Solution was again effected by gentle warming on a water-bath. After cooling the solution overnight in a refrigerator, the crystalline product which separated was filtered with suction and then recrystallized from alcohol until the melting point was constant: m. p. 63.0° (Averill, Roche and King,[16] 62.6°).

Discussion

Molecular weight determinations and iodine values were found to be excellent criteria for the purity of the unsaturated triglycerides. The percentage of carbon and hydrogen in possible contaminate (monoglyceride and/or diglyceride) approaches the theoretical percentages for the triglycerides. Therefore, the determination of purity on the basis of these percentages was of little value and only one such determination is reported to indicate that no gross errors were involved.

When esterification of 1-monoölein was carried out at a temperature of 45° for three days, average yields of 90–95% of triglycerides were obtained. The time and temperature of reaction for this series of triglycerides were greater than is customarily required during the course of esterification.

In order to determine the melting points, melted samples were placed in a capillary tube, cooled slowly to $-20°$ and allowed to stand at $-20°$ for at least twenty-four hours.

The melting points and refractive indices for this series of unsymmetrical monoöleo-disaturated triglycerides increased with increasing carbon length of the saturated fatty acid. The change in refractive index with temperature ($dn/dt = 0.00038$) agreed in value with that previously determined for a similar series of saturated mixed triglycerides.[18]

Summary

Data are reported for a series of monoöleo-disaturated triglycerides, 1-oleo-2,3-dicaprin, 1-oleo-2,3-dilaurin, 1-oleo-2,3-dimyristin, 1-oleo-2,3-dipalmitin, and 1-oleo-2,3-distearin.

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(18) Robinson, Roche and King, THIS JOURNAL, 54, 705 (1932).

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Unsaturated Synthetic Glycerides. II. Unsymmetrical Dioleo-monosaturated Triglycerides[1]

BY B. F. DAUBERT, C. J. SPIEGL AND H. E. LONGENECKER

In the first paper of this series[2] it was shown that the usual methods available for the preparation of mixed triglycerides are readily adaptable to the preparation of glycerides containing oleic acid.

Unsymmetrical dioleo-monosaturated triglycerides were prepared from oleyl chloride and 1-monoglycerides that had been synthesized by the method of Malkin and Shurbagy.[3] Physical data for this series of unsaturated triglycerides are reported.

By hydrogenation of the dioleo-monosaturated triglycerides, a series of unsymmetrical distearo-monoacyl triglycerides was obtained identical with that prepared by Robinson, Roche and King.[4]

Experimental

Saturated fatty acids, oleic acid, and oleyl chloride were prepared according to the methods given in the previous paper of this series.[2]

Preparation of 1-Monocaprylin.—Dry hydrogen chloride was passed into a mixture of caprylic acid (30 g.) and acetone-glycerol (50 g.). After forty-five minutes, liquefaction had occurred and the solution was dissolved in 300 ml. of cold ether. The product was then hydrolyzed with an ice-cold solution of hydrochloric acid saturated with calcium chloride. Following one-half hour of standing, with occasional shaking, the mixture was washed successively with ice water, saturated sodium bicarbonate solution, and again with water. After the solution had been dried over anhydrous sodium sulfate and filtered, the ether was removed and the monoglyceride dissolved in petroleum ether for crystallization; yield, 33.5 g. (74%). 1-Monocaprin, 1-monolaurin, 1-monomyristin, 1-monopalmitin, and 1-monostearin were prepared in a similar manner. The yields with the higher members of the series were generally found to be better than the yields with the lower members.

Preparation of 1-Monocaproin.—1-Monocaproin was prepared by the reaction of caproyl chloride on acetone-glycerol in the presence of quinoline, melting point 19.4°.

Preparation of 1-Capryl-2,3-diolein.—1-Monocaprin (3.1 g.) was added to 4 g. of dry quinoline and 5 ml. of absolute chloroform in a small flask. Oleyl chloride (8 g.) was added with constant shaking and the mixture allowed to reflux on a steam-bath. The reflux condenser was closed with a drying tube to avoid exposure of the reactants to the moisture of the atmosphere. After four hours, the mixture was dissolved in 200 ml. of petroleum ether and then washed successively with cold 0.5 *N* sulfuric acid, 5% potassium carbonate solution, and distilled water. The petroleum ether solution was dried over anhydrous sodium sulfate and then filtered. The product was fractionated by removing successive crops of crystals at $-20°$. Iodine values (Wijs) determined on each of the fractions showed a progressive increase and an approach toward the theoretical value for 1-capryl-2,3-diolein (51.6, 53.2, 64.7, filtrate 65.2, calcd. 65.5). The petroleum ether was then removed from the filtrate under reduced pressure, and the product crystallized from a mixture of ether and alcohol. Finally, the triglyceride was recrystallized from ether until the iodine value was constant at 65.6 (theory 65.5); melting point, -0.5 to $0.5°$. The melting points of all compounds were determined on samples that had been allowed to

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(1) The authors are indebted to Swift and Company and to the Buhl Foundation for grants in support of this investigation.

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

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

(4) Robinson, Roche and King, THIS JOURNAL, 54, 705 (1932).

TABLE I

DIOLEO-MONOSATURATED TRIGLYCERIDES, 1-ACYL-2,3-DIOLEIN

The average d*n*/d*t* for the series is 0.00037.

Acyl	Molecular weight[a] Calcd.	Molecular weight[a] Found	Wijs iodine value[a] Calcd.	Wijs iodine value[a] Found	Melting point, °C.	n^{35}_D
1-Caproyl-	719	709 ± 9	70.6	70.9	−11.0 to −10.0	1.46114
1-Caprylyl-	747	754 ± 7	67.9	68.0	− 6.6 to − 5.6	1.45998
1-Capryl-	775	774 ± 6	65.5	65.6	− 0.5 to 0.5	1.45941
1-Lauryl-	803	795 ± 9	63.2	63.5	5.5 to 6.5	1.45932
1-Myristyl-	831	825 ± 9	61.1	60.8	12.5 to 13.5	1.45995
1-Palmityl-	859	852 ± 9	59.1	58.8	18.0 to 19.0	1.46060
1-Stearyl-[b]	887	878 ± 9	57.2	57.4	22.5 to 23.5	1.46190

[a] Molecular weights and iodine values were found to be much more reliable criteria for these compounds than carbon and hydrogen values. [b] *Anal.* Calculated for 1-stearyl-2,3-diolein, $C_{57}H_{104}O_6$: C, 77.14; H, 12.04. Found: C, 77.21 77.09; H, 12.01, 11.96.

stand at −20° for at least twenty-four hours after solidification. The molecular weight, determined by the method of Menzies and Wright,[5] as modified by Hanson and Bowman,[6] was 774 ± 6 (calcd. 775.3); refractive index at 35°, 1.45941. 1-Caproyl-2,3-diolein, 1-caprylyl-2,3-diolein, 1-lauryl-2,3-diolein, 1-myristyl-2,3-diolein, 1-palmityl-2,3-diolein, 1-stearyl-2,3-diolein were prepared in a similar manner. The constants for these compounds are given in Table I. The low melting points and high solubility of the triglycerides in organic solvents made it necessary to resort to fractional crystallization from petroleum ether in order to remove the less soluble mono- and diglycerides. Progressively increasing iodine values of the fractions indicated that considerable purification was accomplished in this manner. In order to remove any oleic acid present, the triglycerides were crystallized from a mixture of ether and alcohol at −20°. Titration of the dioleo-monosaturated triglycerides for free fatty acid indicated less than 0.01% in every case.

Amberger and Bromig[7] prepared 1-palmityl-2,3-diolein which they reported to be an oil with an iodine value of 59.82 (calcd. 59.13). Using their experimental conditions it was impossible to duplicate their results in this Laboratory. The only products that could be isolated were the 1-acyl-3-oleo diglycerides. 1-Monostearin and oleyl chloride reacted to give 1-stearo-3-oleyl glycerol, melting point, 54°; iodine value (Wijs), 40.9 (calcd. 40.7); molecular weight, 625 ± 5 (calcd. 623.0). Hydrogenation of the 1-stearo-3-oleyl glycerol gave 1,3-distearin with a melting point of 79°. The saturated diglyceride gave no melting point depression when it was mixed with 1,3-distearin synthesized by another method.

Preparation of 1-Palmityl-2,3-distearin.—1-Palmityl-2,3-diolein (0.5 g.) was dissolved in approximately 25 ml. of absolute alcohol, and to this solution there was added 0.5 g. of palladium black. After hydrogenating for two hours at room temperature under 20 pounds pressure, the mixture was filtered and the filtrate reduced in volume. The 1-palmityl-2,3-distearin crystallized at 5° and, after several crystallizations from ether, reached a constant melting point at 62.3°. 1-Caproyl-2,3-distearin, 1-caprylyl-2,3-distearin, 1-capryl-2,3-distearin, 1-lauryl-2,3-distearin, and 1-myristyl-2,3-distearin were prepared in a similar manner. The melting points of these compounds are given in Table II.

TABLE II

1-ACYL-2,3-DISTEARINS

Hydrogenated product	Melting point of product, °C. Reported[4]	Melting point of product, °C. Found
1-Caproyl-2,3-distearin	42.7	44.0
1-Caprylyl-2,3-distearin	47.6	47.5
1-Capryl-2,3-distearin	48.2	47.8
1-Lauryl-2,3-distearin	50.6	49.7
1-Myristyl-2,3-distearin	58.5	58.2
1-Palmityl-2,3-distearin	62.6	62.3

Summary

A series of new dioleo-monosaturated triglycerides, including 1-caproyl-2,3-diolein, 1-caprylyl-2,3-diolein, 1-capryl-2,3-diolein, 1-lauryl-2,3-diolein, 1-myristyl-2,3-diolein, and 1-stearyl-2,3-diolein, was prepared. Physical and chemical data for each triglyceride are reported. In addition, data are reported for 1-palmityl-2,3-diolein and 1-stearyl-3-oleyl glycerol.

The melting points of the unsymmetrical dioleo-monosaturated triglycerides increase with increasing length of the carbon chain of the saturated fatty acid.

The average change in refractive index with change in temperature (d*n*/d*t*) for the compounds prepared is 0.00037.

Hydrogenation of the dioleo-monosaturated triglycerides gave 1-acyl-2,3-distearins comparable to those prepared previously by other methods.

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

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

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