have been prepared and several physical constants have been determined.

2. The dehydrochlorination of the two isomers has been studied and the lower boiling isomer (α) is appreciably more reactive than the higher boiling isomer (β).

3. Propargyl alcohol has been prepared in good yields from the lower boiling isomer (α) and from a mixture of the two isomers.

4. It is impossible to assign definite geometrical structures to the two isomers from the data available.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

The Preparation of Some Unsaturated Fatty Acid Chlorides[1]

BY THOMAS R. WOOD, F. L. JACKSON, A. R. BALDWIN AND H. E. LONGENECKER

A valuable approach to an understanding of the physical nature and physiological properties of natural fats is afforded by the synthesis of mixed triglycerides of known constitution.[2,3] As our attention turned to the important group of unsaturated triglycerides,[4,5,6] it became desirable to develop a satisfactory method for making unsaturated acyl chlorides of oleic, elaidic, linoleic and linolenic acids.

Attempts to prepare the unsaturated chlorides with thionyl chloride were unsatisfactory.[7] The use of oxalyl chloride had been suggested[8] for some saturated fatty acids and was found in this work to be distinctly preferable for the unsaturated acids.

The possibility of double bond rearrangement during the reaction and subsequent purification merits attention. We have considered the possible formation of conjugated systems, known to arise in polyene acids during alkali treatment or following oxidative changes.[9] No consideration has been given here to possible changes in geometric configuration during reaction. Evidence has been presented[10] for the existence of isomers of the *cis-trans* type in debromination linoleic and linolenic acids, such as were employed in the present study.

Conjugated diene, triene and tetraene linkages in preparations of linoleic and linolenic acids and their acid chlorides were estimated by comparison of the ultraviolet absorption of these compounds in appropriate spectral regions with that of pure 18-carbon conjugated polyene acids. We have employed standard absorption values compiled by Bradley and Richardson[11] for 9,11-(or 10,12)-linoleic, eleostearic and parinaric acids, whose molecular extinction coefficients (ϵ) are 33,600 (232 mμ), 46,700 (270 mμ), and 57,700 (320 mμ), respectively.

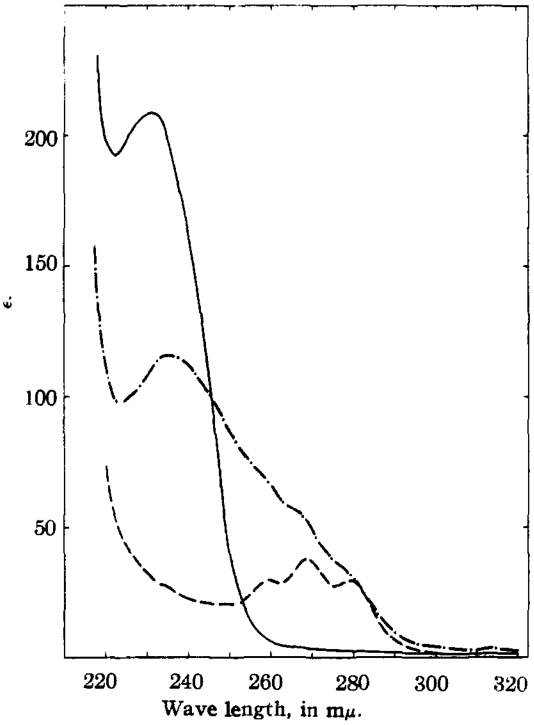

Fig. 1.—Molecular extinction curves in heptane: ———, undistilled linoleic acid; -------, distilled linoleic acid; -·-·-·-, linoleyl chloride.

The ultraviolet absorption spectra of our linoleic acid and linoleyl chloride are plotted in Fig. 1, while Fig. 2 presents similar data for linolenic acid and linolenyl chloride. It is evident that conversion of the acids to the acid chlorides was in each instance accompanied by an increase in conjugation. In no case, however, was more than 1% of the total acid or acid chloride conjugated (Table II). Moreover, it has been our experience that any manipulation of these highly unsaturated compounds tends to introduce conjugation. Con-

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(1) The authors are indebted to the Buhl Foundation for support of this investigation.

This paper was presented before the Division of Biological Chemistry of the American Chemical Society, Pittsburgh, September, 1943.

(2) Daubert and King, *Chem. Rev.*, **29**, 269 (1941).

(3) Daubert and Longenecker, *Oil and Soap*, in press.

(4) Jackson, Longenecker, Daubert and King, THIS JOURNAL, **66**, 289 (1944).

(5) Daubert, Fricke and Longenecker, *ibid.*, **65**, 2142 (1943).

(6) Daubert, Spiegl and Longenecker, *ibid.*, **65**, 2144 (1943).

(7) Jackson, F. L., Ph.D. Thesis, University of Pittsburgh, 1943.

(8) Adams and Ulich, THIS JOURNAL, **42**, 599 (1920).

(9) Mitchell and Kraybill, *ibid.*, **64**, 988 (1942).

(10) Mathews, Brode and Brown, *ibid.*, **63**, 1064 (1941).

(11) Bradley and Richardson, *Ind. Eng. Chem.*, **34**, 237 (1942).

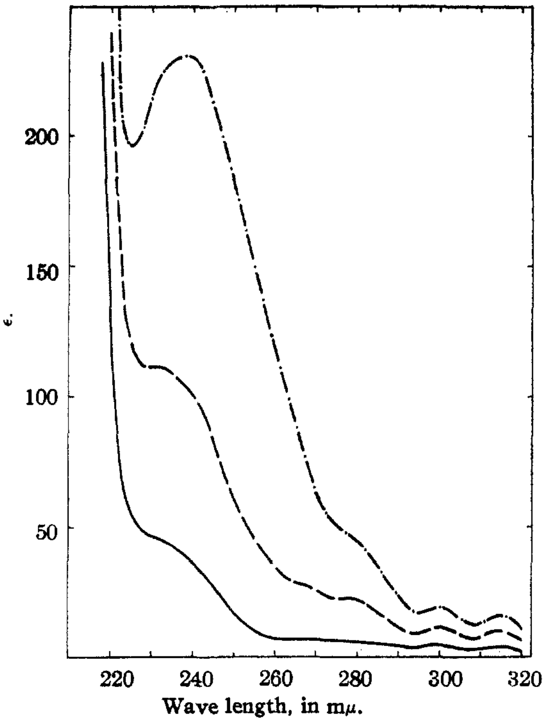

Fig. 2.—Molecular extinction curves in heptane: ———, undistilled linolenic acid; -·-·-·-, distilled linolenic acid; -·-·-·-·-, linolenyl chloride.

sequently, it is evident that the use of oxalyl chloride in the preparation of these acid chlorides does not effect changes which result in the appearance of a significant amount of conjugation. It is of interest to note the disappearance of diene conjugation in linoleic acid during distillation and the appearance of a small amount (0.08%) of conjugation of the trienoid type. The latter phenomenon may be related to the behavior of vegetable oils during bleaching with fuller's earth.[9]

As a further check on the purity of linoleic and linolenic acids and the corresponding acid chlorides, a modification of the spectral analysis method of Mitchell, Kraybill and Zscheile[12] was used. This procedure depends upon the measurement of conjugation induced in polyene acids under conditions of high temperature saponification. Kass and Skell[13] postulated that this type of isomerization is effected by the removal of a proton from central active methylene groups in 1,4-diene systems with a final stabilization in conjugated linkages. In any case, it is unlikely that conjugation would be induced in 1,4- and 1,5-diene systems at equal rates. Since the molecular extinction coefficients at 232 and 270 mμ of the soaps derived from either acid and its corresponding acid chloride were identical within experimental error (Table II) it may be assumed that little or no "spreading" of the double bonds within the diene or triene systems takes place during the reaction of the acid with oxalyl chloride.

As previously indicated, migration of double bonds in the opposite direction with resultant conjugated configuration does not occur. Consideration of the remaining possibility of the formation of geometric isomers during acid chloride synthesis must await the preparation of linoleic and linolenic acids by the low-temperature crystallization technique.

Experimental

Instrument and Methods.—All of the absorption data were obtained from measurements made with a Beckmann quartz spectrophotometer. Solutions of the acids and the acid chlorides were made in purified heptane. The absorption curves are plotted using the value of the molecular extinction coefficient on the ordinate and the wave length in mμ on the abscissa.

Molecular extinction coefficient (ϵ) = $\log_{10} I_0/I/cl$
I_0 = intensity of radiation transmitted by the solvent
I = intensity of radiation transmitted by the solution
c = concentration of solute in moles per liter
l = length in cm. of solution through which the light passes

Preparation of Highly Purified Fatty Acids.—Oleic acid was prepared by the crystallization technique of Brown and Shinowara,[14] and elaidic acid by the elaidinization of oleic acid according to the method of Lyutenberg.[15] Linoleic and linolenic acids were obtained by the debromination of tetrabromostearic acid (m. p. 115°, cor.) and hexabromostearic acid (m. p. 185°, cor.), respectively.

TABLE I

ANALYSES OF ACIDS

Acid	Iodine value (Wijs, 1 hr.) Calcd.	Found	$n^{50.0}D$	M. p.,[a] °C.
Oleic	89.9	89.7	1.4487	13.5
Elaidic	89.9	89.9	1.4468	44.5
Linoleic	181.0	182.0	1.4588	−6.5 to −6.0
Linolenic	273.5	273.1	1.4678	−15 to −14

[a] Filled capillaries were allowed to stand for twenty-four hours at −25° prior to observation of the melting point.

TABLE II

SPECTROPHOTOMETRIC ANALYSES OF LINOLEIC AND LINOLENIC ACIDS AND ACID CHLORIDES

	Conjugation,[a] %			Molecular extinction coefficients of alkali-isomerized compounds (× 10^{-4})	
	Diene	Triene	Tetraene	at 232 mμ	at 270 mμ
Linoleic acid					
Undistilled	0.6	Trace	Trace	2.34	0.01
Distilled	< 0.08	0.08	< 0.003	2.35	0.01
Linoleyl chloride	.34	< .12	< .006	2.33	0.01
Linolenic acid					
Undistilled	< .13	< .015	.007		
Distilled	< .34	< .06	.018	1.55	1.29
Linolenyl chloride	.69	< .15	.029	1.54	1.25

[a] Calculated as per cent. of 18-carbon conjugated acid. Where no absorption peaks were observed, values are indicated as maximal.

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(12) Mitchell, Kraybill and Zscheile, *Ind. Eng. Chem., Anal. Ed.*, **15**, 1 (1943).

(13) Kass and Skell, presented at the Detroit meeting of the American Chemical Society in April, 1943.

(14) Brown and Shinowara, THIS JOURNAL, **59**, 6 (1937).

(15) Lyutenberg, *Fettchem. Umschau*, **42**, 89 (1935).

The debrominations were carried out by the addition of zinc and hydrochloric acid to an ether solution of the bromides.[16] Analytical data for the above acids are presented in Table I.

Preparation of Fatty Acid Chlorides.—The acid chlorides of oleic, elaidic, linoleic and linolenic acids were prepared by the action of oxalyl chloride on the pure acids. As an example of the method, the preparation of linoleyl chloride is given.

Linoleic acid (16.5 g., 0.06 mole) was refluxed at 65 to 70° with 22.4 g. (0.18 mole) of oxalyl chloride (Eastman Kodak Company) for four hours in an all glass still. The excess oxalyl chloride was removed by warming the mixture to 100° *in vacuo*. The acid chloride was distilled under 2 to 3 mm. pressure. The yield was 14.5 g. (82% of the calculated amount) of water-white linoleyl chloride.

Anal. Calcd. for linoleyl chloride, $C_{18}H_{31}OCl$: Cl, 11.87. Found: Cl, 11.68, 11.77.

For the other acid chlorides:

Anal. Calcd. for oleyl chloride, $C_{18}H_{33}OCl$: Cl, 11.78. Found: Cl, 11.68, 11.68.

Anal. Calcd. for elaidyl chloride, $C_{18}H_{33}OCl$: Cl, 11.78. Found: Cl, 11.73, 11.83.

Anal. Calcd. for linolenyl chloride, $C_{18}H_{29}OCl$: Cl, 11.95. Found: Cl, 11.86, 12.08.

Summary

The preparation of oleyl, elaidyl, linoleyl, and linolenyl chlorides has been successfully accomplished through the use of oxalyl chloride.

Linoleic and linolenic acids and the corresponding chlorides were examined spectrophotometrically, and the results demonstrate that the reaction of the acids with oxalyl chloride was not accompanied by rearrangements of the double bonds to produce conjugated systems.

PITTSBURGH, PA.

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(16) Frankel and Brown, THIS JOURNAL, 65, 415 (1943).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

Unsaturated Synthetic Glycerides. IV. Symmetrical Monoöleo-disaturated Triglycerides[1]

BY F. L. JACKSON, B. F. DAUBERT, C. G. KING AND H. E. LONGENECKER

In other papers[2,3] of this series it was shown that methods available for the synthesis of unsymmetrical mixed triglycerides containing saturated acids were suitable, with little modification, for the preparation of 1-oleyl-2,3-disaturated triglycerides and 1-acyl-2,3-dioleins. This investigation likewise shows that methods suitable for the preparation of symmetrical mixed triglycerides containing saturated fatty acids can be adapted to the synthesis of those containing unsaturated acids. However, the reaction between the symmetrical diglyceride and the unsaturated acyl chloride cannot be completed under less rigorous conditions than refluxing for several hours on a steam-bath.[3] Amberger and Bromig[4] attempted to prepare 2-oleyl-1,3-distearin by treating 1,3-distearin with oleyl chloride in quinoline and pyridine solution at room temperature for several days. Their results were unsatisfactory as they succeeded only in isolating the original diglyceride. It has been our experience that good yields of unsaturated triglycerides may be obtained, in general, only when the acylation of the 1-mono- or 1,3-diglyceride with an unsaturated acyl chloride is carried out at 70 to 85° for three to six hours.

Although the methods of Fischer[5] and Verkade and associates[6,7,8] both were used in this work to prepare the symmetrical diglycerides which later were used as intermediates, it was found that the use of 1-monotrityl glycerol was unsatisfactory for preparing 1,3-dilaurin and 1,3-dicaprin. Poor yields of 1,3-dilaurin were obtained on hydrolysis of 1-trityl-2,3-dilauryl glycerol and successful isolation of 1,3-dicaprin was not accomplished. Hydrolytic cleavage of the low molecular weight fatty acids no doubt occurred simultaneously with removal of the trityl (triphenylmethyl) group during hydrolysis of the 1,2-diacyl-3-tritylglycerol.

The melting points of the symmetrical monooleo-disaturated triglycerides are, with one exception, two to five degrees higher than the unsymmetrical isomers reported in a previous paper.[2] The melting points were determined on melted samples contained in capillary tubes cooled slowly to −20° and held at −20° for at least twenty-four hours.

Although measurable differences in refractive indices were obtained when compared with the unsymmetrical isomers, no definite conclusions can be drawn concerning this particular physical property.

Experimental

Preparation of Intermediates.—All saturated fatty acids and the corresponding acyl chlorides, oleic acid and oleyl chloride were prepared by the methods given in the first paper of this series.[2]

Two symmetrical diglycerides, 1,3-dipalmitin (m. p. 72.5°) and 1,3-dicaprin (m. p. 45.5°) were prepared using 1-iodohydrin (Alival) as the intermediate by the method described by Fischer.[5] 1-Monotritylglycerol, prepared as described by Verkade and Meerburg,[7] was used for the synthesis of 1,3-distearin (m. p. 79.5°), 1,3-dimyristin (m. p. 64.7°) and 1,3-dilaurin (m .p. 58°). The method is given in detail for 1,3-distearin.

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(1) The authors are indebted to the Buhl Foundation for a grant in support of this investigation.

(2) Daubert, Fricke and Longenecker, THIS JOURNAL, 65, 2142 (1943).

(3) Daubert, Spiegl and Longenecker, *ibid.*, 65, 2144 (1943).

(4) Amberger and Bromig, *Biochem. Z.*, 130, 252 (1922).

(5) Fischer, Bergmann and Barwind, *Ber.*, 53, 1589 (1920).

(6) Verkade, van der Lee, de Quant and Zuydewijn, *Proc. Acad. Sci., Amsterdam*, 40, 580 (1937).

(7) Verkade and Meerburg, *Rec. trav. chim.*, 54, 716 (1935).

(8) Verkade and van der Lee, *ibid.*, 55, 267 (1936).