

of 2,4-bis-(benzyloxy)-benzoyl chloride resulted in the formation of tarry amorphous products. Since tarry products resulted from warming the acid chloride alone in pyridine, it appears that the compound is capable of reacting with itself. The use of alkali bases instead of pyridine resulted in the same behavior.

Free Depsides.—The depside benzyl ethers—benzyl esters were dissolved in dioxane and reduced at 50° with spongy palladium catalyst⁵ under about 40 lb. pressure. After thirty to sixty minutes, the hydrogenolysis was complete as measured by the hydrogen absorption. The catalyst was filtered off, the dioxane distilled off under

reduced pressure and the depside recrystallized from 70% ethanol.

Summary

Simple depsides have been prepared by treating benzyloxybenzoyl chlorides with benzyl esters of phenolic acids to form the benzyl ethers—benzyl esters of depsides which are then catalytically hydrogenolyzed to form the free depsides. The synthesis has been used to prepare ortho, meta and para depsides.

(5) Willstätter, *Ber.*, **54**, 123 (1921).

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Unsaturated Synthetic Glycerides. I. Unsymmetrical Monoöleo-Disaturated Triglycerides¹

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Much of the investigation concerning synthetic glycerides has been focused on the establishment of adequate methods of synthesis for glycerides containing only saturated acids from intermediates of proved configuration and structure. The saturated rather than unsaturated glycerides have occupied the attention of many workers primarily because of the availability of saturated acids of high purity and the comparative simplicity of obtaining crystalline products of relatively high melting point and purity. On the basis of the comprehensive work done on the synthesis of glycerides during the past few years, it seems reasonably certain that satisfactory methods are now available for the preparation of mixed triglycerides.

Relatively little attention has been devoted to the synthesis of glycerides containing unsaturated acids. Kreis and Hafner² heated symmetrical distearin with oleic acid under reduced pressure and reported a small yield of 2-oleo-1,3-distearin. Grün and co-workers^{3,4} reported the preparation of the same compound by heating distearin with oleic anhydride. The isomeric 1-oleo-2,3-distearin was prepared by Amberger and Bromig⁵ from 1-monoölein and stearyl chloride.

In view of the fact that an oleic acid of satisfactory purity has been prepared by simplified methods, only recently, by Wheeler and Riemenschneider,⁶ Brown and Shinowara⁷ and others, it is doubtful whether the earlier investigators had available an oleic acid of sufficient purity to warrant its use in the synthesis of glycerides.

In 1937, Bömer and Kappeller⁸ reported the preparation of several mixed triglycerides con-

taining elaidic acid. The synthesis of 1-mono-linolein by debromination of 1-mono-(9,10,12,13-tetrabromo)-stearin has been reported by Black and Overley.⁹

The nomenclature of the fatty acid derivatives of glycerol, used in past literature references, has been somewhat inconsistent, Greek letters and numbers both being used to designate the carbons in the glycerol molecule. Since Greek letters are used to differentiate the geometrical isomers of unsaturated fatty acids, polymorphism in glycerides, etc., we have chosen to adopt the numerical nomenclature for the purpose of avoiding possible confusion. In this and succeeding publications from this Laboratory, alpha monoglycerides will be referred to as 1-monoglycerides, beta monoglycerides as 2-monoglycerides, symmetrical and unsymmetrical diglycerides as 1,3- and 1,2-diglycerides, respectively. The same nomenclature will be applied to symmetrical and unsymmetrical mixed triglycerides and to those mixed triglycerides containing three fatty acids.

Glycerides containing unsaturated acids are an important group of naturally occurring components of fats and oils. Because of the paucity of information concerning unsaturated synthetic glycerides, there is an evident necessity of obtaining physical and chemical data for this group of compounds. The postulated structures of those triglycerides isolated from natural sources will need to be checked against the evidence and data provided by synthesis.

The purpose of the present paper is to report the physical and chemical data for a series of unsymmetrical monoöleo-disaturated triglycerides. Data on the symmetrical isomers will be reported at a later date.

Experimental

Fatty Acids.—All saturated fatty acids, including capric, lauric, myristic, palmitic, and stearic, were obtained by careful purification of crude acids.

(9) Black and Overley, *THIS JOURNAL*, **61**, 3051 (1939).

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

(2) Kreis and Hafner, *Ber.*, **36**, 1123 (1903).

(3) Grün and Schacht, *ibid.*, **40**, 1778 (1907).

(4) Grün and Theimer, *ibid.*, **40**, 1792 (1907).

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

(6) Wheeler and Riemenschneider, *Oil and Soap*, **16**, 207 (1939).

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

(8) Bömer and Kappeller, *Fette u. Seifen*, **44**, 340 (1937).

TABLE I
 CONSTANTS FOR SATURATED ACIDS

Fatty acid	Melting point, °C.	Iodine value	Saponification equivalent	
			Found	Calcd.
Caprylic	16.5	0.0	144.3	144.2
Capric	32.2	.1	172.4	172.3
Lauric	45.0	.0	200.5	200.3
Myristic	56.3	.0	228.3	228.4
Palmitic	64.0	.1	256.4	256.4
Stearic	70.7	.2	284.6	284.5

Oleic acid was prepared by the low temperature crystallization methods of Wheeler and Riemenschneider⁶ and Brown and Shinowara.⁷ The oleic acid obtained had the following constants: m. p., 13.5°; iodine value, 89.8; thiocyanogen value, 89.8; refractive index at 30°, 1.45625. Spectrophotometric examination¹⁰ indicated less than 0.2% linoleic acid.

Fatty Acid Chlorides.—Saturated fatty acid chlorides were prepared by the method of MacMasters and Ahmann.¹¹

Oleyl chloride was prepared by an adaptation of the method of Adams and Uhlisch.¹² Oleic acid (20 g.) was refluxed in a fractionating column with oxalyl chloride (30 g.) for two hours. The temperature of the reaction mixture was then gradually raised to remove unreacted oxalyl chloride. Finally, the oleyl chloride was quickly distilled at 163° and 2 mm. pressure; yield, 20.2 g. (90%). Consistent yields of 90% or better were obtained when prolonged heating of the crude chloride during distillation was avoided.

Anal. Calculated for C₁₉H₃₅OCl: Cl, 11.78. Found: Cl, 11.73, 11.83.

Preparation of 1-Monoolein.—Oleyl chloride (14 g.) was added slowly, with shaking, to acetone-glycerol (9.2 g.) and dry quinoline (10 g.) dissolved in dry chloroform (50 ml.) contained in a glass-stoppered flask. The mixture was allowed to stand at room temperature for two days and then dissolved in ether (400 ml.). The ether solution was washed successively with 0.5 N sulfuric acid, 5% potassium carbonate solution, distilled water, and finally dried over anhydrous sodium sulfate. The ether solution of oleyl acetone-glycerol was reduced in volume to approximately 50 ml. *in vacuo*, and then cooled in an ice-bath. The product was hydrolyzed by the addition of 50 ml. of hydrochloric acid to the cooled solution. After thirty minutes ice water (400 ml.) was added and the 1-monoolein separated as a liquid. The liquid was dissolved in ether (200 ml.) and the solution washed with distilled water several times. The solution was then dried over anhydrous sodium sulfate and filtered. The filtrate was reduced to one-half its volume by distillation *in vacuo* and placed in a refrigerator at 5° to crystallize. The flaky crystals which separated were filtered with suction and dried for several days in a vacuum desiccator. It was necessary to make several careful fractional crystallizations from mixtures of ether and petroleum ether to obtain a 1-monoolein with an iodine value of 71.2 (calcd. 71.2) and a constant melting point of 35.5°; yield, 15.6 g. (94%), molecular weight, 355 = 4 (calcd. 356.53), refractive index at 40°, 1.46262.

Amberger and Bromig⁸ prepared this unsaturated mono-glyceride as a liquid but did not report all the experimental details or indicate the purity of the oleic acid used in its preparation. The low iodine value (67.2) which they reported would seem to indicate an impure product.

Preparation of 1-Oleo-2,3-disaturated Triglycerides.—All triglycerides were prepared essentially by the method of Fischer, Bergmann and Barwind,¹³ given in detail for 1-oleo-2,3-dipalmitin.

(10) Thanks are due Dr. T. R. Wood for the spectrophotometric determinations.

(11) MacMasters and Ahmann, *THIS JOURNAL*, **50**, 147 (1928).

(12) Adams and Uhlisch, *ibid.*, **42**, 599 (1920).

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

1-Monoolein (5 g.) was dissolved in a mixture of dry chloroform (50 ml.) and dry quinoline (5 ml.) in a glass-stoppered flask. Palmityl chloride (8 g.) was added slowly, with shaking, to the solution. The mixture was placed in an incubator at 45° for three days. The mixture was then dissolved in ether (400 ml.) and washed successively with cold 0.5 N sulfuric acid, 5% potassium carbonate solution and distilled water. The solution was dried over anhydrous sodium sulfate and the ether removed from the filtered liquid by distillation under reduced pressure. The residue was crystallized several times from a 1:1 mixture of ether and ethyl alcohol, and finally crystallized from ether; yield, 10.5 g. (90%); m. p., 34.5°; molecular weight, 820 = 8 (calcd., 833.34); refractive index at 40°, 1.45562.

Constants for 1-oleo-2,3-dicaprin, 1-oleo-2,3-dilaurin, 1-oleo-2,3-dimyristin, and 1-oleo-2,3-distearin, prepared in the same manner, are given in Table II.

Anal. Calculated for 1-oleo-2,3-dilaurin, C₄₅H₈₄O₆: C, 74.95; H, 11.74. Found: C, 74.69, 74.75; H, 11.79, 11.69.

 TABLE II
 MONOOLEO-DISATURATED TRIGLYCERIDES, 1-OLEO-2,3-DIACYLIN

Compound, 1-oleo-2,3-	Molecular weight ^a		Iodine value ^b		Melting point, °C.	n _D ²⁰
	Calcd.	Found	Calcd.	Found		
Dicaprin	665.03	659 = 7	38.2	38.1	3-4	1.45185
Dilaurin	721.13	730 = 10	35.2	35.1	20.0	1.45322
Dimyristin	777.24	771 = 7	32.7	32.7	25.0	1.45458
Dipalmitin	833.34	820 = 8	30.5	30.5	34.5	1.45562
Distearin ^c	889.44	889 = 6	28.4	28.4	38.5	1.45700

^a Molecular weights were determined by the ebullioscopic method of Menzies and Wright,¹⁴ as modified by Hanson and Bowman.¹⁵ ^b All iodine values are averages of triplicates which agreed to within = 0.1 iodine value unit. The Wijs method was used for all iodine values. ^c Amberger and Bromig reported a melting point of 42° and an iodine value of 31.2 for this compound.

Hydrogenation of the Triglycerides.—For further identification of structure, the monooleo-disaturated triglycerides were hydrogenated to products identical with those prepared by other independent methods (Table III). The hydrogenation procedure is given in detail for 1-oleo-2,3-dipalmitin.

1-Oleo-2,3-dipalmitin (0.25 g.) was dissolved in 30 ml. of absolute alcohol. Palladium black (0.2 g.) was added to the solution and it was then transferred to the hydrogenation bottle of a Burgess-Parr apparatus. After evacuation of the air from the system, the hydrogenation was carried out at room temperature and 20 lb. hydrogen pressure. The time required for complete hydrogenation varied from thirty to sixty minutes. After removal of the catalyst by filtration, the solution was reduced to approximately one-half its volume *in vacuo*. In many instances, triglyceride began to separate during the removal of the alcohol.

 TABLE III
 HYDROGENATION OF MONOOLEO-DISATURATED TRIGLYCERIDES^a

Hydrogenated product	Melting point, °C.	
	Reported	Found
1-Stearyl-2,3-dicaprin	41.0 ^b	44.0
1-Stearyl-2,3-dilaurin	45.4 ^c	45.2
1-Stearyl-2,3-dimyristin	56.0 ^b	57.0
1-Stearyl-2,3-dipalmitin	62.6 ^c	63.0

^a 1-Oleo-2,3-distearin was not hydrogenated. ^b Carter and Malkin.¹⁷ ^c Averill, Roche and King.¹⁶

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

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

(16) Averill, Roche and King, *THIS JOURNAL*, **51**, 866 (1929).

(17) Carter and Malkin, *J. Chem. Soc.*, 1518 (1939).

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.

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

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Unsaturated Synthetic Glycerides. II. Unsymmetrical Dioleo-monosaturated Triglycerides¹

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In the first paper of this series² 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

(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).