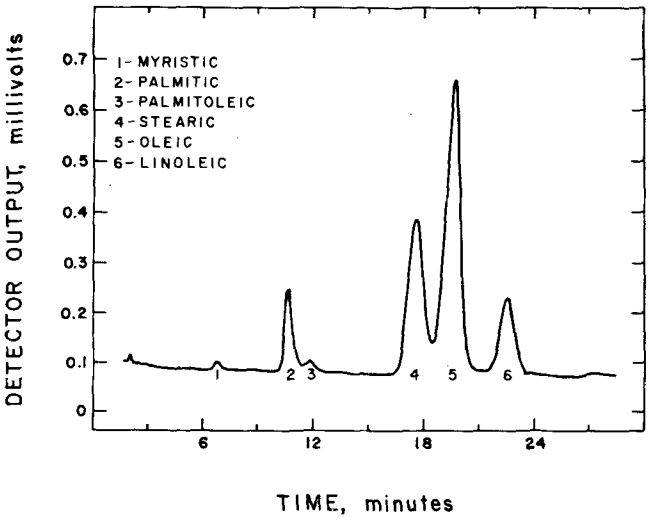

FIG. 3. Chromatograph chart for liberated fatty acids from pork fat.

min. hydrolysis times. There was no change in the composition of the liberated fatty acids over this time-interval. Hydrolysis of a sample of symmetrical oleodistearin prepared synthetically showed less than 1% oleic acid in the liberated fatty acids. The hydrolysis appeared therefore to be completely selective for the 1 and 3 positions under the conditions used.

The compositions of the original fats were also obtained by gas-phase chromatography. The fats were converted to their methyl esters by refluxing 100 mg. of fat in 10 ml. of methanol containing 1 mg. of sodium methoxide for one hour. A few drops of acetic acid were added to destroy the catalyst and the solvent evaporated to give the esters which were injected into the chromatographic unit.

Summary

A theory has been presented for the formation of fats which gives the amounts of the various glyceride types equivalent to a random or modified restricted random distribution and at the same time gives a predominance of specific positional isomers. The basis of the theory is a random attachment of the fatty acids at each stage of glyceride synthesis with an intramolecular rearrangement to a preferred form at the 1,2-diglyceride level of fat formation. The theory gives a good correlation of much of the data available on glyceride structure at the present time.

Like all previous theories, the present proposal is based on the analysis of the final products of fat synthesis without any definite knowledge of the mechanism of the synthesis. Much more work is required on the glyceride structure of fats and the mechanism of their biosynthesis before the distribution pattern of the fatty acids in natural fats can be definitely established.

Acknowledgments

Appreciation is expressed to D. K. Kline, biochemistry department, University of Saskatchewan, who supplied the majority of the animal fats, and to R. Altchul, department of anatomy, University of Saskatchewan, who donated the test animals.

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New Fat Products: Glyceride Esters of Adipic Acid[1]

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MANY practical applications as lubricants and coatings for the food industry have been visualized for highly viscous edible oils. A previous publication (6) has shown that the acylation of symmetrical diglycerides of edible fat-forming acids with dibasic acids like fumaric, succinic, and adipic produces compounds which possess a high viscosity and other unusual properties. Structurally these compounds are essentially two diglyceride molecules joined by simple ester linkages to a molecule of short-chain dibasic acid.

These esters might be expected to be edible and digestible since fumaric and succinic acids occur as metabolites in the Krebs cycle for the metabolism of fats. Recently Horn and co-workers (9) have provided evidence, based on the acute and chronic administration of adipic acid to laboratory animals, that adipic acid is physiologically comparable to citric and tartaric acids and can be added to food products with safety. While available information indicates that the glyceride esters of adipic acid as well as those of fumaric and succinic acids are edible, recommendations as to whether or not these compounds can be used as foods must await the outcome of tests now under way.

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Compounds of the type under discussion have been described only twice heretofore, in our earlier work (6) and in a very brief mention by Blake of bis(glycerol dioleate) malate (3). Several esters of short-chain dibasic acids, other than but somewhat related to the glyceride esters with which we are concerned, have been shown to be suitable for use as lubricants and coatings. Roberts (12) describes the preparation of a related compound suitable for use as a demulsifying agent.

The present investigation was concerned primarily with extending the information available on diglyceride esters of dibasic acids, particularly as to the manner in which symmetry and types of fatty acids affect the physical properties. In this investigation adipic acid was the only dibasic acid used.

Experimental

Materials and Methods of Preparation. The glycerol employed in the preparation of the distearins was U.S.P. grade. In the preparation of 1,2-*O*-isopropylideneglycerol (acetoneglycerol), the glycerol was first dehydrated by distillation under reduced pressure, and a middle fraction was collected.

The 1-monostearin employed was prepared by repeated crystallization, first from hexane and then from acetone, of a molecularly distilled 1-monostearin prepared from a commercial stearic acid, Hystrene S-97, which originally had a purity of about 97%. By the periodic acid oxidation method of analysis (8) the final product contained better than 99% of 1-monostearin and had a hydroxyl value of 312.5 (theoretical value, 314.7). The latter value was determined by the method of West *et al.* (14) except that an acetic anhydride to pyridine ratio of 1:3 instead of 1:7 was used.

The 1,3-diacetin used in the preparations was obtained as Eastman grade from the Eastman Organic Chemicals Department of Eastman Kodak Company.

The 1-aceto-3-stearin and 1-butyro-3-stearin used were prepared by the direct esterification in chloroform and pyridine solution of 1-monostearin with acetyl and butyryl chlorides, employing a modification of the procedure of Malkin *et al.* (10). The 1-aceto-3-stearin contained 0.60% monoglyceride and had a hydroxyl value of 143.8 (theoretical value, 140.0). The 1-butyro-3-stearin contained 0.43% monoglyceride and had a hydroxyl value of 122.8 (theoretical value, 130.6).

The 1,3-distearin was prepared from purified stearic acid obtained by repeated crystallization of Hystrene S-97 from acetone. The stearic acid was converted into a mixture of mono-, di-, and tristearin by reaction with glycerol in the presence of stannous chloride dihydrate under conditions which favored the formation of distearin (5). After purification by fractional crystallization from solvents, the 1,3-distearin contained 0.0% of monoglyceride and had a hydroxyl value of 85.0 (theoretical value, 89.7).

The 1,3-diolein was obtained by repeated crystallization from acetone of a product containing 85% diolein, which was obtained in turn as a fraction during the molecular distillation of a mixture of mono-, di-, and trioleins. The purified 1,3-diolein possessed the theoretical iodine value (81.75), contained 0.48% monoglyceride, and had a hydroxyl value of 91.7 (theoretical value, 90.3).

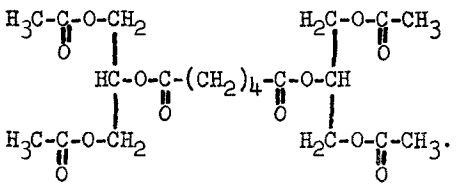
The acetyl chloride was Baker's Analyzed grade, obtained from the J. T. Baker Chemical Company, and was used without further purification. The butyryl and adipyl chlorides were Eastman grade, obtained from the Eastman Organic Chemicals Department, Eastman Kodak Company. They too were used without further purification.

The method of Youngs *et al.* (15) was used in the preparation of the stearoyl chloride. Pure stearic acid was dissolved in commercial pentane and allowed to react with phosphorus pentachloride. The reaction product was purified by washing the hydrocarbon solution with ice water. After drying the solution, the commercial pentane was removed by distillation and stripping with an inert gas. A reduced molybdate colorimetric test for phosphorus revealed that the stearoyl chloride contained only 0.05% phosphorus. By infrared spectrophotometric analysis of a carbon tetrachloride solution, the quantity of stearic acid in the stearoyl chloride was estimated to be approximately 1 to 2%.

Oleoyl chloride was prepared by reacting oleic acid, obtained by the saponification and subsequent acidulation and purification of methyl oleate derived from pecan oil, with oxalyl chloride or phosphorus pentachloride. The oleoyl chloride obtained with the last-mentioned reagent contained 0.26% phosphorus.

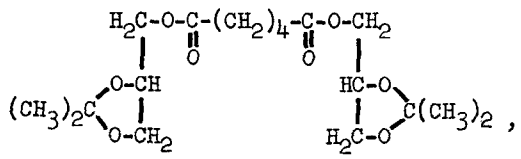
The various solvents and other reagents employed in the preparations were given a special purification whenever this was deemed necessary. The pyridine was refluxed and then distilled over porous barium oxide to remove all traces of moisture. The chloroform was washed to remove the ethanol which had been added as a preservative, dried over Drierite, decanted, and distilled.

The preparation of the 1,3-mono-acid- and the 1,3-diacid-diglyceride esters of adipic acid simply involved reaction of the proper diglyceride with adipyl chloride in the presence of solvents under conditions which assured complete esterification of the free hydroxyl group and minimized the formation of by-products (6). The esters were purified by repeated crystallization from commercial hexane and acetone except in the case of bis[1-(acetoxymethyl)-2-(acetoxy)ethyl] adipate,



The latter product was purified simply by washing a chloroform solution with water.

For the preparation of bis(2,2-dimethyl-1,3-dioxolan-4-ylmethyl) adipate,



the 1,2-*O*-isopropylideneglycerol was prepared by the classical method of Fischer and Pfähler (7). Specifically, 200.0 g. (2.18 moles) of anhydrous glycerol were allowed to react with 950 g. (16.36 moles) of an-

TABLE I

Characteristics of Glyceride Esters of Adipic Acid

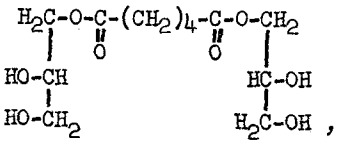
Compound	Number-average molecular weight[a]		Content of carbon and hydrogen, %				Hydroxyl value	Monoglyceride content, %	Acid value
	Found	Theoretical	Found		Theoretical				
			C	H	C	H			
Bis(2,3-dihydroxypropyl) adipate	306	294	48.22	7.42	48.97	7.54	754.0	98.3[c]	0.75
Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethyl) adipate	433	374	57.77	8.01	57.74	8.08	1.26[b]	0.1	0.12
Bis[1-(acetoxymethyl)-2-(acetoxy)ethyl] adipate	478	462	52.36	6.62	51.94	6.54	0.34[b]	0.0	0.72
Bis[1-(acetoxymethyl)-2-(stearoyloxy)ethyl] adipate	920	911	68.88	10.44	68.53	10.40	6.23	0.3	0.42
Bis[1-(butyroxymethyl)-2-(stearoyloxy)ethyl] adipate	930	939	69.29	10.42	69.04	10.52	3.96	0.1	0.00
Bis[1-(hydroxymethyl)-2-(stearoyloxy)ethyl] adipate	.....	827	69.78	10.69	69.69	10.97	138.12	.....	.....
Bis(2,3-distearoyloxypropyl) adipate	1383	1360	74.04	11.63	74.17	11.71	3.77	0.2	0.21
Bis[1-(stearoyloxymethyl)-2-(stearoyloxy)ethyl] adipate[d]	1245	1360	74.34	11.74	74.17	11.71	0.07[b]	0.5	1.65
Bis[1-(oleoyloxymethyl)-2-(stearoyloxy)ethyl] adipate	1350	1356	73.98	11.08	74.39	11.45	0.0	.....	.....
Bis[1-(oleoyloxymethyl)-2-(oleoyloxy)ethyl] adipate[d]	1318	1352	74.18	11.25	74.61	11.63	0.07[b]	.....	0.56

Compound	Melting point,[e] °C.	Kinematic viscosity, centistokes at		Density, g./ml. at			Refractive index $N^{95/D}$
		37.8°C.	98.9°C.	30.0°C.	50.0°C.	98.9°C.	
Bis(2,3-dihydroxypropyl) adipate	No crystals at −70	311.0	63.1	1.3450	1.3326	1.2985	1.44831
Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethyl) adipate	56.0	.....	7.70	.....	.....	1.0702	1.43938
Bis[1-(acetoxymethyl)-2-(acetoxy)ethyl] adipate	No crystals at −70	205.0	29.9	1.3010	1.2797	1.2438	1.43400
Bis[1-(acetoxymethyl)-2-(stearoyloxy)ethyl] adipate	43.0	.....	25.4	.....	1.0085	0.9522	1.43649
Bis[1-(butyroxymethyl)-2-(stearoyloxy)ethyl] adipate	71.8	.....	20.3	.....	.....	0.9030	1.43571
Bis[1-(hydroxymethyl)-2-(stearoyloxy)ethyl] adipate	75.9	.....	18.6	.....	.....	1.0066	1.48175
Bis(2,3-distearoyloxypropyl) adipate	75.2	.....	16.5	.....	.....	0.8787	1.43685
Bis[1-(stearoyloxymethyl)-2-(stearoyloxy)ethyl] adipate[d]	82.1	.....	18.9	.....	.....	0.8882	1.43844
Bis[1-(oleoyloxymethyl)-2-(stearoyloxy)ethyl] adipate	20.8	116.0	17.6	0.9235	0.9108	0.8778	1.44492
Bis[1-(oleoyloxymethyl)-2-(oleoyloxy)ethyl] adipate[d]	No crystals at −70	92.0	15.0	0.9435	0.9354	0.9148	1.44754

[a] Menzies-Wright ebullioscopic procedure and apparatus (10). [b] Micro method. [c] Calculated by assuming the molecular weight of the monoglyceride to be equal to half the molecular weight of the indicated compound. [d] Reference 6. [e] Corrected melting point, capillary tube method.

hydrous acetone containing 1% (by weight) of hydrogen chloride, which served as a catalyst. Water formed by the reaction was absorbed by anhydrous sodium sulfate. At the end of the reaction the excess hydrogen chloride gas was removed with lead carbonate. The acetone was removed, and the product was distilled at 82.5°C. and a pressure of 11 mm. of mercury. To a mixture of 132.2 g. (1.00 mole) of 1,2-*O*-isopropylideneglycerol and 87.0 g. (1.10 moles) of dry pyridine in dry chloroform there were added, while the mixture was cooling in an ice bath, 82.4 g. (0.45 mole) of adipyl chloride. After standing at room temperature for two days, the mixture was diluted with ethyl ether, then washed with a 0.25 *N* hydrochloric acid solution, and finally washed with water. The solvents were removed by distillation, which was followed by stripping at about 100°C. with nitrogen gas below atmospheric pressure. Further purification consisted of repeated crystallizations from commercial hexane and acetone.

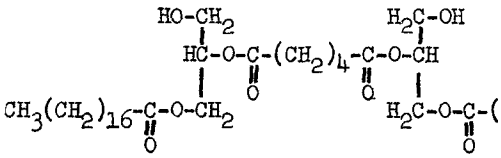
To convert bis(2,2-dimethyl-1,3-dioxolan-4-ylmethyl) adipate to bis(2,3-dihydroxypropyl) adipate,



the 1,2-*O*-isopropylideneglycerol complex was broken by hydrolysis in a 10% solution of acetic acid (2). The hydrolysis was continued with constant stirring for 4 hrs. at 60°C. Subsequently the volatile components of the mixture were removed by warming and stripping with nitrogen gas while under reduced pressure.

To prepare bis(2,3-distearoyloxypropyl) adipate, 40.0 g. (0.136 mole) of bis(2,3-dihydroxypropyl) adipate were acylated with 164.8 g. (0.544 mole) of stearoyl chloride under the same conditions as described previously. The ester was purified by repeated solvent crystallization from commercial hexane and acetone.

A method similar to that outlined by Verkade and van der Lee (13) for the preparation of unsymmetrical diglycerides, which involves tritylation and subsequent reductive detritylation of the 1,2-diacyl-3-trityl glycerol, was used to prepare the diacid diglyceride-containing adipates. First, bis[1-(hydroxymethyl)-2-(stearoyloxy)ethyl] adipate,



was prepared by the reaction of 100.0 g. (0.279 mole) of 1-monostearin and 80.0 g. (0.289 mole) of triphenylchloromethane in a pyridine solution for 3 hrs. on a steam bath. The reaction mixture was diluted with ethyl ether and washed in the same manner as were the other products. After several crystallizations from 96% ethanol the product melted at 66.5–67.0°C. A quinoline solution of 1-stearoyl-3-tritylglycerol was acylated with adipyl chloride in the manner described previously. The resulting ester was purified by solvent crystallization from acetone and detritylated by hydrogenolysis in glacial acetic acid solution. A palladium-on-carbon catalyst and a reaction time of 6.5 hrs. at 45 to 50°C. were used. Work at this laboratory on reductive detritylation in glacial acetic acid solution has shown that no rearrangement occurs under these conditions. The resulting bis[1-(hydroxymethyl)-2-(stearoyloxy)ethyl] adipate was purified by low-temperature crystallization from a solution in commercial hexane.

To prepare bis[1-(oleoyloxymethyl)-2-(stearoyloxy)ethyl] adipate, a portion of the bis[1-(hydroxymethyl)-2-(stearoyloxy)ethyl] adipate was acylated with oleoyl chloride in the presence of quinoline under the usual conditions for acylation described above.

Analysis. The purities of the glyceride esters were determined by chemical analyses, including elemental carbon and hydrogen analyses, and number-average of molecular weights. The values obtained are re-

corded in Table I. The viscosities were measured with Ostwald-Cannon-Fenske viscometers or microviscometers, as described by Cannon and Fenske (4). Temperatures were selected to correspond with those for which viscosities of various vegetable oils have been reported. The densities of the products were determined by the pycnometer method. The refractive indices were determined with an Abbé refractometer at 95°C. in order to compare these values with values reported previously for distearin and diolein esters of adipic acid (6).

Results and Discussion

The melting points, viscosities, densities, and refractive indices determined for the adipic acid esters are recorded in Table I. The melting points listed are those for the highest melting polymorph obtained by tempering the sample or crystallizing it from solvent. No significant premelting was observed with any of the compounds. There is evidence that one or more additional melting points exist for each compound, but these have not yet been determined accurately. The highest melting point, 82.1°C. for bis[1-(stearoyloxymethyl)-2-(stearoyloxy)ethyl] adipate, is above that of tristearin, 72.5°C., and 1,3-distearin, 78°C. The melting point of this ester is close to that for carnauba wax, m.p. about 83.5°C. The melting points of all of the other adipic acid esters are below the melting points of the corresponding glycerides. For instance, the melting point of bis-[1-(acetoxymethyl)-2-(stearoyloxy)ethyl] adipate is 43.0°C. while that of 1-aceto-3-stearin is 47.5°C. Some melting points of the adipic acid esters are far below the melting points of the glycerides. An example of this is bis[1-(oleoyloxymethyl)-2-(oleoyloxy)ethyl] adipate, which did not crystallize even at −70°C., and 1,3-diolein, which melts at 25°C. In addition to the bis[1-(oleoyloxymethyl)-2-(oleoyloxy)ethyl] adipate, bis(2,3-dihydroxypropyl) adipate and bis[1-(acetoxymethyl)-2-(acetoxy)ethyl] adipate did not appear to crystallize when stored at −70°C. for a long time. Crystallization could not be induced by scratching the side of the containers in which these esters were stored. On being cooled, the products became increasingly viscous and eventually vitreous in nature.

The effect of the constituents in the glyceride moiety can be determined by an examination of the melting points of the compounds. On comparison of the values for bis[1-(stearoyloxymethyl)-2-(stearoyloxy) ethyl] adipate, bis[1-(hydroxymethyl)-2-(stearoyloxy)ethyl] adipate, and bis(2,3-dihydroxypropyl) adipate, it is observed that free hydroxyl groups lower the melting point; the effect is additive. The effect of length of fatty acid in the glyceride moiety is illustrated by a comparison of the series bis[1-stearoyloxymethyl)-2-(stearoyloxy)ethyl] adipate; bis[1-(butyroxymethyl)-2-(stearoyloxy)ethyl] adipate; bis-[1-acetoxymethyl)-2-(stearoyloxy)ethyl] adipate; and bis[1-(acetoxymethyl)-2-(acetoxy)ethyl] adipate. Decreasing the chain lengths of the fatty acid groups decreases the melting points. The unsymmetrical bis-(2,3-distearoyloxypropyl) adipate has a lower melting point than has the symmetrical bis[1-(stearoyloxymethyl)-2-(stearoyloxy)ethyl] adipate. Also the melting point is lowered as the degree of unsaturation of the glyceride increases. These observations are in agreement with the effects normally encountered on comparison of melting points of ordinary glycerides.

When crystallized from solvents, the solid esters tend to form long needle-like crystals. As reported previously (6), this tendency appears to be enhanced by the presence of impurities. In this property the esters differ considerably from ordinary glycerides, such as tristearin.

The characteristic which distinguishes the glyceride esters of dibasic acids most markedly is viscosity. This characteristic is of great practical importance in their utilization in edible lubricants and coatings. The differences in the viscosities of the distearin and diolein esters of dibasic acids and the viscosities of coconut, cottonseed, and castor oils have been observed previously (6). In Table I are recorded the kinematic viscosities at one or two temperatures of a series of glyceride esters of adipic acid. A comparison of the values at 98.9°C. reveals the following effects. The viscosity increases as the number of hydroxyl groups in the glyceride moiety increases. Lengthening of the fatty acid groups decreases the viscosity. The symmetrical distearin ester is more viscous than is the unsymmetrical distearin ester. The greater the extent of unsaturation, the less viscous is the compound. These relationships are important in "tailoring" glyceride esters of dibasic acids to a desired viscosity.

Examination of the values for density recorded in Table I reveals that the values for the glyceride esters of adipic acid do not differ greatly from the values for cottonseed oil at the same temperature. As a further comparison, the density for tristearin at 80°C. is 0.8632 g./ml. and for triolein at 25°C. is 0.9078 g./ml. It was observed that the density increases as the number of hydroxyl groups in the glyceride moiety increases. As the length of the fatty acid groups increases, the density decreases. The symmetrical distearin ester is slightly more dense than is the unsymmetrical distearin ester. The greater the extent of unsaturation, the greater the density.

The effects of various substituents on the refractive index have been investigated by Backer (1) and others, and their generalizations seem to be in agreement with the findings in the present investigation. In fact, the values found in the present investigation differ little from those of ordinary glycerides containing fatty acid groups. For purposes of comparison, the refractive indices, $n^{95/D}$, for several of the ordinary glycerides are: tristearin, 1.4338; triolein, 1.4415; 1-oleo-3-stearin, 1.4374. For the compounds listed in the table the refractive index tends to increase as the number of hydroxyl groups increases. The refractive index of bis[1-(hydroxymethyl)-2-(stearoyloxy)ethyl] adipate is the highest value recorded in the table, 1.48175. It might appear to be higher than expected; however the refractive indices of monoglycerides are known to be considerably higher than the refractive indices of the corresponding simple triglycerides. The refractive indices increase with an increase in the length of the fatty acid groups and an increase in the degree of unsaturation. In addition, the refractive index for the more symmetrical compound is larger than that for the unsymmetrical compound.

Summary

Six new glyceride esters of adipic acid were prepared, and their properties were determined. By the

use of acetals and trityl groups the number, type, and positions of the fatty acid groups in the glycerol moiety were varied systematically. The reaction products were purified, their purities were established, and their melting points, viscosities, densities, and refractive indices were determined.

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ABSTRACTS . . . . R. A. REINERS, Editor

ABSTRACTORS: Lenore Petschaft Africk, R. R. Allen, S. S. Chang, Sini'tiro Kawamura, F. A. Kummerow, E. G. Perkins, and Dorothy M. Rathmann

• Fats and Oils

NEPHELOMETRIC DETECTION OF LIPIDES IN CHROMATOGRAPHIC COLUMN EFFLUENTS. A. C. Arcus (Nutrition Research Dept., Medical School, Dunedin, New Zealand). *Anal. Chem.* 31, 1618–1620 (1959). A relatively nonspecific method of roughly estimating lipides in chromatographic column effluents is based on the light-scattering power of the suspension formed when the lipide is precipitated from methanolic solution containing 0 to 1 mg. per ml. by the addition of water. The method is applicable only to substances soluble in pure methanol and insoluble in a mixture of 1 part of methanol with 2 parts of water, but suggestions are made for its extension to other substances. The smallest detectable concentration is of the order of 2 to 20 γ per ml., depending on the substance. Application to chromatography is illustrated.

PAPER CHROMATOGRAPHY OF THE SATURATED FATTY ACIDS. M. A. Buchanan (The Inst. of Paper Chemistry, Appleton, Wis.). *Anal. Chem.* 31, 1616–1618 (1959). In a new procedure for the paper chromatography of the saturated fatty acids, the developer reacts with the unsaturated acids to form products which readily separate from the saturated acids. Hydrogen peroxide and formic acid are added to the usual acetic acid-water developers used for reverse-phase chromatography of the fatty acids. The new procedure permits the separation of small amounts of saturated acids from large amounts of the unsaturated acids, and is suitable for tentative identification of the even-numbered straight-chain acids from lauric acid to lignoceric acid.

DESIGN CONSIDERATIONS OF A GAS CHROMATOGRAPHY SYSTEM EMPLOYING HIGH EFFICIENCY GOLAY COLUMNS. R. D. Condon (The Perkin-Elmer Corp., Norwalk, Conn.). *Anal. Chem.* 31, 1717–22 (1959). The application of Golay columns, using highly sensitive ionization detectors, to gas chromatography is described. Samples with a wide boiling point range, as well as those with close range boiling points, can be separated in a relatively short time with high efficiencies. Samples with low vapor pressures can also be analyzed. Low concentration analysis should also benefit from these disclosures. Gas chromatography as an analytical tool may be extended to new areas not heretofore possible with current instrumentation.

DETERMINATION OF HYDROXYL NUMBERS BY NEAR-INFRARED ABSORPTION. C. L. Hilton (Research Center, U. S. Rubber Co., Wayne, N.J.). *Anal. Chem.* 31, 1610–12 (1959). Duplicate analyses by the acetylation procedure for hydroxyl number require 1.5 man-hours and 3 hours of elapsed time. A faster method of analysis was desired. Duplicate determinations of hydroxyl numbers of certain polyesters and polyethers by near-infrared absorption analysis in the region from 2.0 to 3.2 microns can be accomplished in 0.5 hour using a Beckman Model DK-2 spectrophotometer. This represents a saving of 1 man-hour and 2.4 elapsed hours per duplicate determination. Results with samples thus far analyzed show an average difference of less than 1.0% relative between the chemical and the near-infrared methods.

BUTTERFAT OXIDATION. EVALUATION OF LEA'S ALDEHYDE DETERMINATION METHOD. A. Tamsma and R. D. Powell (Dairy Industry Section, Iowa Agr. Exptl. Sta., Ames, Iowa). *J. Agr. Food Chem.* 7, 643–6 (1959). Lea's method for determination of aldehyde in fats in excellent for *n*-heptanal. For normal aldehydes with more than seven carbon atoms, recovery decreased with increasing chain length and limiting values were reached with C_9 and C_{10} aldehydes. For "aldehydes" from autoxidized milk fat the value found by Lea's method is arbitrary, because these carbonylic compounds do not behave like heptanal. Incomplete recovery can be caused by low solubility in water and low reactivity with bisulfite. Too high recovery may be obtained with unsaturated carbonyl compounds as a result of reaction of the double bonds. Reaction products and yields were examined by isolation of the aldehyde by solvent extraction after decomposition of the bisulfite complex. "Milk-fat aldehyde" was of ketonic character; the yield was about one-third to one-tenth as compared to synthetic aldehyde.

CONTINUOUS RECTIFICATION OF SYNTHETIC FATTY ACIDS. A. Ya. Koldovkin. *Khim. i Tekhnol. Topliv i Masel* 4(6), 67–9 (1959). A critical discussion of the paper by Levin (*C. A.* 52, 5856). (*C. A.* 53, 17573)

IDENTIFICATION OF OLEUROPEIN IN OLIVE OIL AND ITS APPLICATION IN ANALYSIS OF MIXTURES OF EDIBLE OILS. R. Diaz Blasco and L. N. Pizzorno. *Anales direc. nacl. quím.* (Buenos Aires) 10(19), 13–6 (1957). Oleuropein, a glucoside, is present to the extent of 1% in olives and 0.3% in olive leaves. Principal method of analysis is Hoepfner's reaction (*C. A.* 53, 9112) which can be used in paper chromatography after ascending development with 80 parts of 1.25% sodium chloride and 20 parts of 95% ethanol for 8 hours. Sensitivity of the test allows identification of 2 parts per million or 10 micrograms of oleuropein. A method for detection of adulteration with olive oil based upon these tests is proposed. As rancidity increases, oleuropein concentration decreases. The possibility that oleuropein is a natural antioxidant is being investigated. (*C. A.* 53, 17539)

SOME LIMITATIONS TO THE KINETIC STUDIES ON AUTOXIDATION OF FATTY-ACID ESTERS OF DIFFERENT UNSATURATION. N. A. Khan (East Regional Labs., Dacca, India). *Pakistan J. Sci. Research* 10(4), 149–54 (1958). Reduction of the oxygenated products which are formed by autoxidation of methyl oleate at 24–6°, 45°, and 350° to 5% peroxide content yielded no polymer. Reduction of the oxygenated products formed by autoxidation of methyl oleate at 60°, 75°, and 100° for 3 weeks, 3 days and 30 hours, respectively, yield 60, 9, and 26% of polymers, respectively. Methyl linoleate was autoxidized to 5% peroxide content in the dark at 0°. The peroxides were concentrated by countercurrent extraction. Reduction gave monohydroxystearic acids. Analysis indicated the production of almost 100% methyl *cis, trans*-conjugated-monohydroxylinoleate. Thus methyl linoleate forms monomeric monohydro-