A New Polymorphic Form of Elaidic Acid

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Abstract

A new polymorphic modification of elaidic acid has been prepared and characterized. The common crystalline form, mp 43.7C, is shown to be metastable. The crystals of the new, stable form have a higher melting point, 44.8C, and a lower solubility. The two modifications give distinctive x-ray diffraction patterns: stable form, long spacing 94.0Å (or possibly 47.0Å), characteristic short spacings at 4.55Å (s), 4.44Å (vs), 3.81Å (vs), and 3.68Å (s); metastable form, long spacing 48.7Å, characteristic short spacings at 4.12Å (vs) and 3.71Å (s). The short spacings of the stable form are similar to those reported for the *trans*-6-, 8-, 10-, and 12-octadecenoic acils, and the short spacings of metastable form are essentially the same as those of the *trans*-7- and 11-octadecenoic acids. Solubility data have been obtained for both polymorphic forms in methanol.

Introduction

IT HAS LONG BEEN KNOWN that long-chain normal saturated organic compounds tend to exhibit polymorphism. Most of the common *n*-alkanoic acids occur in at least three crystalline forms. Of the long-chain alkenoic acids however, oleic acid (*cis*-9-octadecenoic acid) is apparently the only one for which the existence of polymorphism has been established. The two crystal modifications have been characterized by different melting points, 13.6 and 16.3C, and by x-ray diffraction measurements (1). No polymorphism was observed for elaidic acid by Benedict and Daubert (2) or for elaidic acid or any of the other *trans*-6- through 12-octadecenoic acids by Lutton and Kolp (3) or Swern et al. (4).

The existence of a new, higher-melting, stable modification of elaidic acid was first observed in connection with the recent investigation of the freezing points of binary mixtures of *cis* and *trans*, 6- and 9-octadecenoic acids (5). Two distinct solubility curves were obtained for elaidic acid in oleic acid, also in petroselinic and petroselaidic acids. The present report deals with the isolation and characterization of the new crystalline modification of elaidic acid.

Experimental Section

The elaidic acid was prepared from pure oleic acid, as previously described (6).

Solubilities and melting points were determined by the thermostatic sealed-tube method. For each composition weighed amounts of the acid and the solvent were sealed in a glass tube. Two glass beads were included to insure efficient stirring as the sample tube was turned end-over-end in a constant temperature bath. Two temperatures about 0.20 of a degree apart were noted, at one of which the last crystals just disappeared and at the other a few crystals remained undissolved after prolonged agitation. The melting point or solubility temperature was taken as the mean of these two temperatures, corrected for both thermometer calibration and emergent stem.

X-ray diffraction patterns were obtained by the direct measurement technique. An XRD5 General Electric diffractometer was used. The instrument was equipped with a copper-target x-ray tube, a Xenon-filled proportional counter tube, and a 0.007-in. nickel filter. A one-degree slit was used in collimating the 2θ angle between 0 and 50 degrees. The unit was operated at 46 KVP and 15ma.

Results and Discussion

Preparation of High-Melting Crystal Modification

The melting point of the pure solvent-crystallized elaidic acid was 43.7C by the thermostatic method. It was found however that a higher melting-point could be obtained by manipulation of the bath temperature as the rotation of the sample tube was continued. If the molten sample is heated to about 48C and then allowed to crystallize slowly at about 42C, the crystals contain a very small proportion of the higher-melting modification. The bulk of the crystals melt at 43.7C, leaving a slight turbidity. The turbidity increases perceptibly as the sample tube is turned end-over-end if the bath temperature is held between 43.7 and 44.8C, but it always disappears to form a clear melt if the temperature is raised above 44.8C. The proportion of the high-melting form can be increased by manipulating the bath temperature so as to equilibrate the sample repeatedly at 42C and just below 44.8C successively, but the rate of build-up is relatively slow. A much more rapid build-up was accomplished when the conversion procedure was carried out in an open test tube while pressing the crystals and stirring with a stirring rod as they formed. The opacity of the crystal mass increases with the degree of conversion. Melting and resolidification result in reconversion to the low-melting form.

X-Ray Diffraction Measurements

The increase in the proportion of the high-melting form can be followed by the change in the x-ray diffraction pattern of the crystals, i.e., by the decrease in intensity and eventual disappearance of the characteristic spacings of the low-melting form. Complete disappearance of some of these spacings was attained only after a lengthy storage of the highly converted samples. Table I shows the diffraction patterns of A, the low-melting form; B, a partially converted sample; C, an extensively converted sample; and D, a completely converted sample obtained by storing Sample C at room temperature for about two years. The values given are averages based on two or more experimental measurements.

The two crystal modifications have distinctive x-ray diffraction patterns (Table I). The long-spacing value, 48.7Å, found for the common low-melting form crystals, is in good agreement with the value 48.9Å, reported by Benedict and Daubert (2), and the average values, 49.5 and 49.0Å, reported by Lutton and Kolp (3) and Swern et al. (4), respectively, for the *trans*-7-, 9-, and 11-octadecenoic acids.

The long-spacing patterns for the high-melting (opaque) modification was unusual for a crystalline long-chain compound. The only orders represented were the 4th (very weak) and the 12th to 18th, correspond-

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TABLE I
X-Ray Diffraction Data for Elaidic Acid, in Å

A Metastable form		B Partially converted	C Extensively converted	D Stable form	
Long Spacings					
d/n	n	d/n	d/n	d/n	n
49.0vs	1	47.8vs	49.3m	23.7vw	4
24.1m	2	24.2w			
16.1vs	3	16.2s	16.4vw		
12.2w	4				
9.70vs	5	9.74m	9.84vw		
8.18vw	6	7.82vw	7.84w	7.84w	12
			7.22vw	7.23vw	13
6.98m	7	6.98w	6.97vw	6.99vw	
6.11vw	8		5.22vw	6.22vw	15
5.42vw	9		5.88vw	5.88vw	16
4.88w	10			5.24vw	18
Av.d 48.7		48.5	49.1	94.0	
Short Spacings					
		4.55s	4.56s	4.55s	
		4.44s	4.44vs	4.44vs	
4.12vs		4.12vs	4.12m	4.07vw	
3.71s		3.81s	3.81vs	3.81vs	
3.50s		3.69s	3.68s	3.68s	
3.06m		3.52m	3.52s	3.52s	
2.72m		3.35vw	3.35	3.35w	
2.33w		2.33m	2.33w	2.33m	
2.24s		2.24m			
		2.20w	2.20w	2.20w	
2.15m		2.15w	2.04w	2.04w	

ing to a long-spacing value of 94.0Å, or possibly 47.0Å. There were no lines of even medium intensity above 4.55Å, and the 4th order was observed in only one sample. Other examples of this unusual type of pattern have been reported in the literature. For the high-melting, opaque form of oleic acid Lutton (1) observed long-spacing lines for only the 2nd order and the 9th to 16th orders, all of weak or very weak intensities. He reported a probable long-spacing value of 84.4Å, or possibly 42.2Å, as compared with 40.5Å for the low-melting form. A complete absence of the long-spacing lines was also observed by Lomer (7) for the γ modifications of lauric and myristic acids, which formed from the α-modifications "by spontaneous but slow transformation in the solid state."

The two modifications of elaidic acid also have distinctive short-spacing patterns. The low-melting crystals give a very strong line at 4.12Å and a prominent line at 3.71Å. The high-melting form is characterized by strong lines at 4.55, 4.44, 3.81, and 3.68Å.

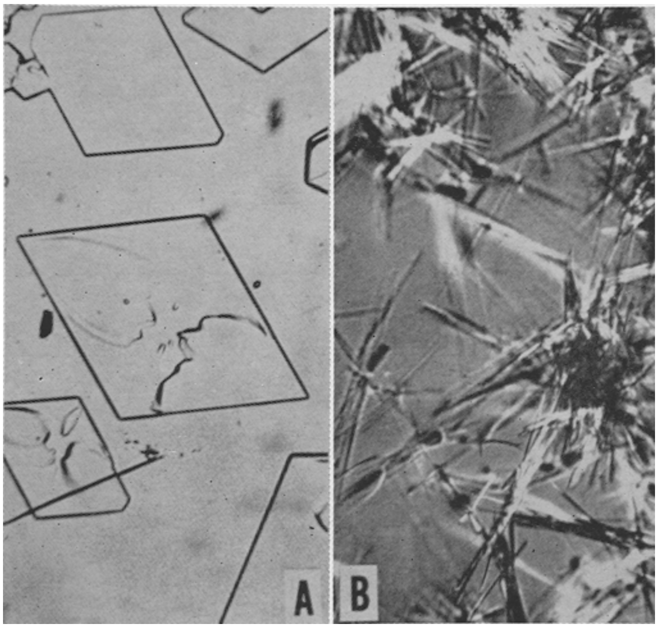

FIG. 1. Photomicrographs of elaidic acid crystals (195X): *A*, metastable form; *B*, stable form.

TABLE II
X-Ray Diffraction and Melting-Point Data for Elaidic Acid and Its Positional Isomers

	mp °C	Long spacing Å	Principal short spacings Å
Elaidic acid			
Metastable	43.7	48.7	4.12vs, 3.71s
Stable	44.8	94.0	4.55s, 4.44vs, 3.81vs, 3.68s
Trans-m-octadecenoic acids			
m = 7, 9, or 11	43.5–44.0	49.5[a]	4.15vs, 3.74s[a]
m = 6, 8, 10, or 12	50.5–53.4	45.5[a]	4.61s, 4.43s, 3.87s, 3.72s+[a]

[a] Reported as average values (3).

Because of their relatively high intensities these short spacings afford a sensitive test for contamination of either crystalline form by the other. The data for Sample C in Table I show that a small proportion of the low-melting form can be detected by the presence of the 4.12Å short spacing. It is interesting to note that the short-spacing pattern reported by Benedict and Daubert (2) for elaidic acid shows two strong lines, at 3.74 and 3.65Å, instead of a single strong line at 3.71Å; there is also a line at 4.57Å(m-). This may indicate the presence of a small amount of the high-melting modification in their sample.

There is an interesting relationship between the x-ray diffraction patterns of the two forms of elaidic acid and the patterns of the isomeric *trans*-octadecenoic acids. Table II summarizes the data as average values (3,4) for the *trans*-6- through 12-octadecenoic acids. This series exhibits alternation of melting points and also of x-ray diffraction patterns. The "odd" (7-, 9-, and 11-) members of the series have a crystal long-spacing of about 49.5Å, and their short-spacing patterns are characterized by two strong lines, at about 4.15 and 3.74Å. The "even" members of the series have ling spacings of about 45.5Å and a more complex short-spacing pattern with strong lines at about 4.61, 4.43, 3.87, and 3.72Å. For the odd members the short-spacing pattern is similar to that of the low-melting form of elaidic acid. For the even members it resembles that of the high-melting form. The simpler short-spacing pattern in both instances is associated with the lower melting-point and the higher angle of tilt.

Short-spacing patterns similar to those for the two forms of elaidic acid have also been reported for polymorphic forms of other long-chain derivatives. For example, the principal short-spacings reported for the C form of stearic acid are 4.14 and 3.70Å, and for the A form, 4.65, 4.51, 3.79, and 3.63Å (8). Those reported for Lutton's "beta-prime" modification of tristearin (mp 64C)are 4.18 and 3.78Å and for his "beta" form (mp 73.1C) they include 4.61, 3.84, and 3.68Å (9). The spacings for the β (opaque) form of ethyl stearate are 4.08 and 3.69Å (8,10), and for the opaque form of octadecane they are 4.58, 3.80, and 3.66Å (11). Because of the lack of an accepted, consistent system of nomenclature for the polymorphs of long-chain fatty derivatives, the two polymorphic forms of elaidic acid

TABLE III
Solubility Data for the Two Polymorphic Forms of Elaidic Acid in Methanol

Mole % elaidic acid	Freezing point, °C	
	Stable form	Metastable form
0.0474	− 7.7	
0.39	8.0	
1.08	15.3	15.1
2.90	20.6	20.2
10.14	26.2	25.6
49.90	38.1	37.1
100.00	44.8	43.7

are referred to only as the common, low-melting or metastable form and the new, high-melting or stable form.

Microscopic Examination

Photomicrographs of the crystals of each of the modifications were obtained as they were formed from the melt by careful manipulation of the hot-stage temperature. The crystals of the low-melting modification were transparent, parallelogram platelets (Fig. 1A). There were formed by spontaneous crystallization. The high-melting crystals were opaque rod clusters (Fig. 1B). These were obtained in localized areas of the microscope slide either by partially melting crystals of the high-melting form and partial resolidification or by seeding a melt with fine crystals of the high-melting form, followed by partial solidification.

Solubility Determinations

Solubility data were obtained for the two modifications in absolute methanol. The low-melting form has a slightly greater solubility and was the only form that could be obtained once the crystals had gone into solution. Therefore crystals of the high-melting modification had to be used in preparing the sample tubes for measuring the solubilities of this form, and the solubility temperature had to be approached from below.

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