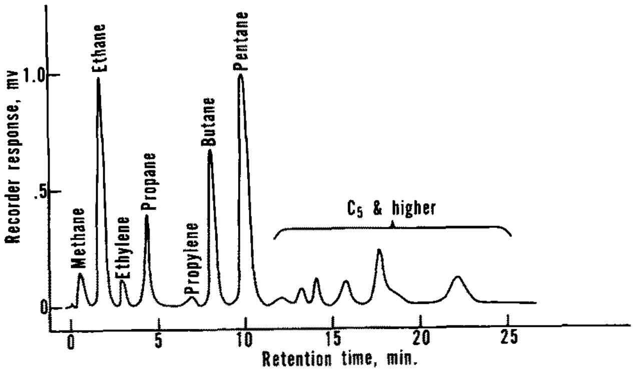

FIG. 5. Saturated and unsaturated hydrocarbons taken from the headspace gas of a home kitchen-type potato chip fryer. Temperature programmed from 75–300C at 21C/min in a 4 ft × ¼ in. column. Sample size 2.5 ml.

ture programming (21C/min from 75–300C) a headspace gas sample of 2.5 ml. Only the saturated and unsaturated hydrocarbons appear in the chromatogram. Polar oxygen-containing components in the sample are irreversibly adsorbed on the active sites of the alumina and have no effect on the hydrocarbon separations. Alumina GSC offers a direct and quantitative method for hydrocarbon analysis in fat autoxidation systems without prior removal of more polar materials which would complicate the interpretation of the chromatogram and identification of the component peaks. A limited number of injections may be made of samples dissolved in polar solvents (diethyl ether, methanol) before the adsorptive capacity of the column is exceeded. These columns can be regenerated to their original activity by a short baking period at 350C.

Gas-chromatographic analysis of low-boiling mixtures frequently requires refrigerated columns. Alumina adsorption gas chromatography is ideal for low molecular-weight hydrocarbons, whose boiling points vary over a wide range, because the troublesome use of refrigerated columns is avoided. Alumina is a unique substrate for these separations because it is stable even at elevated temperatures, and since no liquid phase is employed, column bleeding is eliminated making an ideal system for temperature programming. Separations are achieved at conditions well within the range of commercial gas chromatographs.

Chromatographic studies of aromatic hydrocarbons on alumina by Klemm et al. (15) are useful for interpretation of our results even though their investigations dealt with liquid-solid adsorption phenomena. Solute adsorption increased with the number of double bonds present, molecular approach to coplanarity, symmetry number, extent of conjugation and the number of sterically unhindered methyl or alkylene groups. In GSC systems of activated alumina the saturated hydrocarbons are eluted before olefins of equivalent carbon number because the electron-rich unsaturated bonds of the olefin are more firmly bound to the electropositive sites of the alumina lattice. Separation of branched-chain from straight-chain compounds is possible because of differences in individual vapor pressures. Behavior of diene, cyclic and isomeric hydrocarbons in GSC will be treated in a separate publication.

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Preparation of Linseed Acid Chlorides[1]

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Abstract

A method is described for the preparation of linseed acid chlorides in excellent yields and functional purity. After linseed acids are reacted with phosphorus trichloride, the mixture is briefly heated in vacuo, cooled, and decanted. The linseed acid chlorides were also distilled in a specially modified molecular still to obtain a nearly colorless product.

RECENT WORK at this laboratory required the use of linseed acid chlorides (LAC). Various chlorinating agents such as oxalyl and thionyl chloride or phosphorus tri- and pentachloride have been used to prepare the acyl chlorides of long-chain fatty acids. Bauer (1) studied the use of various chlorinating agents in the preparation of saturated and unsaturated C_{18}-acyl chlorides. Yields reported by Bauer for linoleoyl chloride were 26.6 and 89.9%, using phosphorus trichloride and oxalyl chloride, respectively. Craig et al. (2) used an improved vacuum-distillation technique to eliminate resinification and decomposition of the product and increase the yields of palmitoyl, stearoyl, and oleoyl chlorides. Ralston et al. (3) eliminated the distillation procedure for purification of the long-chain acyl chlorides by washing the reaction mixture with water to remove the various phosphorus byproducts. Youngs, Epp, Craig, and Sallans (4) obtained excellent results by carrying out the washing procedure in an inert solvent to minimize the hydrolysis of the acyl chloride.

Numerous attempts to purify LAC by washing with water as described by Youngs et al. gave products that analyzed 75 to 94% pure. However, when the chlorination mixture was heated rapidly to 150C in vacuo, LAC were obtained in nearly quantitative yields and with almost 100% purity.

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[1] Presented at AOCS meeting in Cincinnati, Ohio, 1965.

[2] A laboratory of the No. Util. Res. and Dev. Div., ARS, USDA.

TABLE I

Analysis of Acyl Chlorides

Sample	Single titration	Double titration	% Cl^-	% RCOOH I.R.	I. V.	N_D^{25}
Benzoyl chloride	100	99.5				
Linseed acid chloride (LAC)			(11.88 calc.)			
Run Ia Water washed	81.5	89.0	10.07	3.5	167.2	1.4722
b Vac. heated to 150C	100.4	99.4	12.03	0.9	168.1	1.4732
c Vac. distilled	98.6	99.8	12.09	1.0	171.5	1.4708
d Run IC + linseed acid calc. 88.2% LAC	88.4	88.6	10.53	7.4		
Run IIa Water washed	90.3	92.5	11.09		167.5	1.4724
b Water washed	87.7	93.5	10.95	3.7	168.0	1.4725
c Water washed	88.8	92.6	10.68		167.2	1.4726
d Vac. heated to 150C	101.9	101.7	12.25	0.6	168.7	1.4729
Run IIIa Vac. distilled	100.3	99.8				1.4706
b Run IIIa water washed	89.2	91.7				1.4716
c Run IIIa + linseed acid calc. 85.5% LAC	85.7	85.2	10.11			
Vac. heated to 150C calc. 75.5% from HCl lost	74.5	85.7	9.18			
d Run IIIa + linseed acid calc. 49.5% LAC	49.1	49.6				1.4694
Vac. heated to 150C then 160C calc. 17.2% LAC from HCl lost	15.9	47.7	1.91			1.4732

Discussion

Numerous attempts to prepare LAC from linseed acid (LA) and phosphorus trichloride according to the procedure of Youngs et al. consistently gave impure products when analyzed by a double titration procedure (methanolysis and hydrolysis). The water-washing step can now be eliminated and the crude product purified (for most reactions) simply by heating it rapidly to 145–150C in vacuo (water aspirator), cooling, and decanting from the insoluble residue that forms. This procedure gives LAC in near quantitative yields (98–100%) and near 100% purity.

In Table I are shown the analytical results of various treatments of crude LAC. In run I, the crude reaction mixture was divided into two portions after decantation from the phosphorus acid residues. A 25 g portion was taken, dissolved in 100 ml of hexane, washed twice with ice water as described by Youngs, dried with sodium sulfate, stripped of solvent, and analyzed. The remaining portion was heated to 150C in vacuo, cooled, decanted from a small amount of insoluble residue, and analyzed. Finally, the vacuum-heated product was distilled in an all-glass falling film still (Fig. 1). This still differs from those available commercially in that the annular space between the evaporating and condensing surfaces was increased to 17 mm to prevent spray from contaminating the distillate.

For run II, three 25 g portions were taken and dissolved in hexane. Each was washed with water as described above. A fourth portion was again heated to 150C in vacuo. For run III, a 20 g portion of distilled LAC was washed with ice water as described.

Table I gives data on analyses of the acyl chlorides by single and double titrations (see Fig. 2), chloride determination, and infrared analysis for free acid (4). All the LAC heated to 150C in vacuo are about 99% pure, whereas those obtained by the water-wash technique were always below 94% and sometimes (not listed) as low as 75%.

In this work the analysis for free fatty acid in the acid chlorides by infrared methods as reported by Youngs et al. (4) apparently gave low results for samples containing more than a few percent of free acid. A known sample of LAC containing 11.8% free fatty acid contained only 7.4% free acid by infrared methods (run Id). Correct results for acid chloride content were, however, obtained for this sample by the single and double titration methods described.

The data in Table I show a consistently lower value for the acid chloride content of water-washed products when analyzed by the single titration method as compared with the double titration method. The two analytical methods are not equivalent since the single titration method depends on titration of the hydrochloric acid produced by hydrolysis of LAC, whereas the double titration method depends on the difference in the total acid produced by hydrolysis before and after treatment with methanol. The double titration method is not capable of distinguishing between acid chloride and anhydride. The differences observed between the analytical results by the two methods are believed, therefore, to be due to the presence of linseed acid anhydrides (LAA) which are formed during the water-washing procedure and subsequent heating. Run IIIc shows that good quality acid chloride is appreciably hydrolyzed by water-washing according to the procedure of Youngs et al. (4). The acid produced is apparently involved in an equilibrium with the acid chloride and the HCl

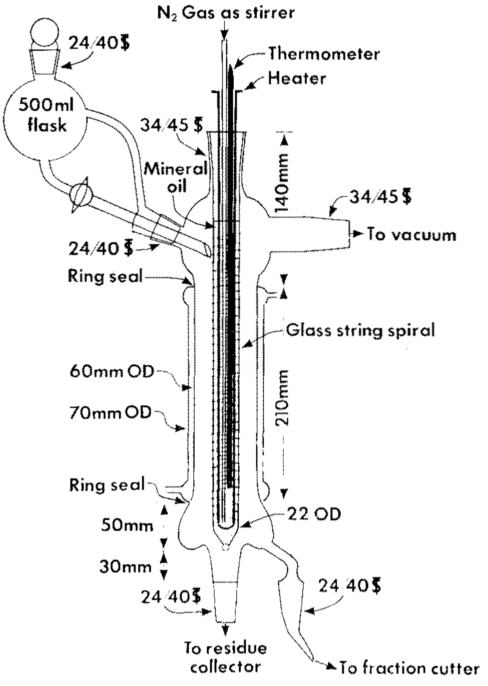

FIG. 1. All-glass falling film still.

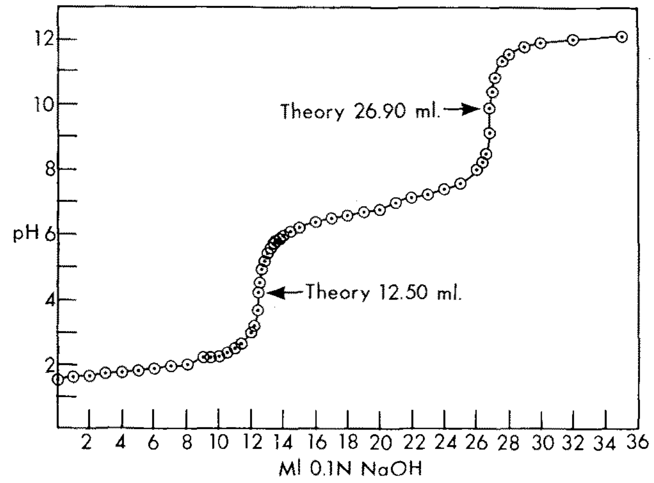

FIG. 2. Titration of linseed acid chloride containing 11.8% linseed acid.

$$RCOCl + RCO_2H \rightleftarrows (RCO)_2H + HCl$$

is removed by water or during in vacuo removal of the hexane resulting in formation of small amounts of anhydride. The anhydride is not formed in the phosphorus trichloride reaction [in agreement with Galbraith et al. (5)] as evidenced by the analyses of runs Ib and IId.

A mixture of LAC and LA (85.5% LAC) was prepared (run IIIc) and heated to 150C in vacuo and cooled immediately. Hydrogen chloride was evolved and trapped in a soda lime-calcium sulfate absorption tube. The double titration method indicated no change in LAC (85.7%) content, whereas the single titration method indicated an LAC content of 74.5% or a loss of 11.2%. Apparently, the LAC and LA reacted with evolution of hydrogen chloride forming LAA.

An attempt to prepare LAA (run IIId) was made by heating a mixture of LAC and LA (49.5% LAC) at 150C for 1 hr in vacuo and then at 160C for 1 hr in vacuo. Only a small amount of HCl was evolved during the second period of heating. The reaction product contained 15.9% and 47.7% LAC by the respective single and double titration procedures. Chloride analysis (1.91%) indicated 16.1% LAC. From the amount of HCl trapped, the calculated amount of LAC present in the mixture was 17.2%. Infrared absorption spectra shows strong carbonyl bands for acid anhydride at 5.51 and 5.71 μ, acid chloride at 5.55 μ, and acid at 5.85 μ.

Phosphorous analysis of 0.27% and 0.37% (< 1.0% calc. as H_3PO_3), respectively, for the water-washed (run Ia) and the vacuum-heated (run Ib) LAC indicated that both methods are equally effective in removal of phosphorous compounds.

Linoleic acid (94.8% C_{18} diene) was converted to linoleoyl chloride with no appreciable loss in diene content.

Experimental

Linseed Acid

For this work LA with the following properties was used: bp 185–190C/0.35 mm; N_D^{25} 1.4690; I.V. 183.9; N.E. 280.2.

Linseed Acid Chloride

LA (100 g, 0.35 mole) was heated to 70–75C on a steam bath in a flask equipped with a thermometer, dropping funnel, magnetic stirrer, and a condenser capped with a drying tube. Phosphorus trichloride (48.9 g, 0.35 mole) was added dropwise in 30 min. The solution was maintained at 70–75C for 2 hr, cooled, and carefully decanted from the viscous residue. The crude product was heated rapidly to 150C in vacuo (water aspirator), cooled, and again decanted from a small amount of viscous material. Yields in various runs were 104 to 105 g (98 to 99%). The analysis is shown in Table I.

Distillation through an all-glass falling film still gave 89.9 to 96.6 g (84.3–90.4%) bp 145–150C at 0.14 mm.

Linoleoyl Chloride

Linoleic acid (6) with the following properties was used: bp 162–164C/0.07 mm; N_D^{25} 1.4683; I.V. 174.5; N.E. 280.3. A sample of the acid was esterified with methanol and analyzed by GLC. The composition of the ester was 1.3% palmitate, 2.6% oleate, 94.8% linoleate, and 1.3% linolenate.

Linoleoyl chloride heated to 150C in vacuo as described was 98.9% acid chloride (99.2% yield) and contained 95.5% linoleoyl chloride when analyzed as the methyl ester by GLC. Distillation at 150–153C/0.2 mm gave 99.1% pure acid chloride (84.4% yield) and I.V. 163.0; N_D^{25} 1.4700. The composition of the methyl esters from this acyl chloride was 1.2% palmitate, 2.9% oleate, 95.8% linoleate and a trace of linolenate.

Analysis of Linseed Acid Chlorides

Single Titration-Neutral Hydrolysis. The acyl chloride sample (approximately 1.5 mmoles) was added to 30 ml of acetone and 5 ml of water in a pressure bottle. The bottle was stoppered with a rubber stopper and the solution heated at 60C for 30 min, cooled, and transferred to a beaker. After adding 50 ml of acetone the solution was titrated potentiometrically with 0.1*N* aqueous NaOH. The results were plotted to obtain the end point (Fig. 2). The first end point is for total hydrochloric acid. A blank was run.

$$\text{Percent LAC} = \frac{\text{ml NaOH}^{\Delta}\text{ (sample-blank)} \times N \times 298.2^{*} \times 100}{\text{g sample} \times 1{,}000}$$

$^{\Delta}$ For first end-point.
* For linoleoyl chloride.

Double Titration-Basic Hydrolysis and Methanolysis. Hydrolysis was carried out as in A with 30 ml of acetone, 5 ml of water, and 1 ml of pyridine. Basic methanolysis was performed as in A with 20 ml of methanol and 1 ml of pyridine. After adding 50 ml of acetone to each sample, the solutions were titrated potentiometrically with 0.1*N* NaOH, and the results plotted to determine the end points.

$$\left[\text{Percent LAC} = \frac{\text{ml NaOH (hydrolysis-blank)}}{\text{g sample}} - \frac{\text{ml NaOH (methanolysis-blank)}}{\text{g sample}}\right] \times \frac{N \times 298.2 \times 100}{1{,}000}$$

ACKNOWLEDGMENTS

Mrs. Clara McCrew performed the microanalyses; George McManis, the infrared analyses; and Frank Castle constructed the falling film still.

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