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.

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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).

TABLE I

SYMMETRICAL MONOÖLEO-DISATURATED TRIGLYCERIDES AND THEIR HYDROGENATED PRODUCTS

	2-Oleyl-1,3-diacyl glycerides						2-Stearyl-1,3-diacyl glycerides	
	Molecular weight		Iodine value		Melting point, °C.		Melting point, °C.	
Acyl radical	Calcd.	Found	Calcd.	Found		$n^{45.6}_{D}$	Reported	Found
Capryl	665	654 ± 1	38.2	38.0	5 to 6	1.45018[e]	44.5[a]	45.0
Lauryl	721	728 ± 1	35.2	35.1	14.5 to 15	1.45164	50.9[b]	51.5
Myristyl	777	792 ± 2	32.7	32.7	26 to 27	1.45244	55.5[a]	56.0
Palmityl	833	819 ± 2	30.5	30.6	35.5 to 36	1.45347	68.0[c]	68.0
Stearyl	889	890 ± 3	28.5	28.7	42.5 to 43	1.45417	71.5[d]	71.5

[a] Malkin and Meara, *J. Chem. Soc.*, 1141 (1939). [b] Averill, Roche and King, THIS JOURNAL, **51**, 866 (1929). [c] Malkin and Meara, *J. Chem. Soc.*, 103 (1939). [d] Clarkson and Malkin, *ibid.*, 666 (1934). [e] Average d*n*/d*t* = 0.00038.

1-Monotrityl glycerol (8.0 g.) was dissolved in a mixture of 25 ml. of chloroform and 13 g. of pyridine. While cooling the solution in an ice-bath, 19 g. of stearyl chloride was added slowly. After standing for four days at room temperature, the mixture was dissolved in ether and the solution was washed successively with water, 0.5 *N* sulfuric acid, 5% potassium carbonate solution and again with water. After drying over anhydrous sodium sulfate and distilling the ether from the filtered liquid, a pale yellow, viscid liquid remained. The liquid solidified slowly on standing at room temperature. The product was dissolved in 400 ml. of petroleum ether and cooled to 0°. Dry hydrogen chloride was passed into the solution for thirty minutes, during which time the diglyceride separated as a white solid. The mixture was allowed to stand at room temperature for one hour. After the addition of sufficient ether to effect solution, it was washed successively with 5% potassium carbonate solution and water. The solution was dried over anhydrous sodium sulfate, filtered, and evaporated to dryness. The 1,3-distearin was crystallized repeatedly from 95% alcohol; yield, 12 g. (80%); m. p. 79.5°.

Preparation of 2-Oleyl-1,3-dilaurin.—Oleyl chloride (3.6 g.) was added slowly to a solution of 1,3-dilaurin (5 g. in 13 g. of chloroform and 5 g. of quinoline) in a glass-stoppered flask. After refluxing for three hours on a steam-bath, the reaction mixture was allowed to stand overnight. It was then dissolved in petroleum ether and washed successively with 0.5 *N* sulfuric acid, 10% potassium carbonate solution and water. After drying over anhydrous sodium sulfate, the solution was filtered and evaporated to dryness under reduced pressure. The yellow liquid remaining was dissolved in ethyl ether and refluxed with activated charcoal for twenty minutes. After filtration the ether was removed from the filtrate and the colorless liquid remaining was redissolved in petroleum ether. Several crops of crystals were obtained as the solution was progressively cooled to −30°. The iodine values of the successive crops of crystals were 34.8, 35.0 and 35.2, respectively (calcd. for 2-oleyl-1,3-dilaurin, 35.2). The iodine value of the residue recovered from the mother liquor was 33.9. The two fractions having iodine values of 35.0 and 35.2 were combined and recrystallized several times from petroleum ether; yield, 6 g. (75%).

Anal. Calcd. for $C_{45}H_{84}O_6$: C, 74.95; H, 11.74. Found: C, 74.81, 74.78; H, 11.69, 11.60.

The physical and chemical constants for 2-oleyl-1,3-distearin, 2-oleyl-1,3-dipalmitin, 2-oleyl-1,3-dimyristin, and 2-oleyl-1,3-dicaprin, prepared in a similar manner, are given in Table I.

Proof of Structure.—Hydrogenation of the symmetrical monoöleo-disaturated triglycerides to the corresponding saturated analogs gave added support to the symmetrical structure (Table I). The hydrogenation procedure was similar to that described previously.[2,3]

Summary

2-Oleyl-1,3-dicaprin, -dilaurin, -dimyristin, -dipalmitin and -distearin have been prepared in high purity, their structure demonstrated by hydrogenation, and their melting points and refractive indices measured. These properties both increase numerically with increasing length of the carbon chain of the saturated fatty acids.

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

Unsaturated Synthetic Glycerides. V. Unsymmetrical Monoelaidyl-Disaturated and Monosaturated-Dielaidyl Triglycerides[1]

BY B. F. DAUBERT

The evident need of obtaining physical and chemical data on synthetic mixed triglycerides containing unsaturated acids for the purpose of characterizing more adequately those glycerides present as components in natural fats has been discussed recently in previous communications of this series.[2,3]

Elaidic acid, the *trans* isomer of oleic acid, does not occur free or combined in glycerides of natural fats so far as the author is aware. Notwithstanding this fact, however, the physical and chemical properties of this group of glycerides are of considerable interest for the purpose of comparison with the corresponding synthetic oleyl- and stearyl-glycerides.

It is well known that the melting point of a fat may be increased considerably through the process of elaidinization. The melting point data for the synthetic glycerides reported in this paper give ample verification to this observation.

Therefore, physical and chemical data are reported for a series of unsymmetrical monoelaidyl-

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[1] The author is 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 and Longenecker, *Oil and Soap*, in press.