Table I

Symmetrical Monoöleo-disaturated Triglycerides and their Hydrogenated Products

Acyl radical	2-Oleyl-1,3-diacyl glycerides Molecular weight Calcd.	 Molecular weight Found	 Iodine value Calcd.	 Iodine value Found	 Melting point, °C.	 $n^{45.0}_D$	2-Stearyl-1,3-diacyl glycerides Melting point, °C. Reported	 Melting point, °C. 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 [illegible]3.9. 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.

Pittsburgh, Pa. Received October 30, 1943

[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.

TABLE I

Acyl radical	Molecular weight[a] Calcd.	Molecular weight[a] Found	Iodine value[b] Calcd.	Iodine value[b] Found	M. p.,[c] °C.	$n^{45.0}_{D}$	M. p. of 1-stearyl-2,3 diacyl glycerol, °C.
			1-Elaidyl-2,3-diacyl Glycerols				
Myristyl	777.24	772 ± 8	32.7	32.8	39.5	1.45136	56.0
Lauryl	721.13	719 ± 6	35.2	35.0	27.0	1.45023	45.5
Capryl	665.03	658 ± 6	38.1	37.8	15.0	1.44895	41.0
Caprylyl	608.91	601 ± 9	41.7	41.4	3.0	1.44786	32.0[d]
			1-Acyl-2,3-dielaidins				
							1-Acyl-2,3-distearin
Myristyl	831.31	821 ± 8	61.1	60.8	40.0	1.45619	62.5
Lauryl	803.25	796 ± 6	63.2	63.0	35.5	1.45507	54.0
Capryl	775.20	770 ± 3	65.5	65.1	25.0	1.45391	49.0

[a] Molecular weights determined by the method of Menzies and Wright,[10] as modified by Hanson and Bowman.[11] [b] Iodine values (Wijs) are averages of triplicates differing by not more than 0.1 unit. [c] Melting points were determined by the capillary tube method. Fused samples were cooled to −20° and held at −20° for at least twenty-four hours. [d] 1-Stearyl-2,3-dicaprylin was also prepared from 1-monostearin and caprylyl chloride; m. p. 31.5°; molecular weight, 603 ± 6 (calcd. 610.93); *anal.* calcd. for $C_{37}H_{70}O_6$: C, 72.73; H, 11.55. Found: C, 72.56, 72.62; H, 11.36, 11.42.

disaturated and monosaturated-dielaidyl triglycerides.

Experimental

All saturated fatty acids used in this investigation were prepared as described in the first paper of this series.[2]

Elaidic acid was prepared by the method of Lyutenberg[4] using a highly purified oleic acid. Final crystallization of the acid from ethyl ether yielded a product melting at 44.5°. Saponification equivalent, 282.1 (calcd. 282.2); iodine value (Wijs), 89.8 (calcd. 89.9); refractive index at 50.0°, 1.44682.

Preparation of Elaidyl Chloride.—In a previous communication[5] from this Laboratory it was indicated that oxalyl chloride serves as a satisfactory acylating agent for elaidic acid.

Elaidic acid (38 g.) in a round-bottom flask was treated with oxalyl chloride (38 g.) and the mixture warmed at a bath temperature of 70–80°. After one-half hour the vigorous reaction ceased, but the reaction mixture was refluxed for an additional three hours at 70–80°. Excess oxalyl chloride was removed by distillation at a bath temperature of 100°. The elaidyl chloride was then rapidly distilled at 168–170° under reduced pressure (1 mm.). The distillation yielded 27 g. (91%) of a water-white product.

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

All saturated fatty acid chlorides were prepared with thionyl chloride after the method described by McMasters and Ahmann.[6]

Preparation of 1-Monoelaidin.—Elaidyl chloride (21 g.) was added slowly to a mixture of acetone-glycerol[7] (8 g.), quinoline (15 ml.) and chloroform (20 ml.). The mixture after standing at room temperature twenty-four hours was dissolved in ethyl ether (300 ml.) and the solution washed successively with cold 0.5 *N* sulfuric acid, 5% potassium carbonate solution and distilled water. After drying the ether solution over anhydrous sodium sulfate, it was reduced, *in vacuo*, to a volume of 50 ml. Concentrated hydrochloric acid (100 ml.) was added with constant stirring to the solution, cooled in an ice-bath. After standing one-half hour, ice-water (400 ml.) was added and the flocculent white precipitate which separated was washed repeatedly with ice water until free of mineral acid. The product, after solution in ethyl ether, was dried over anhydrous sodium sulfate. On cooling the filtered liquid to 5° for twenty-four hours crystallization occurred. A constant melting point of 58.5° was obtained after crystallization from a 1:1 mixture of ether and petroleum ether. Molecular weight, 354 ± 2 (calcd. 356.23); iodine value, 71.0 (calcd. 71.2).

The 1-monoglyceride of elaidic acid was also prepared by a slight modification of the method of Malkin and Shurbagy.[7]

Dry hydrogen chloride was passed into a mixture of elaidic acid (7 g.) and acetone-glycerol (15 g.) until the mixture liquefied (about 20 minutes). The mixture was diluted to a total volume of 50 ml. with ethyl ether and treated with concentrated hydrochloric acid (50 ml.). The precipitated product was crystallized from a 1:1 mixture of ethyl ether and petroleum ether as described under the preceding method; m. p. 58.5°. Mixed with the 1-monoelaidin prepared above, no melting point depression was observed.

For further identification each compound prepared by the two independent methods was hydrogenated to 1-monostearin, m. p. 81.5°. Mixed melting points with a 1-monostearin prepared from acetone-glycerol and stearyl chloride[8] showed no depression. Preliminary X-ray investigations show the 1-monoelaidin to have a diffraction pattern typical of all 1-monoglycerides examined to date.[9]

Preparation of 1-Elaidyl-2,3-dimyristin.—1-Monoelaidin (2 g.) was dissolved in a mixture of quinoline (10 ml.) and chloroform (10 ml.) and to this solution myristyl chloride (2.8 g.) was added slowly. The mixture was refluxed on a steam-bath for four hours. After the addition of ethyl ether (200 ml.), the solution was washed successively with cold 0.5 *N* sulfuric acid, 5% potassium carbonate solution, distilled water and dried over anhydrous sodium sulfate. The solution was filtered and the ether removed by distillation under reduced pressure. Fractional crystallizations from mixtures of ether and petroleum ether, and ether and 95% alcohol, yielded a product melting at 39.5°.

Anal. Calcd. for $C_{49}H_{92}O_6$: C, 75.72; H, 11.93. Found: C, 75.49, 75.61; H, 11.84, 11.79.

Other analytical constants together with the melting points of the saturated analogs obtained by a hydrogenation procedure described in a previous paper,[2] for this compound and 1-elaidyl-2,3-dilaurin, 1-elaidyl-2,3-dicaprin, 1-elaidyl-2,3-dicaprylin are listed in Table I.

Preparation of 1-Myristyl-2,3-dielaidin.—To a solution of 1-monomyristin (3.5 g.) in a mixture of quinoline (5 ml.) and chloroform (10 ml.), elaidyl chloride (8.5 g.) was added slowly. The mixture, after refluxing on a steam-bath for four hours, was dissolved in petroleum ether (200 ml.) and the solution washed successively with 0.5 *N* sulfuric acid, 5% potassium carbonate solution and distilled water. The solution was then dried over anhydrous

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

(5) Wood, Jackson, Baldwin and Longenecker, THIS JOURNAL, **66**, 287 (1944).

(6) McMasters and Ahmann, *ibid.*, **50**, 147 (1928).

(7) Malkin and Shurbagy, *J. Chem. Soc.*, 1628 (1936).

(8) Fischer, *Ber.*, **53**, 1621 (1920).

(9) Unpublished results.

(10) Menzies and Wright, THIS JOURNAL, **43**, 2309, 2314 (1921).

(11) Hanson and Bowman, *Ind. Eng. Chem.*, *Anal. Ed.*, **11**, 440 (1939).

sodium sulfate and filtered. Crystallization occurred on cooling the solution to −20° overnight. Repeated fractional crystallizations from petroleum ether and finally 95% alcohol gave a product melting at 40.0°.

Other analytical constants and melting points of the saturated analogs obtained by hydrogenation for this compound and for 1-lauryl-2,3-dielaidin, and 1-capryl-2,3-dielaidin are also given in Table I.

Discussion

Bömer and Kappeller[12] reported a melting point of 44.8° for the 1-monoelaidin they prepared from elaidyl chloride and acetone-glycerol. Unfortunately, these investigators did not report the method by which they determined the melting point nor did they report other physical and chemical constants for the compound. Preliminary warming and cooling curves have established the existence of at least three forms for 1-monoelaidin. Form I melts at 58.5°, Form II at 44.0° and Form III at 17.6°. The melting point reported by Bömer is in good agreement with the melting point of Form II. This suggests, perhaps, that the melting point (44.8°) of the 1-monoelaidin prepared by these investigators was not that of the stable phase.

The mixed triglycerides, 1-elaidyl-2,3-distearin (m. p. 61.0°), and 1-elaidyl-2,3-dipalmitin (m. p. 51.0°) prepared from 1-monoelaidin were in good agreement with those previously reported by Bömer and Kappeller, as also were 1-stearyl-2,3-dielaidin (m. p. 49.5°) and 1-palmityl-2,3-dielaidin (m. p. 46.0°).

It will be observed from the data in Table I that the melting points of the 1-elaidyl-2,3-disaturated triglycerides are, on the average, approximately 20° lower than their fully saturated analogs, and, on the average, approximately 15° higher than the same triglycerides containing an oleyl in place of the elaidyl group. Data for the latter have been reported in a previous paper.[2] Thus, the melting point relationships show the mixed triglycerides containing one elaidyl group to be intermediate between those containing one oleyl group and one stearyl group, respectively, the other saturated acids in the molecule, of course, being the same.

The above relationship also holds true for the series of unsymmetrical monosaturated-dielaidins, except that the magnitude of difference in average melting point is larger between those glycerides containing two elaidyl and those containing two oleyl groups. The average difference in melting point is about 30°.

It may also be observed, in comparing the melting point data of the two series of triglycerides (Table I) that the double bond in the single elaidyl group has the greater influence on the melting point, particularly in lower members of the series. The converse seems to be true for the monosaturated-dielaidins, *i.e.*, the chain length of the elaidyl groups has the greater influence on the melting point.

The refractive indices of the new monoelaidyl-disaturated triglycerides and the monosaturated-dielaidins are measurably lower than the corresponding synthetic mixed triglycerides containing oleic acid. The change in refractive index with change in temperature (dn/dt = 0.00038) is approximately the same as that reported previously for other series.

Molecular weights and iodine values were used as criteria for purity in preference to combustion data. The carbon and hydrogen values, however, were determined for one compound as proof against errors or confusion.

Summary

Physical and chemical data are reported for seven new unsaturated synthetic glycerides, 1-elaidyl-2,3-dimyristin, 1-elaidyl-2,3-dilaurin, 1-elaidyl-2,3-dicaprin, 1-elaidyl-2,3-dicaprylin, 1-myristyl-2,3-dielaidin, 1-lauryl-2,3-dielaidin and 1-capryl-2,3-dielaidin.

Data are also reported for 1-stearyl-2,3-dicaprylin.

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[12] Bömer and Kappeller, *Fette und Seifen*, **44**, 340 (1937).