ABSTRACTS OF PAPERS
39TH FALL MEETING
CINCINNATI, OHIO

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ISOMERIC LINEAR ALKYLBENZENES AND SODIUM ALKYLBENZENESULFONATES

F. D. Smith, A. J. Stirton and M. V. Nunez-Ponzoa

Linear alkylbenzenes made from α-olefins and benzene, with aluminum chloride or methanesulfonic acid as the condensing agent, were found by gas-liquid chromatography of the acetophenone homologs obtained by chromic acid oxidation to be a mixture of all theoretically possible internal position isomers (5, 6, 7 and 8 from the 12, 14, 16 and 18 carbon α-olefins, respectively).

Product distribution showed a maximum of the 2-phenyl and a minimum of the 3-phenyl isomer, with a submaximum depending upon the chain length of the α-olefin. The 2-phenyl isomer, formed in largest amount and presumably the highest melting isomer, was separated by low temperature crystallization from acetone. Partial separation of isomeric alkylbenzenes was possible by fractional distillation or selective adsorption on a picric acid column.

The alkylbenzene product mixtures and the isolated 2-alkylbenzenes were sulfonated and detergent and surface active properties were compared. The sodium 2-alkyl-p-benzenesulfonates were more biodegradable than the mixtures in the river water die-away test.

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SYNTHESIS AND SURFACE ACTIVE PROPERTIES OF SULFONATED BRANCHED CHAIN FATTY ACID ESTERS

T. J. Micich, E. A. Diamond, R. G. Bistline, Jr., A. J. Stirton and W. C. Ault

In continuation of work reported a year ago describing branched chain fatty acids, a series of monosodium methyl 2-sulfo-2-alkylcarboxylates was synthesized. The surface active properties of these compounds were evaluated and compared with the corresponding disodium 2-sulfo-2-alkylcarboxylates. The alkylcarboxylic acids were obtained by peroxide catalyzed addition of aliphatic acids to normal terminal olefins in 50-70% yields and purified by distillation. The 2-alkylcarboxylic acids were sulfonated with sulfur trioxide-dioxane adduct, esterified with methanol, and neutralized with anhydrous sodium carbonate to yield 25-80% sodium methyl sulfocarboxylates after repeated crystallizations. Relative to the disodium salts the sodium methyl sulfoesters are characterized by better wetting properties, greater calcium ion stability and more stable foams.

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POLYETHOXYLATED ALKYL PHENOLS: RELATIONSHIP OF STRUCTURE TO BIODEGRADATION MECHANISM

Q. W. Osburn and J. H. Benedict

The mechanism of biodegradation of the polyethoxylated alkyl phenols in the river water die-away test has been ascertained using various isolation procedures and measurement by infrared spectroscopy. In this study degradation was found to proceed by carboxylation of the alkyl chain and, in certain cases, by degradation of the ethylene oxide chain. The ether chain was found to degrade only when it contained ten or less units of ethylene oxide. The analytical evidence points to the degradation of the ether chain by a hydrolysis mechanism.

Test results show both branched and straight chain structures containing ten or less units of ethylene oxide per mole to degrade by both routes, straight chain structures containing more than ten units of ethylene oxide per mole to degrade only by carboxylation of the alkyl group, and branched chain structures containing more than ten units of ethylene oxide per mole to be essentially nonbiodegradable. An exception to the above is the isooctyl alkyl group which, by the nature of its structure, is resistant to biodegradation by the carboxylation route.

The effect of ether chain degradation on the measurement of residual surfactant by ultraviolet spectroscopy and the cobalt thiocyanate procedures will be discussed.

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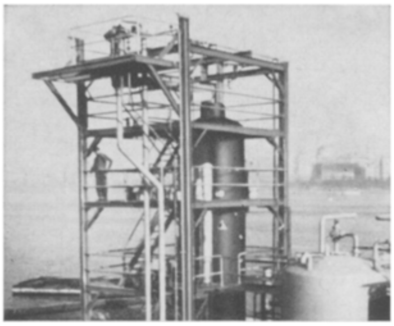
A PROCEDURE AND STANDARDS FOR THE DETERMINATION OF THE BIODEGRADABILITY OF ALKYL BENZENE SULFONATE AND LINEAR ALKYLATE SULFONATE

T. E. Brenner, Subcommittee on Biodegradation Test Methods, The Soap and Detergent Assn.

For over three years the Subcommittee on Biodegradation Test Methods of The Soap and Detergent Association has been developing and evaluating test procedures for the measurement of surfactant biodegradability. This has been a cooperative effort involving some twenty companies taking part in round-robin evaluations of the several methods proposed.

A two-step procedure has been developed and tested and is described in this paper. Both steps are microbiological in nature and were designed with a view towards simplicity and reproducibility. The first or presumptive step employs a procedure described as the shake-flask technique and involves the exposure of the surfactant under test to preadapted organisms in a basal medium. The second or confirmatory step operates under conditions similar to those found in modern sec-



ondary sewage treatment plants. In this step, using a method called the semicontinuous activated sludge procedure, the surfactant under test is exposed to bacteria obtained from sewage. The bacteria, the surfactant under test, and a synthetic sewage used as an energy source are intimately mixed and aerated in a specially designed chamber.

In both steps, samples are regularly withdrawn and analyzed to follow the course of surfactant biodegradation.

A discussion of the supporting statistical evaluation will be given in the description of biodegradability standards established for surfactants of the alkyl benzene sulfonate and linear alkylate sulfonate groups.

— 5 —

DETECTION AND ESTIMATION OF LAS IN WATERS AND EFFLUENTS

R. D. Swisher

The detergent industry of the United States has replaced tetrapropylene ABS by linear alkylate sulfonate (LAS) in its formulations in an effort to eliminate waste surfactants from the nation's pollution load. The effectiveness of this move will be assessed by the monitoring of sewage treatment plant effluents and receiving waters by numerous agencies during the next several years. Most of the analytical methods available respond to a whole range of surfactants and are not specific for LAS. This deficiency can be avoided by use of the desulfonation-gas chromatography technique, which gives unequivocal proof of the presence or absence of LAS and is readily applicable at the range of interest in the neighborhood of one part per million. Examples are given of examination of various effluents for presence and semiquantitative estimation of LAS. A simple procedure is described for preconcentration and separation of anionic surfactants from other components of the sample.

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BIODEGRADATION OF LAS DETERGENT BASE MATERIALS IN AN OPERATING TRICKLING FILTER SEWAGE TREATMENT PLANT

C. E. Renn and Gordon Kumke

Field Test experience on detergent removal in a conventional trickling filter system treating institutional domestic wastes demonstrates that LAS-based materials undergo biological breakdown equal to that of sewage. The field test rates of LAS breakdown are found to be comparable to those recorded in laboratory trickling filters and field and laboratory activated sludge unit.s The findings from the field tests on trickling filters suggest that differences in the biological systems involved in activated sludge treatment and various trickling filters are not critical in estimating the behavior of LAS base detergents in secondary treatment. Data is presented in tabular and graph form to illustrate specific history of performance during the field test. Equipment experience and performance during the test is also presented.

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HETEROGENEOUS CATALYTIC DEUTERATION OF METHYL OLEATE. I. REDUCTION AND SEPARATION OF ISOLOGS AND ISOMERS

C. R. Scholfield, W. K. Rohwedder, J. Barter and H. J. Dutton

Methyl oleate was reduced at 40C and atmospheric pressure with deuterium gas and either platinum or palladium catalysts. Samples of the esters and of the gas phase were removed during the reaction. The hydrogen-to-deuterium ratios in the gas phase were determined by mass spectrometry. Withdrawn ester samples were fractionated by reverse phase chromatography on rubber columns into saturate and monoene fatty esters, and the monoenes, into *cis* and *trans* isomers by argentation chromatography.

Experimental conditions, fractionation procedures, and results of infrared analysis, argentation chromatography, mass spectrometry, and nuclear magnetic resonance will be described.

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HETEROGENEOUS CATALYTIC DEUTERATION OF METHYL OLEATE. II. BOND MIGRATION, GEOMETRIC ISOMERIZATION AND DEUTERIUM DISTRIBUTION

E. Selke, W. K. Rohwedder, V. L. Davison, T. Nieman and H. J. Dutton

Separated isomers from the heterogeneous catalytic deuteration of methyl oleate were subjected to mass spectrometric analysis to determine their deuterium content. The saturated ester fraction varied from less than 1 deuterium atom per molecule at the 20% saturation level to more than 2 at the 100% level, whereas the still unsaturated esters reached 2 atoms of deuterium per molecule at the 80% level. Oxidative cleavage of the separated unsaturated esters showed a symmetrical and normal distribution of the double bonds about the Δ 9 position; bonds ranged from the 6th to the 13th position, and less than 40% of the bonds remained in the Δ 9 position at the 80% saturation level. Mass spectra of the individual monobasic and dibasic acids from the oxidative cleavage showed the greater the double bond movement, the greater the deuterium content.

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MASS SPECTROMETRY AND DIMER ACID STRUCTURES

D. H. Wheeler and L. E. Peterson

Mass spectrometry has proven to be a valuable tool in studying the structure of the dimers of fatty acids. Three model dimers were prepared and studied chemically, as well as by mass spectrometry.

Dehydrostearate dimer from methyl stearate and di-t-butyl peroxide was shown to contain noncyclic structures with joining of the stearate chains by a carbon-carbon bond at the α-methylene, as well as randomly at other methylenes.

Dehydro-oleate was shown to be predominantly joined at positions 8, 9, 10, and 11 of the oleate chains, with only 5-10% at the α- or 2-position.

In contrast to these two noncyclic dimers, the thermal dimer of the conjugated 10-*trans*, 12-*trans* linoleate contains the cyclic cyclohexene structure resulting from a Diels-Alder addition, with a double bond of one molecule acting as dieneophile, adding to the conjugated diene of a second molecule.

Complete hydrogenation of the unsaturation in the dehydro-oleate and the conjugated linoleate dimers gave the saturated dimers which were specially valuable in deducing skeletal structures by mass spectrometry.

Other chemical reactions, including ozonolysis of double bonds, dehydrogenation and chemical synthesis supported the proposed structures. Other physical methods including infrared, ultraviolet and nuclear magnetic responance spectroscopy, and thin-layer chromatography were also valuable.

Some unexpected patterns of fragmentation in the mass spectrometer will be discussed in addition to the usual patterns which were used for deducing skeletal structures.

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MASS SPECTRAL STUDIES OF HIGH MOLECULAR WEIGHT ESTERS

T. H. Kinstle and K. L. Rinehart, Jr.

The introduction of samples directly into the ion source of a mass spectrometer, coupled with rapid recording of the mass spectrum, allows the determination of the mass spectral fragmentation patterns of relatively nonvolatile compounds of high molecular weights. The present studies employed an Atlas CH-4 mass spectrometer equipped with vacuum lock and TO4 ion source, and an ultraviolet light spot recorder with 250 cps and1500 cps galvanometers. Mass spectral studies have been carried out on a wide variety of compounds, including derivatives of sterculic acid, other cyclopropenoid compounds, and intact triglycerides. Of particular interest due to their complex structures and high molecular weights are the neutral macrolide antibiotics. Although their acetyl derivatives are somewhat more volatile and give better spectra, quite good spectra have been determined for the intact antibiotics to molecular weights above 800. Fragmentation patterns of these compounds will be discussed.

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THE UROPYGIOLS

H. M. Fales and E. O. A. Haahti

Recently a series of lipids was isolated from the uropygial glands of chickens and preliminary structural data were presented.

We have reinvestigated the substance with the aid of high-resolution mass spectrometry and identified the material as a homologous series of saturated, straight-chain, 2,3-diols.

$$CH_3\ (CH_2)_n - CHOH - CHOH - CH_3$$
$$n = C_{19} - C_{22}$$

The products exhibit no molecular ions, but cleave between the hydroxy functions, giving rise to intense peaks at m/e 236, 250 and 264 which have accurate masses corresponding to $C_{20}H_{41}0$, $C_{21}H_{43}0$, and $C_{22}H_{45}0$. In addition a large peak is present at m/e 45, corresponding to C_2H_50. Oxidation of this material and Wolff-Kishner reduction of the ketones gave a series of saturated chain hydrocarbons identified by gas chomatography as $n\text{–}C_{19}H_{40}$ to $n\text{–}C_{24}H_{50}$. The mass spectra of the series will be discussed in detail.

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THE AOCS STATISTICS COMMITTEE — ITS FUNCTIONS AND OBJECTIVES

H. P. Andrews

A committee of industry and associated statisticians is available to provide the following services and work toward the following objectives for the Society and its membership.

1. Consult in the design of committee studies and in the analysis and interpretation of data from those studies.
2. Advise the Uniform Methods Committee upon the statistical adequacy and validity of method studies pursuant to their being made Official.
3. Institute and promote education in statistical methology beneficial to the industry through special short courses, basic training courses, and symposia on annual meeting programs.
4. Investigate the contribution which statistical review of papers submitted to the Journal might make to the quality of the publications.

Progress in some of these and other objectives will be discussed along with further ideas for their increased utilization and implementation.

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STATISTICS FOR BETTER SPECS!

R. C. Manring

Specifications result from the desire or need to outline or describe a necessary aspect of product performance. As such, they are a vital business tool, both with a producer's organization and in the producer-consumer relationship.

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Various aspects of the specification development procedure will be discussed, such as:

1. Historical review of methods of establishing specifications.
2. Statistical methods for designing better specifications.
    - (a) Measurements and their relationship to specification limits.
    - (b) How each step in the process contributes to process variability.
    - (c) How multiple specifications affect overall process capability.

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EFFICIENT DESIGN FOR INTERLABORATORY STUDY OF VARIABILITY IN ANALYTICAL PROCEDURES

R. D. Snee and H. P. Andrews

"Heirarchic" or "nested" designs have been widely used for characterizing the variability in analytical procedures within and among laboratories.

Although these designs are flexible to almost any objective they are usually fully balanced in order to simplify the calculations for statistical analysis of the data. The requirement of full balance may result in expenditure of time and money not merited to estimate the variability from certain sources, particularly sources where the variability is small. Introduction of imbalance into the design gives greater flexibility and greater efficiency by permitting more rational expenditure of analytical effort to obtain the variance estimates. The computational procedures are only slightly more complex and an exposition of these and of their use in the interpretation of such studies is the purpose of this paper.

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HYDROGENATION OF SOYBEAN OIL - THE EFFECTS OF PROCESS VARIABLES ON SELECTIVITY AND ISOMER FORMATION, A STATISTICAL APPROACH

L. H. Going, E. R. Purves and A. M. Lopez

A half-replicate factorial design was used to study the effects of five process variables on selectivity and fatty acid isomer formation during batch hydrogenation of soybean oil. The variables were temperature, pressure, mass transfer (agitation), catalyst type, and catalyst concentration. Two levels of each variable were used, corresponding approximately to the range of normal commercial practice. With the aid of a digital computer, expressions have been developed relating selectivity and isomer formation to the operating variables. This has permitted quantitation of the significant comparative effects. Temperature was the dominant factor, contributing more than half of the total variation in both selectivity and isomer content. Interactions between variables were relatively unimportant.

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CORRELATION OF NONIONIC SURFACTANT STRUCTURE AND SOLUBILITY WITH TEXTILE WETTING

J. A. Komor and J. P. G. Beiswanger

The effect of nonionic surfactant structure with respect to textile wetting efficiency has been studied. A correlation has been shown to exist between wetting speed and molecular diffusion rate, critical micelle concentration, area per molecule (as deduced from surface tension versus concentration measurements), extent of adsorption and temperature. The slope of the log wetting time versus log concentration curve is dependent upon temperature, product cloud point, critical micelle concentration and area per molecule. Log concentration for ten-second wetting is shown to be inversely proportional to the diffusion constant which in turn is a function of the critical micelle concentration. Concentration coefficients of wetting indicate that the most efficient wetting is obtained at or very near to the critical micelle concentration.

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PROPERTIES OF ETHOXYLATE DERIVATIVES OF NONRANDOM ALKYLPHENOLS

L. H. Smithson

Performance evaluation data for the highly biodegradable nonrandom linear alkylphenol ethoxylates and ethoxysulfates are presented for typical heavy- and light-duty detergent formulations. The effect of the derivatives' molecular weights on performance characteristics is also discussed, including variations in the hydrophobic and hydrophilic parts of the molecule.

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THE SOLUTION PROPERTIES OF SOME POLYOXYETHYLENE-POLYOXYPROPYLENE SURFACTANTS IN NONAQUEOUS SOLVENTS

J. M. G. Cowie and A. F. Sirianni

Results obtained with pluronic polyol homologues in benzene and in dioxane by light-scattering, ultracentrifugal and vapour pressure lowering measurements in addition to data obtained in water and in butyl chloride by light-scattering and ultracentrifugal determinations will be described. The systems are examined over a wide range of solute concentrations at about 37C. Considerable difference appears to exist between weight and number-average micellar weight obtained by light-scattering and two methods of measuring vapour pressure lowering of the solutions. Divergence in micellar weight values appears to be less pronounced between the latter technique and ultracentrifugal determinations. A possible micellar configuration of these pluronic polyols will be discussed.

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MICELLE FORMATION IN MIXTURES OF NONIONIC AND ANIONIC DETERGENTS

M. J. Schick and D. J. Manning

It has been shown previously that the temperature dependence of the critical micelle concentration (cmc) of sodium n-dodecyl ether alcohol sulfate with a short polyether group follows the pattern of sodium n-dodecyl alcohol sulfate; in contrast the corresponding data of the homolog with a long polyether group follow that of polyoxyethylene n-dodecanol. In order to amplify these findings, the cmc's of intermolecular combinations of nonionic and anionic detergents with comparable hydrophobic groups have been studied as a function of composition and temperature.

This paper describes the effect of a homologous series of polyoxyethylene n-dodecanols on the cmc of n-dodecyl alcohol sulfate. The cmc of the nonionic component of the mixed micelles is about one-hundredth of that of the anionic. Only a gradual increase in the cmc values of the mixed micelles above the values of the nonionic components was observed in the composition range of 0-90% M anionic detergent. This is followed by an abrupt transition to the high cmc values of the anionic component. The magnitude of the gradual increase in the range below 90% M anionic detergent is inversely proportional to the number of ethylene oxide units in the polyoxyethylene n-dodecanols. It is postulated that the degree of ionic repulsion of the ionic component in mixed micelles is markedly decreased as the proportion of nonionic component reaches a threshold range of 10% M. This effect is more pronounced with large ethylene oxide coils operating at the micellar periphery than with short ethylene oxide coils. Thermodynamic data have been included.

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REFRACTIVE INDEXES OF ALCOHOL NONIONICS

D. R. Weimer, L. D. Lindemuth and W. L. Groves

Refractive index is a rapid and consistent method of analysis for alcohols and nonionics from normal alcohols and ethylene oxide. Correlations of refractive index with hydroxyl number of alcohols and nonionics are excellent, and measurement error is considerably lower for refractive index. Refractive index affords a measurement of the amount of ethylene oxide in nonionics and can be used as a replacement for the 1% cloud point analysis. The ethylene oxide adduct distribution has no effect on refractive index. Specific adducts, a narrow range of adducts made by acid catalyzed ethoxylation, and a broad range of adducts made by base-catalyzed ethoxylation give the same refractive index value for any given ethylene oxide content.

Applications for the refractive index method for the laboratory and plant are: alcohol blending control, calculation of ethylene oxide requirements for ethoxylation, nonionic control analysis, calculations of hydroxyl number for sulfations. Also, refractive index can help identify laboratory samples, indicate the 1% cloud point, and predict the phase character of nonionics.

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VISCOSITIES OF AQUEOUS SOLUTIONS OF BLOCK COPOLYMERS OF PROPYLENE AND ETHYLENE OXIDES

I. R. Schmolka and L. R. Bacon

Brookfield viscosity measurements were made on aqueous solutions of surface-active agents composed of block copolymers of propylene and ethylene oxides in which the molecular weights of the polymers varied from 1100 to over 15,000. The hydrophobic bases were polyoxypropylene glycols varying in molecular weight from 750 to over 3000. To these were added varying amounts of ethylene oxide so that the polyoxyethylene hydrophil comprised from 15 to 80% of the surfactant total weight. It was found that the surface active agents with hydrophobe base molecular weights from 750 to 1100, and in which the polyoxyethylene sections comprised from 15 to 80% of the total weight, did not form gels in aqueous solution.

Some surfactants with a hydrophobe base molecular weight of 1750 to 2750, to which varying amounts of polyoxyethyene were added, formed gels in water at a surfactant concentration range of 40 to 80%. With a hydrophobe molecular weight of 3250, gels formed at from 30 to 90% surfactant concentration. The behavior of these surfactants in forming gels is explained on the basis of hydrate formation. The moles of water per ethylene oxide group in the adduct varied with the hydrophobe base weight and with the polyoxyethylene hydrophil, and ranged from 0.3 to 17.1, at 25C.

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THE OXYPROPYLATION OF FATTY ALCOHOLS AND THE SULFATION PRODUCTS

J. K. Weil, A. J. Stirton and Elizabeth A. Barr

The reaction of propylene oxide, rather than ethylene oxide, with fatty alcohols gives a higher yield (50%) of the mono-oxyalkylation product because the secondary alcohol formed is less reactive than the primary alcohol formed with ethylene oxide. Rate of further reaction (poly-oxypropylation) is about half the rate of reaction of the parent primary alcohol. Distribution of the propylene oxide reaction products is in accordance with the Weibull-Nycander equation.

Analysis of the reaction products was best accomplished by gas-liquid chromatography after acetylation of the ether alcohol mixtures. Pure mono-oxypropylated alcohols $ROCH_2CHOHCH_3$ and in some cases di-oxypropylated alcohols $R[OCH_2CH(CH_3)]_2OH$ were separated by fractional vacuum distillation and characterized.

Individual ether alcohols and reaction products with a known average number of oxypropyl groups were sulfated and evaluated in terms of Krafft point, critical micelle concentration, detergency, foam height and lime soap dispersing properties. Compared to the parent alcohol sulfates incorporation of one oxypropyl group was somewhat more effective than the corresponding degree of oxyethylation, and improved solubility with no significant loss in good foaming and detergent properties. Ether alcohol sulfates from propylene oxide are stable to alkaline hydrolysis and nearly equal to ether alcohol sulfates from ethylene oxide in their stability to acid hydrolysis.

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CHARACTERIZATION OF UNSATURATED FATTY ESTERS BY MASS SPECTROMETRY

J. A. McCloskey, M. J. McClelland and R. E. Wolff

Mass spectra of various derivatives of unsaturated long chain esters indicate the potential usefulness of this technique for the complete characterization (i.e., of positional and geometrical isomers) of these compounds. Use of a gas chromatographic inlet system provides the additional advantages of retention-time data, and permits the rapid recording of mass spectra from samples in the microgram range.

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GAS CHROMATOGRAPHIC AND MASS SPECTROMETRIC CHARACTERIZATION OF CYCLOPROPANE FATTY ACID ESTERS

W. W. Christie, W. E. Brugger and R. T. Holman

Mono and polycyclopropane fatty acid esters have been prepared in good yield from the appropriate unsaturated fatty acid esters using a highly active zinc-copper couple and methylene iodide gas chromatographic and mass spectrometric characterizations have been performed upon these derivatives and will be presented.

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A MASS-SPECTROMETRIC INVESTIGATION OF VITAMIN B_6 COMPOUNDS

D. C. DeJongh and Walter Korytnyk

Three substances as a group are designated vitamin B_6: pyridoxine (I), pyridoxal (II), and pyridoxamine (III). Detailed study of the metabolic role of the vitamin has resulted in the isolation of metabolic precursors and of products of metabolic-transformations and in the synthesis of model systems and various vitamin B_6 derivatives.

A mass-spectrometric investigation of vitamin B_6 compounds was undertaken in order to use the correlation of structure and mass spectra in structure-elucidation problems encountered in syntheses and isolation of new pyridoxine compounds and in the investigation of a number of published structures thought to be incorrect. From an electron-impact-mechanisms standpoint, these compounds are interesting since they can be viewed as substituted pyridine, benzaldehyde, benzyl alcohol, *o*- and *m*-hydroxybenzyl alcohols, and phenol. Their spectra can be interpreted in terms of the interplay of the various functions in the one molecule.

The compounds which have been studied include compounds I-III, their homologs, deoxy-analogs, and isomers, as well as 5- and 6 membered cyclic ketal derivatives, oxidation products and their derivatives, acyl derivatives, and O- and N-methyl derivatives. A number of deuterated analogs have been studied to corroborate the proposed fragmentation schemes.

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PYROLYSIS-GAS CHROMATOGRAPHY-MASS SPECTROMETRY APPLIED TO SOME SIMPLE LIPID MOLECULES

R. T. Holman, Manfred Deubig and H. W. Hayes

In order to correlate pyrolysis products with structure of lipids, pyrolysis-gas chromatography has been applied to characterization of hydrocarbons and methyl esters of fatty acids. The position of a methyl group in a branched molecule can be distinguished. To identify the products of hydrolysis produced empirically, the major pyrolysis products of a few compounds have been identified by their mass spectra obtained using a direct pyrolysis-gas chromatograph-mass spectrometer hookup on samples of approximately 0.5 mg.

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IDENTIFICATION OF PRODUCTS FROM OXIDATION OF METHYL LINOLEATE BY MASS SPECTROMETRY

R. J. Horvat, W. H. McFadden, H. Ng and W. G. Lane

In a continuing study of the autoxidation of methyl linoleate the compounds methyl octanoate, methyl azelaaldehydate, 8-formoxy methyl octanoate, and five trialkyl trioxanes were identified from among the nonvolatile compounds isolated. Mass spectrometry was the principal means of identification for the compounds which were separated and purified by preparative gas-liquid chromatography. Material for analysis was obtained by oxidizing methyl linoleate on purified glass wool under a slight positive pressure of oxygen (90 mm Hg) under ambient conditions. Two different procedures were used to obtain samples for analysis. They were: (1) isooctane extraction of the oily oxidized material and (2) room temperature distillation of the oil at 20 to 40μ pressure. Most fractions collected were checked for purity on a 200-ft by 0.01-in. capillary column coated with SF 96-50 Silicone oil or a 75-ft by 0.01-in. capillary coated with Dow-Corning 550 Silicone oil.

Except where noted, the mass spectral data were compared with those of authentic compounds, members of an homologous series, or with literature data. In addition, most compounds were examined by nuclear magnetic resonance and infrared spectroscopy, and GLC retention times were determined. All reference compounds were synthesized by standard organic reactions.

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GAS CHROMATOGRAPHIC AND MASS SPECTRAL IDENTIFICATION OF SOME VOLATILES FROM GAMMA IRRADIATED MILK FAT

L. L. Khatri, L. M. Libbey and E. A. Day

Milk fat irradiated at 4.5 Mrads under vacuum was subjected to vacuum steam distillation at 40C. The volatiles thus obtained were extracted into ethyl ether, and the ether concentrate was subsequently used for analysis by means of gas liquid chromatography (GLC) in conjunction with fast-scan mass spectrometry (MS). The Barber-Colman series 5000 gas chromatograph equipped with packed columns and flame ionization detection was coupled to an Atlas CH 4 mass spectrometer. Several gas chromatographic techniques were necessary to remove certain interferring GLC peaks or for concentrating certain small but odorously potent peaks for subsequent mass spectral analysis. Among the components identified in irradiated milk fat by the above techniques were: alkanes and alkenes up to C_{17}, *n*-alkanals, *n*-alkanones, γ- and δ-lactones and other compounds.

The above GLC-MS technique has recently been improved by utilizing temperature-programmed capillaries and a dual ion source; in this case the mass spectrometer behaves both as a GLC detector (with the 20 eV source) as well as furnishing the usual fragmentation pattern with 70 eV.

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THE STABILITY OF SOYBEAN OIL: EFFECT OF TIME AND TEMPERATURE ON DEODORIZATION

Helen A. Moser, Patricia C. Cooney and C. D. Evans

The effect of the time and temperature of deodorization on stability of soybean oil was studied in the laboratory at 190, 210, 230, 250, and 270C for periods of ½, 1, 2, and 3 hr. Evaluation was based on organoleptic tests and oxidative stability data. Statistical analyses showed that time of deodorization was important and that for each temperature there were times of deodorization significantly better than others. A deodorizer temperature of 270C was detrimental to the quality and stability of the oil.

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STABILITY EVALUATION OF EDIBLE LINSEED OIL

C. D. Evans, Helen A. Moser, G. R. List and J. C. Cowan

Glyceride structure of linseed oil shows that only 8.5% of the triglyceride molecules are free of linolenic acid. However, linseed oil containing 56% linolenic acid can be processed as an edible oil to yield a bland, odorless product comparable to other vegetable oils. When freshly prepared and packaged under nitrogen, the oil can be stored and flavor quality maintained for an adequate shelf life. Organoleptic and oxidative tests show that metal inactivating agents improve the stability and flavor of linseed oil. Evaluations made under accelerated storage conditions indicate that added butylated hydroxy anisole imparts little, if any, improvement to the keeping quality of linseed oil. Oils exposed to air and under 60C storage conditions show a relatively short shelf life. Various organoleptic and oxidative evaluations for stabilized and unstabilized oils exposed to air, light, heat, and under inert packaging will be presented and results discussed.

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A CHEMICAL STUDY OF THE VOLATILE DECOMPOSITION PRODUCTS OF A SLIGHTLY AUTOXIDIZED COTTONSEED OIL

B. D. Mookherjee and S. S. Chang

The volatile autoxidative decomposition products in a stored cottonseed oil with a peroxide number of 2.09 meq/kg were isolated by semi-continuous counter-current vacuum steam distillation. The isolated decomposition products were separated into acidic and nonacidic compounds.

A small portion of the nonacidic compounds was reacted with 2,4-dinitrophenyl-hydrazine and the 2,4-dinitrophenylhydrazones of the monocarbonyl compounds were characterized by means of adsorption and liquid-liquid partition chromatography. A total of fourteen monocarbonyl compounds were identified by this method.

The rest of the nonacidic compounds were fractionated into eight broad fractions by gas chromatography using a preparative column of Silicone SE-30. Each fraction was rechromatographed with a carbowax 100 analytical column and seventy-one fractions were collected. Each of these fractions was again gas chromatographed with a Silicone SE-30 analytical column. One hundred and nineteen fractions were thus collected which were studied by infrared and mass spectrophotometry. Forty-six different compounds have been positively identified. The spectrum of compounds identified included six saturated hydrocarbons, six unsaturated hydrocarbons, four acetylenic compounds, eight alcohols, five esters, sixteen aliphatic aldehydes, three ketones and an aromatic compound. The mechanisms of their formation will be discussed.

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INVESTIGATION OF ANTIOXIDANTS FOR POLYUNSATURATED EDIBLE OILS

J. W. Thompson and E. R. Sherwin

The recent trend toward increased use of polyunsaturated vegetable oils in the human diet has emphasized the need for better antioxidant systems than those currently available. This need led to a research program in which a variety of experimental antioxidants were evaluated. Their selection was influenced by general requirements for food additives and by the results of prior antioxidant studies in various fields. Emphasis was placed on hydroxybenzene types, particularly substituted hydroquinones. Oxidative stability tests employing the standard AOM procedure and 110F shelf storage were used to screen the antioxidants in polyunsaturated oils. The type and number of substituent groups on hydroquinone had considerable effect on antioxidant potency. Some of the experimental compounds, such as 4,4′-methylenebis(5-acenaphthenol) and monoalkylhydroquinones, were several times as effective in the test oils as the food-approved antioxidants currently available.

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TURNIP LIPIDS. STORAGE EFFECT ON FATTY ACID COMPOSITION

M. Lepage

Lipids of turnip, a member of the mustard family (Cruciferae) were examined for their fatty acid composition and changes during storage at 40F. Laurentian, a highly pigmented variety and Wye, a nonpigmented variety, were used for this study. Lipids were first separated into classes by thin-layer chromatography. Phospholipids appeared to be predominant, although there were appreciable quantities of galactolipids in turnips stored at 40F. Linolenic acid was found to be the main fatty acid in both varieties and showed a decrease in Laurentian variety after storage. Attempts were made to relate loss in linolenic acid to autoxidation. Tocopherols and related alcohols are being investigated.

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SIMPLIFIED DESCRIPTION OF SOME PATTERNS OF TRIGLYCERIDE COMPOSITION

A. S. Richardson

A confusing superabundance of mathematical formulas has been proposed for calculating the hypothetical patterns of triglyceride composition commonly supposed to embody pure random (I), restricted random (II) and 1-3-random-2-random (III) distribution of the component acids. A clear understanding of these extremely simple and intimately interrelated patterns requires a simplified mathematical description affording clues to similarities and differences which are independent of the concept of random distribution. Hence it is suggested that the older descriptions be replaced by use of equations (1) and (2) below for describing all three patterns.

$$(Sx + Ux)(Sy + Uy)^2 = 1 \tag{1}$$

$$(Ax + Bx + Cx \text{ etc.})(Ay + By + Cy \text{ etc.})^2 = 1 \tag{2}$$

Equation (1), dealing with saturated and unsaturated acids collectively as required in pattern II, can be made to describe all three patterns by simple changes in the meaning of terms and in the values assigned to them. Similarly patterns I and III can be described in complete detail by equation (2), for any number of component acids. The terms as shown identify component acids and also denote mol fractions thereof. Terms of the expanded equations identify all possible triglycerides and denote mol fractions thereof. The equations were selected primarily for describing only the chemical composition characteristics of these known patterns. The paper offers suggestions for making the equations descriptive also of hypothetical reaction processes resulting in the described composition.

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FATTY ACIDS OF LINDERA UMBELLATA AND OTHER LAURACEAE SEED OILS

C. Y. Hopkins, Mary J. Chisholm and Linda Prince

Seed oils of six species of Lauraceae (laurel family) were examined and their fatty acid composition was determined. The acids of four species consisted almost entirely of capric and lauric acids. One species, *Lindera umbellata*, not previously studied, contained 50% of 4-dodecenoic acid, 4% of 4-decenoic acid. and 3% of 4-tetradecenoic acid. Positive identification of these acids was made and new derivatives were prepared. The seed is thus a convenient source of 4-dodecenoic acid. The occurrence of this group of unsaturated acids and possible biosynthetic routes are discussed.

The other five species did not contain more than a trace of unsaturated C_{10}–C_{14} acids, although all had unsaturated C_{18} acids in varying amounts. There was some GLC evidence of traces of odd-numbered carbon acids (e.g. C_{15}).

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CONJUGATED TETRAENE FROM IMPATIENS EDGEWORTHII SEED OIL: A PROGRESS REPORT

M. O. Bagby, C. R. Smith, Jr., and I. A. Wolff

Seed of *Impatiens edgeworthii* Hook. F. contains 50% of pentane-hexane extractable oil, which affords 48% of conjugated tetraenoic acid. Methyl tetraenoate readily absorbs 4 mole equivalents of hydrogen to yield methyl stearate. Oxidative cleavage of the methyl octadecatetraenoate yielded propionic and azelaic acids. Partial reduction of the tetraene with hydrazine yielded the expected mixture of acids. Mixtures of *cis-* and *trans-* monoenes; *trans,trans-* and *cis,trans*-dienes; and *cis, trans,trans*-trienes were isolated and analyzed by spectroscopy. Results suggest that there are two adjacent *trans*-double bonds and that the parent acid is *cis,trans,trans,cis-tetraene.* Oxidative cleavage of a fraction rich in *trans,trans*-conjugated diene yielded fragments that indicated 71% of 11,13-diene. Formation of a maleic anhydride adduct from the tetraene provides additional evidence for conjugated *trans, trans*-unsaturation.

Other investigators [Kaufmann and Sud, Chem. Ber. *92,* 2797 (1959)] working with conjugated tetraenes from different sources have not found adjacent *trans*-double bonds.

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THE OCCURRENCE OF CIS-5, CIS-9, CIS-12-OCTADECATRIENOIC ACID IN XERANTHEMUM ANNUUM SEED OIL

R. G. Powell, C. R. Smith, Jr., and I. A. Wolff

The seed oil of *Xeranthemum annuum* (family Compositae) contains *cis*-5,*cis*-9,*cis*-12-octadecatrienoic acid (I) in addition to palmitic, stearic, oleic, and linoleic acids. Evidence obtained by NMR, IR, TLC, and GLC indicated that I was a straight-chain C_{18} acid having 3 *cis* double bonds, only 2 of which had methylene-interrupted spacing. The double bond positions of I were determined by partial reduction with hydrazine, isolation of the monoene fraction by chromatography on silver nitrate-impregnated silica, oxidative cleavage of the monoene mixture, and identification of the oxidation products by GLC. Although *trans*-5,*cis*-9,*cis*-12-octadecatrienoic acid is known to occur in seed oils, the all-*cis* isomer, to our knowledge, has previously been reported only as a constituent of a Finnish tall oil [cf. Y. Aho, et al., Teknillisen Kemian Aikakauslehti *19,* 390–392 (1962)]. The unusual constituents of X.

annuum oil also include epoxystearic acid, 3%; epoxyoleic acid, 10%; and a mixture of hydroxy-*cis,trans*-conjugated dienoic acids, 11%.

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LIPID-PROTEIN INTERACTIONS AND COHESIONAL FORCES IN THE LIPOPROTEIN SYSTEM OF MEMBRANES

F. A. Vandenheuvel

Ultimately the integrity and function of biological membranes depends on the cohesional forces among the lipid and protein components of the membranes as they exist in aqueous media. On the basis of 3-dimensional structural models an effort has been made to understand the forces operating in biological membranes. These forces are of several types—London-van der Waals forces, hydrogen bonds, ionic bonds and dipole-dipole interactions. It is not possible to arrive at a final conclusion about the system of cohesional forces in biological membranes, but from the molecular models supported by much experimental data it is possible to develop an approximate picture and to deduce the nature of changes in the force relationships as the ionic or other composition aspects of the biological media change.

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ON THE ORIENTATION OF SULFOLIPIDS, GALACTOLIPIDS, AND PHOSPHOLIPIDS IN CHLOROPLAST MEMBRANES

A. A. Benson

The widespread recognition of the corpuscular nature of membrane ultrastructure demands re-evaluation of established concepts of its molecular structure. Many aspects of membrane physiology, composition, and metabolism provide support for the proposal that most membranes consist of two-dimensional polymers of lipoprotein subunits. Such a model allows the specificity, activity, and adaptability attributed to biological membranes. Evidence which supports this corpuscular model for membranes will be presented and some of the inadequacies of the bimolecular lipid leaflet model will be pointed out.

The lamellae of plant chloroplasts are membranes which clearly consist of subunits (quantasomes). These lipoprotein complexes of pigments, galactosyl dilinolenins, sulfoquinovosyl diglyceride, and phosphatidyl glycerol possess properties which may be studied experimentally. They serve as important reservoirs of carbohydrate and reduced sulfur in photosynthetic metabolism. Since each of these surfactant lipids possesses a specific spectrum of fatty ester components it is suggested that the nature of the fatty acid chain determines the location in the membrane where the lipid will be most firmly bound in the protein component. Reconstitution of quantasomal lipoprotein and restoration of biological activity has been achieved by Shibuya and Maruo. Behavior of these structures and the nature of hydrophobic lipid-protein association in membranes will be discussed.

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THE STRUCTURE OF PHOTORECEPTORS

J. J. Wolken

It is essential to know the molecular structure and the chemistry of photoreceptors in order to understand how they function physiologically. Chloroplasts and the outer segments of the retinal rods and cones of the eye are photoreceptors of plant and animal cells; they are able to receive, convert and transfer light energy to chemical and to electrical energy in the processes of photosynthesis, vision and nervous excitation. Chemically, their major constituents are pigments, lipids and proteins. Structurally, they are an ordered system of tightly-packed plates, discs, or tubes. Their *fine structure* in electron micrographs appears as electron dense double layers (lamellae) with a total thickness of the order of 250Å; each lamella or membrane at the interface is of the order of 50Å. Because of their staining, it is evident that the electron dense layers are associated with lipids; the less dense interspaces, with aqueous proteins.

To discover how the pigment molecules are associated with these lamellae in the photoreceptors, the geometry (that is, the length, diameter, and number of lamellae) was measured and the pigment concentration determined spectroscopically. These data were then used to calculate the area that each pigment molecule would occupy if spread as a monolayer on the lamellar surfaces. In addition, pigment-lipid-protein micelle structures have also been studied.

On the basis of these physical-chemical studies, molecular models for the photoreceptors have been proposed. In this paper, I will illustrate and discuss the structure of the photoreceptors in relation to the structure of cell membranes.

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THE BEHAVIOR OF STEROLS OF SILICA SURFACES AND AT OTHER INTERFACES

P. D. Klein, J. C. Knight and Patricia A. Szczepanik

The specific manner in which a molecule is oriented at an interface determines the reactions in which the molecule can participate. Sterols, being highly anisotropic molecules, present "ends" and "sides" to surfaces which differ greatly in their reactivity and interaction with the surface. Seen from the 3B-hydroxy end, as at an air-water interface, sterols are largely indistinguishable from one another in their behavior. On the other hand, at an organized interface, such as that of an adsorbent, a great many differences in structure can be demonstrated. These include the distinction between nuclear and sidechain double bonds, the number and location of nuclear double bonds, the substituents in the side chain and the number of methyl groups in the molecule.

We have been interested in the degree of specificity which such interaction can display because of the obvious parallel to sterol-protein interactions of a structural or enzymatic nature. Through the synthesis of a variety of sterol structures possessing the desired arrangement of double bonds and numbers of methyl groups, we have established a reproducible correlation between adsorptive interaction and double bonds in the Δ^5, Δ^7, Δ^8, $\Delta^{5,7}$, and $\Delta^{7,9}$ positions, as well as for the saturated stanol. These correlations have been extended for the 4α, 4β, 4,4 dimethyl and 4,4,14α trimethyl series as well. The elucidation of the structure of macdougallin by Djerassi, Knight and Wilkinson (J. Am. Chem. Soc. *85*, 835 (1963) as a 14α methyl sterol in which the 4,4, *gem* dimethyl grouping was absent prompted a further study of the 14α methyl sterols, of which the Δ^7, Δ^8, $\Delta^{7,9}$ and unsaturated varieties have been prepared and tested. The presence of a 14α methyl group in the absence of other methyl groups confers a unique behavior on the molecule in that this series does not fit into the adsorptive scheme for the other sterols. Instead, the interaction of the double bond with the surface is almost completely independent of its position, suggesting that the molecule is "perched" on the 14α methyl group when adsorbed in the surface. This appears to be a highly significant feature in the orientation of the molecule, since the removal of this methyl group is usually regarded as an essential first step in the conversion of lanosterol to cholesterol.

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THE PREPARATION AND PROPERTIES OF SOME PETROSELINYLAMINE DERIVATIVES

Lida L. Placek and F. G. Dollear

Petroselinylamine (*cis*-6-octadecenylamine) has been prepared by a new and more efficient process in which petroselinic acid in xylene is subjected to ammonolysis and treated further to yield the primary amine without isolating the intermediate products. In addition the petroselinylamine has been reacted with acrylonitrile followed by reduction with metallic sodium and alcohol to give N,N-petroselinylamine-trimethylenamine adducts, and with ethylene oxide under pressure to yield the oxyethylated tertiary amine derivatives. The crude products in each case were mixtures of derivatives of various molecular weights. It was possible to isolate the N,N-petroselinyl-1,3-trimethylene diamine in pure form from the crude mixture of hydrochloride salts by repeated recrystallizations from aqueous ethanol. Attempts to separate mixtures of petroselinylamine-ethylene oxide derivatives were unsuccessful.

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ACRYLIC ACID DERIVATIVES OF PARTIALLY EPOXIDIZED LINSEED OIL

A. E. Rheineck and P. R. Lakshmanan

Coating intermediates obtained by reacting partially epoxidized linseed oil with acrylic acid are of interest to oil chemists. Partially epoxidized linseed oil with 2.5% oxirane dries by oxidation-polymerization and therefore the hydroxyl group and acryloxy side chain formed during the oxirane opening gives an added reactivity to the oil, namely the ability to copolymerize with other vinyl monomers.

The preparation of these oil monomers is relatively simple. The reaction can be followed by the decrease in oxirane content. The final reaction product has *vicinal* hydroxy-acryloxy and/or diacryloxy groups with some residual oxirane. Factors influencing the final properties and composition of the oil are ratio of acid/oxirane, temperature and time of reaction, and the oxirane content of the starting linseed oil.

The acryloxy side chain incorporated in the oil moiety was found to undergo additional polymerization with a number of vinyl monomers. The copolymerization can be effected at temperatures of 80-90C in the presence of a peroxide initiator. The site of copolymerization of the vinyl monomers was found to be predominantly on the acryloxy side chain although some copolymerization at the fatty acid unsaturation was also detected.

These copolymers have improved rates of drying and film properties. Improvements are dependent upon the choice of vinyl monomers and the ratio of these to the oil. Synthetic vehicles with a wide range of properties have been prepared.

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ASYMMETRIC SYNTHESIS OF GLYCEROL DERIVATIVES

Dmytro Buchnea

The investigation of the glyceryl-1,2-isopropylideneglyceryl-3,3′-ether revealed that this ether under certain conditions undergoes disproportionation to bis(1,2-isopropylideneglyceryl) ether and bisglyceryl ether.

There are two different possibilities by which this disproportionation can take place: firstly, an intermolecular exchange between isopropylidene group and two hydrogen atoms, and secondly cleavage and reformation of the ether bond resulting in bis(1,2-isopropylideneglyceryl) ether and bisglyceryl ether.

To decide between the two possibilities an optically active D-1,2-isopropylidene-glyceryl-3-allyl ether, $[\alpha]^{20}_{D}$ + 23°, was synthesized with the prospect that on hydroxylation of its double bond and subsequent disproportionation of glyceryl-D-1,2-isopropylideneglyceryl-3,3′-ether, $[\alpha]^{20}_{D}$ + 10°, an optically active bis(D-1,2-isopropylideneglyceryl) ether and a racemic bisglyceryl ether would result, if disproportionation takes place via dissociation of the ether bond; otherwise both disproportionation products would be racemic if it follows the first mechanism.

It was found that the disproportionation of glyceryl-D-1,2-isopropylideneglyceryl-3,3-ether resulted, as anticipated, in an optically active bis(D-1,2-isopropylideneglyceryl) ether, $[\alpha]^{20}_{D}$ + 16°, and surprisingly, an optically active bisglyceryl ether, $[\alpha]^{20}_{D}$ − 8.5°, which on acetonation gave bis(D-1,2-isopropylideneglyceryl) ether, $[\alpha]^{20}_{D}$ + 16°. These results prove irrevocably that the hydroxylation of an optically active 1,2-isopropylideneglyceryl-3-allyl ether is specific and that the position of the central hydroxyl group in glyceryl moiety is determined by the 1,2-isopropylideneglyceryl moiety.

If, for example, 1,2-isopropylideneglyceryl moiety is of "D" form then through the hydroxylation of the double bond of allyl moiety the central carbon atom takes the "D" form; conversely L-1,2-isopropylideneglyceryl-3-allyl ether on hydroxylation of its double bond is expected to result in L-glyceryl-L-1,2-isopropylideneglyceryl-3,3-ether.

The conversion of an optically inactive moiety of glyceryl ether to an optically active bisglyceryl ether, by chemical means, has been demonstrated for the first time in glycerol chemistry.

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PREPARATION AND EVALUATION OF VERNOLIC ACID ESTERS AS PLASTICIZERS FOR POLY(VINYL CHLORIDE)

G. R. Riser, R. W. Riemenschneider and L. P. Witnauer

Several esters of vernolic (epoxyoleic) acid, a naturally occurring epoxy acid, were prepared and evaluated as plasticizers of poly(vinyl chloride). All the esters showed good compatibility. The data indicated that they are excellent low temperature plasticizers with the added advantage of greatly increasing the heat stability of the poly(vinyl chloride), in addition to improving light stability. The results are compared with DOP and other epoxy-containing plasticizers now being used as primary plasticizers but also in combination with other plasticizers as plasticizer-stabilizers.

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CATALYTIC DEHYDROGENATION OF METHYL 12-HYDROXYSTEARATE TO METHYL 12-KETOSTEARATE

Bernard Freedman and T. H. Applewhite

Economically attractive catalytic methods for the conversion of methyl 12-hydroxystearate to methyl 12-ketostearate have been developed on a laboratory scale. With 1 weight percent copper chromite catalyst pure methyl 12-hydroxystearate is dehydrogenated to methyl 12-ketostearate in 99% yield and 97% purity. The conversion occurs by simply heating catalyst and hydroxystearate at atmospheric pressure for about 0.5 hr at 180-263C with vigorous stirring. The reaction was followed by hydrogen evolution and GLC. Commercial methyl 12-hydroxystearate required 3% catalyst and somewhat higher temperature but gave a 98% conversion. Three copper-containing catalysts were evaluated and compared to Raney nickel for this reaction. Methyl ricinoleate, methyl ricinelaidate, and hydrogenated castor oil when treated with copper chromite as above gave mainly undesirable byproducts. The synthetic and analytical techniques and advantages and limitations of the method will be discussed.

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SYNTHESIS OF GLYCERYL MONOETHERS OF ANTEISO FATTY ALCOHOLS AND RE-INVESTIGATION OF THE BENZYLIDENE GLYCEROL INTERMEDIATE

B. Serdarevich and K. K. Carroll

Glyceryl monoethers were prepared by standard methods from C_{15}- and C_{17}- anteiso alcohols derived from the corresponding fatty acids isolated from lipids of the bacterium *Listeria monocytogenes.* The 1- and 2-glyceryl monoethers were obtained in 60% yields following purification by column chromatography on Florisil. Thin-layer chromatography on Silica Gel G impregnated with boric acid gave good separation of 1- and 2- glyceryl monoethers and was useful for following the course of reactions used in their synthesis. Gas-liquid chromatography was also used to analyze the ethers and intermediate products. The structures of the 1- and 2-glyceryl monoethers were confirmed by nuclear magnetic resonance.

The synthesis of benzylidene glycerol, an intermediate in the preparation of 2-glyceryl monoethers and 2-monoglycerides, was reinvestigated and evidence was obtained that the primary product of reaction is the 1,2-benzylidine derivative which subsequently isomerizes to the 1,3-derivative. These isomers were separated by chromatography on Florisil and their structures determined by nuclear magnetic resonance.

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FRAGMENTATION IN ABNORMAL OZONIDE DECOMPOSITIONS

A. N. Wrigley

Abnormal rearrangements resulting in loss of carbon are compared on one hand to nucleophilic 1,2-migrations with a pair of bonding electrons and on the other to *abcdx* fragmentations (C A. Grob, Kekule Symposium, 114, Butterworth's, 1959). In analogy with the former, electron pairs of ortho and para ether oxygen assist aryl bridging migrations in ozonolysis of methoxylated cinnamates by increase in covalence transmitted through the aromatic ring.

In zwitterion rearrangements of allylic compounds, ether or amino

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functions cannot so assist bridging; and on the basis of migratory aptitudes it has been puzzling that acrylic systems rearrange with similar readiness. In analogy with Grob, the ether zwitterion from ozonolysis of ethyl crotyl ether undergoes fragmentation to formate and ethyl methylene oxonium ion, an ion pair whose further reactions explain the products observed by Young (J. Am. Chem. Soc. *68*, 283 (1946).

By assigning a consistent role to electron pairs of heteroatoms, a fragmentation mechanism rationalizes the comparable activity of carbonyl and of alcohol, ether, and amino substituents, and accounts for common abnormal products, including evolution of carbon monoxide and some carbon dioxide.

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SECONDARY AND TERTIARY AMINES FROM ALDEHYDES DERIVED FROM OZONIZATION OF SOYBEAN ESTERS

E. H. Pryde, D. E. Anders and J. C. Cowan

We have reported previously the preparation of 9-aminononanoate esters in more than 90% yield from azelaaldehydate esters upon reductive amination with a nickel catalyst in an excess of ammonia when a nonpolar solvent, such as cyclohexane, is used. We now find that secondary amines can be prepared in good yield with nearly stoichiometric amounts of ammonia in a two-phase solvent system. For example, pelargonaldehyde gives 81% yield of dinonylamine when reductively aminated at 75C and 1,000 psig of hydrogen for 4 hr in a mixture of equal parts of heptane and methanol. By-products are nonyl alcohol (4-12%), nonylamine (5-8%) and trinonylamine (1-3%). Under similar conditions, methyl azelaaldehydate gives bis(9-carbomethoxynonyl)amine, also in 81% yield. Negligible tertiary amine formation probably is the result of diffusion of $RCH{=}NCH_2R$ and $(RCH_2)_2NH$ into the nonpolar phase containing only low concentrations of RCHO and $RCH{=}NH$. Undesired hydrogenation of carbonyl to hydroxyl was controlled, to some extent, by pretreatment of the Ni catalyst with amine. With excess ammonia, methyl azelaaldehydate give 97.2% of methyl 9-aminononanoate and 2.8% of methyl 9-hydroxynonanoate. In the absence of solvent, pelargonaldehyde and methyl azelaaldehydate gave their respective tertiary amines in 85% yield over Pd/C catalyst.

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URETHANE FOAMS FROM ANIMAL FATS. II. REACTION OF PROPYLENE OXIDE WITH FATTY ACIDS

Frank Scholnick, H. A. Monroe, Jr., E. J. Saggese and A. N. Wrigley

Propylene oxide has been reacted with 9,10-dihydroxystearic acid to form polyol components for urethane foams. Using stearic acid as a model compound, the alkalicatalyzed reaction proceeds slowly until the first mole of propylene oxide is absorbed and thereafter at a higher rate. For other substrates, the initial reaction proceeds most readily with alcohols and decreases in speed with increasing acidity of the hydroxyl group. Thus, octadecanol is considerably more reactive than stearic or oleic acid, whereas phenolic hydroxyls are intermediate. This rank of reactivities was the same when either ethylene or propylene oxide was used.

Threo- and *erythro*-9,10-dihydroxystearic acids were reacted with approximately 1, 2, 4, 6 and 8 moles of propylene oxide. The resulting polyols are all liquids unlike corresponding oxyethylated derivatives, whose *erythro* series are solids. A small amount of unsaturation was observed in the reaction products in accord with previous studies. The liquid polyols can be conveniently used in the preparation of rigid urethane foams.

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URETHANE FOAMS FROM ANIMAL FATS. III. OXYPROPYLATED DIHYDROXYSTEARIC ACIDS IN RIGID FOAMS

E. J. Saggese, Frank Scholnick, Marta Zubillaga,
W. C. Ault and A. N. Wrigley

Liquid polyols consisting of *threo-* or *erythro*-9,10-dihydroxystearic acid previously reacted with 1, 2, 4, 6 and 8 moles of propylene oxide were adjusted with triisopropanolamine to equivalent weight 100. Using Freon as blowing agent and triethylenediamine as catalyst, the adjusted polyols were foamed by reaction with a prepolymer of 32,000 cps viscosity made from oxypropylated sorbitol and excess disocyanate.

The resulting rigid foams had densities between 1.6 and 2.0 lb/ft^3, the densities for the *threo* series being parallel to but higher at each stage of oxypropylation than those of the *erythro* series. Compressive strengths (10% compression) in the *erythro* series ranged from 19 psi for the monooxypropylated compound to 38 psi for the octaoxypropylated member. Compressive strengths in the *threo* series ranged from 27 to 39 psi. Properties generally improved in both series as the degree of polyol oxypropylation increased. This contrasted with foams prepared earlier from oxyethylated polyols, whose properties generally reached maxima at intermediate degrees of oxyethylation. Using the tetra- and hexaoxypropylated *threo* polyols, the proportion of Freon was varied to relate compressive strength to density of foams between 1.4 and 4 lb/ft^3.

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STANDARDIZATION OF NUCLEAR MAGNETIC RESONANCE MEASUREMENTS OF SOLIDS IN FATS AND SHORTENINGS

W. D. Pohle and R. L. Gregory

An investigation of factors that influence the measurement of solids in fats and shortenings by nuclear magnetic resonance has been directed toward standardization of method, the aim being to select conditions that would yield results comparable to those existing at temperature equilibrium and with an accuracy and in a sufficiently short time that the method would be suitable for both research and control purposes. The following factors were investigated: setting up the calibration curve, the chilling time, the tempering time and the sample temperature when tested. Conditions will be reported that give results almost identical with or close to those attained at equilibrium and in less than an hour.

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A METHOD FOR ADSORBENT FRACTIONATION OF COTTONSEED OIL FOR INTRAVENOUS FAT EMULSIONS

W. S. Singleton, M. L. Brown and H. J. Zeringue

Based on animal screening tests of emulsions of several cottonseed oils, including a commercially processed oil, a cold-extracted oil, and a glandless variety, the oil must be modified by removal of pigments and minor polar components. A clay treatment, alumina-fractionation method for removal of color and polar components of cottonseed oil was developed whereby the triglyceride portion was obtained as an essentially pure water-white fraction. The combination of bleaching clay and chromatographic alumina were very satisfactory adsorbents, at concentrations of 15% of clay and a 1-to-1 ratio of alumina-to-oil. Adsorption fractionation on alumina alone did not effectively remove both pigments and polar components except at high alumina-oil ratios (5-to-1 and higher). Treatment with clay alone had no effect on removal of polar components, but did remove some of the pigments. The clay-treated oil was fractionated on alumina either by column chromatography or by vacuum filtration. The color characteristics of the fractionated oil, by light transmission at 465 mμ, were 92.4% prior to deodorization and 98.6% after deodorization, against distilled water as the transmission standard. The peroxide value of the deodorized oil was 0.18 meq/kg, and free fatty acid content 0.015%. Thin-layer chromatography indicated the presence of sterol esters in the fractionated oil, but no polar components.

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FLOCCULATION OF PHOSPHATIDE STABILIZED FAT EMULSIONS BY ELECTROLYTE SOLUTIONS

M. S. Gray and W. S. Singleton

Effects of electrolytes on flocculation rates of emulsions of cottonseed or soybean oils have been investigated by measuring the changes in light transmission as a function of time. The emulsions were stabilized with egg yolk phosphatides or soybean phosphatides of different degrees of purity. The differences in stability of the emulsions to the electrolyte solutions apparently were due to the differences in composition, or purity, of the phosphatide emulsifiers, and to the differences in properties of the respective oils. Emulsions of cottonseed or soybean oils stabilized with chromatographically homogeneous lecithin differed only slightly in degree of flocculation and were less stable than emulsions of the same oils stabilized with impure phosphatides. In the latter, emulsions of cottonseed oil were more stable than emulsions of soybean oil.

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CONVERSION OF ALDEHYDE OILS TO ACETALS WITH CATION RESIN CATALYSTS

R. E. Beal, D. E. Anders and L. T. Black

Aldehyde oils produced by partial or complete ozonization of soybean or linseed oils at unsaturated centers, followed by reduction to aldehydes, are being studied for new applications in coatings and in other products. Although aldehyde oils having satisfactory color and viscosity can be produced on a pilot-plant scale, they gradually polymerize at room temperature and solidify in a few weeks. Conversion to acetals stabilizes them. Certain weakly acidic salts catalyze acetal formation without transesterification of glyceride bonds; however, they also promote polymerization and are difficult to remove and to recover. Strong cation resins in the hydrogen form were therefore examined for catalyzing acetal formation. Molecular weight determination indicated that some transesterification accompanied acetal formation when fresh resin was used, but this was slight with reused resin. Aldehyde conversion was determined by infrared absorbance near 2720 cm^{-1}. Conditions for obtaining maximum conversion to the dimethyl acetal were also studied by using varying amounts of methanol, dimethoxypropane and cation resin under reflux.

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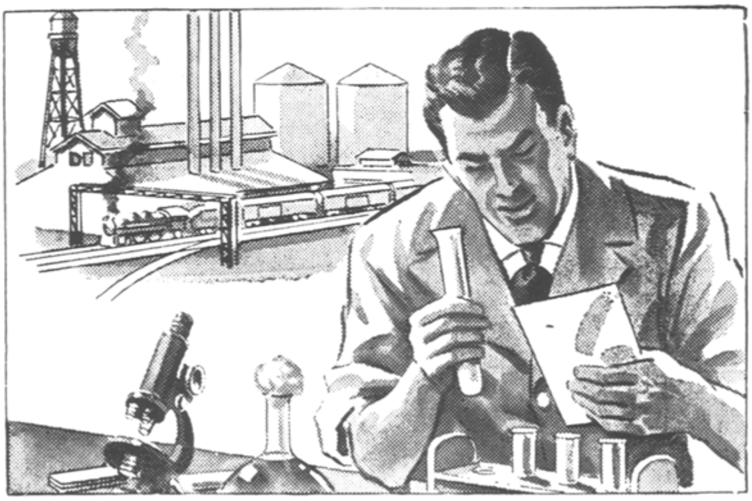
NEW COATING COMPOSITION BASED ON DIMORPHOTHECA OIL

A. E. Rheineck and G. M. Sastry

The fatty acids of *Dimorphotheca* oil contain up to about 60% of 9-hydroxy-*trans*-10, *trans*-12, octadecadienoic acid. The oil itself dries poorly in the presence of conventional driers. In this study the addition of nonconjugated *cis*, triglycerides, e.g. 5% of linseed oil, has been shown to bring about a marked improvement in the drying properties of this oil.

The hydroxyl group of the dimorphecolic acid was used advantageously in the preparation of film-forming compositions.



Coatings with excellent properties have been prepared by reacting the oil with several mono- and polyisocyanates. The combination of the oil modified with rosin esters via polyfunctional isocyanates has been studied.

It was shown that both the types of isocyanates and modifying rosin resins have a significant effect on the physical properties of the films.

When used as a modifying agent in the preparation of alkyd resins, *Dimorphotheca* oil improves the film properties to the same extent as tung oil.

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COUNTERCURRENT CENTRIFUGAL EXTRACTION OF RAW COTTONSEED FLAKES WITH THE ACETONE-HEXANE-WATER AZEOTROPE

V. L. Frampton, A. B. Pepperman and Joseph Simmons

It is demonstrated that the oil from raw moist cottonseed flakes is rendered in 60-90 seconds by the acetone-hexane-water azeotrope. Data obtained through the use of the basket centrifuge show that the oil contents of marcs and miscellas obtained in a countercurrent extraction obey the universal dilution law, and that the extraction is a washing extraction. The oil content of the finished meal is reduced to 0.1-0.2% in a countercurrent extraction where the residence time of the marc in the system need not exceed 3 min. The native lysine of the seed is retained as available lysine. The total gossypol of the meal is also reduced to a low level.

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THE APPLICATION OF A CAPILLARY EXTRUSION RHEOMETER TO THE DETERMINATION OF THE FLOW CHARACTERISTICS OF LARD

H. J. Scherr and L. P. Witnauer

A capillary extrusion rheometer was designed and techniques were developed to make a more meaningful study of the flow behavior of lard. Since constant and adjustable shearing rates are a necessary feature for the study of the basic rheological behavior of a material, the rheometer was designed for use in conjunction with a tensile tester having a wide selection of crosshead rates. Various techniques were developed for accurately measuring flow behavior and for treating the data obtained. A comparison study on a Newtonian liquid sample proved the validity of the approach employed. Lard at 23.4C was tested to obtain its flow parameters. From the data obtained the rheological parameters of apparent viscosity, consistency and degree of non-Newtonian behavior (flow behavior index) were obtained.

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LIPOPROTEIN DISTRIBUTION IN SERUM

F. T. Lindgren, N. K. Freeman and A. M. Ewing

Among unusual macromolecular systems are the low and high-density lipoprotein spectra in human serum. The low-density $S_f 0$ - 400 lipoprotein spectra consist of nearly a continuous distribution of molecules differing in hydrated density, particle-size and lipid composition. Development of a computer analysis of Schlieren Diagrams allows a more detailed profile analysis and comparison of one population with another. Such a program has been combined with a classical moving boundary flotation rate measurement, permitting corrections for concentration dependence and nonstandard conditions of the analytical run. The significance of interrelationship between such lipoprotein distributions, flotation rates of the major low-density lipoprotein group, lipoprotein composition, and other blood parameters will be considered.

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ENZYMATIC HYDROLYSIS AT AN OIL/WATER INTERFACE

F. H. Mattson

Triglycerides are metabolized by most of the organs and tissues of the body. However, the conditions in the lumen of the intestinal tract are unique, for it is only here that triglycerides are found in the free state. Elsewhere these lipids are associated with water soluble materials. Since enzymes are water soluble, the enzyme, lipase, responsible for the hydrolysis of triglycerides in the intestinal tract has the special property of being capable of functioning efficiently at an oil/water interface. Any material that can alter the nature of this oil/water interface can markedly influence the digestion of triglycerides.

Because of the unusual conditions under which the hydrolysis of triglycerides occurs, the usual methods of studying enzyme kinetics are not applicable. Besides the enzyme-substrate reaction itself, one must consider also such matters as diffusion of the substrate to the oil/water interface, removal of the products of hydrolysis from the oil/water interface, and the subsequent diffusion of these into the bulk phase. All of these steps can be influenced by such variables as efficiency of agitation, electrolyte concentration, and the presence of surface active agents.

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CONTROL OF FATTY ACID COMPOSITION IN GLYCEROLIPIDS

W. E. M. Lands

The continued suggestion that the ratio of saturated to unsaturated acids in the diet can influence the general health of a mammal is still not easily explained at a biochemical level. Studies on the metabolism of glycerophosphatides show that the enzymes involved appear to differ in the degree of selectivity toward substrates with different amounts of unsaturation. In general, each individual acid will have its own characteristic metabolic fate. The acyl-CoA:acyl-GPC acyl-transferases have a marked specificity for both the position to be acylated and the particular acyl-CoA involved. In some cases, the observed distributions of fatty acids in naturally occurring lecithins and triglycerides are similar to the distributions predicted from in vitro studies of the acyltransferase enzymes. Other enzymatic steps, such as acid activation and N-methylation, can also be shown to influence the fatty acid composition of the glycerolipids. The relative importance of these metabolic processes must now be determined.

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STRUCTURAL INVESTIGATIONS ON PHOSPHOLIPIDS FROM CELLULAR AND INTRACELLULAR MEMBRANES

L. L. M. van Deenen

A complete chemical characterization of phosphatidyl glycerol from green leaves and algae demonstrated that 1-linoleneoyl-2-*trans*-Δ^3-hexadecenoyl-glycero-3-phosphoryl-1′-glycerol represented the major molecular species and its occurrence appeared to be related to photosynthesis.

Beef-heart cardiolipin was demonstrated to be identical to synthetic diphosphatidyl glycerol.

Chemical structures of synthetic amino acid esters of phosphatidyl glycerol were compared with those of amino acid and glucosamine containing phospholipids from bacterial cell membranes.

The molecular species of lecithin from animal tissues were recognized and the influence of dietary fats on their composition was determined.

Physical characteristics of natural and synthetic phospholipids indicate that nature is eloquent to preserve the properties offered by particular fatty acid combinations in the phospholipid molecule.

Mammalian tissues were found to contain phospholipase A activity which produces two structurally isomeric monoacyl-phosphoglycerides.

Utilizing five isomeric lysolecithins of known structure micro methods involving enzymic hydrolysis were developed to distinguish among these isomers. Lysolecithins from different natural sources were demonstrated to consist of both 1-acyl-glycero-3-phosphorylcholine and 2-acyl-glycero-3-phosphorylcholine.

In connection with the nonrandom distribution of fatty acids of different apolarity at the two positions of phosphoglycerides, the various metabolic pathways of lysolecithin enantiomers in red cell ghosts, yeast and liver were investigated using different doubly-labeled substrates.

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THE DETECTION OF EPOXIDES IN HEATED OILS

J. A. Fioriti, A. P. Bentz and R. J. Sims

A colorimetric method, which involves the reaction of epoxides with picric acid, has been used to measure the oxirane content of heated vegetable oils. Cottonseed, soybean, and olive oils were heated for prolonged periods in air at 80C, 150C, and 250C and were then assayed for epoxide content.

The reaction with picric acid to form hydroxy-picryl ethers was shown to be specific for epoxides and to be a useful method for determining trace quantities in heated oils. Also it is applicable to the assay of nonfatty epoxides including both the internal and terminal types.

Thin-layer chromatography on silver nitrate-impregnated plates was successfully applied to the separation of picrates derived from *cis* and *trans*-methyl epoxystearate and methyl epoxyoleate. Subsequently, it was demonstrated that, after transmethylation, the TLC technique is applicable to the epoxides in heated oils. In each case the heated samples were found to contain at least two epoxides. Olive oil heated at 80C contained both *cis* and *trans*-methyl epoxystearates as well as methyl epoxyoleate. Whenever possible, the identities of the epoxides were confirmed by NMR, GLC, and infrared methods.

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DIRECT CLEAVAGE OF INTERNAL EPOXIDES WITH PERIODIC ACIDS

Gerhard Maerker and Elizabeth T. Haeberer

A direct method for the cleavage of epoxides was required for use in structural determinations of oxirane compounds. Previously, epoxides were cleaved via the glycol route. The new cleavage method has the advantages of being both direct and fast. It consists of the reaction of the epoxide group with paraperiodic acid in an aqueous dioxane system, yielding the corresponding aldehyde products. Methyl 9,10-epoxystearate was cleaved quantitatively by this reaction yielding pelargonyl aldehyde and methyl azelaaldehydrate.

The procedure is primarily useful for saturated internal epoxides. Unsaturated epoxides such as methyl vernolate were cleaved, but the yield of reaction products was much lower than for saturated compounds due to involvement of the double bond.

The effect of altering reaction variables was studied. Investigation of various solvents showed that aqueous nitromethane and aqueous methyl acetate gave acceptable yields, while acetone and acetic acid gave objectionable by-products. Other solvent systems were tried, but found unsuitable for various reasons. The reaction, which was normally run at room temperature, was found to produce lower and inconsistent yields of cleavage products at elevated temperatures due to polymerization of products.

Reaction products were analyzed by infrared spectroscopy and gas liquid chromatography (GLC). Quantitative results were obtained by GLC with the use of an internal standard.

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THE QUESTION OF POSITIONAL PREFERENCE IN THE MONOEPOXIDATION OF METHYL LINOLEATE

G. Maerker, E. T. Haeberer and W. C. Ault

Epoxidation of methyl linoleate with sufficient peroxyacetic acid to oxidize only one of the two double bonds permits the formation of two positional isomers: methyl vernolate, formed by epoxidation of 12,13-double bond and methyl coronate, formed by epoxidation of the 9,10-double bond. The present study was undertaken to determine whether there is preferential epoxidation of either bond.

The product obtained by monoepoxidation of methyl linoleate was analyzed by two methods: (a) reduction, followed by periodic acid cleavage of the saturated epoxides, and (b) a series of reactions including acetoxylation, catalytic reduction, saponification, esterification and finally periodic acid cleavage of the resulting dihydroxyesters. In both cases the cleavage products were aliphatic aldehydes and ω-formyl esters. The relative amounts of methyl vernolate and methyl coronate were calculated from a quantitative GLC determination of the relative amounts of methyl brassyaldehydate and methyl azelaaldehydate among the cleavage products. Results of both methods were in agreement. No significant preference in epoxidation at either of the two double bonds could be detected.

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QUANTITATIVE ESTIMATION OF THE TOTAL GLYCERYL ETHER CONCENTRATION IN LIPIDS

D. G. Cornwell, T. D. Beardmore, K. E. Guyer and K. S. Holla

Saturated and unsaturated glyceryl ethers are readily converted to alkyl monoiodide and alkyl diiodide derivatives which may be separated by gas-liquid chromatography in order to determine the relative composition of a glyceryl ether mixture. Furthermore, alkylmonoiodides are particularly well suited for the estimation of total glyceryl ether content of a lipid. Alkyl iodides were reacted with lithium aluminum hydride yielding hydrocarbons and the metal iodide. The metal iodide was then titrated quantitatively with ceric sulfate to a visual end-point. The indicator was orthrophenanthroline ferrous ion. The ceric sulfate was standardized against potassium dichromate by an indirect procedure using ferrous sulfate. This procedure estimated glyceryl ethers in lipid samples containing from 15 to 400 μmoles of glyceryl ether. Total glycerol ethers (alkyl and vinyl) were measured directly in naturally occurring diacyl neutral lipids and phospholipids after preliminary hydrogenation with a platinum oxide catalyst. When hydrogenation was preceded by the liberation and separation of aldehydes, the procedure measured only the alkyl ether concentration.

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GAS-LIQUID CHROMATOGRAPHIC ANALYSIS OF ISOMERIC GLYCEROL ETHERS

Randall Wood and Fred Snyder

The existing methods for the preparation of suitable derivatives for the gas-liquid chromatographic (GLC) analysis of glycerol ethers are for the most part unsatisfactory. Most of the derivatives are formed from incomplete reactions which require laborious clean-up procedures, while other methods do not yield derivatives of the 2-isomer.

A procedure for the GLC analysis of glycerol ethers as their trifluoroacetic acid (TFA) and their trimethylsilyl ether (TMS) derivatives will be described. The TFA derivatives allow the resolution of the 1- and 2-isomers and this resolution has not been reported previously. The TFA and TMS derivatives are prepared at room temperature and are ready for GLC analysis within 15 min. Analyses were carried out on packed columns of ethylene glycol succinate (EGS), 50% β-Cyanoethylmethylsiloxane (XE-60) and methylsiloxane (SE-30). The 1- and 2-isomers of a mixture of C_{10}, C_{12}, C_{14}, C_{16}, and C_{18} glycerol ethers have also been resolved with the 1-isomer eluting ahead of the 2-isomer. Isomeric mixtures of both $C_{18:1}$ and $C_{18:2}$ glycerol ethers also have been resolved.

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ANALYSIS OF ETHYLENE, DIETHYLENE AND PROPYLENE GLYCOL MONOSTEARATES BY QUANTITATIVE THIN-LAYER CHROMATOGRAPHY USING DENSITOMETRY

G. L. Anderson and A. R. Tallman

Quantitative thin-layer chromatography using densitometry has been applied to the analysis of commercial ethylene, diethylene and propylene glycol monostearates to determine the relative amounts of mono and diester present. Techniques and conditions are given that improve the accuracy of this method. The method offers many advantages over the previously used wet methods.

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DETERMINATION OF CYCLOPROPENES BY HYDROGENATION AND FRACTIONATION

Zigrida Zarins and R. O. Feuge

The cyclopropene acids malvalic and sterculic, which occur in the glycerides of cottonseed oil and other seed oils, are highly reactive and the free acids and their methyl esters are easily degraded. However, the methyl esters can readily be obtained without degradation by a sodium methoxide catalyzed methanolysis. Hydrogenation of the malvalate and sterculate with the aid of platinum and palladium catalysts results in the simultaneous formation of a number of products, the exact composition depending upon the hydrogenation conditions. However, conducting the hydrogenation with a highly reactive, zirconium promoted nickel catalyst at atmospheric pressure in a hydrocarbon solvent and at a temperature between 30C and 80C results in a practically quantitative conversion of cyclopropenes to their dihydro forms. Any epoxides present also will hydrogenate quantitatively. Linoleate and oleate are affected relatively little. Mixtures containing the hydrogenated cyclopropenes can be fractionated readily on a silicic acid-silver nitrate column. The first emerging, saturated fraction contains the dihydro forms of the cyclopropenes but no unsaturated esters or hydroxy esters from any epoxides. In a subsequent analysis of the saturated fraction by gas-liquid chromatography using a polyester column, the dihydro forms of the cyclopropenes appear at equivalent chain length 0.4 unit greater than those of the saturated acids having the same number of carbon atoms.

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A PRECISION HYDROGENATION APPARATUS

W. K. Rohwedder

A unique high-speed hydrogenation apparatus has been designed and built of stainless steel to give highly reproducible results. Unusual features include: a reaction chamber with an enclosed top that prevents the sample or catalyst from leaving the stirred region, a stirring paddle that comes within 0.010 inch of the fluted walled reaction chamber producing shear and turbulence in the reaction mixture, and a directly driven stirrer whose speed is controlled by a tachometer that can be varied from 100 to 4,000 rpm. The pressure of the system is sensed by an electronic micromanometer and controlled by a stainless steel piston-type volume control.

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THE STATUS OF SAFFLOWER

J. A. Kneeland

Safflower as a source of linoleic-rich oil has become widely available. The U.S. safflower industry has matured in the relatively short period of 15 years to a position of stable oil prices, modern processing, and world-wide distribution. This dry-land Western U.S. oilseed crop is grown in rotation with barley, wheat, rice and other grains. The higher oil content seed developed by the agronomists' reduction of hull content has made safflower more valuable to domestic and foreign markets. Production has increased to more than 300,000 tons in the United States. Safflower is unique in that it is grown for its oil, whereas the other significant edible oil crops are actually by-products of protein feeds, fibers, or starch. Processing of the seed and oil is done by conventional methods, preferably continuous screw-pressing and solvent extraction.

The future of safflower will depend primarily upon the demand for linoleic-acid based products — either in foods such as the new margarines and other polyunsaturated products, or industrial uses of nonyellowing drying oils, and chemical modifications of linoleic acid. Secondarily, it will depend upon more sophisticated utilization of the protein by-products. Safflower continues to be a growth situation.

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THE COMPOSITION OF SAFFLOWER SEED

T. H. Applewhite

Safflower is an increasingly important U. S. oilseed crop. Current commercial seed types have compositions in the range of 40% hull, 37% oil and 23% meal. Varieties have been described, however, with hull percentages ranging from 59% to 18% and inversely varying oil and meal percentages. In the linoleic acid type oils the fatty acid compositions are quite constant with typical percentages as follows: linoleic 78%, oleic 11%, stearic 3% and palmitic 6%. Experimental types have been described with about equal oleic-linoleic contents, with high oleic-low linoleic contents, and with relatively high stearic contents. Compositional data will be reviewed with particular attention to major and minor constituents (especially linolenic acid) influencing safflower utilization.

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SAFFLOWER OIL UTILIZATION IN SURFACE COATINGS

A. E. Rheineck and Lowell Cummings

The unique high linoleic acid content (78%) in safflower oil makes it an especially suitable oil in the coatings industry. The high content of linoleic acid, low amount of saturated acids, and absence of linolenic acid constitute an oil which forms fast-drying, nonyellowing films that have an excellent through dry and low wrinkling characteristics.

More safflower oil is utilized in the manufacture of alkyd resins than in any other single use. The oil alcoholizes rapidly with polyols and heat bleaches to very light colors in cooking the alkyd resins. These alkyds have the best combination of fast drying and nonyellowing properties of any drying oil alkyd of equal oil content.

Heat bodied safflower oil has very uniform polymer structure as shown by its viscosity reduction curves. Heat bodied and low viscosity safflower oils are used extensively in exterior house paints. These paints show good through dry, low wrinkling and resistance to dew flatting.

Specialty uses for safflower oil include urethane resins, caulks and putties, linoleum, oil emulsion exterior house paints and as conjugated safflower oil.

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THE ROLE OF SAFFLOWER OIL IN EDIBLE OIL APPLICATIONS

J. E. Blum

Safflower oil has been used as an edible oil in numerous countries for many years. In this country, commercial use of safflower oil as an edible product was noted in the 1950's and the use continues at progressively higher levels each year.

One use of safflower oil in "dressing" type products is related to the natural cold resistance of the oil. Other applications include oil, margarine and some imitation dairy products. Additional development work has been done on other food products so that the scope of usage could be broadened if there should be increased demands for safflower oil.

The susceptibility of safflower oil to oxidation has been minimized by improved processing and packaging.

Further use of safflower oil appears to be dependent upon availability, pricing, abnormally good cold resistance and the role of polyunsaturates in the diet.

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SAFFLOWER MEAL

G. O. Kohler

The composition and nutritional value of commercially and experimentally produced safflower meals will be reviewed including their utilization in rations of poultry, swine and ruminant animals. Available evidence from chick assays shows that safflower meals contain little or no deleterious components such as are found in most other oilseed meals. Primary utilization problems in feeds revolve around low metabolizable energy due to the content of relatively indigestible hull in the meal and the low content of methionine and lysine in safflower protein. When properly supplemented with energy, lysine, and methionine, outstanding growth rates are obtained in broiler chicks fed corn-safflower meal type rations. When lower fiber meals can be produced, expanded markets can be expected in rations for poultry and swine. Potential markets exist for such products and for safflower protein isolates as food for human beings here and abroad.

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LIPID CHANGES IN MATURING OIL-BEARING PLANTS. IV. CHANGES IN LIPID CLASSES IN RAPE AND CRAMBE OILS

Mary E. McKillican

Seeds of crambe abyssinica and golden and zero-erucic rape were collected at increasing maturity and the free lipid extracted with hexane. The lipid thus obtained was separated into lipid classes by silicic acid chromatography using increasing concentrations of diethyl ether in hexane, followed by methanol to elute phospholipids and glycolipids. The lipid classes were further examined by thin-layer and gas-liquid chromatography.

In crambe and both rape varieties the relative amounts of the lipid classes varied as the seed matured. The greatest change was in triglycerides and phospholipids plus glycolipids. Free fatty acids, present in immature seeds, had disappeared at maturity. The lipid classes of crambe and both types of rape were in similar proportion at maturity. Differences in phospholipid and glycolipid composition were found between crambe and rape and between immature and mature rape. The fatty acid composition was different in different lipid classes and changed with maturity. Changes in 18-carbon acids in zero-erucic rape paralleled the development of erucic acid in golden rape. The sterol compositions were also compared.

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FATTY ACIDS IN TISSUES OF RATS FED HUMAN FOOD, RAT RATION AND SYNTHETIC DIETS

Margaret O. Osborn

Fatty acids in serum and tissues of albino rats maintained on controlled diets have been studied. One group was fed a human food diet obtained from the professional staff dining room of the University Hospitals. The diet provided approximately 17% of the calories as protein and 41% as fat. A second group was fed a synthetic diet similar in protein and fat content to consumption studies of people in the United States. A third group was fed a commercial rat ration which provided 28% of the calories as protein and 14% as fat. Animals were placed on diets when approximately three weeks of age and sacrificed at seven weeks. Fatty acids in serum, liver and lung tissues were determined using gas chromatography. Data were analyzed statistically.

Diet seemed to influence the amounts of myristic, palmitic, palmitoleic, stearic, oleic, behenic and arachidonic acids in the tissues. Levels of oleic and linoleic acids in tissues appeared to follow levels in the diets. Arachidonic and behenic acids were found in tissues but not in the diet. Lung tissue appeared to be higher in palmitic but lower in stearic and oleic acids than liver or serum. Liver seemed to have larger amounts of arachidonic acid than serum or lung tissue.

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BIOSYNTHESIS OF DOCOSAPENTAENOIC AND OTHER FATTY ACIDS BY RAT TESTES

J. T. Davis and J. G. Coniglio

The possibility of active fatty acid synthesis by rat testes was suggested by the increase in concentration of pentaenoic acid in this organ in the rat during sexual maturation (Kirschman and Coniglio, Arch. Biochem. Biophys. *93*, 297, 1961). The characterization of this fatty acid as 4, 7, 10, 13, 16 docosapentaenoic acid in rat testes (Davis, Bridges, Coniglio, Fed. Proc. 24, 663, 1965) and in bovine and porcine testes (Holman and Hofstetter, J. Am. Oil Chem. Soc. *42*, 540, 1965) and its increase in liver following feeding of linoleic acid (Mohrhauer and Holman, J. Lipid Res. *4*, 346, 1963) lead to the hypothesis that arachidonic acid is its precursor. We have investigated the biosynthesis of the docosapentaenoic acid by using C^{14}-acetate, C^{14}-linoleate, and C^{14}-arachidonate as precursors injected directly into rat testes. C^{14} was incorporated into the docosapentaenoate from all three substrates. C^{14} from labeled linoleate was incorporated into eicosatrienoic, eicosatetraenoic, docosatetraenoic and docosapentaenoic acids, the specific activities peaking in that order. By chemical degradation of the docosapentaenoate biosynthesized from arachidonate-1-C^{14} it was found that over 98% of C^{14} activity was in carbon 3, indicating elongation of the 20 carbon to the 22 carbon fatty acid. Chemical degradation of isolated pure fatty acids obtained after acetate-1-C^{14} injection established that palmitic acid was synthesized predominantly by *de novo* synthesis while stearic acid was formed to a larger extent by elongation of shorter chains. The pattern of labeling of oleic acid was identical to that of stearic acid.

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STUDIES OF THE METABOLIC CONVERSIONS AND THE POSITIONAL DISTRIBUTION IN LIVER LECITHIN OF SOME UNNATURAL DIENOIC ACIDS

H. W. Sprecher, H. J. Dutton, F. D. Gunstone, P. J. Sykes and R. T. Holman

The acids, 7,13-eicosadienoate, 9,15-octadecadienoate, and 12,15-octadecadienoate were fed to rats, which had been maintained on a fat-deficient diet, to establish whether they could be converted to unsaturated acids with the normal skipped unsaturation pattern. The liver lipids were isolated, converted to methyl esters, and the amounts of the various fatty acids determined by gas-liquid chromatography. All of the experimental acids were incorporated into tissue lipids. However, none of the acids were converted to naturally occurring polyunsaturated acids. The positional distribution of the two octadecadienoate isomers in liver lecithin was determined.

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DEGRADATION OF ERUCIC ACID TO EICOSENOIC AND OLEIC ACIDS BY THE INTACT RAT

B. M. Craig and Joyce L. Beare Rogers

Previous investigations have shown that rats fed rapeseed oil have body lipids which contain oleic, eicosenoic and erucic acids in proportions of 45, 10 and 8%, respectively. Other studies on the relations between dietary and body fats indicate that the proportion of oleic is higher and erucic is lower than expected. This can only be explained by assuming that the rat can degrade erucic acid, presumably by beta oxidation to eicosenoic and oleic acids which are then deposited in the body fat.

The 11-docosenoic acid found in herring oil has been used to study the proposed degradation which would proceed according to the following sequence:

11-docosenoic → 9-eicosenoic → 7-octadecenoic

The analyses of body fats of rats which were fed a mixed oil containing 30% of 11-docosenoic acid showed 8% docosenoic acid and 4-5% each of the 9-eicosenoic and 7-octadecenoic acids.

The metabolism of erucic acid in the rat then involves some deposition of the acid as such coupled with a degradation to produce C_{20} and C_{18} monoene acids which also appear in the body fats. This partial degradation can be used to explain some unusual effects which have been found in nutritional studies on rapeseed oil.

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FATTY ACID COMPOSITION OF LIPIDS OF BULL AND BOAR SEMEN

Balwant Ahluwalia, E. F. Graham and R. T. Holman

Ejaculates from several bulls were pooled, and from one boar, sperm-poor and sperm-rich fractions of semen were collected. The semen was centrifuged to separate seminal plasma and the spermatozoa. The spermatozoa were disintegrated by ultrasonic vibration, and fractions containing sperm heads and the sperm tails were obtained by centrifugation. Lipids from each fraction were extracted and separated into neutral lipids and phospholipids through thin-layer chromatography. The neutral lipids were further fractionated into diglyceride, triglyceride and cholesterol esters by TLC, and the phospholipids into phosphatidyl choline and phosphatidyl ethanolamine by DEAE column chromatography. Methyl esters of each fraction were analyzed by GLC. Individual methyl esters were identified by equivalent chain length and ozonolysis. The data indicate that bull semen contains highly unsaturated fatty acids of C22 chain length which constitute approximately 40-45% of the total fatty acids in the semen. Phosphatidyl choline contains the highest amount of unsaturated fatty acids. In neutral lipid fractions, diglyceride is more unsaturated than triglyceride or cholesterol esters. In boar semen, the sperm-poor fraction contains fatty acids less unsaturated than in the sperm-rich fraction. The fatty acid composition of lipids from bull and boar semen are quantitatively different. The total lipids of boar semen were less unsaturated than those of bull semen. The relationship between fatty acid composition of semen lipids and fertility of the semen will be discussed.

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STUDIES ON THE METABOLISM OF TRANS ACIDS IN THE RAT. INTERCONVERSION OF TRANS-11, TRANS-14- AND CIS-11, CIS-14-EICOSADIENOIC ACIDS

O. S. Privett, E. M. Stearns, J. D. Nadenicek and F. J. Pusch

Adult male rats of the Sprague-Dawley strain with well-advanced symptoms of essential fatty acid deficiency from prolonged feeding of a fat-free diet were fed supplements of 5% methyl *trans*-11, *trans*-14-eicosadienoate or 5% *cis*-11,*cis*-14-eicosadienoate for 10 days and sacrificed. Five animals fed the basic fat-free diet were also sacrificed to serve as a control group. The hearts, livers, epididymal fat pads and kidneys of each animal were excised. The lipids of these tissues were extracted with chloroform-methanol and fractionated by a combination of acetone precipitation and preparative thin-layer chromatography into triglycerides, a fraction consisting mainly of cholesteryl esters and polar lipids. The fatty acids of the lipids of these fractions in each group were fractionated by a combination of selective argentation, mercuric acetate adduct formation and reversed-phase partition chromatography, and analyzed. The composition of the fatty acids of the control animals was typical of animals with an essential fatty acid deficiency, namely, a high ratio of trienoic to tetraenoic acids and a low dienoic acid content. The ratio of trienoic to tetraenoic acids was also high in the lipids of the animals which received the methyl *trans*-11,*trans*-14-eicosadienoate, but was reversed by the feeding of methyl *cis*-11,*cis*-14-eicosadienoate. The deposition in the lipids of the acids of these esters was determined and possible pathways of their conversion proposed.

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PHOSPHOLIPASE A PROPERTIES OF SEVERAL SNAKE VENOM PREPARATIONS

L. J. Nutter and O. S. Privett

The hydrolytic properties of seven snake venom preparations, *Crotalus adamanteus, Ancistrodon contortrix, Naja naja, Bothrops atrox, Ophiophagus hannah, Crotalus atrox,* and *Vipera russeli,* were studied with highly purified lecithins and mixtures of lecithins of known fatty acid and class composition as substrates.

The relative rates of hydrolysis of the fatty acids by the above venoms were determined by analysis of the products of the reaction at frequent intervals during the course of the reaction. All venoms selectively hydrolyzed the fatty acids in the β-position but there was considerable variability in the rate of release of individual fatty acids. With some venoms, the saturated fatty acids were hydrolyzed much faster than unsaturated fatty acids; with others the reverse was true. The type of fatty acid in the α-position did not appear to have any influence on the rate of liberation of the individual fatty acids in the β-position, other factors being equal.

Of the seven venoms examined, that of King Cobra was the only one which did not give some degree of preferential rate of hydrolysis of individual fatty acids. The venom of *Crotalus adamenteus,* which has been used extensively in investigations of lecithin structure, exerted a strong preferential rate of hydrolysis of saturated fatty acids in the early stages of the reaction.

The results are discussed in relation to the use of snake venoms for the determination of lecithin structure and the general mode of phospholipase A action in phospholipid metabolism.

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A SIMPLE MICROMETHOD FOR THE DETERMINATION OF THE STRUCTURE OF UNSATURATED FATTY ACIDS VIA OZONOLYSIS

E. C. Nickell and O. S. Privett

Techniques for the preparation, purification and cleavage of ozonides are described and incorporated into a simple procedure for the determination of the structure of unsaturated fatty acids. The method involves, essentially, preparation of ozonides via ozonization of fatty acid esters in pentane at –70C, fission of the ozonides by pyrolysis and analysis of the fragments of the reaction by GLC. The positions of the double bonds in the original molecule are derived from the chain length of the fragments. An analysis may be carried out on samples of the order of 100 μg and completed in less than 1 hr. The method is illustrated on highly purified methyl oleate, linoleate, linolenate and arachidonate.

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HETEROGENEOUS CATALYTIC DEUTERATION OF METHYL OLEATE. I. REDUCTION AND SEPARATION OF ISOLOGS AND ISOMERS

C. R. Scholfield, W. K. Rohwedder, J. Barter and H. J. Dutton

Methyl oleate was reduced at 40C and atmospheric pressure with deuterium gas and either platinum or palladium catalysts. Samples of the esters and of the gas phase were removed during the reaction. The hydrogen-to-deuterium ratios in the gas phase were determined by mass spectrometry. Withdrawn ester samples were fractionated by reverse phase chromatography on rubber columns into saturate and monoene fatty esters, and the monoenes, into *cis* and *trans* isomers by argentation chromatography.

Experimental conditions, fractionation procedures, and results of infrared analysis, argentation chromatography, mass spectrometry, and nuclear magnetic resonance will be described.

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HETEROGENEOUS CATALYTIC DEUTERATION OF METHYL OLEATE. II. BOND MIGRATION, GEOMETRIC ISOMERIZATION, AND DEUTERIUM DISTRIBUTION

E. Selke, W. K. Rohwedder, V. L. Davison,
T. Nieman and H. J. Dutton

Separated isomers from the heterogeneous catalytic deuteration of methyl oleate were subjected to mass spectrometric analysis to determine their deuterium content. The saturated ester fraction varied from less than 1 deuterium atom per molecule at the 20% saturation level to more than 2 at the 100% level, whereas the still unsaturated esters reached 2 atoms of deuterium per molecule at the 80% level. Oxidative cleavage of the separated unsaturated esters showed a symmetrical and normal distribution of the double bonds about the Δ 9 position; bonds ranged from the 6th to the 13th position, and less than 40% of the bonds remained in the Δ 9 position at the 80% saturation level. Mass spectra of the individual monobasic and dibasic acids from the oxidative cleavage showed the greater the double bond movement, the greater the deuterium content.

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SEPARATION OF CONJUGATED METHYL OCTADECADIENOATE AND TRIENOATE GEOMETRIC ISOMERS BY SILVER-RESIN COLUMN AND PREPARATIVE GAS-LIQUID CHROMATOGRAPHY

E. A. Emken, E. N. Frankel, V. L. Davison and C. R. Scholfield

The separation of geometric fatty ester isomers by silver-cation exchange resin chromatography was extended to conjugated methyl octadecadienoates and trienoates. This technique in combination with preparative gas-liquid chromatography (GLC) was developed to analyze conjugated isomers in hydrogenated fatty esters.

The analytical procedure consisted of separating the nonconjugated dienes from the conjugated dienes by preparative GLC and fractionating the conjugated diene isomers by silver-resin chromatography. The preparative GLC step was tested with a model mixture of methyl oleate, linoleate and linolenate and with a concentrate of methyl *trans,trans*-9,11-octadecadienoate. The unconjugated fatty esters were obtained pure with recoveries averaging 90%. The conjugated fatty ester showed 5% geometric and positional isomerization after preparative GLC.

Conjugated dienes from alkali-conjugated methyl linoleate and from dehydrated methyl ricinoleate, and a mixture of methyl α- and β-eleostearate were fractionated by silver-resin column chromatography. The alkali-conjugated methyl linoleate gave pure *cis,trans*-conjugated diene. Dehydrated methyl ricinoleate gave *cis,cis-*, *cis,trans-* and *trans,trans*-conjugated dienes in 94 to 99% purity. Oxidative cleavage analysis showed double bond scattering increasing in the order: *cis,cis-*, *cis,trans-* and *trans,trans*-conjugated dienes. Silver-resin chromatography of a mixture of methyl α- and β-eleostearate yielded the α-isomer in 92% purity.

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GAS-LIQUID CHROMATOGRAPHY OF THE POSITIONAL ISOMERS OF METHYL NONYNOATE

Henry Rakoff and R. E. Anderson

A mixture of all the positional isomers of methyl nonynoate is poorly resolved by gas-liquid chromatography on packed polar (diethylene glycol succinate) and packed nonpolar (Apiezon L) columns. Better resolution is obtained on capillary columns, with the polar liquid phase giving baseline separations between all the isomers except 9:T4 and 9:T5. The nonynoic esters elute later than methyl nonanoate on either liquid phase. The isomers with the triple bond near the center of the molecule come off first, and the elution time increases as the triple bond moves toward either end of the chain. Methyl 8-nonynoate, the only isomer with a terminal triple bond, does not follow this pattern.

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COMPARISON OF GAS CHROMOTOGRAPHIC TECHNIQUES

F. H. Fryer and O. D. Decker

Several parameters of GLC fatty acid analysis were compared. Preparation of esters by saponification followed by catalytic methylation was compared with direct transmethylation. DEGS liquid phase was compared with EGS liquid phase for resolution and quantization. Triangulation of peak areas was compared with planimeter measurements, and area response was compared with known mixtures.

It is hoped the variations indicated in this study will be useful in the future establishment of an official GLC fatty acid analysis method.

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COLLECTION OF METHYL ESTERS IN PREPARATIVE GAS-LIQUID CHROMATOGRAPHY VIA ELECTROSTATIC PRECIPITATION TECHNIQUES

L. Borka and O. S. Privett

The effect of the operating variables of electrostatic precipitators on the recovery and structure of methyl esters and related compounds collected via these devices in preparative gas-liquid chromatography was studied.

Aerosol formation was prevented by AC or DC voltages of 5,000 to 12,000 volts. AC was more effective than DC but caused changes in structure which were detectable by both thin-layer and gas-liquid chromatographic methods of analysis.

An apparatus of simple construction and operation was designed for the collection of methyl esters and its use demonstrated with several model compounds.

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SILANE TREATMENT OF SOLID SUPPORTS FOR GAS CHROMATOGRAPHY

W. R. Supina, R. S. Henly and R. S. Krupa

A variety of techniques have been reported in the literature for silane treatment of solid supports. Often one will be recommended as

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being superior to some of the other techniques. It has been our experience that many important variables are involved which are only briefly mentioned or even omitted in the literature. It is therefore possible to follow the procedures exactly as reported, and yet the support may not be properly silane-treated.

While the methods used for the silanization are important, too often the preliminary treatment of the support is neglected. We have examined many of the variables and found that a few are particularly important.

Proper evaluation of the silane-treated support is important; the common test to determine whether or not all particles float in water is inadequate. A support which passes this test may still cause catalytic decomposition of the sample being analyzed.

The detailed procedure for preparing a satisfactory support will be described and use of this support in analyzing steroids and pesticides will be illustrated.

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SIMPLIFIED MICRO-OZONOLYSIS PROCEDURES FOR QUANTITATIVE DETERMINATION OF DOUBLE BOND POSITIONS

V. L. Davison and H. J. Dutton

Direct injection of ozonized fatty esters into the heated inlet port of a gas chromatograph offers a one-step procedure for decomposing ozonides and for analyzing the resulting aldehydic fragments to determine double bond positions. In this manner microliter samples of ozonides, prepared on any convenient scale, may be analyzed.

Acidic functional groups, formed during thermal cleavage, have been effectively eliminated by inserting a short column, containing well-oxidized zinc granules or zinc oxide on an inert support, between the injector port exit and the fractionating column.

A microreactor has been developed in which 5 µl may be successively ozonized, thermally cleaved and injected without sample transfer and attendant losses. This procedure provides an easy and rapid analysis; it also permits analyzing samples available only in limited amounts.

When either the direct injection of ozonides or the microreactor procedure was used with a temperature-programmed gas chromatograph, equipped with a column containing a mixed polyester-silicone liquid phase, effective separation was achieved for mono- and difunctional aldehydes from 3 to 16 carbons in length.

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PLASMALOGENS IN PHOSPHOLIPIDS OF CHICKEN MUSCLE

C. Y. Peng and L. R. Dugan

The phosphoglycerides phosphatidyl choline, phosphatidyl ethanolamine, and phosphatidyl serine from the lipids of white and dark meat chicken muscle were found to contain varying amounts of plasmalogens. Qualitative evaluation was made by colorimetric methods, thin-layer chromatography and column chromatography. Quantitative evaluation was accomplished by a procedure involving iodination and by gravimetric analysis. The fatty aldehyde moieties of the plasmalogens were determined by gas-liquid chromatography of the dimethylacetal derivative.

The plasmalogen content of white meat phospholipids was greater than that of the dark meat phospholipids. Phosphatidyl ethanolamine was found in relatively greater amounts than phosphatidyl choline or phosphatidyl serine. The major aldehydes found were palmitaldehyde, stearaldehyde, oleylaldehyde, and capraldehyde with palmitaldehyde being predominant.

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AVIDIN INHIBITION OF LONG-CHAIN FATTY ACID SYNTHESIS IN MITOCHONDRIA

J. P. Jordan and E. B. Harris

The effect of avidin on the synthesis of long-chain fatty acids was studied using a sonically solubilized enzyme preparation from rat liver mitochondria. Using acetate-1-C^{14} or acetyl-1-C^{14}-CoA as substrate, the avidin concentration was varied from 0 to 300µg. Nearly maximum inhibition was observed in the presence of 100 µg of avidin and increased very little at 300 µg. This represented a reduction of approximately 47% in the synthesis of fatty acids.

The effect of avidin on the synthesis of particular fatty acids was studied by measuring the incorporation of C^{14} into individual fatty acids which were separated by gas-liquid chromatography. The relationship of avidin sensitivity to *de novo* synthesis and elongation was studied by decarboxylation of palmitic and stearic acids and by permanganate-periodate oxidation of palmitoleic and oleic acids.

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METABOLISM OF THE ALKOXY, ALKENYL, AND DIACYL ETHANOLAMINE PHOSPHOLIPIDS IN BRAINS OF ADULT RATS

L. A. Horrocks and G. B. Ansell

Adult rat brain phospholipids contain 13% diacyl glycerylphosphorylethanolamine, 23% alkenyl acyl GPE (ethanolamine plasmalogen), and 3.1% alkoxy acyl GPE. Some aspects of the metabolism of these types of phospholipid were studied in vivo after intracerebral injection of C^{14}-ethanolamine. The ethanolamine phospholipids were separated from the other brain lipids by DEAE cellulose chromatography and specific activities determined after mild alkaline and acid hydrolysis (Horrocks and Ansell, Biochem. J., in press).

At all times studied the specific activities were diacyl GPE > alkoxy acyl GPE > alkenyl acyl GPE. Thus the ethanolamine plasmalogens are not precursors of alkoxy acyl GPE. The possibility of alkoxy acyl GPE being a precursor of alkenyl acyl GPE and the significance of these compounds in membranes will be discussed.

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THE DEPOSITION AND METABOLISM OF α-BATYL ALCOHOL-1-^{14}C IN THE RAT

Fred Snyder, Claude Piantadosi and Ed Oswald

The distribution, metabolism, and excretion of batyl alcohol occurring 6 hr after oral administration of this radioactive glyceryl ether were investigated in the female rat. Thin-layer chromatographic zonal scans were used to determine the degree and type of metabolic changes in the lipid fraction of various tissues. Under the conditions of this experiment most of the ingested label was found in the intestines but 11% was found in the liver. Other tissues contained less than 0.3% of the administered dose. TLC scans of the lipids found in intestinal contents and in cells showed that significant cleavage of the ether bond occurred in this location. Labeled di- and monoethers, free fatty acids, and fatty alcohols were found in addition to the original glyceryl ether. The lipids isolated from the intestinal tract only, contained labeled triglycerides and phospholipids also. Approximately 30 and 24% of the lipid label found in the contents and tract, respectively, was the unchanged batyl-1-^{14}C alcohol.

The major portion of the radioactive plasma lipids contained the carbon-14 label as glyceryl ether diesters (53%) and phospholipids (25%). In the liver, most of the ^{14}C was in the phospholipids (70%; of this, 58% in the lecithin and 26% in the cephalin fractions).

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FURTHER STUDIES ON A SERIAL METHOD FOR OIL DETERMINATION IN OIL SEED

Lars-Åke Appelqvist

The routine method for determination of oil content in rape and mustard seeds, developed by Troeng, has been in use for 10 years with good results. Each year 30,000–50,000 samples have been analysed. Cumulated data from analyses performed during many years on samples sent to different laboratories in Sweden as well as in Denmark, England, Germany and Holland have shown that results obtained with the serial method are more accurate than those obtained with official methods using Butt-type or Twisselman extractors.

Besides its present major use, viz., for determination of oil content in rape and mustard seeds, it has potential uses for flax, safflower, poppy and sunflower.

The extraction conditions, 1 hr at 25–30 C, are favorable for the utilization of the extraction tubes for the preparation of oil which is to be studied further, e.g., in determination of the peroxide number of the oil extracted. Details will be given of the special care that has to be taken in using the tubes for other purposes than determination of oil content.

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A STUDY OF "THE SWEDISH METHOD" FOR DETERMINATION OF OIL CONTENT IN PLANT SEEDS

F. W. Hougen and Mrs. V. Bodo

Troeng in 1955 published a rapid method for determination of oil content in oil seed. His method is used extensively in Swedish laboratories for rapeseed analyses. The method is based on simultaneous ball-milling and extraction of the samples in stoppered steel tubes containing steel balls and a measured volume of solvent. The tubes are shaken lengthwise for grinding of the samples and subsequently centrifuged for sedimentation of suspended solids. For each tube, a measured aliquot of clear solution is transferred to a beaker and the solvent is evaporated. The oil contents of the samples are computed from the weights of oil recovered in the beakers.

Troeng's method, with modifications, has been adapted for the extraction of various oil seeds and cereal grains. Sources of error have been examined and comparisons have been made with the Soxhlet method. The Swedish method was found precise, accurate, and well suited for routine work.

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GAS-LIQUID CHROMATOGRAPHY OF NATURAL TRIGLYCERIDES CONTAINING C$_{20}$, C$_{22}$, AND C$_{24}$ FATTY ACIDS

R. D. Harlow, Carter Litchfield and Raymond Reiser

Although GLC of natural triglycerides containing C$_8$ through C$_{18}$ fatty acids is now used in many laboratories, erucic acid oils and marine oils have not been analyzed by this technique. Triglycerides containing long chain fatty acids usually show poor peak resolution and substantial losses during GLC. By critically selecting optimum operating conditions and using accurate calibration, we have successfully overcome these problems and achieved quantitative analysis of natural triglycerides containing C$_{20}$, C$_{22}$, and C$_{24}$ acids.

The triglycerides of four erucic acid oils (rapeseed, nasturtium, water cress, and *Lunaria annua*) and two fully hydrogenated fish oils, (menhaden and tuna) have been separated by GLC. Chromatograms showed adequate peak resolution for accurate quantitation by triangulation. The average fatty acid chain length calculated from the triglyceride composition of each oil agreed closely with that determined by GLC of its fatty acid methyl esters.

Several conclusions about the triglyceride compositions of the fats analyzed will be discussed.

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CHROMATOGRAPHY OF POLAR TRIGLYCERIDES ON SILICIC ACID COLUMNS

C. D. Evans, D. G. McConnell, R. L. Hoffman and Helen M. Peters

Triglycerides containing polar fatty acids are resolved by silicic acid chromatography into molecular species with increasing amounts of polar acids. Natural fats like isano, oiticica, castor or kamala seed oils containing both nonpolar fatty acids and polar hydroxy or keto acids have been resolved into component glycerides according to degree of polarity. The application of the silicic acid column offers a means of obtaining specific glycerides from fats for detailed studies on glyceride composition and structure.

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PREPARATION OF THE VINYL ESTER OF THE DIELS-ALDER ADDUCT OF PETROSELINIC ACID AND HEXACHLOROCYCLOPENTADIENE

J. P. Moreau, R. L. Holmes and G. Sumrell

Vinyl 5-(1,4,5,6,7,7-hexachloro-3-undecylbicyclo [2.2.1]-5-hepten-2-yl)-pentanoate (I) was prepared by the vinylation of the Diels-Alder adduct of *cis*-6-octadecenoic (petroselinic) acid and hexachlorocyclopentadiene (HCCPD). The acid adduct was prepared by heating petroselinic acid with an excess of HCCPD at 134 C for 28 hr. The excess HCCPD was distilled off and the unreacted petroselinic acid removed from the acid adduct by urea complexing. (I) was formed by treating the acid adduct with vinyl acetate in the presence of mercuric sulfate catalyst for 72 hr at room temperature. The excess vinly acetate was removed by distillation under reduced pressure below 40 C. Unreacted acid adduct was removed by alkaline washings on an alumina column.

The HCCPD adduct of methyl petroselinate was also prepared, and distilled.

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THE 1,2-CYCLOADDITION OF HALOALKENES TO CONJUGATED FATTY ESTERS

E. W. Bell, J. P. Friedrich, L. E. Gast and J. C. Cowan

The reaction has been studied of 1,1-dichloro-2,2-difluoro, chlorotrifluoro and tetrafluoroethylenes and hexafluoropropylene with the *cis,-trans* and *trans,trans* isomers of conjugated methyl linoleate. All reactions gave 50–75% yields of 1,2-cycloaddition products. The presence of the vinylcyclobutane structure in the addition products was shown by IR and NMR spectra, elemental analyses, and IV. The formation of 1,2-versus 1,4-cycloaddition products will be discussed. The reactions were best carried out with inert solvent, hydroquinone inhibitor, autogenous pressure, and a temperature of 200 C for 5 hr. The distilled adducts are colorless liquids with viscosities ranging from 11 to 19 centistokes at 100 F. These products exhibit low pour points (down to −55 C) and may be useful as low-temperature plasticizers or lubricant additives. Stabilities of the halogen atoms toward hydrogenation will be discussed.

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ESTERIFICATION OF FATTY ACID DOUBLE BONDS

L. T. Black and R. E. Beal

Unsaturated fatty acid methyl esters react with short-chain carboxylic acids in the presence of a reticulated cation exchange resin and produce esters at fatty acid double bonds. Hydrolysis of these esters by saponification and subsequent acidification yields hydroxy fatty acids.

The following variables were studied in the preparation of the acetate esters of methyl oleate: yield versus time, temperature, acid ratio and resin ration. In addition to acetic acid, several other carboxylic acids were tried. The reaction with acetate acid appeared to reach equilibrium at about 45% of theoretical yield.

Physical constants and derivatives were obtained for identification and characterization of the products. Interaction of the unsaturated fatty acid methyl esters produces an ester polymer, formation of which could be minimized by increased acetic acid ratios. The acetate esters were easily separated from unreacted methyl oleate and ester polymers by fractional distillation.

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PREPARATION OF LINSEED ACID CHLORIDES

E. J. Dufek, L. E. Gast, and W. J. DeJarlais

The preparation in excellent yields and with functional purity of linseed acid chlorides from linseed acids by reaction with phosphorus trichloride is described. In vacuo heating followed by decantation furnished good quality acid chloride with low phosphorus content. The acid chlorides were also distilled in a modified molecular still to obtain a nearly colorless product. Water-washing the crude acid chloride mixtures in hexane solution to remove phosphorus compounds was unsatisfactory since tests with purified acid chlorides in hexane showed that this treatment resulted in an appreciable amount of hydrolysis. Two analytical methods depending upon hydrolysis of the acid chloride were used and results compared. The use of infrared absorption and elemental chlorine analyses to determine the acid chloride contents was also investigated. Evidence was obtained for the existence of an equilibrium betweeen linseed acid chlorides, linseed acids, hydrogen chloride, and linseed acid anhydrides. Yield of about 70% of linseed acid anhydrides was obtained by reaction of linseed acid chlorides with linseed acids.

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NMR SPECTRA OF SUBSTITUTED FATTY ESTERS

A. P. Tulloch

High resolution NMR spectra have been recorded, at 100 megacycles, for all the isomeric methyl acetoxy-, hydroxy-, and oxostearates. Hydroxy esters of other chain lengths, various dihydroxy esters, epoxy esters, and some monoenoic and dienoic esters have also been examined. Splitting of the methylene signal was observed for a number of the esters which were substituted near the middle of the fatty acid chain. The terminal methyl group signal was modified in those esters which were substituted at any of the neighboring 4 carbon atoms. Substitution within 4 or 5 carbon atoms of the carboxyl end of the chain also affected the spectrum. The theoretical and practical aspects of these observations will be discussed.