[CONTRIBUTION FROM THE CHEMICAL DIVISION OF THE PROCTER & GAMBLE COMPANY]

A Study of *n*-Octadecenoic Acids. V. The Polymorphism of Some Elaidyl and Petroselaidyl Triglycerides

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Phase behavior has been studied for the triglycerides obtained by introducing (separately) elaidyl and petroselaidyl radicals into glycerol, 1-monopalmitin and -stearin, and 1,3-dipalmitin and -stearin—also for the triglycerides 2-palmityl- and 2-stearyl dielaidin. There is considerable similarity especially between corresponding elaidyl and petroselaidyl individuals. The familiar alpha, beta prime and beta double-chain-length forms of the C_{16}–C_{18} saturated triglycerides may be called typical for the present compounds, although beta prime forms are lacking for 5 of the 12 individuals. No triple-chain-length structures such as are common with mixed oleyl-saturated triglycerides have appeared. In the few cases where comparison can be made with earlier work there is fair agreement especially with regard to diffraction pattern. However, modifications in the association of pattern with melting point are necessary, since, as in previous cases, Malkin's so-called "vitreous" form was not confirmed. Three separate preparations of 1-palmityl dielaidin gave a compound melting 6° lower than has been reported in the literature.

In this paper are reported phase studies of the triglycerides EEE, PEE, SEE, PEP and SES, where E, P and S stand for elaidyl, palmityl and stearyl radicals, respectively—and also phase studies of the corresponding glycerides in which Pe (petroselaidyl) replaces E. In addition, results for EPE and ESE are reported.

Carter and Malkin[1] and Malkin and Wilson[2] have reported work on EEE, PEP and SES. As in previous instances,[3] their so-called "vitreous" forms were not confirmed in this Laboratory, and different association of diffraction pattern with melting point is required. With the results of Filer, *et al.*,[4] on EEE, the present data are in essential agreement.

Daubert[5] has reported the preparation of PEE and SEE. Present data are in agreement with his m.p. for SEE, but three preparations of PEE have given a m.p. of 40° which is 6° lower than his value. This lower m.p. is not due to a metastable polymorph since the normally highest melting beta form was obtained here.

Of the petroselaidyl glycerides, only PePePe has been previously reported. Steger and Van Loon[6] have reported a m.p. in fair agreement with the value found here.

Experimental

The triglycerides were prepared, according to recognized procedures, by treating elaidyl or petroselaidyl chloride with glycerol, monoglycerides or diglycerides as required by the configuration of the desired product. The mono- and diglycerides were prepared[7] by directed interesterification.[8] The acid chlorides were prepared by the reaction of purified elaidic and petroselaidic acids with oxalyl chloride followed by vacuum distillation. After synthesis, the triglycerides were crystallized four to six times from solvents—acetone, petroleum ether or ether. Analytical data for the triglycerides are given in Table I. Sufficient description of procedures for studying triglyceride polymorphism has been presented in earlier papers from this[3] and other laboratories. Characteristic thermal and diffraction data appear in Table II. Relative stability of the various forms is indicated in Table III.

TABLE I

ANALYTICAL CONSTANTS OF TRIGLYCERIDES

	Iodine value		*trans* I.V.[a]	M.p., °C.	
	Exptl.	Theory	(by infrared)	Exptl.	Lit.
EEE	85.8	86.0	84.5	42.4	42.0[4]
PEE	58.8	59.1	58.1	40.3	46.0[5]
SEE	56.4	57.2	55.9	49.9	49.5[6]
PEP	28.7	30.5	28.5	53.3	
SES	27.0	28.5	26.7	59.5	
EPE	56.5	59.2	58.4	44.5	
SES	54.6	57.3	55.7	50.1	
PePePe	85.4	86.0	85.6	52.5	50.1[6]
PPePe	58.6	59.1	59.5	46.4	
SPePe	56.7	57.2	55.9	55.0	
PPeP	29.8	30.5	30.1	54.2	
SPeS	28.1	28.5	29.1	62.6	

[a] *trans* I.V. is used to express *trans* double bonds in terms of iodine value.

Discussion

As in numerous previous instances it is observed that the lowest melting forms of these glycerides are alpha with definite long spacings. Thus present results are in disagreement with those of Malkin, *et al.*,[1,2] on EEE, PEP and SES (but are in essential agreement with Filer, *et al.*,[4] on EEE). After dispensing with the vitreous form, there is observed one less form and generally one less melting level than reported by Malkin, *et al.* Otherwise data for m.p. and diffraction spacing are in moderate agreement, with the exception of X-ray data on the beta form of PEP.

The elaidyl and petroselaidyl glycerides all show double-chain-length structures in all forms. This is like tristearin and various C_{16}–C_{18} saturated mixed triglycerides and rather unlike the corresponding oleyl compounds which commonly show triple-chain-length structures. This difference shows the greater tendency of oleyl chains to segregate, or alternatively the greater compatibility of elaidyl or petroselaidyl with saturated chains.

There is a very high degree of similarity in behavior between the corresponding elaidyl and petroselaidyl compounds. This is indicated by absence of beta prime for EEE, PePePe, SEE and SPePe. An exception occurs with the appearance of beta prime for SES but not SPeS. It is notable that both PEP and PPeP have beta prime forms which appear to melt about as high as the corresponding beta forms. The petroselaidyl glycerides melt

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[1] M. G. R. Carter and T. Malkin, *J. Chem. Soc.*, 554 (1947).

[2] T. Malkin and B. R. Wilson, *ibid.*, 369 (1949).

[3] E. S. Lutton, F. L. Jackson and O. T. Quimby, THIS JOURNAL, **70**, 2441 (1948).

[4] L. J. Filer, Jr., S. S. Sidhu, B. F. Daubert and H. E. Longenecker, *ibid.*, **68**, 167 (1946).

[5] B. F. Daubert, *ibid.*, **66**, 290 (1944).

[6] A. Steger and J. Van Loon, *Rec. trav. chim.*, **46**, 703 (1927).

[7] By Dr. F. J. Baur of this Laboratory.

[8] (a) E. W. Eckey and M. W. Formo, *J. Am. Oil. Chem. Soc.*, **26**, 207 (1949); (b) F. J. Baur and W. Lange, THIS JOURNAL, **73**, 3926 (1951).

TABLE II

CHARACTERISTIC THERMAL AND X-RAY DIFFRACTION DATA

	EEE	PEE	SEE	PEP	SES	EPE	ESE	PePePe	PPePe	SPePe	PPeP	SPeS
M.p., °C.												
Alpha	15.3	22.8	28.8	36.8	42.9	26.0	34.0	18.8	26.4	31.5	35.9	43.4
Beta prime		33		53.2	47	32.0	43.2		35.9		54.3	
Beta	42.4	40.3	49.6	53.3	59.5	44.5	50.1	52.5	46.4	55.0	54.9	62.6
X-Ray data: long spacings, Å.												
Alpha	49.6	48.8	50.5	45.5	50.8	48.6	48.7	49.5	48.9	50.5	47.5	50.8
Beta prime		44.3		43.0	46.9	44.1	45.9		45.3		42.7	
Beta	44.6	44.1	44.75	42.05	45.0	43.2	44.8	44.6	43.4	44.6	41.7	44.8
Short spacings, Å.												
Alpha	4.15S	4.15S	4.15S	4.15S	4.15S	4.12S	4.12S	4.15S	4.12S	4.13S	4.13S	4.13S
Beta prime		4.18S		4.20S	4.36S	4.09S	4.2S(diff.)		4.21S		4.20S	
					4.16S							
		3.83M		3.85M	3.82M	3.81S−	3.82S−		3.86M		3.82S	
Beta	5.6W	5.32M	5.25W	5.30M	5.35W	5.30W+	5.34M	5.32W	5.34W	5.34M	5.32M	5.45W
	4.58S	4.60VS	4.87W	4.60S+	4.61S	4.58S+	4.56S	4.56S	4.55S	4.55S	4.58S	4.58S
	3.93M	3.90M	4.56S	3.87S−	3.90S−	3.82S+	3.87S	3.88M	3.86S	3.86S	3.82S	3.87M
	3.71M	3.72M	3.91M	3.78S	3.75S−		3.63S	3.80S	3.80S	3.77S		3.75M
			3.70W+									

TABLE III

STABILITY OF VARIOUS FORMS OF GLYCERIDES

U, unstable; S, stable; V, very; M, moderately; MM, more than moderately

EEE	PEE	SEE	PEP	SES	EPE	ESE
Elaidyl glycerides						
α(U)	α(U)	α(MMS)	α(MS)	α(U)	α(MS)	α(U)
....	β'(MS)	......	β'(S)	β'(U)	β'(MS)	β'(MS)
β(S)	β(S)	β(S)	β(S)	β(S)	β(S)	β(S)
Petroselaidyl glycerides						
PePePe	PPePe	SPePe	PPeP	SPeS		
α(VU)	α(U)	α(U)	α(U)	α(MS)		
....	β'(U)	......	β'(MMS)	....		
β(S)	β(S)	β(S)	β(S)	β(S)		
Comparable stearyl glycerides						
SSS	PSS	SSS	PSP	SSS	SPS	SSS
α(U)	α(U)	α(U)	α(VU)	α(U)	α(MMS)	α(U)
β'(VU)	β'(S)	β'(VU)	β'(S)	β'(VU)		β'(VU)
β(S)	β(S)	β(S)		β(S)	β(S)	β(S)

above the elaidyl glycerides by about 3° for each chain difference. The present m.p. value for PEE, 6° lower than the literature, seems definitely better in line with values for related compounds. Moreover, one of the present PEE preparations was hydrogenated to an authentic PSS of m.p. 65.0°,[3]

It is interesting to compare EEE and PePePe in the light of known differences in their fatty acid m.p.'s, 45.5° and 53.6°[9] for elaidic and petroselaidic, respectively. The glycerides in their tilted stable forms shows as much difference, but in their perpendicular alpha forms show only 3° m.p. difference. It is suggested that a m.p. alternation[10] occurs in the case of stable forms of *trans*-octadecenoic glycerides as for the corresponding acids, but a lesser alternation or perhaps none is anticipated for non-tilted alpha forms.

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[9] W. F. Huber, THIS JOURNAL, **73**, 2730 (1951).

[10] An alternation in m.p. between compounds with double bond in "odd" position, *e.g.*, *trans* 9-octadecenoic (elaidic), and compounds with double bond in "even" position, *e.g.*, *trans*-6-octadecenoic (petroselaidic) compounds.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ARKANSAS]

A Tracer Study of the Reaction of Isocyanates with Carboxylic Acids[1,2]

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By the use of C^{14}-carboxyl labeled acids, the carbon dioxide evolved during the reaction of isocyanates with carboxylic acids has been shown to come from the isocyanate. In a similar manner, the carbon dioxide produced from the reaction of carbanilide with acetic anhydride has been shown to come from the carbanilide.

The reaction between isocyanates and carboxylic acids may proceed by two different paths.[3]

$$\mathrm{RNCO + R'COOH \longrightarrow CO_2 + R'CONHR} \tag{1}$$

$$\mathrm{2RNCO + 2R'COOH \longrightarrow CO_2 + (R'CO)_2O + (RNH)_2CO} \tag{2}$$

A mixture of products corresponding to partial reaction by both paths is usually obtained. The products from reaction (2), the carboxylic acid anhydride and the urea, have been shown to undergo further reaction at higher temperatures to give carbon dioxide and two moles of the amide, R'CONHR.[3]

Dieckmann and Breest[4] showed that the first product obtained from the reaction of isocyanates with carboxylic acids was the mixed carbamic acid–carboxylic acid anhydride of the general formula

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[1] This work was supported in part by the A.E.C.

[2] Presented at the Eighth Southwest Regional American Chemical Society Meeting, Little Rock, Arkansas, December 4–6, 1952.

[3] C. Naegeli and A. Tyabji, *Helv. Chim. Acta*, **17**, 931 (1934); **18**, 142 (1935); and earlier references cited there.

[4] W. Dieckmann and F. Breest, *Ber.*, **39**, 3052 (1906).