REVIEW OF SCIENTIFIC LITERATURE ON FATS AND OILS FOR 1937

PART II

By M. M. PISKUR

SWIFT & COMPANY, CHICAGO, ILL.

BIOCHEMICAL

Resumés of the biochemistry and physiology of fats were prepared by R. G. Sinclair [*Ann. Rev. Biochem.* **6,** 245-8] and J. S. Hepburn [*Hahnemannian Monthly* **72,** 329-36]. The information in these is the result of recent investigations published prior to 1937.

In the past, the extent of fat absorption by the intestine was assumed to be inversely related to the melting points; the fats excreted had higher melting points than those ingested. Conclusions drawn from fat balance studies and from data on the fat content of the intestine at various intervals following ingestion have recently been placed in doubt. Shapiro and co-workers [*Am. J. Physiol.* **117,** 525-8] have shown that on excluding the bile from the intestines of a human subject, the fat in the feces was equal to or exceeded the intake. Fats labeled with deuterium have demonstrated that even though there may be a large amount of fecal fat, 60 to 70 per cent of the ingested fats was absorbed. S. Baglioni and V. Famioni [*Nuva riv. olii vegetali e saponi* **3,** 33] found that hydrogenated lard and whale oil were superior to the softer unhydrogenated fats in respect to growth, general nutrition and survival. E. Rost *et al.* [*Arch. Hyg. Bakt.* **118,** 193-259] reported that the feces of dogs which had been fed hardened fat contained an abnormal amount of fat. R. Lecoq [*Compt. rend.* **204,** 1001-3] studied the hard and liquid fat acids from the standpoint of the alimentary imbalance which they cause in pigeons; fat acids melting between 55 and 57° C. had the same effect as those liquid at the body temperature. It was suggested that the hard fatty acids became soaps and were rapidly assimilated. Feeding of calcium salts, according to Y. Nakamura [*Z. ges. exptl. Med.* **99,** 494-7], increased the excretion of calcium, fat and fat acids in the feces.

A few investigations on the absorption of fats were made on isolated loops of intestine. S. Fillippon and L. Bellini [*Boll. soc. ital. sper.* **12,** 135-7] reported 45 per cent absorption of oleic acid by a loop of dog intestine. Poisoning the dog with phlorizin reduced the absorption to about 6 per cent; absorption became normal after glucosuria had ceased. T. Onozaki [*Tohoku J. Exptl. Med.* **29,** 224-43] with similar technic showed that by adding dispersed fat to the isolated washed intestine the amount of absorption depended upon time of contact with intestine and degree of dispersion of fat. Histological studies of the intestines after fat absorption were also reported. When hydrolyzed fat was used, fat acids were found in the epithelial cells; but in the deeper underlying cells the acids had been reconverted into neutral fat. The literature on mechanism of penetration of fat acids into the epithelium of the small intestines was reviewed by G. Rossi [*Arch. fisiol.* **36,** 365-9].

N. N. Dastur and K. V. Giri [*Proc. Soc. Biol. Chem. India* **1,** 40-1] evaluated the rates of hydrolysis of fats by castor seed lipase. The speed of hydrolysis of fats in decreasing order was butter fat, coconut oil, sesame oil, and peanut oil. With pancreatic lipase butter fat was the most slowly hydrolyzed at pH of 12.6, but at pH of 9.3 it was rapidly digested. The addition of the bile salt, sodium taurocholate, accelerated the digestion of the fats. A. K. Balls *et al.* [*J. Biol. Chem.* **122,** 125-37] showed that in the *in vitro* digestion of fat with pancreatic lipase the substrate remains in the form of the triglyceride, because the mono- and diglyceride intermediates hydrolyze much more quickly than the triglycerides and therefore quickly disappear. The hydrolysis of the higher saturated triglycerides was dependent on the temperature. The glycerides of 7 to 10 carbon atom acids exhibited a maximum rate of splitting at moderate temperatures. The above did not apply to unsaturated glycerides. Olein acted as though it contained acids of 9 carbon atoms rather than 18.

H. J. Deuel, Jr., with coworkers [*J. Biol. Chem.* **117,** 119-29, 131-3; **119,** 257-68; **120,** 277-88] reported a series of studies on fat metabolism. Much larger amounts of glycogen were found in the livers of fasting rats after feeding triglycerides of odd chain acids than could be accounted for from the glycerol moiety. This was interpreted as further proof of the convertibility of odd chain acids into carbohydrates. It was suggested that those fats which cannot be stored as such in the tissues, *i.e.*, triglycerides up to tricaprylin, were decomposed yielding glycerin for glycogen synthesis, other fats being stored away as such and yielding no glycogen. In a later report it was shown that ethyl esters of odd-carbon-chain fat acids gave rise to glycogen formation when fed to fasting rats while those of even-carbon-chain gave entirely negative results. The relation of fatty livers to fasting ketonuria was also studied by this group. On the second or third day of fast after a high fat diet a considerable ketonuria occurred and persisted for five days. There was no relationship between the amount of liver fat and the magnitude of the ketonuria. After a diet high in fat and cholesterol the rate of decrease of accumulated liver fat was slowest of all. Rats on high-butter fat diet supplemented with choline did not accumulate fat in the liver. Administration of choline to fasting rats which had previously received choline-butterfat diets, prevented infiltration of fat into livers and lowered ketonuria values.

C. Brentano and S. Markees [*Z. ges. exptl. med.* **99,** 498-517] fed fat acids to rabbits and recorded the rise in ketones in the blood. Injections of adrenaline or a creatinuria or a combination of these inhibited the disappearance of ketones from the blood stream. S. Kauvar [*Am. J. Med. Sci.* **193,** 617-26] also studied blood-ketone curves. Hyperketonemia did not normally develop after a fat tolerance test. If the secretion of ketogenic hormone was increased after the fat meal, fat combustion was increased and hyperketonemia developed.

C. Artom [*Z. physiol. chem.* **245,** 276-7] reported that only small amounts of dicarboxylic acid were found in urine of dogs after feeding

triglycerides; most after tricaprylin and very little after triheptylin or triundecylin.

Abnormal deposition of liver fat was the subject of several reports. O. Rosenthal [*Arch. neerland. physiol.* **21,** 503-16] presented a morphological study of fatty degeneration of the rat livers. Fat was histologically recognized at 2 per cent concentration in liver cells. Phosphatide and cholesterol had no visible effect on the degree and form of histological degeneration. According to Eunice V. Flock and Jesse L. Bollman [*Proc. Soc. Exptl. Biol. Med.* **36,** 853-5] the neutral fats of blood plasma were not elevated beyond the normal range during the production of fatty livers by a high fat diet. R. P. Cook [*Biochem. J.* **31,** 410-5] studied the effect of cholesterol with various percentages of fat in the diet of growing rats. Fatty livers were more apparent on the high fat diet. About 30 per cent of the cholesterol fed remained unaccounted for in the feces and the animal's body. H. F. Tucker and H. C. Eckstein [*J. Biol. Chem.* **121,** 479-84] recorded that there were over 57 per cent more lipids in the liver of rats fed a diet containing 5 per cent casein and 40 per cent lard than in the livers of rats fed the same diet and a supplement of 0.5 per cent cystine. A supplement of 0.5 per cent methionine in the diet yielded rat livers with 41 per cent less fat. H. J. Channon *et al.* [*Biochem. J.* **31,** 41-54, 1736-42] recorded data on the fatty liver production of various fats in diets of low choline content. The liver fat varied from 30.7 per cent wet weight in the case of butter fat diet to 7.2 per cent for the codliver oil diet. No relationship was found between the amount of fat in the livers and that in the carcasses. Homocholine was found more effective and triethyl-β-ethylammonium hydroxide not greatly less effective than choline in preventing fat deposition in the livers. J. M. Munoz [*Anales asoc. quim argentina* **24,** 15B] reported that repeated injections of posterior lobe extract of hypophysis produced glycemia, glucosuria, and excess fat in the liver. Fatty livers were produced in animals by L. Califano [*Biochem. Z.* **289,** 354-64] by feeding small amounts of phosphorus. F. Verzar and L. Laszt [*Biochem. Z.* **288,** 351-5, 356-8] did not obtain fatty infiltration of livers in adrenalectomized animals after five days' poisoning with phosphorus. However, on administration of phosphorus together with cortical hormone fatty livers developed. The hormone was replaceable by flavin-phosphate or yeast.

Mary E. C. Rogers and H. C. Eckstein [*Proc. Soc. Exptl. Biol. Med.* **36,** 738-40] were unable to find any effect on weight or histology of the thyroid gland of rats after feeding diets containing various types and amounts of fats over periods of 50 to 60 days. A weak antithyroid effect by oleic and linolenic acids on female rats but not on males was reported by H. Zain [*Klin. Wochschr.* **15,** 1722].

Several investigators studied the relation of fats to other constituents of the diets. M. Miyazaki [*J. Biochem. Japan* **24,** 407-22] reported that high fat diets increased fat deposition and decreased liver glycogen in dogs. This effect was offset by the addition of carbohydrate to the diet. During inanition, according to Emile F. Terroine and Simone Synephias [*Compt. rend.* **205,** 390-3] the fat supplied different proportions of the energy for various mammals. Thus for the rabbit it was 70 per cent, for man 85 per cent and for the pig, mouse and rat 90 to 96 per cent; the remainder was supplied by protein. A comparison of three grades of meat meal containing 18.82, 11.08 and 3.17 per cent fat reported by H. E. Woodman and R. E. Evans [*J. Agr. Sci.* **27,** 465-73] showed that the crude protein and total organic matter in the medium fat meal had the highest digestibility in pigs. L. S. Gorschkova and A. A. Dorodnitsyna [*Voprosy Pitaniya* **3,** No. 6, 28-33] found that protein assimilation by dogs was highest with addition of butter fat, less with margarine and soybean oil and lowest with lard and sunflower seed oil. It was assumed that the variations were due to differences in vitamin content.

Recent literature associates the role of vitamin B_1 with the metabolism of fat and carbohydrate. As discussed by E. W. McHenry [*Science* **86,** 200] carbohydrate metabolism proceeds to the pyruvic acid stage and is halted there in the absence of vitamin B_1, thus allowing the pyruvic acid to accumulate. In the presence of the vitamin, fat is synthesized, presumably with pyruvic acid as an intermediate stage. Further, the action of dietary fats in sparing vitamin B_1 might be through providing the body with necessary fat, thus not requiring the synthesis from carbohydrates in the animal, which process requires the aid of the vitamin. W. D. Salmon and J. G. Goodman [*J. Nutrition* **13,** 477-500] reported that coconut fat was most effective in alleviating vitamin B_1 deficiency in the rat. With synthetic esters, the effectiveness was maximum with esters containing fatty acids of 8 carbon atoms; and decreased in each direction from this molecular composition. Determinations of caprylic and caproic acids in fats from the brains and livers of the rats showed no differences that could be attributed to vitamin B_1 deficiency. E. W. McHenry [*J. physiol.* **89,** 287-95] reported that rats on a fatty liver producing diet without vitamin B_1 showed an original increase in liver fat until the vitamin B_1 stores were exhausted and then the liver fat decreased. The fat in the liver could be greatly increased by feeding the vitamin. The same was also true when a fat-free, high-carbohydrate diet was used. A lowering of the iodine number of skin fat of animals on a diet deficient in vitamin B was reported by T. Kalaja [*Suomen Kemistilehti* **9B,** 21-2]. In animals which synthesize vitamin B in the alimentary tract the addition of fat according to N. G. Guerrant *et al.* [*J. Nutrition* **13,** 305-15] did not lead to a more favorable production of vitamin B_1.

Recent investigations on the chemistry of the phospholipids were reviewed by E. Klenk and K. Schuwirth [*Ann. Rev. Biochem.* **6,** 115-38]. Recent reports of W. R. Bloor and E. M. Boyd were discussed by H. H. Williams and W. E. Anderson [OIL AND SOAP **14,** 122-4]. The evidence presented favors the view that as the histological appearance of a tissue varies with its state of physiological activity, in like manner the lipid composition of the tissue varies. Active tissues contain a greater percentage of phospholipids. Degeneration, retrogression or inactivity were found associated with decreasing or low values of phospholipids and cholesterol and high values for cholesterol esters and neutral fat.

The synthesis of phospholipids was studied by C. Perrier *et al.* [*Nature* **139,** 1105-6] and G. Hevesy and E. Lundsgaard [*Nature* **140,** 275-6] by feeding animals fat and radioactive phosphates and soon after determining the destiny of the "labelled" phosphorus. Perrier *et al.* found a large part of the radioactive phosphorus in the phospholipids of the liver and the intestines, while the heart, spleen and skeletal muscles showed none. Hevesy and Lundsgaard reported that the

amount of radioactive phospholipid in the blood was small. He suggested that the phospholipids were formed outside of the intestines.

New information on the effects of food fats on the fat and other lipids of the body was produced. S. H. Rubin *et al.* [*J. Biol. Chem.* **121,** 19-26] analyzed the liver lipids of dogs fed a diet containing various types of fats. The total lipids and the individual lipid fractions, except for the iodine value of the total fat acids, showed no statistically significant difference as between cod liver oil, Mazola or Crisco. A. E. Hansen and W. R. Brown [*J. Nutrition* **13,** 351-7] recorded data on body fats of rats reared on a fat free diet. The serum lipids had a lower degree of unsaturation than those of rats on stock diet. The serum lipids of young animals tended to have lower iodine values than those of adult animals. Esters of oleic acid given in fairly large quantities to animals on the fat deficient diet caused a definite increase in the iodine values of the total lipids even though they effected only a partial clinical cure of unsaturated acid deficiency disease. According to K. Miura [*Biochem. Japan* **25,** 579-93] feeding rats with linseed oil increased the iodine number of fat acids of both mother and fetus while coconut oil decreased it. However, with linseed oil the iodine value of the phosphatide fat acids was also increased; while feeding coconut oil yielded no marked changes. Elaidic acid affected the phosphatide fat acids of both mother and fetus.

S. Schmidt-Nielson and A. Astad [*Kgl. Norske Videnskab. Selskab. Forh.* **9,** No. 15, 54-7] reported the effect of certain cattle feeds on the characteristics of butter. Turnip feed yielded a high Polenske value butter fat whereas coconut meals lowered the Reichert-Meissl, iodine and butyric acid values. V. Horn and E. Muhl [*Biedermanns Z. B. Tierernahr.* **9,** 1-31] suggested the addition of 30 per cent palm kernel cake to cattle feed concentrate containing soybeans in order to increase the milk yield and improve the quality of butter produced. S. M. Hauge, J. W. Wilbur and J. H. Hilton [*J. Dairy Sci.* **20,** 87-91] attempted to locate the factor in soybeans which interferes with the transference of vitamin A activity of the feed to the butterfat secreted by the cow. The factor was said to be present in the bean, and prolonged extraction of soy beans with ethyl ether and ethyl alcohol failed to remove it.

T. P. Hilditch [*Analyst* **62,** 250-7] recorded the fat acid composition of milk fat produced under winter feeding and pasture feeding in England, New Zealand and India, and also the effect of cod-liver oil feeding. When cod-liver oil was fed to cows there was a lowering of milk-fat production and a very marked alteration in the composition. The lower fatty acids were reduced to half their usual proportion; the myristic and stearic acid content was reduced to a lesser extent while oleic acid content was considerably increased and several per cent of highly unsaturated C_{20} and C_{22} acids appeared in the butter fat. Linseed or rape oil feeds did not affect the milk fats except that with rape oil the milk contained a small amount of C_{22} mono-ethenoid (erucic) acid. The hypothesis suggested was that "if the formation of the lower fatty glycerides of butter is due to enzymic oxidation-reduction of oleo-glycerides, highly unsaturated glycerides of the cod-liver oil will undoubtedly be preferentially absorbed by the enzymes concerned, which would therefore be partially 'poisoned' or hindered from carrying out their normal functions." By comparing daily production of component acids rather than percentage of butter fat acids, it was shown that the glycerides which suffer most in production were precisely those which, on the hypothesis suggested, were produced by oxidation-reduction processes from oleo-glycerides.

Several therapeutically active oils are toxic. Some Japanese investigators believe that the toxicity of several fish liver oils is due to higher unsaturated acids in the oil. M. Yoshida [*J. Agr. Chem. Soc. Japan* **13,** 120-47] found that the toxicity of the liver oil of *Squalus wakiyae* was prevented by administration of yeast, liver or the extracts of these containing the flavin fraction. The findings were important because the nutritive value of the liver oil of *Squalus wakiyae* is superior to that of cod liver oil and the toxicity seemed to run proportional to its vitamin activity. I. Yamanto [*Bull. Inst. Phys. Chem. Research Tokyo* **15,** 590-4] showed that ingestion of yeast reduced the toxicity caused by consuming large amounts of cod liver; the result from yeast extracts was less marked. G. M. Dorrance and E. F. Ciccone [*Proc. Soc. Exptl. Biol. Med.* **36,** 426-7] produced spindle cell sarcomas in 34 rats by feeding crude wheat germ oil. The tumors were successfully transplanted both subcutaneously and intraperitoneally in 260 rats through 15 successive generations.

Data on the vitamin A and D value of butter produced in various European countries and New Zealand were tabulated by R. S. Morgan and H. Pritchard [*Analyst* **62,** 354-62]. The summer average values were vitamin A 27.2 and vitamin D 0.49 International Units per gram; the winter values were 15.4 and 0.16 respectively. Data by J. Krizenecky [*Chem. Listy* **31,** 88-93, 114-21] showed that the vitamin A content of premier jus was 0.3 to 0.5 that of average butter, and the vitamin D content was 0.5 that of autumn butter. The vitamin A and D content of lard was less than that of beef tallow. The vitamin activities of the above mentioned materials throughout the year were tabulated. T. A. Buckley [*Mahayan Agr. J.* **24,** 485-8] reported that palm oil from ripe fruit had a vitamin A potency of 1900 International Units per gram and that this value was increased by removing solid components by settling and filtering.

Many investigators prepared communications on the vitamin activity of fish liver oils. Among these A. D. Holmes *et al.* [*Ind. Eng. Chem. Anal. Ed.* **9,** 456-7] found that spectrophotometric and chemical methods for determining the vitamin A content of cod-liver oils gave values of the same order. The presence of free fatty acids or various amounts of unsaponifiable affected neither method. H. I. Milne [*Poultry Sci.* **16,** 383-7] recommended that values for the vitamin A content of pilchard oil be measured spectrophotometrically on the unsaponifiable fraction of the oil. The vitamin A content of Australasian fish liver oils was tabulated by W. Davis and D. J. Field [*Biochem. J.* **31,** 248-50]. L. I. Pugsley [*Prog. Rept. Can. Pac. Biol. Sta. & Pac. Fisheries Expt. Sta.* **1937,** No. 34, 3-7] tabulated similar data on grayfish, *Squalus sucklii,* liver oil. T.-H. Wang and C.-H. Kan [*J. Chinese Chem. Soc.* **4,** 393-401] report that biological tests showed that liver oils from *Dasytis akijei* were rich in vitamins A and D.

The vitamin D content of various fish liver oils varies considerably with the species of fish, the location and season of catch and the amount of oil in the livers. To give a good picture of the value of the various sources one must consider all the variables from tabulated results. Data of this type tabulating the vitamin D content of West Indian shark liver oils were presented by C. F. Asenjo [*Puerto Rico J. Pub. Health*

Trop. Med. **12,** 358-62], of New Zealand fish liver oils by M. M. Cunningham [*New Zealand J. Sci. Tech.* **18,** 898-9], of Burbot liver oil by T. Myers [*J. Lancet* **57,** 110-1] and of menhaden body oil by W. C. Supplee [*Ind. Eng. Chem.* **29,** 190-1].

The curative effect of certain unsaturated fat acids on lesions caused by the lack of fat in the diet has been associated with vitamins because it seems to be of the same nature. T. Moore [*Biochem. J.* **31,** 138-154] confirmed the earlier work of Burr and Burr on this subject. He attempted to associate the curative effect with spectroscopic absorption of the fats. O. Turpeinen [*Proc. Soc. & Med.* **37,** 37-40] found arachidonic acid approximately three times as effective as linoleic (or lenolenic) acid in curing the fat deficiency disease. It was suggested that the need of the animal was primarily for arachidonic acid and that linoleic acid was beneficial solely on account of its conversion into arachidonic acid in the body. W. R. Brown and A. E. Hansen [*Proc. Soc. Exptl. Biol. Med.* **36,** 113-7] reported that the content of linoleic and arachidonic acids in the fat of blood serum was definitely diminished in children with eczema and suggested that the disturbance in unsaturated fat acid metabolism may be one of many factors at fault in the condition. Contrary to this report N. N. Epstein and D. Glick [*Arch. Dermatol. Syphilol.* **35,** 427-32] found no abnormal variation in blood fat composition in patients with eczema and psoriasis but high fat in acne vulgaris. No improvement was obtained on administration of linseed oil to the patients.

Schiff and C. Hirschberger [*Jahrbuch. f. Kinderheilkunde* **150,** 247] reported an increase in the number of thrombocytes in the blood of children, owing to the presence of the fat-soluble "T factor," found in sesame oil and egg yolk. Its activity is destroyed by ultra violet radiation, it is not present in cod liver or olive oil and seems to be distinct from vitamin A.

The question of introducing vitamins through the skin with special reference to vitamin containing cosmetics and skin creams were reviewed by M. Schieblick [*Fette u. Seifen* **44,** 64-7]. Many favorable reports were assembled in this review. The editor of the Journal of American Medical Association [*J. A. M. A.* **108,** 1279; **109,** 509-10], however, presented reports unfavorable to the practice of exploiting vitamin-containing cosmetics. H. S. Redgrove [*Pharm. J.*, Apr. 17] questioned whether there was any additional cosmetic value in the vitamin cosmetics even though they may be absorbed by the skin. A. L. Bacharach [*Manufg. Perfumer London,* May] discussed the flimsiness of the evidence for vitamin F cosmetic promotion. T. Durfee [*Drug Trade News* (May 24)] published a complaint issued by the Federal Trade Commission against manufacturers who made extraordinary claims as to the therapeutic value of vitamin-containing cosmetics.

A patent issued to J. McKee [*U. S.* 2,083,572] described a method of ozonizing oils. The oils treated with ozone were said to have some therapeutic value for both external and internal use.

DETERIORATION OF FATS AND OILS

Monographs on spoilage of fats were prepared by N. Maravalhes [*Rev. alimentar* **1,** 10-2], K. Täufel [*Fette u. Seifen* **44,** 179-87] and E. E. Russell [*Can. Chem. Met.* **20,** 346-8].

R. Rouzaut [*Anales asoc. quim. argentina* **24,** 160] compared the various tests for detecting rancidity in fats. The Kreis reaction as modified by Täufel, Sadler and Russow was preferred; and if this test is negative, the test for peroxides should be used as a supplement. Modifications of the Kreis test were proposed by W. P. Walters, M. M. Muers and E. B. Anderson [*Chem. & Industry* **56,** 1055] and R. Neu [*Chem.-Ztg.* **61,** 733-6]. Walters *et al.* substituted an organic acid, trichloroacetic, for the mineral acid used in the test and recommended amyl acetate as a solvent for the phloroglucinol. The advantage of this method is that the color appears in one phase and is measured directly by the Lovibond tintometer or the Zeiss photometer, thus increasing the accuracy. Neu recommended adding two centimeters of fat to 10-12 grams of granulated silica gel in such a way that the fat is absorbed immediately by the gel. The gel is placed in a calcium chloride drying tube. Hydrogen chloride is passed through the gel and then it is allowed to bubble through the phloroglucinol reagent. The color is examined spectroscopically. J. P. Harris and W. S. Welch [Oil & Soap **14,** 3-5] reported that some bleaching carbons completely removed the compounds that were responsible for the Kreis test in cottonseed and corn oils. Other carbons and fullers earth caused a development of bodies that react positively in the test.

H. L. Roschen and W. J. Lehmann [Oil & Soap **14,** 17-9] recorded data that showed that the Korpaczy modification of the Stamm reaction for detecting rancidity in fats was applicable to lard and beef fat but generally inapplicable to vegetable seed and marine oils. They agreed with the suggestion of Korpaczy that a value of five defined the boundary between rancid and nonrancid lard.

The use of solvents containing ketones is a source of error in evaluating the extent of spoilage by tests for ketones. F. Kiermeier and K. Täufel [*Fette u. Seifen* **44,** 508-9] reported that synthetic octane and benzol gave negative peroxide reactions; a few samples of ether, ethyl alcohol, carbon tetrachloride and chloroform gave slightly positive reactions and ether, petroleum ether and benzine gave strongly positive tests.

A. A. Zinovev and S. V. Drukker [*Masloboino Zhirovoe Delo* **13,** No. 2, 6-8] recorded the rate of development of peroxides and ketone rancidity in lard and in unsaturated fats. It was shown that the peroxides were formed before the ketones. This report was criticized by K. Täufel and F. Kiermeier [*Fette u. Seifen* **44,** 423-4]. These investigators obtained a positive ketone reaction in lard samples stored one month at —8.5° C. and whose final Lea's reaction was 0.08. Under all conditions of rancidity tests with various samples that stood in light, in dark and at low temperatures, the ketone reaction of fat spoilage appeared positive before or at the same time as other tests now in current use. K. Täufel, H. Thaler and H. Hohner [*Z. Untersuch. Lebensm.* **74,** 119-33] reported that higher methyl ketones were formed from fatty acids: (1) by the action of hydrogen peroxides in ammoniacal solutions, (2) by bacterial action and (3) by the action of light and heat. They described the salicylic aldehyde reaction and the use of photometers for the detection and estimation of methyl ketones.

J. C. Smith [*Chem. & Industry* **56,** 833-9] reviewed the possible effects of and the mechanism of formation of active oxygen in organic compounds. H. Böhme and G. Steinke [*Ber.* **70B,** 1709-13] recommended that data on the oxidation velocities of fat constituents be determined in order to develop knowledge on the oxidative susceptibility of individual double bonds. The

rates of oxidation with oxidizing agents of several fat acids and oils were plotted. In some oils the peracid oxidizing agent consumed corresponded to the iodine numbers. For oils having a diene value the amount of peracid consumed was less. This was interpreted to indicate that poppy, linseed and sesame oils contain double bonds which add halogen but are not oxidized by peracids.

L. A. Hamilton and H. S. Olcott [*Ind. & Eng. Chem.* **29,** 217-23] studied the course of oxidation of oleic acid, methyl oleate and oleyl alcohol. In the initial reactions of the double bonds, each molecule of methyl oleate and oleic acid absorbed approximately four and each molecule of oleyl alcohol approximately five atoms of oxygen. Simultaneously each of the three compounds lost one molecule of water. The peroxide level in the early stages of oxidation was higher in oleyl alcohol and methyl oleate than in oleic acid. The destruction of the double bond occurred faster than was expected for an unimolecular reaction, presumably because of secondary reactions, which became more prominent as the oxidation progressed.

H. Schmalfuss, H. Werner and A. Gehrke [*Margarine Ind.* **29,** 31-2] added new evidence toward proving that free aldehydes may be liberated from saturated compounds. A very pure methyl ester of lauric acid was converted to free aldehyde on heating in the presence of oxygen. These authors [*Fette u. Seifen* **43,** 211-4, 43-7] also reviewed their work on deterioration and discussed the significance to economy of the investigations on fat spoilage.

The rate of peroxide development under constant intensity of light was recorded by M. R. Coe [Oil & Soap **14,** 171-3]. It was shown that the induction period of an oil which had been protected by sextant green filter was unaffected by the peroxides which were developed during protection and was equal to that of a fresh sample of the same oil. This suggested that the peroxides which developed under the light filter did not increase the susceptibility of the oil to becoming rancid. The fat materials which are usually packaged in transparent containers can be protected from the accelerating action of light according to patent issued to Sylvania Industrial Corp. [*Brit.* 453,438] in which the packaging material is colored so that it is opaque to light of wave lengths 2900 to 4700 A.° N. I. Kozin and F. M. Fridlyanskaya [*Masloboino Zhirovoe Delo* **12,** 529-33] reported that a sample of sunflower oil that was kept 24 years in a hermetically sealed flask and was protected from light by opaque coverings showed no marked changes. He concluded that oils decompose only by oxidation reactions. B. N. Banerjee and N. N. Dastur [*Agr. Livestock India* **6,** 433-40] recorded data on the destruction of vitamin A in ghee on exposure to light. Colored cellophane wrappers decreased the destruction of the vitamins only to the extent that they reduced the intensity of the light.

The action of ozone and ultraviolet light on fats is significant at the present time because various writers in trade journals and concerns have promoted the use of ozone or ultra-violet for the preservation of meat. C. H. Lea [*Dept. Sci. Ind. Rept. Food Invest. Bd.* **1935,** 25; **1936,** 33-8] showed that both practices cause a rapid development of foreign odor or rancidity in the beef and pork fat. Beef fat exposed at a distance of 25 cm. from a cold type mercury-in-quartz lamp acquired a foreign odor that was detectable by some observers in five minutes and by all after 10 minutes exposure. Foreign flavor was detectable in cooked, five-minute irradiated samples and those irradiated 10 minutes were unpalatable. It was shown that the superficial fat was oxidized.

C. H. Lea [*Dept. Sci. Ind. Rept. Food Invest. Bd.* **1935,** 79-81] recommended low temperatures for storage of herring oil. The rate of oxidation at 0° was 2.55 times that at —10° and 6.8 times that at —20°. A. Banks [*J. Soc. Chem. Ind.* **56,** 13-15T] reported similar data on the same oil. In addition he reported that herring muscle catalyzes the oxidation. The effect was destroyed by heat. C. H. Lea [*J. Soc. Chem. Ind.* **56,** 376-801; *Dept. Sci. Ind. Rept. Food Invest. Bd.* **1936,** 77-9] also reported that a tissue oxidase accelerates development of rancidity in bacon fat. The activity of the enzyme was high at pH between 4 and 5 and in the presence of salt. The same author [*Dept. Sci. Ind. Rept. Food Invest. Bd.* **1936,** 39-40] recorded that the following water soluble substances affect the rate of oxidation of lard: (a) at pH values below 5, nitrite was a powerful pro-oxidant; (b) copper and iron salts accelerated oxidation; (c) glycerol and sugars were weak antioxidants; (d) aliphatic hydroxy acids were moderate and polybasic hydroxy acids powerful antioxidants; (e) aliphatic amino acids and proteins were antioxidants; (f) in small concentrations the pro-oxidant effect of copper was inhibited by proteins; (g) orthophosphoric acid was fairly good, pyro-phosphoric acid very good and phosphorous acid effective antioxidants.

A comprehensive investigation on formation and decomposition of peroxides in oils was presented in a series of eight papers by M. Nakamura [*J. Soc. Chem. Ind. Japan* **40,** 203-32B]. Sixty minutes' heating reduced the peroxides in rancid soybean oil 99 per cent and aldehydes 27 per cent. Optimum temperature for peroxide formation in soybean oil was 135°; at higher temperatures the peroxides decomposed. Antioxidants raised the optimum temperature of peroxide formation while pro-oxidants, *i.e.,* driers, decreased this critical temperature even to as low as 60°. The optimum temperature of formation of peroxides in tung, linseed, tsubaki and castor oils were 95°, 105°, 125-40° and 155°, respectively. The effect of carotene differed with the oils and the amount used.

Reviews on antioxidants and methods of preventing autoxidation of fats were contributed by F. Wittka [*Chem.-Ztg.* **61,** 386-9], J. M. Butler [*New Zealand Inst. Chem.* **1,** 26-30] and R. Fussteig [*Öle, Fette, Wachse, Seife, Kosmetik* **1937,** No. 3, 7-10]. K. Hinsberg and R. Ammon [*Z. physiol. Chem.* **246,** 139-48] showed that isouroporphyrin, coproporphyrin and hematoporphyrin inhibited the autoxidation of linoleic and linolenic acids. H. C. Cohen [*Verkroniek* **10,** 3-4] showed that one of the natural antioxidants of linseed oil was cephalin. H. S. Olcott and O. H. Emerson [*J. Am. Chem. Soc.* **59,** 1008-9] reported that α, β, and γ tocopherols and their allophanates were effective antioxidants for lard. They were increasingly effective in the order α, β, and γ. A description of properties of the antioxidants obtained from some vegetable oils which was previously reported by H. S. Olcott and H. A. Mattill was confirmed by T. G. Green and T. P. Hilditch [*J. Soc. Chem. Ind.* **56,** 23-26T], who obtained higher yields of the concentrate from extracted soy bean cake than from the oils themselves. S. H. Bertram [*Internatl. Tin Res. Development Council Tech. Publ. Ser. A,* No. **45,** 3-10] recommended tin salts as antioxidants for textile oils. F. Wittka [*Seifensieder-Ztg.*

64, 194-5, 210] warned soap makers that soap perfumes should be selected from the viewpoint of their effect on rancidity. Some perfume constituents were reported to have an antioxidant effect while others were pro-oxidants.

Seed flours as antioxidants especially oat flour, or their extracts as patented by S. Musher [*U. S.* 2,069,265; 2,075,824; 2,093,971; 2,097,252] during the year 1937 and other patents by the same inventor that were reported in preceding years received considerable attention in both the scientific and trade journals. F. N. Peters and S. Musher [*Ind. Eng. Chem.* **29,** 146-51] reviewed the patents and tabulated data of comparative tests on treated and untreated fatty substances. R. C. Conn and R. E. Asnis [*Ind. Eng. Chem.* **29,** 951-2] recorded data on the inhibiting action of this material on potato chips. Methods of use and data on stabilizing butter were recorded by C. D. Dahle and D. V. Josephson [*Natl. Butter Cheese J.* **28,** No. 15, 6-7; No. 18, 18-21], V. L. Koenig [*Natl. Butter Cheese J.* **28,** No. 15, 26-30] and W. H. Sproule and F. W. Hamilton [*Can. Dairy and Ice Cream J.* **16,** No. 2, 19-21]. Parallel work on fatty fish and fish oils was reported by J. M. Lemon *et al.* [*Food Industries* **8,** 576-7, 583] and L. Lowen *et al.* [*Ind. Eng. Chem.* **29,** 151-6] respectively. C. L. Bedford and M. A. Joslyn [*Food Research* **2,** 455-69] compared the oat flour antioxidant with other antioxidants. All the investigators reported favorably on this product for the various uses mentioned.

H. A. Mattill and H. S. Olcott [*U. S.* 2,098,254] concentrated antioxidants from vegetable material. The process comprised extracting fat from the vegetable material, separating the unsaponifiable constituents and subjecting this portion to fractional distillation. The antioxidants, "inhibitols," were separated as a fraction distilling within the range 90-220° C. at 0.05 to 0.2 mm. pressure.

The inventors and the materials patented as an antioxidant for food fats during the year were as follows: D. P. Grettie [*U. S.* 2,095,740; *Ger.* 650,285 *Cl.* 53*h*] a distillate secured by the deodorization of hydrogenated sesame oil; A. Eisenstein [*Austrian* 147,701 *Cl.* 23*a*] a small amount of several kinds of crude oil; A. K. Epstein and B. R. Harris [*U. S.* 2,075,806; 2,075,807] phosphoric acid esters of partially esterified polyhydroxy compounds; M. R. Coe [*U. S.* 2,097,516] catalase in either pure form or in the form of a cheese or liver extract; and W. F. Douglass [*U. S.* 2,071,457] lipin containing animal organs, *i. e.*, brain and parts of nervous system, or an extract of the same. Antioxidants patented for technical oils were: J. K. Hunt [*U. S.* 2,064,610], ortho-alkoxy phenols in which at least one of the positions was substituted by a CHO group; J. K. Hunt and G. H. Latham [*U. S.* 2,063,602], sugar amine compounds, such as methyl glucamine; M. S. Carpenter [*U. S.* 2,064,885] polyalkyl-substituted phenols; C. P. Wilson, Jr. [*U. S.* 2,060,965] a product obtained by condensing pyrogallol or catechol with a sulfur dioxide extract of a hydrocarbon oil in the presence of dilute sulfuric acid; and W. H. Carothers and G. J. Berchet [*U. S.* 2,073,363] butadienyl derivatives. E. C. Crocker [*U. S.* 2,073,923] patented the use of glutamic and aspartic acids or their acid salts as antioxidants for soap.

L. B. Jensen [*J. Bact,* **33,** 98] showed that bacteria may induce: (a) oxidative rancidity (lipase-peroxidase formers), (b) hydrolysis with high free fatty acid (lipase formers), (c) tallowiness (oxidizers) in beef and mutton fats, and (d) flavor reversion and production of flavor adjuvants. Also fat-soluble pigments of various microörganisms caused "pink" fats and purple discolorations by oxidation-reduction mechanisms. Data on the lipolytic action of 38 different strains of staphylococci and two strains of *Micrococcus tetragenus* on eight different glycerides, were secured by R. E. Trussell and L. A. Weed [*J. Bact.* **33,** 381-8]. The action of the fat splitting enzymes of yeast according to R. Murakami [*Bull. Agr. Chem. Soc. Japan* **12,** 115-6] were weakest in the dark, weak in red or yellow light and strong in green violet.

Deterioration of butter was in most cases associated with molding. T. R. Vernon [*Dairy Ind.* **2,** 63-5, 133-5, 255-6] found that the molds associated with discoloration of more than 2,000 samples of butter consisted of *Cladosporium, Penicillium, Aspergillus, Stemphylium, Fusarium* and *Phoma.* The types of discoloration caused by each were described. It was shown that some molds affect quality; others have no effect on quality, yet in mold count both types receive the same consideration. He suggested that the organism be classified according to its lipolytic or caseolytic activity. However, the present method for mold and yeast count was said to be of value as a check on plant methods. Some of these same points were also discussed by E. C. Beck [*Can. Dairy and Ice Cream J.* **16,** No. 5, 69-71, 73]. General recommendations and a discussion on the factors relating to manufacturing butter of good keeping qualities were presented by O. R. Overman [*Natl. Butter Cheese J.* **27,** No. 24, 6-7].

Data on the storage of butter was recorded by C. R. Barnicoat [*Refrigerating Eng.* **32,** 335-6]. After storage of five months in white pine wooden boxes butter that was kept at 32° F. scored 3½ points lower than samples of the same butter kept at 14° F. Under the same conditions tin foil wrapped butter showed a one point difference when compared between the two temperatures. Sweet cream butter stored at -5° F. lost 1.5 points in score after eight months' storage. W. Riddet and J. C. Neill [*New Zealand J. Agr.* **53,** 129-39] reported that aluminum foil parchment wrapper prevents mold penetrating from infected boxes to the surface of butter while a double layer of 28-30 pound parchment was ineffective. They obtained promising results on mold control by immersing wooden boxes for 10 minutes in a 0.1 per cent solution of sodium salicylanilide. The chemical was not detected in the surface butter that had been packed in the treated boxes. D. H. Jacobsen [*S. Dak. State Coll. Agr. Bull.* 308] recommended that a sample of each batch of butter be held at room temperature for 10 days so as to give information on the storage quality of the product.

V. C. Stebnitz and H. H. Sommer [*J. Dairy Sci.* **20,** 181-196, 265-80; Oil & Soap **14,** 228-32] presented data which show that a tallowy flavor will develop in butterfat as a result of oxidation by air and heat in the absence of light. The tallowy flavor did not appear at any definite peroxide value but seemed to vary with the different samples of butterfat. Other evidence showed that when cows were on grass the butterfat was less saturated and more susceptible to oxidation. L. Erlandsen [*Fette u. Seifen* **44,** 462-4] summarized the work published by Sommers on this problem in 1923, and showed that Sommers' conclusions were substantiated by several European investigators. W. Ritter [*Schweiz. Milch-Ztg.* **62,** 529-30 538, 541-2, 543-4] also attributed the flavor reversion of butter to the same process.

J. O. Clarke *et al* [*J. Assocn. Off.*

Agr. Chem. **20,** 475-505] investigated the possibility of determining decomposition products as indices of the decomposition in butter made from unfit cream. It was shown that lactic acid fermentation of the cream did not increase the indole content of the butter. Decomposition of cream caused an increase in indole. In many cases butter made from decomposed cream showed high values for indole, acidity of fat and mold.

Three deaths by asphyxiation in an oxygen-deficient air are of interest in connection with fat spoilage because the accidents resulted from deterioration of an oil. According to E. J. Powers [*Am. J. Pub. Health* **27,** 880-2] one man was overcome in an attempt to clean out the foots at the bottom of an oil reservoir; two others were overcome in rescue attempts. The reservoir had been closed for three months, during which time the fine meal which had passed through the filter presses, had accumulated at the bottom and had begun to ferment giving off carbon dioxide. This gas being heavier displaced the air upward and the deterioration of the oil further diminished the oxygen content; thus giving the asphyxiating atmosphere.

COMPOSITION AND CHARACTERISTICS OF FATS AND OILS

The recent data on composition and characteristics of fats and oils are appended to this section of the review. For arriving at the fat acid composition several methods were used. T. P. Hilditch and co-workers usually separated the fat acids into several fractions by distillation, analyzed the fractions and computed the original percentage composition. H. P. Kaufmann with co-workers depended on the characteristics, *i. e.*, iodine, thiocyanogen, hexabromide and diene numbers and determination of saturated acids for ascertaining the composition. His analysis of tung oil is tabulated. Oiticica oil [*Ber.* **69**B, 2674-83] was reported to contain: licanic acid 70.0, unsaturated nonconjugated acids 15.2, saturated acids 9.9 and glycerol 4.5 per cent. G. S. Jamieson and R. S. McKinney [Oil & Soap **13,** 202] used the lead salt method of separating the saturated from unsaturated fat acids of walnut oil and then determined the composition of the saturated acid by distillation of its ethyl esters and the composition of the unsaturated portion by means of the characteristics. In a similar manner these same authors obtained the data on tung and lumbang oil which are tabulated in the chart. With tung oil they presented evidence that indicated that linoleic and linolenic acids were absent. This permitted development of equations to determine the amount of oleic and eleaostearic acids present. The iodine and thiocyanogen values, per cent unsaponifiable and per cent of saturated acids were required for the calculations. In addition to the characteristics and composition of the fats and oils that are given in the charts most authors suggested several uses for the newer oils.

In addition to the tabulated information several reports contained tabulations of similar data for many oils. An anonymous writer [*Bull. Imp. Inst.* **35,** 147-57] tabulated and discussed the character of the tung fruit, nuts, kernels, and oils from British Empire sources. Similar data on 56 and 129 Indian vegetable oils were tabulated, respectively, by S. Krishna *et al* [*Indian Forest Records Chemistry* **1,** 1-44 (1936)] and in an Indian government, Industrial Research Bureau, pamphlet. H. Matsuo [*Repts. Imp. Ind. Research Inst. Osaka Japan* **17,** No. 12, 1-36] recorded information on vegetable seed oils of Southern Pacific islands. Market samples of edible oils sold in Japan were analyzed by S.-S Ueno and Y. Ota [*J. Soc. Chem. Ind. Japan* **40,** 291-2B]. H. Chen's report [*Ind. Research China* **6,** 92-3] on camphor seed oil indicated that it was similar to coconut oil. A comparison of the chemical composition and properties of illipe nut fat and cacao butter by P. A. Rowaan [*Ber. Afdeel, Handelsmusem Koninkl. ver Kolon. Inst. No.* 113, 30 *pp.*] showed that they are very similar.

Several factors may influence the amount of oil in seeds and the quality of the oils. K. Schmalfuss [*Angew. Botan.* **18,** 345-7] obtained poppy seed oil of lowest iodine value from plants receiving a complete fertilizer. Fertilization of the flax with potassium and ammonium salts resulted in increasing the proportion of linoleic acid in the oil produced at the expense of oleic and linolenic acids. R. A. Gross and C. H. Bailey [Oil & Soap **14,** 260-3] report that all seed oils of the Bison flax variety contained a higher percentage of oleic acids and a lower percentage of linolenic acids than the Abyssinian yellow flax variety. W. G. McGregor [*Can. J. Research* **15***C*, 362-79] associated high oil content flax seeds with a long period between blossoming and maturity. U. Gerloff [*Planta* **25,** 667-88] determined the composition of the oil from different parts of plants. Oils from the roots of the plants investigated contained significantly more saturated acids than the oils from the seeds. C. K. McClelland [*Ark. Agr. Expt. Sta. Bull.* **334,** 3-44] recorded the oil content of 160 varieties of soybeans. The oil content ranged from 13 to 23 per cent with an average of 18 per cent. According to R. Salgwes [*Compt. rend. soc. biol.* **124,** 817-9], olives infected with *Macrophoma dalmatica* yielded 20 per cent less oil than healthy fruit from the same orchard. Oil from the diseased fruit had an iodine number of 106 as compared to 81 for the normal fruit. A report by M. Bifano [*Boll. soc. ital. biol. sper.* **11,** 847-8] showed that the unsaponifiable content of tunny oil from various sources varied. S.-I. Ueno and S.-I. Makaguchi [*J. Soc. Chem. Ind. Japan* **40,** 86-6B] reported the characteristics and unsaponifiable content of several sea fishes. The unsaponifiable matter was highest in the liver oil.

Analytical contributions by T. P. Hilditch [*J. Soc. Chem. Ind.* **56,** 310-5T, 315-22T, 322-9T, 434-8T; *Biochem. J.* **31,** 1805-9, 1964-72; *J. Chem. Soc.* **1936,** 1750-5] include a general review of the analytical procedure employed, a discussion on the method, analysis of marine animal, tea seed, ox-fat, soybean and rape seed oils and seed wax of *Simmondsia californica.* Molar percentage composition of Antarctic whale and cod liver oils, respectively, were myristic 9, 2; myristoleic 4, 2; palmitic 2, 1; C_{18} unsaturated 35 (mean unsaturation —2.6H), 26 (—3.3H); C_{20} unsaturated 12 (—5.6H), 25 (—5.5H); C_{22} unsaturated 4 (—9H), 20 (—7.4H); and C_{24} unsaturated ———, less than 1 per cent. He showed by distillation of the ethyl esters and by means of oxidation that hexadecenoic was present in small amounts in olive and teaseed oils. The work on soybean and ox depot fat demonstrated that results of analysis of these fats based on characteristics of mixed fatty acids or glycerides alone were of little value without some form of detailed analysis. The structure of the component acids of ox fat and the constituents of *Simmondsia californica* seed wax were determined. M. Tsujimota and co-workers [*J. Soc. Chem. Ind. Japan* **40,** 191-3B, 272-4B] fractionated sperm and pilot-whale head oil. The characteristics of the fractions with suggestions as to their composition were presented. An efficient fractionation equipment for the quantitative examination of natural fats was described by H. E. Longenecker [*J. Soc. Chem. Ind.* **56,** 199-202T].

S. H. Bertram [*Öle, Fette, Wachse, Seife, Kosmetik* **1936** *No.* 14, 2-4], R. C. Stillman and J. T. R. Andrews [OIL & SOAP **14,** 257-60] and S.-I. Ueno and C. Yonese [*J. Chem. Soc. Japan* **58,** 430-70] issued notes on the separation of saturated fat acids from oils by the lead-salt method. The method with several oils yielded saturated acids of high iodine number. Bertram showed that the high iodine number of the lead salts separated from fat acid of hazelnut oil was due to the presence of oleic acid. There was no explanation of this behavior. Stillman and Andrews attributed similar experiences on other oils to a low linoleic-oleic acid ratio in the oils. S.-I. Ueno and C. Yonese reported that the solid acid separated from tunny oil had an iodine value of 98.2. G. Canneri and D. Bigalli (*Ann. chim. applicata* **26,** 430-6] suggested that separations of fat acids could be accomplished when in the form of their thallium salts. The solubility of the thallium salts of several fat acids in acetone and diethyl ketone were recorded.

Practically pure cerotic acid, melting at 80.5° C., was separated from butterfat by G. E. Helz and A. W. Bosworth [*J. Biol. Chem.* **116,** 203-6]. J. M. Spadola and R. W. Riemenschneider [*J. Biol. Chem.* **121,** 787-90] reported that the unsaturated C_{16} acid of goat milk fat, egg yolk glycerides and depot fat of white rat was chiefly $\Delta^{9,\ 10}$ hexadecenoic acid. Only one solid tetrabromide, α-linoleic acid tetrabromide, was obtained by D. M. Birosel [*J. Am. Chem. Soc.* **59,** 689-92] from the bromination of soybean and cottonseed oils. R. S. Morrell and W. R. Davis [*Paint, Varnish, Production Mgr.* **15,** 15-6, 18, 20, Dec. 19; *J. Oil Colour Chem. Assoc.* **19,** 359-62] reported that oiticica oil contains 16 per cent of nonconjugated unsaturated acids that as yet are not identified.

Several Japanese investigators, S. Komori and S.-I. Ueno [*Bull. Chem. Soc. Japan* **12,** 226], Y. Toyama and Tsuchya [*Ibid.* **11,** 741-4], S.-I. Ueno and M. Iwai [*Ibid.* **11,** 643-9], T. Kuwata and Y. Ishii [*J. Soc. Chem. Ind.* **39,** 317] and M. Takano [*J. Soc. Chem. Ind. Japan* **40,** 165B] reported investigations on identifying the lesser known fat acids of several oils.

A method for the direct determination of eleostearic acid in tung oil was developed by P. S. Ku [*Ind. Eng. Chem. Anal. Ed.* **9,** 103-6]. It was based on the different solubilities of the fat acids in 76 per cent ethyl alcohol at 0° C. The method can detect 2 per cent or more of the common adulterants.

Mixed glycerides of elaidic acid and isoöleic acid, respectively, with palmitic, stearic and their triglycerides were prepared and the melting points recorded by A. Bömer and co-workers [*Fette u. Seifen* **44,** 29-31, 340-3].

H. Kurz [*Fette u. Seifen* **44,** 144-5] tabulated data on the alcoholysis of olive, sesame, linseed, linseed-stand, tung and tung-stand oils. Due to the intermediate formation of mono- and diglycerides as shown by acetyl values, the glyceride splitting was far advanced before large proportions of glycerol were liberated. Substantial differences in the rate of alcoholysis of the different fat acids in stand oils were not observed.

Data on the characteristics of glycol, methyl, ethyl, butyl, amyl, cyclohexyl and methyl-cyclohexyl esters of the fat acids of castor oil were contributed by Y. Toyama and T. Ishikawa [*J. Soc. Chem. Ind. Japan* **40,** 172-3B]. The use of the esters for lubrication was discussed.

A general discussion on the non-glyceride constituents of fats giving their structural formulas and properties was contributed by H A. Boekenoogen [*Allgem. Oel- u. Fett-Ztg.* **33,** 461-8]. The information on the pigments associated with both animal and vegetable fats and oils was reviewed by I. M. Heilbron and A. E. Gillam [*Nature* **139,** 612-5, 657-60]. The latter author with M. S. el Ridi [*Biochem. J.* **31,** 251-3] reported that α-carotene was either absent or was present in negligible amounts in butter. Butter carotene was shown by analysis, melting point, absorption spectra and optical rotation to be the pure β-carotene. H. A. Schuette and R. C. Palmer [OIL & SOAP **14,** 295-7] demonstrated the presence of α- and β-carotene accompanied perhaps by the γ- form in rye germ oil; two xanthophylls, lutein and zeaxanthine were found present, and the existence of a third unidentified pigment of this class was suggested.

Three alcohols, α-tritisterol, β-tritisterol and an unidentified alcohol were separated from the unsaponifiable fraction of wheat-germ oil by P. Karrer and H. Salomon [*Helv. chim. Acta* **20,** 424-36]. H. Marcelet [*J. pharm. chim.* **24,** 213-25; *Bull. inst. Egypte* **19,** pt. 1, 1-3] separated the hydrocarbons $C_{15}H_{30}$ and $C_{19}H_{38}$ from peanut oil and $C_{13}H_{24}$, $C_{16}H_{30}$, $C_{19}H_{36}$, $C_{23}H_{42}$, $C_{28}H_{50}$, $C_{36}H_{68}$, $C_{24}H_{50}$ and $C_{26}H_{54}$ from olive oil. The sugar, stachyose, was isolated from soybean foots by K. Okano and co-workers [*J. Agr. Chem. Soc. Japan* **12,** 714-20].

Modifications of the methods for extraction of gossypol from cottonseed oil were proposed by J. O. Halverson and G. H. Smith [*Ind. Eng. Chem. Analyt. Ed.* **29,** 516-8] and L. K. Kozhevnikova and Gil'tburg [*Masloboino Zhirovoe Delo* **12,** 545-6]. Specific precautions as to the type of solvents and the temperatures used during the extractions were given. The structure of this compound was studied by R. Adams *et al* [*J. Am. Chem. Soc.* **59,** 1723-8, 1729-31, 1731-5, 1736-8]. The tin tetrachloride complex, the dipyridine salt, the formate, the acetate, the propionate, the hexabenzoate, several ethers and other derivatives of gossypol were prepared, their characteristics recorded and notes on the possible structure of the gossypol discussed. Gossypol hexapalmitate was prepared by V. E. Gil'tburg [*Masloboino Zhirovoe Delo* **12,** 546-7] by the condensation of palmityl chloride with gossypol.

A. D. Holmes *et al* [*J. Am. Pharm. Assoc.* **26,** 525-40] and C. L. Barthen and C. S. Leonard [*J. Am. Pharm. Assoc.* **26,** 515-24] demonstrated that the spectrophotometric method for the assay of vitamin A was practical. In order to correlate the readings with the vitamin value, a reference cod-liver oil is necessary, such as the United States Pharmacopoeia reference oil which is evaluated biologically.

A few new recommendations on determining oil content of material were endeavors for increasing the accuracy and shortening the time necessary. K. Szahlender and G. Sulyok [*Ber. ungar pharm. Ges.* **13,** 185-8] recommend that seeds be rubbed with a pestle in the presence of solvent before the usual extraction. Because of the susceptibility of fish oils to oxidation and polymerization M. E. Stansby and J. M. Lemon [*Ind. Eng. Chem. Anal. Ed.* **9,** 341-3] reported that a rapid method for determining oil content of fish flesh was necessary. The method they suggested involves extraction of the flesh with acetone, evaporating the acetone and water and extracting the residue with ethyl ether. According to R. W. Harrison [*J. Assocn. Off. Agr. Chem.* **20,** 447-50] the fat in fish meal experiences a considerable change during storage and in so doing becomes less soluble in the type of solvents now used for analysis. Studies to devise a method for the determination of the actual fat content of meal are

now in progress. The oil in fish liver emulsions can be determined according to H. Werner and H. Schmalfuss [*Fette u. Seifen* **44,** 348-51] by mixing the emulsion with anhydrous sodium sulfate and extracting in a Soxhlet apparatus. During extraction and evaporation the oil was protected by blowing nitrogen over it.

For determining fat in wool the colorimetric method described by E. K. Zil'berkveil and L. A. Vasil'ev [*J. Applied Chem. (U.S.S.R.)* **10,** 570-7] can be applied. The wool is refluxed with trichloroethylene, filtered; a small aliquot of the combined solvent is treated with 1 cc. acetic anhydride and 10 drops of sulfuric acid and after 3 minutes colorimetrically compared with standard solutions prepared from solutions of copper nitrate and potassium dichromate.

Procedures and data for the refractometric determination of fat in chocolate and cacao products were contributed by W. Leithe and R. J. Heinz [*Z. Untersuch. Lebensm.* **72,** 414-8], J. Stanley [*Ind. Eng. Chem. Anal. Ed.* **9,** 132-5] and C. Zäch [*Mitt. Lebensm. Hyg.* **28,** 1-5]. Leithe and Heinz's data were for use of bromonaphthalene and petroleum fractions as solvents; Stanley's information was on dibutyl phthalate and diethyl phthalate solvents, and Zäch's data were similar to Leithe's and included the method for fat in cheese. W. Leithe and H. Lamel [*Fette u. Seifen* **44,** 247-8] and N. Rubinskii [*Masloboino Zhirovoe Delo* **13,** No. 2, 23-4] developed the necessary data for using the method on castor beans and press cake, respectively. The accuracy of the method on flax seeds was investigated by L. Lompe [*Angew. Chem.* **50,** 296-8], L. Zeleny [*J. Assoc. Off. Agr. Chem.* **20,** 421-7] and N. Rubinskii and Barmicheva [*Masloboino Zhirovoe Delo* **13,** No. 3, 32]. The latter reported favorable results. Lompe found that samples from different locations did not give comparable values. He, therefore, recommended that the refractive index of each oil be determined and corrections made for variations. Zeleny contributed tables for converting refractive index reading of halowax solutions to per cent oil and tables for correcting for the variability of the refractive index in oil from different samples of flax seed.

W. Leithe and H. Lamel [*Fette u. Seifen* **44,** 140-2] recommended that a mixture of solvents be used in the refractometric determination of fat in oil seeds to adapt the process to instruments having limited range. Mixtures of benzine with cyclohexane were suggested for this purpose. G. Kluin [*Pharm. Weekbl.* **74,** 1234-49] compared the use of *o*-dichlorobenzol, bromobenzol, nitrobenzol, *o*-toluidin, anilin, methyl benzoate, amyl acetate, butyl propionate and monochloronaphthalene as solvents for the refractometric determination of oil in peanuts, rape seeds, palm kernels and cacao seeds. High values were usually obtained with amyl acetate. Butyl propionate gave best results when considering determinations on all the materials but methyl benzoate and monochloronaphthalene were preferred for palm kernels. The data for the solvents were graphically presented. A description of several instruments for determining refractive index and a discussion of their uses in the oil and fat industry was contributed by L. Ivanovsky [*Öle, Fette, Wachse, Seife, Kosmetik* **1937,** No. 2, 1-11]

The procedure for determining moisture in fats and oils by a modified Fischer [*Angew. Chemie* **48,** 394-6] volumetric method was described by H. P. Kaufmann and S. Funke [*Fette u. Seifen* **44,** 345-6]. The method depends on absorption of iodine in sulfur dioxide-methyl alcohol solution in presence of water. The same authors [*Fette u. Seifen* **44,** 386-7] reported that the Smith and Bryant volumetric method compared well with the above method and gravimetric methods. A refractometric moisture determination method was described by P. Z. Zaichenko [*J. Applied Chem. (U.S.S.R.)* **10,** 908-15]. The oil sample was shaken with 90 per cent glycerol, centrifuged for 2 minutes and the refractive index of the glycerol fraction determined. Equations for converting readings to moisture content were given. L. B. Parsons and C. O. Holmberg [Oil & Soap **14,** 239-41] devised a simple apparatus in which oil samples can be dried in a current of hydrogen at elevated temperatures. Tabulated data indicate that good results are obtainable in a very short time.

Color scales for a wide range of linseed, tung, soybean, cottonseed, peanut, sardine and shark oils were prepared by D. L. Tilleard [*J. Oil Colour Chem. Assoc.* **20,** 124-48] from data obtained by means of a Guild trichromatic colorimeter both with respect to the three primary colors and to brightness. The points on the scales correspond to various combinations of Lovibond tintometer glasses. Due to lack of correlation between lightness and darkness of an oil and the Lovibond grade assigned to it by the practical color grader, K. S. Gibson [Oil & Soap **14,** 286-9] recommended that spectral transmittance by colorimetric methods be used to compute the Lovibond color. Disputes among oil chemists can thus be settled. W. Mohr and H. Ahrens [*Milchw. Forsch.* **18,** 1-14] recommend that the color of butter be determined by measuring the percentage absorption of light filtered through a blue glass. Artificial butter colors can be mixed with white fat and their strength determined in the same manner.

The viscosities of several Indian vegetable oils at various temperatures were tabulated by G. N. Bhattacharyya [*Ind. J. Phys.* **10,** 403-11]. The data were discussed from the standpoint of using the oils for lubricating purposes. Data on the viscosity of the fatty matter in butter was contributed by M. Goryaev [*Lait* **16,** 943-5]. Experiments by M. Tobia [*Olii minerali olii e grassi, colori e vernici* **15,** 172-6] indicated that the values for the viscosities of vegetable oils lie so close together that they cannot be used as distinguishing characteristics. Castor oil was the only exception.

A method for determining melting point of fats, described by J. A. Scarrow [*Can. Chem. & Met.* **20,** 305-6] a regulated pressure was used to move the sample as soon as it softened; this movement was taken as the end-point rather than the gradually developing transparency as in conventional methods. W. D. Gallup *et al* [Oil & Soap **14,** 124-6] demonstrated that hardness and melting point of butterfat were directly proportional to melting time and a less definite relationship existed between iodine value and melting time. M. I. Goryaev [*Milchw. Zentr.* **66,** 65-9] recommended that the cooling of butter during determination of solidification point take place at such a rate that its temperature changes from 40 to 25° in 20 minutes. The solidification point of butter was appreciably affected by changes in rates of cooling. G. A. Richardson [*J. Dairy Sci.* **19,** 749-52] described technic for cooling fat slowly and uniformly. Cooling curves and fat constants for nine fats were contributed. Similar information was presented by T. Hinko [*Öle, Fette, Wachse, Seife, Kosmetik* **1937,** No. 7, 1-2].

The cold test on refined oils proposed by an American Oil Chemists' Society committee [Oil & Soap **14,** 104-5] was comprised of filling a 4-ounce bottle half full of sample, stoppering tightly and immersing in a mixture of ice and

water for 5½ hours. Winter oil must be clear, brilliant and limpid at the end of the test.

An investigation on indicators for determining free fat acids in dark colored oils was reported by P. M. Shuey [OIL & SOAP **14,** 232-3]. Thymol blue gave a sharper end point in dark oils than did phenolphthalein. Thymolphthalein was intermediate. Several other indicators tested were affected by carbon dioxide. Y. Volmar [*Documentation sci.* **5,** 33-9] recommended fluorescent indicators. Umbelliferone which gave an intense blue fluorescence below a pH of 6.6 was especially recommended for the titration of fats and oils. A. C. Rolfe and G. P. Alcock [*J. Soc. Chem. Ind.* **56,** 294-8T] favored potentiometric titration methods using the glass electrode for the colored oils. A microcolorimetric method for determining acidity of oils as described by V. V. Ilarionov and I. S. Kogan [*Mikrochemie* **21,** 11-6] comprised extracting the free fat acid with alcohol, adding a small amount of bromocresol indicator and comparing against standards prepared from pure oleic acid. Due to the insolubility of castor oil fat acid in alcohol, the method was not applicable to castor oil. A micro method for the free fat acid determination on castor oil was described by K. Szahlender [*Arch. Pharm.* **275,** 1-5].

An important characteristic in the purchase and sale of an oil is its refining loss. A method for determining this characteristic for soybean oil has been developed by an American Oil Chemists' Society committee [OIL & SOAP **14,** 173, 174-89]. The general procedure and apparatus was similar to that for hydraulic pressed crude cottonseed oil except for a few alterations in strength and amounts of lye, temperature, and durations of various manipulations.

Methods for the determination of soap in refined edible oils described by K. Butkoskii and Y. Vasilenko [*Masloboino Zhirovoe Delo* **12,** 389-90] and L. A. Spielman *et al* [OIL & SOAP **13,** 177-8, 205] depended on the difference between the acidity of the original oil and a sample of the oil in which the soap was hydrolyzed with hydrochloric acid and the inorganic acid removed by washing.

E. Rossmann [*Angew. Chem.* **50,** 187-90] compared the various methods for determining the iodine value of oils. He emphasized the advantages of the bromine vapor method. E. Yamaguchi *et al* [*Waseda Applied Chem. Soc. Bull.* **13,** No. 4, 7-11] found that the results by this method varied 2 to 6 units from the Wijs iodine value on sesame, soy, linseed, whale and several other oils and more than 40 to 70 on Japanese and China wood oils. New information on the refractometric determination of iodine value of linseed oil was contributed by T. H. Hooper and L. L. Nesbitt [OIL & SOAP **14,** 34-6] and F. H. Lehberg and W. F. Geddes [*Can. J. Research* **15**C, 349-61]. The method was applicable only to surveys of quality of flaxseeds and also to linseed crushers for securing a measure of the drying value of their raw material because it was accurate only with fresh oils.

Work on the method for determining the thiocyanogen value of oils dealt with stabilizing the thiocyanogen solution. H. P. Kaufmann and H. G. Oetringhaus [*Ber.* **69**B, 2670-6] reported that iodine prevented the thiocyanogen from polymerizing. However, in certain solvents and at high temperatures iodine thiocyanate was formed. This compound reacted with elaidic acid to give a derivative which was hydrolyzed, for removing iodine, to give thiocyanostearic acid. Further hydrolysis yielded 10 - oxostearic acid. Oleic and erucic acids gave corresponding reactions with the iodine thiocyanate.

The determinations of hexabromide and acetyl value were the subjects of collaborative work by committees of Deutsche Gesellschaft für Fettforschung [*Fette u. Seifen* **44,** 15-9, 113-4, 150-3]. During the year the current methods were reviewed, modified methods were proposed and some collaborative results were contributed. K. Hinsberg [*Biochem. Z.* **289,** 294] described a method for determining acetyl value in which a solution of acetic anhydride in pyridine was used as the acetylating reagent.

H. P. Kaufmann and co-workers [*Ber.* **70**B, 903-11] added new information on the reaction of maleic anhydride on fats, so called diene value. The method was slightly modified, and the diene values for several oils determined. The work indicated that there are many fats containing unsaturated substances which are as yet unknown. A comprehensive treatise on the diene reaction by K. Alder and G. Stein [*Angew. Chem.* **50,** 510-9] contained information on its many uses and chemistry. W. Bickford *et al* [*J. Am. Chem. Soc.* **59,** 2744-5] reported that the diene value of castor oil fell to zero after acetylation, that of tung oil exhibited a decrease, those of linseed and soybean oil increased after acetylation and were accompanied by an increase in refractive index and decrease in drying time. The findings were interpreted to indicate that in the latter a shift of the polyethenoid bonds toward a conjugated system occurs during acetylation. The diene value was recommended for the characterization and analysis of essential oils by H. P. Kaufmann and co-workers [*Ber.* **70**B, 908-11] and of sterols by A. B. Maggy and R. Robinson [*Nature* **140,** 282].

A method for determining conjugated double bonds had been proposed by B. A. Ellis who recommended that the characteristic be called maleic acid value. H. P. Kaufmann [*Ber.* **70**B, 900-2] reported that the work was not new in principle. K. A. Pelikan and J. D. Mikusch [OIL & SOAP **14,** 209-10] compared the Kaufmann method with that of Ellis and Jones. The Ellis and Jones procedure yielded result for certain oils which were too high. The Kaufmann diene value was found to indicate exact quantitative evaluation of conjugated double bonds.

Work on Meinel's bromine-combining value by K. Meinel [*Fette u. Seifen* **44,** 9-13] and H. Scheiber [*Farbe u. Lack* **1937,** 140] dealt with recording data on this characteristic for several drying oils before and after various heat treatments.

To increase the rapidity of the saponification value determination for control work, J. Hübscher [*Seifensieder-Ztg.* **64,** 315-6] suggested that 8 to 10 grams fat sample, 40° Bé potassium hydroxide and 0.5 *N* acid titrating solution be used. The procedure dispenses with the analytical balance.

This review will be continued in the June issue.

The committee which assisted the chairman in preparing this paper by reviewing and submitting additions, suggestions and corrections is composed of:

R. C. NEWTON
H. A. MATTILL
GEO. S. JAMIESON
G. R. GREENBANK
M. M. PISKUR, Chairman.