

The Effect of Positional and Geometrical Isomerism on the Dilatometric Properties of Some Octadecenoic Acids¹

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HYDROGENATION of the glycerides of polyunsaturated acids produces some glycerides containing positional and geometrical isomers of normal oleic or *cis* 9 octadecenoic acid. These oleic acid isomers differ from normal oleic acid in melting point and other physical properties although their degree of unsaturation is identical. Undoubtedly the presence of these iso-oleic acid isomers in the glycerides of shortening and other plastic fats prepared by hydrogenation has an influence on the properties of these products; yet, surprisingly, only a small amount of fundamental physico-chemical information on the isomers is available.

Among the types of information which should prove desirable in elucidating the behavior of plastic fats would be data relating the effect of positional and geometrical isomerism in oleic acid to expansibility, melting dilation, and density. Norman (8) determined relative rates of expansion for impure oleic acid and its trans isomer, elaidic acid, but without taking into consideration polymorphic changes in the former acid.

The present investigation was undertaken to obtain data on the effect of isomerism on some physical properties. Four octadecenoic acids, normal oleic, elaidic, petroselinic, and petroselaidic were examined. The latter two are the *cis* and trans isomers, respectively, of 6 octadecenoic acid.

Experimental

Materials. Oleic acid was prepared from pecan oil by the interesterification of the oil with methanol, subsequent separation and purification of the methyl oleate by the method of Wheeler and Riemenschneider (14), and conversion of the purified methyl oleate to oleic acid which was repeatedly crystallized from acetone. The purified acid had an iodine value of 89.7 and a dilatometric melting point of 16.3°C.

Elaidic acid was derived from a portion of the oleic acid by elaidinization with oxides of nitrogen (7). The reaction product was crystallized from acetone until there was obtained a purified elaidic acid having an iodine value of 89.8 and a melting point of 43.9°C.

Petroselinic acid was prepared from the extracted oil of commercial parsley seed by the same method used to prepare and purify the oleic acid. The iodine value of the recrystallized acid was 89.4, melting point 30.0°C.

Petroselaidic acid was derived from a portion of the petroselinic acid by the same methods used to obtain elaidic acid from oleic. Repeated crystallization from acetone yielded a purified petroselaidic acid having an iodine value of 89.5 and a melting point of 51.9°C.

Spectrophotometric curves of the four isomeric acids following alkali isomerization (9) indicated that

they were entirely free of polyunsaturated components. As a further check on the purity of the acids, both the oleic and petroselinic acids were oxidized with alkaline potassium permanganate to the corresponding dihydroxystearic acids by the method of Lapworth and Mottram (5). The melting points of the dihydroxystearic acid derivatives of petroselinic and oleic acids were found to be 122° and 132°C., respectively, which are in agreement with the published values of Steger and van Loon (13) for these materials.

The dilatometric procedure has been described in previous publications (1, 4). Each sample of acid was placed in a dilatometer, tempered for two hours just below its determined melting point, slowly cooled to approximately -40°C., then placed in a controlled-temperature bath at between -36° and -20°C. The expansibility determinations were then begun. The expansion of each sample was determined over a range starting at a temperature where it was completely solid and extending approximately 10° above its melting point.

Densities in the liquid state were determined by the pycnometer method.

Results and Discussion

The expansibilities and melting dilations of the acids are recorded in Table I. The specific volumes of the acid samples at representative temperatures over their complete ranges of melting were calculated (1). Table II contains the densities used in

TABLE I
Expansibility and Melting Dilation

Acid	Expansibility		Melting dilation ml./g.
	Solid state ml./g./°C.	Liquid state ml./g./°C.	
Oleic.....	0.000269 ^a 0.000308 ^b	0.000957	0.1183
Petroselinic.....	0.000369	0.000895	0.1314
Elaidic.....	0.000253	0.000968	0.1615
Petroselaidic.....	0.000308	0.000900	0.1403

^a Below -5°C.
^b Between -4° and 10°C.

TABLE II
Density in the Liquid and Solid States

Acid	Liquid state		Solid state	
	Temp. °C.	Specific volume ml./g.	Temp. °C.	Specific volume ml./g.
Oleic.....	20.0	1.1230	-36.96	0.9853
Petroselinic.....	45.0	1.1442	-36.96	0.9726
Elaidic.....	55.0	1.1555	-17.0	0.9678
Petroselaidic.....	55.0	1.1537	-17.2	0.9892

making these calculations. Specific volumes of the acids plotted as functions of temperature are shown in Figure 1.

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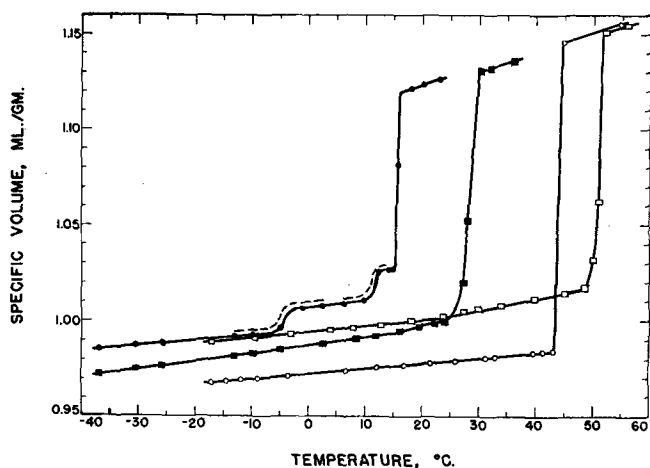


FIG. 1. Specific volume of the acids in relation to temperature. Closed circles, oleic acid; open circles, elaidic acid; closed squares, petroselinic acid; open squares, petroselaidic acid.

It is apparent from Figure 1 that at temperatures above 52°C., where all four acids are in the liquid state, the absolute specific volumes (and therefore the densities) of the acids are very nearly equal whereas at temperatures below -7°C., at which all are in the solid state, the specific volumes of petroselinic and elaidic acids are at variance with the specific volumes of oleic and petroselaidic acids. The mode of crystalline packing therefore can be said to vary among these acids. The order of increasing density of the acids in the solid state was oleic, petroselaidic, petroselinic, and elaidic. Hence greatest density difference in the solid state was between oleic and elaidic acids. The double bonds of these two acids are in the center of the carbon chains, thus allowing the *cis* and *trans* configurations to exert their full effect on crystal packing. Petroselaidic and petroselinic acids are more unsymmetrical with respect to the position of their double bond, and the difference in densities of these isomers was not as great as in the case of oleic and elaidic acids.

The melting points of the *cis* acids and *trans* acids increased in the order oleic, petroselinic, elaidic, and petroselaidic, which is in agreement with the results of Huber (2). However the melting dilations of the four acids did not follow this pattern. Melting dilations of the acids increased in the order oleic, petroselinic, petroselaidic, and elaidic. For each position of the double bond, the melting dilation of the *trans* isomer was greater than that of its *cis* isomer. It was also found that the melting dilation of the *cis* and of the *trans* isomers decreased as the position of the double bond was farther away from the carboxyl end of the carbon chain, this pattern was the same as that observed for the melting points. A comparison of the melting dilations of these acids with the melting dilation of stearic acid, which is 0.1857 ml./g. (11), shows that the C_{18} mono-unsaturated acids approach stearic acid in the magnitude of this property as the position of the double bond approaches the carboxyl end of the carbon chain.

Oleic acid is unique among the four acids investigated in that it alone, although tempered at 15°C. and slowly cooled, exhibited evidence of polymorphic transformation during the course of the dilation measurements. It has been established on the bases of

melting points (3, 12) and x-ray diffraction patterns (6) that oleic acid is capable of existing in two polymorphic forms, which melt at 16.2° and 13.4°C. In the specific volume, temperature curve for tempered oleic acid, the abrupt volume increase shown between 11° and 13°, Figure 1, is evidence of the established polymorphic transformation, accompanied by a small amount of melting, of the lower melting form to the high melting form. The oleic acid sample was found to undergo this transformation regardless of the rate of cooling of the melted sample, which indicated that below 11°C. the acid was always in the lower melting form. Furthermore tempering of the oleic acid at 12.35°C. apparently did not prevent the reappearance of the lower melting form on subsequent cooling. Thus lowering of the temperature of the tempered sample from 12.35°C. to 3.0°C. and then proceeding in the normal manner of raising the temperature by small increments reproduced the original values of dilation obtained with the same sample before tempering. These observations indicate that either the polymorphic transformation of this acid was completely reversible or alternatively, the partial melting and resolidification was of incomplete conversion. The range of temperature over which the transformation was determined is indicated by the broken lines of the oleic acid curve, Figure 1.

There were indications that there is a third polymorphic form of oleic acid, which exists below -6°C. Transformation of what appeared to be this third form to the intermediate form (m.p. 13.4°C.) at about -5°C. was accompanied by a volume increase of 0.014 ml./g. This transformation was apparently reversible (with the same alternative previously mentioned), as was established by lowering the temperature of the sample from 8°C., which is above the observed transition temperature to -12°C., and then proceeding in the normal manner. The original dilation behavior was reproduced by this procedure. The temperature range over which the polymorphic transformation was determined is indicated by the broken lines in Figure 1.

The observed transformation of oleic acid at about -5°C. was similar to that observed by the authors during expansibility measurements on triolein. The latter material was found sharply to increase in volume by 0.004 ml./g. at about -22°C., indicating transformation of polymorphic forms.

Since the melting dilations of fatty acids and their glycerides are in direct relationship (10), it can be assumed that the magnitude of the specific volumes of the glycerides of these four acids would be in the same order as the acids themselves. Therefore some predictions can be made as to how hydrogenated products containing the glycerides of these acids might differ under different conditions of hydrogenation if the content of saturated glycerides is equal. If the predominant glycerides were those of oleic acid, the hydrogenated product would have a relatively low melting point and density. If hydrogenation produced elaidic acid glycerides, the product would be more dense and higher melting. Should the double bond be shifted to the 6:7 position, either *cis* or *trans* configuration, the product would have a density intermediate between that of the oleic and elaidic acid glycerides and a high melting point if petroselaidic acid glycerides predominated. Hydrogenation conditions favoring any of these four acid

glycerides would therefore give products of differing characteristics.

Summary

Four isomeric octadecenoic acids, oleic, elaidic, petroselinic, and petroselaidic, were prepared and their expansibility determined. The melting dilation of each acid was calculated and found to increase in the order oleic, petroselinic, petroselaidic, and elaidic. In each instance the melting dilation of the trans acid was greater than that of its cis isomer. Of the two cis acids studied, the melting dilation was less for the acid with the double bond farther from the carboxyl end of the carbon chain. The trans acids did not follow this pattern.

At temperatures above 52°C., at which all acids were liquid, the absolute specific volumes of the acids were very nearly equal whereas at temperatures below -7°C. at which all were in the solid state, the specific volumes of petroselinic and elaidic acids were at variance with the specific volumes of oleic and petroselaidic acids. This variance must be attributed to differences in crystal packing.

Oleic acid clearly showed the two polymorphic forms previously recognized and, in addition, apparently reversibly transformed at about -5°C., indicating the possible existence of a third polymorphic

form. These transformations of oleic acid occurred regardless of tempering, and without visual melting. The other three acids did not exhibit polymorphism under the conditions employed in the dilatometric measurements.

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Simplified Procedure for Water Determination by the Karl Fischer Method.¹ I. Application to Drycleaning Detergents and Solvents

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PRIOR to 1949 the literature on the Karl Fischer method for determination of water was rather discouraging to one in search of a routine procedure for systems where the oven method could not be used. The discouraging aspects of the method were several. The reagent was unstable, and frequent standardization was necessary; electrometric titrations and apparatus of considerable complexity were usually recommended; the method was overburdened by well-meant but exaggerated precautions.

In 1949 Seaman, McComas, and Allen (5) described a rather drastic modification of the conventional Fischer procedure. This procedure, with the further modifications described in the present paper, appears to meet all of the above objections. The simplified procedure to be described has been in constant use in this laboratory since June 1949 in a variety of research projects and routine analyses. Six different technicians have used it successfully, and none has reported any difficulties.

The principal distinction between Seaman, McComas, and Allen's method and the older ones is that the newer procedure makes use of the reagent in the form of two solutions that are mixed in the presence of the sample during titration.

In the present paper there are offered some simplifications to make the method suitable for routine use where a large number of determinations need to be made. In addition, the method of standardization is

improved by substitution of n-propanol for methanol in the standard water solution. Propanol has three advantages over methanol for this purpose. It is less hygroscopic hence the standard solution is more stable on exposure to the air; it is less volatile so that the pipet is not cooled by rapid evaporation of the solvent film; and finally it is more viscous, therefore pipetting is easier.

Propanol could probably be substituted elsewhere in the procedure but for the fact that it is more difficult to dry than is methanol. To obtain satisfactory results with our procedure, we have found that the methanol should be as dry as possible. Methanol can be dried satisfactorily by means of magnesium methyllate (3). Fortunately this time-consuming step can be avoided by the purchase of a drum of synthetic methanol. We have found that methanol taken directly from the drum is as dry as we can get it by the magnesium method. This is not generally the case with bottled methanol. The time and expense saved by avoiding the drying operation will amply repay the investment in methanol.

Reagents and Chemicals. The reagents were prepared in the same manner as by Seaman *et al.* (5) except that a number of precautions observed by these workers were found to be unnecessary.

It was not found necessary to cool the methanol before addition of sulfur dioxide. The gas is absorbed very rapidly at room temperature, and the small amount that escapes can be disposed of by using a hood, or an open window and electric fan.

¹The Karl Fischer procedure, as modified by Seaman and coworkers, has been further simplified so that it may be used as a routine analytical tool, using merely the visible end-point. Some applications to organic solvents and drycleaning detergents are described.