Abstracts

EDITOR: S. KORITALA • ABSTRACTORS: J.C. Harris, M.G. Kokatnur, F.A. Kummerow, G. List, B. Matijasevic, K.D. Mukherjee, D.B.S. Min, R.A. Reiners, and P.Y. Vigneron

• Fats and Oils

RESOLUTION OF DESMOSTEROL, CHOLESTEROL, AND OTHER STEROL INTERMEDIATES BY REVERSE-PHASE HIGH-PRESSURE LIQUID CHROMATOGRAPHY. E. Hansbury and T.J. Scallen, *J. Lipid Res.* 19, 742–6 (1978). A highly efficient technique has been developed for the resolution of several sterols that are intermediates in the biosynthesis of cholesterol and that differ only by one carbon-carbon double bond or by one methyl group. The technique described utilizes reverse-phase high-pressure liquid chromatography on a μBondapak-C_{18} column with acetonitrile as eluting solvent.

METHOD FOR THE EXTRACTION AND CLEANUP OF ANIMAL FEED FOR THE DETERMINATION OF LIPOSOLUBLE VITAMINS D, A, AND E BY HIGH-PRESSURE LIQUID CHROMATOGRAPHY. H. Cohen and M. Lapointe, *J. Agric. Food Chem.* 26, 1210–3 (1978). A high-pressure liquid chromatography (LC) procedure and cleanup has been developed for the determination of vitamins A, D, and E in feeds. The method is quantitative for all three vitamins. Recovery studies on different feeds showed an average recovery of vitamin A (acetate), 96.4% ± 2.4; vitamin E acetate, 92.6% ± 2.92; vitamin D_3, 91.25% ± 5.9. Minimum detectable amounts are: vitamin A, 250 IU/kg; vitamin D_3, 10,000 IU/kg; vitamin E, 5 IU/kg. The LC procedure was compared with an AOAC colorimetric procedure for the vitamins A and E.

OXIDATION OF CHOLESTEROL BY DIOXYGEN SPECIES. L.L. Smith, *et al.*, *J. Am. Chem. Soc.* 100, 6206–11 (1978). Reaction between cholesterol in aqueous sodium stearate dispersions and H_2O_2 yielded many products of which 12 were isolated and identified. Products included 5,6α-epoxy-5α-cholestan-3β-ol and 5,6β-epoxy-5β cholestan-3β-ol in 1:8 ratio representing direct reaction between cholesterol and H_2O_2 and 5α-cholestane-3β, 5,6β-triol formed by hydration of the 5,6-epoxides; epimeric cholesterol 7-hydroperoxides, epimeric cholest-5-ene-3β,7-diols, and 3β-hydroxycholest-5-en-7-one representing free-radical oxidation of cholesterol by molecular oxygen derived by H_2O_2 disproportionation; 5α-cholest-6-ene-3β,5-diol, cholest-4,6-dien-3-one, and 7α-stearatoxycholest-5-en-3β-ol possibly derived from singlet molecular oxygen released in H_2O_2 disproportionation; and 5α-cholestane-3β,6β-diol. These results complete our studies of reactions between cholesterol and dioxygen species, revealing for the first time the several pathways of oxidation of a biologically important substrate by dioxygen species.

CONFORMATIONAL STRUCTURE OF GLYCEROL TRIVALERATE AND ITS RELATION TO PHOSPHOLIPIDS: STUDIES BY NMR AND POTENTIAL ENERGY CALCULATIONS. G. Govil, R.V. Hosur and A. Saran, *Chem. Phys. Lipids* 21, 77–96 (1978). The structure of a model lipid (glycerol trivalerate, GTV) has been investigated by ^1H and ^{13}C NMR, and energy calculations based on classical potential functions (CPF). The structure of glycerol-ester pivot in GTV is characterized by a dynamic equilibrium between two dominant conformations. The conformational picture of the hydrocarbon chains and glycerol moiety in GTV is very similar to that in phospholipids. These results indicate caution in using the reported crystal structure of 1,2-dilauroyl-*D,L*-phosphatidylethamolamine as the only model for the organization of lipid molecules in biological membranes.

HIGH-SENSITIVITY SCANNING CALORIMETRIC STUDY OF MIXTURES OF CHOLESTEROL WITH DIMYRISTOYL- AND DIPALMITOYLPHOSPHATIDYLCHOLINES. S. Mabrey, P.L. Mateo, and J.M. Sturtevant, *Biochemistry* 17, 2464–8 (1978). A highly sensitive and stable scanning microcalorimeter is employed in a reinvestigation of the effect of cholesterol on multilamellar suspensions of dimyristoylphosphatidylcholine (DMPC) and dipalmitoylphosphatidylcholine (DPPC). Below 20 mol % cholesterol the DPPC mixtures give heat-capacity curves each of which can be resolved into a narrow and a broad peak, suggesting the coexistence of two immiscible solid phases; above 20 mol % only the broad peak is observed and this disappears at about 50 mol %.

EFFECTS OF AIR, OZONE, AND NITROGEN DIOXIDE EXPOSURE ON THE OXIDATION OF CORN AND SOYBEAN LIPIDS. R.I. Brooks and A.S. Csallany, *J. Agric. Food Chem.* 26, 1203–9 (1978). This study was conducted to determine the oxidative effects induced by exposure of corn and soybean seeds to air, nitrogen dioxide (NO_2) and ozone (O_3). Whole halves, and ground samples of soybean seeds and whole corn kernels were exposed to air, 15 ppm NO_2, or 1.5 ppm O_3 continuously for 100 h at room temperature. Ground soybean samples exposed to air, 15 ppm NO_2, or 1.5 ppm O_3 incurred the greatest PUFA and tocopherol destruction and lipofuscin-like pigment formation.

STEREOSPECIFIC ^1H-NMR ANALYSIS OF TRIMETHYLSILYL DERIVATIVES OF GLYCERIDES WITH A CHIRAL SHIFT REAGENT. J. Bus and C.M. Lok, *Chem. Phys. Lipids* 21, 253–60 (1978). A proton magnetic resonance procedure with tri(3-heptafluorobutyryl-*d*-camphorato)praseodymium(III) as a chiral shift reagent has been developed to determine the enantiomeric purity of monoglycerides, 1,2-diglycerides and triglycerides with one mono-unsaturated fatty acid at position *sn*-1 or *sn*-3 and two saturated fatty acids at the two other glycerol positions. The addition of a chiral shift reagent induces a useful enantiomeric splitting which allows the accurate determination of the ratio of both enantiomers. The trimethylsilyl ethers of 1,2-diglycerides are better suited for this purpose than the acetyl compounds. For monoglycerides, the earlier published method with the diacetates gives a better line separation in the ^1H-NMR spectra.

STUDIES ON THE PROPERTIES OF THE SINGLET OXYGEN-LIKE FACTOR PRODUCED DURING LIPID PEROXIDATION. E.K. Lai, K.L. Fong and P.B. McCay, *Biochim. Biophys. Acta* 528, 497–506 (1978). The singlet oxygen reaction product of various trapping agents is observed during enzymic and nonenzymic peroxidation of microsomes as well as during the peroxidation of pure lipids extracted from microsomes. We now wish to report that purified fatty acid hydroperoxide alone, as well as peroxidized microsomal lipid and cumene hydroperoxide also form the singlet oxygen reaction product with 2,5-diphenylfuran. The reaction product (*cis*-1,2-dibenzoylethylene) was observed to be formed in an anaerobic system, with or without EDTA. The data indicate that a reaction of hydroxyl radicals with 2,5-diphenylfuran cannot account for the formation of dibenzoylethylene in these systems.

TOTAL SYNTHESIS OF DL-19-HYDROXYPROSTAGLANDIN E_1 AND DL-13-CIS-15-EPI-19-HYDROXYPROSTAGLANDIN E_1. C. Luthy *et al.*, *J. Am. Chem. Soc.* 100, 6211–7 (1978). A total synthesis of *dl*-19-hydroxyprostaglandin E_1 (34) and *dl*-13-*cis*-15-*epi*-19-hydroxyprostaglandin E_1 (35) via the conjugate addition of the dioctenyl cuprate reagent 21 derived from *dl*-1-iodo-3-hydroxy-7-*tert*-butyldimethylsilyloxyoct-1-*cis*-ene (14) to *dl*-2-(6-carbomethoxyhexyl)-4-tetrahydropyranyloxycyclopent-2-en-1-one (23), followed by the stereospecific sulfenate-sulfoxide transformation on the resultant 13-*cis*-prostaglandin analogue, is reported. The preparation of the requisite *cis*-iodooctene 14, prepared by two synthetic sequences starting from either α-methylcyclopentanone or acrylonitrile, is described as well as the separation of the C-19 α and β isomers.

TWO NEW VITAMIN D ISOMERS. FORMATION OF (3S,10R)-(Z,Z)-9,10-SECOCHOLESTA-5,7,14-TRIEN-3-OL AND ITS 10S-EPIMER FROM CIS-ISOTACHYSTEROL$_3$ VIA FACILE (1,7) SIGMATROPIC REARRANGEMENTS. B.L. Onisko, H.K. Schnoes, and H.F. Deluca, *J. Org. Chem.* 43, 3441–4 (1978). Warming a solution of (3*S*)-(*Z*)-9,10-secocholesta-5(10), 6,8(14)-trien-3-ol (*cis*-isotachysterol$_3$) in decane produced two new isomers of vitamin D: (3*S*,10*S*)-(*Z*,*Z*)-9,10-secocholesta-5,7,14-trien-3-ol (5a) and (3*S*,10*R*)-(*Z*,*Z*)-9,10-secocholesta-5,7,14-trien-3-ol (5b). The reaction has been shown to be reversible, and to occur via an

intramolecular (1,7) hydrogen transfer.

Optimum configuration of large-scale technical plants for straight distillation and fractionation of natural fatty acids. H. Stage, *Seifen, Ole, Fette, Wachse* **104**(16), 445–53 (1978). The review deals with the question as to how suitable connection and design of component elements can contribute to a reduction in operating costs in the light of ever rising energy prices and how, at the same time, the quality can be improved by careful treatment of the thermally and oxidatively very sensitive higher fatty acids, especially those with double bonds.

Detection of waxes with UV radiation. W. Schmidt. *Coating 1978,* 11(1), 32 (1978). Fluorescence given by the different waxes is shown in a table. (World Surface Coatings Abs No. 435)

Reactions of fatty acids with amines. II. Sequential thermal reactions of stearic (octadecanoic) acid with some 1,2- and 1,3-aminoalcohols and bis-amines. R.N. Butler, C.B. O'Regan and P. Moynihan, *J. Chem. Soc, Perkin Trans.* 1(4), 373–7 (1978). Thermal reactions of stearic acid with 2-aminoethanol and 3-aminopropanol in a heavy hydrocarbon oil as solvent involved (1) salt formation, (2) stearoylation of the amino nitrogen, and (3) a stearoyl transfer between two molecules of the stearamidoalcohol to give the amidoester. Each successive step took place at a higher temperature. The reaction of the stearamidoalcohols with thionyl chloride involved rearrangements, and did not yield stable cyclised products. Thermal reactions of stearic acid with propane-1,3-diamine and with bis(2-hydroxyethyl)amine gave diamides and amidoesters. (World Surface Coatings Abs. No. 436)

Structure and synthesis of polyunsaturated fatty acids. E. Ucciani, *Rev. Fr. Corps Gras.* **25**, 397-404 (1978). Natural polyunsaturated fatty acids have various structures. Almost all the possibilities which can occur between several double and triple bonds are represented. These structures are studied with respect to isomery and stereochemistry as well as in respect to conformation. Consequences at the level of chemical and catalytic reactivity are seen by some representative structures. Thanks to analytical progress since a few years limits of the reasonable structural pureness have diminished and synthesis methods had to fit to this new situation. The improvement of organic synthesis permits actually univocal and selectif couplings C-C, the creation of highly stereoselectif bonds C = C and all the necessary synthons. Several examples are given and discussed in order to show this simultaneous evolution in analysis and synthesis of polyunsaturated fatty acids.

Structure-chemical reactivity relations of polyunsaturated fatty acids. J. Graille, *Rev. Fr. Corps Gras,* **25**, 405–12 (1978). The reactional sites of polyunsaturated fatty acids are reviewed with regard to their interaction with antagonists of different electronic nature: free radicals, anions. Some examples of substitution reactions by halogen atoms are given and structural consequences are seen. Catalytic oxidation and autoxidation of polyunsaturated acids are studied similarly. The ionic antagonists can cause conjugation reactions and, in consequence, typical cyclisation in the case of polyunsaturated. The particular structure of natural polyunsaturated is well suited to concerted participation reactions (anchimeric reactions). Some examples of simultaneous participation of two double bonds in intramolecular heterocyclisation processes are discussed. In conclusion, the eventual importance of actual knowledge on polyunsaturated specific reactivity is shown.

Structure-catalytic reactivity of polyunsaturated fatty acids. G. Cecchi, *Rev. Fr. Corps Gras,* **25**, 413–21 (1978). The structure of polyunsaturated fatty acids determines a certain, complex and sometimes misunderstood catalytic reactivity. Some examples of reactions are discussed. Using as examples, isomerisation and hydrogenation, several elements of general catalytic theory are reviewed. Emphasis is placed on activated complexes which result from olefin-metal interactions. The organometallic intermediaries are discussed, particularly in homogeneous catalysis; their contribution to selectivity is studied with several examples. The structural consequences of polyunsaturated activation by metals or their complexes are reviewed. In conclusion, fundamental data on catalysis are used to explain the catalytic transformation of an oil.

Optimization of the yield in soybean crushing plants. R. Leysen, *Rev. Fr. Corps Gras,* 25, 349–52 (1978). The different factors which occur in expenses for soybeans crushing installations are very important. A control of material balance is necessary: quantity of unloaded beans, manufactured meals, produced oil and lecithin, and, a laboratory control of manufactured products which have to meet commercial specifications. Used energy and preventive maintenance of installations are two important points which are successively reviewed.

Recent advances in direct extraction processes of oils from oil rich seeds. M. Bernardini, *Rev. Fr. Corps Gras,* 25, 361–4 (1978). The oil extraction from seeds having a high content of oil (40–60%) is carried out according to two systems. The first system is using continuous presses (expellers) and a traditional solvent extraction device for residual oil from the press-cakes. The second system is using one direct solvent extraction device with two extractors in series. Comparative data of both processes show a significant advantage for direct extraction. Results concerning the treatments of different oilseeds are given.

Adsorption of stearic acid on pure and mixed oxides. R.L. Madan and N.K. Sandle, *J. Indian Chem. Soc.* **54**, 1113–6 (1977). The adsorption of stearic acid from solutions in cyclohexane on tin oxide (in the form of gel and precipitate), antimony oxide and tin-antimony mixed oxides having various ratios of tin to antimony, has been investigated. It is observed that the mode of adsorption depends upon the surface acidity of the oxide. In the case of tin oxide gel, tin oxide ppt. and the mixed oxides with Sb:Sn as 1:5 and 1:10, stearic acid is adsorbed with its hydrocarbon chain parallel to the surface. With antimony oxide and mixed oxides with higher percentage of antimony, the perpendicular orientation is adopted.

• Drying Oils and Paints

The fenugreek oil:composition, properties, possible uses in paints and varnishes industry. J.C. Baccou *et al., Rev. Fr. Corps Gras,* 25, 353–9 (1978). The oil of Trigonella foenum graecum L. (Fenugreek) contains interesting proportions of linoleic and linolenic acids which are relatively steady, whatever geographic origin and growing conditions of this plant may be. This led to siccativity and standolization experiments. An oleoglycerophtalic resin has been obtained after classical refining treatments (desodorisation, decoloration, wintering). It was technologically suitable to be used in paints industry instead of drying oils and derivations. This oil is an interesting by-product in extraction from Fenugreek steroïdic sapogenins. Its recovery contributes to valorization of this leguminous.

Linseed oil/metal acetylacetonate systems. IV. Thermogravimetry. N. Indicator *et al., J. Coatings Tech.* **60**, No 638, 54-61 (1978). Thermogravimetric data are presented for linseed oil containing small quantities of 15 metal acetylacetonates in the temperature range of 20–100 C. in air. Inhibition period, rate of increase in weight, maximum weight achieved and subsequent weight decrease are reported. Temperature parameters are presented. Results are discussed in terms of oil drying mechanisms which have appeared in the literature. (World Surface Coatings Abs. No. 435).

Drier composition and yellowing of linseed oil films. H. Rakoff, W.F. Kwolek and L.E. Gast. *J. Coatings Tech.* **50**, No 637, 51–5 (1978). The effect of drier composition on yellowing was studied spectrophotometrically with linseed oil as the vehicle and Morest paper as the substrate. The yellowness indices produced by the naphthenates and octoates of Co, Mn and Pb, either alone or in combinations of two or three driers, were analysed statistically. The results show that time of exposure, thickness of the film, and cation type had significant effects on yellowing, while the role of concentration and type of anion were less apparent. Films that contain two driers yellow in a way that indicates that the effects of single driers are additive. (World Surface Coatings Abs. No. 435)

Studies on non-traditional oils. II. Acid catalysed alcoholysis of tobacco seed oil. A.S. Kulkarni, D. Pradhan and H.A. Bhakare. *J. Col. Soc.* 16(3), 29–32 (1977). Alcoholysis of tobacco seed oil using methanol and ethanol with various acid catalysts such as hydrochloric, sulphuric and perchloric acids has been carried out. It has been shown that for methanolysis sulphuric acid gives best yields of esters, while for ethanolysis hydrochloric acid gives best yields. (World Surface Coatings Abs. No. 436)

RECENT APPLICATIONS OF GEL PERMEATION CHROMATOGRAPHY IN PAINT INDUSTRY. I. R.A. Ellis. *Pig. Resin Tech.* 7(4), 4(6 pp), (1978). The use of GPC for the analysis of oils, fatty acids and their derivatives, polyamide-modified alkyds, oligomeric polyethers, esters and polyesters, polyisocyanates and phenol-formaldehyde resins is reviewed. (World Surface Coatings Abs. No. 435)

HYDROGENATED CASTOR OIL (CASTOR OIL WAX). E. Plunsch. *Coating* 11(2), 69 (1978). Uses of hydrogenated castor oil are outlined. (World Surface Coatings Abs. No. 436)

EFFICIENT UTILISATION OF ROSIN ACIDS DURING TALL OIL DISTILLATION. A.A. Mariev and B.S. Filippov. *Izv. VUZ, Lesnoi Zh.* 20(1), 105–11 (1977). An investigation of product distribution from the distillation of tall oil indicated that about half of the rosin acids which are lost in distillation tars are degradation products. Rosin acid yields can be increased by using columns with Z-shaped titanium packing instead of ceramic saddle packing. (World Surface Coatings Abs. No. 436)

SOLVENT SELECTION FOR SEPARATING NEUTRAL SUBSTANCES FROM TALL OIL PRODUCTS. I.P. Zhukova, A.N. Trofimov and V.B. Kogan. *Zh. Prikl. Khim.* 30(6), 1420–2 (1977). The selectivities of 32 different solvents toward the pairs fatty acids/neutral components, fatty acid and rosin acid soaps/neutral components, neutral components/beta-sitosterol and soap/beta-sitosterol were determined and tabulated. The most highly selective solvents for pairs of acid/neutral component type were hydrocarbons, ketones and esters; the least selective were alcohols. (World Surface Coatings Abs. No. 436)

• Biochemistry and Nutrition

EFFECTS OF GEMFIBROZIL (CI-719), GEMCADIOL (CI-720), CLOFIBRATE AND U-41792 ON CHOLESTEROL DISTRIBUTION IN RAT PLASMA FRACTIONS OBTAINED BY POLYANION PRECIPITATION. R.E. Maxwell, J.W. Nawrocki and P.D. Uhlendorf *Artery* 4, 303–13 (1978). Rats fed a diet containing cholesterol and cholic acid develop a marked depression of plasma HDL as measured by polyacrylamide gel electrophoresis or by the amount of cholesterol in the supernatant from precipitation with heparin + Mn^{++} (SN–C). Evidence is summarized indicating that these two measurements, while qualitatively related, are not necessarily equivalent, the latter representing cholesterol associated with lipoproteins deficient in B and arginine-rich apoproteins. Since there is evidence that the B and arginine-rich apoproteins are responsible for the initial atherogenic event of attachment of lipoproteins to cells, the ability of a compound to elevate SN–C may be of therapeutic potential.

APOPROTEIN (E—A-II) COMPLEX OF HUMAN PLASMA LIPOPROTEINS. I. CHARACTERIZATION OF THIS MIXED DISULFIDE AND ITS IDENTIFICATION IN HIGH DENSITY LIPOPROTEIN SUBFRACTION. K.H. Weisgraber and R.W. Mahley *J. Biol. Chem.* 253, 6281–8 (1978). A $M_r = 46,000$ apoprotein designated as the apo(E—A-II) complex has been isolated from the $d < 1.006$ fraction of human type III hyperlipoproteinemic plasma and from the $d = 1.063$ to 1.125 fraction of normal human plasma. The apo(E—A-II) complex was stable to treatment with 4 M guanidine, 8 M urea, and 2% sodium dodecyl sulfate but was dissociated into two subunits following reduction with β-mercaptoethanol or dithiothreitol. The possible interconversion between the apo(E—A-II) complex and the E and A-II apoproteins *in vivo* and its importance in lipoprotein metabolism remains to be determined.

KINETICS OF RAC-1-OLEYL-2-(4-(3-PYRENYL)BUTANOYL)GLYCEROL TRANSFER BETWEEN HIGH DENSITY LIPOPROTEINS. S.C. Charlton, K. Hong and L.C. Smith, *Biochemistry* 17, 3304–9 (1978). The mechanism of transfer of diglyceride between high density lipoproteins (HDL) was investigated with a pyrene-containing analogue whose fluorescent properties depend on the microscopic concentration in the lipoprotein. These results support a mechanism in which rate-limiting dissociation of the diglyceride analogue from one HDL particle into the aqueous phase precedes rapid diffusion and subsequent uptake by another such particle.

LIQUID CRYSTALS AND CHOLESTEROL NUCLEATION DURING EQUILIBRATION IN SUPERSATURATED BILE ANALOGS. R.T. Holzbach and C. Corbusier *Biochim. Biophys. Acta* 528, 436–44 (1978). In recent work, apparent liquid crystal agglomeration to form typical solid cholesterol microcrystals was frequently observed photomicrographically in bile samples from prairie dogs fed a cholesterol-enriched diet, prior to solid crystal formation. We therefore have conducted a systematic study of time-course lipid compositional changes in the mesophase and micellar phase constituents of bile analog solutions while undergoing cholesterol nucleation during equilibration. In keeping with theoretical considerations, structural evidence for increased hydration is demonstrable near the point of complete equilibration when the mesophase is dissolving.

MOLECULAR ORDER IN CIS AND TRANS UNSATURATED PHOSPHOLIPID BILAYERS. J. Seelig and N. Waespe-Sarcevic, *Biochemistry* 17, 3310–5 (1978). The influence of *cis* and *trans* double bonds on the hydrocarbon-chain organization of fluid lipid bilayers is investigated by means of deuterium nuclear magnetic resonance. Oleic acid and elaidic acid have been deuterated selectively at six and three different carbon atoms, respectively. The C = C bond vector is found to be aligned almost perpendicular to the bilayer surface; i.e., the angle between the bilayer normal and the C = C bond vector is only 7–8°. A similar orientation is likely for the trans double bond.

PLASMA LEVELS OF APOLIPOPROTEIN AI AND APOLIPOPROTEIN B IN HUMAN ATHEROSCLEROSIS. P. Avogaro *et al.*, *Artery* 4, 385–94 (1978). In two series of patients affected by post infarction cardiopathy or complaining of angina the plasma levels of apo-B and apo-A_1 were recorded. Apo-B levels are higher and apo-A_1 levels are lower in atherosclerotics than in controls; these findings have been recorded also in patients showing normal lipid plasma levels.

LIPID-PROTEIN ASSOCIATIONS IN CHROMATOPHORES FROM THE PHOTOSYNTHETIC BACTERIUM RHODOPSEUDOMONAS SPHAEROIDES. G.B. Birrell, W.R. Sistrom, and O.H. Griffith, *Biochemistry* 17, 3768–73 (1978). Lipid-protein interactions were examined in chromatophores isolated from the photosynthetic bacterium *Rhodopseudomonas sphaeroides* using lipid spin-labels. The chromatophores contain fluid bilayer and a significant amount of lipid immobilized by membrane proteins. For a typical preparation of cells grown under 600 ft-c illumination, 59% of the spin-labeled fatty acids were bound. Essentially the entire length of the 18-carbon fatty acid chain was immobilized, judging from results obtained with the spin-label at the 7, 12, and 16 positions. The changes in immobilized lipid with light level and polar head group suggest that the anntenna bacteriochlorophyll-binding proteins preferentially associate with negatively charged lipids.

CHAIN SHORTENING OF ERUCIC ACID BY SUBCELLULAR PARTICLES ISOLATED FROM LIVER AND HEART OF RAT. P. Clouet and J. Bezard *FEBS Lett.* 93, 165–8 (1978). In several animal species, the presence in the diet of rape-seed oil rich in erucic acid (*cis*-13-docosenoic) causes various pathological disorders, especially in the heart. Many workers have dealt with the morphological aspects of the affected organs; others with the metabolic modifications brought about by the diet. As erucic acid has often been considered responsible for such disorders, many studies have been made on the metabolism of this fatty acid. The purpose of this work was to determine in which cellular organelles, mitochondria or microsomes, these chain-shortening reactions in liver and heart occur.

LONG-TERM TREATMENT WITH METFORMIN IN A LARGE COHORT OF HYPERLIPIDEMIC PATIENTS. G. Descovich *et al.*, *Artery* 4, 348–59 (1978). Metformin (N,N-dimethyl biguanide) was given to a large cohort of hyperlipidemic patients (daily dose of 2,550 g) in an effort to control hyperlipidemia and to analyse possible cardiovascular changes. 254 patients completed a 6 month follow up; of these (134 males and 120 females), 92 were diagnosed as type IIA, 87 IIB and 81 type IV. This study shows the applicability of a hypolipidemic drug regimen in a relatively large patient sample from a medium sized town. The preliminary results also suggest that this regimen may favourably affect vascular function tests in treated patients.

Distribution of radioactivity in myelin lipids following subcutaneous injection of (^{14}C)stearate. N. Gozlan-Devillierre, N. Baumann and J. Bourre, *Biochim. Biophys. Acta* **528**, 490–6 (1978). Blood fatty acids are an important parameter for the synthesis of brain myelin as exogenous stearic acid is needed: after subcutaneous injection to 18-day-old mice this labelled stearic acid is transported into brain myelin and incorporated into its lipids. However the acid is partly metabolized in the brain by elongation (thus providing very long chain fatty acids, mainly lignoceric acid) or by degradation to acetate units (utilized for synthesis of medium chain fatty acids as palmitic acid, and cholesterol). These metabolites are further incorporated into myelin lipids.

Biosynthesis in Escherichia coli of sn-glycerol 3-phosphate, a precursor of phospholipid. J.R. Edgar and R.M. Bell, *J. Biol. Chem.* **253**, 6348–53 (1978). The biosynthesis of *sn*-glycerol 3-phosphate (glycerol-P), a precursor for the synthesis of phospholipids, in *Escherichia coli* is accomplished in a single step by reduction of the glycolytic intermediate, dihydroxyacetone-phosphate. The enzyme which catalyzes this reaction, the biosynthetic glycerol-P dehydrogenase (EC 1.1.1.8), is strongly inhibited *in vitro* by glycerol-P. These data establish that the physical properties of the wild type and feedback-resistant glycerol-P dehydrogenases are similar and that the mechanism of glycerol-P inhibition does not involve association or dissociation.

Effect of membrane phospholipid compositional changes on adenylate cyclase in LM cells. V.H. Engelhard, M. Glaser, and D.R. Storm, *Biochemistry* **17**, 3191–200 (1978). Adenylate cyclase activities were examined in mouse LM cell membranes which had been supplemented with polar head groups and/or fatty acids. Basal, fluoride-, and PGE$_1$-stimulated activities varied systematically with changes in phospholipid composition, and PGE$_1$-stimulated activities correlated with the average degree of unsaturation of the phospholipid fatty acids or with the primary amino group character of the phospholipid polar head groups. In addition, the K_m for ATP of basal adenylate cyclase was systematically changed by both polar head group and fatty acid supplementation. It is proposed that adenylate cyclase can exist in several different conformations in the membrane depending upon the phospholipid composition.

Effect of specific fatty acyl enrichments on membrane physical properties detected with a spin label probe. M.E. King and A.A. Spector, *J. Biol. Chem.* **253**, 6493–501 (1978). The fatty acyl composition of the Ehrlich ascites cell plasma membrane was modified by exposure of intact cells to media containing various fatty acids during short term, stationary culture. Differences in the fatty acyl composition of the isolated plasma membrane fraction were most apparent in the choline phosphoglycerides, where enrichments of 10 to 20% occurred after 3 h of culture. Some modifications also were noted in the ethanolamine phosphoglycerides, but the other membrane phospholipid fractions were only slightly affected. These results indicate that plasma membrane lipid mobility, as measured with a spin label probe, is sensitive to relatively small changes in membrane fatty acyl composition. Moreover, these changes occur in cells that are not growing or dividing and appear to be produced as a result of the rapid turnover of certain phospholipid pools in the membrane.

Stereospecific side chain hydroxylations in the biosynthesis of chenodeoxycholic acid. S. Shefer *et al.*, *J. Biol. Chem.* **253**, 6386–92 (1978). This paper describes stereospecific side chain hydroxylations in the biosynthesis of chenodeoxycholic acid by liver mitochondria and microsomes. The hydroxylation of 5β-cholestane-3α,7α-diol was studied in subcellular fractions of rat, guinea pig, and rabbit livers. Incubation of 5β-cholestane-3α,7α-diol resulted in hydroxylations at C-12, C-24, C-25, and C-26. On the basis of these results it is not possible to draw firm conclusions concerning the relative importance of the microsomal 25-hydroxylase or the mitochondrial 26-hydroxylase in chenodeoxycholic acid synthesis.

Quantitative aspects of free and esterified sterols in Saccharomyces cerevisiae under various conditions. S. Taketani, J. Nagai and H. Katsuki, *Biochim. Biophys. Acta* **528**, 416–23 (1978). For extraction of free and esterified sterols from yeast cells, a method was devised in which both forms of sterols were extracted with light petroleum after the treatment of the cells with acetone, and then with dimethylsulfoxide. The content of sterol esters in the cells under aerobic conditions markedly increased with time, amounting to 95% of the total sterols under some conditions. In the cells under aerobic conditions, the free sterols were found to consist mainly of ergosterol, whereas the esterified sterols contained considerable amounts of zymosterol, lanosterol, and other intermediate sterols besides ergosterol.

Regulation of cholesterol ester synthesis in cultured glial and neuronal cells. Relation to control of cholesterol synthesis. J.J. Volpe, S.W. Hennessy and T. Wong, *Biochim. Biophys. Acta* **528**, 424–35 (1978). Regulation of cholesterol ester synthesis was studied in cultured C-6 glial and neuroblastoma cells. Particular emphasis was placed on the relation of this regulation to control of cholesterol synthesis. The effectors studied were low density lipoprotein (LDL) and desmosterol. Distinct differences in regulation were observed between the glial and neuronal cells. Suitable experiments indicated that alterations in pool sizes of intermediates did not contribute to the genesis of the observed responses and suggested that LDL and desmosterol produced their effects by stimulating esterification of primarily endogenous cholesterol.

(^{14}C)Palmitate uptake in isolated rat liver mitochondria: effects of fasting, diabetes mellitus and inhibitors of carnitine acyltransferase. J.M. Amatruda, *et al.*, *J. Lipid Res.* **19**, 688–94 (1978). The rapid association of Na-(16-^{14}C) palmitate with isolated rat liver mitochondria was measured by an oil separation method. This association was time and temperature-dependent and as absolutely dependent on the presence of exogenous ATP and CoASH and partially dependent on exogenous carnitine. Carnitine dependence was enhanced at lower concentrations of (^{14}C)palmitate. These studies demonstrate a method of evaluating fatty acid association with mitochondria which, because of its dependence on carnitine and carnitine acyltransferase I activity, most likely represents true uptake into mitochrondria. Furthermore, these studies indicate that the carnitine-dependent uptake of fatty acids into mitochondria is enhanced in the two ketotic states evaluated and that the carnitine acyltransferase system may be a regulatory site in ketone body production.

Cyclic AMP metabolism in adipose tissue of exercise-trained rats. E.W. Askew, *et al.*, *J. Lipid Res.* **19**, 729–36 (1978). Cyclic AMP metabolism in epididymal adipose tissue of exercise-trained rats was examined to determine if training induced changes in cyclic AMP production or inactivation. Beginning at 7 weeks of age, male rats were physically trained by 12 weeks of treadmill running. Pair-fed control rats remained sedentary in their cages for the duration of the experiment. The results of this study indicate that cyclic AMP production in response to norepinephrine stimulation is not increased by training and may even be reduced, implying that adipose tissue cyclic AMP levels may be under a greater degree of control in trained rats. Modulation of adipose tissue cyclic AMP levels may function to regulate more closely the duration of lipolysis in exercise-trained rats.

Effects of ascorbic acid deficiency on adrenal mitochondrial hydroxylations in guinea pigs. I. Bjorkhem, A. Kallner, and K. Karlmar, *J. Lipid Res.* **19**, 695–704 (1978). The effect of ascorbic acid deficiency on adrenal hydroxylation of cholesterol and deoxycorticosterone in guinea pigs was studied by using mitochondria and isolated cytochrome P-450 fractions. The effects obtained were compared with the effects of long-term treatment with ACTH. Advanced scurvy as well as treatment with ACTH resulted in an increase in the weight of the adrenals, the total amount of cytochrome P-450, the cholesterol side-chain cleavage activity, the cortisol level in plasma, and the excretion of unconjugated cortisol in urine. It is concluded that the level of ascorbate in the adrenals might be of some importance for the capacity to convert cholesterol into pregnenolone.

Metabolism of cholesterol-enriched chylomicrons. Catabolism of triglyceride by lipoprotein lipase of perfused heart and adipose tissues. C.J. Fielding, J.P. Renston, and P.E. Fielding, *J. Lipid Res.* **19**, 705–11 (1978). The chemical and biochemical properties of cholesterol-enriched and cholesterol-poor chylomicrons from rat lymph have been compared. The enriched particles, prepared from cholesterol-containing lipid dispersions, passed into the duodenum, had four to ten times the cholesteryl ester content of the control chylomicrons but had the same content of total "core" (cholesteryl ester + triglyceride) lipid. Both chylomicron species had the same protein composition, the same phospholipid composition, and the same composition of triglyceride fatty acids. It is concluded that cholesteryl ester content of chylomicrons under the conditions neither affects their protein composition nor has a major effect on their rate of reaction with liproprotein lipase.

Cyclic AMP-sensitive activation of hepatic sterol synthesis and 3-hydroxy-3-methyl-glutaryl coenzyme A reductase. C.D. Goodwin and S. Margolis, *J. Lipid Res.* **19**, 747–56 (1978). We previously showed that preincubation of a 10,000 g supernatant (S_{10}) from rat liver for 20 min at 37°C dramatically increased the subsequent incorporation of (^{14}C)acetate into sterols. No activation was seen with (^{14}C) mevalonate as substrate. In the present studies we have examined the effect of preincubation on HMG CoA reductase. These results suggest that hormone-induced changes in the cellular level of cyclic AMP may regulate the activity of HMG CoA reductase and the rate of hepatic cholesterol synthesis.

Composition of proteins of mesenteric lymph chylomicrons in the rat and alterations produced upon exposure of chylomicrons to blood serum proteins. K. Imaizumi, M. Fainaru, and R.J. Havel, *J Lipid Res.* **19**, 712–22 (1978). Protein composition was determined in mesenteric lymph chylomicrons from fat-fed rats. Among the proteins of intermediate molecular weight, apoproteins A-I and the arginine-rich apoprotein accounted for 31% and 4% of the total protein mass, respectively. Apoprotein B and apoprotein A-IV each accounted for about 10% and proteins of low molecular weight (C apoproteins and apoprotein A-II) accounted for most of the remainder. Apoprotein A-I also accounted for more than 30% of the protein mass of mesenteric lymph lipoproteins of density less than 1.006 g/ml (small chylomicrons) obtained from rats fed glucose.

Changes in biliary lipid and biliary bile acid composition in patients after administration of ursodeoxycholic acid. I. Makino and S. Nakagawa, *J. Lipid Res.* **19**, 723–8 (1978). Twenty-three patients with gallstones were treated with two dosage levels of ursodeoxycholic acid, 600 mg/day and 150 mg/day. Two to three months after the treatment, the molar percentage of cholesterol in bile significantly decreased (from 7.4 to 4.5 mole% in the 600 mg group and from 7.6 to 4.0 mole% in the 150 mg group), so that bile became unsaturated in most patients in both treatment groups. However, there was no significant difference between the two groups.

Effects of acetate, acetaldehyde, and ethanol on lipolysis in isolated rat adipocytes. N.Ö. Nilsson and P. Belfrage, *J. Lipid Res.* **19**, 737–41 (1978). The effects of different concentrations of acetate, acetaldehyde, and ethonal, alone or in combination, on the lipolysis rate, measured as glycerol release, were studied in isolated adipocytes from fed or fasted rats, in the basal state and at various levels of norepinephrine stimulation. Ethanol, acetaldehyde, and acetate in combination inhibited glycerol release to an extent similar to that of acetate alone.

Lipids of the streptomycetes. Structural investigation and biological interrelation. S.G.Batrakov and L.D. Bergelson, *Chem, Phys. Lipids* **21**, 1–29 (1978). During a systematic investigation of lipids of *Streptomycetes* a series of compounds of biochemical and microbiological interest have been isolated and characterized. These include several menaquinones, glycosyl diglycerides (glucuronosyl and isoaldobinosyl diglycerides), two ornithino lipids and a diol phospholipid. Some of these lipids were not known previously as constituents of streptomycete cells although they have been encountered elsewhere; others have proved to be novel lipids. The results of structural studies of these lipids are reviewed and some of their possible biological functions are discussed.

Photogenerated reagents for membrane labeling. 2. Phenylcarbene and adamantylidene formed within the lipid bilayer. H. Bayley and J.R. Knowles, *Biochemistry* **17**, 2420–3 (1978). Phenylcarbene and adamantylidene have been generated photochemically from the corresponding diazirines within lipid bilayers. Reasonable yields of labeled fatty acid side chains have been observed. The products have been characterized by gas chromatography-mass spectrometry and derive both from the insertion of the carbene into carbon-hydrogen bonds of saturated fatty acids and from the addition of the carbene to the carbon-carbon double bonds of unsaturated fatty acids. Carbenes generated from diazirines are evidently superior reagents for the photolabeling of lipids and should be useful for identifying the intrinsic hydrophobic sections of membrane proteins.

Photogenerated reagents for membrane labeling. 1. Phenylnitrene formed within the lipid bilayer. H. Bayley and J.R. Knowles, *Biochemistry* **17**, 2414–9 (1978). Phenylnitrene generated photochemically from phenyl azide that is bound to artificial phospholipid vesicles labels the fatty acid chains of the lipids in low yield. The labeling yield varies from approximately 3.3% with soybean lecithin (which is highly unsaturated) to approximately 0.25% with dimyristoyllecithin (which is completely saturated). Labeling is largely eliminated by reduced glutathione in the aqueous phase. Phenyl azide itself is further compromised as a lipophilic reagent by its rather low partition coefficient into lipid bilayers, as measured by equilibrium dialysis.

The modulation of lipid bilayer fluidity by intrinsic polypeptides and proteins. B.A. Cornell *et al.*, *FEBS Letters* **90** (1), 29–35 (1978). The importance of lipid-bilayer fluidity for biomembrane structure and function is now well appreciated. The presence of molecules such as cholesterol within the lipid bilayer structure is known to modulate the bilayer fluidity. Early results using monolayer systems and described as 'condensation effects' were explained and rationalised in terms of this lipid-modulation effect. A whole range of physical techniques have supported this interpretation including the use of NMR spectroscopic methods.

Benzene-lecithin interaction in lecithin-benzene solutions. Part II: Optical studies and quantum mechanical calculations. H. Frischleder *et al.*, *Chem. Phys. Lipids* **21**, 131–7 (1978). UV absorption and CD spectra of dipalmitoyl-*sn*-glycerine phosphatidylcholine (DPPC)- benzene and DPPC-cyclohexane systems at different temperatures (in the micellar and gel state) as well as quantum chemical calculations of a benzene-trimethyl ammonium supermolecule demonstrate that in the gel state of the DPPC-benzene system a molar fraction of benezene molecules forms a weak charge transfer complex with the $-N^+$ $(CH_3)_3$ moeity of DPPC. In the gel state there exists a second fraction of benzene molecules, the reorientation freedom of which is restricted by a liquid crystal-like structure.

Measurement of repulsive forces between charged phospholipid bilayers. A.C. Cowley *et al.*, *Biochemistry* **17**, 3163–8 (1978). By using an osmotic stress technique (Le Neveu, D.M., *et al.* (1977) *Biophys. J.* **18**, 209), we have measured the net repulsive force between egg lecithin bilayers containing various amounts of the charged lipids phosphatidylglycerol and phosphatidylinositol. We conclude that the hydration force demands more attention than it has enjoyed hitherto in attempts to understand bilayer membrane interaction and fusion.

Lateral diffusion in phospholipid bilayer membranes and multilamellar liquid crystals. P.F. Fahey and W.W. Webb, *Biochemistry* **17**, 3046–53 (1978). The lateral-diffusion coefficients (*D*) of a fluorescent lipid analogue, 3,3′-dioctadecylindotricarbocyanine (diI), have been measured in black lipid membranes (BLMs), in large (20–50-μm diameter) solvent-free bilayer and multilayer membrane vesicles, and in multilamellar liquid crystals of dipalmitoylphosphatidylcholine, dimyristoylphosphatidylcholine, and egg lecithin. They show that *D* changes by several orders of magnitude at the liquid-crystal transformations of the solvent-free bilayers and multilayers. A simple method of forming small numbers of large solvent-free vesicles is described.

Phase behavior of synthetic phosphatidylglycerols and binary mixtures with phosphatidylcholines in the presence and absence of calcium ions. E.J. Findlay and P.G. Barton, *Biochemistry* **17**(12), 2400–5 (1978). Using differential thermal analysis, scanning calorimetry and light scattering, transition temperatures and enthalpy data for the gel to liquid crystalline phase transitions of five synthetic phosphatidylglycerol sodium salts ($PG\text{-}Na^+$) were measured. The values obtained were almost identical with literature values for the corresponding phosphatidylcholines (PC). However, transition temperatures for the fully protonated forms of the saturated phosphatidylglycerols (PG-H^+) were approximately 20°C higher. In sum, these results provide evidence for a high degree of miscibility of the phosphoglycerol and phosphocholine head groups, either in the presence or absence of Ca^{2+}, such that the characteristic phase behavior of each mixture is determined primarily by differences in the hydrocarbon chain structure.

DIETARY FAT AND CHOLESTEROL METABOLISM IN ADULT RATS UNDERGOING RAPID TISSUE REPLETION. S.E. Carlson, C.N, Shiver and L. Arnrich, *J. Nutr.* **108**, 1170-9 (1978). An experimental model in which adult rats underwent rapid rates of tissue repletion after dietary restriction served to explore the influence of dietary fat on cholesterol metabolism. Adult rats severely restricted in protein and energy were refed either 8 or 24 hours per day for 10 days. Refeeding diets contained approximately 0% or 20% fat by weight as safflower oil or beef tallow and 4% or 17% protein on an energy basis. Concentration or source of dietary fat did not significantly influence either serum or hepatic cholesterol concentrations. The data suggest that, in the absence of exogenous cholesterol, high levels of polyunsaturated fat may influence cholesterol metabolism primarily by increasing synthesis and excretion of bile acids. ●

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