know, is what happened.

But what of the future? Can these two charts be useful for projections into crop year 1967–68? We think the answer is yes. The same basic supply, demand, and economic factors still apply. The question is, how much meal will be needed? We can expect fewer animals on feed. Farrowing intentions for this fall's pig crop are off 3%. Cattle on feed will be down. Broiler hatchery supply flocks are down. The cottonseed crop is not expected to be any larger than last year. We can expect more fish meal. More urea is likely at prices less than this year due to improved production techniques. This seems to add up to less soybean meal demand and consequently lower prices, based on Chart 4. But with fewer animals and improved economic conditions by the end of 1967 we should have higher animal prices and higher feeding rates. So the prospect is for meal production and prices to average about the same as this season, which should result in little change in soybean oil prices.

* * * *

Now, what of the lard situation? For production in the current season (October through September) we can use two billion pounds. This is derived from Fig. 5 which was constructed like Fig. 3 for soybean crush. The range of cumulative percentage through May of annual total is 68% to 72%, a slightly wider range than for soybean crush. The current situation leads us to believe that through May 70% of this year's total lard had been produced.

The June 1 Pig Crop Report indicates there were 9% more market hogs on farms than a year ago in the 180 lb plus category. In the 120 to 179 lb range there were only 1% more. In the 60 to 119 lb range there were 4% more, while below 60 lb there were 5% less. June hog marketings were up about 9%. This phase was completed in June. July to early August should drop back to only 1% over last year. This should be followed by a 4% higher rate through August and September. Then the indicated rate is lower for several months. As for farrowings next December to May, we will watch the hog-corn ratio this fall. There is a good correlation between this ratio and farrowing decisions (Fig. 6). Lard prices? They look steady to easier into July. Then some recovery this summer. A little easier in the fall. Then stronger.

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Fall Meeting Abstracts

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cleavage is lower than that for more unsaturated oil and fewer low molecular weight fragments are formed. Other applications where high-oleic safflower oil has a potential economic advantage will be discussed.

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ISOMERIC PHENYLSTEARIC ACIDS AND RELATED COMPOUNDS. COMPOSITION AND PARTIAL SEPARATION

F. D. Smith and A. J. Stirton

The effect of variables such as aluminum chloride ratio and order of addition of reactants was explored in the Friedel-Crafts reaction of benzene with oleic acid, oleyl alcohol and oleonitrile. In each case the product was a viscous oil which failed to crystallize. Gas-liquid chromatography of the ketone fraction obtained by chromic acid oxidation showed phenylstearonitrile, phenylstearic acid, and phenyloctadecanol were mixtures of 11, 12 and 13 isomers with the benzene ring attached at carbon numbers 7 to 17, 6 to 17 and 5 to 17 on the aliphatic chain resepectively. A partial resolution of the oily reaction products by analytical GLC showed a similarity in composition. Partial resolution by preparative GLC effected isolation of the 17-, 16- and 15-phenyl isomers in a pure state from phenylstearic acid; and of the 17- and 16-phenyl isomers from phenylstearonitrile and phenyloctadecanol.

Repeated low temperature crystallization from acetone separated the 17-phenyl isomer from phenylstearic acid, phenyloctadecanol, phenyloctadecyl acetate, and phenylstearonitrile. Because of a higher melting point (42.2–42.9C vs. 31.0–31.8C) low temperature crystallization of methyl phenylstearate gave the 16-phenyl rather than the 17-phenyl isomer.

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CORRELATION OF FATTY ACID STRUCTURE WITH PREFERENTIAL ORDER OF UREA COMPLEX FORMATION

J. L. Iverson and R. W. Weik

The selective order in which methyl esters of fatty acids form urea complexes was correlated with fatty acid structure. Detailed information about the preferential order in which inclusion compounds are formed was obtained by fractionating complex oils (e.g., butter, lanolin, cod liver and a special polyunsaturated fraction of cod liver oil). The preferential order was correlated with GLC retention times and the detection of trace amounts of fatty acids (<0.1%) was possible. Urea adduct valves (UAV) are proposed as a useful means of expressing preferential order at the formation of inclusion compounds. The preferential order can be used to identify structural isomers of unsaturated fatty acids and tentatively indicate the presence of additional members of a homologous series of compounds such as multibranched isoprenoid acids.

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FATTY ACID COMPOSITION OF COD LIVER OIL DETERMINED BY UREA FRACTIONATION AND MODIFIED PTGC

J. L. Iverson

Cod liver oil contains all odd and even chain length saturated fatty acids from C_{12} to C_{24} and branched chain iso and anteiso acids from C_{14} to C_{24}. A series of multibranched acids composed of a basic saturatrd isoprenoid unit beginning with a C_{16} member, including the C_{20} member (3,7,11,15-tetramethyl hexadecanoic acid) and extending to a C_{28} member has been found together with several additional unidentified saturated components. The presence of monounsaturated acids, including positional isomers, from C_{14} to C_{28}, and polyunsaturated acids, including positional isomers, from C_{16} to C_{26} has been confirmed. In addition, trace amounts of C_{28}, C_{30} and C_{32} polyunsaturated acids of undetermined structure have been detected.

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MOLECULAR SIEVES AS CATALYSTS FOR CYCLIC FATTY ACID FORMATION

R. A. Eisenhauer and R. E. Beal

A method has been developed for producing cyclic fatty acids by the use of molecular sieves to catalyze the reaction. Previously, the triene system of linolenic acid was cyclized by heating with excess alkali in an appropriate solvent. To recover the cyclic fatty acids, soaps and excess alkali were neutralized with acid. Alkali addition and subsequent neutralization are eliminated with the molecular sieve procedure. To conduct the reaction, molecular sieves, linseed fatty acids and dodecane solvent were heated and stirred in an autoclave. Such reaction variables were investigated as type of sieve, sieve-fatty acid ratio, solvent ratio, temperature and time. GLC data show that cyclic fatty acids made by both methods contain the same isomers; however, the predominant isomers differ. The cyclic fatty acids produced by molecular sieve catalysts are similar to those from a thermal treatment.

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STUDIES ON THE AUTOXIDATION OF HUMAN SERUM LIPOPROTEINS USING ULTRAVIOLET SPECTROPHOTOMETRY

W. L. Robison and Gary J. Nelson

Changes in the ultraviolet spectra of purified human serum lipoproteins isolated by ultracentrifugal procedures are a sensitive measure of autoxidative changes in the lipoprotein molecule. The extent of the autoxidative changes can be determined quantitatively by the intensity of ultraviolet absorption in the region from 250 to 350 mμ. In this study total serum lipoprotein with density 1.21 gm/ml, high density lipoproteins (HDL_3), and a low density lipoprotein fraction, $S_{f\,3-9}$ were isolated ultracentrifugally and then exposed to oxygen. The ultraviolet spectra were recorded at various intervals up to one week after the initial isolation. In addition, solutions of fatty acid-free bovine serum albumin (BSA) and various pure fatty acids—saturated, monoene, and polyenes—were exposed to oxygen using the same conditions. BSA, saturated and monoene fatty acids showed little change in their ultraviolet absorption, but the spectra of the polyunsaturated fatty acid underwent changes similar to those of the lipoprotein samples. When double sector cells were used with BSA in one compartment and autoxidized polyunsaturated fatty acids in the other, the spectra of the autoxidized lipoproteins could be approximated. Hence, it was concluded that the changes in the ultraviolet spectra of the autoxidized lipoproteins were due to the autoxidation of the polyunsaturated fatty acids in the molecule. Ultracentrifugal flotation patterns on autoxidized lipoproteins were found to be essentially normal despite gross alterations in the ultraviolet spectra of the samples, and, hence, are a poor criterion for the degree of autoxidation of a lipoprotein sample.

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QUANTITATIVE DETERMINATION OF GLYCERYL ALK-L-ENYL AND ALKYL-ALKENYL ETHERS IN NEUTRAL AND PHOSPHOLIPIDS

Randall Wood and Fred Snyder

A quantitative method for the simultaneous determination of glyceryl alk-l-enyl and alkyl-alkenyl ethers is described. Complete hydrogenolysis of carboxylate and phosphate esters of neutral and phospholipids was achieved with lithium aluminum hydride. The hydrogenolysis products of the glyceryl ether-containing lipids, glyceryl alk-l-enyl and alkyl-alkenyl ethers and alcohols, were identified by thin-layer chromatography (TLC), gas-liquid chromatography (GLC), and infrared spectroscopy. The glyceryl alk-l-enyl and alkyl-alkenyl ethers were quantitated by TLC photodensitometry. The specificity of this method can also be extended when used in conjunction with GLC, ion-complexing TLC, zonal scanning, and autoradiography to study composition, isomeric form, and the biosynthesis of glyceryl ethers in neutral and phospholipids.

The percentage of glyceryl alk-l-enyl and alkyl-alkenyl ethers in both the neutral and phospholipids of various rat tissues was determined by the described method. Glyceryl ether glycerides of various tissues represent 0.3–1.2% of the total neutral lipids, whereas the glyceryl ether phosphatides of brain, heart, marrow, muscle, and spleen represent 4.5–12.0% of their total phopholipids. Higher concentrations of glyceryl alkyl-alkenyl than of alk-l-enyl ethers were found in the neutral lipids, whereas the glyceryl alk-l-enyl ethers were found to predominate in the phospholipids.

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THE SUBCELLULAR DISTRIBUTION AND METABOLISM OF GLYCERYL ETHER DIESTERS IN EHRLICH ASCITES CELLS

Fred Snyder and Randall Wood

Total lipids from Ehrlich ascites carcinoma cells contain approximately 2% glyceryl ether dieseters. Carcinoma cells were disrupted in a French pressure cell, and subcellular fractions were examined for glyceryl ether diester and triglyceride content by thin-layer chromatography and gas-liquid chromatography. The highest proportion of the neutral lipid-ethers was found in the mitochondria and the least amount in the microsomes. After the mice bearing the tumor were given 5 daily injections of palmitic-1-^{14}C acid, only the mitochondrial fraction had a significant peak of radioactivity in the glyceryl ether diesters as detected by zonal ^{14}C profile scans.

The phospholipid composition of intact Ehrlich ascites cells and subcellular fractions, including their alkyl-alkenyl and alk-l-enyl content, will also be reported.

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AN IMPROVED METHOD FOR THE PREPARATION OF CYCLIC ACETAL DERIVATIVES FROM PLASMALOGENS

Grace Y. Sun and L. A. Horrocks

The cyclic acetal derivatives of alk-l-enyl ethers (Venkata Rao, Ramachandran, and Cornwell, J. Lipid Res., in press) have several advantages for analysis by gas chromatography when compared with the dimethyl acetal derivatives, but the method recommended by Venkata Rao et al. for cyclic acetals requires more time and equipment than that required for the preparation of dimethyl acetals. The following micro-procedure has been developed for the preparation of cyclic acetal derivatives: Place a lipid sample having an alk-l-enyl ether content of 5–20 μmoles, 1,3-propanediol (0.05 ml), *p*-toluenesulfonic acid (2–5 mg), and chloroform (5 ml) in a culture tube sealed with a Teflon-lined screw cap and keep at 90C for 2 hr. Take to dryness and extract with hexane. Purify the hexane extract by preparative thin-layer chromatography with toluene development. The dimethyl acetals. The following micromon-1K–withpmeSHRDLUCM residue not extracted by hexane is suitable for the preparation of fatty acid methyl esters. No differences in compositions of the cyclic acetal and the dimethyl acetal derivatives were found for beef heart lecithin and mouse brain phospholipids. The present method for the preparation of cyclic acetal derivatives is convenient, requires only small quantities of phosphoglycerides, produces a derivative that is more stable than the dimethyl acetals, and is recommended for the determination of the alk-l-enyl ether composition of plasmalogens.

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CHARACTERIZATION OF SIALYLGALACTOSYLCERAMIDE (SGC) FROM HUMAN BRAIN

Bader Siddiqui and R. H. McCluer

Kuhn and Wiegandt (Z. Naturforschg. *19b*, 256, 1964) reported the isolation of brain ganglioside which yielded 3′ neuraminyl galactose following ozone degradation. Thus in this ganglioside, sphingosine is directly linked to galactose, whereas in other gangliosides sphingosine is linked to glucose (R. Kuhn and H. Wiegandt, Chem. Ber. *96*, 866, 1963). Since the fatty acid and sphingosine composition of brain gangliosides and cerebrosides are clearly distinct, examination of the sphingosine and fatty acid composition of SGC should contribute to an understanding of its metabolic relationships.

Mixed gangliosides were prepared as previously reported (K. Sambasivarao and R. H. McCluer, J. Lipid Res. 5, 103, 1964). SGC was further purified on silicic acid columns. TLC of SGC gave one resorcinol-positive spot in four different solvent systems. Treatment of this ganglioside with neuraminidase gave galactosylceramide and N-acetylneuraminic acid (NANA). Galactosylceramide was identified by borate TLC method of Kean (J. Lipid Res. 7, 449, 1966).

Quantitative molar ratio of total hexose, NANA, and sphingosine was 1:1:1. Qualitative analysis of sphingosine was determined by gas-liquid chromatography. C_{18} spingosine and C_{20} sphingosine, present in roughly equal amounts, were the major components; small amounts of dihydrosphingosine and C_{20} dihydrosphingosine were also found. Hydroxy and nonhydroxy fatty acids were separated by TLC and then analyzed by GLC. Nonhydroxy fatty acids found were 16:0, 18:0, 18:1. Hydroxy fatty acids found were C_{20}, C_{22}, C_{23}, C_{24}, C_{25}.

In conclusion, the sphingosine composition of SGC was the same as found in gangliosides, whereas the fatty acid composition was different. The hydroxy fatty acid composition of SGC was similar to that found in cerebroside (galactosylceramide).

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LIPIDS OF THE PREPUTIAL GLAND OF THE MOUSE

Gail Sansone and J. G. Hamilton

The mouse preputial gland is a bilaterally symmetrical, subcutaneous organ located on each side of the midline just superior to the symphysis pubis. The gland contains large amounts of lipid including wax esters, neutral plasmalogens, glyceryl ether diesters, triglycerides, phosphatidyl ethanolamine (PE), phosphatidyl choline (PC), and PE and PC plasmalogens. Fractions containing neutral plasmalogens, diacylglyceryl ethers and acyl dialkyl glyceryl ethers were isolated by thin layer chromatography. Saponification of the diaclyglyceryl ethers and analyses of the glyyceryl ether and fatty acid methyl esters were performed. The glycerl ethers were predominantly chimyl and shorter chain ethers. The methyl esters were mainly myristic, palmitic palmitoleic and oleic. The acyl dialkylglyceryl ethers were saponified and the methyl esters of the fatty acids obtained were identified by gas chromatography. This fraction contained palmitic, stearic, oleic and linoleic acids.

A fraction from thin layer chromatograms corresponding to wax esters and cholesterol esters was saponified. This yielded fatty acids, fatty alcohols and a non-saponifiable fraction. Upon analysis, the non-saponifiable fraction appeared to contain long chain trialkyl glyceryl ethers.

Analysis of the neutral plasmalogens fraction was performed by cleaving the vinyl ether group. The resultant aldehydes were reduced to alcohols and the acetates of the alcohols were gas chromatographed. The alcohols were primarily cetyl and myristyl. The methyl esters of the fatty acids obtained from the neutral plasmalogens were myristic, palmitic, stearic, oleic and linoleic.

The mouse preputial gland is an excellent source of glyceryl ethers, neutral plasmalogens and wax esters. It contains relatively high concentrations of acyl dialkyl glyceryl ethers and is the only source as yet reported of tentatively identified trialkylglyceryl ethers.

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SOME EFFECTS ON FATTY ACIDS INDUCED BY EXERCISE

J. B. Saddler, H. M. Krueger, I. J. Tinsley and R. R. Lowry

Coho salmon were taken from the river and maintained in the laboratory for an average of 16 days on an ad libitum diet of tubificid worms. The total lipids were extracted and the fatty acids were detected by gas-liquid chromatography. The change in fatty acid composition was observed when 38 salmon were forced to swim against a constant water velocity for a maximum of 24 hr or until they failed and related to the fatty acid composition of 32 control salmon. At the water velocity of 59 cm/sec, the average swimming time for the 38 salmon placed to swim was 398 min.

The average length for control salmon was 8.06 cm and the average length for swimming salmon was 7.90 cm. The average weight loss for salmon swimming at 59 cm/sec was 480 mg, and the average fatty acid loss was 11.5 mg. An alteration in the relative amounts of individual fatty acids present accompanied the total fatty acid loss. The total loss in saturated fatty acids was 1.9 mg or 18% of the total fatty acid loss for swimming salmon. Three monene fatty acids accounted for 7.4% of the loss while one hexene acid with 22 carbons accounted for 24% of the total loss.

In control salmon saturated fatty acids represented 27% of the total fatty acids while the decrease in saturated fatty acids for swimming salmon represented 18% of the total fatty acid loss. This relationship suggests that salmon swimming for shorter distances at high velocities preferentially metabolize a higher percentage of unsaturated fatty acids.

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THE INFLUENCE OF ω6 FATTY ACIDS ON THE COMPOSITION OF THE ω3 GROUP OF FATTY ACIDS IN THE LIPIDS OF THE COHO SALMON

I. J. Tinsley, J. B. Sadler, R. R. Lowry and H. M. Krueger

The relation between the proportion of ω6 fatty acids in the total lipids and the composition of the ω3 fatty acids has been studied in a group of juvenile salmon. Product/precursor ratios of fatty acids of the ω3 sequence were plotted as a function of the proportion of an ω6 fatty acid in the total lipid. Statistically significant correlations were observed between the 18:2,ω6 level and the 18:4,ω3/18:3,ω3 and 20:5,ω3/18:4,ω3 ratios. The first correlation suggests a competitive interaction between 18:2,ω6 and 18:3,ω3 in the synthesis of polyunsaturated fatty acids since an increase in the proportion of 18:2,ω6 was associated with a decrease in the 18:4,ω3/18:3,ω3 ratio. In contrast an increase in the proportion of 18:2,ω6 was correlated with an increase in the 20:5,ω2/18:4,ω3 ratio. This correlation might be explained by a higher degree of conversion of 18:4,ω3 to 20:5,ω3 when smaller quantities of the former are available as a result of the inhibition of the 18:3,ω3-18:4,ω3 transformation by 18:2,ω6. The subsequent transformations of 20:5,ω3 to 22:5,ω3 and 22:6,ω3 were not influenced by the proportions of ω6 acids present. These relationships will be interpreted with reference to a model system which simulates the type of competitive interactions which are apparently in the salmon as well as the rat.

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ACETOACETATE METABOLISM IN RATS ON "KETOGENIC" DIETS

Li Hsin Chung and Jacqueline Dupont

Young adult female rats were fed nutritionally adequate diets as follows: a) high carbohydrate (2% corn oil); b) one-half of ad libitum consumption of a); c) high beef tallow (no carbohydrate); d) high corn oil (no carbohydrate). At the end of 2 weeks each rat was given an intraperitoneal injection of ethyl acetoacetate-3-^{14}C. The animal was placed in a respiration chamber and expired CO_2 collected for 3 hours. The rat was then anesthetized with Na-pentobarbital and a blood sample and the liver removed. Serum was analyzed immediately for acetoacetate. Serum and liver were frozen and later analyzed for total lipid and cholesterol and ^{14}C in those fractions.

Rats fed one-half calories (group b) or beef tallow (group c) had significantly grater serum acetoacetate than controls (group a). Rats fed high corn oil had serum acetoacetate concentration similar to controls. There was no difference among groups in rate of oxidation of ^{14}C-acetoacetate. Incorporation of ^{14}C-acetoacetate into cholesterol was less in beef tallow and corn oil rats than in control and half-calorie groups; the latter 2 were equal to each other. Incorporation of label into total lipid was one-fourth as great in half-calorie rats as in controls and only about one-tenth as great in high beef tallow and high corn oil groups as in controls.

Previous experiments using ^{14}C-acetate as a tracer have shown stimulation of ^{14}C incorporation into cholesterol by high corn oil diets. It thus appears that whatever the mechanism for stimulus of cholesterol synthesis from acetate by corn oil, it is not operative for syntheesis from acetoacetate. It is also evident from this experiment that a high corn oil diet does not exert a ketogenic effect on the female rat as does high beef tallow.

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THE INFLUENCE OF VARIOUS SURFACTANTS ON THE ANTIMICROBIAL ACTIVITY OF BROMSALANS AND OTHER RING-HALOGENATED SUBSTANCES

N. M. Molnar

Test methods used in the assessment of activity are discussed, utilizing the gradient plate dilution technique for screening work and skin and finger imprint studies to show residence in skin. Also given are extraction studies in fabric to demonstrate the substantivity to fabric.

The various classes of surfactants studied are *anionics,* such as soap and sodium salt of dodecyl benzene sulfonic acid and dibasic sulfosuccinate one-half esters (esterified with a hydroxy acid amide); *nonionics* such as tridodecyloxypoly (ethyleneoxy) ethanol and nonyl phenoxy poly (ethyleneoxy) ethanol; *amphoterics* such as imidazolinium surfactants and substituted imidazoline such as 1-hydroxy-ethyl-2-alkyl imidazoline; and *cationics* such as cetyl trimethyl ammonium bromide and benzalkonium chloride.

The data thus obtained may be utilized for formulation of fabric softeners, and the tests employed aid in the selection of the proper surfactant for textile and skin applications.

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NEW TERTIARY AMINE BASED SURFACE ACTIVE POLYMERS

I. R. Schmolka and R. K. Seizinger

There has been a growing interest in new nontoxic nitrogen-containing surface active agents for use in cosmetic applications. An investigation was carried out into the synthesis of high molecular weight block polymers of ethylene and propylene oxides which are derived from hydrophobes higher in molecular weight than have been prepared previously. Using polyoxypropylene glycol adducts of ethylene diamine, ranging in molecular weight from 4750 up to 6750, surface active polymers with molecular weights ranging from 5600 up to 30,000 were synthesized.

The toxicological properties of some of these new nonionics indicated that they would be nontoxic when used in contact with the skin and scalp. Their typical physical properties, such as wetting, emulsifying, foaming, and thickening, are reported. A variety of cosmetic specialties have been prepared. Formulations are presented based upon these new nonionic surface active polymers which illustrate their versatility when used in products as diverse as a floating bath oil, an antiperspirant gel, a cold cream, and a sun screen cream.

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METHYL GLUCOSIDE ESTERS IN COSMETICS

O. E. Libman and Howard Packer

A series of methyl glucoside esters (mono, di and tri) were prepared using oleic, stearic, and lauric acids.

Poloxyethylene derivatives of methyl glucoside esters using different mole ratios of ethylene oxide were also prepared for a cosmetic testing program.

The calculated HLB values of the methyl glucoside monoesters were higher than those of corresponding sorbitan monoesters. The calculated HLB values of the 10 mole polyoxyethylene methyl glucoside monoesters were lower, and those of the 20 mole polyoxyethylene monoesters were higher than the HLB values of the corresponding polysorbates (20 mole polyoxyethylene sorbitan monoesters).

Cosmetic type emulsions, lotions and ointment bases were prepared with lyophile/hydrophile emulsion pairs. A comparison was made between formulations based on emulsion pairs based on sorbitan esters/poly-sorbate pairs and methyl glucoside esters/polyoxyethylene methyl glucoside ester pairs. The ratio of lyophile/hydrophile were adjusted for the methyl glucoside emulsifier pair to approximate the HLB values of the sorbitan emulsifier pair.

Stable lotion and ointment emulsions were obtainable from the methyl glucoside emulsifier pairs.

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FATTY GLYCOLS AND ISOSTEARYL ALCOHOL AS LIPSTICK COMPONENTS

R. R. Egan and B. J. Hoffman

Castor oil and oleyl alcohol have long been the basic raw materials used in lipsticks because of their solvent power for the halogenated fluorescein dyes. They have the disadvantages of being unsaturated and subject to rancidity, and immiscible with waxy materials which must be added to them to produce a solid.

A new series of fatty glycols and liquid saturated isostearyl alcohol can follow formulation of nonoxidizing, high-strain lipstick bases. The fatty glycols, both in internal and terminal forms, having chain lengths from C_{11} to C_{20}, have been studied. They are all excellent solvents for halogenated fluoresceins, are nontoxic, colorless and virtually tasteless and water-insoluble. They can be used to produce lipstick bases with a wide range of physical properties. The C_{11-14} internal glycol can be used by itself as a lipstick.

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REDUCED LANOLINS: THE SYNTHESIS, PROPERTIES AND COSMETIC APPLICATIONS

F. P. Siegel, Theodore Kritchevsky and S. T. Goode

Reduced lanolin was prepared by one of two routes: 1) high pressure catalytic hydrogenolysis and 2) sodium reduction.

The chemical and physical properties of the two reduced lanolins will be discussed.

A number of cosmetic formulations were prepared to compare the properties of the two reduced lanolins.

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PROTEINS—SOME NEW STUDIES

R. R. Risso

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SOME SPECIAL SAFETY PROBLEMS IN PLANTS OUTSIDE THE US

Les Watkins

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SAFETY PROBLEMS IN OPERATING DT MACHINES

H. James

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A REVIEW OF OPERATING RULES RELATING TO EXTRACTION PLANT SAFETY

W. Pearson

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SELECTIVE HYDROGENATION OF CYCLOPROPENOIDS IN COTTONSEED OIL

J. P. Hutchins, A. Z. Ullman and L. H. Going

A new process has been developed in which the cyclopropenoid groups in cottonseed oil can be selectively and continuously hydrogenated under mild conditions. This process utilizes nickel in a fixed bed reactor, thereby eliminating the expensive filtration commonly associated with slurry reactors.

In pilot plant runs at essentially atmospheric pressure, and temperatures from 150F to 315F, Halphen-negative oils (oils which do not give a positive response to the Halphen test; estimated cyclopropenoid concentration is less than 0.01%) were produced in as short a contact time as 2 minutes. Little or no hydrogenation or isomerization of normal fatty acids occurred during the process.

Catalyst half-life (50% reduction in initial activity) for one commercial nickel catalyst has been estimated at 60,000 lb oil hydrogenated/lb catalyst.

Kinetic data and reactor scale-up will be presented.

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AUTOXIDATION OF MONOLAYERS OF LINOLEIC ACID ON SILICA GEL

W. L. Porter, A. S. Henick, S. R. Cunnold, M. A. Sharkey and S. Warrington

To approximate in a model system the autoxidation of monomolecular layers of lipids on the cell surfaces of freeze-dried foods, the autoxidation of presumed monolayers of linoleic acid adsorbed from solution onto silica gel has been studied as a function of time and tocopherol content. The method of Honn (JAOCS *28*, 129, 1951) was used, modified by the substitution of linoleic acid for soybean oil, the addition of anti-oxidants, and the use of gas chromatography to follow oxygen disappearance at 80C.

It was found that adsorption of linoleic acid onto silica gel from petroleum ether solution conforms to a Langmuir isotherm, indicating the formation of a statistical monolayer. Confirming Honn's finding with soybean oil, it was found that the most rapid uptake of oxygen occurred at a linoleic acid/silica ratio close to that for the statistical monolayer.

Without included anti-oxidant, oxidation at a linear rate commences without observable induction period. Time to consumption of one-half mole of oxygen per mole of linoleic acid is about 30 min, during which the rate remains linear. If very small amounts of tocopherol are included in the layer, virtually no oxygen uptake measurable in this system occurs during an induction period whose length is approximately proportional to tocopherol content. The inflection point at the commencement of rapid oxidation is very sharp; the ensuing linear oxidation rate approximates that of the unprotected acid.

The induction period of linoleic acid with the same tocopherol content is as much as 100% longer when exposed in monolayer than in a bulk form. However, the rate after commencement of rapid oxidation is 8 to 10 times greater in the monolayer.

In the same system, butylated hydroxytoluene (BHT) merely reduces the rate without producing an induction period. It was shown experimentally that BHT is competitively desorbed from the monolayer by linoleic acid and apparently superimposed upon it if the solvent is totally evaporated.

In studies using mixtures of silicas containing linoleic acid with and without tocopherol, it was shown that there is little evidence for inter-particle diffusional transfer of tocopherol at 80C. It would appear therefore, that in spite of reduced mobility, tocopherol may give protection over considerable distances against autoxidation of linoleic acid in a monolayer adsorbed on silica.

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THE COLOR PROBLEM IN EXPERIMENTAL VARIETIES OF SAFFLOWER

H. J. Burkhardt

The dark color found in commercially extracted oils from two new thin-hull safflower varieties is formed from a colorless precursor. This precursor is extracted into the oil from the kernel portion of the seed with hot hexane. It condenses to a dark pigment if heated for prolonged times in excess of 100C and was found in decreasing amounts in hot extracted oils of a pigmentless, a brown-striped, and the commercial Gila variety. The color precursor can be removed by extraction with water or standard alkali refinement and the dark pigment by treatment with dilute alkaline peroxide. All the oil of the investigated varieties can be easily obtained free of pigment and pigment precursor if the press cake or whole cracked seeds are extracted with hexane at room temperature. The presence and content of dark pigment in oils of investigated varieties was directly dependent on the content of precursor in the kernel but not melanin content of the hull. A microtest has been devised to screen existing collections and new breeds of safflower varieties for color precursor. Isolation and identification of this color precursor are in progress.

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PHOSPHOLIPID OXIDATION IN EMULSIONS

G. A. Corliss and L. R. Dugan

Phospholipids from egg yolk and a commercial soybean phosphatide preparation were separated into fractions by silicic acid column chromatography. The purity of individual fractions was ascertained by thin-layer chromatography. Purified phosphatidyl ethanolamine (PE) and phosphatidyl choline (PC) were emulsified in a Tween 20-borate buffer by a Braun cell-disintegrator and their oxygen uptake was followed manometrically at various temperatures with a Gilson Differential Respirometer. Oxygen uptake was temperature dependent for both PE and PC, and that by PE was greater at all temperature and pH values studied.

The rates of oxygen uptake at different temperatures were utilized to determine activation energies for PE and PC from egg and soybean. The energy of activation for the autoxidation of PE and PC from egg and soybean were comparable; however, the values obtained for PE and PC were approximately one-half of that reported for the autoxidation of methyl linoleate and linoleic acid emulsions.

Oxidized and non-oxidized samples of PE and PC were methylated and their fatty acid compositions were determined by GLC. Autoxidation resulted in a large reduction in the concentration of linoelic and arachidonic acids in egg phospholipids and linoleic and linolenic acids in soybean phospholipids.

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HIGH "OLEIC" OILS BY SELECTIVE HYDROGENATION OF SOYBEAN OIL

H. J. Dutton, O. Popescu and S. Koritala

Copper-containing catalysts possess high linoleic selectivity as well as high linolenic. This characteristic implies that they do not produce stearate under normal conditions of hydrogenation while reducing linolenyl and linoleyl groups. It suggests the possibility of producing essentially monoene oils from soybean and other polyunsaturated oils. Usually the activity of commercially available copper catalysts decreases from more than 1000 to less than 100 ml H_2 (0C, 760 mm Hg) min/1000 ml oil after only about 45 min of hydrogenation. Consequently, they are not so practical for producing high "oleic" acid-containing oils.

High-monoene oils were prepared in a 2.8 gal hydrogenator. Three different hydrogenation methods were used: 1) with commercial catalysts in a two-step process, Ni-hydrogenation followed by copper hydrogenation at low pressure, 2) with commercial copper-containing catalysts at high pressure and 3) with a new laboratory-prepared copper catalyst on a support with a large surface area at low pressure. All oils contained about 62–72% monoenic acid, 13.8–22.6% dienoic acid and only about 1% more stearic acid than the original oil; they remained liquid at about 28C and had a *trans* isomer acid content of about 32%.

More than 55% of the double bonds were located in the 9-position for the *cis*-monoenoic acids, but more than 50% were in the 10- and 11-positions in the *trans*-monoenoic acids. Double bonds appeared along the monoene molecules from C_8 to C_{15} (6 to 14% at C_{12}).

It is concluded that the two-step hydrogenation technique or the new selective and more active laboratory-prepared copper catalyst may be used industrially to produce oils containing a high percentage of "oleic" acid.

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SELECTIVE HYDROGENATION OF SOYBEAN OIL. III. COPPER-EXCHANGED MOLECULAR SIEVE AND OTHER SUPPORTED COPPER CATALYSTS

Sambasivarao Koritala

Although copper-chromium catalysts selectively reduce linolenate groups in soybean oil, such commercial catalysts have only moderate activity. To obtain catalysts with higher activities for selective hydrogenation of soybean oil, copper has been dispersed on high surface silica, alumina and molecular sieves. Activity of catalysts so prepared varied depending upon the support. The highest activity was achieved when copper was precipitated on Cab-O-Sil, a pure form of silica with a large external surface. Selectivity ratios (K_{Le}/K_{Lo}) of all the catalysts prepared varied from 6 to 15.

Treatment of some supports with hydrochloric acid before precipitation of copper improved both selectivity and activity. For example, copper precipitated on acid-washed Celite hydrogenated soybean oil in 54 min with a selectivity ratio of 9.9. Untreated Celite required 165 min and gave a selectivity ratio of 5.9.

To ensure maximum activity with copper catalysts, soybean oil must be bleached more thoroughly than is customarily done for hydrogenation with nickel catalysts. Further refining and bleaching of a refined, bleached, commercial soybean oil improve catalyst activity. For example, copper-on-Cab-O-Sil catalyst hydrogenated commercial oil in 18 min and retreated oil in 11.5 min.

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ARTIFACT FORMATION IN THE FRACTIONAL DISTILLATION OF LONG-CHAIN POLYUNSATURATED METHYL ESTERS

O. S. Privett, E. C. Nickell, J. D. Nadenicek and F. J. Pusch

Studies are reported on the fractionation and structural analysis of artifacts that are formed by alteration of methyl docosahexaenoate during fractional distillation. Extensive decomposition, including polymerization that normally occurs on the fractional distillation of methyl esters of polyunsaturated fatty acids through packed columns, can be virtually eliminated through use of a spinning band column operated at high vacuum and with a carrier-chaser. The main artifacts formed under these conditions are geometric isomers. These compounds, as well as artifacts formed in normal distillations, are isolated and their structures determined by a combination of mass spectrometry, NMR, infrared and ultraviolet absorption properties and localization of the *cis* and *trans* double bonds via ozonolysis. Artifacts formed during fractional distillation may be detected and separated by mild physical processes and generally do not constitute a sufficiently serious problem to void the use of this technique in the preparation of polyunsaturated fatty acids.

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DISTILLATION AND THERMAL DECOMPOSITION OF FATTY OZONIDES

E. M. Stearns, Jr. and O. S. Privett

Studies are reported on the high vacuum distillation and thermal decomposition of the ozonides of unsaturated methyl esters and synthetic triglycerides alone and in mixtures with nonozonized synthetic and natural fats.

Ozonides of long chain methyl esters and hydrocarbons may be molecularly distilled at approximately 100C. The yield of methyl ester ozonides and extent of decomposition during distillation depended on the number of ozonide groups in the molecule. Monoozonides distilled with less than 5% decomposition, while triozonides were largely decomposed, the major products being simple aldehydes and minor amounts of polymeric materials.

In the decomposition of ozonides of long chain methyl esters and triglycerides the yield of aldehydic compounds decreased inversely with polymer formation and the number of ozonide groups in the moelcule. Aldehydes apparently are produced as a result of fission of the molecule into radicals, polymer formation occurs largely as a result of interraction of the ozonides.

Polymeric products also were obtained by the interraction of ozonides with synthetic triglycerides and natural fats. The reaction is believed to take place via free radicals produced on decomposition of the ozonides.

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REMOVAL OF COPPER FROM HYDROGENATED SOYBEAN OIL

R. E. Beal, K. J. Moulton and L. T. Black

Removing residual copper from soybean oil is essential to the successful use of copper catalysts for selective hydrogenation. Hydrogenation with a copper chromite catalyst at 170C, 30 psi, increased the copper content of a refined, bleached soybean oil from 0.02 to 3.5 parts per million. Various methods were examined to remove this copper. Alkali refining (1% NaOH in 4% aqueous solution) eliminated 60% of the copper in the hydrogenated oil; one acid wash (1.3% citric acid in 2% aqueous solution), 70%; treatment with a cation exchange resin, 90%; bleaching (2% activated clay), 95%; three acid washes (2.5% aqueous H_2SO_4 solution), 99%; or treatment with aqueous citric acid solution followed by dehydration and filtration, about 99%. Oil samples were analyzed by carefully ashing the oil, dissolving the ash and determining copper in solution colorimetrically. AOM peroxide values of soybean oil, hydrogenated with a copper chromite catalyst, bleached and deodorized with 0.01% citric acid added, indicate that removal of residual copper from the oil should be adequate for the production of stable oils low in linolenic acid content.

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UPTAKE AND METABOLISM OF FREE FATTY ACID BY ISOLATED PERITONEAL MAST CELLS OF RATS

M. S. Cabut, R. J. Ho and H. C. Meng

The uptake and metabolism of free fatty acid (FFA) by isolated peritoneal mast cells (MCS) from normal fed rats were studied. MCS isolated according the Uvnas and Thon, were incubated in a bicarbonate buffer (pH 7.4) containing palmitate-1-^{14}C as a complex with albumin. Incubation was terminated by adding ice-cold buffer. MCS were centrifuged and washed 3 times and resuspended in the same buffer. An aliquot of the washed cells were taken for ^{14}C measurement. The remainder was extracted for lipids. ^{14}C-total lipids and lipid fractions recoverd from thin-layer chromatographs were measured.

At a FFA to albumin molar ratio of 0.78, significant radioactivity of MCS was obesrvd after 1-minute incubation. The MCS radioactivity was a function of the incubation time (1.173×10^3 and 1.62×10^4 cpm/10^6 cells after 1-minute and 1-hour incubation, respectively). The incorporation of palmitate-1-^{14}C into MCS lipids was also increased with time. After short period of incubation, most of the radioactivity was recovered as FFA fraction. However, the percent radioactivity in FFA was decreased and that of esterified lipids was increased when the incubation time was prolonged. The capability of MCS to utilize FFA was temperature dependent. The total uptake of palmitate-1-^{14}C by MCS was a function of the medium palmitate concentration. 0.392 mμmoles/10^6 cells/hr were taken up when the medium palmitate was 0.012 mM. The uptake was increased to 6.65 mμmoles/10^6 cells/hr when the medium palmitate was increased to 3.12 mM. The metabolism was strongly inhibited by both 2,4-dinitrophenol (5×10^{-4} M) and N-ethylmalmeimide (2×10^{-4} M). The results seem to suggest that the uptake of FFA is not rate limiting for metabolism of this substrate by MCS.

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INHIBITION OF LIPOLYTIC ENZYMES BY ORGANOPHOSPHATES AND CARBAMATES

R. G. Jensen and Dorothy L. Carpenter

0,0-diethyl-0-p-nitrophenylphosphorothioate (Parathion), diethyl-p-nitrophenyl phosphate, (DNP) 2,3-dihydro-2,2-dimethyl-7-benzofuranyl-N-methyl carbamate (NIA10242) and *N*-methyl-1-naphthyl carbamate (Sevin) were used in inhibitor studies on the following enzymes; crude and purified pancreatic lipases, *Geotrichum candidum* lipase, *Veronia anthelmintica* seed lipase and a special calf pregastric esterase. The inhibitors were emulsified at the level of 10^{-3} moles into the appropriate buffer. After 30 min of equilibration with the enzyme, an olive oil or butter oil emulsion was added. Inhibition was calculated from the quantities of fatty acids released as compared to a control.

At this level purified pancreatic lipase was inhibited (%), DNP, 90 and parathion 30. Increasing the level to 2×10^{-3} moles resulted in the following inhibitions (%): DNP, 94 Parathion, 40 Sevin, 25 and NIA, 19. Crude pancreatic lipase was inhibited to the extent of 89% by DNP. The other compounds either did not inhibit this enzyme or caused slight activation. The *G. candidum* lipase was inhibited by DNP, 75% and Sevin, 25%. *V. anthelmintica* seed lipase was inhibited 19% by Parathion. Pregastric esterase was inhiibted by Sevin, 37%; DNP 90% and Parathion 33%. These data suggest that a serine residue may be present at the active site of several of the lipases studied.

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ROLE OF LIPIDS IN CA^{++} UPTAKE AND Mg-ATPase ACTIVITY OF RAT SKELETAL MUSCLE SARCOPLASMIC RETICULUM

B. P. Yu, E. J. Masoro and F. D. DeMartinis

Sarcoplasmic reticulum fragments isolated from skeletal muscle homogenates exhibit an ATP-dependent capacity to remove Ca^{++} from the medium in which they are suspended. Presumably an ATPase activity is associated with the Ca^{++} uptake process. That the lipid structure of the sarcoplasmic reticulum is important in both the ATPase and Ca^{++} sequestration activities is indicated by the fact that treatment with phospholipase C destroyed both the ATPase and Ca^{++} sequestering activities. However, neither phospholipase A nor D treatment destroyed these sarcotubular activities, thereby indicating that specific aspects of phospholipid structure are involved. Further evidence concerning this specificity was obtained from experiments with essential fatty acid (EFA) deficient rats and with sarcotubular fragments treated with antibiotics Filipin and Nystatin . Although the EFA components of the lipid esters of the sarcotubular fragments from EFA deficient rats are replaced by nonessential fatty acids, no significant change in Ca^{++} sequestration or ATPase activity is caused by EFA deficiency. The antibiotics which specifically bind to the cholesterol of the membrane structure had no effect on either sarcotubular activity. From these data, it seems likely that the sarcotubular ATPase and Ca^{++} sequestration processes involve a lipoprotein structure. To study this further, attempts to solubilize the lipoprotein from the sarcotubular fragments were made by the following treatments: 0.05% Triton X-100, 0.06 M NaI, 0.05% deoxycholate, mild sonication and aging the microsomes in 0.25 M sucrose. The first three treatments resulted in marked destruction of the ATPase activity while the last two treatments slightly increased the ATPase activity. The conclusion drawn from these experiments is that the ATPase and Ca^{++} sequestration activities of the sarcoplasmic reticulum involve the lipoprotein structure of the membrane and, in particular, require the phosphoryl structure of the phospholipid. No other aspect of the lipid structure appears to be important.

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CHAIN ELONGATION OF POLYUNSATURATED FATTY ACIDS BY MICROSOMES IN VITRO

Kirsten Christiansen, Hans Mohrhauer, Yves Marcel, Minerva Gan and R. T. Holman

The chain elongation of linoleic acid and other long-chain fatty acids has been studied using radioactive substrates incubated with subcellar particles in vitro. Individual fatty acids were separated by gas chromatography and their radioactivities were measured by scintillation counter. The most effective system for the chain elongation of polyunsaturated acids was liver microsomes plus malonyl-CoA with co-factors NADPH and ATP. Temperature and pH optima were determined for the system. Under strict anaerobic conditions, the chain lengthening reaction proceeded without significant dehydrogenation. The chain elongation of polyunsaturated acids can be inhibited by saturated and unsaturated acids. Conversion of 18:2ω6 to 20:2ω6 proceeded in about 30% yield, whereas conversion of 18:3ω6 to 20:3ω6 proceeded at about 60% yield. Oleic acid was converted to about 20% and stearic acid about 5%. From consideration of reaction kinetics and inhibition by other fatty acids the preferred pathway of 18:2ω6 to 20:4ω6 seems to be via 18:3ω6.

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LIPOXIDASE DEACTIVATION TO IMPROVE STABILITY, ODOR AND FLAVOR OF FULL-FAT SOY FLOURS

G. C. Mustakas, W. J. Albrecht, J. E. McGhee, L. T. Black, G. N. Bookwalter and E. L. Griffin

Oxidation of soybean lipids catalyzed by lipoxidase was prevented by heat preconditioning to give a full-fat soy flour free of rancid odor and flavors. Our previous studies showed that the lipids in cracked dehulled whole soybeans were rapidly oxidized in the presence of moisture and an active lipoxidase system. A series of experiments are reported in which dry heat, wet heat and steaming were evaluated as preconditioning treatment for lipoxidase deactivation. A dry heat to 212F or steaming, or both, deactivated lipoxidase to give flours that maintain low values of peroxide, conjugated diene and free fatty acids upon hydrolysis. Dry-heat temperatures as low as 150F were effective if followed by 5-min steaming under conditions where no moisture condensation could occur. Wet-heat deactivation alone was less effective than dry heat followed by wet heat. Protein denaturation (nitrogen solubility index lowering) and reduction in urease activity proceeded rapidly with steaming or with a wet-heat treatment; protein denaturation was markedly less with a dry-heat application. Dry-heat enzyme deactivation was aslo carried out successfully as a continuous operation; in this step, 6–8 min retention in a jacketed, paddle conveyor was required to achieve final temperatures in the range of 218–222F. Thiamine and total tocopherols were very stable under controlled dry-heat conditions.

GLC studies gave evidence that the rapid formation of volatile off-flavors in full-fat soy flours was catalyzed by a lipoxidase system. Chromatograms of heat-deactivated samples dramatically showed amounts of volatile constituents lower than those without treatment. Our data were further substantiated by sensory tesing in which a 10-member taste panel was able to detect significant differences between samples with and without lipoxidase deactivation. The panel could indicate nonrancid vs. rancid flavor and odors. Information from this study can be translated to commercial soybean process operations to improve the quality of soybean products.

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DIFFERENCES IN TRIGLYCERIDE STRUCTURE AFTER REFEEDING WITH MEDIUM CHAIN METHYL ESTERS AND TRIGLYCERIDES

Hans Kanitz, Ruth E. Johnson and Cynthia Belton

Adult male rats were restricted to 5–8 g of Purina Laboratory Chow daily for two months. During this food deprivation, their average weight declined from 400 to 250 g. Half of the animals were then given free access to a mixture of 80% Purina Chow and 20% of medium chain triglycerides (MCT) composed of 61% C 8:0, 32% of C 10:0, and 7% of other acids in a random distribution over the glycerol moieties. The second group was given 80% Purina Chow + 10% MCT and 10% of fatty acid methyl esters having the same composition as MCT. After six weeks, when the average weights of both groups were about 350 g, the animals were sacrificed. The triglyceride fraction was isolated from perirenal adipose tissue and liver lipids by preparative TLC and analyzed by means of argentation chromatography and GLC. The perirenal adipose tissue TG of the rats fed the methyl esters were richer in linoleate and contained fewer saturated TG (smaller S_3 band) than the controls fed only MCT. This suggests that the feeding of fatty acids as TG has metabolic effects. Inasmuch as the principal difference in the intestinal absorption of methyl esters and TG is the occurrence of beta monoglycerides during absorption of the latter, a specific effect of beta monoglycerides is suggested.

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THE ENDOGENOUS TRIGLYCERIDES OF THE PIG

R. E. Anderson, N. R. Bottino and R. Reiser

Two three-week old male pigs were fed a fat-free diet for about five months. Triglycerides were isolated from mesenteric and perirenal fat and from inner and outer back fat. The fatty acid compositions of the two subcutaneous fats resembled each other. The fatty acid compositions of the mesenteric and perirenal fat also resembled each other but differed from the subcutaneous fats in that the internal fats contained more palmitic and stearic acids but less oleic acid than the more peripheral. Fractionation of the four tissue triglyceride mixtures by silver nitrate thin-layer chromatography gave in each case four bands, corresponding to the S_3, S_2M, SM_2 and M_3 types ($S =$ saturated fatty acids, $M =$ monoenoic fatty acids). It was found that each of the four triglyceride types in the four tissues had the same fatty acid composition, and that the distributions of the fatty acids on the respective triglyceride types as determined by pancreatic lipase hydrolysis, were also the same. This suggests that differences in the fatty acid compositions of the four depot fats are due to different proportional amounts of the same triglycerides.

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EPOXIDES IN RAT LIPIDS

J. A. Fioriti and R. J. Sims

Serum, liver and epididymal lipids from Sprague-Dawley rats fed trivernolin containing 86% epoxyoleic acid at 1.6 and 4.8% level in the diet for 90 days, were analyzed by thin-layer and gas-liquid chromatography. No epoxide was detected in the serum lipids and only trace amounts were found in the liver lipids. The epididymal fat pads were found to contain more than 5% epoxyoleic acid. Picric acid reaction on a TLC plate shows three distinct epoxide positive entities which have been tentatively identified as trivernolin (1% or less); divernoyl triglyceride (5–10%), and monovernoyl triglyceride (about 90%). These results suggest that trivernolin is absorbed by rats in a manner similar to common triglycerides.

Two other groups of animals were fed epoxycholesterol at 0.5 and 1.5% level for 90 days. Besides serum, liver and epididymal; kidney and spleen lipids were also investigated in this instance. Results from the GLC and TLC examination of these lipids will be presented.

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ABSORPTION OF LABELED NONVOLATILE OXIDATION PRODUCTS OF RANDOMIZED CORN OIL

E. G. Perkins and Silloo M. Vachha

The metabolic fate of the high molecular weight and polar oxidation products formed from lipids treated under frying conditions has not been clarified. The present experiments were designed to measure the absorption and transport of these materials in the rat. Methyl linoleate-1-C^{14} as well as the uniformly labeled material was transacylated with glycerol using an alkaline catalyst. The resultant labeled mono and diglyceride were separated by column chromatography on silica gel and transesterified with fresh corn oil. The randomly labeled corn oil thus obtained was then moderately oxidized for 24 hr at 200C in the presence of air. The labeled nonvolatile oxidation products were separated by partitioning of the fatty acids of oxidized corn oil with 80% ethanol and hexane. One milliliter of the methyl esters of the oxidized material (6.49 μc/g) was fed to lymph cannulated rats via stomach tube and the lymph collected for a period of 48 hr. Recovery of radioactivity in the lymph after 48 hr was 12.5%. In the liver 0.75% of administered counts were found. When the unoxidized randomized labeled corn oil was fed, 95.9% of the activity was recovered in the lymph in 48 hr.

In simultaneous catabolism experiments, rats, after administration of labeled material, were put in metabolism cages and the urine, feces and respiratory CO_2 collected separately. At the end of 48 hr the percentage of radioactivity recovered from the oxidized polymer and random corn oil fed rats was respectively: respiratory CO_2 18.7, 60.2; urine 4.5, 1.4; feces 62.8, 14.4; gastrointestinal tract 5.9, 1.5; liver 1.0, 1.9; carcass 7.6, 17.7. The data obtained indicated that 31.2% of the nonvolatile material was absorbed in the noncannulated rats, compared to 84.2% of the randomized corn oil in 48 hr. These results indicate that the undesirable nutritional effects of heat damaged oils is caused to some extent by absorption of a considerable amount of the oxidation products present in used oils. Experiments are under way to determine the composition of the material absorbed through the lymph.

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BREEDING RAPESEED FOR OIL AND SEED QUALITY

R. K. Downey, B. M. Craig and C. G. Youngs

Significant variation in fatty acid composition occurs within the seed oils of the *Brassica* genus, which includes the mustards and rapeseed. Research into the inheritance and biosynthesis of fatty acids has shown that at least two biosynthetic pathways exist in the developing rapeseed and some of the steps are under direct genetic control. The plant breeder has the basic knowledge in this oilseed crop to produce seed oils with defined fatty acid compositions, and a practical example is the commercial development of Canbra oil, the rapeseed oil from which erucic acid has been eliminated.

Brassica seed meals contain thioglucosides which may cause metabolic disturbances when fed to certain classes of livestock. The major thioglucosides in rapeseed meal are those giving rise to 3-butenyl and 4-pentenyl isothiocyanate and 5-vinyl-2-oxazolidinethione. Partial success in eliminating these compounds has been achieved by breeding strains of turnip rape (*B. campestris*) which do not contain the glucosides of 4-pentenyl isothiocyanate and oxazolidinethione. The absence of these compounds is under direct genetic control. These findings suggest that complete removal of these sulphur compounds may be possible through plant breeding.

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ALTERING THE GOSSYPOL CONTENT OF COTTONSEED THROUGH BREEDING

J. A. Lee

All species of *Gossypium* have small, pigment-bearing, glands in most parts of the plant. The most important of these pigments, gossypol, is not only toxic to various animals, but produces an obnoxious pigment in expressed oil. Genetical studies reveal that the presence of glands in cottonseed is controlled by alleles at two loci. The size and number of glands and, hence, the relative level of seed gossypol is determined by polygenic systems which act in concert with the major alleles. Reduction in the number of active alleles present reduces gossypol level as gland number and size diminishes. Substitution of mutant alleles for active alleles at both major loci eliminates glands and gossypol from seeds. Glandlessness is thus a characteristic of great potential worth, and breeders seek to develop glandless strains which give high yields of quality fiber. Although some success has been achieved, recent work shows that both of the glandless genes are linked to factors which impair yield. This condition increases breeding problems. A possible solution to this problem might be obtained through inducing glandlessness in high yielding strains with irradiation.

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VARIATION IN COMPOSITION OF SUNFLOWER OIL FROM COMPOSITE SAMPLES AND SINGLE SEEDS OF VARIETIES AND INBRED LINES

E. D. Putt, B. M. Craig and R. B. Carson

Significant differences ($P = .01$) existed between varieties and between stations in mean values for percentage of stearic, oleic, and linoleic acids in the seed oil of eight sunflower varieties grown at 10 locations in 1963 and 14 locations in 1964. The same observations held for three varieties common to seven points in the two years. Significant differences did not occur for palmitic acid. Years × stations was the only significant interaction appearing in these studies. Varieties requiring the same time to mature differed significantly.

Oil from composite samples of inbred lines showed large differences in analyses; e.g. in 56 lines grown in one season at one location ranges in percentage values were: palmitic 4.7–8.2; stearic 1.7–9.1; oleic 13.9–40.3; linoleic 47.9–76.4. Single seeds within seven inbred lines also showed striking variation. The greatest variation occurred in lines inbred for one to three generations and the least in lines inbred for eight to nine generations. Pairs of lines with identical or similar flowering date differed significantly in mean values of all four acids. Variation between seeds within varieties was relatively narrow in Armavirec and Advent, but wide in Peredovik where the range was: palmitic 4.5–9.4; stearic 2.5–12.4; oleic 14.8–46.4; linoleic 34.3–75.5.

The results show that genetic control of oil quality, independent of flowering or maturity date, exists in sunflowers. The wide range in analyses suggests that altering oil quality in the crop by breeding is a practical objective.

— 107A —

MODIFICATION OF QUANTITY AND QUALITY OF SAFFLOWER OIL THROUGH PLANT BREEDING

P. F. Knowles

Increases in the oil content of the seed of safflower (*Carthamus tinctorius* L.) have been achieved mostly by reducing hull. The thin-hull (*th*) gene reduces the thickness of the cell walls of the hull, resulting in a very thin hull when the cells collapse on drying. Several alleles of the striped (*stp*) gene modify hull content and hull characteristics. Using these genes it is possible to raise oil content to 45%, or higher. Oil quality has been modified by genes affecting fatty acid content. Three alleles of the *ol* gene govern proportions of linoleic and oleic acids; *Ol* produces high levels of linoleic acid, as in the usual commercial varieties; *ol* produces high levels of oleic acid, as in the new variety UC-1; and ol^1 produces about equal amounts of linoleic and oleic acids. Normally safflower oil has less than 2% stearic acid, but the allele *st*, for stearic acid, will raise it to 10%.

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BREEDING FOR OIL QUALITY AND QUANTITY IN FLAXSEED

D. M. Yermanos

Seed weight, oil content of the seed, and iodine value of the oil of flaxseed have a high heritability. Absence of strong negative associations among these 3 traits permits effective simultaneous selection for all of them. Efforts to increase seed yield and oil content of the seed through plant breeding have been very successful. Efforts to modify the chemical composition of the oil have not been as effective. Analyses of numerous seed samples from all parts of the world indicate that the 3 major fatty acids in the oil of cultivated flaxseed have the following range; oleic 14–38%, linoleic 7–18%, linolenic 35–66%. While it was not possible to find or breed cultivated flax with oil differing markedly from the above composition, several aberrant types of linseed oil, including types with high linoleic and low linolenic acid content, were found among wild species of flax. Research in process for the utilization of desirable germplasm of the wild species for flax breeding is not sufficiently advanced to base predictions regarding the possibility of producing cultivated varieties of flax with modified oil composition.

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THE COMPLETE CHARACTERIZATION OF UNSATURATED N-ALDEHYDE DINITROPHENYLHYDROZONES BY THIN LAYER CHROMATOGRAPHY

P. W. Meijboom

By analyzing volatile decomposition products from mildly autoxidized oils and fats mainly n-aldehydes of the classes saturated, $\Delta2$- and $\Delta2,4$-unsaturated have so far been identified.

By combining three thin layer chromatographic techniques, a new method of analysis of the DNPHs of these volatiles was devised. By this method aldehydes having one or two isolated double bonds in either cis or trans stereo configuration or having one conjugated and one or two isolated double bonds, again in the two possible configurations, were completely separated and identified.

Application of this technique to mildly autoxidized soyabean oil and to isolinoleic methylesters will be given.

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TRIGLYCERIDE ANALYSIS BY CONSECUTIVE LIQUID-LIQUID PARTITION AND GAS-LIQUID CHROMATOGRAPHY EPHEDRA NEVADENSIS SEED FAT

Carter Litchfield

A method for the preparative separation of triglycerides by liquid-liquid partition chromatography (LLC) has been developed. Thin-layer chromatography (TLC) plates were prepared by dissolving 4 g purified hexadecane in 85 ml petroleum ether, adding 50 g silanized silicic acid, and spreading 0.25 mm thick on 20 × 40 cm glass plates. After standing overnight, 4–10 mg of a triglyceride mixture was applied to each plate using a Radin-Pelick sample streaker, and the plate was developed with 100% nitroethane saturated with hexadecane. Triglyceride bands were located by exposing only the edges of the TLC plate to iodine vapor, and the triglyceride fractions were recovered from the center of the plate. Highly unsaturated triglyceride mixtures were easily resolved on the basis of "partition number" using this hexadecane/nitroethane partition system.

A combination of LLC and GLC was used to characterize the complex triglyceride composition of *Ephedra nevadensis* seed fat, which contains 16 different fatty acids including 17.6% triene and 10.8% tetrane. Triglycerides were first separated according to partition number by LLC. The recovered fractions were then analyzed by GLC to determine the molecular weights of the triglycerides present. A total of 30 different groups of triglycerides were identified and quantitated in *Ephedra nevadensis* seed fat by this combined technique.

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FRACTIONATION OF NATURAL MIXTURES OF DIACYL PHOSPHATIDES CONTAINING ALK-L-ENYL ACYL PHOSPHATIDES

C. V. Viswanathan, S. P. Hoevet and W. O. Lundberg

The fact that different classes of alk-1-enyl phosphatides contain mainly polyenoic fatty acids with very small amounts of saturated fatty acids permits the fractionation, by argentation chromatography, of natural mixtures of 1) diacyl phosphoryl cholines and alk-1-enyl phosphoryl cholines, or 2) diacyl phoshporyl ethanolamines and alk-1-enyl acyl phosphoryl ethanolamines, or 3) diacyl phosphoryl serines and alk-1-enyl acyl phosphoryl serines into molecular species.

The application of this technique for the isolation of native alk-1-enyl acyl phosphatides without destruction of accompanying components is discussed. Data are given also on the fatty acid and fatty aldehyde compositions of the original mixtures and fractions thereof.

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CHROMATOGRAPHIC SEPARATION OF PLASMALOGENS, ALKYL-ACYL PHOSPHATIDES AND DIACYL PHOSPHATIDES

Ossi Renkonen

Certain nonpolar derivatives of phosphatides and glycolipids can be fractionated far more effectively than the native lipids themselves by liquid chromatography. At first the polar parts of the phosphatides were completely removed, but more recently I have "masked" them instead. Derivatives that have proved particularly valuable include dimethyl esters of phosphatidic acids, which are easily obtainable from several classes of glycerophosphatides; dinitrophenylated and methylated "cephalins" also represent a very convenient form of lipids. The important thing in these derivatives is that even the atoms of the polar groups are still available, e.g., for tracer experiments.

Thin-layer chromatography (TLC) of sufficiently high resolving power separates completely the plasmalogenic, the alkyl-acyl, and the diacyl forms of phosphatidic acid dimethyl esters. The same three forms of glyceryl phosphoryl ethanolamine lipids are also completely separated as the methylated and dinitrophenylated derivatives. In both series of derivatives the plasmalogenic lipids run ahead the others on silica gel, the alkyl-acyl phosphatides have intermediate mobility, and the diacyl lipids are the slowest ones in each series. The same order of mobility has been observed in my laboratory also with the three different types of diglyceride acetates. The relatively high resolving power of TLC necessary for these new separations is obtained by using the technique of multiple undimensional development with solvents giving very low mobility of the lipids. The separations discussed have never been reported with the native phosphatides.

Argentation chromatography separates quite effectively many individual molecular species of all three subclasses of phosphatidic acid dimethyl esters, and also those of methylated and dinitrophenylated "cephalins."

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COPPER DETERMINATION OF EDIBLE SOYBEAN OILS

Gary List and C. D. Evans

Soybean oils have been analyzed for their copper content before and after hydrogenation with copper-containing catalysts. Some determinations were made directly without ashing by both activation and atomic absorption analyses. Other samples were ashed and their residues analyzed by atomic absorption, emission spectroscopy and two colorimetric methods. A low-temperature "dry asher," an apparatus in which oxygen plasma is generated in a radio frequency field under high vacuum, was adopted for ashing glyceride oils. Although the five-chambered apparatus can be operated continuously, a 3-g sample boat required 72 hr for ashing. Surface formation of an oxidized-polymerized skin makes dry ashing of triglyceride oils extremely slow.

The various analyses of the alkali-refined and bleached soybean oils showed a natural copper content of 0.02–0.04 ppm. Oils hydrogenated with copper catalyst increased in copper content several ppm, but oils reprocessed after hydrogenation had copper levels equal to those of the original salad oil.

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TITRATION OF CYCLOPROPENE ESTERS WITH HYDROGEN BROMIDE

R. O. Feuge, Zigrida Zarins, J. L. White and R. L. Holmes

Esters of the naturally occurring cyclopropene acids have heretofore been determined by titration with hydrogen bromide in glacial acetic acid. However, highly purified methyl malvalate and sterculate had an apparent purity of only 83–86% by this method. An unwanted catalyzed addition of acetic acid to the cyclopropene moiety during the titration has been shown to occur. Substituting toluene for the acetic acid not only gives the correct cyclopropene content but also sharpens the end point of the titration, undoubtedly because the reaction processed by a different mechanism. The titration is performed at 70–75C and 1,3-diphenylguanidine, which is soluble in toluene, should be used as a primary standard. The indicator solution is 0.03% crystal violet in butyric acid. Mono- and diglycerides and oxidized fatty compounds must be removed before titration. Oxirane oxygen can also be determined by the new procedure, probably with an accuracy greater than that possible with hydrogen bromide titration in glacial acetic acid.

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A BROMOTHYMOL BLUE DYE-BINDING PROCEDURE FOR EVALUATING HEAT PROCESSING OF SOYBEAN MEALS

J. E. McGhee, G. C. Mustakas and W. J. Albrecht

A new dye-binding procedure was studied to follow the extent of heat processing of soybean meals beyond the point of urease deactivation.

Bromothymol blue absorption by the meal demonstrated a linear relationship with time of autoclaving from 1/2 to 5 hr at atmospheric pressure.

In carrying out the procedure, a 0.2% solution of bromothymol blue was prepared by dissolving the dye in an alkaline solution of 90% ethanol. The tests were carried out on samples prepared from hexane-extracted Hawkeye soybeans. A sample was added to the dye solution and the mixture was agitated for exactly 1 min. A portion of the liquid was decanted into a curvette and the transmittance was measured on a spectrophotometer at 570 mμ.

The heat-processed soybean meals were also analyzed for urease activity, available lysine, nitrogen solubility index and trypsin inhibitor.

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AN IMPROVED PROCEDURE FOR QUANTITATIVE ANALYSIS OF LIPID CLASSES VIA TLC BY CHARRING AND DENSITOMETRY

L. J. Nutter and O. S. Privett

Lipid is extracted from fresh tissues *via* homogenation with mixtures of chloroform and methanol and nonlipid impurities separated by Sephadex chromatography by a combination of procedures described by A. N. Sikotas and G. Rouser (JAOCS *42*: 913, 1965) and R. E. Wuthier (J. Lipid Res. 7: 558, 1966).

A qualitative examination of the lipid classes is made by TLC with mixtures of petroleum ether, ethyl ether and acetic acid for the neutral lipids, and two-dimensionally for the polar lipids with chloroform methanol and water in the first dimension and propanol, water and acetic acid in the second dimension.

An amount of sample to permit the analysis of all components is then fully hydrogenated by means of the Adams catalyst, and fractionated by TLC in series of one (or two, if necessary) dimensional systems. The spots of the hydrogenated classes are charred by heating the plates for 45 min at 200C after spraying with a chromic-sulfuric acid reagent prepared by mixing 30 parts (vol) of distilled water saturated with potassium dichromate with 70 parts (vol) concentrated sulfuric acid and analyzed by densitometry. When two-dimensional systems are employed, standards and the sample are also run on the same plate one-dimensionally in each solvent system.

Analysis of a selection of purified polar and non-polar lipid classes gave identical standard curves expressed in terms of carbon content. A linear relationship between peak area and carbon content was obtained from zero to approximately 20 μg of carbon. Application of the method is demonstrated with a number of standard and natural mixtures of lipid classes.

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THE STRUCTURE OF DIMERIC FATTY ACIDS AND THE MECHANISM OF DIMERIZATION

Achintya K. Sen Gupta

Homolytic cleavage of the carbon-carbon single bonds adjacent to the double bond occurs on heating methyl esters of unsaturated fatty acids at 280C in absence of oxygen to produce a number of chain cleavage radicals. The various secondary reactions of these radicals give in addition to the dimers a variety of different substances which were isolated and their constitution elucidated. The thermal dimers of methyl oleate were separated into three classes, viz. acyclic diene, acyclic monoene and monocyclic saturated dimers. The mechanism of dimerization of methyl oleate was investigated in detail and it was found that allyl radicals are first formed from methyl oleate which then add to a second molecule of intact methyl oleate. Intramolecular radical additions also play a part in the dimerization of methyl oleate which lead to saturated cyclic dimers. This phenomenon of intramolecular radical addition is particularly important in the case of methyl $9^c,12^c$-linoleate, which on heating to 280C produces saturated tricyclic, monoolefinic bicyclic, diolefinic monocyclic and triply unsaturated acyclic dimers together with monoolefinic tricyclic and diolefinic bicyclic dehydrodimers. All these types of dimers were either isolated as such or as corresponding epoxides and analysed chemically and also NMR– and mass spectroscopically. The thermal dimers of methyl $9^t,11^t$-linoleate were shown to be of tetrasubstituted cyclohexene (Diels-Alder) structure, whereas thermal dimers obtained from methyl $9^c,12^c$-linoleate at 280C under the exclusion of O_2 do not contain Diels-Alder-dimers.

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NONVOLATILE ALPHA-BRANCHED CHAIN FATTY ESTERS III. ADDITION OF ACID CHLORIDES AND ANHYDRIDES TO TERMINAL OLEFINS

T. Perlstein, A. Eisner, W. C. Ault and P. A. DeHaven

A tert-butyl peroxide initiated free radical reaction was employed for the preparation of α-branched fatty acid chlorides, which were then converted in situ to methyl, tert-butyl, and phenyl esters. An α-branched fatty acid anhydride was similarly prepared and converted to the methyl ester.

The use of the acid chloride or acid anhydride permitted reduction in the molar ratio of reactants to half or less of that used in addition of esters to terminal olefins without affecting the yield. The resultant weight percent increase of product in reaction mixture eased the problem of isolating the product also. The direct addition of these substrates to terminal olefins gives rise to α-branched moieties which can be converted readily to a variety of derivatives such as acids, amides, nitriles and difficultly prepared esters.

The yields of α-branched methyl esters obtained from esters, carboxylic acids, acyl chlorides and acid anhydrides under the same addition reaction conditions were compared.

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A STRUCTURAL BASIS FOR THE DEVELOPMENT OF FUNCTIONAL DEFECTS IN ISOMERIZED LINOLENATES

J. P. Kass

Structural and theoretical considerations will be presented to indicate the ostensibly anomalous defects of catalytically conjugated linolenates as compared with the more normal linoleates in isomerized drying oils are in part attributable to the apparently hitherto overlooked factors consequent upon the known formation of an isolated, dimethylene-interrupted (1,5) nonpolymerizable double bond in the Δ9,13,15, and to a lesser extent Δ9,11,15 triene systems from the doubly monomethylene interrupted (1,4) Δ9,12,15 system of natural linolenic acid.

Similar considerations will be applied to the "reversion" effects of residual Δ15 or Δ14 isolated double bonds remaining after the 1,4 addition of hydrogen to newly formed conjugated systems, or the preferential saturation of the proximate diene systems upon the selective hydrogenation of linolenate.

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METHYLATION OF FATTY ACIDS IN LIPIDS BY LOW-TEMPERATURE BASE CATALYSIS

Barbara Zook and L. R. Dugan

The effect of potassium hydroxide on the methylation of triglyceride and phospholipids by the low temperature-sulfuric acid method was studied. Neutral lipids methylated included corn oil, coconut oil, tallow and butter oil. The phospholipids phosphatidyl choline, phosphatidyl ethanolamine and sphingomyelin prepared from egg yolk were purified by preparative thin-layer chromatography (TLC) and studied in like manner. Portions of each lipid were methylated according to the low temperature-sulfuric acid method using varying amounts of potassium hydroxide for neutralization. TLC of the products of the neutral lipid samples revealed that complete methylation was accomplished with potassium hydroxide at levels of 4.5 g/15 ml methanol and above. The TLC data from neutral lipids also showed that methylation was essentially complete when no acid was used indicating that the methylation was actually base-catalyzed. Gas-liquid chromatography data showed an increase in shorter chain acids (esp. myristic) and in the C_{18} unsaturated acids when lesser amounts of base were used. This release of the shorter chain and less saturated acids is suggestive of the lipid release by lipase hydrolysis.

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PROPERTIES OF WAX ESTERS

R. T. Iyengar and H. Schlenk

Saturated, monounsaturated and some diunsaturated wax esters were synthesized from alcohols and acids of chain lengths C_{12} to C_{22} (even numbered only). The mps generally show increments of 4°–5°/2 C atoms for saturated esters C_{26}, C_{28}, C_{30} . . . . where either the alcohol portion or the acid portion is constant. Increments are about 9°/4 C atoms when both alcohol and acid are homologous, as in wax esters C_{28}, C_{32}, C_{36}. Certain consistencies of mps become also apparent when comparing saturated isomers. However, some exceptions have been encountered and they appear to be characteristic.

Monoenoic wax esters with the double bond in the alcohol group have higher mps than the isomers which have the double bond in the acyl group and the crystals are quite different in appearance.

Preparative as well as analytical separation methods fail with isomeric wax esters which occur in biological materials. Therefore, a study of mass spectra of the synthetic wax esters was undertaken. Saturated esters exhibit patterns which enable identification of components of simple isomeric mixtures.

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SYNTHESIS OF α-METHYL BRANCHED FATTY ACIDS VIA THE FAVORSKY REACTION

T. Gerson and H. Schlenk

Fatty acids substituted with a methyl group in α-position are of biological interest in view of their occurrence in a variety of lipids. Identification of side products from fatty acids synthesis by Wolff rearrangement of diazoketones indicated that α-methyl fatty acids can be prepared from chloromethyl ketones. Accordingly, acid chlorides were converted into diazomethyl ketones and further into chloromethyl ketones. The latter gave α-methyl fatty acids upon treatment with alkali (Favorsky reaction). α-Methylpalmitic and -stearic acids were prepared this way from palmitic and stearic acids and after adsorption chromatography gave the pure compounds, as methyl esters, in yields up to 55%. α-Methylarachidonate was prepared from arachidonic acid with a yield of 40%.

Previously, the Favorsky reaction had not been applied to long chain fatty acids but it seems to offer advantages above syntheses of α-methyl acids utilizing methylmalonate, in particular, for introducing ^{14}C. The reaction was applied also to dihalomethyl ketones from which olefinic acids were obtained. Yields were of the order of 25% in the latter case. The structures of the synthetic compounds were established by a variety of methods.

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HIGH-YIELD PREPARATION OF METHYL STEAROLATE

R. O. Butterfield and H. J. Dutton

A laboratory procedure for preparing methyl stearolate is described. It involves three steps—bromination, dehydrobromination and purification. A variety of starting materials were investigated, including commercial and laboratory "oleic" acids and olive fatty acids and triglycerides. Fatty acids were brominated in diethyl ether, whereas triglycerides were brominated directly and in ether. Dehydrobrominations were done in either boiling 30% KOH-ethylene glycol solutions or 30% KOH-water solutions under pressure. Saponification of the triglycerides also occurred during this second step. After conversion to methyl esters, the product from olive oil analyzed 80% methyl stearolate. Purification by either argentation or acetonitrile-hexane counter current distribution yielded methyl stearolate of 99+% purity. Based on the amount of oleic acid present in the initial oil, overall recoveries averaged 80%. In addition to this laboratory method, a possible manufacturing procedure is outlined.

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RELATIVE REDUCTION RATES OF FATTY ACID ISOMERS BY HYDRAZINE

C. R. Scholfield, R. O. Butterfield and H. J. Dutton

Hydrazine is known to reduce double bonds in fatty acids without a change in position or geometric configuration of remaining double bonds and to be much less selective than catalytic hydrogenation between poly- and monounsaturated acids in mixtures. Previous work at this Laboratory has shown that with linolenic acid, double bonds farthest from the carboxyl are reduced at a slightly faster rate.

Kinetic studies of hydrazine reduction of simple binary mixtures of fatty acids provide a more sensitive method for measurement of differences in reaction rates. *cis* 15-Octadecenoic acid is reduced about 1.3 times faster than *cis*-9-octadecenoic acid. The same difference is found between *cis*-3-octadecene and *cis*-9-octadecene. *cis*-12-Octadecenoic acid is reduced at the same rate as the *cis*-9-isomer, but *trans*-9-octadecenoic acid is reduced slightly faster. The comparative reduction and analyses of these and other isomer mixtures and of some polyenoic acids will be described.

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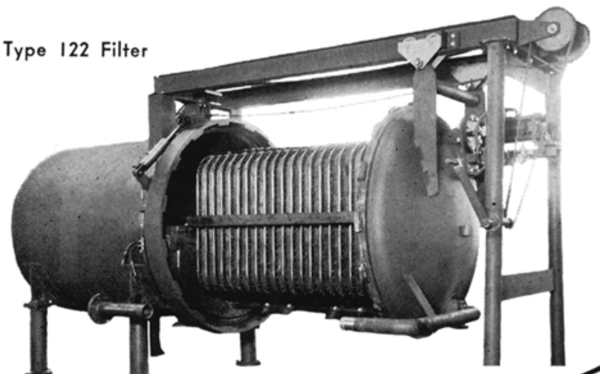
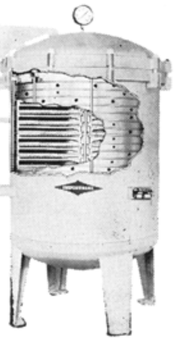
SYNTHESIS OF UNSATURATED ALDEHYDES

Henry Rakoff

Mahadevan, Phillips and Lundberg [Lipids *1*, 183 (1966)] describe the synthesis of unsaturated fatty aldehydes without bond migration or isomerization by oxidation of the corresponding fatty alcohol tosylates





with dimethyl sulfoxide and sodium bicarbonate. In studying the Rosenmund reduction of acid chlorides to aldehydes, White, Sulya and Cain [J. Lipid Res. *8*, 158 (1966)] found that while this method worked well for the preparation of saturated aldehydes, the reduction of oleoyl chloride gave stearaldehyde as well as olealdehyde. Moreover, the olealdehyde contained 26% *trans* bonds and the double bonds were scattered from C_6 through C_{14} with less than half remaining at C_9.

Since a noncatalytic method might give reduction without bond migration or isomerization, the reduction of unsaturated acid chlorides with lithium tri-*t*-butoxyaluminohydride [J. Am. Chem. Soc. *80*, 5377 (1958)] was studied. Infrared analyses of olealdehyde, linolealdehyde and stearolaldehyde prepared from the corresponding acid chlorides revealed no *trans* isomers. Ozonization-reduction of the ethylenic aldehydes or ozonization-hydrolysis-esterification of the acetylenic aldehyde followed by gas-liquid chromatographic analysis of the fragments showed that essentially no bond migration had occurred (at most 3–5%). Ultraviolet analysis of linolealdehyde showed the absence of conjugation. Therefore, lithium tri-*t*-butoxyaluminohydride can be used to reduce monoethylenic, diethylenic and monoacetylenic acid chlorides to the corresponding aldehydes with essentially no bond migration or isomerization.

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Flavor Chemists Elect Merwin President

E. L. MERWIN has been elected to a one-year term as President of the Society of Flavor Chemists, Inc., at its Annual Meeting in New York City.

Other officers elected were: Vice President, ANTHONY CLEMENTE of Fritsche Bros.; Secretary, EUGENE BUDAY of Polak Frutal Works; Treasurer, A. V. SALDARINI of Norda.

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Applications Now Being Accepted for Polymeric Materials Program

Applications for the graduate program in Polymer Chemistry and Technology at Polytechnic Institute of Brooklyn are now being accepted by the Office of Admissions, 333 Jay St., Brooklyn, N. Y. 11201.

Registration will be held Sept. 18–21, 1967. Classes begin Sept. 25. Research fellowships are available for the program, announced Prof. James Conti, Head of the Chemical Engineering Department. Interested students may write to Prof. Conti or call him at (212)643–2852 or 643–2962.

The program, leading to a master's degree in Polymeric Materials, can be pursued full-time in the day or part-time in the evening. A full-time student can complete the program in one calendar year.

Requirements for the program are a B.S. degree in Chemistry or Chemical Engineering or the equivalent from an approved college. Total semester hour credits required for the degree are 30. Of this total, 20 are elective credits.

Planned to make possible specialization in polymer science or engineering or to obtain a diversified training in both *polymer chemistry and technology,* the program conforms fully with the recommendations of the Education Committee of the Society of Plastics Engineers.

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(Continued from page 360A)

SYNERGISTIC SEQUESTERING AGENT. J. S. Pierce. *U.S. 3,294,689.* A synergistic sequestering composition of matter of wide utility is claimed which, when dissolved in water, consists essentially of an aqueous solution of $(HOCH_2)_3CNHCH_2CHOHCH_2NHC(CH_2OH)_3$ and citric acid, in which the molar ratio of polyhydroxyamine to citric acid has limits of 4/1 to 1/4.

SHAVING CREAM CONTAINING POLYSILOXANES. J. L. Bishop, Jr. and C. W. Todd (Dow Corning Corp.). *U.S. 3,298,919.* A shaving cream composition consists of 0.5-9% stearic acid, 0.5-3% lauric acid, 1-15% glycerine, 1-7% triethanolamine, 40-80% water, 2-12% of a propellant and 0.1-5% of a silicone fluid.

LIME SOAP DISPERSANTS. R. R. Irani and K. Moedritzer (Monsanto Co.). *U.S. 3,298,956.* A soap composition is claimed, consisting essentially of soap and at least one per cent by weight of an organo-amino polymethylphosphonic compound of the formula $(R_1)(R_2)N$—C(Y)(Y′)—PO$(OX)_2$, where X is a cation selected from the group consisting of hydrogen, alkali metal ion, ammonium ion and lower molecular weight alkyl, alkylene and alkanol amine ions; Y and Y′ are either hydrogen or lower alkyl groups containing 1-4 atoms; R_1 is either hydrogen, an aliphatic group containing 1 to 30 C atoms or —C(Y)(Y′)—PO$(OX)_2$; R_2 is selected from the class consisting of hydrogen, aliphatic groups containing 1 to 30 C atoms, —C(Y)(Y′)—PO$(OX)_2$ and —$[C(Y)(Y')]_n$—N(Z′)(Z), where n is an integer from 1 to 30; Z is a member selected from the class consisting of hydrogen and —C(Y)(Y′)—PO$(OX)_2$ and Z′ is a member selected from the class consisting of hydrogen, —C(Y)(Y′)—PO(OX_2) and —$[C(Y)(Y')NZ]_m$—C(Y)(Y′)—PO$(OX)_2$, where m is an integer from 1 to 30; with at least one of the groups represented by R_1 and R_2 containing at least one —C(Y)(Y′)—PO$(OX)_2$ group.

DETERGENT BREAKER COMPOSITION. J. S. Frank. *U.S. 3,298,963.* A synthetic detergent breaker composition consists essentially of 2–60% by wt. dialkylpolysiloxane having the general formula $(RSiO)_n$ where n is a positive integer from 2 to 100 and the R radicals are alkyl groups with, at the chain ends, from 1 to 6 C atoms; 2–70% alkylsiloxymetallic complex having the general formula $(RSiO)_3M$, where M is the metallic ion selected from the group consisting of Al, Fe^{2+}, Fe^{3+} and Co and the R consists of alkyl groups from C_1 to C_6; 10–70% metallic sulfate, the metal being Al, Fe^{2+}, Fe^{3+} or Co.; 0.5–20% silica gel; and 0.2–0.5% of a pH controlling material selected from the group consisting of sulfuric acid, sulfurous acid and ascorbic acid.

ALKYLENE OXIDE POLYMER COMPOSITION FLEXIBILIZED WITH SALTS OF CARBOXYLIC ACIDS. R. D. Lundberg and R. W. Callard (Union Carbide Corp.). *U.S. 3,298,980.* An homogeneous composition is claimed, comprising a polyethylene oxide having a reduced viscosity of at least 1 and from about 20 to 40% by wt., based on the weight of the polymer, of a salt containing 4-22 C atoms selected from the group consisting of ammonium or alkali metal salts of aliphatic carboxylic acids or aromatic carboxylic acids.

METHOD OF SELECTING EMULSIONS INTENDED FOR THE PREPARATION OF COSMETICS AND SKIN PRODUCTS. R. R. Aron-Brunetiere and C. F. Aron (Paris, France). *U.S. 3,300,386.* A method is described for testing emulsions as to their suitability in the treatment of dry and greasy skins. The method involves effecting a biopsy of an untreated portion of the shaven skin of an animal, applying the emulsion to be tested on another portion of the shaven skin at spaced intervals for a predetermined interval and effecting biopsies of the treated portion to determine the effect of the treatment. Emulsions for treating dry skins are expected to cause hyperplasia of the sebaceous glands and emulsions for treating greasy skins should fail to cause such an effect.

PRESSED POWDER ANTIPERSPIRANT AND METHOD OF PREPARATION. R. L. Kole (Kolmar Laboratories, Inc.). *U.S. 3,300,387.* A topically applied product for human use consists of a dry pressed powder cosmetic base having dispersed in itself divided particles of a hygroscopic antiperspirant coated with a water-soluble wax-like material selected from one of the following: polyethylene glycols with an average molecular weight of 1000 to 6000; polypropylene glycols with an average molecular weight of 140 to 600; methoxy propylene glycols with an average molecular weight of 350 to 750; lanolin extracts; ethoxylated lanolin; fatty acid esters of polyalcohols containing C_8 to C_{20} fatty acids; ethoxylated fatty acids containing

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