

# Report of the Literature Review Committee

## Annual Review of the Literature on Fats, Oils and Detergents Part VI.

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### NUTRITION, PHYSIOLOGY AND BIOCHEMISTRY

#### NUTRITION

With either rice or sucrose as dietary carbohydrate fed at 22% of calories, no significant difference of serum cholesterol was noted in 5 healthy young men (Irwin et al., *J. Nutr.* 82, 338). Subjects on diets providing 45% of the calories on corn oil were fed varying levels of  $\beta$ -sitosterol. Starting at 300 mg/day  $\beta$ -sitosterol caused progressively larger decreases of serum cholesterol with an increasing dose. It was concluded that  $\beta$ -sitosterol in corn oil may in large part be responsible for its hypocholesterolemic effect (Beveridge et al., *J. Nutr.* 83, 119). Oral administration of paromomycin caused a significant reduction in the serum cholesterol in 7 of 10 patients studied (Samuel et al., *Proc. Soc. Exp. Biol. Med.* 115, 718).

Feeding cholesterol to hens caused an increase in serum and egg cholesterol levels 10 days after feeding commenced. However, levels in both serum and egg tended to return to normal later in the experiment (Edwards and Jones, *Poultry Sci.* 43, 877). Unsaturated fat fed to hens causes an increase in the cholesterol content of eggs (Weiss et al., *Arch. Biochem. Biophys.* 105, 521). Tung oil when fed to chicks at 0.5% level caused slow growth and higher levels in the diet caused high mortality. Neither the methyl esters of tung oil fatty acids nor the unsaponifiable fraction were toxic. Studies of nutritional encephalomalacia in chicks indicated that linolenic acid can displace essential fatty acids and inhibit the conversion of linoleate to arachidonate (Century and Horwitz, *Arch. Biochem. Biophys.* 104, 416).

Rats on a carotenoid-free diet were fed diesters of taraxanthin and zeaxanthin. One third of the pigment was recovered in the feces mostly as the free carotenol. The fate of the other two thirds was unknown (Booth, *Biochem. Biophys. Acta* 84, 188). Pigs fed low levels of dietary linoleate exhibited major changes in serum lipids when dietary linoleate was less than 1% of calories. There was a decreased concentration of linoleic and arachidonic acids and a rise in eicosatrienoic acid. The amount of 70% to 75% of the eicosatrienoic and arachidonic acid was associated with the phospholipids and 60%–70% of the linoleic acid was associated with the sterol esters (Leat, *Biochem. J.* 89, 44). Choline deficiency in rats caused a decrease in the concentrations of all classes of serum lipids in both sexes. Decreases in the phospholipid fractions of both sexes and in cholesterol esters of female rats, were largely due to preferential decreases in arachidonic acid, but the fatty acids of triglycerides decreased uniformly in both sexes (Tinoco et al., *J. Lipid Res.* 5, 57). As little as 0.1% ethyl ester of the polyunsaturated acids of cod liver oil reduced the hypercholesterolemia of rats fed diets supplemented with coconut oil, cholesterol and sodium taurocholate (Kahn, *J. Nutr.* 83, 262).

The nutritional effects of epoxidized oils were determined in rats. The toxicity of epoxidized soybean oil increased with the degree of epoxidation. A daily dose of 5 mg of epoxyoxygen to each rat inhibited growth and 45 mg caused death in 80% of rats within eight days. A drop in protein efficiency and an increase in water consumption were noted (Kieckhefer et al., *vette Seifen Anstrichmittel* 65, 914, (1963)). A study of the essential fatty acid requirement of guinea pigs indicates that 1% of calories as linoleic acid is necessary for normal growth and skin conditions (Reid et al., *J. Nutr.* 82, 401). When peanut oil enriched with elaidinized fatty acids is given to rats, the *trans* fatty acids in the depot fat triglycerides are found in the  $\alpha$  position (Raulin et al., *Biochem. Biophys. Acta* 70, 642). Chickens and rats restricted to eating a diet containing modest amounts of cholesterol for 2 hr/day exhibit double the serum cholesterol levels and four to seven times the incidence of atherosclerotic lesions than animals containing 30% more diet over a 24 hr period. Similar data on man are reviewed (Cohn, *Fed. Proc.* 23, 76). The rate of development of creatinuria in the tocopherol-deficient rat proved to be dependent on the degree of unsaturation of the dietary fatty acids. Muscle fatty acid composition were dependent on the composition of the dietary fatty acids (Witting and Horwitz, *J. Nutr.* 82, 19).

The minimal vitamin D<sub>2</sub> requirement for baby pigs is not greater than 100 IU/kg of diet (Miller et al., *J. Nutr.* 83, 140). Epoxyoleate and 19:2 which are structurally related to linoleate did not function as essential fatty acids. Dietary 20:5 and 22:6 both related to linolenate were less active than linoleate in preventing fat deficiency symptoms, but depressed eicosatrienoate (Rahm and Holman, *J. Lipid Res.* 5, 169).

#### PHYSIOLOGY

##### Digestion and Absorption

Palmitic and stearic acids which are poorly absorbed by the chick when fed singly are well absorbed when fed in a mixture of fatty acids. Oleic acid appears to play a direct role in facilitating the absorption of saturated fatty acids (Young and Garrett, *J. Nutr.* 81, 321). Pancreatic lipase had no intramolecular specificity for glyceryl 1-palmitate-2,3-dibutyrate, which was also hydrolyzed more slowly than glyceryl 1-myristate 2,3-dioleate indicating intramolecular specificity. Position specificity was maintained during 5-minute digestions when glyceryl 2-

butyrate, 1,3 dipalmitate was the substrate (Jensen et al. *J. Dairy Sci.* 47, 727). Phospholipase A does not attack D- $\alpha$ -phospholipids. L- $\alpha$ -lecithins containing fatty acids of varying chain length are hydrolyzed, however water soluble short chain acids are hydrolyzed at a slow rate. Glycol analogues have substrate activity (Van Deenen and De Haas, *Biochim. Biophys. Acta* 70, 538). Erythrocytes from vitamin E deficient rats were susceptible to hemolysis by copper and iron. Those from control animals were hemolyzed by copper but not by iron, but the degree of hemolysis was less than in deficient animals. The changes were more pronounced when corn oil was included in the diet. The action of iron appeared to be associated with oxyhemoglobin in the cell (Walker and Kummerow, *J. Nutr.* 82, 323). Depancreatized chickens absorb both proteins and fats poorly. Incorporation of raw pancreas in the feed returned the absorption to normal levels. Starch was digested better than proteins or fats in depancreatized animals. (Ariyoshi et al., *Poultry Sci.* 43, 2321). Rats fed egg oil were compared to a similar group fed a diet containing an equal amount of cholesterol and fat of the same unsaturation. The rats on the egg oil diet had lower plasma and liver cholesterol levels. Cholic acid caused an increase in lipid levels in both groups (Walker and Emerson, *J. Nutr.* 82, 311). High dietary linoleic acid provided by corn oil resulted in the accumulation of this acid at the expense of oleic (Walker and Kummerow, *Ibid.*, 82, 329).

Injection of vitamin A and vitamin A acetate into the posterior small intestine, duodenum or cecum indicate that the major absorption site is the duodenum. Little absorption took place in the cecum (Shellenberger et al. *J. Nutr.* 82, 99). Growing rats maintained on diets containing 5, 10, or 20% protein absorbed vitamin A acetate more efficiently on the high protein diets. The activity of enzymes hydrolyzing and synthesizing vitamin A esters, and of those oxidizing retinene also correlated well with protein level (Deshmukh et al., *Biochem. J.* 90, 98). In rats fed labeled oleic acid chemical and radiochemical findings in the absorption of fatty acid indicate that the fatty acid enters the chyle primarily as triglyceride, that the triglyceride content of the intestinal wall is increased, and that there is a significant transfer of the label from fatty acid to triglyceride at some stage of absorption. Some of the osmophilic droplets seen with the electron microscope during fatty acid absorption are fatty acid (Ashworth and Johnston, *J. Lipid Res.* 4, 454).

#### Lipid Transport and Body Fat

Cholesterol fed to guinea pigs had no effect on the total lipid levels in adrenals. The cholesterol and cholesterol ester fraction was increased at the expense of triglycerides. Phospholipid levels were unanected. (Ostwald et al., *J. Nutr.* 82, 443). Iso-leucine deficient rats had higher liver triglyceride levels than control rats. Liver slice experiments showed an increased synthesis of triglycerides. There were no difference in serum lipid or lipoprotein concentrations in the two groups (Lyman et al., *Ibid.* 82, 432).

During fermentation of vegetables by lactic acid bacteria, free fatty acids increased. The increase was found in palmitic and short chain acids. Unsaturated C18 acids decreased. (Vorbeck et al., *J. Food Sci.* 28, 495).

Excess niacin added to high fat diets in rats causes increased concentrations of pyridine nucleotides in blood and liver and increased levels of fat in the liver. (Rikans et al., *J. Nutr.* 82, 83).

In rats cholesterol is esterified by the intestinal mucosa and absorbed cholesterol esters are rapidly removed by the liver. A portion of the esters undergoes hydrolysis while another portion appears to participate in a series of transferase reactions with fatty acid donors to form other cholesterol esters. The major ester formed by transferase reactions is cholesterol arachidonate, which is then released into the blood in association with lipoproteins (Swell et al., *Arch. Biochem. Biophys.* 105, 541).

Labeled lignoceric acid intravenously injected into rats accumulated in the liver and was slowly oxidized to CO<sub>2</sub>. It was incorporated into sphingolipids, cholesterol esters and glycerides. After intracerebral administration it was found in brain sphingolipids and glycerides (Gatt, *Biochem. Biophys. Acta* 70, 370).

More 18:2 and less 20:4, 20:5 and 22:6 as percentage of fatty acids was found in total liver lipids of rats with portal fatty liver caused by a deficiency of lysine and threonine. There was a decrease in 20:5, 22:5 and 22:6 in phospholipids. An increase in the amount of 18:2 in neutral fat was found. The absolute amounts of 18:2, 18:3 and 18:1 were increased (Viviani et al., *J. Lipid Res.* 5, 52). Vitamin B<sub>6</sub> deficient rats showed growth inhibition and a decrease in carcass lipids. The lipid changes were partially prevented by the administration of insulin (Huber et al., *J. Nutr.* 82, 371).

Methyl and ethyl esters of higher fatty acids were found in human tissue lipids. (Kaufmann and Viswanathan, *Fette Seifen Anstrichmittel* 65, 925 (1963). The 18:1 fatty acid fraction of animal tissue fatty acids is shown to contain from 20 to 50% cis-vaccenic acid. Cis-vaccenic acid can be derived from palmitic but not from stearic acid (Holloway and Wakil, *J. Biol. Chem.* 239, 2489).

In vivo studies with synthetic glycerides indicate that they are not carcinogenic, do not cause atherosclerosis or hypercholesteremia and are readily available and nutritionally useful to the experimental animal (Uzzan, *Rev. Franc. Corps Gras* 10, 517).

#### Lipid Metabolism in the Intact Animal

Feeding 15% safflower oil to cows caused a decrease in the yield of milk and milk fat. The content of unsaturated fatty acids in the milk was doubled with oleic acid showing the major increase (Perry et al., *J. Dairy Sci.* 47, 37). The proportions of the C<sub>20</sub>-C<sub>22</sub> polyunsaturated fatty acids in plankton crustaceans increased with decreasing temperature. In the crustaceans raised on algae containing no fatty acids longer than C<sub>18</sub>, the C<sub>20</sub>-C<sub>22</sub> acids always appeared as major components. 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 (Farkas and Herodek, *J. Lipid Res.* 5, 369). Biotin was replaceable by oleic and palmitic acid in bakers yeast grown under aerobic conditions. Baker's yeast grew normally with stearate and palmitate under similar conditions. The saturated fatty acids are absorbed and converted into unsaturated acids. Under conditions of biotin deficiency the content of C<sub>18</sub> acids decreased and the content of C<sub>16</sub> acids increased (Suomalainen and Keranen *Biochem. Biophys. Acta* 70, 493).

Triparanol fed to chicken resulted in an increase in serum total sterols and desmosterol. Triparanol caused a cessation of egg production and enhanced the degree and extent of atherosclerosis (Wong, et al., *J. Lipid Res.* 4, 477). Hamsters fed on a fat-free, high sucrose diet develop crystalline bile stones with a high cholesterol content, as well as dark colored, amorphous stones having a high content of bile acids. When the dietary carbohydrate was replaced by fat there is a complete reversal of trend, and in some cases with unsaturated fats disappearing altogether. Chickens did not develop bile stones under similar conditions. Chicken bile has a high bile acid and phospholipid to cholesterol ratio when compared to hamster bile (Dam, *Riv. Ital. Sostanze Grasse, Sympos Issue* 1962, 85). Intravenous injection of various fatty acids in rabbits caused a marked thrombopenia lasting 1-2 hours. Intraperitoneal administration of the fatty acids caused no thrombopenia (Zbinden, *J. Lipid Res.* 5, 378). The onset of laying in chickens is preceded by large increases in plasma FFA and total lipids. The quantities decreased markedly when laying commenced. (Heald and Badman, *Biochem. Biophys. Acta* 70, 381). Acetate was infused intravenously into sheep. Much of the pool acetate was converted into other compounds before oxidation; the turnover time from acetate to CO<sub>2</sub> being 3 hours, in contrast to the acetate pool turnover time of 2 min (Sabine and Johnson, *J. Biol. Chem.* 239, 89). In rats lithocholic acid is converted to chenodeoxycholic, 3 $\alpha$ , 6 $\beta$ -dihydroxy-5 $\beta$ -cholanic,  $\alpha$ -muricholic and  $\beta$ -muricholic acids. No conversion to cholic acid was found (Thomas et al., *Ibid.*, 239, 102). Injection of labeled oleic acid into rat brain indicated that it is not incorporated into nervonic acid of the sphingolipids. The injection of labeled palmitate, stearate, lignocerate, or cerebrone indicate that all four acids are incorporated into sphingolipid. The palmitate and stearate gave to lignocerate and cerebrone. Injected lignocerate gave rise to cerebrone and injected cerebrone was incorporated intact (Kishimoto and Radin, *J. Lipid Res.* 4, 444; Hajra and Radin, *Ibid.*, 448). "Cis-trans" methyl linoleate is converted to cis-cis-cis-trans arachidonic in the rat. "Cis-trans" methyl linoleate is converted to polyenoic acids with trans unsaturation. 4, 7, 10, 13 eicasatetraenoic is shown to be present in liver phospholipids of rats fed a fat-free diet (Blank and Privett, *J. Lipid Res.* 4, 470).

1-C<sup>14</sup>-octadecane and 1-C<sup>14</sup>-hexadecane were directly converted to fatty acids of the same chain length in the goat, rat, and chicken. These studies suggest a widespread omega oxidation in various tissues (McCarthy, *Biochem. Biophys. Acta* 84, 79). Feeding the cis- and trans-isomers of fatty acids to rats indicated that the various isomers were well absorbed, readily oxidized to CO<sub>2</sub> and transported in the lymph mainly as glycerides with no major difference in the distribution of the various acids among the lipid classes. The trans-isomers were metabolized in an efficient and apparently normal manner (Coots *J. Lipid Res.* 5, 473). Ethanol caused a suppression of the incorpora-

tion of labeled acetate into liver lipids. This suppression is explained as being mostly isotopic dilution (Majehrowicz, *Proc. Soc. Exp. Biol. Med.* 115, 615). Administration of  $\alpha$ -ethylcaproic acid increased the absorption of cholesterol. However, no cholesterol- $\alpha$  ethylcaproate was formed. It is suggested that this effect is due to a diversion of fatty acids from other pathways in the mucosa to cholesterol esterification (Hyum et al., *Arch. Biochem. Biophys.* 104, 139).

## BIOCHEMISTRY

### Analytical and Methodology

The amount of lipid present in rat liver nuclei is small, but the pattern of lipids is similar to that in the whole cell with the exception that cardiolipin is absent (Gurr et al., *Biochem. Biophys. Acta.* 70, 406). The present state of our knowledge of lipoxylase of soybeans is reviewed (Andre', *Oleagineux*), 19, 461).

The gas chromatography of fatty acids from human depot fat is described and discussed. Data for some 40-45 fatty acids is presented including for the first time the series of branched-chain acids from C<sub>13</sub> to C<sub>24</sub> (Kingsbury et al., *Biochem. J.* 90, 147). Serum triglycerides are determined by thin layer chromatography of an extract of 1 ml of serum followed by quantitative determination by infrared spectrometry (Krell and Hashim, *J. Lipid Res.* 4, 407). The total lipids of cabbage and lettuce leaves were separated into 19 components. Only a small portion of leaf phospholipids was present in the chloroplast fraction, which contained a novel, unidentified lipid in addition to mono- and di-galactolipids. Free sterols, sterol esters and triglycerides were present in whole leaf extracts, but were absent from chloroplasts (Nichols, *Biochem. Biophys. Acta* 70, 417). Free glycerol was determined in blood serum by GLC using butane-1,4-diol as an internal standard. The acetates were formed and extracted with ether. Normal sera was found to contain 0.4-1.2 mg/100 ml.

Rat liver cardiolipid was fractionated into 5 subclasses by siliic acid column chromatography. Extensive studies of individual fractions failed to explain the fractionation (Rose, *Biochem. Biophys. Acta* 84, 109). The fatty acids of phosphatidyl choline from a number of sources were investigated. The amounts of 36 to 38 mole % of the fatty acids esterified in the  $\alpha$ -position were saturated; 91-99 mole % of the fatty acids in the  $\beta$ -position were unsaturated (Menzel and Olecott, *Ibid.*, 84, 133). A method is described for thin layer separation of individual phospholipids and neutral lipids of serum followed by GLC for determination of fatty acids patterns of the isolated fractions (Bowyer et al., *Ibid.*, 70, 423). A method is described for the quantitative isolation of neutral glycolipids of serum by TLC (Svennerholm and Svennerholm, *Ibid.*, 70, 432). A method for the isolation of pure sphingomyelin from human plasma is described. All even- and odd-carbon saturated fatty acids from C<sub>11</sub> to C<sub>25</sub> are present and most of the corresponding monoenoic acids as well. Palmitic acid is the predominant component. A C<sub>21</sub> dienoic acid is present as a trace component (Sweeley, *J. Lipid Res.* 4, 402). Forty-seven mono- and diunsaturated fatty acids in ester linkage were found in pig brain. Twenty-five had not previously been reported to occur in natural sources. These include the even and odd numbered monoenoic and even numbered dienoic acids 16 to 22 carbons long. Each acid consisted of three to six positional isomers (Kishimoto and Radin, *Ibid.*, 5, 20). Seventeen chemically defined hydroxy acids were found in pig brain sphingolipids, 15 of which have not been previously reported. They include the odd and even numbered hydroxy acids 22 to 26 carbons long. Each acid consists of three to four positional isomers (Kishimoto and Radin, *Ibid.*, 5, 94).

In mammals the richest site of bound glyceryl ethers is bone marrow (Todd and Rizzi, *Proc. Soc. Exp. Biol. Med.* 115, 218). A method for quantitative determination of bile acid production and neutral sterol excretion using a double isotope technique is presented. In the rat the major portion of fecal cholesterol of endogenous origin is derived from or is in equilibrium with that of blood (Wilson, *J. Lipid Res.* 5, 409). Evidence is presented that the phosphoinositide-protein complex exists *in situ* in brain and is not an artifact of preparation (Lebaron, *Biochem. Biophys. Acta* 70, 658). In several *Nocardia* species straight chain saturated fatty acids from C<sub>14</sub> to C<sub>19</sub> have been found. C<sub>16</sub> is the major fatty acid. Branched chain fatty acids C<sub>16</sub>, C<sub>17</sub>, and C<sub>17</sub> belonging to the iso and anteiso series were found. Iso C<sub>21</sub> and 10 methyl-octadecanoic acid were identified. Several unsaturated acids were identified (Bordet and Michel, *Ibid.*, 70, 613).

A spectrophotometric method for the determination of tocopherol in milk and related products is described (Erickson and Dunkley, *Anal. Chem.* 36, 1055). Separation of carotenoids

in vegetable oils by TLC followed by extraction and quantitation is described (Capella et al., *Riv. Ital. Sostanze Grasse*, 40, 666). A method for the determination of serum glycerides, free cholesterol and cholesterol esters using a binary solvent is presented (Galanos et al., *J. Lipid Res.* 5, 242). Simultaneous determination of triglycerides and cholesterol esters in serum by infrared spectrophotometry is presented (Freeman, *Ibid.*, 5, 236). A technique is presented for the cannulation and perfusion of isolated rat epididymal fat pad (Ho and Meng, *Ibid.*, 5, 203). A method for the preparation of brain polyphosphoinositides is presented (Kerr et al. *Ibid.*, 5, 481). A method for the determination of urinary estrogens by TLC and GLC is presented (Wotiz and Chatteraj, *Anal. Chem.* 36, 1466).

### Lipid Biosynthesis

Free labeled (4-<sup>14</sup>C) cholesterol and lecithin labeled in the B-position with fatty acid served as substrates for synthesis of cholesterol esters by rat plasma and extracts of acetone powders of rat plasma. The conversion was prevented by snake venom. Labeled triglycerides did not serve as substrates (Shah et al., *Liochem. Biophys. Acta* 84, 176). The biosyntheses of carotenoids and vitamin A is reviewed. This review stresses the biochemical transformations and the characteristics of the enzymes involved (Olson, *J. Lipid Res.* 5, 281). Propionic acid is incorporated into the branched end of C32-mycoeholic acid and its lower C 26-homolog (Gastambide-Odier and Delaunay, *Biochem. Biophys. Acta* 70, 670). Studies on cholesterol biosynthesis with cell-free homogenates of liver from rats treated with doses of estrone that cause a reduction of blood cholesterol indicate that there is an inhibition of cholesterol synthesis at the stage at which mevalonate is decarboxylated (Merola and Arnold, *Science* 144, 301). The lipid composition of mammalian cells grown in tissue culture on a defined lipid-free medium and a serum supplemented medium were essentially the same. In lipid free medium cell lipids were synthesized *de novo* from C<sup>14</sup>-acetate whereas in serum supplemented medium synthesis from C<sup>14</sup>-acetate was almost completely inhibited (Bailey, *Proc. Soc. Exp. Biol. Med.* 115, 747). The *in vitro* incorporation of acetate into macrophages showed 37% of the activity in palmitic acid, 18% in oleic acid and smaller amounts in myristic, stearic and linoleic acid. Specific activity of myristic acid was high relative to palmitic, stearic and oleic which had similar specific activities. (Day et al. *Biochem. Biophys. Acta* 84, 149). Glycerides are synthesized by two pathways in mammary gland. One pathway involves the direct acylation of monoglycerides. The other proceeds from acylation of  $\alpha$ -glycerophosphate. Perfusion of red cell albumin solutions containing high concentrations of FFA as either palmitate or linoleate were rapidly taken up and gave a net synthesis of triglyceride in the liver. Perfusion with palmitate markedly increased the percentage of palmitate in the perfusate glycerides. Linoleate had less effect on the fatty acid pattern of the liver glycerides and a greater effect on the perfusate glycerides (Nestel and Steinberg, *J. Lipid Res.* 4, 461). Using rat mammary gland slices in the absence of glucose, almost all of the C<sup>14</sup>-activity recovered in the total lipid fraction was found in fatty acids when alanine, leucine, or aspartic acid were used as C<sup>14</sup>-substrates. Under similar conditions with glycine, serine, or methionine little activity was found in fatty acids. (Abraham, et al. *J. Biol. Chem.* 239, 855).

Cholesterol comprises 25% of total red cell lipid. The average percentage distribution of individual phospholipids were: choline glycerophosphatides (CGP) 30%, sphingomyelin (SPL) 24%, ethanolamine glycerophosphatides (EGP) 26% and serine glycerophosphatides (SGP) 15%. EGP are high in 20:4, 22:5 and 22:6 fatty acids while SGP contains large amounts of 18:0 and 20:4, CGP is distinguished by 20:25% 18:2 and SPH by high concentrations of 24:0 and 24:1. (Wars and Hanahan, *J. Lipid Res.* 5, 318). In rat liver homogenates 22, 25-diazacholesterol was shown to block sterol biosynthesis from a number of C-14 precursors similar to triparanol. This is in agreement with the findings of appreciable desmosterol levels in rats treated with 22, 25-diazacholesterol (Dvornik et al. *Proc. Soc. Exp. Biol. Med.* 116, 537). Extracts of Group - A streptococci added to serum markedly increase the esterification of cholesterol in serum incubated at 37C. The streptococcal factor evidently enhances esterification by making bound lecithin more accessible to the serum enzyme involved in fatty acid transfer (Rowen and Martin, *Biochem. Biophys. Acta* 70, 396).

An enzyme system from rat brain was found which oxidatively decarboxylates  $\alpha$ -hydroxystearate and  $\alpha$ -hydroxytrienoic acids. The products were CO<sub>2</sub> and a normal fatty acid (Levis and Mead, *J. Biol. Chem.* 239, 77). The conversion of

## Fourth Chicago Gas Chromatography Course

The Chicago Gas Chromatography Discussion Group will hold its fourth annual introductory course in gas chromatography at Roosevelt University, Chicago, Ill., on Feb. 1-4, 1966. The four-day course is intended to give the student sufficient theoretical and practical background to perform independent work in gas chromatography.

This course is unique in the emphasis placed on practical laboratory training. During the four-day session, each student will spend a total of 16 hours of intensive laboratory work in the areas of column preparation, qualitative analysis, quantitative analysis and studies on column efficiency plus proper column selection.

The fee for the course will be \$50. Registration will be limited to 60 students. Applications of registration along with checks or money orders, made out to the Chicago Gas Chromatography Discussion Group, should be mailed to Dr. Jay Curtice, Chemistry Department, Roosevelt University, 430 S. Michigan Ave., Chicago, Ill., 60605 before Jan. 15, 1966.

## Papers to be Published Soon

### C. M. Scholle Becomes 44th President of Paint Federation

C. M. Scholle, Plant Superintendent of Jewel Paint & Varnish Co., Chicago, became the 44th President of the Federation of Societies for Paint Technology on Oct. 27, 1965, during the Federation's 43rd Annual Meeting in Atlantic City. H. B. Gough, of Finnaren & Haley, Inc., Philadelphia, Pa., was named President-Elect; and H. L. Fenburr, of Hanna Paint Mfg. Co., Columbus, Ohio, was elected treasurer.

Over 50 papers were presented at the meeting, the 43rd in the Federation's history. Most of the papers presented are expected to be published in the November and December 1965 issues of the *Official Digest*, or in the January, 1966 and future issues of the *Journal of Paint Technology*, the new name of the *Official Digest*, commencing with the new year.

Four seminars were also included in the program: 1) Production and Quality Inventory Control; 2) Quality Control; 3) Sand Grinding; 4) IMPACT—Inventory Management Program and Control Techniques.

The Joseph J. Mattiello Memorial Lecture, "Color Measurement and Tolerances," was delivered by D. L. MacAdam, Senior Research Associate, Physics Division, Eastman Kodak Co., Rochester, N. Y.

## ASTM to Publish New Journal

A new journal will be launched by the American Society for Testing and Materials in April, 1966. Called *Journal of Materials*, it is designed for faster dissemination of new developments in materials technology; and to meet the expanding needs of engineers and scientists concerned with materials. To keep pace with the widening scope of knowledge of engineering materials, ASTM will publish this informative and sophisticated journal on a quarterly basis with spring, summer, fall, and winter issues.

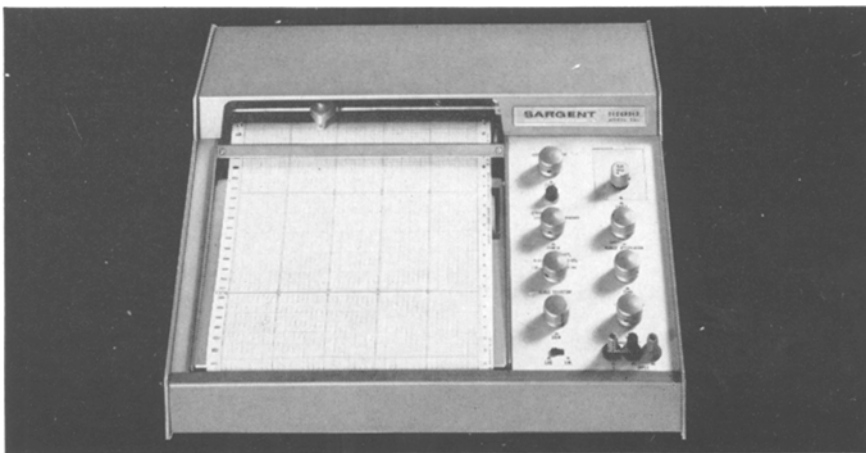
*Journal of Materials* will contain some 60 to 70 articles per year on

subjects in the field of materials technology and materials evaluation methods. To insure inclusion of papers of the highest quality, they will be selected for their timeliness, pertinence, and contribution to the fundamental knowledge. The format and typography have been carefully selected for ease of reading and ready reference. The new journal will not carry advertising, and the cost has been kept low to make it available to as many readers as possible. A year's subscription is \$15.00; to ASTM members: \$10.50. It is also available at lower rates on 2- and 3-year subscriptions.

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stearate to oleate was studied in homogenates and subcellular fractions of liver of diabetic rats untreated and treated with insulin. The site of the reaction is in the microsomes. In diabetes, the microsomal enzymatic conversion of stearate to oleate stops and can be corrected with insulin (Gellhorn and Benjamin, *Biochem. Biophys. Acta* 84, 167). After incubation of intact fat pad of the rat with palmitic- $1-C^{14}$  acid the free fatty acids in different cell fractions and in different parts of a single fat pad had different specific activities. This is interpreted as a small pool of free fatty acids which serves as a precursor pool for glyceride synthesis (Vaughn et al. *Biochem. Biophys. Acta* 84, 154).

In gangliosides from several sources 18:0 was found to be the major fatty acid component while 16:0 and 20:0 were found in small amounts. Hydroxy acids were not found in significant amounts. Sphingosine, a small amount of dihydro-sphingosine, and two  $C_{30}$  bases were not present in other sphingolipids. (Sambasivarao and McCluer, *J. Lipid Res.* 5, 103). Quantities of human cerebral grey and white matter phosphatides decreased from ethanolamine glycerophosphatides (EGP) through choline glycerophosphatides (CGP) to serine glycerophosphatides (SGP) in each locale. The quantities of aldehydes in gray matter 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 oleylaldehyde made up 90% of the aldehydes found (O'Brien et al., *J. Lipid Res.* 5, 329).

Normal human erythrocytes and spherocytic human erythrocytes both synthesize diacyl glycerophosphoryl choline and diacyl glycerophosphoryl ethanolamine at equal rates when incubated with oleic acid and monoacyl 1-phosphatides (Robertson and Lands, *J. Lipid Res.* 5, 88). The effect of the addition of "light" and "intermediate" microsomal fractions from fed and fasted rats were tested for their effect on fatty acid synthesis of supernatant fractions from livers of fed rats. All fractions from fasted rats were more inhibitory from fasted rats than fed rats. Part of the microsomal inhibition was due to ATPase. (Korchak and Marsoro, *Biochem. Biophys. Acta* 70, 647). A supernatant fraction from rat liver converts even numbered fatty acids into their omega hydroxy and into omega dicarboxylic acids. (Preiss and Bloch, *J. Biol. Chem.* 239, 85). *Euglena gracilis* Z grown photoautotrophically contain a diglyceride, galactolipids and a phospholipid fraction containing chiefly phosphatidylserine. The principal acids are linolenic acid and 4, 7, 10, 16-hexadecatetraenoic acid. Heterotrophic cells contain triglycerides and large amounts of phospholipids but no galactolipids. The principal acids are arachidonic and (or) 11, 14, 17-icosatrienoic acid, 5, 8, 11, 14, 17-icosapentaenoic acid and uncharacterized  $C_{22}$  and  $C_{24}$  polyunsaturated acids (Hulanicka et al., *J. Biol. Chem.* 239, 2778).

### Sterols and Steroids

Labeled acetate or mevalonate was incorporated into sterols by rat testicular slices. Labeled acetate and mevalonate were not incorporated into sterols by cell-free homogenate; similar homogenates metabolized labeled lanosterol (Tsai et al., *Arch. Biochem. Biophys.* 105, 329). The two central carbon atoms of squalene appear as carbons 11 and 12 of cholesterol. Conversion of this cholesterol to cholic acid and then to its 12-keto derivative indicate that the same two carbon atoms are labeled in cholic acid (Samuelsson and Goodman, *J. Biol. Chem.* 239, 98). Both "structural" and metabolic functions of sterols were found in insects. Evidence is presented for the existence of mechanisms for the excretion of sterols and their metabolites (Clayton, *J. Lipid Res.* 5, 3).

The concept of steroid number in gas chromatography is extended to several selected phases (Hamilton et al., *Biochem. Biophys. Acta* 70, 679). The incorporation of mevalonic acid into potato plants (*Solanum tuberosum*) gave a higher total and specific activity of sitosterol than in stigmasterol (Johnson et al., *Arch. Biochem. Biophys.* 104, 102). The synthesis of cholesterol esters by rat liver microsomes with ATP and CoA consisted predominantly of saturated and monounsaturated esters. A series of CoA esters gave lower levels of synthesis than added ATP and CoA. It is suggested that the major pathway for cholesterol esterification in liver microsomes does not involve a simple condensation between cholesterol and fatty acid CoA esters (Swell et al., *Arch. Biochem. Biophys.* 104, 128).

The incorporation of  $2-C^{14}$  acetate and  $2-C^{14}$  mevalonate into terpenes and sterols of *Salvia selarea* was studied. Incorporation into selareal was practically nil. Incorporation into sterols and a partially purified acidic triterpene was low but significant (Nicholas, *Biochem. Biophys. Acta* 84, 80).

### Lipoproteins

The fatty acids of goat milk that come from blood are derived from triglycerides of the chylomiera and  $d < 1.019$  low-density lipoproteins. (Barry et al., *Biochem. J.* 89, 6). Fatty acid distribution of cholesterol esters, triglycerides and phospholipids were determined in three lipoprotein fractions of human plasma. The fatty acid distribution of corresponding lipid classes was similar (Goodman and Shiratori, *J. Lipid Res.* 5, 307). Human erythrocytes takes up palmitic acid from  $\alpha$ -lipoprotein until all binding sites are filled. 38% of the  $\alpha$ -lipoprotein free cholesterol does not exchange. Cholesterol and palmitic acid each interferes with the other in the transfer from  $\alpha$ -lipoprotein to erythrocytes (Ashworth and Green, *Biochem. Biophys. Acta* 84, 182). The lipid composition of human plasma chylomicrons was studied. (Wood et al., *J. Lipid Res.* 5, 225). The low-density lipoproteins in egg yolk plasma was studied (Saari et al., *J. Food Sci.* 29, 307). A study of doubly labeled chylomicrons indicates that lipoprotein lipase is involved in the uptake of chylomicron glyceride by mammary gland (McBride and Korn, *J. Lipid Res.* 5, 459). Free fatty acids cross the placental membrane and are rapidly taken up by fetuses at midpregnancy. There is no transfer of chylomicrons across the placental membrane (McBride and Korn, *Ibid.*, 453).

### BOOK REVIEWS

A number of reviews pertaining to various phases of fats and oils appeared during the last year. In a contribution titled "The Chemistry of Lipids," Brody and Trams reviewed the immunochemistry of lipids and the role of lipids in natural and artificial membranes (*Ann. Rev. Biochem.* 33, 75-100). The metabolism of lipids was reviewed by Vagelos (*Ibid.* 33, 139-172). Fat-soluble vitamins were reviewed by Gloor and Weis (*Ibid.* 33, 313-330). Benson reviewed plant membrane lipids (*Ann. Rev. Plant Physiol.* 15, 1-16). A symposium on drugs in lipid metabolism was published (*JAOCS* 41, 697-716; 756-779). Biodegradable detergents were discussed in another symposium (*Ibid.* 41, 732-755; 799-830). A summary of all the papers presented at the First World Fat Congress held under the auspices of the International Society for Fat Research in 1964 was published. A review on thin-layer chromatography by Mangold, Schmid and Stahl appeared (*Methods of Biochemical Analysis*, Vol. XII, 393-451). Another review on thin-layer chromatography by Maier and Mangold was also published (*Advances in Analytical Chemistry and Instrumentation* Vol. 3, 369-477). Several feature and review articles concerning lipid chemistry and biochemistry appeared in the news section of the *JAOCS*.

New books of interest to chemists in lipid research are as follows:

- Boekennoogen, H. A., Ed., "Analysis and Characterization of Oils, Fats and Fat Products," Vol. 1, Interscience Publishers, 421, pp., 1964.
- "Standard Methods for the Analysis of Oils, Fats and Soaps," by the International Union of Pure and Applied Chemistry in Great Britain, 5th Ed., Butterworth Inc., 140 pp., 1964.
- "Detergents and Emulsifiers," 1964 Manual, John W. McCutcheon Inc., 211 pp., 1964.
- Prat, T., and A. Giraud, "The Pollution of Water by Detergents," Organization for Economic Cooperation and Development, Paris, France, 86 pp., 1964.
- Gould, R. F., Ed., "Contact Angle, Wettability and Adhesion," Special Issues Sales, American Chemical Society, Washington, D.C., 389 pp., 1964.
- Hummel, D., "Identification and Analysis of Surface Active Agents," translated by E. M. Wulkow. Interscience Publishers, Vol. I, 386 pp., Vol. II Spectra, 157 pp., 1964.
- Tatton and Drew, "Industrial Paint Applications," Van Nostrand Co., 1964.
- Martens, C. R., "Emulsions and Water-Soluble Paints and Coatings," Reinhold Publishing Corp., 1964.
- "Synthetic Resins," Edited by Kunstsharsfabriek Synthese N. V. Katwijk aan Zee, Netherlands, 386 pp., 1962.
- Peereboom, J. W. C., "Chromatographic Sterol Analysis As Applied to the Investigation of Milk Fat and Other Oils and Fats," Centrum Voor Landbouwpublishates En Landbouwdocumentatie, 157 pp., 1963.
- Lederer, M. Ed., "Chromatographic Reviews, 6," Elsevier Publishing Company, 1963.
- Kaiser, R., "Gas Phase Chromatography," translated by P. H. Scott. Vol. I, Gas Chromatography, 199 pp.; Vol. II, "Capillary Chromatography," 120 pp.; Vol. III, "Tables for Gas Chromatography," 162 pp. Butterworth, Inc.
- Marini-Bettolo, G. B., Ed., "Thin-layer Chromatography," Elsevier Publishing Company, 232 pp., 1964.

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# Report of the AOCS Industrial Oils and Derivatives Committee

All of the Subcommittees of the Industrial Oils and Derivatives Committee met during the fall session of the AOCS in Cincinnati to review work that had been accomplished during the past six months and lay plans for future work. The following is a brief summary of the work being done in each of these Subcommittees, as submitted by K. E. Holt, Chairman.

## **Epoxidized Oils Subcommittee, R. J. Gall, Chairman**

A proposed method for hydroxyl value of epoxidized oils was submitted by letter ballot to the Industrial Oils and Derivatives Committee on July 15. There were a few questions raised and constructive suggestions given by members of the Committee. These have now been resolved and the method will be submitted to the Uniform Methods Committee with the recommendation that it be adopted as a tentative official method of the AOCS.

The Subcommittee began a collaborative study on the "Jay Method" for per cent oxirane using tetraethylammonium bromide and perchloric acid. This method is based on an original paper by Jay [Analyt. Chem. 36, 667 (1964)]. The Subcommittee members found several areas where clarification of the method was needed and the collaborative study was discontinued until the method could be studied more completely and necessary modifications made in the method. This has been accomplished and a collaborative study will be completed prior to the Los Angeles meeting.

## **Dibasic Acids Subcommittee, D. F. Roblin, Chairman**

The Dibasic Acids Subcommittee is cooperating with an ASTM group on Polybasic Acids. The ASTM group is working on the basic methods of analysis and the Subcommittee will review the proposed ASTM methods to determine if they satisfy AOCS method requirements. The Subcommittee will write a recommended practices method and the test methods for polybasic acids (other than polymerized acids) which depend on fatty materials as a raw material, in particular azelaic and sebacic acids.

Since ASTM is working on methods which have a broad scope, the AOCS Subcommittee will concentrate on methods which are more narrow in their application such as heat stability and composition by GLC.

## **Commercial Fatty Acids Subcommittee, R. O. Walker, Chairman**

The Subcommittee is in agreement that AOCS Method Td-3a-64, Color Stability of Fatty Acids, is not good enough to separate different grades of unsaturated fatty acids and is ineffective in separating the saturated acids. Two alternative methods for improving the Color Stability Method have been proposed and will be checked against the present method in a collaborative study. These are; 1) using the present equipment with the bath temperature increased to 240C and the nitrogen flow regulated. 2) Using the present tubes but replacing the nitrogen flushing tubes with 30 in. air condensers and raising the bath temperature to 240C.

## **Drying Oils Subcommittee, D. S. Bolley, Chairman**

The Industrial Oils & Derivatives Committee gave letter ballot approval on a number of proposed changes in AOCS Method To-1b-64, Specific Gravity. The changes will now be recommended to the Uniform Methods Committee for their approval. There is no precision data on the Specific Gravity Method and it is planned to develop this data by collaborative study before submitting the revised method to the Uniform Methods Committee.

The results of the collaborative study on haze or clarity of drying oils by comparison was reviewed by the Subcommittee. It is obvious that the most consistent results on haze can be obtained when a comparison is made against

haze standards. A review will be made of haze standards now used in other industries to determine whether these standards would be suitable for drying oils.

## **Fatty Nitrogen Products, N. O. V. Sonntag, Chairman**

Five laboratories have agreed to participate in a "round robin" on primary fatty amine using the GLC. Three samples including a coco, tallow and a synthetic blend will be used in this study. The work is scheduled to be completed before the spring AOCS meeting.

## **Polymerized Acids Subcommittee, H. Fisher, Chairman**

The methods for sampling, acid value, saponification value, saponifiable matter, Karl Fisher and color will be rewritten to include polymerized fatty acids in their scopes. Methods for unsaturation and composition are needed; however, the available methods are not satisfactory and collaborative work will be held up until more suitable methods have been developed.

## **Hydrogenated Oils, R. O. Walker, Chairman**

This Subcommittee is planning to review approximately 25 existing AOCS analytical methods to determine which methods require modification to make them applicable to hydrogenated products. Subcommittee members are, also, requested to submit other methods used by their laboratories for control or evaluation of hydrogenated oils.

K. E. HOLT, CHAIRMAN

## • *New Product*

WATERS ASSOCIATES, INC., Framingham, Mass., has introduced the Ana-Prep Gel Permeation Chromatography Assembly, a combination unit which can be used for both analytical determinations of molecular weight distribution of rubbers and fractionation of rubber samples to obtain gram quantities of narrow molecular weight fractions.

## • *Literature Review . . .*

(Continued from page 706A)

- James, A. T., and L. J. Morris, Editors, "New Biochemical Separations," D. van Nostrand Company Ltd., 424 pp., 1964.
- Hilditch, T. P., and P. N. Williams, "The Chemical Constitution of Natural Fats," 4th Edition, John Wiley and Sons, Inc., 745 pp., 1964.
- Swern, D., Ed., "Bailey's Industrial Oil and Fat Products," 3rd Edition, Interscience Publishers, 1103 pp., 1964.
- Markley, K. S., Ed., "Fatty Acids: Their Chemistry, Properties, Production and Uses," Second edition, Part 3, Interscience Publishers, 992 pp., 1964.
- Asselineau, T., "Les Lipides Bacteriens, Isolement-Composition-Proprietes" (Actualites Scientifiques et Industrielles No. 1297, Hermann, Paris, 350 pp., 1962.
- Folch-Pi, T., and H. Bauer, Editors, "Brain Lipids and Lipoproteins and the Leucodystrophies," Proceedings of the symposium held in Rome in 1961, Elsevier Publishing Co., 213 pp., 1963.
- Rodahl, K., and B. Issekutz Jr., "Fat as a Tissue," McGraw-Hill Book Co., 428 pp., 1964.
- Meng, H. C., T. G. Coniglio, V. S. Le Quire, G. V. Mann and J. M. Merrill, Editors, "Lipid Transport," International Symposium, Charles C Thomas, 336 pp., 1964.
- Dawson, R. M. C., and D. N. Rhodes, Editors, "Metabolism and Physiological Significance of Lipids," John Wiley and Sons Ltd., 657 pp., 1964.
- Altschull, R., Ed., "Niacin in Vascular Disorders and Hyperlipemias," Charles C Thomas, 320 pp., 1964.
- Holman, R. T., Ed., "Progress in the Chemistry of Fats and Other Lipids," Vol. 7, Pergamon Press, 308 pp., 1964.
- Paoletti, R., and D. Kritechsky, Editors, "Advances in Lipid Research," Vol. 2, Academic Press, 499 pp., 1964.