The Preparation of Fatty Acid Chlorides

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IN connection with the extensive investigation of the physical properties of natural fats now in progress in this laboratory it became evident that some of the data obtained, e.g. calorimetric and dilatometric data, could be interpreted intelligently only in the light of similar data obtained on pure synthetic glycerides of known constitution. For many of these measurements large quantities of pure synthetic glycerides were required, and it was, therefore, of importance to prepare the necessary glycerides as economically as possible.

Pure glycerides of known structure are now almost universally prepared by way of the fatty acid chlorides. A review of many publications devoted to the syntheses of glycerides indicated that different investigators have employed one or another of a variety of chlorinating reagents in the preparation of the required intermediate acid chlorides. The chlorinating agents most commonly used are oxalyl chloride, thionyl chloride, phosphorus trichloride, and phosphorus pentachloride. In most instances the reason for selecting the specific reagent used is not stated. However, preference appears to have been given oxalyl or thionyl chlorides because the byproducts of the reaction are volatile and easily removed from the reaction.

Each of the various chlorinating reagents appears to possess certain advantages and disadvantages which have influenced individual investigators to give one reagent preference over another. For example, Verkade (15) reports that the purification of thionyl chloride by distillation over quinoline and over boiled linseed oil prevented the formation of a dark tarry product during the reaction with oleic acid. He states that oleyl chloride was prepared in a yield of nearly 90% with this reagent and claims that the less satisfactory yields reported by other investigators were due to the use of impure thionyl chloride. McMaster and Ahmann (12) claim that thionyl chloride is easier to handle than solid phosphorus pentachloride. While no data are given on the preparation of a specific fatty acid chloride, the statement is made that, "thionyl chloride readily converts acids of the fatty acid series into acid chlorides." Black and Overley (3) also reported the satisfactory use of thionyl chloride in the preparation of 9,10,12,13-tetrabromostearyl chloride from the tetrabromostearic acid. The acid chloride, however, was not distilled, purification was effected through crystallization.

Bömer and Kapeller (4) used phosphorus pentachloride for the preparation of elaidyl chloride, employed in the synthesis of several glycerides, by the procedure of Krafft and Tritschler (10). They reported a yield of 97.6% of elaidyl chloride prepared by this reagent. Taüfel and Künkele (14) prepared oleyl chloride in yields of 48% and 46%, respectively, by reacting oleic acid with phosphorus pentachloride and phosphorus trichloride. They state that, prior to distillation, complete separation of the phosphorous acid formed during the reaction with phosphorus trichloride is essential for obtaining maximum yields. Bömer and Stather (5) found that isooleyl chloride could be prepared satisfactorily by reacting phosphorus pentachloride with 10,11-isooleic acid.

By treatment of the pure fatty acids with oxalyl chloride, acid chlorides were prepared by Averill, Roche, and King (2) for use as intermediates in the synthesis of glycerides. These authors claimed that stearyl chloride could be distilled only when the distilling flask was immersed up to the sidearm in a special oil bath. Daubert, Fricke, and Longenecker (6) reported the preparation of saturated acid chlorides by reaction of fatty acids with thionyl chloride according to the method of McMaster and Ahmann (12). However, oleyl chloride was prepared by reaction of oleic acid and oxalyl chloride according to a modification of the method of Adams and Ulich (1). Wood, Jackson, Baldwin, and Longenecker (17) prepared the acid chlorides of oleic, elaidic, linoleic and linolenic acids by refluxing the fatty acids with oxalyl chloride. They found that the use of this reagent did not produce appreciable conjugation in the linoleyl and linolenyl chlorides.

It has been known since 1870 that low molecular weight acid chlorides can be produced by treatment of the free fatty acids or their sodium salts with phosgene, but the reaction has not found favor as a method of preparing higher acid chlorides. However, several patents (9, 9a, 13a) have been granted covering the treatment of higher fatty acids for the production of acid chlorides. Generally, these patents claim the production of higher fatty acid chlorides by reaction of fatty acids with phosgene at temperatures of 140° to 150° C. in the presence of a catalyst such as specially activated charcoal. More recently, Prat and Etienne (13) have described the laboratory preparation of higher fatty acid chlorides by reaction of fatty acids with highly dispersed phosgene at temperatures of 140° to 150° C. These investigators prepared the acid chlorides of lauric, palmitic, stearic and oleic acids, as well as those of a mixture of coconut oil fatty acids. They report yields of 85 to 90% for lauryl, and 70 to 75% for palmityl and stearyl chlorides. They state, however, that optimum yields are obtained only when the passage of phosgene gas, through the molten fatty acids, is extremely rapid and highly dispersed (60 grams per hour through 120 grams of fatty acids at 120° to 140° C.).

In the absence of reliable comparative data on the yields and purity of fatty acid chlorides and the relative cost of their preparation with each of the available chlorinating agents, a series of higher fatty acid chlorides was prepared under a variety of conditions in an effort to determine the most efficient method of preparing the required products.

Experimental

Preparation of Pure Saturated Fatty Acids: The saturated fatty acids were prepared from commercial

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fatty acids of approximately 90% purity. The acids were melted on a steam bath and treated with 5% by weight of concentrated sulfuric acid. After about 30 minutes of heating, distilled water was added and the mineral acid and water-soluble sulfo-derivatives of any unsaturated acids were removed by repeated washing with water. The fatty acid was then converted to the methyl ester and fractionally distilled. The purest fraction, based on saponification values, was saponified and the fatty acid obtained after acidification was crystallized several times from acetone. The properties of the fatty acids prepared in this manner are given in Table 1.

TABLE 1

Properties of Purified Fatty Acids

Acid	Melting point	Iodine value	Saponification value of methyl ester	Boiling point of acid chloride
	°C.			°C.
Lauric	44.5-44.9	0.02	260.9	130-132 (7 mm.)
Myristic	54.5-55.5	0.02	232.7	155-157 (7 mm.)
Palmitic	63.0-63.5	0.01	207.3	176-178 (7 mm.)
Stearic	69.8-70.2	0.02	189.3	192-194 (6 mm.)
Oleic	....	89.6	....	187-190 (8 mm.)
Elaidic	43.5-44.5	89.5	....	197-199 (8 mm.)
Linoleic	....	179.7	....	192-194 (7 mm.)

Preparation of Unsaturated Fatty Acids: The oleic acid was prepared from olive oil by means of methyl ester fractionation and low temperature crystallization of the mixed esters as outlined by Wheeler and Riemenschneider (16). The purified oleic acid was also used in the preparation of the elaidic acid according to the procedure of Ellis (7). A portion of the oleic acid was placed in a shallow dish in a desiccator containing sodium nitrite. The desiccator and contents were cooled to 4° C. in an ice box, after which a small amount of dilute nitric acid was poured over the nitrite and the desiccator was securely closed. The oleic acid isomerizes to the solid form on standing overnight. The unreacted oleic acid and oily products were separated from the solid elaidic acid by pressing on a porous plate. The crude elaidic acid was then dissolved in Skellysolve F, filtered to remove insoluble oxidation products, and the solvent removed prior to crystallization from 80% ethyl alcohol.

Pure linoleic acid was prepared by brominating the mixed fatty acids of corn oil and separating and purifying the tetrabromostearic acid which was subsequently debrominated (11). Debromination was carried out in ether solution using zinc dust and concentrated hydrochloric acid as suggested by Frankel and Brown (8). The linoleic acid thus obtained was distilled and sealed in vials until used.

Preparation of Saturated Acid Chlorides: The saturated acids from lauric to stearic were converted to the respective acid chloride by two different methods which are described in detail in the case of the preparation of lauryl chloride.

Method (a)—Four 20.0-gram samples (0.1 mole) were placed in 250-ml. three-necked flasks equipped with stirrers, dropping funnels, and condensers protected with drying tubes. The fatty acid was either melted or dissolved at 50° C. in 25 ml. of benzene or carbon tetrachloride, and one of the following reagents added:

(1) 15.2 grams (0.12 mole) of oxalyl chloride.
(2) 14.3 grams (0.12 mole) of thionyl chloride.
(3) 13.8 grams (0.10 mole) of phosphorus trichloride.
(4) 20.8 grams (0.10 mole) of phosphorus pentachloride, added in small quantities through the third neck of the reaction flask.

After the addition of the chlorinating agent to the acid, the mixtures were heated and stirred at 60-70° C. for two hours. The reaction products were poured into Claisen flasks, and in the case of the phosphorus trichloride reaction, care was taken to avoid transfer of any phosphorous acid. When a solvent was used, it was removed by distillation on a steam bath under reduced pressure, following which the acid chloride was distilled *in vacuo* with the flask immersed in a preheated oil bath. The distilling arm of the Claisen flask was insulated with asbestos paper. The oil bath was preheated to a temperature approximately 40°-50° C. above the boiling point of the respective chloride. The reduced pressure employed during removal of the solvent was produced by means of a water aspirator, and that employed in distillation of the chloride was produced by a water jet exhaustor operating with ice-cold water at 45-50 lbs./sq. in. pressure, under which conditions vacuums of 6 to 8 mm. were obtained.

The solvent-free acid chlorides were analyzed before and after distillation by reacting a sample with an ether solution of aniline to form the corresponding anilide. This method proved advantageous for estimating the percentage conversion of the fatty acid to acid chloride since, unlike the silver nitrate method, it is not affected by the presence of any volatile chlorine compounds.

Method (b)—In the case of phosphorus trichloride an additional series of experiments was made in which the mole ratio of acid to chlorinating agent was 1:0.4 (equivalent to 20% excess of $\frac{1}{3}$ mole). These latter experiments were undertaken to determine whether each chlorine atom of the phosphorus trichloride was equally capable of replacing the hydroxyl group of the fatty acid. The fatty acid was placed in a separatory funnel protected by a drying tube and the calculated amount, 5.4 grams (0.04 mole), of phosphorus trichloride was added directly or in the form of a benzene or carbon tetrachloride solution to 20 grams (0.1 mole) of the solid lauric acid. The mixture was then allowed to stand at room temperature for 24 hours. In the case of palmitic and stearic acids slight warming was necessary at first to effect solution, which became complete as the reaction progressed. The contents of the separatory funnel eventually became liquid and a syrupy layer of the phosphorous acid slowly settled out and was easily removed through the stopcock. The crude acid chlorides were distilled and analyzed as described below.

Action of Phosgene on Saturated Fatty Acids: When stearic acid was heated at 150° C. in the presence of an activated charcoal and phosgene bubbled at a slow rate through the mixture for 6 hours, no appreciable reaction occurred. The mixture solidified on cooling and on analysis was found to contain 92.6% unreacted acid. The above experiment was repeated using 23 g. (130 percent excess) of phosgene which was bubbled through the acid heated to a temperature of 210° C. On distillation of the reaction mixture, there was obtained 11.3 g. or 45.9 percent of stearyl chloride boiling at 190-193° C. at 8 mm. pres-

TABLE 2

Preparation of Lauryl Chloride

Reagent	Solvent	Yield,[1] %	Free fatty acid in lauryl chloride, %		
			Crude product	Distilled product	Distillation residue
Oxalyl chloride	Benzene	98.8	1.51	0.73	....
Oxalyl chloride	None	96.5	0.82	0.61	....
Phosphorus trichloride	None	96.2	2.09	0.96	....
Phosphorus trichloride	Benzene	91.8	3.59	2.51	41.13
Phosphorus trichloride	Carbon tetrachloride	91.8	2.47	2.40	20.82
Oxalyl chloride	Carbon tetrachloride	89.0	....	0.34	....
Phosphorus pentachloride	Carbon tetrachloride	88.7	5.62	1.06	33.84
Thionyl chloride	Benzene	86.8	5.80	0.74	38.57
Phosphorus pentachloride	Benzene	84.5	7.25	1.80	34.50
Thionyl chloride	None	75.9	11.08	0.71	49.16
Phosphorus trichloride	None	70.0	9.10	2.33	43.5
Thionyl chloride	Carbon tetrachloride	67.4	....	0.53	....
Phosphorus pentachloride	None	61.7	3.26	5.18	15.06
Phosphorus pentachloride	Carbon tetrachloride	59.6	....	0.80	....
Phosphorus trichloride[2]	Benzene	59.3	9.21	1.30	11.93
Phosphorus pentachloride	None	57.2	2.91	9.66	11.87
Phosphorus trichloride[2]	Carbon tetrachloride	54.1	....	0.89	....

[1] Corrected for amount removed for analysis and free fatty acid in distillate.

[2] Reaction carried out in separatory funnel with 0.04 mole of phosphorus trichloride to 0.1 mole of fatty acid.

sure. The theoretical amount of phosgene was also bubbled into a solution of myristic acid dissolved in dry xylene which was heated at a temperature of 140-150° C. and stirred. On distillation of the reaction mixture no liquid product was obtained at temperatures up to 250° C. and analysis of the residue indicated that it consisted primarily of unreacted myristic acid.

No attempt was made to follow the procedure of Prat and Etienne (13) as it was assumed that the very considerable amount of phosgene required, its toxicity, and the prolonged reaction time, would offset any advantage to be gained through the use of this reagent.

Preparation of Unsaturated Acid Chlorides: Oleic, elaidic, and linoleic acids were also reacted with a number of chlorinating agents following the general procedure used with the saturated acids.

Method of Analysis: As previously mentioned, the crude acid chlorides were analyzed immediately following removal of the solvent to determine the yield of reaction product and after distillation to determine the degree of purity. In either case, one- to two-gram portions were weighed accurately into glass-stoppered Erlenmeyer flasks. Two ml. of aniline dissolved in 25 ml. of anhydrous ether were then added and the flask swirled to insure complete mixing. Reaction was instantaneous, and the contents of the flask congealed to a thick white paste. The reaction mixture was allowed to stand at room temperature for one hour after which the excess aniline was converted to the hydrochloride by addition of 2 ml. of concentrated hydrochloric acid. After removal of the ether on a steam bath, the aniline hydrochloride was removed by washing several times with distilled water. The crude anilide remaining in the flask was then washed with hot distilled water until free of mineral acid. This was accomplished by allowing the anilides to solidify from the cooled solution and then decanting the supernatant liquid through a filter paper. The solid anilides remaining on the filter were dissolved by pouring 50 ml. of hot, neutralized ethyl alcohol (95%) through the filter. The filtrate was collected in the reaction flask containing the bulk of the anilide remaining after decantation of the wash water. The contents of the flask were then heated to complete solution of the anilide and while still hot titrated with 0.1 N sodium hydroxide solution using phenolphthalein as indicator to determine the extent of the presence of free fatty acid in the sample. The percentage of free fatty acid remaining in the original reaction product was computed by means of the following equation:

$$\text{F.F.A.} = \frac{(\text{ml. of NaOH x normality}) \left(\dfrac{\text{M.W. of fatty acid}}{1000}\right)}{\text{weight of sample}} \times 100$$

The accuracy of the method was checked by analyzing samples of the purified acids and mixtures of these acids with pure acyl chlorides. Samples of 1.705 and 1.867 g. of lauric acid and 1.624 and 1.175 g. of stearic acid when treated as blanks with the various analytical reagents gave free fatty acid values corresponding to 99.2, 99.5, 100.7, and 101.4%. Analysis of a mixture consisting of 0.1143 g. of lauric acid and 2.007 g. of lauryl chloride, equivalent to 5.04% lauric acid, gave a value of 5.17% free fatty acid.

TABLE 3

Preparation of Myristyl and Palmityl Chlorides[a]

Reagent	Solvent	Myristic acid				Palmitic acid			
		Yield,[b] %	Free fatty acid in myristyl chloride, %			Yield,[b] %	Free fatty acid in palmityl chloride, %		
			Crude product	Distilled product	Distillation residue		Crude product	Distilled product	Distillation residue
Oxalyl chloride	Benzene	97.5	2.18	0.71	......	90.7	5.49	1.13	24.31
Phosphorus pentachloride	None	96.6	7.34	5.94	6.59	88.9	5.36	1.12	23.93
Oxalyl chloride	None	95.2	0.89	1.02	......	87.9	2.64	1.03	7.82
Phosphorus trichloride	Carbon tetrachloride	89.4	......	0.72	......	......	......	......	......
Phosphorus pentachloride	Benzene	83.9	3.78	1.85	4.21	72.0	8.66	......	14.51
Phosphorus trichloride	Benzene	82.8	2.59	1.22	18.75	84.7	2.59	2.54	37.30

[a] The data in this table have been selected to show only the conditions under which the highest yields were obtained in a series of experiments similar to those described for lauryl chloride (Table 2).

[b] Corrected for amount removed for analysis and free fatty acid in distillate.

TABLE 4

Preparation of Stearyl Chloride

Reagent	Solvent	Yield,[1] %	Free fatty acid in stearyl chloride, %		
			Crude product	Distilled product	Distillation residue
Oxalyl chloride	Benzene	81.1	2.15	0.63	6.17
Phosphorus pentachloride	None	77.2	......	0.50	......
Phosphorus pentachloride	None	75.3	0.42	0.39	4.63
Oxalyl chloride	Carbon tetrachloride	73.5	......	0.71	7.65
Phosphorus pentachloride	Benzene	72.1	0.37	0.70	5.80
Thionyl chloride	Benzene	70.5	......	0.07	......
Oxalyl chloride	None	65.1	7.21	......	6.15
Thionyl chloride[3]	Carbon tetrachloride	60.9	......	0.25	......
Phosphorus pentachloride	Benzene	57.9	8.80	1.32	51.26
Phosphorus trichloride	Benzene	56.5	......	0.64	......
Thionyl chloride	None	55.4	......	0.23	......
Phosphorus trichloride	None	54.3	9.32	0.89	16.14
Thionyl chloride	None	53.7	12.57	0.49	21.30
Phosphorus pentachloride[4]	Benzene	51.4	2.30	0.60	7.20
Thionyl chloride	Carbon tetrachloride	51.3	......	0.75	......
Thionyl chloride	Carbon tetrachloride	40.5	13.51	0.64	26.22
Phosphorus trichloride	Benzene	36.8	21.31	2.08	39.99
Phosphorus trichloride[2]	Carbon tetrachloride	36.4	......	0.52	23.3
Phosphorus trichloride[2]	Benzene	35.7	......	......	......
Phosphorus trichloride[2]	Carbon tetrachloride	33.0	......	......	......
Phosphorus trichloride	Carbon tetrachloride	30.2	5.86	1.08	16.84
Phosphorus trichloride[2]	Carbon tetrachloride	24.6	7.04	0.51	19.88
Phosphorus pentachloride	Carbon tetrachloride	0[5]	......	......	......

[1] Corrected for amount removed for analysis and free fatty acid in distillate.

[2] Reaction carried out in separatory funnel with 0.04 mole phosphorus trichloride to 0.1 mole of fatty acid.

[3] Sodium soap used in reaction.

[4] Three times usual quantities of fatty acid and reagent.

[5] No liquid distillate obtainable under these conditions.

Discussion of Results

Data relative to the preparation of the saturated acid chlorides are given in Tables 2 to 5, and for the unsaturated chlorides in Table 6. Examination of these data indicates that the higher fatty acid chlorides are as readily prepared with phosphorus trichloride and phosphorus pentachloride as with the oxalyl chloride. Thionyl chloride in all instances is inferior as a chlorinating agent by comparison with the other three reagents. In only one instance, namely, the preparation of lauryl chloride, did this reagent give higher yields of fatty acid chlorides than the phosphorus chlorides.

The poor solubility, relatively poor reactivity at low temperatures, and the toxic nature of phosgene render it an unsuitable laboratory reagent for the preparation of fatty acid chlorides.

Comparison of Reagents: The relative cost of preparing 100 g. of each of the fatty acid chlorides was calculated on the basis of the yields given in Tables 2 to 5 and the retail price of the various reagent grade chlorinating agents. It was calculated that the cost of reagent chlorides used in preparing 100 g. lots of lauryl, myristyl, palmityl, and stearyl chlorides was respectively $8.44, $7.58, $7.32 and $7.43 for oxalyl chloride as compared with $0.32, $0.26, $0.27 and $0.27 for phosphorus pentachloride, and $0.16, $0.16, $0.14 and $0.20 for phosphorus trichloride.

On a basis of the ease of preparation and relative yields of fatty acid chlorides, and the cost of reagent grade chlorinating agents, it is possible to select the most advantageous reagent and method for preparing relatively large quantities of pure products on a laboratory scale which are suitable for the synthesis of fatty acid glycerides of known structure.

Among the advantages and disadvantages of the various chlorinating agents it should be emphasized that complete conversion of the fatty acid to chloride cannot be accomplished with as low a mole ratio as 1 to 0.4 of acid to phosphorus trichloride.

There is no appreciable difference in the ease of handling the various liquid reagents. Solid phosphorus pentachloride is somewhat more difficult to handle than the other reagents which can be readily added through a dropping funnel. However, the short time required for handling the phosphorus pentachloride and the increased yields obtained with it offset to a large extent this slight inconvenience.

When benzene is used as solvent, the yields are greater in most instances than is the case when carbon tetrachloride or no solvent is used. This is especially evident in the preparation of stearyl chloride by means of phosphorus pentachloride. No distillable product was obtained in the presence of carbon tetrachloride as solvent; whereas, with benzene or with no solvent at all, good yields of stearyl chloride are obtained.

TABLE 5

Preparation of Unsaturated Fatty Acid Chlorides

Reagent	Solvent	Oleic acid		Elaidic acid		Linoleic acid	
		Yield %	F.F.A. of distillate	Yield %	F.F.A. of distillate	Yield %	F.F.A. of distillate
Oxalyl chloride[a]	Carbon tetrachloride	86.3	......	......	......	......	......
Oxalyl chloride	Benzene	85.2	0.3	92.2	0.19	89.9	0.31
Oxalyl chloride	None	78.0	0.6	......	......	79.6	3.29
Oxalyl chloride	Carbon tetrachloride	......	......	67.3	......	......	......
Phosphorus trichloride[b]	None	59.8	5.58	......	......	......	......
Phosphorus trichloride[b]	Carbon tetrachloride	36.7	......	49.8	0.48	26.6	......
Thionyl chloride	None	54.9	0.91	......	......	......	......
Thionyl chloride	Carbon tetrachloride	......	......	19.4	......	57.4	......
Phosphorus pentachloride	None	0	......	......	......	......	......

[a] Procedure of Adams and Ulich using oxalyl chloride equal to 2.5 times the weight of the fatty acid.

[b] Reaction carried out in separatory funnel with 0.04 mole of phosphorus trichloride to 0.1 mole of fatty acid.

On the basis of the results shown in Table 5, oxalyl chloride is the only reagent capable of converting the higher unsaturated fatty acids to their acid chlorides in reasonably good yields. The use of phosphorus chloride apparently results in considerable polymerization of the unsaturated acids with corresponding reduction in the yield of acid chloride.

Summary

Fatty acid chlorides of lauric, myristic, palmitic, stearic, oleic, elaidic, and linoleic acids were prepared using phosphorus tri- and pentachlorides, oxalyl chloride, and thionyl chloride as chlorinating agents. On the basis of yields, ease of handling, and cost of reagent, phosphorus tri- and pentachlorides are superior to other chlorinating agents for the preparation of the higher fatty acid chlorides for use as intermediates in the preparation of pure saturated fatty acid glycerides of known structure. The unsaturated fatty acid chlorides are, however, best prepared from oxalyl chloride.

The use of phosgene, which has been patented for the preparation of acid chlorides, failed to effect efficient conversion of the higher fatty acids to the corresponding chlorides.

The analysis of the fatty acid chlorides by conversion to anilides provides a simple and easy means for ascertaining the extent of conversion of fatty acids to chlorides. By means of this method it is possible to follow readily the course of the reaction in order to determine when complete conversion of fatty acid to fatty acid chloride has been effected.

Acknowledgment

The author wishes to acknowledge the assistance of Victor Gastinel, Jr., in the early stages of this work, prior to his induction into military service, and of Miss Maizie Caravella for the preparation of a number of pure acids.

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Spectral Properties of Linoleic and Linolenic Acids Prepared by Debromination

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INCIDENT to studies on the thiocyanogen reagent and method recently described (11) it was found necessary to prepare pure samples of linoleic and linolenic acids. Use of the ultraviolet spectrophotometer to determine the percentage of conjugated isomers present in various preparations of these acids indicated the necessity of introducing certain refinements and precautions into the usual methods of preparation. As a result of these refinements specimens of linoleic and linolenic acids were obtained which were of higher purity spectroscopically than those previously reported (3, 18).

The absorption spectra have been determined for each of the acids which were obtained by the various modifications applied in their preparation. The data obtained offer a striking example of the utility of the spectrophotometer in following the progress of the preparation of a pure compound. The ultraviolet spectra of the pure fatty acids are of considerable importance in view of the increasing use of the spectrophotometric method of determining the composition of fats and oils and in establishing reference values for use in this type of analysis (1, 2, 7, 14, 15).

Preparation of the Acids

The acids were separated and purified by modifications of well recognized and generally accepted methods. However, only by observing additional precautions and introducing successive refinements in these methods was it possible to obtain acids of the highest purity.

Linoleic Acid: Preparation No. 1: Tetrabromostearic acid (m.p. 114.2°-115.0° C., total immersion thermometer) was prepared from the fatty acids of corn oil according to the method of McCutcheon (12). Debromination was carried out in ethyl ether in accordance with the method of Frankel and Brown (5). Excess ether was removed at room temperature under reduced pressure and the ether-free acid was distilled in a Claissen flask submerged in an oil bath. Distillation in this manner yielded two fractions which were collected over a boiling range of 176°-178° C. at 0.4 mm. pressure.

Preparation No. 2: A survey of the literature showed that melting points of tetrabromostearic acid had been reported which were higher than that used for preparation No. 1. Accordingly, the tetrabromides were subjected to purification by a modification of the method recommended by Kass, Lundberg, and Burr

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