

of the reaction product at 170° and 0.02 mm. yielded a white solid which was recrystallized from a mixture of ether and petrol ether; 3.7 g. of colorless needles melting at 75–76° was obtained.

Anal. Calcd. for $C_{16}H_{17}O_2N$: C, 74.07; H, 7.04; N, 5.75. Found: C, 73.75; H, 6.83; N, 5.81.

3,4-Dicarbethoxy-2-furanvaleric Acid (VII).—54 grams of 2-furanvaleric acid (IV) and 62 g. of diethyl-acetylenedicarboxylate were heated on the steam-bath for twelve hours. The oily addition compound (V) was then dissolved in 300 cc. of ethyl acetate and was hydrogenated in the presence of palladium black until 1 mole of hydrogen had been absorbed. The catalyst was then removed by filtration and the ethyl acetate was evaporated. The residue which consists of the partially hydrogenated compound (VI) was then heated at 16 mm. pressure to 190–200° until the evolution of ethylene had stopped. The substance was then distilled and the fraction boiling at 205–210° at 0.02 mm. was collected; 68 g. (68% of the theoretical yield) of 3,4-dicarbethoxy-2-furanvaleric acid was obtained.

3,4-Dicarboxy-2-furanvaleric Acid (VIII).—21.6 grams of the above compound was dissolved in 80 cc. of 5 *N* potassium hydroxide and the solution was heated on the steam-bath for two hours; 80 cc. of water was then added and the solution was acidified to congo red with concentrated hydrochloric acid. The crystalline acid which separated out was collected, washed with water, and dried at 100° *in vacuo*; 16.8 g. (95% of the theoretical yield) of the crude acid melting at 180–182° was obtained. The material was purified by crystallization from a mixture of methanol and ethyl acetate. Needles melting at 188–190° were obtained.

Anal. Calcd. for $C_{11}H_{12}O_7$: C, 51.56; H, 4.72. Found: C, 51.45; H, 4.90.

3,4-Dicarbethoxy-2-furanvaleric Acid Ethyl Ester (IX)—13.5 grams of the above acid, 200 cc. of absolute ethanol and 20 cc. of concentrated sulfuric acid were refluxed for twelve hours. The solution was then concentrated *in vacuo* to one-third of its volume. The residue was diluted with ice-cold water and was extracted with ether. The ether solution was washed with 2 *N* sodium carbonate and water and was dried over sodium sulfate. The ether was removed on the steam-bath and the residue was distilled *in vacuo*; 12.5 g. (70% of the theoretical yield) of the ester boiling at 165–166° at 0.02 mm. was obtained: n_D^{20} 1.4741; d_4^{20} 1.124. The same ester was obtained in 90% yield when 3,4-dicarbethoxy-2-furanvaleric acid (VII) was esterified in the manner described above.

3,4-Dicarbethoxy-2-furanvaleryl Chloride (X).—11.8 grams of 3,4-dicarbethoxy-2-furanvaleric acid (VII) was

mixed with 15 cc. of thionyl chloride and the mixture was heated on the steam-bath until the vigorous reaction was over. The excess of thionyl chloride was removed *in vacuo* and the residue was distilled; 9.4 g. (74% of the theoretical yield) of the acid chloride, boiling at 177–178° at 0.02 mm., was obtained.

3,4-Dicarbethoxy-2-furanvaleric Acid Piperidide (XI).—9.4 grams of the above acid chloride (X) was dissolved in 50 cc. of dry ether and this solution slowly added to a solution of 8 g. of freshly distilled piperidine in 50 cc. of ether. The mixture was kept at room temperature for thirty minutes, then washed with 3 *N* hydrochloric acid, 2 *N* sodium carbonate and water and dried over sodium sulfate. The ether was removed and the resulting oil was distilled *in vacuo*; 9.72 g. (90% of the theoretical yield) of the piperidide boiling at 210–211° at 0.02 mm. was obtained: n_D^{20} 1.5006; d_4^{20} 1.132.

3,4-Dicarboxy-2-furanvaleric Acid Piperidide (XII).—9.5 grams of the above ester piperidide (XI) was dissolved in 20 cc. of 5 *N* potassium hydroxide and 40 cc. of methanol and the mixture refluxed for two hours. The solution was then concentrated *in vacuo* and the residue was acidified to congo red with concentrated hydrochloric acid. The resulting oil crystallized on cooling and scratching with a glass rod. The material was collected, was washed with water and was dried. Crystallization of the material from dilute alcohol yielded 6.4 g. (79% of the theoretical yield) of whetstone shaped needles melting at 132–133°.

Anal. Calcd. for $C_{16}H_{21}O_6N$: C, 59.45; H, 6.55; N, 4.33. Found: C, 59.33; H, 6.72; N, 4.31.

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Summary

1. 3,4-Dicarboxy-2-furanvaleric acid as well as some of its derivatives have been prepared.
2. A satisfactory procedure for the preparation of 2-furanvaleric acid has been described.
3. The ultraviolet absorption curves of 3,4-dicarbethoxy-2-furanvaleric acid as well as 3,4-dicarboxy-furan have been given.

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Unsaturated Synthetic Glycerides. III. Unsaturated Symmetrical Mixed Diglycerides¹

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Of the several reliable methods for the synthesis of diglycerides, all involve the use of a glycerol derivative with two free hydroxyls and one temporarily blocked or potential hydroxyl group. Thus, in the Fisher² method 1-iodohydrin (Alival) is treated with an excess of an acid chloride, producing 1-iodo-2,3-diacylglycerol. During the subsequent replacement of the iodine by an hydroxyl group, acyl migration from

the 2(beta) to the 1(alpha) position of glycerol is known to occur with the resulting production of a symmetrical diglyceride. Similarly, when the 2,3-diacyl derivatives of either the 1-trityl ether of glycerol or 1-carbobenzyloxyglycerol are hydrolyzed, acyl migration occurs to yield the more stable 1,3-diglycerides.^{3,4,5,6} These three independent methods have been useful

(3) Jackson and King, *This Journal*, **55**, 678 (1933).

(4) Daubert and King, *ibid.*, **61**, 3328 (1939).

(5) Verkade, van der Lee and Meerburg, *Rec. trav. chim.*, **51**, 850 (1932); **54**, 716 (1935).

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

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

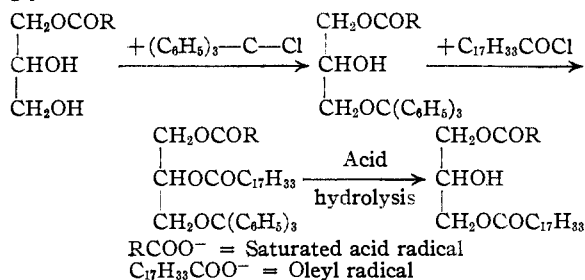
(2) Fisher, *Ber.*, **53**, 1621 (1920).

in preparing symmetrical (1,3-) diglycerides of a single fatty acid.

Verkade⁶ observed that a 1-monoglyceride reacts with trityl chloride to form an easily separable 1-acyl-3-trityl glycerol with the 2-(beta) hydroxyl group unreacted. This fact makes possible the introduction of a second acyl radical differing from the one present in the original monoglyceride. Acid hydrolysis of the trityl group from the resulting 1,2-diacyl-3-tritylglycerol is again accompanied by a shift of the acyl group in the 2-(beta) position to that position formerly occupied by the trityl group. The resulting diglyceride is again symmetrical but may now contain two different acids in the 1 and 3 positions. Verkade⁶ used this method to prepare several mixed symmetrical diglycerides containing two different saturated acids.

Malkin and associates⁷ reported the preparation of symmetrical diglycerides containing saturated acids by the direct esterification of 1-monoglycerides (10 to 15% excess) with fatty acids in the presence of *p*-toluenesulfonic acid. This method could, likewise, be adapted to the preparation of symmetrical diglycerides containing two different fatty acids.

In the present investigation advantage was taken of acyl migration during removal, by acid hydrolysis, of the trityl group from a series of 1,2-diacyl-3-tritylglycerols to prepare symmetrical mixed diglycerides containing oleic acid and either lauric, myristic, palmitic, or stearic acid. The reactions starting with the 1-monoglycerides are as follows



The identity and structure of the unsaturated diglycerides were verified by hydrogenation to the completely saturated symmetrical mixed diglycerides. It was necessary, however, for complete identification of the series, to prepare 1-lauryl-3-stearylglycerol by a method other than hydrogenation, since it had not previously been reported in the literature.

Experimental

1-Myristyl-3-tritylglycerol.—The method used for the preparation of this compound is essentially the same as that described by Verkade and van der Lee.⁶

Five grams of 1-monomyristin was dissolved in 10 ml. of quinoline and 5 g. of trityl (triphenylmethyl) chloride added to the solution. The mixture was refluxed on a steam-bath for two hours. On cooling the mixture to room temperature and allowing it to stand for several hours, a

copious precipitate of quinoline hydrochloride separated. The semi-solid mass was dissolved in 200 ml. of ether and the solution washed successively with 0.5 *N* sulfuric acid, 5% potassium carbonate solution, and water. The solution, after drying over anhydrous sodium sulfate, was filtered and the ether distilled. The sirupy residue remaining was dissolved in 300 ml. of warm petroleum ether and the solution allowed to stand at room temperature for six hours. The small amount (0.1 g.) of unreacted monoglyceride which separated was filtered off and the petroleum ether removed from the filtrate by distillation under reduced pressure. The residue was then dissolved in 30 ml. of 95% ethyl alcohol and the solution cooled to -20° . After several crystallizations from 95% ethyl alcohol and petroleum ether the product melted at 56.0° : molecular weight, 540 ± 4 (theory, 544.74).

Anal. Calcd. for $\text{C}_{36}\text{H}_{58}\text{O}_4$: C, 79.37; H, 8.88. Found: C, 79.22, 79.19; H, 8.79, 8.82.

1-Lauryl-3-tritylglycerol.—This compound was prepared in a manner similar to that described for 1-myristyl-3-tritylglycerol; m.p. 47.0° ; molecular weight, 510 ± 3 (theory, 516.69).

Anal. Calcd. for $\text{C}_{34}\text{H}_{54}\text{O}_4$: C, 79.03; H, 8.58. Found: C, 78.95, 78.99; H, 8.62, 8.65.

1-Stearyl-3-tritylglycerol, m. p. 66.0° , and **1-palmityl-3-tritylglycerol**, m. p. 62.0° (Verkade and van der Lee,⁶ 67° and 62° , respectively), were prepared in an analogous manner.

1-Stearyl-2-oleyl-3-tritylglycerol.—Five grams of 1-stearyl-3-tritylglycerol was dissolved in 5 ml. of quinoline and to this solution there was added 2.5 g. of oleyl chloride dissolved in 10 ml. of dry chloroform. The mixture was shaken over a period of two hours and then allowed to stand two days at room temperature. The mixture was dissolved in 250 ml. of ether and 50 ml. of 0.5 *N* sulfuric acid, and then washed successively with small volumes of 0.5 *N* sulfuric acid, 10% potassium carbonate solution and distilled water. After drying the ether solution over anhydrous sodium sulfate, the ether was removed under reduced pressure. The liquid residue remaining was dissolved in warm petroleum ether. An equal volume of 95% alcohol was then added and the solution cooled to -20° . Repeated attempts to induce crystallization from alcohol, petroleum ether, and mixtures of these two solvents, were not successful. The liquid which separated during cooling was washed repeatedly with cold 95% alcohol. This procedure was necessary to obtain a product of satisfactory purity.

1-Palmityl-2-oleyl-3-tritylglycerol, **1-myristyl-2-oleyl-3-tritylglycerol** and **1-lauryl-2-oleyl-3-tritylglycerol**, all liquids at room temperature, were prepared in a similar manner (Table I).

1-Myristyl-3-oleylglycerol.—Two grams of 1-myristyl-2-oleyl-3-tritylglycerol was dissolved in 15 to 20 ml. of petroleum ether and the solution cooled to about 5° in an ice-bath. Dry hydrogen chloride was passed into the solution for fifteen minutes. After allowing the mixture to stand at room temperature for two hours, it was dissolved in 150 ml. of ether and the ether solution washed three times with 30-ml. portions of 5% potassium carbonate solution, and water. After drying over anhydrous sodium sulfate the solution was filtered and the ether removed from the filtrate by distillation. The solid residue was dissolved in a 1:2 mixture of ether and alcohol. On cooling at 5° for four hours flaky white crystals separated. After several crystallizations from the same mixture of solvents, the vacuum-dried product melted at 41° .

Analytical constants for **1-myristyl-3-oleylglycerol** and also for **1-stearyl-3-oleylglycerol**, **1-palmityl-3-oleylglycerol** and **1-lauryl-3-oleylglycerol**, prepared in a similar manner, are tabulated in Table II.

1-Stearyl-2-lauryl-3-tritylglycerol.—This compound not having been reported previously was prepared by essentially the same procedure as for 1-stearyl-2-oleyl-3-tritylglycerol; m.p. 25.0° ; molecular weight, 775 ± 4 (theory, 783.14).

(7) Malkin, Shurbagy and Meara, *J. Chem. Soc.*, 1409 (1937).

TABLE I
 1-ACYL-2-OLEYL-3-TRITYLGLYCEROLS

Acyl radical	Carbon, %		Hydrogen, %			Molecular weights ^a		Iodine values ^b		
	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found		
Stearyl	80.50	80.32	80.37	10.25	10.09	10.01	865.28	857 ± 6	29.3	29.1
Palmityl	80.33	80.28	80.19	10.11	10.08	10.01	837.23	834 ± 3	30.3	30.0
Myristyl	80.15	80.12	80.06	9.97	9.87	9.96	809.18	801 ± 7	31.4	31.5
Lauryl	79.95	79.73	79.65	9.81	9.63	9.75	781.13	778 ± 5	32.5	32.1

^a Molecular weights determined by the method of Hanson and Bowman.⁸ ^b Wijs method used for all iodine values. Average of triplicates differing not more than ±0.1 iodine value unit.

 TABLE II
 UNSATURATED SYMMETRICAL MIXED DIGLYCERIDES (1-ACYL-3-OLEYLGLYCEROLS)

Acyl radical	Carbon, %		Hydrogen, %			Iodine values		Molecular weights		M. p. °C.	n _D ²⁰ -D _D ^b	
	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found				
Stearyl	75.19	75.22	75.09	11.97	11.87	11.91	40.7	40.5	622.98	615 ± 6	54.0 ^c	1.44690
Palmityl	74.69	74.58	74.56	11.86	11.82	11.78	42.7	42.4	594.93	592 ± 4	46.0	1.44574
Myristyl	74.15	74.20	74.12	11.74	11.70	11.72	44.8	44.5	566.88	561 ± 2	41.0	1.44455
Lauryl	73.55	73.32	73.41	11.60	11.51	11.56	47.1	47.2	538.83	531 ± 4	32.0	1.44335

^a This compound is identical with that prepared by direct esterification of 1-monostearin with oleyl chloride, reported in a previous paper.⁹ ^b Refractive indices were derived from graphs plotted from index readings over a range of about 10 to 15°; dn/dt for each compound of the series was 0.00039.

Anal. Calcd. for C₆₁H₇₈O₃: C, 79.75; H, 10.04. Found: C, 79.69, 79.71; H, 10.02, 9.99.

Hydrolysis in petroleum ether solution with dry hydrogen chloride yielded 1-stearyl-3-laurylglycerol; m. p. 62.0°; molecular weight, 534 ± 4 (theory, 540.84).

Anal. Calcd. for C₅₃H₆₄O₃: C, 73.28; H, 11.93. Found: C, 73.21, 73.16; H, 11.89, 11.88.

Proof of Structure.—The structure and identity of each of the new unsaturated symmetrical mixed diglycerides was proved by hydrogenation to the corresponding saturated analogs and by conversion to 1,2-diacyl-3-oleylglycerols. The latter compounds were identical with

those prepared by an independent method and reported in a previous paper¹⁰ (Table III).

Summary

Physical and chemical data are reported for seven new tritylglycerol intermediates: 1-myristyl-3-tritylglycerol, 1-lauryl-3-tritylglycerol, 1-stearyl-2-oleyl-3-tritylglycerol, 1-palmityl-2-oleyl-3-tritylglycerol, 1-myristyl-2-oleyl-3-tritylglycerol, 1-lauryl-2-oleyl-3-tritylglycerol, and 1-stearyl-2-lauryl-3-tritylglycerol.

Physical and chemical data are also reported for four new unsaturated symmetrical mixed diglycerides: 1-stearyl-3-oleylglycerol, 1-palmityl-3-oleylglycerol, 1-myristyl-3-oleylglycerol, 1-lauryl-3-oleylglycerol, and a new saturated symmetrical mixed diglyceride, 1-stearyl-3-laurylglycerol.

The refractive index and melting point of the unsaturated symmetrical mixed diglycerides increases with increase in the length of the carbon chain of the saturated fatty acid. The change in refractive index with change in temperature agrees in value with that previously reported for other series of synthetic glycerides.

TABLE III

Acyl radical in 1-acyl-3-stearylglycerol	Melting point, °C.	
	Reported	Found
Stearyl	79.1 ^a	79.0
Palmityl	71.0 to 71.5 ^b	71.0
Myristyl	65.5 to 66.5 ^c	66.0
Lauryl	62.0 ^d	62.0

^a Averill, Roche and King, *THIS JOURNAL*, **51**, 870, (1929). ^b Verkade and van der Lee.⁶ ^c Verkade, van der Lee and Meerburg.⁵ ^d Melting point of 1-stearyl-3-laurylglycerol prepared by an independent method as reported in this paper. Mixed with the hydrogenation product of 1-lauryl-3-oleylglycerol there was no depression of the melting point.

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

(9) Daubert, Spiegl and Longenecker, *THIS JOURNAL*, **65**, 2144 (1943).

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