# ABSTRACTS R. A. REINERS, Editor. ABSTRACTORS: J. G. Endres, J. Iavicoli, K. Kitsuta, F. A. Kummerow, C. C. Litchfield, Louise R. Morrow, E. G. Perkins, and T. H. Smouse

## • Fats and Oils

A highly sensitive method for measurement of lipid hydroperoxides by iodimetry and amperometric endpoint. K. Oette, M. L. Peterson and R. L. McAuley (The Rockefeller Inst., New York 21, N. Y.). *J. Lipid Res.* **4**, 212-215 (1963). A simple, accurate, and highly sensitive method is described for measurement of lipid hydroperoxides, utilizing standard iodimetric reactions and an amperometric endpoint. Measurement of $10^{-8}$ equivalents of hydroperoxides is feasible in samples of milligram size. Several parameters of the analysis have been defined.

Diels Alder reaction in the field of fats. H. P. Kaufman (Deut. Inst. Fettforsch, Münster). *Fette Seifen Anstrichmittel* **64**, 1115–1126 (1962). The Diels Alder reaction in the field of fats is discussed in a systematic order. The significance of the diene reaction for fat analysis, structure research, and for preparative work is discussed.

Pro- and antioxidants in fats. VIII. The synthesis of cholesterol esters of hydroxy and keto fatty acids. H. P. Kaufman, G. Garloff, and F. Diecke (Deut. Inst. Fettforschung, Münster). *Fette Seifen Anstrichmittel* **64**, 1104-1109 (1962). The authors attempt to characterize the products of an aqueous reaction of cholestrol linoleate and haemoglobin. Apparently dihydroxy fatty acids are among the products. The effects of α-tocopherol and billirubin upon the oxidation were studied as well.

Carbonyl formation in autoxidized fatty acid esters. K. Taufel and G. Heder (Deut. Inst. Lebensmittelchem. und Technol., Humboldt Univ., Berlin). *Fette Seifen Anstrichmittel* **65**, 85–91 (1963). Esters of oleic acid and linoleic acid were oxidized to peroxide values of 140-200, and subjected to the action of bleaching earth in the presence of acid. An increased formation of steam volatile monocarbonyl compounds was noted. The 2,4-dinitrophenylhydrazones were prepared and characterized with the aid of paper chromatography.

Hydrogenation of acid oils and technical oils at elevated pressure. H. Wissebach (Ohwerke Germania, Emmerich). *Fetté Seifen Anstrichmittel* **64**, 967-970 (1962). The author reports that hydrogenation of acid oils and technical oils (recovered from spent bleaching earth) can be carried out more quickly and with lower catalyst consumption by applying increased hydrogen pressure, 30 atmospheres instead of 3 atmospheres. The cycle time is reduced by 70-80% and nickel consumption lowered by 30-50%.

Isolation of methyl ketones from fats and paper chromatograghic differentiation in the form of 2,4-dinitrophenylhydrazones. K. Taufel, K. Schmidt, and Cl. Franzke (Inst. Lebensmittlechemie, Humboldt Univ., Berlin). *Fette Seifen Anstrichmittel* **64**, 957-961 (1962). Heat treated butter contains the homologeous series of odd numbered methyl ketones from $C_3$ to $C_{15}$. In unheated butter only acetone is detected. Evidence is presented which indicates the possible presence of even numbered and branched chain compounds which also may be ketones.

Mechanism of acyl-migration in partially acylated glycerides. D. Buchnea (Banting and Best, Dept. of Med. Research, Univ. of Toronto, Canada). *Fette Seifen Anstrichmittel* **64**, 887-892 (1962). The author outlines seven schemes in detail which may explain the migration of acyl groups in partial glycerides. Most of the reaction conditions under which these reactions occur are included in the schemes. The acyl migration in mono and diglycerides is shown to be a two stage reaction. The author shows that in such migrations an exchange of the acyl groups between two molecules takes place.

Secondary conversions of autoxidized fatty acid esters. K. Taufel, G. Heder, and Cl. Franzke (Inst. Lebensmittelchemie, Humboldt Univ., Berlin). *Fette Seifen Anstrichmittel* **65**, 6–13 (1963). The influence of cupric, ferric, ferrous and plumbous ions, and of sulfuric, hydrochloric, phosphoric, oxalic, monochloroacetic, citric, and benzoic acids on autoxidized methyl oleate and linoleate was investigated. Cupric ion has a stronger peroxide destroying action on concentrates of methyl oleate hydroperoxide than ferrous ion. This was shown by a decrease in absorption at 232 m$\mu$. Mineral acids and lesser organic acids (especially when warmed) lead to decomposition of hydroperoxides in mixtures of esters and to a deepening of color. Decrease in peroxide value, decrease in the extinction coefficient at 232 m$\mu$, and color deepening were parallel to the strength and concentration of mineral acids.

Studies of the UV spectra of antioxidants. II. a new direct UV spectroscopic method for the determination of antioxidants in fats. B. A. J. Sedlacek (Inst. Ernahningforch., Prague). *Fette Seifen Anstrichmittel* **64**, 962-967 (1962). A new UV method for the determination of gallate esters, BHA, and NDGA is reported. Chloroform has been shown to be a better solvent than toluene in this method. Statistical comparisons of this method with others are included.

New possibilities of applications of vegetable oils in the field of coating materials. J. E. Wiff, P. H. Martin and A. R. Baldwin (The Cargill Corp., Minneapolis, Minnesota). *Fette Seifen Anstrichmittel* **65**, 117-121 (1963). Investigations were carried out with films of zinc oxide containing linseed oil of various viscosities with regard to their resistivity to the formation of bubbles, vapor permeability, and water absorption. The results obtained are compared with those obtained from linseed oil emulsions.

Preparation of erucic acid by low temperature crystallization. K. Taufel, K. O. Heems and C. Franzke (Inst. Lebensmittelchemie, Humboldt Univ., Berlin). *Fette Seifen Anstrichmittel* **64**, 1023-1026 (1962). Low temperature crystallization of rapeseed oil fatty acids or methyl esters from acetone solution yields erucic acid of over 95% purity in one fraction. Repeated crystallizations give a pure product. Yields are about 20% based on the total acids.

Hydrogenation of castor oil in ethanol. J. G. Kane and K. M. Manerkar (Dept. of Chem. Tech., Univ. of Bombay, Bombay, India). *Fette Seifen Anstrichmittel* **64**, 1026-1030 (1962). The course of hydrogenation of castor oil in ethanol was studied. The influence of temperature, pressure, alcohol:oil ratio, and the concentration of alcohol and catalyst was investigated. In the presence of alcohol as solvent, the hydrogenation of castor oil is rapid and little dehydroxylation was observed.

Interesterification of fats V: detection of methanol in fats by interesterification with sodium methylate. H. P. Kaufman and B. Grothues (Deut. Inst. Fettforsch., Münster). *Fette Seifen Anstrichmittel* **64**, 805-807 (1962). The authors have shown that a determination of the methyl esters of fats as methanol by transesterification is not possible. A direct method for the detection of methyl esters in fats utilizing paper chromatography has been developed.

Glycerylethers of cod liver oil. A. Emmerie and C. Engel (Lab. Mikrobiologie, Univ. Utrecht). *Fette Seifen Anstrichmittel* **64**, 813-816 (1962). A new chromatographic method (column) is described for the preparation of the unsaponifiable portion of cod liver oil. Purification and separation of fractions obtained by chromatography and testing of them by microbiological methods aided in the isolation of fractions with high bacteriostatic activity. The activity was shown to be confined to the unsaturated α-glyceryl ethers. Other glyceryl ethers, apart from selachyl alcohol, were isolated.

Isomerization of highly unsaturated nonconjugated fatty acids by heat treatment of sea-animal oils. T. Miyakawa and H. Nomizu (Government Ind. Res. Inst., Osaka, Japan). *Fette Seifen Anstrichmittel* **64**, 593-599 (1962). Heating the methyl esters of cuttle fish oil at 200 to 250 C causes formation first of *cis-cis-trans* and then *trans-cis-trans* triene compounds. These materials then undergo partly inter- and intra-molecular cyclisation. The formation of cyclic compounds was followed by urea fractionation, and UV and IR measurements.

Molecular weight determination of fats and fat polymers in the ultracentrifuge. II. molecular weight determination of fats from the approximation of the sedimentation equilibrium. H. Luck and E. Rickerl (Deut. Inst. Lebensmittelchemie, Munich). *Fette Seifen Anstrichmit-*

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*tel* **64**, 825-831 (1962). Using groundnut oil as an example, it was shown that a molecular weight determination of fats is possible using the ultracentrifuge. The molecular weights obtained in polar and non-polar solvents show no significant differences. At higher oil concentration (5-10%) association phenomena are observed.

Studies on the uv-spectrum of antioxidants I: Influence of solvents and fat on the uv-spectrum. B. A. J. Sedlacek (Inst. Ernahningsforschung, Prague). *Fette Seifen Anstrichmittel* **64**, 683–687 (1962). The UV spectra of methyl, ethyl, propyl, octyl, and dodecyl gallate; BHA, BHT, NDGA, ascorbyl palmitate and ascorbic acid were studied in aqueous and ethanolic solutions. The spectra with fats added in solution and without antioxidants were determined. Chloroform and toluene were suitable solvents. Fat rancidity reduces the extinction values of antioxidant absorption maxima.

Evaluation of the known methods of chromatographic separation of lower fatty acids. J. Churacek (Inst. Anal. Chem. Chemish-Technolog. Hochschule, Pardubice/CSSR). *Fette Seifen Anstrichmittel* **64**, 679–682 (1962). The literature is reviewed. Methods are described briefly and evaluated from the point of simplicity, speed, and sensitivity.

Linseed oil of Rumanian origin. G. Alexa and G. Caraculacu. *Studii Cerc. et Sti. Chim., Iassy* **12**, 137–55 (1961). The oil obtained from the seed of a linen flax of the Concurrent variety was shown to be very similar, in its physical and chemical properties, to oil obtained from linseed grown primarily for its oil content. The oil content of the Concurrent linseed varied from 34 to 35.2%. (Rev. Current Lit. Paint Allied Ind.)

Variation of refractive index as a rapid method for measuring fat oxidation. G. Janíček and J. Pokorný (Inst. of Chem. Tech., Prague). *Papers of the Inst. of Chem. Tech. Prague* **4-I**, 157–83 (1960). The refractive index of oils increases with their degree of oxidation, even though there may be a corresponding decrease in iodine value. The relationship between refractive index and degree of oxidation is dependent on the type of oil, heating time and temperature. During the induction period, however, the refractive index does not change at all even though the peroxide value is gradually increasing. In the second stage of oxidation, the refractive index begins to increase at the same time as the rate of peroxide formation also suddenly increases. In the third stage of oxidation the peroxide content is decreasing while the refractive index continues to increase though at a slower rate. The refractometric method allows the end of the induction period to be accurately determined and provides a nearly linear relationship between refractive index and peroxide value in the region from 100 to 1,000 meq./Kg. (second stage). The advantage of the refractometric method over the peroxide value determination appears to be in the fact that the former measures more than just one of the oxidation products of the oil. In addition, it is both rapid, inexpensive and accurate.

A study of the autoxidation of some vegetable oils at elevated temperatures. VIII. The influence of reaction conditions on the preparation of oxidized linseed oil with optimum drying properties. J. Pokorný (Inst. of Chem. Tech., Prague). *Papers of the Inst. of Chem. Tech. Prague* **4-II**, 223–37 (1960). The drying time of linseed oil can be shortened by subjecting the oil to a previous partial oxidation, with the resultant destruction of natural antioxidants and formation of peroxides. The maximum decrease in drying time (about 40%) corresponds to the stage of oxidation in which the peroxide content of the oil reaches a maximum, while further oxidation causes the drying time to increase slightly once more. Temperature of oxidation (between 65C and 130C) has no great influence on drying time. However, drying rate is not a simple function of peroxide level, being also dependent on the rate at which oxygen is blown through the oil during the oxidation period. This indicates that other oxidation products beside peroxides also affect drying rates. The viscosity increase up to the point of maximum peroxide level is small and not reproducible, therefore it is not a suitable method for following the course of the reaction.

Kinetics of the esterification of diglycerol with stearic acid. E. Mareš and J. Pokorný (Inst. of Chem. Tech., Prague). *Papers of the Inst. of Chem. Tech. Prague* **4-I**, 275–93 (1960). The catalyzed esterification reaction between diglycerol and stearic acid is found to be a second order reaction, with the rate constant greatly affected by temperature (there is a 17-fold increase in rate going from 175C to 250C). Potassium hydroxide is used as a catalyst. A catalyst level of 0.5% (based on the stearic acid) is optimum with respect to rate of esterification, higher catalyst levels not yielding any rate advantage. During esterification, the monoester content increases to a maximum and afterwards decreases due to esterification of the remaining free hydroxyl groups and interesterification. The maximum amount of monoesters increases with decreasing ratios of fatty acid to diglycerol and depends on the reaction temperature. The activation energy of the reaction is calculated at 17,400 cal.

The determination of the peroxide value of cosmetic creams containing vegetable oils. J. Pokorný, J. Cmolík, V. Pokorná and G. Janíček (Inst. of Chem. Tech., Prague). *Papers of the Inst. of Chem. Tech. Prague* **4-II**, 297–310 (1960). The optimum conditions for the analysis of peroxide value in cosmetic creams containing 20–25% of vegetable oils (such as linseed oil, sunflower seed oil and soybean oil) are discussed. Both the weight of sample used in the analysis and the amount of water present during the reaction are found to affect results, probably because of a synergistic effect of the other components of the cream on the oxidation of potassium iodide. Details of the method are given.

The determination of the presence of hardened fats in cocoa butter. J. Pokorný, J. Smíšek, B. Kakáč and G. Janíček (Inst. of Chem. Tech., Prague). *Papers of the Inst. of Chem. Tech. Prague* **4-II**, 313–24 (1960). The presence of hydrogenated fats in cocoa butter can be detected by analysis of the *trans* fatty acid content, preferably by measurement of the optical density of a solution of the fat, since pure cocoa butter contains no more than 1% of *trans* acids. The addition of 5% or more of hydrogenated fats to cocoa butter can be ascertained by this method, with an accuracy of 100%.

A study of the chemistry of oats and its products. III. Changes in the content and properties of oat flakes lipids caused by thermal treatment. G. Janíček and J. Pokorný (Inst. of Chem. Tech., Prague). *Papers of the Inst. of Chem. Tech. Prague* **4-II**, 327-39 (1960). The chemical changes caused in the lipids of oat flakes by heating to 100–200C for 90–300 min. are described. The amount of chloroform extract of oat flakes heated to 135C or higher decreases linearly with the heating temperature. The spectral changes of the oat lipids are rather complicated, indicating the disappearance of chlorophyll and the formation of new color bodies. The determination of refractive index is not suitable as a measurement of the degrees of oxidation.

The composition of waxy substances from oat hulls. I. The composition of the glyceride portion of the extract. J. Pokorný, I. Zeman and G. Janíček (Inst. of Chem. Tech., Prague). *Papers of the Inst. of Chem. Tech. Prague* **4-II**, 343–54 (1960). Extraction of oat hulls with light petroleum fractions or chloroform yields about 1% of a greenish-brown paste-like extract. The extract contains only a small amount (5%) of unsaponifiables, mostly higher alcohols, about 25% fatty acids, probably hydroxyacids, and about 25% of even more highly polar compounds, soluble only in ethanol. The glyceride fraction of the extract contains 50% oleic acid, 25% palmitic acid and 17% linoleic acid.

Esterification of erucic acid with higher alcohols. J. Zajíc and M. Burešová (Inst. of Chem. Tech., Prague). *Papers of the Inst. of Chem. Tech. Prague* **4-II**, 275–94 (1960). The esterification of erucic acid (prepared from rapeseed oil, with an I.V. of 73 and a 30C melting point) with cetyl, stearyl and oleyl alcohols was studied. The reaction was conducted under vacuum (180 mm. Hg), at 160, 200, and 240C in the presence of catalyst. The optimum reaction conditions were found to be: catalyst, 0.5–1.5% phophoric acid; temperature, 240C; cetyl alcohol to erucic acid molar ratio, 1:1. Findings relative to rate constants, activation energy, effect of type and amount of catalyst and molar ratio of reactants are reported upon. The cetyl and stearyl esters are solid substances (m.p. respectively 40 and 48C) while the oleyl ester is liquid at 20C. Dilatation curves and penetration results of the cetyl and stearyl esters show great similarity to those of beeswax. These materials appear therefore to be suitable for the production of synthetic waxes.

Analysis of mixtures of higher aliphatic nitriles by gas-liquid chromatography. J. Pokorný and I. Zeman (Inst. of Chem. Tech., Prague). *Papers of the Inst. of Chem. Tech. Prague.* 4-II, 255–71 (1960). Mixtures of aliphatic nitriles prepared from palmitic, oleic, stearic and coconut fatty acids were analyzed by vapor phase chromatography using a microflame detector. Nitriles were found to have elution times approximately corresponding to those of the respective methyl esters. The high temperature (265C) of the analysis does not affect the results and the correction for combustion heats has only negligible influence on the values of the constants for the individual components. The $C_8$ and the $C_{10}$ components evaporated partially during the reaction and their measurements were not quantitative.

Study of castor oil hydrogenation at low temperatures. J. Hladík and J. Zajíc (Inst. of Chem. Tech., Prague). *Papers of the Inst. of Chem. Tech. Prague* 4-II, 241–52 (1960). The hydrogenation of castor oil was studied, at temperatures between 120 and 180C. The optimum conditions, from the standpoint of the stability of the hydroxyl group and of the formation of the 12-hydroxystearic acid, are: 160C and 0.5% Ni catalyst. In two hours of hydrogenation under these conditions, the I.V. was reduced from 83 to 14 and the hydroxyl value from 171 to 149. Higher temperatures and higher amounts of catalyst favor a larger loss of hydroxyl groups.

Colorimetric determination of fat peroxides by means of titanium chloride, I. G. Janíček and J. Pokorný (Inst. of Chem. Technology, Prague). *Papers of the Inst. of Chem. Tech., Prague* 3, 233–55 (1959). A method of colorimetric determination of peroxides in fats by titanium chloride in glacial acetic acid is described. In comparison to the titanium sulfate method (by Strohecker et al.) the titanium chloride method is 30–50 times more sensitive, requiring very small amounts of fat (as little as 0.1 g) for the determination. The method has good reproducibility and is simple and rapid. One single calibration curve is sufficient for all the more common oils, while special calibration curves are required for such oils as castor oil, conjugated linseed oil and tung oil. The only disadvantage is that it is necessary to observe the reaction time (20–40 seconds) strictly, since the color intensity of the pertitanic complex has a sharp maximum at this time.

II. Determination in a chloroform-propionic acid medium. J. Pokorný, J. Cmolík and G. Janíček *Ibid,* 4-II, 197–207 (1960). The previous method for colorimetric peroxide determniation was modified by replacing acetic acid with propionic acid. A directional advantage of this method is that fats are more soluble in propionic than in acetic acid and also that the colored titanium complex is somewhat more stable in this medium, thus making the previous requirement for observing the reaction time accurately (20 to 40 seconds) slightly less stringent.

III. Influence of lactic acid on results in a propionic acid medium. *Ibid,* 211–20. The addition of lactic acid to a chloroform-propionic acid mixture greatly increases the stability of the colored pertitanic complex formed during colorimetric determination of fat peroxides. The optimum reaction time is twenty minutes. The peroxide values obtained by this method are up to 50% higher than in the method without lactic acid and correlate quite well with the results obtained by the iodometric method, thus showing the reaction to be quantitative. Details of the method are discussed.

Determination of active oxygen in some cosmetic products. J. Pokorný, M. Karvánek, V. Pokorná and G. Janíček (Inst. of Chem. Technology, Prague). *Papers of the Inst. of Chem. Tech. Prague* 4-I, 319–30 (1960). A semimicro colorimetric method for the analysis of active oxygen in cosmetic products is proposed. The method employs titanium chloride as the color-forming reagent. Special procedures for preparing the sample before the analysis are recommended and details of the method are discussed. The iodometric method can also be used for cosmetic products, while the manganometric method was found unsatisfactory in some cases.

Solvent extraction of glycerine from water solutions. J. Dyr, V. Krumphanzl and J. Chudý (Inst. of Chem. Tech., Prague). *Papers of the Inst. of Chem. Tech. Prague* 4-II, 145–64 (1960). The ternary equilibrium diagrams of the systems: *n*-butanol-water-glycerine, isobutanol-water-glycerine and cyclohexanol-water-glycerine have been studied at 25-50-75C. The extraction coefficient increases with increasing temperature and with increasing glycerine concentration in the initial solution, while it decreases with the choice of solvent in the following order: *n*-butanol, isobutanol, benzyl alcohol and cyclohexanol. The two-phase region in the ternary diagram is largest with cyclohexanol and decreases with isobutanol and *n*-butanol.

The refining of oils with high free fatty acid content. J. Zajíc, J. Zalud and J. Hladík (Inst. of Chem. Tech., Prague). *Papers of the Inst. of Chem. Tech. Prague* 4-I, 253–70 (1960). When oils containing high (20% or more) levels of FFA are refined by conventional methods, excessive losses of neutral fat through saponification are encountered. Refining by solvent extraction of the FFA was studied using 96% ethanol as a solvent. The optimum conditions for extraction are found to be: ethanol to fat ratio, 1:1, or as little as 1:2 in the lower range of FFA levels; temperature, 30 to 40C. Losses through solubilization of the fat in ethanol average 0.35%. In most cases, a seven-stage extraction is required to eliminate 97–98% of the original FFA content.

Determination of carbonyl groups in oxidized fats in the presence of peroxides. J. Pokorný, J. Smíšek and G. Janíček (Inst. of Chem. Tech., Prague). *Papers of the Inst. of Chem. Tech. Prague* 4-I, 187–201 (1960). The determination of carbonyl groups (aldehydes and ketones) in oxidized fats is an important complement to peroxide value determination in rancidity studies. The hydroxylamine method generally used is subject to interference by the peroxides present in the oxidized fats, which can also oxidize hydroxylamine and thus cause results to be biased in excess. The method of carbonyl group determination in glacial acetic acid medium (according to Higuchi and Barnstein) was found to require no correction, since none of the various oxidation products examined (peroxides, hydroperoxides, esters, free fatty acids) interfere with the analysis. A modification of the method aimed at optimizing its accuracy is proposed.

Determination of the iodine value of edible oils by a modified hypochlorite method. M. Karvánek and J. Pokorný (Inst. of Chem. Tech., Prague). *Papers of the Inst. of Chem. Tech. Prague* 3, 413–425 (1959). A previous hypochlorite method for iodine value dtermination (by Mukherjee) was modified by using a sodium acetate solution in glacial acetic acid and carbon tetrachloride as a solvent. The modified method has better reproducibility and lower analytical error, while yielding results in good agreement with other methods (e.g., that of Von Mikusch and Frazier). Use of the method is not recommended in the case of drying oils, where consistently low results are obtained.

Relation between the fatty acid composition of hardened fats and their physico-chemical and technical properties. J. Pokorný (Inst. of Chem. Tech., Prague). *Papers of the Inst. of Chem. Tech. Prague* 3, 347–407 (1959). Hydrogenation of peanut oil and soybean oil is described in relation to its effects on melting point, dilatation, penetration, refractive index, isoleic acid formation, stability, specific gravity. The rate of hydrogenation of soybean oil is found to be approximately twice as high as that of peanut oil, all other conditions being equal. The determination of refractive index or iodine value as indices of dilatation changes is valid only if selectivity and rate of isoleic acid formation are constant and the initial fatty acid composition of the oil does not vary.

A study of the preparation of fats with properties similar to those of cocoa butter. I. Hardening of vegetable fats. G. Janíček and J. Pokorný (Inst. of Chem. Tech., Prague). *Papers of the Inst. of Chem. Tech. Prague* 3, 301–42 (1959). Simple hydrogenation of coconut oil, palm oil or palm kernel oil is not sufficient to produce a satisfactory cocoa butter substitute. Hydrogenated coconut oil has the steepest dilatation curve of the three oils examined, coming close to matching cocoa butter in this respect; however, its melting point remains lower, even after *full* hydrogenation, than that of cocoa butter. Hydrogenated palm kernel oil has a less steep dilatation curve but a melting point (37.9C) closer to cocoa butter. Palm oil is definitely unsuitable as a cocoa butter substitute because of its much flatter dilatation curve and excessive content of glycerides melting above 100F.

A study of autoxidation of some vegetable oils at elevated temperatures. VI. Autoxidation of blown linseed oil in films. J. Pokorný (Inst. of Chem. Tech., Prague). *Papers of the Inst. of Chem. Tech* 3, 261–293 (1959). The kinetics of the autoxidation reaction of blown linseed oils was studied. Blown oils are so deeply oxidized that their peroxide content is relatively high and there is not a sufficient amount of fatty acids capable of being oxidized to fully utilize the ability of hydroperoxides to initiate the chain reaction. Consequently, oxidation velocity cannot increase proportionally to peroxide content and autoxidation proceeds as a first order reaction. When blown oils are heated to 65–130C in inert atmosphere to decompose their peroxides and subsequently caused to autoxidize, the reaction proceeds as an autocatalytic second order reaction with a lower initial rate. Once a sufficient amount of peroxides has been formed, the reaction changes again to the first order and the reaction course loses its autocatalytic character.

VII. THE COLOR CHANGES OF BLOWN OILS IN RELATION TO REACTION CONDITIONS AND METHOD OF MEASUREMENT. *Ibid,* 4-I, 205–247 (1960). The color changes of refined and unrefined linseed oil during autoxidation at 70, 100, 130C were measured by colorimetric and spectrophotometric methods. The dominant wavelengths were practically unaffected by oxidation (less than 8 mμ). The optical density at 450 mμ increases sharply at the beginning, reaching a maximum during the induction period, after which it falls rapidly to a value lower than in the original oil at the end of the induction period. Further oxidation causes the optical density to increase again.

A STUDY OF THE CHEMICAL COMPONENTS OF OAT AND ITS PRODUCTS. I. OAT LIPIDS. G. Janíček and J. Pokorný (Inst. of Chem. Tech., Prague). *Papers of Inst. of Chem. Tech. Prague* 3, 503–20 (1959). The properties of lipid fractions of oat extracts were examined after successive extractions with petroleum ether and methanol, before hydrolysis, and with petroleum ether and chloroform after it. A total of approximately 5% fatty acids was found in the four extractions, about 70% of the total being found in the first extraction of oatmeal with petroleum ether. The petroleum ether extract contained 55.6% oleic acid, 33.1% linoleic acid and 12.1% palmitic acid. Only a small percentage of fatty acids came from the hulls, the bulk being found in the hull-free grain. Stability of the oat extracts was comparable to that of rapeseed oil.

II. THERMALLY STABLE ANTIOXIDANTS IN OAT. J. Supová, J. Pokorný and G. Janíček, *Ibid,* 525–44. The antioxidant effect on lard of various oat extracts was studied. Extractions were carried out with methanol, petroleum ether, water and benzene, and the extracts added to lard at the 0.5–1.0% level. Rate of fat oxidation was measured by the increase in peroxide number with time of aeration at 100C. All of the oat extracts exhibited some antioxidant properties increasing the stability of lard by 50 to 100%. The highest activity was found with the lipid-free methanolic extract of oatmeal. The antioxidant effect of these oatmeal extracts is however only one fifth as large as that of propyl gallate.

PARTIAL OXIDATION OF UNSATURATED FATTY ACIDS BY PERIODIC ACIDS AND OTHER PERACIDS. F. D. Gunstone and P. J. Sykes (Univ. of St. Andrews, Fife). *Riv. Ital. Sostanze Grasse* 11, 561–7 (1962). Partial oxidation of unsaturated fatty acids by means of peracids has been studied with two main objectives: as an improved method for determining the position of double bonds in polyunsaturated acids and as a means for distinguishing methylene-interrupted polyene acids (such as linoleic) from monoethenoid acids, such as oleic. The attainment of the first objective and some interesting results in connection with the second are described.

QUANTITATIVE GAS CHROMATOGRAPHY OF BUTTER FATTY ACIDS WITH PROGRAMMED FLOW. S. Valussi and G. Cofleri (Trieste). *Riv. Ital. Sostanze Grasse* 12, 617–9 (1962). Gas chromatography of butter fatty acids with linearly increasing programmed flow (from 10–30 to 60–110 cc./min.) is found to give good results in the quantitative analysis of low molecular weight fatty acids whose peaks are thus well separated and nearly equidistant.

CYCLOTRITERPENIC ALCOHOLS, MINOR CONSTITUENTS OF VEGETABLE OILS. G. Jacini and P. Capella (Staz. Sperim. Oli e Grassi, Milan). *Riv. Ital. Sostanze Grasse* 12, 620–3 (1962). The substances responsible for the F peak in the chromatogram of the unsaponifiable of several vegetable oils have been found to consist of two parts, one of which is precipitated by digitonin and one is not. The digitonin precipitate, that was previously thought to be a mixture of sterols, was analyzed and found to be a mixture of cyclotriterpenic alcohols.

HYDRATION OF SOYBEAN PHOSPHATIDES. A. Jakubowski (Institut Przemyslu Tluszczowego, Warsaw, Poland). *Riv. Ital. Sostanze Grasse* 10, 512–6 (1962). A study of phospholipid hydration (the process through which phospholipids are precipitated from crude oils) confirms the hypothesis of formation of a double monomolecular layer made up of water and phospholipids plus glycerides, provided the minimum amount of water necessary for the process is used. This minimum quantity of water necessary to hydrate the phospholipids depends on the type of phosphatide present, in the case of lecithin being approximately eight moles for each P atom.

THE EFFECT OF REFINING ON THE VISIBLE SPECTRUM OF EDIBLE OILS. M. T. Giordano and V. Pennati (Enologic Bureau, Genoa). *Olearia* 5-6, 168–70 (1962). Refining of edible oils induces alterations in the coloring substances that can be observed by spectrophotometry. In particular, the absorption maximum of chlorophyll in the visible spectrum is shifted from 670 mμ to lower values. This effect is always encountered after deodorizing but not after neutralization of the oil's acidity.

CHROMATOGRAPHIC STUDIES ON ESTERFIED OLIVE OILS. G. Bigoni (Gaslini S.p.A., Genoa). *Riv. Ital. Sostanze Grasse* 9, 428–31 (1962). Bromination of the methyl esters of olive oil is found to increase the structural differences between *cis* and *trans* isomers of oleic acid, thus affording the possibility of quantitatively determining the *trans* acid content of olive oil by gas chromatography. By applying this method, the conclusion is reached that *trans* acid content cannot be used as an index of esterification of the oil, since untreated solvent-extracted olive oil contains approximately the same amount of *trans* acid as esterified oils.

IDENTIFICATION BY GAS CHROMATOGRAPHY OF MINOR FATTY ACIDS PRESENT IN OLIVE OIL. D. Grieco (Chem. Lab. of Grain Association, Milan). *Riv. Ital. Sostanze Grasse* 9, 432–8 (1962). Gas chromatograms of olive oils of different origins indicate that the presence and concentration of minor fatty acids may vary with the sample and the analytical technique employed. Linolenic, arachidic and eicosenoic acids are always present, in maximum concentrations, respectively, of 0.9%, 0.5% and 0.1%. Lauric, myristic, behenic and lignoceric acids are sometimes present as traces. The presence of two fatty acids with 17 C atoms has been established: the heptadecanoic acid is present up to the 0.1% level and the heptadecenoic acid up to the 0.2% level.

CHANGES IN THE LIPID CONTENT OF ALMONDS DURING THE RIPENING OF THE FRUIT. C. Galoppini e G. Lotti (Univ. of Pisa, Italy). *Olearia* 5-6, 164–7 (1962). During maturation of the *Prunus Amygalus S* (a variety of almond) the saponification number remains practically constant, while the I.V. diminishes gradually from about 106 (April) to about 94 (September) and the refractive index also becomes lower. Oleic acid constitutes about 80% of the total lipids at the end of the period, while linoleic acid, initially present at the 35% level, drops to approximately 15%.

STUDY OF GREEK OLIVE OIL. VI. OLIVE OIL CROP, 1961-1962. Anon. (Ministry of Commerce, Kingdom of Greece, Special Experimental Lab., Canningos Sq., Athens, Greece). 85 pp., 35 tables (1962). Analyses are given for 518 samples of olive oil from all producing districts in Greece. Oil from short-sized kernel olives was of lower iodine value than oil from larger-sized kernel olives. Variations in climatic conditions had no effect on oil properties.

COLOR REVERSION IN SAPONIFICATION. ELIMINATION OF REVERSION PRODUCTS BY SALTING OUT. M. G. Lechartier (Lab. Jean Ripert, Paris, Fr.). *Rev. Franc. Corps Gras* 10, 19–23 (1963). It has been shown that by salting out, using a suitable salt concentration, and the successive washing of the different phases used in the manufacture of soap (saponification, cooking, liquidation, etc.) an improvement in the color of finished soap can be accomplished. Oxidized acids which are responsible for color reversion are removed with the salting out procedure.

COMPARATIVE STUDY OF THE INFLUENCE OF CERTAIN PHYSICAL AND CHEMICAL FACTORS UPON THE PEROXIDE AND CARBONYL VALUE. F. Birden, Y. Lauchard and M. Loury (Lab. J. Ripert, Inst. Corps Gras, Paris, Fr.). *Rev. Franc. Corps*

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*Gras* 10, No. 2, 79–85 (1963). In order to better understand the practical significance of the carbonyl value, the authors have been able to demonstrate by this study that the variation of the carbonyl value under the influence of various chemical and physical factors is much smaller than that of the peroxide value under the same conditions. The carbonyl value consequently represents to a better degree the alteration of fatty materials.

## • *Fatty Acid Derivatives*

STEREOISOMER FORMATION ON THE OZONIZATION OF ESTERS OF MONOUNSATURATED FATTY ACIDS. O. S. Privett and E. C. Nickell (Univ. of Minnesota, The Hormel Inst., Austin, Minn.). *J. Lipid Res.* 4, 208–211 (1963). The formation of stereoisomers of ozonides on the ozonization of methyl esters of monounsaturated fatty acids in pentane at −70C was demonstrated by thin-layer chromatography, infrared spectra, and other analyses. The *cis*- and *trans*-isomers of ozonides of *cis*- and *trans*-methyl 9-octadecenoates (methyl oleate and methyl elaidate) were isolated and characterized.

THE SYNTHESIS OF KETONES FROM ACID CHLORIDES WITH THE HELP OF ALUMINUM ALKYLS. H. Bertsch and H. Reinheckel (Inst. Fettchemie, Deut. Akad. Wissenschaften, Berlin-Adlershof). *Fette Seifen Anstrichmittel* 64, 881–886 (1962). A number of aliphatic and some aromatic acid chlorides were treated with ethyl aluminum-sesquichloride in aliphatic hydrocarbons as the solvent. The corresponding ethyl ketones were formed in yields of 80 to 85%. The behavior of dicarboxylic acid half-ester chlorides and dicarboxylic acid dichlorides and the influence of other reaction conditions as well as other ethyl aluminum compounds were investigated. The synthesized compounds were: hexanone-3, octananone-3, decanonane-3, dodecanone-3, teradecanone-3, hexadecanone-3, octadecanone-3 and eicosanone-3. The following keto esters were synthesized: 10-ketolaurate, and 6-ketocaprate (methyl esters). Tetradecadione-3,12,- was also prepared. Complete physical constants and constants of derivatives are given. The preparation of various aluminum alkyls is also given.

DIELS ALDER REACTIONS IN THE FIELD OF FATS: II: THE REACTION OF DRYING OILS WITH ETHYLENE AND ITS HOMOLOGUES. H. P. Kaufmann and F. J. Buscher (Deut. Inst. Fettforsch, Münster). *Fette Seifen Anstrichmittel* 65, 105–108 (1963). Methyl esters of conjugated acids were reacted with ethylene, propylene, and butylene at high pressure and high temperature. The Diels Alder adduct was then transformed into the corresponding aromatic systems. Conjugated polyene oils were also subjected to these reaction conditions. Infrared spectra are given. The adducts prepared were: 1-carbomethexy-4-methyl-cyclohexene 5, the 2,4-dimethyl acid; the 2-ethyl-4-methyl derivative; 1-(carbomethoxy-n-heptyl)-(4-n-hexyl)-cyclohexene-5, the 4-n-hexen-1-yl, 2-methyl-4-(n-hexen-1-yl)-, and the 2-ethyl-4-(n-hexen-1-yl)- derivatives.

HIGHLY UNSATURATED FATTY ACID CHLORIDES. H. P. Kaufmann and E. Gulinsky (Deut. Inst. Fettforschung, Münster), *Fette Seifen Anstrichmittel* 64, 599–601 (1962). The chlorides of linolenic acid, α- and β-elaeostearic acid, and α-parinaric acid were prepared using phosgene and pyridine with appropriate solvents. The rates of autoxidation of these compounds were determined and compared to those of the corresponding acids and methyl esters.

BIS-CYANOETHYLATION OF FATTY AMINES. I. SYNTHESIS OF BIS(β-CYANOETHYL)CETYLAMINE. Seimei Nitanai and Yasuo Saito (Toyo Koatsu Co., Hokkaido). *Yukagaku* 12, 154–8 (1963). The cyanoethylation reaction of cetylamine was investigated. The velocity of formation of monocyanoethyl compound was very rapid. The reaction for formation of bis(cyanoethyl) compound took place after the monocyanoethylation reaction. The formation of the bis-compound was very slow without the solvent. The velocity for formation of bis-compound in polar solvents, such as methanol or ethanol, was very rapid and the yield was quantitative in some cases. The reaction in the non-polar solvent, such as benzene or toluene, gave the mono-compound only and little or no bis-compound. The reaction in methanol in the presence of sodium hydroxide gave quantitative yield of mono-compound. The reaction in methanol was not influenced by the addition of acetic acid.

HYDROXYMETHYLATION OF TALL OIL ROSIN. Choichiro Hirai, Kazumitsu Suzuki, and Taro Matsumoto (Nihon Univ., Tokyo). *Yukagaku* 12, 149–53 (1963). Abietic acid concentrated from tall oil rosin was made to react with formaldehyde for 30–60 minutes in acetic acid or propionic acid to give 8,9-bis(methyleneacetoxy)-abietic acid; the cyclohexylamine salt, m. 180C. Hydrolysis of this compound gave 8,9-dihydroxymethylabietic acid, m. 192–3C. The reaction of tall oil rosin with formaldehyde in the absence of carboxylic acid or inert solvent such as dioxane and benzene did not occur, but the condensation of tall oil rosin with formaldehyde was promoted in the presence of a small amount of acetic acid, or even in higher fatty acid. The above reaction was also carried out in the presence of hydrochloric acid, but this yielded large amounts of ether-insoluble matter.

## • Biology and Nutrition

ENZYMATIC SYNTHESIS OF CYCLOPROPANE FATTY ACIDS CATALYZED BY BACTERIAL EXTRACTS. H. Zalkin, J. H. Law, and H. Goldfine (James Bryant Conant Lab., Harvard Univ., Cambridge 38, Mass.). *J. Biol. Chem.* 238, 1242–1248 (1963). Extracts of either *Serratia marcescens* or *Clostridium butyricum* are capable of forming labeled cyclopropane fatty acids when they are incubated with S-adenosylmethionine labeled in the methyl group. Methionine itself is not an effective precursor; neither are other 1 carbon donors such as formate, formaldehyde, and serine. The enzyme system of *Serratia marcescens* contains endogenous lipid substrates for this reaction which cannot be removed or replaced by simple manipulations. Various unsaturated fatty acid derivatives fail to enhance the rate of the reaction. Operations which are ordinarily employed to remove small cofactor molecules from enzymes do not diminish the rate of reaction catalyzed by these extracts.

RAPID APPEARANCE OF INJECTED FAT IN THE GUT OF A RAT. D. J. Wilkins (New England Inst. for Med. Res., Ridgefield, Conn.). *Proc. Soc. Exp. Biol. Med.* 112, 953–955 (1963). Oil emulsions containing a fluorescent dye were given intravenously to rats. Rate of removal from the blood stream was typical for reticuloendothelial clearance of a colloid. The emulsion accumulated in the liver but appeared in the bile duct and duodenum within minutes after injection. Approximately one-half of the dye was found in the intestinal contents.

CARCINOGENIC EFFECT OF EGG WHITE, EGG YOLK AND LIPIDS IN MICE. J. Szepsenwol (Dept. of Anatomy, Univ. of Puerto Rico School of Med., San Juan). *Proc. Soc. Exp. Biol. Med.* 112, 1073–1076 (1963). Mice of the T. M. Strain were maintained from the age of 4 weeks on the Rockland rat diet (Group 1) supplemented with hard boiled egg white (Group 2), raw egg yolk (Group 3) or with cholesterol and lard (Group 4). In one series of experiments males and females were caged separately, while in the other one they were bred and their offspring maintained on the same diets. Each of the groups of the second series of experiments consisted of mice from 3 to 4 successive generations. The results were: The mice of Groups 2 and 3 developed a very high incidence of lymphosarcoma and lung adenocarcinoma. The mice of Group 3 developed, also a relatively high incidence of mammary cancer (33% of the breeding females) which did not appear in the animals of Group 2 nor in the controls. Incidence of mammary cancer was particularly high in the mice of Group 4. From these results it appears that both egg white and egg yolk are carcinogenic, but that their carcinogenicity differs. A carcinogenic substance causing the development of lymphosarcomas and lung adenocarcinomas, would be present in both, while a mammary carcinogen, lipid in nature, is present in the yolk only.

RUMINANT FAT METABOLISM WITH PARTICULAR REFERENCE TO FACTORS AFFECTING LOW MILK FAT AND FEED EFFICIENCY. A REVIEW. P. J. Van Soest (Animal Husbandry Res. Div., Agr. Res. Service, USDA, Beltsville, Md.). *J. Dairy Sci.* 46, 204–216 (1963). Up to the present time, ruminant nutrition research has followed two principal lines of development. On the one hand, there are feeding experiment studies which deal with input-output measurements, digestibility, and efficiencies. On the other hand, there are numerous biochemical studies dealing with rumen, rumen absorption, and intermediary metabolism. The biochemical approach offers a means of explaining and understanding the observations made from feeding experiments, but research in this area has really only begun. Certain phenomena, such as low milk fat on various rations, offer opportunities to learn more about little-known aspects of ruminant metabolism. The intermediary steps involved in the production of milk solids represent one area in which further research is badly needed. It is proposed here to review the literature on low milk fat and certain environmental and physiological factors known to affect the fat content of milk, and to compare these conditions in light of their apparent effects on the over-all efficiency and performance of cattle.

ESSENTIAL FATTY ACID DEFICIENCY AND RAT LIVER HOMOGENATE OXIDATIONS. J. Smith and H. E. DeLuca (Dept. of Biochem., Univ. of Wisconsin, Madison). *J. Nutr.* **79**, 416–422 (1963). Essential fatty acid deficiency (EFA) in rats, whether induced by a diet containing no fat or a large quantity of saturated fat, results in an increased oxidation of practically all of the citric acid cycle intermediates, pyruvate, and caprylate by liver homogenates. This increase was detectable after rats were fed a high fat diet for two weeks, and a fat-free diet for four weeks. These elevated oxidative rates were reduced to the normal range within one week after feeding a source of EFA. Fractionation of liver homogenates revealed that the greatest effect of EFA deficiency is associated with the debris fraction. However, the isolated mitochondria from deficient rats showed an increased oxidation rate when the results were expressed on an equivalent nitrogen basis.

PURIFICATION OF HUMAN PLASMINOGEN AND PLASMIN BY GEL FILTRATION ON SEPHADEX AND CHROMATOGRAPHY ON DIETHYLAMINOETHYL-SEPHADEX. K. C. Robbins and L. Summaria (Biochem. Res. and Development Dept., Michael Reese Res. Foundation, Chicago 16, Ill.). *J. Biol. Chem.* **238**, 952–962 (1963). Plasminogen can be prepared in a highly purified form from human plasma Fraction III$_{2,3}$ by a modification of the Kline method followed by either gel filtration through Sephadex columns or chromatography on DEAE-Sephadex columns, with starting agent development conditions. The major modification of the Kline method was to precipitate the plasminogen, in the final step, at pH 6.0, with NaH$_2$PO$_4$. Plasminogen, of the same purity, can also be prepared by directly chromatographing extracts of plasma Fraction III$_{2,3}$ on DEAE-Sephadex columns.

STRUCTURE AND SYNTHESIS OF MILK FAT. IV. ROLE OF THE MAMMARY GLAND WITH SPECIAL REFERENCE TO THE CHOLESTEROL ESTERS. S. Patton and R. D. McCarthy (Dept. of Dairy Sci., Penn. State Univ., University Park). *J. Dairy Sci.* **46**, 396–400 (1963). The extent to which milk lipids are synthesized within the mammary gland is not known. The objective of the research was to provide a better definition of what the gland accomplishes, as distinguished from what may be contributed by lipid metabolism in the rest of the body. Using intramammary infusion of both labeled and unlabeled fatty acids, it was demonstrated that cholesterol esters, glycerides, and phospholipids of milk are all made from fatty acids within the gland. Diverse evidence from this and other studies suggests that most, if not all, of the ester lipids of milk are synthesized from a common pool of fatty acids within the mammary gland. A remarkably active metabolic role is indicated for the cholesterol esters of milk. In the case of both labeled (palmitate-1-C$^{14}$) and unlabeled (linoleate) infusates, uptake by the cholesterol ester fraction was more intense and, by tracer, more rapid than for the glycerides or phopholipids. Some compositional data on cholesterol esters of milk are also presented.

MACRO- AND MICROMETHODS FOR THE DETERMINATION OF SERUM VITAMIN A USING TRIFLUOROACETIC ACID. J. E. Neeld, Jr. and W. N. Pearson (Div. of Nutrition, Dept. of Biochem. and Med., Vanderbilt Univ., School of Med., Nashville, Tenn.). *J. Nutr.* **79**, 454–462 (1963). A new method for the determination of plasma or serum vitamin A levels which uses trifluoroacetic acid (TFA) as the chromogen is described. This reagent produces a typical Carr-Price color but does not exhibit the turbidity or film-forming properties of SbCl$_3$ in the presence of moisture. The new procedure gives values that agree well with those obtained by the Carr-Price method when rat, porcine, or human sera are analyzed. Significantly higher values are obtained with TFA, however, when bovine sera were analyzed. A micro- modification of the method permitting the analysis of 50 $\mu$l of serum is described and its advantages over existing methods are discussed.

VITAMIN A AND CHOLESTEROL ABSORPTION IN THE CHICKEN. B. E. March and J. Biely (Dept. of Poultry Sci., Univ. of British Columbia, Vancouver, Canada). *J. Nutr.* **79**, 474–478 (1963). The administration of large amounts of vitamin A to 6- to 7-week-old chickens reduced the increase in serum cholesterol level resulting from the inclusion of 1% of cholesterol in the diet. Vitamin A did not, however, moderate the hyperlipemia and hypercholesterolemia produced in birds fed a low cholesterol diet and treated with diethylstilbestrol. Large doses of vitamin A reduced the level of cholesterol in the intestinal wall and in the liver of birds fed 1% of cholesterol. Conversely, birds receiving large amounts of vitamin A and 1% of cholesterol in the diet did not store as much vitamin A in the liver as birds receiving the same amount of vitamin A in conjunction with a diet low in cholesterol. It is concluded that there is mutual interference between vitamin A and cholesterol during the course of absorption across the intestinal wall.

METABOLISM OF GLYCEROLIPIDS. III. REACTIVITY OF VARIOUS ACYL ESTERS OF COENZYME A WITH $\alpha'$-ACYLGLYCEROPHOSPHORYLCHOLINE, AND POSITIONAL SPECIFICITIES IN LECITHIN SYNTHESIS. W. E. M. Lands and I. Merkl (Dept. of Biol. Chem., Univ. of Michigan, Ann Arbor). *J. Biol. Chem.* **238**, 898–903 (1963). Rat liver microsomes catalyze the transfer of acids from their acyl coenzyme A derivatives to the $\beta$-hydroxyl group of $\alpha'$-acylglycerophosphorylcholine to form lecithin. The unsaturated acyl coenzyme A esters react more rapidly than the saturated derivatives. Hydrolysis of acyl coenzyme A in this system does not appear to be due to transfer of the acyl group to water by the acyl transferase, but rather to a separate hydrolytic enzyme with different kinetic properties. This microsomal system can be used to estimate the relative content of the positional isomers in acylglycerophosphorylcholine preparations. Results with mixed acylglycerophosphorylcholine acceptors indicate that the acyl transfer occurs with a preferential esterification of saturated fatty acids with the $\alpha'$-hydroxyl group and unsaturated acids with the $\beta$-hydroxyl group.

IV. SYNTHESIS OF PHOSPHATIDYLETHANOLAMINE. I. Merkl and W. E. M. Lands. *Ibid*, 905–906. Stereospecifically labeled radioactive diacylglycerophosphorylethanolamine may be synthesized from either $\alpha'$- or $\beta$-acylglycerophosphorylethanolamine by use of a rat liver microsomal preparation. Linoleate was a better substarte than stearate in esterifying $\alpha'$-acylglycerophosphorylethanolamine, whereas the reverse was true with the $\beta$-acyl precursor.

INITIAL REACTIONS IN THE METABOLISM OF D- AND L-GLYCERALDEHYDE BY RAT LIVER. B. R. Landau and W. Merlevede (Dept. of Med. and Biochem., Western Reserve Univ., Cleveland 6, Ohio). *J. Biol. Chem.* **238**, 861–867 (1963). Marked activity in carbon atoms 3 and 4 of glucose from glycogen was observed when D-glyceraldehyde-3-C$^{14}$ was a substrate. This indicates that an initial step in D-glyceraldehyde metabolism is reduction to glycerol. With D-fructose-6-C$^{14}$ as substrate, activity was primarily in carbon atoms 1 and 6 of the glucose, indicating the if D-glyceraldehyde is formed from fructose within the liver, it is not reduced to glycerol but rather enters the Embden-Meyerhof pathway via glyceraldehyde phosphate. Both L-sorbose-6-C$^{14}$ and L-glyceraldehyde-3-C$^{14}$ yield glucose labeled primarily in carbon atoms 1 and 6 with more activity in carbon 6 than carbon 1. This suggests that L-glyceraldehyde presented to the liver and that formed from L-sorbose within the liver traverse the same pathways.

METABOLISM AND BIOLOGICAL ACTIVITY OF VITAMIN A ACID IN THE CHICK. S. Krishnamurthy, J. G. Bieri and E. L. Andrews (Lab. of Nutr. and Endocrinology, Nat'l Inst. of Arthritis and Metabolic Diseases, NIH, Bethesda, Md.). *J. Nutr.* **79**, 503–510 (1963). The amount of vitamin A acid required to prevent vitamin A deficiency symptoms in chicks depended upon the time dosing began relative to the onset of symptoms. The acid was found to have a sparing action on vitamin A in the body. When vitamin A acid was the only source of the vitamin in the diet, chicks grew and developed normally during a 6-week experimental period. When the acid was given in daily oral doses, amounts up to 100 $\mu$g would not completely prevent development of ocular or central nervous system lesions, although growth was normal. When a large oral dose was given, the unchanged vitamin A acid could be detected in the tissue up to 18 hours, but not after this time. No other form of vitamin A was detected. The acid was found to be concentrated primarily in the microsomal fraction of liver. Experiments with C$^{14}$ vitamin A acid confirmed the rapid metabolism or destruction which begins in the digestive tract. Four radioactive fractions, based on solubility, were prepared from chicken liver after a dose of $C^{14}$ vitamin A acid. Two of these represented the unchanged acid while a third fraction, fat soluble, gave no reaction with antimony trichloride. A fourth fraction was water soluble. In a rat curative assay, the third fraction had biological activity but fraction 4 did not. No evidence was obtained for the conversion in the body of vitamin A acid to the aldehyde or alcohol.

BIOSYNTHESIS OF BRANCHED CHAIN FATTY ACIDS. I. ISOLATION AND IDENTIFICATION OF FATTY ACIDS FROM BACILLUS SUBTILIS (ATOC 7059). T. Kaneda (Research Council of Alberta, Edmonton, Alberta, Canada). *J. Biol. Chem.* **238**, 1222–1228 (1963). Six branched chain fatty acids and two straight chain fatty acids have been isolated from *Bacillus subtilis* (ATOC 7059) grown on a glucose-yeast extract-Bacto-peptone medium. The identification of the fatty acids was carried out by gas-liquid chromatography and by their infrared spectra, x-ray diffraction, melting points, and neutralization values. The fatty acids identified are 12-methyltetradecanoic, 14-methylhexadecanoic, isopentadecanoic, isopalmitic, palmitic, isoheptadecanoic, isomyristic, and myristic, in order of abundance.

INFLUENCE OF DIETARY VITAMIN E AND SELENIUM ON DISTRIBUTION OF $SE^{75}$ IN THE CHICK. L. S. Jensen, E. D. Walter and J. S. Dunlap (Dept. of Poultry Sci. and Veterinary Pathology, Washington State Univ., Pullman). *Proc. Soc. Exp. Biol. Med.* **112**, 899–901 (1963). Three-week-old chicks fed either a vitamin E deficient or supplmented diet were intraperitoneally injected with $Se^{75}$, and distribution of the isotope was determined in various tissues at 24, 48, and 168 hours after injection. Similarly, 2-week-old chicks fed a selenium deficient or supplemented diet were given an oral dose of $Se^{75}$ and the distribution of the isotope in several tissues was determined at 24 and 168 hours after administration. Vitamin E had no effect on distribution of selenium, but selenium itself had a marked effect on the uptake and retention of radioselenium. One-half of the dose was retained by selenium-deficient chicks at 7 days, whereas only ⅕ of the dose was retained by chicks fed 1 ppm selenium from day-of-age. Considerable selenium was deposited and retained in the cerebellum of chicks even though this element cannot prevent encephalomalacia.

COMPOSITION OF DIETARY FAT AND THE ACCUMULATION OF LIVER LIPID IN THE CHOLINE-DEFICIENT RAT. A. Iwamoto, E. E. Hellerstein and D. M. Hegsted (Dept. of Nutr., Harvard School of Public Health, Boston, Mass.). *J. Nutr.* **79**, 488–492 (1963). Under the conditions used, a two-week assay period and with a diet containing 12% casein, the accumulation of liver lipid in the choline-deficient rat appears to be inversely related to the degree of unsaturation of the dietary fat. The composition of the fat, rather than the amount in the diet, was th emajor factor influencing the amount of liver lipid. The results obtained are, however, dependent upon the basal diet used and the duration of the experiment. The similarity of the conclusions reached in these studies with those relating dietary oils to serum cholesterol in man indicate that possibly similar factors are involved.

PROTEIN, CARBOHYDRATE AND FAT CONTENT OF THE DIET OF THE RAT AS RELATED TO GROWTH. E. E. Howe and E. W. Gilfillan (Merck Inst. for Therapeutic Res., Rahway, N. J.) *J. Nutr.* **79**, 395–398 (1963). Addition of 9% corn oil to the diet of rats receiving suboptimal protein and corn starch as a source of carbohydrate decreased food consumption and depressed growth. These effects were not observed if glucose replaced starch in the diet. Improvement of the protein of the diet, quantitatively or qualitatively, eliminated the difference in performance of animals receiving starch and glucose. Replacement of corn oil by other fats caused growth depression of rats receiving a starch diet. Linseed oil and cod liver oil also caused a growth depression in glucose low-protein diets. Addition of chlortetracycline eliminated the growth-depressing effect of adding corn oil to the diets of low-protein starch fed rats. Oxytetracycline, penicillin, neomycin, streptomycin and succinylsulfathiazole were less effective or without effect.

LIPID ANTIOXIDANT ACTIVITY IN TISSUES AND PROTEINS OF SELENIUM-FED ANIMALS. J. W. Hamilton and A. L. Tappel (Div. of Agr. Biochem., Univ. of Wyoming, Laramie, Wyoming and Dept. of Food Sci. & Tech., Univ. of Calif., Davis). *J. Nutr.* **79**, 493–502 (1963). Lipid antioxidant activity of lipid-free tissue fractions, from control and selenium-fed chickens, rats, and sheep was studied. Animals were fed 10 or 14 ppm of selenium supplied either as sodium selenite or sodium selenate added to a nutritionally adequate basal ration. Antioxidant activities of the tissue fractions were tested by manometric and polarographic techniques. Kidney fraction from sheep contained the highest antioxidant activity. Antioxidant activity was shown to be associated with the tissue selenoproteins. Selenium antioxidants were found to possess 500 times the antioxidant activity of α-tocopherol by the polarographic method and 50 to 100 times in the manometric method. Synergism between α-tocopherol and the tissue selenium was not large.

STUDIES OF CHOLESTEROL BIOSYNTHESIS. IV. REDUCTION OF LANOSTEROL TO 24,25-DIHYDROLANOSTEROL BY RAT LIVER HOMOGENATES. J. Avigan, D. W. S. Goodman, and D. Steinberg (Lab. of Metabolism, Nat'l Heart Inst., Bethesda 14, Md.). *J. Biol. Chem.* **238**, 1283–1286 (1963). The anaerobic reduction of labeled lanosterol, biosynthetically prepared from 2-$C^{14}$-mevalonic acid, to 24,25-dihydolanosterol has been demonstrated with rat liver homogenates. Enzymatic activity was associated with cell particles, mostly with microsomes, and required reduced triphosphopyridine nucleotide. The enzyme was completely inhibited on addition of N-ethylmaleimide or *p*-chloromercuribenzoate, and did not require a divalent cation for activity. Attempts to demonstrate the reversibility of side chain reduction of lanosterol during both anaerobic and aerobic incubations were not successful. Triparanol and two other inhibitors of cholesterol biosynthesis blocked the reduction of both lanosterol and desmosterol *in vitro*. Unlabeled lanosterol or desmosterol added to the incubation medium caused a comparable inhibition of reduction of $C^{14}$-lanosterol. It is possible that a single enzyme is responsible for the reduction of both sterol substrates.

V. THE TIME COURSE AND PATHWAY OF THE LATER STAGES OF CHOLESTEROL BIOSYNTHESIS IN THE LIVERS OF INTACT RATS. D. W. S. Goodman, J. Avigan and D. Steinberg. *Ibid*, 1287–1293. Studies have been conducted of the time course of the distribution of radioactivity in rat liver nonsaponifiables at several short intervals after the intravenous injection of 2-$C^{14}$-DL-mevalonic acid. Recently developed thin layer chromatographic techniques were employed that permit separation of many of the sterol intermediates in cholesterol biosynthesis. Both normal and triparanol-fed rats were studied, and biochemical techniques were used to aid in the identification of some of the intermediate compounds. The evidence presented suggests that the radioactivity in the intermediate zone from normal rats was contained in a $C_{28}$ sterol mixture containing compounds with both saturated and unsaturated side chains. The results also indicate that in normal rats no significant radioactivity was contained in $\Delta^{7,24}$-cholestadienol or in zymosterol, whereas major amounts of radioactivity were present in one or both of these compounds in triparanol-treated rats.

THE CONDENSATION REACTION OF FATTY ACID BIOSYNTHESIS. II. REQUIREMENT OF THE ENZYMES OF THE CONDENSATION REACTION FOR FATTY ACID SYNTHESIS. P. Goldman, A. W. Alberts, and P. R. Vagelos (Enzyme Sec., Lab of Cellular Physiology, Nat'l Heart Inst., NIH, Bethesda 14, Md.). *J. Biol. Chem.* **238**, 1255–1261 (1963). Soluble bacterial synthetase systems from *Clostridium kluyveri* and *Escherichia coli* have been shown to catalyze the synthesis of long chain fatty acids from malonyl coenzyme A, acetyl coenzyme A, and reduced triphosphopyridine nucleotide. Saturated fatty acids are produced in the system from *C. kluyveri* where a requirement for flavin mononucleotide and an unidentified cofactor have been found, whereas in the *E. coli* system both saturated and unsaturated fatty acids are produced. The two synthetase systems have been fractionated, and over-all fatty acid synthesis has been shown to be dependent on the same heat-stable and heat-labile enzymes that catalyze the condensation reaction as measured by the malonyl coenzyme A-$CO^2$ exchange reaction. In contrast, the synthesis of butyrate in *C. kluyveri* extracts requires neither malonyl coenzyme A nor the enzymes that catalyze the condensation reaction.

THE INCORPORATION OF LABELED PALMITIC ACID INTO THE PHOSPHOLIPIDS OF NORMAL AND FATTY LIVERS. J. L. Glenn, E. Opalka, and K. Tischer (Dept. of Biochem., Albany Med. College of Union Univ., Albany 8, N. Y.). *J. Biol. Chem.* **238**, 1249–1254 (1963). Palmitic acid-1-$C^{14}$ was rapidly incorporated into normal rat liver phosphatides, with the exception of phosphatidylserine. Phosphatidylserine was re-

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solved and identified as a separate fraction by silicic acid column chromatography. A pronounced decrease in palmitate incorporation into phosphatidylethanolamine occurred in fatty liver after cerium administration. This decrease occurred at a time when greater palmitate incorporation was observed into phosphatidylinositol and cardiolipin.

Inhibitory and activating effects of polyanions on lipoprotein lipase. P. Bernfeld and T. F. Kelley (Bio-Res. Inst., Cambridge 41, Mass.). *J. Biol. Chem.* **238**, 1236–1241 (1963). The effect of more than 25 different sulfated polysaccharides and of a few other polyanions on the activity *in vitro* of mouse heart lipoprotein lipase was measured. All polysaccharide sulfates which contained no sulfoamino groups and which had at least 0.6 sulfate ester group per repeating unit proved to be potent inhibitors of the enzyme. This inhibition was independent of the chemical nature of the polysaccharide, of the presence or absence of branchings therein, of the type and configuration of its glycosidic bonds, of the presence or absence of carboxyl or N-acetyl groups, as well as of its molecular weight. The simultaneous occurrence of O-sulfate and N-sulfate groups in heparin and in other activators of lipoprotein lipase is believed to be the cause for the coexistence of an inhibitory effect at high concentrations and of an activating power at lower concentrations of the same polyanion. O-Sulfation of a polysaccharide was always accompanied by an increase in its inhibitory potency; but prior blocking of some of its free hydroxyl groups, *e.g.* by nitration, protected it against O-sulfation and, hence, prevented its conversion into an inhibitor.

Sterile aqueous solutions of vitamin D and calcium salts and method of making the same. J. Schenk (Wander Co.). *U.S. 3,089,822.* A stable heat sterilizable aqueous solution of a therapeutically active vitamin D compound and a nontoxic calcium salt suitable for parenteral administration comprises: a clear water solution of a non-toxic water soluble therapeutically active calcium salt and a therapeutically active vitamin D ester of a fatty acid having from 1 to 5 carbon atoms. The solution contains a fatty acid ester of a polyoxyalkylene compound as a solubilizing agent for the vitamin D ester, the polyoxyalkylene compound having between 20 and 50 oxyalkylene groups per molecule.

Aqueous vitamin a oil emulsion. R. F. Czarnecki (Eastman Kodak Co.). *U. S. 3,089,823.* A stable, aqueous vitamin A oil emulsion consists of an oily vitamin A-active concentrate at a concentration of about 1–10 weight %; 30–95 weight % water; 1.55–3.5 methyl cellulose; and gelatin at a concentration effective to suppress development of coloring under normal storage conditions but ineffective to cause gelation of the water phase of the emulsion.

## • Drying Oils and Paints

Use of dimer fatty acids in the paint and the plastics industry. G. J. Van Veersen (Unilever-Emery, Gouda). *Riv. Ital. Sostanze Grasse* **10**, 517–21 (1962). Fatty acid dimers have been used experimentally to replace phthalic anhydride or linseed oil in the preparation of alkyd resins, with advantages both in manufacture and in finished product characteristics (reduced stickiness, improved stability and drying). When added to some epoxy resins, dimers increase degree of hardening and improve stability. Other applications of fatty acid dimers in the areas of polyamides and polyurethanes are discussed.

Properties, uses and application techniques of baked unmodified phenolic coatings. Anon. *Materials Protection* **1**, No. 8, 87–90 (1962). Baked unmodified phenolic coatings were tested in more than 500 chemical media and general recommendations made regarding their corrosion resistance to each environment. Phenolics were less affected by solvents than any other type organic coating. Aliphatic hydrocarbons, aromatic hydrocarbons, alcohols, esters, ethers, ketones and chlorinated solvents had no effect on phenolic coatings. Phenolics also showed excellent high temperature resistance (180–200F) to aqueous solutions of mild acids and acidic and neutral salts. They effectively resisted fermentation conditions as well as exposure to hot animal and vegetable oils. When properly cured they proved odourless, tasteless and non-toxic, making them suitable for use with food products. Uses of high-bake pure phenolics are reviewed briefly. Other topics discussed include forms available, compounding, surface preparation and application techniques and general physical properties. (Rev. Current Lit. Paint Allied Ind.)

Reaction lacquers distinguish themselves by superior adhesion. A. Foulon. *Wochbl. Papierfabrik* **1962**, 90:248, 250. ''Reaction lacquers'' are defined as originating on a substrate by a chemical reaction between the components of a synthetic lacquer vehicle (binder), such as an isocyanate and polyester or alkyd components. Reaction lacquers can be formulated to give either air-drying or oven-drying (baking) types of coatings. Both types have excellent pigment-binding properties and superior adhesion to a variety of substrates, including ferrous and non-ferrous metals (such as Al and Zn), plastics, glass and porcelain. Solvents with reactive groups as well as water, should be avoided. Suitable catalysts accelerate the drying time of air-drying lacquers and lower the baking temperature of oven-drying formulations (from 160–180 to 125–140C). Outstanding characteristics of reaction lacquers include permanent adhesion and elasticity, abrasion resistance, high dielectric properties, low inflammability and excellent resistance to weathering, solvents and chemicals. The addition of plasticisers may impair solvent resistance but improve adhesion and elasticity. Passivating pigments provide corrosion-resistant coatings. (Rev. Current Lit. Paint Allied Ind.)

Survey of the profit history of the British paint and printing ink industries and the availability of raw materials. Anon. *Fisk's Paint Year Book* **1962**, 181–204. Profit histories of groups of British paint and printing ink companies, all of which are public companies and publish their accounts, are analysed and tabulated. Part 2 shows an analysis of the British production and imports of the main raw materials used by the paint and printing ink industries. (Rev. Current Lit. Paint Allied Ind.)

Materials and men. E. Sunderland. *Fisk's Paint Year Book* **1962**, 95–101. A survey of the development of technology in the paint industry. The emergence of the industry from the craft state, the impact of two world wars and the effects of immediate post-war shortages of technical personnel are discussed. The requirements of technologists and the form of technical service which should be available are described. (Rev. Current Lit. Paint Allied Ind.)

Air inhibition of unsaturated polyester lacquers. G. Whale. *Continental Paints & Resins* **1962**, No. 66, 4. A short bibliography of recent patents is given. These deal mainly with additives for conventional polyesters which prevent air inhibition. Polyisocyanates, allyl compounds and long-chain fatty esters are suggested, whilst an improved method using paraffin wax has been described. (Rev. Current Lit. Paint Allied Ind.)

Quality control in the paint industry. J. Hall. *Austral. Paint J.* **6**, 13–16 (1961). An outline based on the paint technology courses conducted at the University of New South Wales. (Rev. Current Lit. Paint Allied Ind.)

Peering ahead. P. J. Gay. *Fisk's Paint Year Book* **1962**, 61–8. The author looks at changes in administration and technical development to be expected in the paint industry in coming years. The uniting of paint manufacturers into large groups, the absorption of paint making units into the chemical industry and the closer control of paint companies over the sales and use of their products are the movements considered. Technical advances foreshadowed are improvements in colour fastness, increased ability to control surface characteristics of paints, better paint making methods and better handling.

Chemicals for the paint industry: availability or requirements? M. H. M. Arnold. *Fisk's Paint Year Book* **1962**, 85–93. A survey is made of the raw materials used in the manufacture of resins *etc.* in the paint industry. The availability and economics of raw materials are discussed and potential new materials are assessed. (Rev. Current Lit. Paint Allied Ind.)

Coating composition and method. D. B. Sheldahl and G. Entwistle (Sinclair Refining Co.). *U.S. 3,086,870.* A water-in-oil emulsion consists of 50–80% water, 10–30% low-boiling petroleum hydrocarbons, 1–6% petroleum wax having a melting point of 125–140F, and 2.0–6.5% of a mixture containing 4–6% of a sulfonate selected from the group consisting of ammonium mahogany sulfonate and sodium mahogany sulfonate, 5–50% of a sorbitan mono-fatty acid ester and the rest a high-boiling petroleum hydrocarbon. *U. S. 3,086,871,* COATING COMPOSITION, describes a composition which consists of 0.05–1% of a sulfonate (oil-soluble ammonium aromatic sulfonate or an oil-soluble sodium aromatic sulfonate), 0.25–2% sorbitan mono fatty acid ester, 1–10% petroleum paraffin wax having a melting point of 125–145F, 0.5–10% boiled linseed oil, up to about 9% high-boiling petroleum hydrocarbon, 1–80% low-boiling hydrocarbon and 5–8% water.

PROCESS OF CONVERTING FREE CARBOXYLIC ACID GROUPS IN LIQUID ESTER COATING COMPOSITIONS TO HALF-ESTER GROUPS WITH RETENTION OF THE COATING COMPOSITION IN THE LIQUID STATE. H. W. Chatfield (Roberts & Co., Ltd.). *U.S. 3,086,949.* The process for inhibiting free carboxylic acidity in liquid coating compositions containing as an essential film-forming ingredient, acid esters of organic acids (natural resins, modified natural resins, synthetic resins) which have a free acid number of over 6, comprises mixing the liquid composition with an epoxidized fatty oil having internal oxirane briding 2 adjacent carbons on the fatty chain portion of the oil and heating the resulting mixture to a temperature of from 170–240C. The retained –COOH groups of the film-forming ingredient are reacted with the oxirane groups to form glycolic half ester groups while retaining the film-forming property of the composition.

## • Detergents

SURFACE ACTIVE POLYHYDROXY-COMPOUNDS 18: CONVERSION OF D,L-MANNITOL WITH N-OCTYL, N-DECYL, AND N-DODECYLISOCYANATE TO ELECTRO-NEUTRAL SURFACE ACTIVE URETHANES. E. Ulsperger and H. D. Jacobi (Deut. Akademie Wissenschaften, Berlin). *Fette Seifen Anstrichmittel* **64**, 1093–1098 (1962). The synthesis of nonionic surface active mono and diesters of D,L-mannitol and N-*n*-alkyl carbamic acid from D,L-mannitol and *n*-alkyl isocyanates of chain length $C_8$, $C_{10}$ and $C_{12}$ is reported. The structure of the products is established and their properties reported.

PREPARATION AND PROPERTIES OF LINOLEATE ESTERS OF SUCROSE. E. G. Bobalek, A. P. De Mendoza, A. G. Causa, W. J. Collings, and G. Kapo (Case Inst. of Tech., Cleveland 6, Ohio). *I&EC Product Res. & Dev.* **2**, 9–16 (1963). A pilot plant process is described for production of sucrose esters by catalytic trans-esterification between the methyl esters of fatty acids and sucrose in dimethylformamide solvent. The process can be controlled to accomplish degrees of esterification from 1 to about 7, based upon the hydroxyl equivalents per mole of sucrose. Superior drying oil qualities develop at degrees of esterification exceeding 4, if the iodine value of the fatty acids exceeds about 140 and all unreacted methyl esters are removed by solvent extraction or absorption on silica gel. In further chemical modification of these purified esters to produce more complex vehicles for paints and printing inks, either the hydroxyl or the olefinic reactive functions can be utilized. Examples are given where these products are converted to emulsions, urethane polymers, and styrenated oils.

DETERGENCY OF NONIONIC SURFACTANT. I. EFFECTS OF SOME INORGANIC BUILDERS. Masaharu Kame, Seiichiro Kishima, Yasuhiko Danjo, and Katsuji Kamijo (Nippon Oils & Fats Co., Amagasaki). *Yukagaku* **12**, 108–10 (1963). Tests on foaming and detergency of aqueous solutions of polyoxyethylene nonylphenyl ether (PEG-N) 0.05–0.5 g./l. and inorganic builder 0.1–1.0 g./l. were made. The result indicated that polyphosphates (hexametaphosphate, tripolyphosphate, and pyrophosphate) were more effective than the other builders (slicate, carbonate and neutral salts) in both soft and hard water. In the detergency tests carried out in water of various hardness and containing PEG-N 0.1 g./l., there was some relationship between the concentration of added builders and washing efficiency. For example, addition of 0.5 mole of pyrophosphate/mole of $Ca^{++}$ showed remarkable increase in washing power.

BUILDERS FOR SOAPS AND DETERGENTS. C. Gomez (Instituto de la Grasa y sus Derivados, Seville, Spain). *Grasas y Aceites (Seville, Spain)* **13**, 247–252 (1962). A review.

A SIMPLE METHOD FOR CALCULATION SOAP FORMULAS. R. Clara. *Afinidad* **19**, 458 (1962). A nomograph has been developed for relating the water, caustic, and fatty acid content of finished soap to the saponification value of the fat and the caustic concentration used during saponification.

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