Dilatometric Investigations of Fats. VI. Melting Dilation as a Function of Chain Length in Fatty Acids and Their Glyceryl Esters[1]

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THE transition of fatty materials from the solid to the liquid state is accompanied by a considerable increase in volume which can readily be measured. This increase in volume has been determined for some of the even-numbered, saturated *n*-fatty acids in the series lauric through stearic (4, 9, 10), the triglycerides of these acids (2), and the monoglycerides of stearic and palmitic acids (6, 8). Apparently no data on melting dilation other than those indicated have been published for the mono- and diglycerides of these fatty acids.

Heat of fusion is a thermal property closely related to volume change on melting. It has been shown by Garner, Madden, and Rushbrooke (3) that a definite relationship exists between the number of carbon atoms in an even-numbered, saturated *n*-fatty acid and its heat of fusion. They found a constant increment in both the heat of fusion and the entropy with each addition of two methylene groups to the fatty acid chain. The effect of the end group or component on the heat of fusion reached a constant value for *n*-fatty acids containing more than 10 carbon atoms. These workers developed a simple equation, involving the number of carbon atoms in a fatty acid chain and an end group constant, by means of which the heat of fusion of a saturated fatty acid can be calculated. Likewise it has been shown from limited data (2) that the volume change accompanying the melting of some simple, saturated triglycerides is a function of the length of the fatty acid chain. The relationship of the heat of fusion of a fatty material to its volume change on melting, both functions of chain length, suggests that the melting dilation of fatty acids and their mono-, di-, and triglycerides should have a definite relationship to each other and that this relationship could be expressed by a set of equations of a type similar to those expressing heat of fusion.

It was the purpose of the present investigation to determine the melting dilations of some additional saturated *n*-fatty acids and their mono- and diglycerides; to correlate these data with existing melting-volume data; from the pattern of variation in the volume effects accompanying the melting of these materials, to determine the melting dilation relationship between fatty acids and the mono-, di-, and trilgycerides of these acids; and to express these relationships in the form of equations.

Experimental

Materials. The monoglycerides of caprylic, lauric, and myristic acids were prepared by reacting one mole of the commercial acids of 99% purity with 4.39, 3.51, and 1.76 moles, respectively, of U.S.P. glycerol in the presence of a small amount of sodium hydroxide (0.1% on a fatty acid basis). The reactions were carried out under hydrogen, using a reaction time of three hours and a temperature of 200°C. Before reducing the temperature at the end of the three-hour period, a glycerol-phosphoric acid solution sufficient to provide 0.75 mole of phosphoric acid per mole of sodium hydroxide originally present was added to decompose the soaps which had formed. The crude products were washed with water, dried, and fractionally crystallized from commercial hexane. Mono-olein was prepared from methyl oleate by the same method. Analysis of the final monoglyceride products by the Handschumaker and Linteris modification of the periodic acid oxidation method (5) indicated the following purities: monocaprylin, 92.8%; monolaurin, 96.8%; monomyristin, 97.6%; and mono-olein, 94.4%. The dilatometric melting points of these materials were 22.9°, 61.4°, 67.8°, and 34.9°C., respectively.

Symmetrical diglycerides of lauric and myristic acids were prepared by reacting the monoglyceride with the corresponding acyl chloride at a low temperature in the presence of pyridine (7). Each diglyceride was crystallized from isopropanol and from commercial hexane. By the dilatometric method the melting points were found to be 57.7°C. for dilaurin and 66.2°C. for dimyristin.

The caproic and capric acids obtained from a commercial source were purified by fractional distillation. The dilatometric melting points of these samples were —3.4°C. for caproic acid and 30.2°C. for capric acid.

Expansibility Measurement. The acids, monoglycerides, and diglycerides, each in the most stable or highest-melting form as determined by the capillary melting point, were confined in dilatometers of the gravimetric type, employing mercury as the confining liquid. All samples were cooled in a controlled-temperature bath to an initial temperature of —32.2° C. and the expansibility determinations begun. Measurement of the dilation of each sample was continued to a temperature approximately 10°C. above its melting point. The dilatometric method and calculations employed have been explained in detail in previous publications (1, 2).

The expansibility in both solid and liquid states and the volume change on melting of each sample were calculated and are recorded in Table I. Included in this table for comparison are the melting dilations of palmitic and stearic acids, monostearin, and the triglycerides from trilaurin through tristearin, all from previous publications (2, 8, 9, 10).

Discussion of Results

A comparison of the melting dilations of the stable forms of stearic acid and its mono- and triglyceride, as pointed out in a previous report (8), revealed that the melting dilations of these materials, in ml./g., were proportional to the stearyl group content of each.

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TABLE I

Expansibilities and Melting Dilations of Some Fatty Acids and Their Glyceryl Esters

Material	Expansibility		Melting dilation[a]			
	Solid	Liquid	Observed		Calculated	
	ml./g./°C.		*ml. /g.*	*ml. /mole*	*ml. /g.*	*ml. /mole*
Stearic acid	0.00026	0.00097	0.186	52.9	0.186	52.9
Monostearin	0.00024	0.00092	0.137	49.1	0.139	49.8
Tristearin	0.00023	0.00092	0.167	148.9	0.167	148.9
Palmitic acid	0.00028	0.00097	0.181	46.4	0.182	46.7
Tripalmitin	0.00022	0.00092	0.162	130.8	0.162	130.0
Myristic acid	0.000191	0.000972	0.172	39.3	0.173	39.5
Monomyristin	0.000345	0.000844	0.118	35.7	0.121	36.6
Dimyristin	0.000435	0.00100	0.141	72.3	0.143	73.3
Trimyristin	0.00021	0.00091	0.152	109.9	0.152	109.9
Lauric acid	0.000190	0.000963	0.166	33.2	0.166	33.2
Monolaurin	0.000341	0.000956	0.110	30.2	0.111	30.5
Dilaurin	0.000391	0.000874	0.126	57.5	0.133	60.7
Trilaurin	0.00019	0.00090	0.143	91.5	0.143	91.5
Capric acid	0.000329	0.000984	0.124	21.4	0.124	21.4
Monocaprylin	0.000204	0.000736	0.052	11.3	0.052	11.3
Caproic acid	0.00035	0.00098	0.116	13.5	0.116	13.5
Mono-olein	0.00034	0.00081	0.067	24.0	0.067	24.0

[a] Calculations based on proportion of acid radical present in each compound.

When the melting dilation of stearic acid was multiplied by the stearyl residue or radical ($C_{17}H_{35}CO$-) content of mono- and tristearin (74.6 and 90.0%, respectively), values for the melting dilation of these latter compounds were obtained which were almost identical with the observed values. By applying this calculation to other series consisting of a fatty acid and its mono-, di-, and triglyceride, values for the melting dilations of these materials were calculated which were close to those obtained experimentally. Both observed and calculated values for the melting dilations of the saturated, even-numbered, *n*-fatty acids and glyceryl esters of the acids are included in Table I. The dilations are expressed on the basis of milliliters per gram of sample, and also on ml. per gram-mole of sample.

Figure 1 is a representation of the melting dilation of four series of compounds, each series comprising one of the fatty acids from lauric through stearic, and their mono-, di-, and triglycerides plotted as a function of the percentage acid residue (RCO-) of the components of each series. It is apparent from this figure that the volume change on melting a gram of sample was greatest for the material having the greatest percentage of acid residue, and therefore the least percentage of end-group components.

A comparison of the observed melting dilations, on a mole basis, of the mono-, di-, and triglycerides of each fatty acid indicated the melting dilation of the monoglyceride to be very nearly one-half that of the diglyceride and one-third that of the triglyceride. This would indicate that the end-group component of the glyceryl esters of the various acids contribute approximately the same effect to the melting dilation of these compounds and that the increment in volume change is regular with each addition of two methylene groups, similar to the increments in the heat effects observed by Garner, *et al.* (3). It was therefore possible to determine to what extent the volume change on melting is affected by both the end-group on the carbon chain and the number of carbon atoms of the acid residue and to relate melting dilation to these two entities. Accordingly, equations were developed for expressing on a gram-mole basis the melting dilation, (ΔV), of a mono-, di-, or triglyceride of an even-numbered saturated *n*-fatty acid having a chain length greater than 10 carbon atoms. In the equations shown below a and b are constants, and n represents the number of carbon atoms in the fatty acid chain.

Monoglycerides	$\Delta V = (n-2)a + b$
Diglycerides	$\Delta V = 2[(n-2)a + b]$
Triglycerides	$\Delta V = 3[(n-2)a + b]$

The calculated values of a and b are 3.24 and -2.08, respectively.

The same procedure was followed for calculating the constants for the fatty acids. The values of a and b are 3.57 and -3.24, respectively, in the following equation:

$$\Delta V = (n-2)a + b$$

The melting dilation per acyl radical for each type of glyceride is approximately 3 ml./mole less than

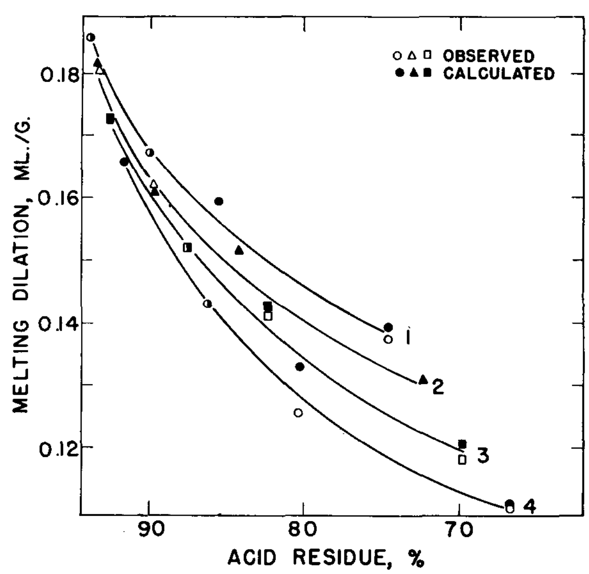

FIG. 1. Melting dilations of the fatty acids lauric through stearic and their glyceryl esters plotted as a function of the percentage of acid residue of each compound: (1) stearyl, (2) palmityl, (3) myristyl, (4) lauryl.

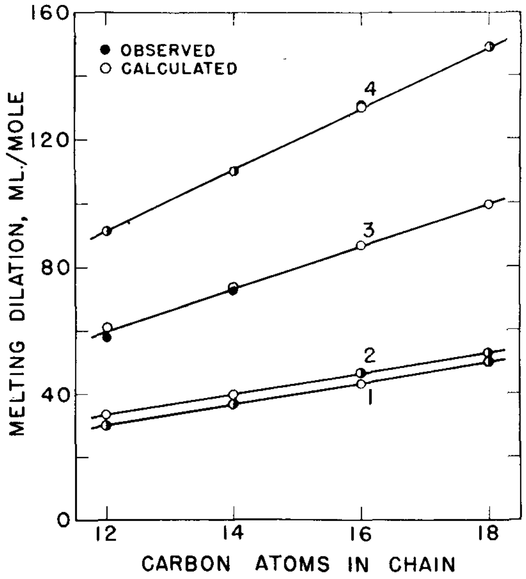

FIG. 2. Melting dilation as a function of chain length for fatty acids lauric through stearic and their glyceryl esters: (1) monoglycerides, (2) acids, (3) diglycerides, (4) triglycerides.

the melting dilation of the corresponding fatty acid.

The melting dilations of the fatty acids and their glyceryl esters, as functions of the chain length, are plotted in Figure 2, which includes both observed values and values calculated by means of the equations.

When calculated by the equations given the melting dilations of those compounds which contain less than 10 carbon atoms deviate from the observed values because of the increased importance of the end-group as the length of the carbon chain decreases. This result was experienced by Garner and associates (3) in their work on heats of fusion. Consequently the equations are not valid for such materials. Also unsaturation in a fatty acid or its glyceryl esters greatly influences melting dilation (2), and the equations herein presented are not valid for unsaturated compounds. The melting dilation of mono-olein was approximately one-half that of monostearin although the number of carbon atoms is the same for each.

Summary

Melting dilations have been determined for the even-numbered, saturated *n*-fatty acids in the series lauric through stearic, and some of their glyceryl esters. These data have been correlated with data obtained previously to determine the relationship between melting dilation and the effective chain length of these compounds.

The melting dilations of the mono-, di-, and triglyceryl esters of a fatty acid were found to be proportional to the acid residue content of each compound. The melting dilation of a monoglyceride was one-half that of the diglyceride and one-third that of the triglyceride of the same fatty acid.

The increment of melting dilation of the fatty acids and glyceryl esters increased regularly with each addition of two methylene groups, with the end group components exerting a contant effect on the volume change.

Equations were developed for calculating the melting dilation of the *n*-fatty acids and their glycerides as a function of chain length of the fatty acid radical.

The melting dilations of those compounds which are unsaturated, or have less than 10 carbon atoms, cannot be calculated by these equations.

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Biochemical Studies on Vitamin A. X. A Nutritional Investigation of Synthetic Vitamin A in Margarine[1,2]

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CERTAIN types of natural vitamin A are currently permitted for use in margarine at a level of at least 9,000 U.S.P. units per pound (5). Actually the level of fortification generally used in the U.S.A. is 15,000 U.S.P. units of vitamin A per pound. Margarine is thus an important food source of vitamin A. Two ounces supply 1,875 units or 47% of the F.D.A. minimum daily requirement for humans (6). With the availability of commercially produced synthetic vitamin A (2), its addition to margarine is of current interest. Synthetic vitamin A concentrates are suitable for use since their blandness and high concentration obviate objectionable flavors and odors in the margarine.

This investigation was designed to study the effect in margarine of vitamin A in the form of synthetic vitamin A palmitate in amounts larger than usual. Three generations of rats were maintained on adequate diets containing 7.5% of margarine oil, one containing natural vitamin A ester at the usual level (18,500 U.S.P. units/gram) and the other fortified with synthetic vitamin A palmitate at a level 100 times that ordinarily used. The criteria of response were growth rate, reproductive performance, and lactation ability. No differences of practical or statistical significance were discovered in the nutritional value of the two margarine oils.

Experimental

Diets. The detailed composition of the diets used in this study is given in Table I. These diets are composed of natural materials and a similar diet with hydrogenated vegetable shortening in place of margarine oil as the source of fat has proven to be adequate for growth, reproduction, and lactation of our stock colony rats over a period of many years. The margarine oil constituted 7.5% of the diet. Fresh diets were prepared weekly, and the prepared diets were stored in the refrigerator until used. All diets were fed *ad libitum.*

Supplements. The margarine oil used to prepare the "regular margarine oil diet" was obtained by the clarification of commercial margarine ("Mayflower" brand made by Armour and Company) labeled as containing 15,000 units of vitamin A per pound of

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