

zation of the protein and the amount of water so held will depend upon a number of factors among them being the arrangement of the protein molecules in the undissolved state. The amount of water held by a protein molecule in solution should be principally dependent upon the extent of the total hydrophilic surface exposed to the water. Bull and Cooper¹⁷ have estimated this water held by dissolved proteins from a consideration of viscosity and diffusion and conclude that the volume of water so held is on the average about 28% of the volume of the protein. This would correspond on weight basis to about 21% hydration.

Acknowledgment.—It is a pleasure to acknowledge the financial assistance of the Abbott Research Fund of Northwestern University which permitted this research problem to be completed.

(17) Bull and Cooper, "Surface Chemistry," *Am. Assoc. Adv. Sci.*, Pub. No. 21, page 150 (1943).

Summary

1. The weight of water vapor adsorbed by a series of purified proteins has been studied as a function of the aqueous vapor pressure at 25 and at 40°. These results are reported.

2. The free energy changes and the heat changes of the adsorption of water vapor by proteins have been calculated and reported.

3. It has been found that the theory of multi-layer adsorption as proposed by Brunauer, Emmett and Teller is able to describe water adsorption by proteins in a very satisfactory manner. The B. E. T. constants have been evaluated and reported.

4. It is believed that the results obtained are consistent with the view that protein molecules in the solid state are linked together to form coherent planes whose exposed surfaces are hydrophilic. Water is adsorbed between these planes.

CHICAGO, ILL.

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[CONTRIBUTION NO. 535 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

Unsaturated Synthetic Glycerides. VIII. Unsymmetrical Mixed Triglycerides Containing Linoleic Acid¹

BY B. F. DAUBERT AND A. R. BALDWIN²

Many of the earlier contributions on the synthesis of mixed triglycerides containing linoleic acid resulted from the investigations of Grün³ and Izar.⁴ Grün³ reported the successful preparation of 1-linoleyl-2,3-distearin, m. p. 33.5–34°, and 1-linoleyl-2,3-dipalmitin, m. p. 11.5–13°, from linoleic anhydride and the corresponding 1,2-diglyceride. Because of the uncertainty regarding the structure of the supposed 1,2-diglycerides, which were synthesized by methods conducive to migration, the mixed triglycerides prepared from these intermediates were undoubtedly mixtures of the symmetrical and unsymmetrical isomers. This fact may account for the magnitude of difference in the reported melting points of the homologous triglycerides. The difference is much too large to be attributed to the carbon chain length increase or decrease of the saturated acids in the triglyceride molecule.

The efforts of Grün³ to obtain the mixed triglycerides mentioned above by heating potassium linoleate and the 1,2-distearyl ester of chlorohydrin were not successful.

Since mixed triglycerides containing linoleic acid are important components of many natural fats and oils, the purpose of the present paper is to report physical and chemical data for a series of

1-linoleyl-2,3-disaturated triglycerides and 1-monosaturated-2,3-dilinoleins.

Experimental

Preparation of Intermediates.—All saturated fatty acids and saturated fatty acid chlorides were prepared by methods described previously.⁵

Linoleyl chloride was prepared from a linoleic acid obtained by debromination of tetrabromostearic acid (m. p. 115°) and oxalyl chloride.⁶

1-Monolinolein was prepared as described in a previous paper of this series⁷ and all saturated 1-monglycerides were synthesized after the method of Malkin and Shurbagy.⁸

Preparation of 1-Stearyl-2,3-dilinolein.—To a solution of 1-monostearin (3 g.) in a mixture of quinoline (5 ml.) and chloroform (30 ml.), linoleyl chloride was added slowly. The mixture, after refluxing on a steam-bath for four hours, was dissolved in petroleum ether (300 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 sodium sulfate. Repeated fractional crystallizations from petroleum ether and finally 95% alcohol yielded a product melting at 5 to 6°.

Other analytical constants together with the melting points of the saturated analogs obtained by hydrogenation for this compound and for 1-palmityl-2,3-dilinolein, 1-myristyl-2,3-dilinolein and 1-lauryl-2,3-dilinolein are listed in Table I.

Preparation of 1-Linoleyl-2,3-distearin.—1-Monolinolein (4 g.) was dissolved in a mixture of quinoline (5 ml.) and

(1) The authors are indebted to The Buhl Foundation for a grant in support of this investigation.

(2) Nutrition Foundation, Inc., Fellow.

(3) Grün and Schonfeld, *Z. angew. Chem.*, **39**, 48 (1916).

(4) Izar, *Biochem. Z.*, **60**, 320 (1914).

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

(6) Wood, Jackson, Baldwin and Longenecker, *ibid.*, **66**, 287 (1944).

(7) Daubert and Baldwin, *ibid.*, **66**, 997 (1944).

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

TABLE I

Acyl radical	Molecular weight ^a		Iodine value ^b		M. p., °C.	n_D^{20} ^d	M. p., °C. 1-Stearyl-2,3-diacyl glycerol
	Calcd.	Found	Calcd.	Found			
1-Linoleyl-2,3-diacyl Glycerols							
Stearyl	887	893	57.2	56.9	32-33	1.45462	71.5
Palmityl	831	826	61.1	61.5	26-27	1.45385	63.0
Myristyl	775	783	65.5	65.2	20-21	1.45335	57.0
Lauryl	719	715	70.6	69.9	15-16	1.45287	45.5
Capryl	663	659	76.6	76.4	-1 to 0	1.45226	41.0
Caprylyl	606	602	83.6	83.5	-13 to -12	1.45183	32.0
1-Acyl-2,3-dilinoleins							
Stearyl	883	868	114.9	113.9	5 to 6	1.47193	71.5
Palmityl	855	849	118.7	117.8	-4 to -3	1.47090	65.0
Myristyl	827	833	122.7	122.1	-9 to -8	1.47010	62.1
Lauryl	799	791	127.0	127.2	-12 to -11	1.46895	54.0

^a Molecular weights determined by the method of Menzies and Wright,⁹ as modified by Hanson and Bowman.¹⁰
^b Wijs method used with one hour reaction time. ^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 Average difference in refractive index, 0.00056; dn/dt , 0.00040. ^e Average difference in refractive index, 0.00100; dn/dt , 0.00039.

chloroform (30 ml.). The mixture, after the slow addition of stearyl chloride (6.8 g.), was refluxed for four hours on a steam-bath. The cooled mixture was then dissolved in peroxide-free ether (300 ml.) and 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 32 to 33°.

Other analytical constants together with the melting points of the saturated analogs obtained by hydrogenation for this compound and 1-linoleyl-2,3-dipalmitin, 1-linoleyl-2,3-dimyristin, 1-linoleyl-2,3-dilaurin, 1-linoleyl-2,3-dicaprin and 1-linoleyl-2,3-dicaprylin are also given in Table I.

Spectrophotometric Analysis.—The unsaturated mixed triglycerides were all examined for preformed conjugation of two and three double bonds by measuring the absorption in iso-octane solution using a Beckmann Spectrophotometer, Model DU.

Small amounts of conjugated diene materials were found to be present in each triglyceride, which when calculated on the basis of standard absorption values for 9,11-(or 10,12)-linoleic acid,^{11,12} were less than 1.5%. The calculated percentages of conjugated diene and triene material in each of the synthetic triglycerides, are listed in Table II.

Only a negligible amount of triene material was present as indicated by absorption maxima in the region of 268 $m\mu$. However, most of the absorption above 260 $m\mu$ is a typical general absorption with the exception of the small peak representing conjugated triene material.

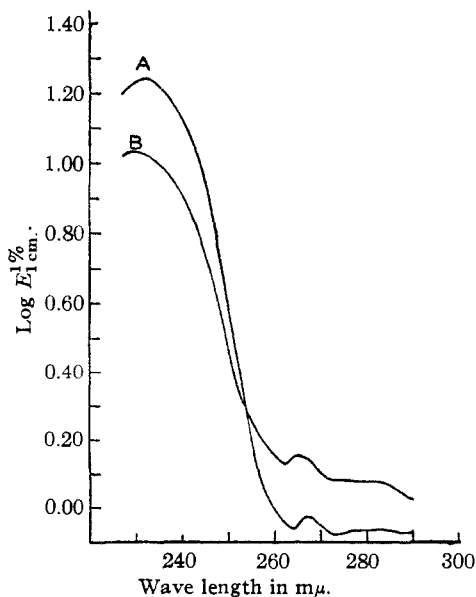


Fig. 1.—Absorption curves in iso-octane: A, 1-lauryl-2,3-dilinolein, and B, 1-stearyl-2,3-dilinolein.

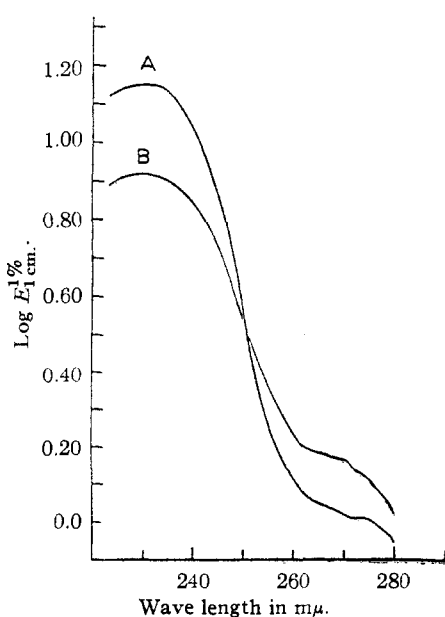


Fig. 2.—Absorption curves in iso-octane: A, 1-linoleyl-2,3-dilaurin, and B, 1-linoleyl-2,3-distearin.

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

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

(11) Kaufmann, Baltes and Funk, *Fette u. Seifen*, **45**, 302 (1938).

(12) Miller and Kass, A. C. S. Meeting, St. Louis, April, 1941.

TABLE II
SPECTROPHOTOMETRIC ANALYSES OF MIXED TRIGLYCERIDES

Acyl radical	Conjugation, % ^a	
	Diene	Triene
1-Linoleyl-2,3-diacyl Glycerols		
Caprylyl	0.55	< 0.06
Capryl	.89	< .07
Lauryl	1.18	< .07
Myristyl	1.35	< .08
Palmityl	0.89	< .08
Stearyl	.71	< .08
1-Acyl-2,3-dilinoleins		
Lauryl	1.45	< 0.06
Myristyl	0.91	< .18
Palmityl	.57	< .14
Stearyl	.84	< .08

^a Calculated as per cent. of 18-carbon conjugated acid. Where no absorption peaks were observed values are indicated as maximal.

In the instance of both conjugated diene and triene absorption peaks for these compounds, the maxima were

shifted to wave lengths shorter than those expected from consideration of the absorption curves for 9,11-linoleic acid or isomerized 9,12-linoleic acid. The absorption curves, represented in Figs. 1 and 2, are typical for the triglycerides reported in this investigation.

Brode, *et al.*,¹³ found as much as 0.46% conjugated diene material in their crystallization linoleic acid and 1.2% in their debromination acids. However, Wood, *et al.*,⁶ obtained a debromination linoleic acid which after distillation had less than 0.1% of diene material. The preparation of linoleyl chloride from this acid increased the percentage of conjugated diene to only 0.34%. The conjugation in each of the triglycerides reported in this paper did not increase significantly beyond the percentage reported by Wood, *et al.*, considering the extensive manipulation necessary in their preparation.

Summary

Physical and chemical data are reported for a series of 1-linoleyl-2,3-disaturated triglycerides and 1-monosaturated-2,3-dilinoleins.

(13) Brode, Patterson and Brown, *Ind. Eng. Chem., Anal. Ed.*, **16**, 77 (1944).

PITTSBURGH, PA.

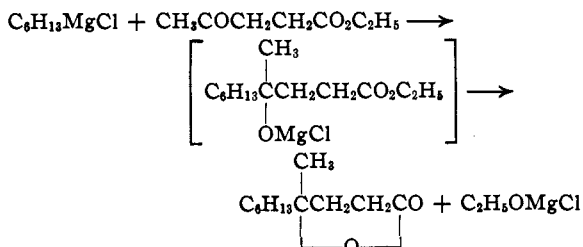
RECEIVED JUNE 23, 1944

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

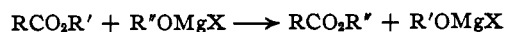
Ester Interchange by Means of the Grignard Complex

BY ROBERT L. FRANK, HORACE R. DAVIS, JR., STEVENS S. DRAKE AND JAMES B. MCPHERSON, JR.

A recent investigation in this Laboratory involved the preparation of γ -methyl- γ -decanolactone by the addition of *n*-hexylmagnesium chloride to ethyl levulinate.¹ It was remarkable that the peach-like fragrance of the lactone was noticed as soon as the Grignard reagent was added to the keto ester. It was subsequently found that the lactone could be isolated directly from the reaction mixture without intermediate saponification, which indicates the reaction



Examination of the literature showed that this type of reaction was known to Grignard² and that it is also known to take place intermolecularly as follows:



Stadnikoff³ has studied the intermolecular reac-

(1) Frank, Arvan, Richter and Vanneman, *THIS JOURNAL*, **66**, 4 (1944).

(2) Grignard, *Compt. rend.*, **135**, 627 (1902); *Bull. soc. chim.*, **39**, 1304 (1926).

(3) Stadnikoff, *J. Russ. Phys.-Chem. Soc.*, **46**, 887 (1914); **47**, 1113, 1122, 2037, 2115 (1915); *C. A.*, **9**, 1755, 3051, 3052 (1915); **10**, 1355 (1916).

tion and obtained such esters as menthyl acetate, menthyl propionate and menthyl benzoate in high yields.

Further study of Stadnikoff's method has provided a practical means of preparing certain esters which are not otherwise easy to obtain. The method is particularly applicable for the preparation of acrylates and substituted acrylates of primary and secondary alcohols, higher alkyl carbonates and higher esters of malonic acid, as shown in the accompanying table. It was not successful, however, for the preparation of cyclohexyl acetoacetate from ethyl acetoacetate, probably due to chelation of the enol form of the acetoacetate. Unsuccessful attempts also were made to prepare *t*-butyl acetate, *t*-butyl methacrylate, phenyl acrylate, furfuryl formate and *s*-butyl γ -hydroxyvalerate.

Experimental

The experimental procedure was essentially the same for the synthesis of each ester, a typical example of which, the preparation of *s*-butyl methacrylate, is here described in detail:

A 500-cc., three-necked, round-bottomed flask was fitted with a reflux condenser, a 125-cc. dropping funnel and a mechanical stirrer. Calcium chloride tubes were placed on the end of the condenser and on the top of the dropping funnel. An ethylmagnesium bromide solution was prepared in the flask in the usual manner from 6.08 g. (0.25 g. atom) of magnesium turnings, 19.0 cc. (27.2 g.; 0.25 mole) of freshly-distilled ethyl bromide and 100 cc. of dry ether. A solution of 23.0 cc. (18.5 g., 0.25 mole) of anhydrous *s*-butyl alcohol in 50 cc. of dry ether was then