

ABSTRACTS

R. A. REINERS, Editor. ABSTRACTORS: J. G. Endres, Kazuo Fukuzumi, J. Iavicoli, K. Kitsuta, F. A. Kummerow, C. C. Litchfield, Gladys Macy,

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• Fats and Oils

COMPOSITION OF STEARIC ACID MONOLAYERS FROM CALCIUM-CONTAINING SUBSTRATES. J. Bagg, M. B. Abramson, M. Fichman, M. D. Haber and H. P. Gregor (Dept. of Chemistry, Polytechnic Inst. of Brooklyn, Brooklyn, N.Y.). *J. Am. Chem. Soc.* **86**, 2759-63 (1964). Monomolecular layers were formed from stearic acid on substrates 10^{-4} M in calcium chloride containing sodium phosphate, sodium bicarbonate or ammonium chloride as a buffer. Analyses of skimmed or plated films were performed by the evaluation of their infrared spectra. On all buffers no calcium stearate was observed at $\text{pH} < 4$ and complete conversion was observed at $\text{pH} > 9$. In the pH range 5-7, less calcium stearate was formed in the monolayer on the sodium phosphate buffer than on the other buffers. These results were found to be in satisfactory agreement with the force-area characteristics of stearic acid monolayers spread on calcium-containing substrates observed by earlier workers. When the monolayer was removed by plating to build up multilayers, the calcium stearate was shown to be present as the monohydrate and not as the anhydrous salt. Heating a multilayer to 50C caused the loss of water and also of a substantial proportion of stearic acid.

DETERMINATION OF THE MAJOR FREE FATTY ACIDS OF CHEDDAR CHEESE. D. D. Bills and E. A. Day (Dept. of Food Sci. and Tech., Oregon State Univ., Corvallis). *J. Dairy Sci.* **47**, 733-8 (1964). The major individual free fatty acids (FFA), acetic through linolenic, were determined in 14 samples of Cheddar cheese. A technique utilizing two methods of column chromatography plus gas-liquid chromatography was necessary for resolution of the complete series of FFA. Formic and propionic acids were not observed in any of the cheeses. Acetic acid showed the greatest variability in concentration and was usually the most abundant. Among the FFA which can arise through the hydrolysis of milk fat, free butyric acid was always found in about twice the percentage reported for esterified butyric acid. The individual FFA from caproic through linolenic, however, were present in nearly the same ratio as the same esterified acids in milk fat.

HYDROCARBON COMPOSITION OF SOME CRUDE AND REFINED EDIBLE SEED OILS. A. Kuksis (Dept. of Biochem., Queen's Univ., Kingston, Ontario, Canada). *Biochem.* **3**, 1086-93 (1964). The hydrocarbon portions (1-10% of the total unsaponifiable matter) of crude corn and wheat germ oils and refined corn, cottonseed, olive, safflower, soybean and sunflower oils were isolated on silicic acid and analyzed by gas chromatography. All the oils were shown to contain mixtures of both odd and even carbon number saturated hydrocarbons ranging in chain length from C_{13} to C_{35} , but the odd carbon number derivatives were present in somewhat greater proportions. While sunflower, safflower and olive oils contained mainly the normal homologs of the odd and even series, the others contained in addition significant amounts of nonnormal chain paraffins which were tentatively identified as the mixed iso- and the 1-cyclohexyl derivatives. Only olive and wheat germ oils contained large concentrations of unsaturated material, a great proportion of which could be accounted for as squalene. The paraffin portions of crude, refined and molecularly distilled corn oils had comparable compositions.

RAPID, ACCURATE MICROANALYSIS OF THE LOWER FATTY ACIDS WITH PARTICULAR REFERENCE TO SERIAL DETERMINATION. F. A. Vandenheuvel (Animal Res. Inst., Canada Dept. of Ag., Ottawa, Ontario). *Anal. Chem.* **36**, 1930-36 (1964). Isolation of the lower fatty acids by steam distillation is efficiently carried out with the described apparatus which permits the simultaneous processing of ten 0.5-ml samples under preset, controlled conditions. About 20 minutes are required to recover over 99% of all acids except formic acid of which a precisely known percentage is obtained. Desiccated aliquots of the neutralized distillates are mixed with measured volumes of a standard solution of formic acid in carbon disulfide which quantitatively

releases the acid from their salts. The resulting solutions are injected into a chromatograph equipped with a flame ionization detector. Statistical analysis of results obtained with standard solutions of mixed acids indicates a relative error of $\pm 1\%$ for injected solutions containing 2 μ moles of acid per ml when xylene is used as an internal standard.

THE AMOUNT OF TOTALLY OXIDIZED ACIDS IN OLIVE OILS. M. Naudet (Lab. of Chem. Fats and Oils and Nat. Lab. of Fatty Materials, Marseille, Fr.). *Oleagineux* **19**, 449-53 (1964). Natural fats always contain small amounts of oxidized chains. The formation and structure of these chains is briefly discussed. The author feels that because of the practical consequences which can result from their presence, the oxidized chains should be studied and determined in their totality. Recourse to various indices is without significance in this regard; insolubility in petroleum ether does not permit a precise separation of the components. Separation can be made using chromatography on reversed phase polyethylene powder following a volumetric titration of the eluant. The method permits the determination with a precision of $\pm 5\%$ of the levels in oxidized acids as low as 0.25%. Examples of the method's application to various olive oils are given and their significance is discussed.

THE FORMATION OF VOLATILE COMPOUNDS DURING THE AUTOXIDATION OF LIPIDS. II. COMPOSITION OF THE VOLATILE CARBONYL COMPOUNDS IN AUTOXIDIZED FATTY MATERIALS. J. Hrdlicka and J. Pokorný. *Sbornik Vys. Skoly Chem. Tech. Praz. Potravn. Tech.* **7**, 113-24 (1963). Ten diverse representative types of economically important fatty materials (linseed oil, cod liver oil, soybean oil, peanut oil, rapeseed oil, olive oil, lard, tallow, cacao butter and coconut oil) have been oxidized at 180C with air passing through the oils. The volatile compounds were converted to their corresponding 2,4-dinitrophenylhydrazones and separated by paper chromatography. The diverse components were identified by their R_f values and spectral properties. The results correspond to data presented in the literature on the oxidation of pure fatty acids. However, homologous series of compounds are formed such as C_1 - C_4 , which are not found during the oxidation of similar materials at ambient temperatures. At the elevated temperatures, the scission of the carbon chain is not limited to the double bond. (Rev. Franc. Corps Gras)

TEN YEARS OF DEVELOPMENT AND APPLICATION IN GAS-LIQUID CHROMATOGRAPHY. J. Van Rysselberge. *Ind. Chem. Belge.* **6**, 575-90 (1964). Ten years' progress in gas-liquid chromatography is previewed. Progress in the design of the various parts of the chromatographic apparatus are considered particularly improvements in carrier gases, the stationary phases and detectors. The chromatographic accessories are examined and special attention is given to qualitative identification of substances, particularly by use of infrared analysis. Quantitative analysis is briefly considered.

DECOMPOSITION OF METHYL OLEATE HYDROPEROXIDE ON THE CELITE/DINITROPHENYLHYDRAZINE-HYDROCHLORIC ACID COLUMN. M. M. Horikx (Unilever Res. Lab. Vlaardingen, Netherlands). *J. Appl. Chem. (London)* **14**, 50-52 (1964). The hydroperoxides in oxidized methyl oleate can be converted in high yield into the dinitrophenylhydrazones of aldehydes and aldehyde esters by reaction on a Celite/dinitrophenylhydrazine-hydrochloric acid column. The aldehydes and aldehyde esters formed are the same as those produced during the thermal decomposition of methyl oleate hydroperoxide. The dinitrophenylhydrazones of unsaturated conjugated C_{18} keto esters are also formed.

FRACTIONATING PLANT FOR SPECIALIZED EDIBLE OILS AND FATS. Anon. *Food Process. Packaging* **33**, 9-13 (1964). A description of the plant built by Loders and Nucleon Ltd. at Silvertown, England for obtaining selected glycerides by continuous solvent fractional crystallization. The glycerides are used for producing specialized fats for the food industry.

FRACTIONATION OF GLYCERIDES BY LIQUID EXTRACTION. M. Naudet (National Lab. of Fats and Oils (ITERG), Marseille, Fr.). *Rev. Franc. Corps Gras* **11**, 326-34 (1964). The application of liquid-liquid extraction theory to glyceride fractionation is discussed. The differences of the affinity of the components of a blend towards a solvent is the basic principle. The causes of variations of the affinity for the solvent, i.e. molecular weight, polarity, compatibility, nature and specific gravity of solvent, are discussed. The design of the solubility curves, solubility isotherms and diagrams of distribution and of selectivity is also discussed. The principles of continuous counter- and co-current operations are described.

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CONTRIBUTIONS TO THE STUDY OF THE OXIDATION OF FATS. R. Francois and M. Loury (Inst. of Fats and Oils, Paris, Fr.). *Chim. Ind. (Paris)* 91, 650-53 (1964). The authors describe the working model which was chosen for the study of the degradation products by the oxidation of fats (in this special case, oleic acid), products which are always the same no matter the temperature up to 100C. The mechanisms of reactions occurring in the course of oxidative rancidity were studied and two hypotheses are given to explain the presence of aldehydes and formic acid.

REACTION OF METHYL ESTERS OF FATTY ACID OF LINSEED OIL ON AUTOXIDATION AND HEATING. Gaku Izumi and Yutaka Yamada (Gov. Ind. Research Inst., Nagoya, Japan). *Yukagaku* 13, 418-26 (1964). Linseed oil is a typical casting oil, the methyl esters of this oil have been used in these experiments. The experimental treatments of the sample were carried out under the conditions similar to the industrial operation. As the catalysts, lead and cobalt naphthenates were added to the sample ester. Esters were autoxidized at 40C by bubbling air into the sample. The reaction proceeded rapidly and the content of ethylenic linkage decreased with time, the *cis*-double bonds were converted into *trans*-isomers and conjugated double bonds, and most of the peroxides produced were of the hydroperoxide type. When autoxidized samples were heated for 1 hour at 200C, the hydroperoxides decomposed vigorously and polymerization proceeded partly. Yet the conjugated double bonds and *trans*-isolated double bonds were still present in appreciable amounts. When above samples heated at 200C were heated to 300C, the content of -OH decreased by the progress of polymerization while there was only a little residual conjugated double bonds, through the content of the *trans*-isolated double bonds increased. Heating at 400C or 500C caused an increase in the formation of cleaved products of low molecular weight and the content of -OH decreased with the progress of polymerization and there was the disappearance of double bonds although some *trans*-isolated double bonds remained. The reaction mechanisms of each treatment were discussed.

STUDIES ON THE VOLATILE CARBONYL COMPOUNDS EVOLVED FROM THE OXIDATION OF METHYL ERUCATE WITH DRIED AIR. Yoshihito Suzuki and Tsugio Takeuchi (Nagoya Univ., Japan). *Yukagaku* 13, 431-4 (1964). Methyl erucate was synthesized from erucic acid and then oxidized with dry air at 96 ± 1 C. The volatile carbonyl compounds from methyl erucate were identified by means of paper chromatography and ultraviolet absorption spectra. The carbonyl compounds from methyl erucate were mostly evolved between 36 and 48 hours of oxidation. Most of the carbonyl compounds contained 10-14 carbon atoms. With the progress of oxidation, the proportion of saturated carbonyl compounds in the fractions having 2-4 and 6-8 carbon atoms was increased, while in carbonyl compounds having 10-14 carbon atoms, there was a tendency of increase of unsaturated carbonyl compounds after oxidation for 36 hours. A small amount of aliphatic ketones was formed simultaneously during the oxidation and it was 8% by weight after oxidation for 24-36 hours.

FOAMING TENDENCIES OF FRYING OILS. III. CHEMICAL CHARACTER OF THERMALLY OXIDIZED TRILINOLEIN. Shizuyuki Ota, Akira Mukai and Iwao Yamamoto (Ajinomoto Co., Tokyo). *Yukagaku* 13, 264-8 (1964). Trilinolein was heated for 5 and 9 hours, respectively, at 200C. The time required for breaking of foams was zero and 12 seconds for samples with 5- and 9-hour heating and the time required for disappearance of foams from samples with 5- and 9-hour heating was 14 and 196 seconds, respectively. Trilinolein showed greater coloration on heating than the commercial frying oils. The tendencies of the change of constants of trilinolein by heating were nearly the same as those of general vegetable oils. The fatty acid monomer was decreased with an increase of time of heating, while the amounts of dimer and the products of further reaction was increased.

STUDIES ON THE LOWER MELTING HYDROGENATED OILS AND FATS. II. TRANS ISOMERIZATION AND BEHAVIOR OF POLYUNSATURATED COMPONENT IN THE PROCESS OF HYDROGENATION OF FISH OIL WITH CATALYST HAVING AN ADDITION OF DIMETHYL POLYSILOXANE

(MPS) AND STABILITY AGAINST OXIDATION OF THE RESULTANT OIL. Umajiro Shimamura, Sadamitsu Maekawa and Shinji Mitsunaga (Nippon Oils and Fats Co., Tokyo). *Yukagaku* 13, 365-9 (1964). Selective hydrogenation and stability against oxidation of fish oils have been investigated. Catalyst consisting of reduced nickel and MPS gave less *trans* acid than the catalyst of reduced nickel alone. The effect of MPS is affected by its viscosity and the higher viscosity indicated greater effect than the low viscosity. When the resultant oil was hydrogenated with catalyst of nickel alone until its iodine value reached to 86, there was the disappearance of conjugated dienic acid but the addition of MPS caused the lowering of iodine value to 81. On the other hand, the formation of *trans* acid showed a tendency of sharp increase in iodine value with the disappearance of this dienic acid. Trienic acid had disappeared, when an iodine value of 90 was reached by use of nickel catalyst alone, while it had to be 88 in case of catalyst containing MPS. There was no difference in stability against oxidation between catalyst of nickel and that of nickel and MPS in the AOM and oven tests. In the hydrogenation of oil with iodine value higher than 90 reversion of fish flavor was recognized before showing rancid flavor.

FATTY ACIDS, INCLUDING POLYENOIC AND TRANS COMPONENTS, AND GLYCERIDES OF INDIAN GOAT TALLOW. N. S. Rajagopal and K. T. Achaya (Regional Research Lab., Hyderabad, India). *J. Sci. Food Agr.* 15, 497-503 (1964). Average analysis of 5 Indian goat tallows by ester fractionation showed (as mole-%): myristic 4.3, palmitic 30.2, stearic 23.8, arachidic 2.3, tetradecenoic 0.3, hexadecenoic 3.6, oleic 34.8, octadecadienoic 0.5 and C_{20-22} acids 0.2. Solvent crystallization, GS_2 determination and component acid analysis of 1 specimen showed GS_2 , 30.3; GS_2U , 25.8; GSU_2 , 41.5 and GU_2 , 2.4 (mole-%). Major individual components (mole-%) were: palmitodistearin 14.4, dipalmitostearin 11.7, palmitostearoolein 18.4, steardiolein 19.2, palmitodiolein 21.2 and triolein 2.4. Indian goat tallows resemble in glyceride structure a saturated Western beef tallow rather than an Indian, which is high in GS_2U . Polyene- and *trans*-acid contents were both low: non-conjugated diene 1.12, non-conjugated triene 0.21, conjugated diene 0.05, conjugated triene 0.02 and isolated *trans*-acid 5.5 (wt-%).

DETERMINATION OF THE VOLATILE OR "FREE" CARBONYL CONTENT OF FATS. C. H. Lea and H. A. F. Jackson (Low Temperature Research Station, Cambridge). *Chem. Ind. (London)* 1964, 1429-30. Sunflower and linseed oils were oxidized at 37C to peroxide values of approximately 100 μ moles/g. The oxidized oils were then examined for volatile carbonyl content by vacuum distillation and by chromatographic methods. By distillation the unheated oils were found to contain 0.14-0.22 μ moles per gram of volatile carbonyls of oil and the same oils after heating contained 15-22 μ moles/g of oil. The chromatographic method applied directly to oils of low peroxide and high carbonyl content gave results reasonably close to those obtained by distillation, but for oils of high peroxide value and low volatile carbonyl content the free carbonyls found were too high, indicating that a considerable breakdown of peroxidic precursors to carbonyls not retained by the column had occurred.

SHORTENING PRODUCT, N. B. Howard (Procter & Gamble Co.). *U.S. 3,145,107*. A glyceride shortening composition which can be used in the preparation of recipe cake batters with single-stage mixing contains as additives from 1-8%, by weight, of the condensation product of a material selected from the group consisting of glycolic acid and lactic acid with a mixture of fatty acid mono- and diglycerides in ratios of 1:9 to 9:1 (the fatty acid radicals containing 14-22 carbons), and from 0.25-4% of materials selected from the group consisting of 1) saturated fatty acids containing 14-22 carbons; 2) the condensation product of material selected from the group consisting of a) a partial fatty acid glyceride containing an average of 1 to 2 fatty acid radicals having from 14 to 22 carbon atoms, but not more than enough unsaturated fatty acid radicals to give a condensation product having an iodine value of 60, and b) a monoester of a straight chain aliphatic diol with a saturated fatty acid, the diol containing 3-5 carbon atoms and the saturated fatty containing 14-22 carbon atoms, with a polycarboxylic acid having from 0 to 4 hydroxy groups, the polycarboxylic acid containing 3-6 carbons, and the condensation product having at least 1 free carboxyl group per molecule; 3) the condensation product of a saturated fatty acid (14-22 carbons) with a polycarboxylic acid (3-6 carbon atoms and 1-4 hydroxyl groups), the condensation product having at least 1 free carboxyl group per molecule; 4) the condensation product of a saturated straight chain fatty alcohol (14-22 carbons) with a dicarboxylic acid (3-6 carbons, 0 hydroxy groups), the condensation product having at least 1 free

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carboxyl group per molecule; 5) mixtures of the preceding materials.

SHORTENING PRODUCT. N. B. Howard (Procter & Gamble Co.). *U.S. 3,145,108*. A glyceride shortening composition which can be used in the preparation of recipe cake batters with single-stage mixing contains as additives 1.5–12%, by weight, of monoester of straight chain aliphatic diol (3–5 carbon atoms) with saturated fatty acid (16–22 carbon atoms), and from 0.25–4% of material selected from the group consisting of 1) saturated fatty acids containing 14–22 carbon atoms; 2) the condensation product of material selected from the group consisting of a) a partial fatty acid glyceride containing an average of 1–2 fatty acid radicals having from 14–22 carbons, but not more than enough unsaturated fatty acid radicals to give a condensation product having an Iodine Value of 60 and b) a monoester of a straight chain aliphatic diol (3–5 carbons) with a saturated fatty (14–22 carbons) with a polycarboxylic acid (0–4 hydroxy groups and 3–6 carbons), the condensation product having at least one free carboxyl group per molecule; 3) the condensation product of a saturated fatty acid (14–22 carbons) with a polycarboxylic acid (1–4 hydroxy groups, 3–6 carbons), the product having at least 1 free carboxyl group per molecule; 4) the condensation product of a saturated straight chain fatty alcohol (14–22 carbons) with a dicarboxylic acid having no hydroxy groups and containing 3–6 carbons, the condensation product having at least 1 free carboxyl group per molecule; and 5) mixtures of the preceding materials.

SHORTENING PRODUCT AND METHOD OF MAKING THEREOF. N. B. Howard (Procter & Gamble Co.). *U.S. 3,145,109*. A glyceride shortening composition contains as additives: A) 1.5–16% by weight of material selected from the group consisting of 1) 1,3-diglyceride containing a saturated fatty acid chain containing 16–22 carbons and a saturated fatty acid chain containing 2–4 carbons; 2) 1,2-diglyceride containing a saturated fatty acid chain containing 16–22 carbons and a saturated fatty acid chain containing 12–18 carbons; 3) mixtures of the 1,3- and the 1,2-diglycerides in which the weight of the 1,2-diglycerides does not substantially exceed the weight of the 1,3-diglyceride; and 4) mixtures thereof; and B) 0.25–4% of material selected from the group consisting of 1) saturated fatty acids containing 14–22 carbon atoms; 2) a condensation product having at least 1 free carboxyl group per molecule of a polycarboxylic acid having from 0 to 4 hydroxy groups and containing 3–6 carbon atoms with a material selected from the group consisting of a) a partial fatty acid glyceride containing an average of 1 to 2 fatty acid radicals having 14–22 carbon atoms, but not more than enough unsaturated fatty acid radicals to give a condensation product having an Iodine Value of 60, and b) a monoester of a straight chain aliphatic diol (3–5 carbons) with a saturated fatty acid (14–22 carbons); 3) the condensation product of a saturated fatty acid (14–22 carbons) with a polycarboxylic acid (3–6 carbon atoms and 1–4 hydroxy groups), the condensation product having at least 1 free carboxyl group per molecule; 4) the condensation product of a saturated straight chain fatty alcohol (14–22 carbons) with a dicarboxylic acid (no hydroxy groups and 3–6 carbon atoms), the condensation product having at least 1 free carboxyl group per molecule; and 5) mixtures of the preceding materials.

SHORTENING PRODUCT. C. T. Abbott, Jr. (Procter & Gamble Co.). *U.S. 3,145,110*. A stable fluid shortening composition, suitable for use in the preparation of recipe cake batters with a single mixing step in large scale commercial baking operations, comprises a normally liquid glyceride containing 0.5–8% by weight of a mono-ester of propylene glycol and saturated fatty acid containing 14–22 carbon atoms. The shortening composition also contains 1–5% of a normally solid triglyceride fat and about 0.5–10% of saturated fatty acid having from 14–22 carbon atoms. The triglyceride fat should be at least 80% in beta phase.

WINTERIZING GLYCERIDE OILS. T. H. Little (Pennsalt Chemicals Corp.). *U.S. 3,145,223*. The process of winterizing a glyceride oil in the absence of solution in a solvent includes the following

steps a) lowering the temperature of the oil to 50–35F to solidify at least a portion of the higher melting glycerides; b) continuously introducing a stream of the chilled oil and solids to a zone of centrifugation; c) building up the solids to a pre-established depth of at least 1/2 of the distance from the periphery of the zone to the axis at which depth the solids obstruct the entrance of a passage in the zone blocking the supply of oil to a segregated chamber, the chamber having a leak passage outward to the outside of the zone and the chamber and the zone having a common partition facing the outside of the zone and movable radially of the zone and carrying a valving surface normally closing an opening in the periphery of the zone, the blocking of supply of oil to the segregated chamber causing a pressure drop in the chamber to move the partition and valving surface inward exposing the peripheral opening; d) extruding a portion of the built-up solids out of the zone through the opening to reduce the depth of solids accumulated, thereby unobstructing the entrance and restoring supply of oil to the segregated chamber to cause a pressure increase in the chamber, the partition and valving surface moving outward under centrifugal force to close the peripheral opening to stop the extruding of solids; e) continually repeating the building up and extruding steps; and f) continuously discharging winterized oil separated from the solids from a locus spaced inward from the periphery of the zone and spaced along the axis from the point of extrusion of solids, and thus in building up to the pre-established depth the solids are compacted to displace inwardly of the zone entrained and occluded portions of the oil.

• Fatty Acid Derivatives

NEAR-INFRARED SPECTRA OF OLEAMIDE AND SATURATED FATTY ACID AMIDES (C₈–C₁₈). Akio Kato, Masakazu Oguro and Yoshio Tsutsui (Gov. Chem. Ind. Research Inst., Tokyo). *Yukugaku* 13, 426–31 (1964). Near infrared spectrum of oleamide was measured in carbon tetrachloride solution between 1.0 and 2.5 μ . From the experimental results, the band characteristic of the amide structure was determined. In particular, presence of an intense absorption band can be ascertained at 1.960 μ . This band is due to a combination of N–H stretching and N–H bending vibrations. The spectra of C₈–C₁₈ saturated fatty acid amides were measured in chloroform solution between 1.9 and 2.2 μ . These amide are characterized by an intense absorption band at 1.96 μ . The absorption band is available for both the qualitative analysis of primary amides and quantitative analysis of nitrogen in the crude amides.

STUDIES ON BIS-CYANOETHYLATION OF FATTY AMINES. IV. INVESTIGATION FOR THE AMINE VALUE AND SYNTHESIS OF N,N,N',N'-TETRA-(β -CYANOETHYL)-HEXAMETHYLENEDIAMINE. Seimei Nitani (Toyo Koatsu Co., Yokohama). *Yukugaku* 13, 369–73 (1964). Reaction of hexamethylenediamine with acrylonitrile gave tetracyanoethylate in high yield. The reaction was carried out in polar solvent. Refluxing a mixture of 6 moles acrylonitrile per mole of amine and 2 parts of methanol for a part of amine for 24 hours gave maximum yield.

V. SYNTHESIS OF TETRA-(β -CYANOETHYL)ETHYLENEDIAMINE AND NONAMETHYLENEDIAMINE. *Ibid.* 374–8. Syntheses of tetracyanoethylate by the reaction of ethylenediamine or nonamethylenediamine with acrylonitrile have been investigated. The reaction in methanol containing water was effective in the tetracyanoethylation of ethylenediamine. Nonamethylenediamine had approximately the same reactivity as hexamethylenediamine. N,N,N',N'-Tetra-(β -cyanoethyl)-alkylenediamine was obtained in stoichiometric quantity under the optimum condition of using twice as much of methanol or methanol containing water based on weight of amine, six moles of acrylonitrile per mole of amine and refluxing for 24–48 hours.

STUDIES ON 8-HYDROXYCAPRYLIC ACID AND ITS DERIVATIVES. Tada-shi Yasukawa and Shozo Abe. *Yukugaku* 13, 360–4 (1964). Methyl 8-hydroxycaprylate was prepared by means of Brown-Walker electrolytic oxidation of methyl hydrogen azelate. The free acid was separated from the product using maleic anhydride as a reagent. Or, 8-hydroxycaprylic acid was prepared from methyl hydrogen azelate by converting the ester into the silver salt, followed by bromination, acetylation and hydrolysis. The solubility of the acid in water and benzene, the velocity of the formation of polyester at different temperatures were given. Ethyl, isopropyl, isobutyl and isoamyl esters of 8-hydroxycaprylate were synthesized. By the *trans*-esterification of the monoglyceride of the acid, the dimeric lactone of 8-hydroxycaprylic acid was obtained.

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SYNTHESIS OF METHYL HYDROGEN AZELATE. Tadashi Yasukawa and Shozo Abe (Univ. Tokyo). *Yukagaku* 13, 317-21 (1964). Attempts have been made to find the best method for preparation of methyl hydrogen azelate by the esterification of azelaic acid in methanol. In the first place, an equilibrium constant was determined, this specified the composition of azelaic acid, methyl hydrogen azelate and dimethyl azelate in equilibrium at 90°C and 1 atmosphere. Practical operating conditions to obtain equilibrium were established. Hydrolysis of dimethyl azelate was also discussed by using sodium hydroxide and barium hydroxide in methanol. The results indicated that the equilibrium method was superior than the other methods.

PREPARATION OF UNSATURATED HIGHER ALCOHOL. Isao Ikeda and Saburo Komori (Osaka Univ.). *Yukagaku* 13, 313-17 (1964). A new method of using a combined catalyst Cu-Cr-oxide and cadmium soap has been investigated. The Cu-Cr-oxide catalyst has been used for long period of time in the preparation of saturated higher alcohols in plant and the cadmium soap is soluble in raw fatty esters. This new method can be performed with the equipment and technique that was established for preparation of saturated higher alcohols. Desirable unsaturated higher alcohols can be prepared for use as a detergent base with a yield over 93% using pressure of 218-205 kg/cm² for 2 hours at 290 ± 3°C and using 0.4 g Cu-Ba-Cr-oxide catalyst and 1.5 g cadmium soap for 4 g raw methyl ester.

PROCESS FOR PRODUCING PRIME STEAM LARD. J. E. Thompson. *U.S. 3,142,576*. A process for recovering fats from fatty tissue of animals comprises: a) introducing the fats into a jacketed kettle to fill the kettle up to approximately half full, b) applying heat to the walls of the kettle to maintain at least 40°F temperature differential between the load in the kettle and the saturated water vapor surrounding the kettle, and simultaneously, c) applying a vacuum of about 15 inches of mercury during rendering, d) introducing live steam into the kettle during the entire cooking cycle, e) heating until equilibrium between condensation and evaporation is reached at approximately 250°F and f) removing the separated fats from the protein tissue.

• Biology and Nutrition

ACCEPTORS OF FATTY ACID FOR GLYCERIDE SYNTHESIS IN GUINEA PIG MAMMARY GLAND. O. W. McBride and E. D. Korn (Lab. of Biochemistry, Section on Cellular Physiology, Nat'l. Heart Inst., NIH, Bethesda, Md.). *J. Lipid Res.* 5, 448-52 (1964). Glycerides are shown to be synthesized by two pathways in mammary tissue of lactating guinea pigs. One pathway involves the direct acylation of monoglycerides. The other pathway proceeds from the acylation of α -glycerophosphate through L- α -phosphatidic acids and D- α , β -diglycerides. Ethanol is also esterified by homogenates of lactating mammary gland.

EFFECTS OF 22,25-DIAZACHOLESTANOL ON SYNTHESIS OF CHOLESTEROL BY RAT LIVER HOMOGENATES. D. Dvornik, M. Kraml and J. Dubuc (Dept. of Biochemistry, Ayerst Res. Lab., Montreal, Canada). *Proc. Soc. Exp. Biol. Med.* 116, 537-9 (1964). In rat liver homogenates 22,25-diazacholesterol blocked to the same extent the incorporation into cholesterol of 2-C¹⁴-acetate, 2-C¹⁴-mevalonate and of 26, 27-C¹⁴-desmosterol. Thus, direct evidence is provided for a triparanol-like interference with hepatic cholesterologenesis *in vitro*. This is in agreement with the finding of appreciable desmosterol levels in humans and rats treated with 22,25-diazacholesterol per os.

TRANSIENT THROMBOPENIA AFTER INTRAVENOUS INJECTION OF CERTAIN FATTY ACIDS. G. Zbinden (Research Division, Hoffmann-La Roche Inc., Nutley, N.J.). *J. Lipid Res.* 5, 378-84 (1964). Intravenous injections of various fatty acids in rabbits caused marked thrombopenia lasting 1-2 hr. The most active saturated fatty acids were myristic acid (14:0) and lauric acid (12:0). Activity decreased with increasing and decreasing chain length, but behenic acid (22:0) had, on a molar basis, activity similar to that of lauric acid. Of the unsaturated fatty acids, oleic acid (18:1) was active only at high doses, whereas linoleic (18:2) and linolenic acid (18:3) had an effect com-

parable to palmitic acid (16:0). Intraperitoneal administration of the fatty acids caused no thrombopenia.

MAGNITUDE OF THE HYPOCHOLESTEROLEMIC EFFECT OF DIETARY SITOSTEROL IN MAN. J. M. R. Beveridge, H. L. Haust and W. Ford Connell (Depts. of Biochemistry and Med., Queen's Univ., Kingston, Ontario, Canada). *J. Nutr.* 83, 119-22 (1964). Ninety-two university students (73 men and 19 women) consumed for 7 days a homogenized formula ration providing 45% of calories as butter fat. The subjects were then divided into 10 groups and continued for 8 days on the same regimen supplemented by a commercial preparation of β -sitosterol in amounts of 50, 100, 200, 300, 400, 600, 800, 1600, 3200 and 6400 mg/950 kcal. Eighty-five subjects (69 men and 16 women) completed the experiment. Starting with the 300-mg level, the β -sitosterol increments caused progressively larger decreases in plasma cholesterol concentrations which were significant in all instances. The implications of these results are discussed in the light of the large amount of plant sterols present in corn oil and it is concluded that these compounds are important factors in accounting in large part for its hypocholesterolemic property.

BENZO(A)PYRENE AND OTHER POLYNUCLEAR HYDROCARBONS IN CHARCOAL-BROILED MEATS. W. Lijinsky and P. Shubik (Div. of Oncology, Chicago Med. School, Chicago, Ill.). *Science* 145, 53-5 (1964). The possible production of carcinogenic polynuclear hydrocarbons in the charcoal broiling of food has been investigated. Fifteen steaks were cooked and the polynuclear compounds were extracted, separated by chromatography and identified spectrometrically. Many polynuclear hydrocarbons were identified, but no nitrogen heterocyclic compounds were detected. The carcinogen, benzo(a)pyrene, was present in the average amount of 8 micrograms per kilogram of steak.

THE EFFECT OF ENVIRONMENTAL TEMPERATURE ON THE FATTY ACID COMPOSITION OF CRUSTACEAN PLANKTON. T. Farkas and S. Herodek (The Biological Res. Inst. of the Hungarian Academy of Science, Tihany, Hungary). *J. Lipid Res.* 5, 369-73 (1964). Measurements of the iodine value made over a period of three years demonstrate a regular yearly cycle in the composition of the fat of crustacean plankton in Lake Balaton. The melting point of the lipid of the planktonic copepods remained during the whole year somewhat lower than the water temperature. The proportions of the C₂₀-C₂₂ polyunsaturated acids in the planktonic crustaceans increased with decreasing temperature and in some species exceeded the values characteristic of marine animals. In fresh-water fish, kept at room temperature and fed on freshly collected fresh-water plankton, the lipids formed in winter resembled marine fish oil. In the crustaceans raised on algae containing no fatty acids longer than C₁₈, the C₂₀-C₂₂ acids always appeared as major components of the copepods.

QUANTIFICATION AND FATTY ACID AND FATTY ALDEHYDE COMPOSITION OF ETHANOLAMINE, CHOLINE AND SERINE GLYCEROPHOSPHATIDES IN HUMAN CEREBRAL GREY AND WHITE MATTER. J. S. O'Brien, D. L. Fillerup, and J. F. Mead (Dept. of Biophysics and Nuclear Med., Univ. of Calif. School of Med., Los Angeles, Calif.). *J. Lipid Res.* 5, 329-38 (1964). The quantities of ethanolamine glycerophosphatides (EGP), choline glycerophosphatides (CGP) and serine glycerophosphatides (SGP) were determined in the grey and white matter from three apparently normal adult human brains. In each locale the quantities decreased from EGP through CGP to SGP. The quantities of aldehydes in these lipids were also determined. In grey matter the aldehyde content (expressed as per cent of fatty acids plus aldehydes) of EGP, CGP and SGP was 22, 0.3 and 0.2%, respectively; while in white matter the proportions were 49, 0.8 and 13%, respectively. Palmitaldehyde, stearaldehyde and olealdehyde made up 90% of the aldehydes found. White matter glycerophosphatides contained more olealdehyde than those from grey matter.

CHARACTERIZATION AND QUANTIFICATION OF RED CELL LIPIDS IN NORMAL MAN. P. Ways and D. J. Hanahan (Depts. of Biochemistry and Med., Univ. of Washington, Seattle, Wash.). *J. Lipid Res.* 5, 318-28 (1964). Human red cell lipids have been studied in a series of normal individuals. Cholesterol comprises 25% of total red cell lipid and free fatty acid is present. Evidence is presented that the total amount of lipid phosphorus per average red cell is 1.40×10^{-11} mg and that most extraction procedures fail to extract 8% or more (some as much as 40-50%) of red cell phospholipid. The average percentage distribution of the individual phospholipid was: choline glycerophosphatides 30%, sphingomyelin 24%, ethanolamine glycerophosphatides 26% and serine glycerophosphatides 15%. The normal range for total red cell plasmalogen was found to be 4.65-

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5.85×10^{-11} μ mole/cell. Ethanolamine glycerophosphatides are high in 20:4, 22:5 and 22:6, while serine and inositol glycerophosphatides contain large amounts of 18:0 and 20:4. Lecithin is distinguished by 20-25 moles % 18:2 and sphingomyelin by high concentrations of 24:0 and 24:1.

QUANTITATIVE GAS-LIQUID CHROMATOGRAPHIC DETERMINATION OF FREE GLYCEROL IN BLOOD SERUM. E. Jellum and P. Björnstad (Inst. of Clinical Biochemistry, Rikshospitalet, Univ. of Oslo, Oslo, Norway). *J. Lipid Res.* 5, 314-7 (1964). Quantitative gas-liquid chromatographic determination of free glycerol in blood serum was accomplished through the use of butane-1,4-diol as internal standard. After removal of proteins with phosphotungstic acid, the glycerol and butanediol were acetylated for 1 hr with acetic anhydride. The acetate thus formed were extracted with diethyl ether, the solvent was removed and the butanediol diacetate and glycerol triacetate were separated on a column with butanediol succinate as stationary phase at temperatures programmed from 150 to 190C. Normal sera were found to contain 0.4-1.2 mg of glycerol per 100 ml, the estimation having a range of $\pm 5-10\%$. The method can be exploited to determine as little as 0.01 mg of glycerol per 100 ml when a sensitive flame ionization detector is used.

FATTY ACID COMPOSITION OF HUMAN PLASMA LIPOPROTEIN FRACTIONS. D. W. S. Goodman and T. Shiratori (Dept. of Med., Columbia Univ. College of Physicians and Surgeons and the Presbyterian Hosp., New York, N.Y.). *J. Lipid Res.* 5, 307-13 (1964). Serial samples of plasma were obtained from two fasting normal adult men who had consumed a diet with a slightly reduced fat content for 1 week previously. Three lipoprotein fractions were collected from each sample by ultracentrifugation at densities of 1.019, 1.063 and 1.21. The fatty acid distribution of cholesterol esters, triglycerides and phospholipids of each lipoprotein fraction was determined. The fatty acid compositions of corresponding lipid classes were very similar in the three lipoprotein fractions in each subject, although small but distinct differences did exist. Linoleic acid predominated in the cholesterol esters, oleic acid in the triglycerides and palmitic acid was the major fatty acid in the phospholipids.

THE BIOSYNTHESIS AND METABOLISM OF CAROTENOIDS AND RETINOL (VITAMIN A). J. A. Olson (Dept. of Biochemistry, Univ. of Florida College of Med., Gainesville, Fla.). *J. Lipid Res.* 5, 281-99 (1964). Acetate, by condensation and decarboxylation reaction, is converted to isopentenyl pyrophosphate, which condenses to form C_{20} terpenol pyrophosphates. These latter compounds condense to yield the initial C_{10} carotenoid precursor which is presumably phytoene. By a series of dehydrogenation, cyclization, isomerization and hydration reactions, various acyclic and alicyclic carotenoids are formed. Subsequently, hydroxylation, epoxidation and oxidation-reduction reactions may occur. Several carotenoids and β -apocarotenals may be converted into retinol in mammalian tissues. Thereafter, retinol may be esterified, oxidized to retinal and retinoic acid, isomerized and further metabolized. This review has stressed the route by which these transformations occur and the characteristics of the enzymes involved rather than nutritional, functional, or chemical aspects of carotenoids.

THE QUANTIFICATION OF CHOLESTEROL EXCRETION AND DEGRADATION IN THE ISOTOPIC STEADY STATE IN THE RAT: THE INFLUENCE OF DIETARY CHOLESTEROL. J. D. Wilson (Dept. of Internal Med., Univ. of Texas Southwestern Med. School, Dallas, Texas). *J. Lipid Res.* 5, 409-17 (1964). A means of quantifying the two major pathways of cholesterol elimination from the body, bile acid production and neutral sterol excretion, has been devised for use in the intact rat. Increase in bile acid formation following cholesterol feeding has been demonstrated directly; this increase has been shown to be sufficient in magnitude to account for the entire positive balance for neutral sterol which occurs in the cholesterol-fed animal after equilibrium has been attained. Utilizing a double isotopic steady state in animals fed cholesterol- 7α - H^3 and implanted with cholesterol- 4 - C^{14} , it has been possible to demonstrate that the major portion of fecal cholesterol of endogenous origin is derived from or is in equilibrium with that of the blood.

STUDIES ON THE MOLECULAR STRUCTURE OF RAT LIVER CARDIOLIPIN. H. G. Rose (Bronx Veterans Admin. Hosp., Bronx, N.Y.). *Biochim. Biophys. Acta* 84, 109-27 (1964). Rat liver cardiolipin, isolated by silicic acid column chromatography, has been resolved into five subfractions by discontinuous gradient elution from a silicic acid column. Comparison of these lipids with authentic beef heart cardiolipin established their essential identity; the beef heart lipid differed only in having a more unsaturated fatty acid composition. A comparison between the five subfractions with regard to phosphorus and amino nitrogen content, ester/phosphorus ratios, fatty acid composition, infrared spectra, presence of salt forms, extent of peroxidation, component glycerophosphoric esters, and hydrolysis characteristics failed to explain the molecular basis for the fractionation. The presence of a free hydroxyl group in cardiolipin could not be confirmed by acetylation or acetonation.

POSITIONAL DISTRIBUTION OF FATTY ACIDS IN FISH AND OTHER ANIMAL LECITHINS. D. B. Menzel and H. S. Oleott (Inst. of Marine Resources, Dept. of Nutritional Sciences, Univ. of Calif., Berkeley, Calif.). *Biochim. Biophys. Acta* 84, 133-9 (1964). Phosphatidyl choline (lecithin) fractions were prepared from tuna, salmon and menhaden muscle, from egg yolk, and from rat and beef liver. Hydrolysis by snake-venom phospholipase A (phosphatide acyl-hydrolase, EC 3.1.1.4) was used to determine the positional distribution of the fatty acids. The fatty acid composition of the hydrolyzed fatty acids (β -position) and those remaining with the phosphatidyl moiety (α' -position) were separately determined by gas-liquid chromatography of the methyl esters. Of the fatty acids esterified in the α' -position 36 to 38 mole % were saturated; 91-99 mole % of the fatty acids in the β -position were unsaturated. Palmitic and stearic acids were the predominant saturated acids in the α' -position. Some similarity was noted in the β -position distribution of linoleic, arachidonic, eicosapentaenoic, docosaenoic, docosapentaenoic and docosahexaenoic acids.

THE INCORPORATION OF C^{14} -LABELLED ACETATE INTO LONG CHAIN FATTY ACIDS BY MACROPHAGES IN VITRO. A. J. Day, N. H. Fidge and G. K. Wilkinson (Dept. of Human Physiology and Pharmacology, Univ. of Adelaide, Adelaide, Australia). *Biochim. Biophys. Acta* 84, 149-53 (1964). The incorporation of C^{14} -labelled acetate into fatty acids by macrophages *in vitro* was investigated by gas phase chromatography. Of the C^{14} -labelled acetate 37.3% was incorporated into palmitic acid, 18.4% into oleic acid and smaller amounts into myristic, stearic and linoleic acid. The specific activity of myristic acid was high relative to palmitic acid, but that of stearic and oleic acid similar to that of palmitic. Linoleic acid was only labelled at low specific activity. The inter-relationship of the synthesis of

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different fatty acids in the metabolism of macrophages is discussed.

ON THE INTERPRETATION OF STUDIES MEASURING UPTAKE AND ESTERIFICATION OF PALMITIC-1-C¹⁴ ACID BY RAT ADIPOSE TISSUE IN VITRO. M. Vaughan, D. Steinberg and R. Pittman (Lab. of Metabolism, Nat'l Heart Inst., Bethesda, Md.). *Biochim. Biophys. Acta* **84**, 154-66 (1964). The effects of glucose and a number of hormones on the incorporation of palmitic-1-C¹⁴ acid from the medium into glycerides in rat epididymal fat pads have been reported. It has been demonstrated that the free fatty acids in different cell fractions and in different parts of a single fat pad have different specific radioactivities after incubation of the intact fat pad in the presence of palmitate-1-C¹⁴, suggesting that there are kinetically distinguishable pools of free fatty acids within the tissue. Evidence is presented to support the view that free fatty acids from the medium can, as such, enter adipose tissue cells, and it is suggested that there is a pool of free fatty acids, perhaps very small, within the tissue which serves as the precursor pool for glyceride synthesis.

THE INTRACELLULAR LOCALIZATION OF AN ENZYMATIC DEFECT OF LIPID METABOLISM IN DIABETIC RATS. A. Gellhorn and W. Benjamin (Dept. of Medicine, College of Physicians and Surgeons, Columbia Univ., New York, N.Y.). *Biochim. Biophys. Acta* **84**, 167-75 (1964). The conversion of stearic acid to oleic acid has been studied in homogenates and other subcellular fractions of adipose tissues and liver of untreated and insulin treated diabetic rats and rats maintained on a fat-free diet. The synthesis of the mono-unsaturated fatty acid is an oxygenase reaction requiring molecular oxygen and DPNH or TPNH. The site of the reaction has been localized to the microsomes. In diabetes, the microsomal enzymatic conversion of stearate to oleate stops. This defect in lipid metabolism, which is separable from the overall depression of lipid biosynthesis, is corrected by insulin therapy.

THE ESTERIFICATION OF CHOLESTEROL IN VITRO BY RAT PLASMA. I. RELATIVE PARTICIPATION OF TRIGLYCERIDES AND PHOSPHOLIPIDS. II. EFFECT OF SNAKE VENOM. S. N. Shah, W. J. Lossow and I. L. Chaikoff (Dept. of Physiology, Univ. of Calif., Berkeley, Calif.). *Biochim. Biophys. Acta* **84**, 176-81 (1964). The synthesis of cholesterol esters by plasma and extracts of acetone powders of rat plasma was studied with the following substrates: a) lecithin labeled in the β position with either oleic-1-C¹⁴ acid, palmitic-1-C¹⁴ acid; b) triglycerides labeled with either palmitic-1-C¹⁴ acid or oleic-1-C¹⁴ acid; c) cholesterol-4-C¹⁴. As much as 24 and 50% of the incubated C¹⁴ was recovered as cholesterol esters when the labeled lecithins and free cholesterol, respectively, were incubated and less than 1% was so recovered when the labeled triglycerides served as substrates. Snake venom completely prevented the formation of labeled cholesterol esters by acetone powder extracts in the experiments with the fatty acid-labeled lecithin and the labeled free cholesterol.

THE SPLITTING OF CAROTENOID ESTERS IN THE ALIMENTARY TRACT OF THE RAT. V. H. Booth (Dunn Nutritional Lab., Univ. of Cambridge and Med. Res. Council, Cambridge, Great Britain). *Biochim. Biophys. Acta* **84**, 188-91 (1964). Female rats subsisting on a carotenoid-free diet were given doses of diesters of taraxanthin and of zeaxanthin dissolved in oil. Pigments recovered from the faeces were examined chromatographically. One-third of the ingested pigment was recovered after passage through the alimentary tract. Most of the recovered pigment had been hydrolysed to the free carotenol. The fate of the two-thirds that disappeared is unknown.

THE TRANSFER OF LIPIDS BETWEEN HUMAN α -LIPOPROTEIN AND ERYTHROCYTES. L. A. E. Ashworth and C. Green (Dept. of Biochemistry, Univ. of Liverpool, Liverpool, Great Britain). *Biochim. Biophys. Acta* **84**, 182-7 (1964). The transfer of palmitic acid and sterol between human α -lipoprotein and erythrocytes has been studied. Human erythrocytes take up palmitic acid from α -lipoprotein until all binding sites are filled. The process is very much more rapid if the lipoprotein also bears extra cholesterol. Of the endogeneous unesterified sterol

of human α -lipoprotein 38% does not exchange with that of rat erythrocytes. C¹⁴-cholesterol taken up by the lipoprotein after dispersion on Celite exchanges with that of human erythrocytes but it does not behave in exactly the same way as the endogeneous sterol. When α -lipoprotein is labelled with both cholesterol and palmitic acid and then incubated with human erythrocytes, each interferes with the transfer to the cells of the other.

A COMPARISON OF THE METABOLISM OF CIS, CIS-LINOLEIC, TRANS, TRANS-LINOLEIC AND A MIXTURE OF CIS, TRANS- AND TRANS, CIS-LINOLEIC ACIDS IN THE RAT. R. H. Coots (Procter and Gamble Co., Miami Valley Lab., Cincinnati, Ohio). *J. Lipid Res.* **5**, 473-6 (1964). A comparison has been made of the metabolism of *cis, cis*-linoleic, *trans, trans*-linoleic and a mixture of *cis, trans*- and *trans, cis*-linoleic acids in the rat. The data show that linoleic acid and its geometric isomers were well adsorbed. These acids were readily oxidized to CO₂ with no apparent difference in rate or extent of catabolism between the *trans*-isomers. However, the *trans*-isomers of linoleic acid were catabolized to CO₂ to a somewhat greater extent than was *cis, cis*-linoleic acid. The *trans*-linoleic acids, like the *cis, cis*-linoleic acid, were transported in the lymph mainly as glycerides. There were no major differences in the distribution of the various acids among the lymph lipid classes, indicating that the rat does not distinguish among the linoleic acid isomers as far as digestion and adsorption are concerned. Linoleic acid and its *trans*-isomers were metabolized in an efficient and apparently normal manner.

ROLE OF ARACHIDONIC ACID IN NUTRITIONAL ENCEPHALOMALACIA: INTERRELATIONSHIP OF ESSENTIAL AND NONESSENTIAL POLYUNSATURATED FATTY ACIDS. B. Century and M. K. Horwitz (Elgin State Hospital). *Arch. Biochem. Biophys.* **104**, 416-22 (1964). Combining 8% reconstituted cod liver oil with 8% reconstituted corn oil in a tocopherol-free diet prevented the appearance of nutritional encephalomalacia in chicks. Adding 8% reconstituted cod liver oil to a diet containing 1% ethyl arachidonate enhanced the incidence of encephalomalacia in tocopherol-deficient chicks and resulted in lower tissue arachidonate levels than in the group fed 1% ethyl arachidonate alone. Adding 8% reconstituted cod liver oil, from which tocopherol was removed, to a diet containing 8% reconstituted corn oil depressed arachidonate and higher essential fatty acids in tissues and markedly increased the levels of the nonessential unsaturated fatty acids of the linolenic series. These data are consistent with the hypothesis that fatty acids of the linolenic series, found in cod liver oil, can readily displace essential fatty acids in tissues, even in brain, and inhibit the conversion of linoleic to arachidonic acid.

TESTICULAR STEROLS. I. INCORPORATION OF MEVALONATE AND ACETATE INTO STEROLS BY TESTICULAR TISSUE FROM RATS. Su-Chen Tsai, Beatrice P. Ying and J. L. Gaylor (Cornell University). *Arch. Biochem. Biophys.* **105**, 329-38 (1964). After incubation with acetate-1-C¹⁴ *in vitro*, relative amounts of activity in the various fractions of the nonsaponifiable lipids were: squalene, 34%; lanosterol and companion C₃₀, C₂₈ and C₂₅ sterols, 19%; cholesterol and companion C₂₇ sterols, 16%; and unfractionated steroids, 26%. After incubation with mevalonate-2-C¹⁴, the relative activities were 32, 21, 12 and 8%, respectively, of the total label that was isolated in the nonsaponifiable fraction. Labeled acetate was incorporated into all fractions of testicular sterols *in vivo*. Labeled acetate and mevalonate were not incorporated into sterols by cell-free homogenates of testicular tissue in fortified media; similar homogenates metabolized labeled lanosterol.

THE BIOSYNTHESIS OF STEROLS IN SOLANUM TUBEROSUM. D. F. Johnson, E. Heftmann and G. V. C. Houghland (National Institutes of Arthritis and Metabolic Diseases). *Arch. Biochem. Biophys.* **104**, 102-5 (1964). The incorporation of mevalonic acid-2-C¹⁴ into the Katahdin variety of *Solanum tuberosum* was studied for an extended period of growth. The largest incorporation into the major sterols, stigmasterol and β -sitosterol, occurred in 1 week. Incorporation into β -sitosterol started sooner and occurred to a greater degree than in the case of stigmasterol.

EFFECT OF DIETARY FAT AND OTHER FACTORS ON EGG YOLK CHOLESTEROL. I. THE "CHOLESTEROL" CONTENT OF EGG YOLK AS INFLUENCED BY DIETARY UNSATURATED FAT AND THE METHOD OF DETERMINATION. J. F. Weiss, E. C. Nabel and R. M. Johnson (Ohio State University). *Arch. Biochem. Biophys.* **105**, 521-6 (1964). Polyunsaturated fatty acids in eggs from hens fed diets containing large amounts of unsaturated fat react with the Zlatkis reagent to give a color that interferes with the determination of cholesterol. The apparent cholesterol concentra-

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tion increased as the unsaturation of the yolk lipids increased. The percentage increase in yolk cholesterol content, measured by the direct Zlatkis method after feeding a diet containing safflower oil at a level of 30% for 3 weeks, was approximately 36%. Upon feeding a diet containing linseed oil at a level of 30%, the increase was 43%. When a modification of the Zlatkis method that included a saponification and extraction procedure was used, the increase in the cholesterol content of eggs from hens fed the diet containing safflower oil was 19% and the increase was 27% when hens were fed the diet containing linseed oil. The increases in the cholesterol content of the eggs, which paralleled the increases in unsaturation of the yolk lipids, were highly significant even after the removal of the interfering unsaturated fatty acids. Unsaturated carotenoid compounds contributed little to the color development when the modified Zlatkis method was used.

ROLE OF THE LIVER IN THE METABOLISM OF EXOGENOUS CHOLESTEROL ESTERS. L. Swell, M. D. Law and C. R. Treadwell (George Washington University). *Arch. Biochem. Biophys.* 105, 541-53 (1964). Rats were fed a test meal containing cholesterol, no fatty acids, or different fatty acids. A control group received a test meal with only a tracer amount of labeled cholesterol. Substantial amounts of cholesterol esters accumulated in the liver in 24 hours. The degree of accumulation was greatest when unsaturated fatty acids were fed. The ester which accumulated to the greatest extent, irrespective of the fatty acid fed, was cholesterol oleate. The fatty acid composition of the serum cholesterol esters was essentially unchanged by cholesterol feeding. The cholesterol-C¹⁴ ester pattern in the liver at 24 hours was similar in all groups irrespective of the fatty acid fed and showed a general shift toward C¹⁴-monounsaturated esters. In all groups, the principal cholesterol ester found in the blood at the end of 24 hours was cholesterol arachidonate. The specific activity data on the free and individual cholesterol esters of the liver indicate that a major portion of the incoming cholesterol esters undergoes transferase reactions with fatty acid donors to form other cholesterol esters. The specific activity of the serum cholesterol esters did not exceed the specific activity of the corresponding liver cholesterol esters. The results of this study suggest that intestinal cholesterol esters are rapidly removed by the liver. A portion of these esters undergoes hydrolysis to free cholesterol while another portion appears to participate in a series of transferase reactions with fatty acid donors to form other cholesterol esters. A major ester formed in this fashion is cholesterol arachidonate, which is then released into the blood in association with the lipoproteins.

EFFECT OF DIETARY CHOLESTEROL ON SERUM AND EGG CHOLESTEROL LEVELS OVER A PERIOD OF TIME. H. M. Edwards, Jr. and Vivian Jones (Poultry Dept., Univ. of Georgia, Athens, Ga.). *Poultry Sci.* 43, 877-79 (1964). Two experiments with Single Comb White Leghorn hens showed that feeding cholesterol caused increases in the serum and egg cholesterol levels 10 days after feeding commenced. However, the hen appeared to adjust to the increased level of dietary cholesterol. In both experiments serum cholesterol levels had returned to normal by 20 days and in one of the experiments, the egg cholesterol levels had also returned to normal. The differences in the responses obtained in the two experiments indicate that some other factors as yet unidentified are influencing the type of response obtained from cholesterol feeding.

OBSERVATIONS ON FEEDING TUNG OIL TO CHICKENS. H. M. Edwards, Jr. (Poultry Dept., Univ. of Georgia, Athens, Ga.). *J. Nutr.* 83, 365-68 (1964). The inclusion of commercially available crude tung oil in the rations of chicks at levels as low as 0.5% caused slow growth. Higher levels (2.0% to 5%) of tung oil in the diet caused high mortality. Upon autopsy the affected chicks showed enlarged gallbladders, fluid in the abdominal, thoracic and pericardial cavities, variable liver size, enlarged hearts and had an odor of tung oil. Methyl esters of the fatty acids from tung oil were not toxic. The unsaponifiable fraction from tung oil isolated after alkaline hydrolysis also was not toxic.

EFFECT OF EXPERIMENTAL DIABETES ON STEROID METABOLISM. II. ALTERATIONS IN ANDROST-4-ENE-3,17-DIONE AND CORTISOL METABOLISM. N. I. Gold and L. D. Garren (Dept. of Pediatrics, Harvard Med. School and Dept. of Medicine, The Children's Hospital Med. Center, Boston 14, Mass.). *J. Biol. Chem.* 239, 2796-2803 (1964). Androst-4-ene-3,17-dione-4-C¹⁴ and cortisol-4-C (11 β ,17,21-trihydroxypregn-4-ene-3,20-dione-4-C¹⁴) were incubated in a reduced triphosphopyridine nucleotide-generating system with microsomal and supernatant fractions prepared from livers of adult female control and alloxan-diabetic rats. With more than 84% of the total radioactivity recovered, the major metabolites formed were identified and determined quantitatively by isotope dilution procedures in which paper and thin layer chromatography were used.

SYNTHESIS OF FATTY ACIDS IN ANIMAL TISSUES. II. THE OCCURRENCE AND BIOSYNTHESIS OF CIS-VACCENIC ACID. P. W. Holloway and S. J. Wakil (Dept. of Biochem., Duke Univ. Medical Center, Durham, N.C.). *J. Biol. Chem.* 239, 2489-95 (1964). Evidence is presented to indicate that *cis*-vaccenic acid is a normal constituent of animal tissue fatty acids. This conclusion is based on the isolation of the C_{18:1} fatty acid fraction from rat liver cells and their subcellular fractions by a combination of thin layer and gas-liquid chromatography. Catalytic hydrogenation of the C_{18:1} fraction yields stearic acid. Periodate-permanganate oxidation of the C_{18:1} fraction yields C₆- and C₁₀-monocarboxylic acids and C₆- and C₁₁-dicarboxylic acids indicating the C_{18:1} fraction is a mixture of both oleic and *cis*-vaccenic acids. The *cis*-vaccenic acid content appears to range between 20 and 50% of the total C_{18:1} acids. *cis*-Vaccenic acid can be derived from palmitic acid but not from stearic acid as evidenced by the incorporation of C¹⁴-palmitic acid, but not C¹⁴-stearic acid into the *cis*-vaccenic acid.

LIPID METABOLISM OF EUGLENA GRACILIS. D. Hulanicka, J. Erwin and K. Bloch (James Bryant Conant Lab., Harvard Univ., Cambridge 38, Mass.). *J. Biol. Chem.* 239, 2778-87 (1964). The lipid and fatty acid composition of *Euglena gracilis* Z has been investigated. Cells grown as strict photoautotrophs and cells grown heterotrophically after dark-adaptation were analyzed. The major polyunsaturated fatty acids of photoautotrophic cells are linolenic acid and 4,7,10,16-hexadecatetraenoic acid. The principal lipids in these cells are a diglyceride, galactolipids and a phospholipid fraction containing chiefly phosphatidylserine. The principal polyunsaturated fatty acids of heterotrophic cells are arachidonic acid and (or) 11,14,17-eicosatrienoic acid, 5,8,11,14,17-eicosapentaenoic acid and uncharacterized C₂₂ and C₂₃ polyunsaturated acids. Heterotrophic cells contain triglycerides and large amounts of phospholipids, but lack galactolipids.

INTERMOLECULAR SPECIFICITY OF PANCREATIC LIPASE AND THE STRUCTURAL ANALYSIS OF MILK TRIGLYCERIDES. R. G. Jensen, J. Sampugna and R. L. Pereira (Dept. of Animal Industries, Univ. of Connecticut, Storrs, Conn.). *J. Dairy Sci.* 47, 727-32 (1964). Pancreatic lipase released butyrate and palmitate in equimolar quantities from glyceryl 1-palmitate 2,3-dibutyrate (PBB), an absence of intramolecular specificity. However, when glyceryl 1-myristate 2,3-dioleate (MOO) was mixed with PBB, the latter was hydrolyzed more rapidly, indicating intermolecular specificity. Primary position specificity was maintained during 5-min digestions when glyceryl 2-butyrate 1,3-dipalmitate was the substrate. Data from the pancreatic lipase digestions of milk fat are presented. It is concluded that pancreatic lipase digests some classes of milk triglycerides more rapidly than others.

A STUDY OF THE HYPOCHOLESTEROLEMIC ACTIVITY OF THE ETHYL ESTERS OF THE POLYUNSATURATED FATTY ACIDS OF COD LIVER OIL IN THE RAT. S. G. Kahn (Squibb Inst. for Med. Res., New Brunswick, N.J.). *J. Nutr.* 83, 262-6 (1964). The ethyl esters of the polyunsaturated fatty acids of cod liver oil reduced the hypercholesterolemia produced in rats fed diets supplemented with a coconut oil, cholesterol and sodium taurocholate. As little as 0.1% ethyl ester added to the diet caused a reduction of blood cholesterol concentration in the hypercholesterolemic rat. The hypocholesterolemic activity of the polyunsaturated fatty esters was sustained after withdrawal of the fatty esters from the ration. Long-term feeding of the polyunsaturated fatty esters resulted in a consistent lower blood cholesterol through the duration of a 154-day feeding experiment. Control animals fed the hypercholesterolemic diet attained high blood cholesterol values which declined after 7 weeks; however, their blood cholesterol level never reached the lower value of the polyunsaturated fatty ester supplemented rats.

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ON LIPOXYDASE OF SOYBEANS. PRESENT STATE OF OUR KNOWLEDGE. E. André. *Oleagineux* 19, 461-63 (1964). This account is divided into four paragraphs: 1) Vegetables in which lipoxydase has been found; 2) Isolation of lipoxydase in the form of a globuline which has been obtained in a crystalline form in spite of its very high molecular weight; 3) Lipoxydase biochemical activity, particularly its action on linoleic acid and on highly unsaturated acids of the elupanodonic group; 4) Lipoxydase action on carotene and carotinoids, specifically application in the bleaching of wheat meal.

ADAPTATION OF THE CARPENTER METHOD FOR THE AMOUNT OF ASSIMILABLE LYSINE IN FISH FLOUR. J. Janicki and J. Skupin. *Rocz. Tech. Chem. Zgw.* 10, 67-75 (1964). The classical method of Carpenter using fluorodinitrobenzene (FDNB) has been used to determine the amount of lysine in fish flour. In order to eliminate the secondary reaction of FDNB with the elimination of the alpha-NH₂ of lysine, a modification of the method was developed, in which methoxycarbonyl chloride is used to block the aforementioned amine group. The amount of assimilable lysine as determined by the classical method is considerably higher than that determined by the modified method. It has been therefore possible to study the amino acid composition of an acid hydrolysate of fish flour by paper chromatography. It has been determined that fish flour contains about 2.6 grams of usable lysine in 100 grams of protein. The quantity of usable lysine is not only an index of the biological value of the protein product, but is also an index of the quality of the process used to obtain the fish protein. (Rev. Franc. Corps Gras)

DISTRIBUTION OF LIPIDS IN SUBCELLULAR PARTICLES OF GUINEA-PIG BRAIN. J. Eichberg, Jr., V. P. Whittaker and R. M. C. Dawson (Agr. Res. Council Institute of Animal Physiology). *Biochem. J.* 92, 91-100 (1964). Guinea-pig forebrain was fractionated by differential and gradient-density centrifuging and the distribution of lipids measured in the subcellular fractions. The large myelin particles contained cholesterol, phospholipid and cerebroside in the molar proportions 2:1.94:1. The phospholipids of myelin contained 25% of both lecithin and ethanolamine plasmalogen and much of the phosphatidic acid of the original homogenate. The mitochondrial phospholipids consisted predominantly of lecithin and ethanolamine-containing phosphoglycerides and contained 11% of cardiolipin phosphorus. Ganglioside and cerebroside were virtually absent. The microsomes were rich in phosphatidylinositol and ganglioside. The synaptosomes (nerve-ending particles) contained no cerebroside, but their phospholipids were similar to those of the original homogenate. The phospholipids of synaptic vesicles resembled those of microsomes. The distributions of individual gangliosides in the cell fractions were remarkably similar except that the large myelin particles contained proportionally more of one monosialoganglioside.

THE HYDROGENATION OF UNSATURATED FATTY ACIDS IN THE OVINE DIGESTIVE TRACT. P. F. V. Ward, T. W. Scott and R. M. C. Dawson (Agr. Res. Council Inst. of Animal Physiology). *Biochem. J.* 92, 60-8 (1964). When labeled linolenic acid was incubated for short periods in an artificial rumen, it was rapidly hydrogenated to 2 types of dienoic acids, subsequently to a C₁₈ monoenoic acid and finally into stearic acid. The isomers in the major dienoic acid fraction had *cis-cis* non conjugated configurations and the double bonds were largely at C-11 or C-12 and C-15 or C-16. The monoenoic acids formed were largely *trans*, with the double bond predominantly at C-13 or C-14. Rapid

hydrogenation of labeled linoleic acid and oleic acid occurred in the artificial rumen; the former gave a *trans* monoenoic acid as an intermediary. The *trans* C₁₈ monoenoic acids passing from the rumen were almost quantitatively absorbed in the ileum. The unsaturated C₁₈ acids present in the ileum digesta were hydrogenated in the caecum and colon, so that nearly all the acids in the excreta were saturated. The hydrogenation of labeled linoleic acid by caecal and colon contents resulted again in the formation of substantial amounts of *trans* C₁₈ monoenoic acids.

FATTY ACID SPECIFICITIES AND RATES OF CHOLESTEROL ESTERIFICATION IN VIVO AND IN VITRO. M. Sugano and O. W. Portman (Harvard School of Public Health). *Arch. Biochem. Biophys.* 107, 341-51 (1964). After injection of mevalonate-2-C¹⁴ into rats or Cebus monkeys or cholesterol-4-C¹⁴ into rats, the specific activity of plasma cholesteryl arachidonate was higher and that of cholesteryl oleate lower than the specific activity of total plasma cholesterol esters for at least 6 hours. After the administration of labeled cholesterol intravenously, the free cholesterol specific activity of liver was equal to that of plasma within 1 hour, but the ester cholesterol specific activity of plasma was 3 times greater than that of liver after 1 hour. The liver and plasma cholesterol ester specific activities did not become equal for nearly 12 hours. Cholesterol-4-C¹⁴ esterification by plasma *in vitro* resulted in a heterogeneous pattern similar to that seen in the early periods of the *in vivo* experiments. Esterification of radiocholesterol with different fatty acids by liver preparations *in vitro* was not similar to that seen in plasma. It was concluded from estimates of the rates of cholesterol esterification *in vivo* and *in vitro* that the plasma esterification activity was of considerable significance in maintenance of the level of plasma cholesterol esters. The authors propose that the early heterogeneity of labeling of different cholesterol esters *in vivo* resulted from the initial preponderant effect of the plasma esterification activity.

CHEMICAL AND NUTRITIONAL ASPECTS OF OXIDISED AND HEATED FATS. N. W. Hanson, compiler. *Chem. Ind. (London)* 1964, 1541-9. Summary of a symposium held in March, 1964, at the Imperial College of Science and Technology, London. Papers included: *Introductory Lecture*, C. H. Lea; *Biological Effects of Oxidised and Heated Fats*, by A. C. Frazer; *The Effects of Hydroperoxides on Mitochondrial Metabolism* by P. J. O'Brien; *Metabolism of Linoleic Acid Hydroperoxides* by I. P. Freeman; *Biological Properties of Blown Oils*, by K. Lang; *Nutritional and Chemical Changes Occurring in Heated and Oxidised Fats: A Review of Some American Work* by P. V. Johnston; *Some Chemical Effects of Heat on Edible Fats* by C. B. Barrett.


VITAMIN-CONTAINING GELATIN BEADLETS AND THE PROCESS OF PREPARING THEM. A. Koff and P. F. Widmer (Hoffmann-La Roche Inc.). *U.S.* 3,143,475. The described process comprises the following steps: 1) forming an aqueous emulsion in which is dispersed a fat-soluble vitamin-active material and gelatin; 2) forming discrete droplets of the emulsion entirely above the surface of a vegetable oil; 3) allowing the droplets to fall through an inert atmosphere into the vegetable oil which is maintained at a temperature of 15 to 25°C; 4) cooling the oil to a temperature of 0 to 15°C and 5) dehydrating the gelatin beadlets formed thereby with a lower alkanol.

METHOD FOR PRODUCING 2-TRANS-VITAMIN A ACID. M. Matsui, S. Saijo, K. Ohizumi, T. Nishida and S. Okano (Sumitomo Chemical Co., Ltd.). *U.S.* 3,143,564. A method for producing 2-*trans*-vitamin A acid compounds comprises contacting one member of the group consisting of 2-*cis*-vitamin A acid, its lower alkyl ester and unsubstituted amides with potassium amide in an amount of at least 1 mol per mol of the 2-*cis*-vitamin A acid compound to be isomerized in an inert medium for 0.5 to 20 hours to give the corresponding 2-*trans*-vitamin A acid compound.

• Drying Oils and Paints

COMPARATIVE EVALUATION OF NYASALAND (MONTANA) AND FORDII TUNG OILS IN MEDIA FOR ZINC CHROMATE PRIMERS. H. W. Chatfield. *Paint Oil Colour J.* 146, 228-230 (1964). Under salt spray conditions the protective performance of the two oils was comparable. Under accelerated weathering conditions there was a slight preference for the Chinese tung oil. Performance could be equalized by an adjustment of the tung-linseed oil ratio.

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MEDIUM OIL LENGTH LACTIC ACID MODIFIED LINSEED GLYCEROL ALKYDS. H. R. Touchin. *Paint Technol.* 28, 14-19 (1964). In linseed glycerol alkyds, lactic acid modification appears to be more effective at the shorter oil length, where good hardening of the film results. Finishes so prepared were in some cases superior. At the longer oil length, the modification seemed to give somewhat inferior performance. Good industrial enamels can be made from the shorter oil length resin. Some evidence of improved pigment dispersion was found. As primers, the lactic modified resins have superior water and humidity resistance and are noted also for a reduced tendency for corrosion to spread under the film from areas of bare metal. The primers have very poor resistance to salt water immersion but will withstand salt spray reasonably well.

• Detergents

METAL-CONTAINING SURFACTANTS. Hiroshi Suzuki (Government Industrial Research Institute). *Yukagaku* 13, 399-412 (1964). A review with 100 references.

APPLICATION OF SURFACTANTS ON WOOL INDUSTRY. II. EFFECT OF ANIONIC SURFACTANTS ON WOOL SHRINKAGE. Chiaki Sakai and Saburo Komori. *Yukagaku* 13, 275-8 (1964). The shrinkage of wool was the highest when it was immersed in a solution of sodium saturated primary alcohol sulfate at a certain concentration of detergent, in which the concentration was lower than the critical micelle concentration obtained from surface tension. In the solution of sodium oleyl alcohol sulfate, this phenomenon was not observed and the wool shrinkage became more or less constant when the concentration of solution was 0.1% or higher. Wool shrinkage was less when it was immersed in 0.1% solution of sodium alkylbenzenesulfonate than when treated with water only. In sodium laurate solution, the wool shrinkage was maximum at a concentration around critical micelle concentration while the solution of sodium oleate did not show such phenomenon. Commercial soaps showed nearly a fixed value for wool shrinkage when its concentration was higher than 0.3%.

ON THE SURFACE OF SUCROSE ESTERS AND OTHER EMULSIFIERS. K. I. Orlova *et al.* *Trudy Vniiz* 23, 298-308 (1963). Various techniques have been used to study the surface activity of the mono- and distearates of sucrose, lecithin and glycerol monostearate, at the air-water interface, the water-benzene interface and at the benzene-emulsified water interface at various temperatures. It was found the esters of sucrose lower the interfacial tension to a greater degree than glycerol monostearate. (Rev. Frane. Corps Gras)

ON THE PROBLEM OF THE SOLUBILITY OF NEW, NONIONIC, EDIBLE EMULSIFIERS—THE SUCROSE ESTERS. K. I. Orlova *et al.* *Trudy Vniiz* 23, 286-97 (1963). The authors studied the solubility at various temperatures of preparations of the sucrose stearates (mono and distearate) in water and in the nonpolar solvents benzene, cyclohexane, *n*-hexane, mineral oil and in sunflower seed oil. Sucrose stearates are practically insoluble in water between 20°C and 40°C, but as the temperature is elevated towards the softening point of the esters, the esters form semi-colloidal solutions which are stable. The solubility of the sucrose stearates in nonpolar solvents is much greater than in water, but the solubility still depends upon the solvent. Solubility decreases in the following order: benzene > cyclohexane > hexane > mineral oil > sunflower seed oil. The mono and distearates of sucrose notably decrease the surface tension of aqueous as well as non-aqueous solutions. (Rev. Frane. Corps Gras)

SURFACE-ACTIVE AGENTS—THEIR BEHAVIOR AND INDUSTRIAL USE. E. G. Schwarz and W. G. Reid (Union Carbide Corp., Silicones Div.). *Ind. Eng. Chem.* 56, 26-31 (1964). The composition of a surfactant molecule—both as a whole and also in part—affects the fundamental properties that define surface activity. Proper balancing of these properties is required for both profoamers and antifoamers. Specific examples are given from the author's industrial experience.

FATTY AMINE OXIDES. E. Jungermann and M. E. Ginn (Armour Grocery Products Co.). *Soap Chem. Specialties* 40(9), 59-62 (1964). The authors discuss the chemistry and preparation, methods of analysis and performance properties of fatty amine oxides. Their greatest utility lies in the area of foam boosting and detergency improvement. Important secondary effects are also imparted, such as skin emolliency in dishwashing and lustre and manageability from shampoos. Textile softening action is also evident.

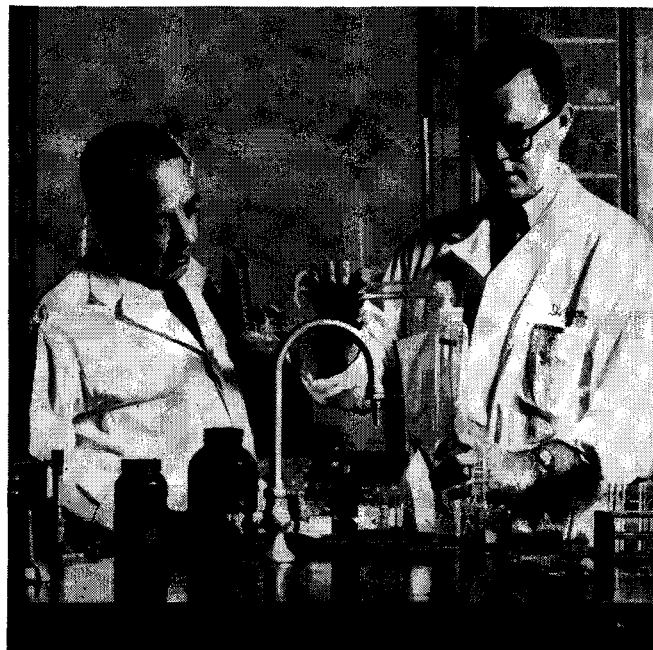
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