oils could be prepared; for example, one such product esterified for 5 hours at 200° C. and 20 mm. pressure with 0.0008 mole of tin chloride per 100 g. fatty acids had a Lovibond color of 10 yellow, 1.5 red without refining or bleaching.

Summary

1. An investigation has been made of the esterification of glycerol and peanut oil fatty acids under reduced pressure, with and without the assistance of various metal chlorides and oxides as catalysts.

2. The uncatalyzed reaction is bimolecular in character but proceeds in two successive stages, of which the latter has the lower velocity constant. Velocity constants have been determined for the initial and final stages of the reaction, at intervals between 166° and 241° C. The calculated heats of activation for the initial and final stages of the reaction are respectively 12,300 and 10,800 calories per mole. The free fatty acid concentration corresponding to the termination of the first stage decreases progressively as the temperature of the reaction is increased.

3. Of a wide variety of metal oxides and chlorides tested, zinc and tin chlorides were outstanding in catalytic activity. The reaction, when catalyzed with these materials, is complex and no longer simply bimolecular. It is believed that tin and zinc chlorides react initially with free fatty acids and free glycerol to form metal soaps and chlorohydrins, and that esterification proceeds through interaction of these two initial reaction products. Other metal chlorides, including the chlorides of aluminum, antimony, mercury, nickel, magnesium, manganese, lead, iron, and cadmium, do not appear to be capable of reacting in this manner, and are relatively poor catalysts. The oxides of tin and zinc are also deficient in catalytic activity, as is hydrochloric acid.

4. The reaction proceeds at a reasonable speed, i.e., the FFA content of the product is reduced to about 3% in 6 hours, if 0.0008 mole of tin chloride per 100 g. of fatty acids is used as a catalyst at 175° C. or if a similar amount of zinc chloride is used as a catalyst at 200° C. Equally rapid esterification is obtained without a catalyst only above 250° C. Esterification is assisted by maintaining a vacuum upon the reaction vessel to remove water vapor from the reacting material as rapidly as it is formed. A vacuum of about 20 mm. pressure of mercury is satisfactory.

5. If zinc or tin chloride catalysts are employed, the metals may be completely removed from the esterified oils by ordinary alkali refining. These catalysts do not cause the oil to polymerize during the course of esterification, do not cause conjugation in the oils, and are not detrimental to the color of the product.

Acknowledgment

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Abstracts

Oils and Fats

Edited by
M. M. PISKUR and SARAH HICKS

DEVELOPMENT OF COMMERCIAL LECITHIN. M. Schofield. *Manufg. Chemist 16*, 135-7 (1945). New outlets for the cheaper commercial forms of lecithin are being found in a number of directions other than in the processing of foods or of fats. It is being used with plant sprays, in creosote emulsions, as softening and wetting agents and in many other ways. This paper reviews the scattered literature of the subject up to date, and indicates the major applications found and suggested.

THE VITAMIN A POTENCY OF CREAMERY BUTTER PRODUCED IN MINNESOTA. R. Jenness and L. S. Palmer. *J. Dairy Sci. 28*, 473-94 (1945). In 1,019 samples analyzed in 1943 the unweighted mean vitamin A and carotene contents were respectively 6.21 ± 0.03 and 3.68 ± 0.04 *ug.* per g. The means weighted by regional and seasonal butter production were respectively 6.14 and 3.71 *ug.* per g.; these values correspond to a total potency of 13,958 I. U. per pound if vitamin A itself is considered to have a potency of 4.00 I. U. per *ug.* With a few exceptions, and for all practical purposes the butters of the state were rather uniform in vitamin A potency in any given season of the year. Marked seasonal fluctuations in potency, similar to those reported elsewhere, and undoubtedly attributable to variations in feeding conditions were found to occur. From Jan. 1 to April 22, 1943, the samples averaged 9,000-10,000 I. U. per pound. With the beginning of pasturing, a rapid rise occurred until the summer level of 16,500- 18,500 I. U. per pound was attained in the period May 21 to June 17. This level persisted until early October whereupon the potency gradually declined nearly to the winter level during the remainder of the year. The picture for the first half of the year was corroborated by analyses of samples secured from Jan. 1 to June 15, 1944. No evidence was found for loss of vitamin A potency by butter during storage.

THE DETERMINATION OF THE PEROXIDE VALUE OF EDIBLE FATS AND OILS: THE INFLUENCE OF ATMOSPHERIC OXYGEN IN THE CHAPMAN AND MCFARLANE METHOD. C. H. Lea. *J. Soc. Chem. Industry 64*, 106-9 (1945).

The Chapman and McFarlane photometric ferric thiocyanate method has been shown to be very sensitive to the presence of atmospheric O_2, the values obtained being reduced to about ¼ when O_2 is rigorously excluded. The necessity for assuming an equivalent of 8 for peroxide O in order to correlate peroxide values with O_2 absorption is thereby eliminated. The degree of further oxidation which occurs during the determination is roughly proportional to the quantity of peroxide already present.

DETERMINING THE HYDROXYL CONTENT OF CERTAIN ORGANIC COMPOUNDS. Macro- and semimicromethods. C. L. Ogg, W. L. Porter and C. O. Willits. *Ind. Eng. Chem., Anal. Ed. 17,* 394-7 (1945). A modification of macroprocedures for determining the hydroxyl content of hydroxylated fatty acids and alcohols is described, in which an internal indicator is used. For colored solutions a potentiometric method has been developed. A semimicroprocedure using an internal indicator is also presented. An acetylating solution of 1 volume of acetic anhydride in 3 volumes of pyridine and a hot-water hydrolysis are used.

THE POLYETHENOID ACIDS OF THE C_{18} SERIES PRESENT IN MILK AND GRASS FATS. T. P. Hilditch and H. Jasperson. *J. Soc. Chem. Industry 64,* 109-11 (1945). Spectrographic measurement of the proportions of conjugated diene and triene acids present after isomerization by alkali at 170° and 180° of unsaturated C_{18} acid fractions from cow milk fat, goat milk fat and grass fat has demonstrated the presence in the milk fats of octadecadienoic acids and in grass fat, in addition, of large amounts of octadecatrienoic acids. Taken in conjunction with earlier evidence, these observations support the view that the diethenoid C_{18} acids of the milk fats consist of cis-Δ^9-trans-Δ^{12}-and/or trans-Δ^9-cis-Δ^{12}-octadecadienoic acids.

SPECTROPHOTOMETRIC STUDIES OF THE OXIDATION OF FATS. IV. ULTRAVIOLET ABSORPTION SPECTRA OF LIPOXIDASE OXIDIZED FATS. R. T. Holman and G. O. Burr. *Arch. Biochem. 7,* 47-54 (1945). Using spectrophotometric measurements as a means of detecting changes in substrates, it has been shown that oleic acid, Et oleate, conjugated linoleic acid, linolelaidic acid, elaidolinolenic acid and α-eleostearic acid are not substrates for lipoxidase. Linoleic acid, Et linoleate, linolenic acid, Et linolenate and Me arachidonate showed increased absorption near 2300 and 2700 Å indicating that these substances were changed by the lipoxidase. Pseudoeleostearic acid and its ester showed decreased absorption near 2700 Å indicating the destruction of the conjugated triene substrate. The products which give the increased absorption in the cases of the naturally occurring substrates are probably conjugated unsaturated carbonyl compounds.

SOUTH AFRICAN FISH PRODUCTS. PART XV. MODE AND DEGREE OF FAT STORAGE AS FACTORS INFLUENCING THE RELATIVE COMPOSITIONS OF FATS FROM THE DIFFERENT ORGANS OF MARINE TELEOSTID FISHES. W. S. Rapson, H. M. Schwartz and N. J. Van Rensburg. *J. Soc. Chem. Industry 64,* 114-18 (1945). Available data on the relative compositions of the fats from the different organs of fishes are reviewed with special reference to the influence of mode and degree of fat storage—factors that seem never to have been adequately stressed in earlier work. It is demonstrated that among fishes with diffuse systems of fat storage, the available data point mostly to the occurrence of definite organ characteristics in the liver oils as contrasted with the oils from the head and body. The nature of these characteristics is discussed and variations associated with degree of fat storage are stressed as of significance for the study of fat metabolism. Exceptions are noted. Where the fat storage is localized in the liver, however, the organ characteristics noted above have not been observed in the liver oils of any of the species so far studied. It is indicated that in such species the compositions of the liver oils correspond to what might be expected from the dilution of a liver oil with organ characteristics with an excess of oil of non-liver type.

THE USE OF SIMPLIFIED DIETS IN THE STUDY OF THE FAT METABOLISM OF THE MAMMARY GLAND. O. W. Kaufmann and J. C. Shaw. *J. Dairy Sci. 28,* 467-72 (1945). The data show that carbohydrate, when fed as the sole diet, provides the precursors for the synthesis of the lower fatty acids of milk fat. As blood glucose does not appear to be the blood precursor of the lower acids, the dietary carbohydrate must act indirectly. Possibly, the carbohydrate is converted into the necessary precursors in the rumen by the action of certain micro-organisms. It is also possible that it may exert a sparing action on the utilization by other body tissues of substances which act as precursors of the lower fatty acids of milk fat.

THE EFFECT OF TOCOPHEROL ON ESSENTIAL FATTY ACID UTILIZATION. E. L. Hove and P. L. Harris. *Federation Proc. 4,* 156 (1945). Tocopherols greatly increase the effectiveness of Me linolate in curing essential fatty acid deficiencies in rats. When tocopherol is fed to weanling rats on the fat free diet the development of the essential fatty acid deficiency is delayed. This offers some evidence that the synergy between tocopherol and linolate is not restricted to the gastrointestinal tract.

THE NUTRITIVE VALUE OF FATS. R. K. Boutwell, R. P. Geyer and E. B. Hart. *Federation Proc. 4,* 152 (1945). Rats on purified diets which contained a medium but not excessive levels of B vitamins maintained a normal growth rate if fed butter fat in combination with the following carbohydrates: starch, dextrin, dextrin-maltose, sucrose and a mixture of equal parts of fructose and glucose. Growth was subnormal if corn oil was substituted for butter fat in these rations. In contrast, equal and excellent growth was produced on any of the possible fat-carbohydrate combinations by a 3-fold increase of synthetic B vitamins plus the addition of a liver concentrate as a source of unknown nutritional factors. The 2 fats in combination with a mixture of glucose and galactose, or glucose and galactose alone, were comparable in nutritive value at all levels of vitamins.

STUDIES ON THE INTERRELATION OF FATS, CARBOHYDRATES AND B-VITAMINS IN RAT NUTRITION. R. K. Boutwell, R. P. Geyer, C. A. Elvehjem and E. B. Hart. *Arch. Biochem. 7,* 143-57 (1945). A change in the kind of dietary fat altered the apparent requirement of the rat for vitamins of the B-complex when sucrose, a fructose-glucose mixture, starch, dextrin, dextrimaltose or lactose was the carbohydrate in certain rations. On any of the above carbohydrates, rats which received butterfat and a medium level of a thiamine, riboflavin, pyridoxin, pantothenic acid and choline grew at a faster rate than comparable rats fed corn oil. This inferiority of corn oil could be reduced on lactose rations and eliminated on all other rations by raising the level of these vitamins and adding high levels of inositol, *p*-aminobenzoic acid and nicotinic acid plus 1% of whole liver powder. No difference in growth between the rats receiving butterfat and those fed corn oil was obtained at any vitamin level when glucose of galactose-glucose mixture was the carbohydrate portion of the ration. Rats receiving either of the 2 fats on the lactose ration grew less than animals fed similar rations containing other carbohydrates, but this inferiority decreased as the level of the water-soluble vitamins was increased. The galactose per se was not responsible for this retarded growth.

DENTAL CARIES AS INFLUENCED BY FAT VERSUS CARBOHYDRATE IN THE DIET. J. D. Boyd. *Am. J. Diseases Children 67*, 278-81 (1944). The dental history of diabetic children observed intermittently for long periods was reviewed in connection with the dietary regimes to determine whether any change in caries experience occurred with the sharp break in dietetic policy which involved replacement of the high fat diets by diets which offered only ½ as much fat and twice the amount of carbohydrate. "No constant or significant differences in the average rates of progression of caries was found between 2 groups of children whose fat ingestion differed by 100%. Protection against caries is thought to depend on the common high nutritive worth of the contrasted diets." (*Exper. Sta. Rec.*)

PATENTS

STABILIZATION OF FAT PRODUCTS. F. A. Norris (General Mills, Inc.). *U. S. 2,377,031.* Process of stabilizing an oleaginous material comprises incorporating therein a compound containing an ene-diol group, *p*-aminobenzoic acid and a tocopherol.

STABILIZATION OF FAT PRODUCTS. F. A. Norris (General Mills, Inc.). *U. S. 2,377,029.* A combination of *p*-amino benzoic acid and a compound having the ene-diol grouping (Ex. I-ascorbic acid) is used as an antioxidant.

STABILIZATION OF FATTY PRODUCTS. F. A. Norris (General Mills, Inc.). *U. S. 2,377,030.* Process of stabilizing fatty products against rancidity comprises incorporating therein a compound having an ene-diol grouping and a compound selected from the group consisting of morpholine, mono-, di- and triethanolamines.

TREATMENT OF OILSEEDS. A. M. Altschul and M. L. Karon (Sec. of Agr.). *U. S. 2,376,852.* The process comprises treating oilseeds with a volatile base to raise the pH to not less than 8, storing for not less than 1 week, and thereafter extracting oil therefrom, whereby the oil is considerably lightened in color.

TREATMENT OF OILSEEDS. A. M. Altschul and M. L. Karon (Sec. of Agr.). *U. S. 2,376,568.* The process comprises treating oilseeds with morpholine to raise the pH to not less than 8, storing for not less than 1 week, and thereafter extracting oil, whereby the oil is considerably lightened in color.

PREPARATION OF VITAMIN E OR TOCOPHEROLS. J. D. Cawley (Distillation Products, Inc.). *U. S. 2,375,078.* The process for preparing a vitamin E concentrate comprises subjecting a crude scum which contains tocopherol and which is derived from the steam deodorization of vegetable and animal fats to hydrogenation, dissolving the hydrogenated scum in acetone to form a solution of between 10 and 40% scum, cooling this mixture to a temperature below —20° to cause precipitation of at least the free fatty acid part of the scum, separating the liquid acetone portion, subjecting it to distillation to remove the acetone as a distillate and leaving vitamin E as a residue.

REFINING TALL OIL. J. N. Borglin (Hercules Powder Co.). *U. S. 2,374,975.* The method of refining tall oil includes heating tall oil in the presence of a B compound capable of removing the visible or latent color bodies of said tall oil and subjecting the treated tall oil to a distillation operation.

REFINING OF ANIMAL AND VEGETABLE OILS. B. Clayton (Refining, Unincorp.). *U. S. 2,374,924.* The process of refining animal and vegetable oils comprises neutralizing free fatty acids in said oil in the presence of an oil solvent to form a mixture containing oil, said solvent and soap stock, vaporizing volatile substances including substantially all of said solvent from said mixture and separating said soap stock from said oil.

PURIFICATION OF TALL OIL. A. Pollak and T. A. Willingham. (West Virginia Pulp and Paper Co.). *U. S. 2,374,700.* In the purification of tall oil, the step of improving the color thereof, comprises heating crude tall oil in the absence of air to in excess of 400° F. and below that at which substantial decomposition of the oil substance occurs for the period of time during which the oil is heated, and maintaining such temperature until a substantial part of the color bodies contained in said oil is destroyed and rendered less volatile, but terminating said treatment before any substantial pyrolysis of the oil substance has taken place and thereafter distilling the so treated oil, leaving behind a substantial portion of the color bodies originally present.

VITAMIN A CONTAINING PREPARATION AND THE MANNER OF ITS PRODUCTION. B. T. Sokoloff (World Products Corp.). *U. S. 2,375,501.* A process for producing an edible preparation in dry powder form in which the stability of vitamin A potency is relatively high, comprises macerating animal livers, extracting the water soluble constituents by mixing the macerated livers with warm water in the presence of lactic acid and separating the fluid from the residue of water insoluble constituents, and drying the residue of water insoluble constituents in vacuo at a relatively low temperature.

EXTRACTION METHOD. C. F. Dinley and W. L. McCracken (Detroit Rex Products Co.). *U. S. 2,377,-135-6.* Designs for a continuous oil extractor are described. A novel means of completely recovering the solvent volatilized is explained.

VITAMIN FORTIFIED PRODUCT. L. O. Buxton (National Oil Products Co.). *U. S. 2,375,278.* A process of preparing a dry vitamin food product devoid of oiliness, consists in comminuting raw fish livers selected from the class consisting of fish livers having a difficultly removable oil content which cannot be liberated by finely grinding said livers and admixing the comminuted fish livers with dry, comminuted hydrophilic vegetable material in the ratio of 1 part of livers to 2-5 parts of said vegetable material to produce a mass wherein the fat-soluble vitamins remain locked in the individual liver particles.

CHROMANS AND INTERMEDIATES AND PROCESS OF PRODUCING SAME. L. I. Smith and H. C. Miller (Regents of the University of Minnesota). *U. S. 2,372,132.* The process of making tocopherol-like chromans comprises reacting β-(3,6-dialkoxy methylphenyl) Et Mg halide with Me-4,8,12-trimethyl tridecyl ketone and thereafter refluxing the resultant tertiary alcohol under acidic conditions to de-alkylate the ether linkages thereof and cyclize to the corresponding 6-hydroxy tocopherol-like chroman.

Stabilization of organic substances. C. J. Pedersen. (E. I. du Pont de Nemours & Co.). *U. S. 2,373,049.* Thiourea, in which a single H has been replaced by an electronegative aromatic radical, is used to protect fat and oil against the oxidation accelerated by catalyst metals.

Phosphatide composition. P. L. Julian and E. W. Meyer (American Lecithin Co.). *U. S. 2,374,681.* A small amount of organic sulfonic acid is added to phosphatides to reduce emulsification properties and to reduce viscosity and thus improve their utility as lubricant adjuncts.

Oil-phosphatide composition. P. L. Julian and E. W. Meyer (American Lecithin Co.). *U. S. 2,374,682.* A difficultly emulsifiable lubricating composition suitable for lubricating high pressure internal combustion engines without substantial varnish formation, comprises a major amount of mineral lubricating oil and a minor amount of phosphatide which latter has been treated with such an amount of acid material that the charges upon the "zwitter" ions which tend to cause water solubility have been neutralized and the phosphatidic material is therefore at or near its isoelectric point.

Method of forming fatty acid substituted amino compounds. F. C. Bersworth (Martin Dennis Co.). *U. S. 2,374,915.* The amide compounds of the unsaturated fatty acids are converted into substituted amino acid amides by reacting the amide with an amine in the presence of a hydrogenating catalyst under conditions inhibiting oxidation and hydrolysis.

Lubricating grease composition. J. C. Zimmer and A. J. Morway (Standard Oil Development Co.). *U. S. 2,374,966.* The grease is a mineral oil product containing Al soap and an organic amine.

Stabilized lubricants. N. D. Williams and W. J. Backkoff (Pure Oil Co.). *U. S. 2,375,060-1.* The lubricant improving agents are prepared by treating fats or waxes with a small amount of P_4S_3 and converting about 50% of the product to the Sn or Pb soaps.

Antioxidant compositions. R. W. Riemenschneider and J. Turer (Sec. of Agr.). *U. S. 2,375,250.* An antioxidant composition comprises an ascorbyl monoester of a saturated aliphatic monocarboxylic acid containing from 12-18 C atoms per molecule, and a compound selected from the groups consisting of α-tocopherol and the isomers and analogues of α-tocopherol.

Lubricating greases. J. D. Morgan and R. E. Lowe (Cities Service Oil Co.). *U. S. 2,375,485.* A turret lubricating grease, comprises about 7% by weight of Ca stearate, about 2% by weight of Li stearate, about 0.6% by weight of Al stearate, about 1% by weight of Pb oleate, the remainder of the lubricant consisting essentially of a mixture of neutral mineral oil and naphthenic oil, said grease being prepared by mixing the stearates with the oils then adding the Pb oleate, heating the mixture to a maximum temperature of about 420° F. and then rapidly chilling the mixture.

Catalytic hydrogenation processes. A. S. Richardson and J. E. Taylor (Procter and Gamble Co.). *U. S. 2,375,495.* In the catalytic hydrogenation of compounds selected from the group consisting of fatty acids and esters thereof to form fatty alcohols, in the presence of a Cu containing catalyst at high temperature and pressure is a step of incorporating a substantial yet not predominant proportion of Cd soap in the mixture to be hydrogenated.

Lubricating oil. C. M. Blair, Jr. (Petrolite Corp. Ltd.). *U. S. 2,375,516.* An amount of a straight chain saturated fat alcohol-citraconic acid monoethylenic straight chain fat alcohol condensation polymer is used to improve lubricants.

Constant viscosity greases. J. D. Morgan (Cities Service Oil Co.). *U. S. 2,376,312.* A comparatively constant viscosity lubricating grease comprises a major portion of a polyalkyl phosphate in which the alkyl group has 5 C atoms per molecule or less and a minor portion of polymerized castor oil dissolved therein and a Li fatty acid soap blended therewith to form a grease.

Neutral organic esters of sulphurous acid as pest-control agents. I. Hechenbleikner (American Cyanamid Co.). *U. S. 2,377,148.* The pest-control composition contains a toxic amount of dilauryl sulphite and a carrier therefor.

Hydrogenation catalysts and other catalysts. J. A. V. Turck, Jr., (Colgate-Palmolive-Peet Co.). *U. S. 2,375,506.* Very porous, low density (2-10% of normal) metallic catalysts are prepared by precipitating the metal as the hydroxide, siphoning off the liquid, washing the precipitate with alcohol or acetone to reduce the water 1-3%, adding isopropyl alcohol or other reducing organic compound and heating in absence of O_2 at the critical reducing temperature.

Abstracts

Drying Oils

Edited by
HOWARD M. TEETER

Saving linseed oil and thinner in paints by improvement of linseed oil. E. Asser. *Lack-u. Farben. Z 1933,* 185-6. A discussion of the economy effected by the Bisöl process [Chem. Abs. 31, 3308 (1937)], by which the viscosity of the oil is decreased and its wetting power is increased. Various suitable paint formulations for rust control are given. (*Chem. Abs.*)

PATENTS

Solvent extraction of oil from seeds. P. A. Singer and H. J. Deobald (Allied Mills, Inc.). *U. S. 2,377,975; 2,377,976.* Continuous extraction of oil from seeds by countercurrent flow of seeds and a solvent consisting of 70 to 80 parts of ethanol and 20 to 30 parts by volume of isopropanol. Extraction