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The Polymorphism of the Mixed Triglycerides of Palmitic and Stearic Acids

By E. S. LUTTON, F. L. JACKSON AND O. T. QUIMBY

Introduction

The four mixed triglycerides of palmitic and stearic acid are of practical as well as academic interest. Among them are generally to be found important and frequently the predominating components of most of the highly hydrogenated fats and oils of commercial significance. These compounds, as would be expected, show many similarities in polymorphism to the single fatty acid triglycerides, but there are differences more significant than is apparent in the valuable papers of Malkin.^{1,2}

The work of Clarkson and Malkin³ on the simple triglycerides was corrected by other observers.^{4,5,6} None of these later authors was in disagreement

connection with unsymmetrical glycerides, but it is generally felt that this is a matter of little physical significance for longer acyl groups. In this paper only such "racemic" mixtures as are prepared by ordinary synthesis are discussed.)

Experimental

The four mixed glycerides were made by established methods from the corresponding mono- or diglyceride by reaction with the proper fatty acid chloride. The mono- and diglycerides were prepared by directed rearrangement according to the method of Eckey.⁸ Fatty acids were purified by distillation and by crystallization from glacial acetic acid. From the acids the corresponding chlorides were prepared by reaction with thionyl chloride and subsequent distillation. Constants for the starting materials are given in Table I along with those of the final products.

TABLE I

ANALYSES OF STARTING MATERIALS AND PRODUCTS

I. V. = iodine value, S. V. = saponification value, H. V. = hydroxyl value, % monoglyceride is by the Mehlenbacher periodic acid method.

	I. V.		S. V.		H. V.		% Mono-glyceride	Setting pt., °C.		M. p., °C.	
	Exp.	Theory	Exp.	Theory	Exp.	Theory		Exp.	Lit. ⁹	Exp.	Lit. ^{10,11,5,6}
Palmitic acid	0.1		220	219				62.6	62.60		
Stearic acid	.1		196	197				69.5	69.39		
1-Monopalmitin	.0		169	169.6			98.4			76.5	77
1-Monostearin	.1		156.3	156.4			101.9			81.5	81.5
1,3-Dipalmitin	.0		197.4	197.3	99	98	0.45			72.4	72.5
1,3-Distearin	.1		179.4	179.7	92	90	0.4			78.2	78
SPS			194.7	195.2						68.5	68
PSS			194.9	195.2						65.2	65
PSP			201.6	201.6						68.6	68
SPP			201.4	201.6						62.7	62.5

with Malkin as to number of forms and melting points. The differences from Malkin arose in association of melting points with diffraction patterns and in nomenclature. It is to be emphasized, however, that the nomenclature of the present authors⁷ follows the lead of Malkin in designation of X-ray patterns, except in details particularly involving the term "beta prime." Here a form is called "beta prime" on the basis of X-ray pattern type rather than order of melting.

In view of the situation with regard to the simple triglycerides, there has been great need for reexamination of the four important mixed glycerides of palmitic and stearic acids—namely, the symmetrical glycerides, 2-palmitylidistearin (SPS) and 2-stearylidipalmitin (PSP), and the unsymmetrical glycerides, 1-palmitylidistearin (PSS) and 1-stearylidipalmitin (SPP). (Theoretically the matter of optical isomerism is to be considered in

A typical synthesis, that of 1-palmitylidistearin, is described in some detail. Twenty grams (0.061 mole) of 1-monopalmitin was dissolved in 50 g. (0.632 mole) of pyridine and 20 ml. of anhydrous chloroform. To this mixture, 41.5 g. (0.137 mole) of stearyl chloride was added slowly while the reaction vessel was cooled in an ice-bath. The mixture was then warmed on a steam-bath for six hours in order to complete the reaction. After this step, the reaction mixture was dissolved in ether and washed consecutively, twice with water, four times with 10% potassium carbonate, three times with dilute sulfuric acid and finally with water until neutral to litmus paper. The ether solution was dried over anhydrous sodium sulfate and filtered. Final purification was accomplished by four crystallizations, one from ether and three from Skellysolve B-ethyl alcohol (1:1) mixtures.

The symmetrical glycerides showed good crystallinity as compared with the chalk-like appearance of unsymmetrical compounds.

The polymorphism of the glycerides was studied by the X-ray and melting point techniques described previously.⁵ Briefly flat film patterns were obtained with a regular General Electric XRD unit. The pinhole was 0.025" and film distances were 2.5 cm. for exploratory patterns, 5.0 cm. for most short spacing determinations and 10.0 cm. for detailed short spacing and for long spacing pat-

(1) Malkin and Meara, *J. Chem. Soc.*, 103 (1939).(2) Carter and Malkin, *ibid.*, 577 (1939).(3) Clarkson and Malkin, *ibid.*, 666 (1934).(4) Bailey, *et al.*, *Oil & Soap*, **22**, 10 (1945).(5) Lutton, *THIS JOURNAL*, **67**, 524 (1945).(6) Filer, *et al.*, *ibid.*, **68**, 168 (1946).(7) Lutton, *ibid.*, **79**, 248 (1948).

(8) Eckey, U. S. Patent 2,442,534 (June 1, 1948).

(9) Francis and Piper, *THIS JOURNAL*, **61**, 578 (1939).(10) Malkin, *et al.*, *J. Chem. Soc.*, 1628 (1936).(11) Malkin, *et al.*, *ibid.*, 1409 (1937).

terns. In the case of 2-palmitoyldistearin, it was necessary to take 10 cm. patterns with a 0.005" slit system for sufficient resolution of certain prominent lines.

For alpha forms three types of capillary thermal points were obtained:

Softening Point.—Sample melted, chilled two seconds at 0°, thrust into bath for observation. Softening point is half-way between the highest point of no increased translucence and the lowest point of definite increase in translucence.

Rapid Complete Melting Point.—Sample melted, cooled rapidly to minimum cloud, thrust into bath. This determination is completed as for the softening point except that complete clarity instead of increased translucence is observed.

Regular Complete Melting Point.—Sample melted, chilled, observed for complete clarity on raising the temperature 0.5° or less per minute.

Beta prime forms were obtained in three ways—from alpha by tempering near the alpha melting point, from melt just above the alpha melting point, and in one case by solvent crystallization (usually Skellysolve B). Melting points were obtained by observing the sample while raising the temperature 0.5° or less per minute.

Beta forms were obtained from beta prime by tempering near the beta prime melting point (or from alpha) and by solvent crystallization (usually Skellysolve B). Melting points were obtained by observing the sample while raising the temperature 0.5° or less per minute.

Detailed melting point and X-ray data are recorded in Tables II and III, respectively. Characterizing data compared with those for tripalmitin and tristearin are to be found in Table IV.

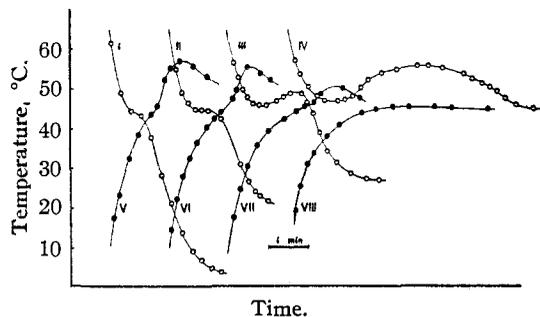


Fig. 1.—Cooling and heating curves indicating the alpha m. p. for PSP. Cooling curves—O, samples melted 100°, placed at temperature without jacket—I, 0°; II, 17°; III, 27°; IV, 44°. Heating curves—●, samples melted, chilled 10°, placed at temperature without jacket—V, 49°; VI, 47°; VII, 45°; VIII, 44°.

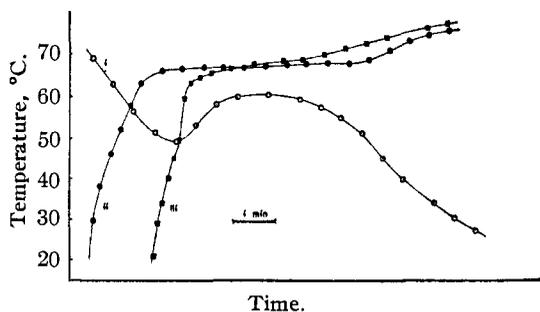


Fig. 2.—Cooling and heating curves involving beta prime for PSP, jacketed samples—I, melted, placed 0°—○; II after I, placed 80°—●; III melted, chilled 10° (no jacket), jacketed at 80°—■.

Thermal curves were run on a 1-g. sample of PSP after the manner of Clarkson and Malkin.³ The procedure has been described previously in some detail.¹² Examples of the curves are shown in Figs. 1 and 2.

TABLE II

THERMAL DATA FOR MIXED PALMITIC-STEARIC TRIGLYCERIDES

		SPS	PSS	PSP	SPP
S. P. = softening point, C. M. P. = complete m. p.					
Alpha	S. P.	50.8	49.6	46.5	46.8
	Rapid C. M. P.	51.0	50.6		47.4
	Regular C. M. P.	51.8			
Beta prime	S. P.		61.1	65.0	57.7
	Rapid C. M. P.		62.1		58.3
	Regular C. M. P.		65.0	68.6	61.7
	Solvent C. M. P.			68.6	
Beta	Regular C. M. P.	67.7			62.4
	Solvent C. M. P.	68.5	65.2		62.7

Discussion

These glycerides are more striking in their individuality than in their similarity. Thus one of them is quite unstable as alpha, another is relatively stable. While two are normal in being thermodynamically beta stable, one is beta prime stable and the fourth is apparently equally stable as beta prime or beta.

No vitreous (or gamma) form was found for any of these glycerides. Accordingly no more than three forms, never four, were found for each compound. For a given form of a given glyceride, *actual variation of complete melting point with extent of stabilization is common* and must be the basis for the excess "characteristic" melting points which have been previously reported.^{1,2} As much as three degrees variation was observed. It was observed that long spacings were constant with such m. p. variation, while short spacings showed only differences in sharpness.

The two symmetrical glycerides offer a most interesting contrast. It is the alpha form of SPS that is unusually stable while that of PSP is so unstable that no complete melting point for it can be obtained, and the observer must be content with a softening point. Neither glyceride shows more than one form beside alpha. Most startling is the fact that, while beta is the stable form for SPS, as would be expected, beta prime is stable for PSP. The short spacing data of Malkin,¹ by the present nomenclature⁷, lead to this same conclusion with regard to PSP, for the form he called beta had no 4.6 Å. spacing but only slightly modified beta prime spacings. The absence of a beta prime form for SPS is a matter of some concern especially since later work has revealed this form for the closely related homolog, 2-myristoyldistearin.¹³ Moreover, it is known that small amounts of impurity permit beta prime development in SPS. However, there can be no doubt that if the beta prime form exists for pure SPS it is extremely fleet-

(12) Ferguson and Lutton, *THIS JOURNAL*, **69**, 1445 (1947).

(13) Jackson and Lutton, unpublished.

TABLE III
 DETAILED d/n VALUES FOR MIXED PALMITIC-STEARIC TRIGLYCERIDES

(hkl)	SPS		PSS			PSP		SPP		
	Alpha	Beta	Alpha	Beta prime	Beta	Alpha	Beta prime	Alpha	Beta prime	Beta
001	48.9 VVS	42.75 VS	48.5 VS	44.9 VS	44.4 VS	47.0 VS	42.8 VS	47.7 VS	43.7 VS	42.0 VS
002	24.5 W	21.7 M	24.3 W-	22.3 VW-	22.7 VW	..	(21.2 VW)	24.0 VW	21.4 VW-	21.4 VW
003	16.5 S+	14.3 S+	16.1 S	15.0 S	14.8 M	15.55 M	14.22 M	14.1 S	14.5 S	14.2 S
004				11.5 VW-				11.8 VW-	11.2 W	10.6 VW-
005	9.86 W	8.66 W	9.75 W+	9.00 M	8.94 VW-	9.30 W	8.59 W	9.50 W	8.88 W	8.36 W
006	8.22 W-	7.22 W	8.13 W	7.50 M		7.75 VW	7.05 W	7.97 W	7.30 W	6.88 VW
007									6.26 VW	
008									5.45 M	
Av. d	49.2	43.1	48.5	45.1	44.7	46.65	42.75	47.6	43.8	42.1
Long Spacings										
	4.14 VS	5.34 M	4.14 VS	4.37 M	5.34 M	4.13 VS	4.34 M	4.13 VS	4.30 VS	5.33 M
	2.40 VW	5.20 M-	2.41 VW	4.23 VS	4.90 W	2.40 VW	4.18 VS	2.40 W	4.15 S	4.61 VS
		4.57 VS		4.07 M	4.61 VS		3.99 M		3.83 VS	4.29 W
		4.44 M		3.81 S	4.28 W		3.75 S		3.13 VW	4.12 VW
		4.24 W		3.48 VW	4.07 W		3.35 VW		2.83 VW-	3.85 S
		4.12 W		3.13 W	3.87 S		3.12 VW		2.57 VW	3.67 S
		3.97 M		3.02 VW-	3.67 S		3.00 VW-		2.98 VW-	2.85 VW-
		3.81 S ^a		2.82 VW-	3.43 VW-		2.79 VW		2.29 VW	2.58 M
		3.72 S+ ^a		2.78 VW	3.30 VW		2.58 VW-			2.41 W
		3.62 W		2.56 VW	2.84 VW		2.52 VW			2.31 W
		3.30 W-		2.40 VW-	2.58 M		2.26 VW+			2.23 VW
		3.21 W		2.27 W	2.40W					2.14 VW
		2.84 VW		2.10 VW-	2.28 W					2.07 W
		2.54 M-		1.89 VW-	2.07 W					1.96 VW-
		2.49 W			1.97 VW-					
		2.27 W								
		2.20 VW								
		2.12 VW								
		2.06 W								
		1.93 W								
		1.85 VW								
		1.79 VW								
		1.68 VW								

^a Resolved by 0.005" slit, 10 cm. sample to film distance.

 TABLE IV
 CHARACTERISTIC THERMAL AND X-RAY DATA FOR PALMITIC-STEARIC TRIGLYCERIDES

	SSS ^{5,14}	SPS	PSS	PSP	SPP	PPP ^{5,14}
Melting Points						
Alpha	54.9	51.8	50.6	46.5	47.4	44.7
Beta Prime	64	..	61.1-65.0	68.6	57.7-61.7	56.6
Beta	73.1	68.5	65.2	..	62.7	66.4
X-Ray Data: Long Spacings						
Alpha	50.6	49.2	48.5	46.65	47.6	46.8
Beta Prime	46.8	..	45.1	42.75	43.8	42.3
Beta	45.15	43.1	44.7	..	42.1	40.9
Short Spacings						
Alpha	4.14 VS	4.14 VS	4.14 VS	4.13 VS	4.14 VS	4.14 VS
Beta Prime	4.18 VS	..	4.37 VS	4.34 M	4.30 VS	4.18 VS
	3.78 S		4.23 VS	4.18 VS	4.15 S	3.78 S
			4.07 M	3.99 M	3.83 S	
			3.81 S	3.75 S		
Beta	5.24 M	5.34 M	5.34 M		5.33 M	5.24 M
		5.20 M-				
	4.61 VS	4.57 VS	4.61 VS		4.61 VS	4.61 VS
	3.84 S	3.81 S	3.87 S		3.85 S	3.84 S
	3.68 S	3.72 S+	3.67 S		3.67 S	3.68 S

ing. The beta form of SPS is characterized by the closeness of the two spacings near 3.8 Å., unresolved on ordinary patterns of 5-cm. sample to film distance.

(14) Quimby, unpublished.

Cooling and heating curves have been used often by Malkin and by others to study the polymorphism of triglycerides. Properly interpreted they can give valuable information, but there are pitfalls. Complicated relationships existing between

environment, sample and thermocouple and the imperfection of quickly formed crystals are some of the factors which can result in apparently shifting the characteristic level of thermal change. Actually one may obtain halts, bends or nicks in thermal curves at practically any temperature from the minimum to the maximum melting point of a pure triglyceride. It is necessary to confirm the significance of breaks by showing that they occur at approximately the same level with fairly wide variations in surrounding conditions.

Among the mixed glycerides discussed here only PSP has been subjected to thorough examination by thermal curves. It is particularly worthy of investigation since only two forms, instead of the previously reported four,¹ have been found. The curves, Figs. 1 and 2, while they actually support the conclusion that only two forms occur, do show how one may be led astray.

The cooling curves of Fig. 1 plainly show a thermal effect (halt, nick or minimum) at 45 to 47° in spite of large variations in cooling rate. The value is in good agreement with the alpha melting point level for PSP, Table II, and is in line with the general experience of agreement between alpha m. p. and supercooling limit for triglycerides. The heating curves of Fig. 1 also reveal this characteristic thermal point. At the inflections of these latter curves the phenomena are not simple for there are involved (1) melting of alpha, (2) transformation of alpha to beta prime and (3) beta prime crystallization from melt.

The level of beta prime melting is indicated by the heating curves of Fig. 2. Curve I, a cooling curve, shows how one may, from minima and maxima, obtain values between alpha and beta prime m. p. values, but a real significance for these values cannot be confirmed visually, nor by X-ray nor by a series of systematically varied thermal curves. Curve II of Fig. 2, following after I, shows only beta prime melting at the normal level. Curve III, run on a quickly chilled (alpha) sample, shows a slight inflection indicative of alpha melting below 50° but the main feature is beta prime melting in the neighborhood of 68°. Thus only alpha and beta prime forms were confirmed.

The differences between the unsymmetrical glycerides, while not so striking as for the symmetrical glycerides, are of equal interest. Both 1-palmityl-distearin (PSS) and 1-stearylpalmitin (SPP) show the three forms—alpha, beta prime and beta. For PSS, however, beta is obtained only from solvent. The stable form from the melt is beta prime. Accordingly, it is found on stabilization to rise in m. p. almost to the level of the beta m. p. obtained after solvent crystallization.

These four mixed glycerides may be conveniently grouped with regard to the stable form from the melt according to the nature of the acyl residue in the 2-position. This is indicated in Table V.

One must infer from the evidence here presented that many of the homologs of these glycerides

TABLE V
STABLE FORMS FROM THE MELT

	Beta prime stable	Beta stable
Unsymmetrical	PSS	SPP
Symmetrical	PSP	SPS
Acyl in 2- position	S	P

which have been discussed by Malkin, *et al.*, must also in many cases have only three, perhaps only two, forms instead of four as reported. For example Malkin's own X-ray data¹ indicate that the glycerides grouped with PSP on the basis of similarity in molecular geometry (namely, 2-palmityl-dimyristin, 2-myristyldilaurin and 2-lauryldicaprin) must have only two forms, metastable alpha and stable beta prime.

Important differences from the evidence of Malkin, *et al.*, for these four mixed glycerides are here summarized: (1) As in the case of tristearin, no glassy forms were observed, *alpha* actually being the lowest melting form in each case. (2) The number of forms for a given glyceride in no case exceeded three and in two cases was two in contrast to Malkin's recording of four forms. (The variation in melting point here reported for a given form of a given compound seemingly is responsible for Malkin's reporting of superfluous melting points.) (3) The stable form of PSP is called beta prime (instead of beta) according to the modification of Malkin's nomenclature, which has been used in the present work. (4) Also for PSP is reported the impossibility of achieving a complete melting point for the alpha form. The observed softening point is 3° below Malkin's "melting point" value. (5) For SPS no beta prime form is here reported and beta has a characterizing feature; this is the closeness of the two smaller main short spacings so that they are unresolved on an ordinary 5 cm.-0.025" pinhole pattern (Malkin's values for these spacings are farther apart). (6) Differences in long spacing data are best discussed in relation to Table VI.

TABLE VI

COMPARISON WITH MALKIN'S LONG SPACINGS
(LJQ) are data of Lutton, Jackson and Quimby.
(M) are data of Malkin and co-workers

	SPS			PSP		
	α	β'	β	α	β'	β
(LJQ)	49.2	..	43.1	46.65	42.75	..
(M)	50.5	47.5	44.2	50.2	44.7	43.2

	PSS			SPP		
	α	β'	β	α	β'	β
(LJQ)	48.5	45.1	44.7	47.6	43.8	42.1
(M)	48.8	44.7	46.5	47.8	43.9	42.5

In several cases agreement is within experimental error; in a few instances differences are of the order of 1.0 Å. Serious differences are a 3.55 Å. difference for the alpha form of PSP, a 1.8 Å. difference for the beta form of PSS and difference as to the existence of a beta value for PSP. It is presumed that Malkin's value reported for beta

prime PSP is not correct but that his value for "beta" is the true beta prime long spacing value. Malkin's beta prime value for a pure SPS is tentatively questioned on the basis of the present authors' failure to obtain such a form.

Acknowledgment.—The authors wish to express their appreciation for permission from the Procter & Gamble Co. to publish the portions of this investigation which are of general interest, and to the members of this laboratory who have assisted in the experimental work and have given advice in the preparation of the manuscript.

Summary

As compared with the great similarity in polymorphic behavior of the single fatty acid saturated triglycerides, the mixed palmitic-stearic triglycerides show a remarkable individuality. Many of the conclusions here reached with regard to their behavior are at variance with those of Malkin and co-workers.

The symmetrical isomers show a high degree of crystallinity; the unsymmetrical compounds are

microcrystalline. All four compounds exhibit a lowest melting alpha form—unusually stable in the case of 2-palmitoyldistearin and unusually labile in the case of 2-stearoyldipalmitin.

Occurrence of forms other than alpha can be briefly tabulated:

Glyceride	Forms beside <i>alpha</i>
2-Palmitoyldistearin	Only beta
2-Stearoyldipalmitin	Only beta prime
1-Palmitoyldistearin	Only beta prime from melt, beta from solvent (beta prime and beta equally stable)
1-Stearoyldipalmitin	Beta prime and beta (beta stable)

A given form of a given glyceride may vary several degrees in melting point depending on its degree of stabilization. This variation may account for the fact that previous workers have reported more characteristic thermal points for a given glyceride than can be substantiated by X-ray diffraction patterns.

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RECEIVED FEBRUARY 6, 1948

[CONTRIBUTION FROM THE PROCTER & GAMBLE CO.]

The Polymorphism of 1-Monostearin and 1-Monopalmitin

By E. S. LUTTON AND F. L. JACKSON

Introduction

The polymorphism of the compounds 1-monocaprylin through 1-monostearin has been studied by Rewadikar and Watson¹ by means of capillary melting point methods but without the help of X-ray diffraction data. Malkin and co-workers,^{2,3,4} using X-ray diffraction and thermal techniques, have studied the polymorphism of saturated 1-mono-, 1,3-di- and triglycerides. However, further work has led to corrections and new interpretations in the field of triglycerides.^{5,6,7} Similarly, re-examination of the 1-monoglycerides, specifically 1-monostearin and 1-monopalmitin, as reported in the present paper has shed new light on the polymorphic behavior of this class of compounds.

As in the case of the triglycerides⁶ every effort has been made to maintain the nomenclature introduced by Malkin.³ However, the discovery of four polymorphic forms (here called subalpha, alpha, beta prime and beta) instead of three for the 1-monoglycerides and the fact that subalpha and beta prime have very similar X-ray patterns required some revision and refinement of Malkin's basis for nomenclature. A particular compli-

cation is the subalpha form, a distinct form accounting for the reversible thermal effects reported by Malkin on cooling alpha and subsequent reheating.

The basis for monoglyceride nomenclature may be summarized as follows.

Subalpha has a single strong short spacing line at 4.15 Å., other medium lines at 3.9, 3.75 and 3.55 Å. This form undergoes a reversible transformation to alpha and therefore has no m. p.

Alpha has a single strong short spacing line at 4.15 Å. with other weak short spacing lines. This form has the lowest complete m. p. Triglyceride alpha similarly has a single strong short spacing line at 4.15 Å. and is the lowest melting form.

Beta prime has a strong short spacing line at 4.15 Å., and a 3.65 Å. medium line which is the strongest one between 4.2 and 2.6 Å. This form has an intermediate complete m. p. Triglyceride beta prime has strong spacings at 4.2 and 3.8 Å., and is normally the intermediate melting form.

Beta has a strong short spacing line at 4.55 Å. and is the highest melting form. Triglyceride beta has a strong line at 4.6 Å. and is generally the highest melting form.

It is apparent from the preceding paragraphs that the bases for nomenclature are similar for the mono- and triglycerides.

Experimental

The monoglycerides were prepared according to the

- (1) Rewadikar and Watson, *J. Indian Inst. Sci.*, **13**, A, 128 (1930).
- (2) Clarkson and Malkin, *J. Chem. Soc.*, 666 (1934).
- (3) Malkin and Shurbagy, *ibid.*, 1628 (1936).
- (4) Malkin, Shurbagy and Meara, *ibid.*, 1409 (1937).
- (5) Bailey, *et al.*, *Oil & Soap*, **22**, 10 (1945).
- (6) Lutton, *THIS JOURNAL*, **67**, 524 (1945).
- (7) Filer, *et al.*, *ibid.*, **68**, 168 (1946).