

# Expansion of Solidifying Saturated Fats

A. HVOLBY, Dansk Sojakagefabrik, Copenhagen, Denmark

## ABSTRACT

From literature it appears that simple saturated triglycerides and commercial fats contract to a considerable extent when they undergo transformation from liquid to solid state and from an instable to a more stable crystalline form. In spite of these facts, the simple saturated even triglycerides and some fully hydrogenated fats exhibit violent solidification expansion by voluntary cooling. Solidification experiments carried out with several saturated even triglycerides and fats under various solidification conditions have shown that the solidification expansion tendency depends upon the chemical composition of the fat, as well as on the solidification conditions. The solidification expansion tendency is increased by various more or less independent factors, namely decreasing iodine value, increasing fatty acid and triglyceride uniformity, increasing triglyceride symmetry, increasing tendency to rapid formation of the stable  $\beta$  crystals, seeding with  $\beta$  crystals, voluntary cooling, moderate cooling velocity, and increasing bulk amount of fat. All the expanded solidified fats ended up being in the  $\beta$  crystalline form, whereas the nonexpanded fats ended up with the  $\beta'$  form. The solidification expansion is avoidable by careful control of the cooling procedure.

## INTRODUCTION

From literature (1-7), it appears that simple saturated

triglycerides and saturated (fully hydrogenated) fats contract to a considerable extent when they undergo transformation from liquid to solid state and from an instable to a more stable crystalline form. Some of the published data on tristearin phase transformations are shown in Table I. As the specific volume of liquid tristearin at 72.5 C is 1.152 ml/g (3), the melting dilatation value for  $\beta$  tristearin (Table I) implies that solidification of tristearin in  $\beta$  form causes a calculated solidification contraction of ca. 14% (2).

In spite of the published data on solidification contraction, in practice, simple saturated even triglycerides and several fully hydrogenated fats expand violently by solidification by voluntary cooling (1, 5, 8-10). In Figure 1 ca. 20% w/w of the fully hydrogenated soybean oil has expanded above the original level of the liquid oil. Since the block of fat, furthermore, has expanded to some extent laterally, the total expansion must imply the occurrence of ca. 35% v/v cavities in the original fat volume which is controllable by cutting the block of fat into pieces. The expansion forces can be so violent that breakage has occurred, not only of cardboard and wood packages, but also of metallic fat moulding boxes. In the laboratory the expansion forces often result in breakage of glass containers (Fig. 2) or expansion of the solidifying fat out of the container (Fig. 3).

## EXPERIMENTAL PROCEDURES

### Materials

The lots of fully hydrogenated fats used were produced

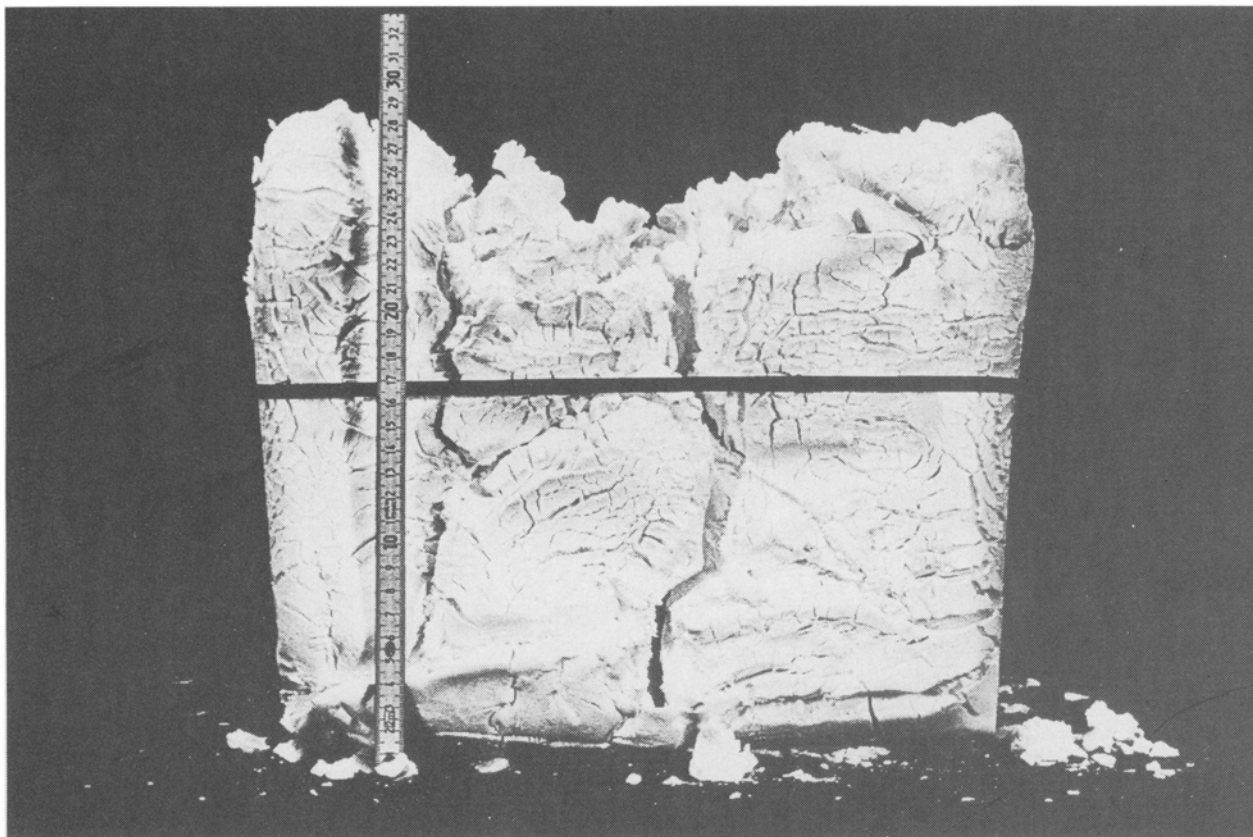


FIG. 1. A solidified expanded block (12 kg) of fully hydrogenated soybean oil after removal of the package. The upper limit of the horizontal black line indicates the level to which the liquid oil was filled into the package (chip board box lined with polyethylene bag). The vertical scale has graduation in cm.

TABLE I  
Expansion and Heat Absorption of Tristearin by Some  
Physical State Transformations

Transformation			Expansion <sup>b</sup> ml/g	Heat absorption <sup>c</sup> cal/g
From	To	Temperature <sup>a</sup> , C		
α crystal	Liquid	54.5	0.119	38.9
β' crystal	Liquid	64.5	0.132	
β crystal	Liquid	72.5	0.167	54.5
α crystal	β' crystal	54.5	-0.006	
α' crystal	β crystal	64.5	-0.030	
α crystal	β crystal	54.5	-0.035	-13.7

<sup>a</sup>The mp of the crystalline forms of tristearin are: α form (unstable): 54.7 C; β' form (metastable): 64.0 C; β form (stable): 73.3 C (10).

<sup>b</sup>See ref. 3.

<sup>c</sup>See ref. 22.

by hydrogenation of commercial nonhydrogenated fats in the laboratory. The esterified triglycerides were produced in the laboratory by esterifying glycerol with saturated even fatty acids or fatty acid methyl esters purified by fractionated distillation. The analytical data for the investigated fats and triglycerides appear in Table II. Only one sample of each type of fat and triglyceride was investigated (Tables II and III). Most of the experiments, carried out to elucidate the influence of the solidification conditions, were carried out with fully hydrogenated soybean oil.

#### Analyses

The fatty acid composition of the fats and triglycerides

was determined by gas chromatography. The crystalline form of the solidified fats and triglycerides was determined by X-ray diffraction (Guinier-De Wolff Camera). The solidification experiments were carried out with varying volumes of fat solidified in containers of different size, form, and construction material (Fig. 1-3).

## RESULTS AND DISCUSSION

### Dependence upon Chemical Composition

Apart from some lots of cocoa butter and some fractions of solvent fractionated natural fats, e.g. shea butter

TABLE II  
Chemical Composition of the Investigated Saturated Fats

Fat	Iodine value	Fatty acid composition <sup>a</sup> , percent w/w							Glyceride composition, ref. no.
		12:0	14:0	16:0	18:0	20:0	22:0	Others	
Vegetable fats, fully hydrogenated									
Cocoa butter	3.0	0.0	0.1	22.6	75.4	1.4	0.2	0.3	(23) <sup>e</sup>
Coconut oil	0.1	43.2	19.6	10.2	12.7	0.1	0.0	14.2	(24) <sup>e,f</sup>
Corn oil	1.2	0.1	0.1	12.0	85.6	1.0	0.9	0.3	(25) <sup>e</sup>
Cottonseed oil	1.4	0.1	0.9	23.2	74.0	0.5	0.3	1.0	(25) <sup>e</sup>
Linseed oil	1.8	0.1	0.1	5.9	92.6	0.5	0.3	0.5	(27) <sup>e</sup>
Olive oil	0.7	0.0	0.1	17.3	79.8	0.3	1.1	1.4	(25) <sup>e</sup>
Palm kernel oil	0.9	46.6	17.0	9.2	21.1	0.1	0.0	5.3	f
Palm oil	0.8	0.2	1.5	45.5	51.5	0.7	0.2	0.4	(24) <sup>e</sup>
Peanut oil	0.6	0.1	0.1	11.7	81.0	2.5	3.0	1.6	(26) <sup>e</sup>
Rapeseed oil	1.3	0.1	0.1	5.3	50.8	9.1	33.5	1.1	(23) <sup>e</sup>
Sesame oil	1.1	0.1	0.2	9.6	88.5	1.0	0.4	0.2	g
Shea butter	8.6 <sup>d</sup>	0.3	0.5	6.2	90.8	1.7	0.0	0.5	(24) <sup>e</sup>
Soybean oil <sup>b</sup>	1.2	0.0	0.3	12.3	83.1	1.8	0.0	2.5	(25) <sup>e</sup>
Sunflowerseed oil	1.2	0.1	0.1	6.3	92.2	0.5	0.7	0.1	g
Animal fats, fully hydrogenated									
Butterfat	0.4	5.4	16.1	33.4	24.3	0.3	0.0	20.5	f
Lard	0.3	0.5	2.1	30.2	63.5	2.1	0.4	1.2	(24) <sup>e</sup>
Tallow	0.2	0.6	4.6	28.5	59.9	0.9	0.3	5.2	(24) <sup>e</sup>
Marine fats, fully hydrogenated									
Fish oil	3.8	0.1	6.7	21.4	20.6	20.3	27.1	3.8	f
Seal oil	1.2	0.1	4.7	22.1	32.4	22.1	16.1	2.5	f
Esterified triglycerides									
Trilaurin	0.8	99.1	0.3	0.1	0.1	0.0	0.0	0.4	g
Trimyristin	0.1	3.3	88.8	6.9	0.6	0.0	0.0	0.4	g
Tripalmitin	0.2	0.0	0.7	98.6	0.4	0.1	0.0	0.2	g
Tristearin	0.2	0.0	0.0	1.6	97.9	0.2	0.0	0.3	g
Tristearopalmitin <sup>c</sup>	0.4	0.2	0.4	50.1	48.5	0.0	0.0	0.8	c,g

<sup>a</sup>Chain length: number of double bonds

<sup>b</sup>Solidification temperature = 64 C.

<sup>c</sup>Random distribution of the fatty acids.

<sup>d</sup>Originating from unsaponifiable components.

<sup>e</sup>The glyceride composition of the fully hydrogenated fat is calculable on the basis of the published glyceride composition of the nonhydrogenated fat.

<sup>f</sup>The wide spread in fatty acid composition might lead one to suppose that the fully hydrogenated fat contains considerable quantities of unsymmetrical triglycerides.

<sup>g</sup>The minimum content of the quantitatively dominating triglyceride is calculable from the fatty acid composition.

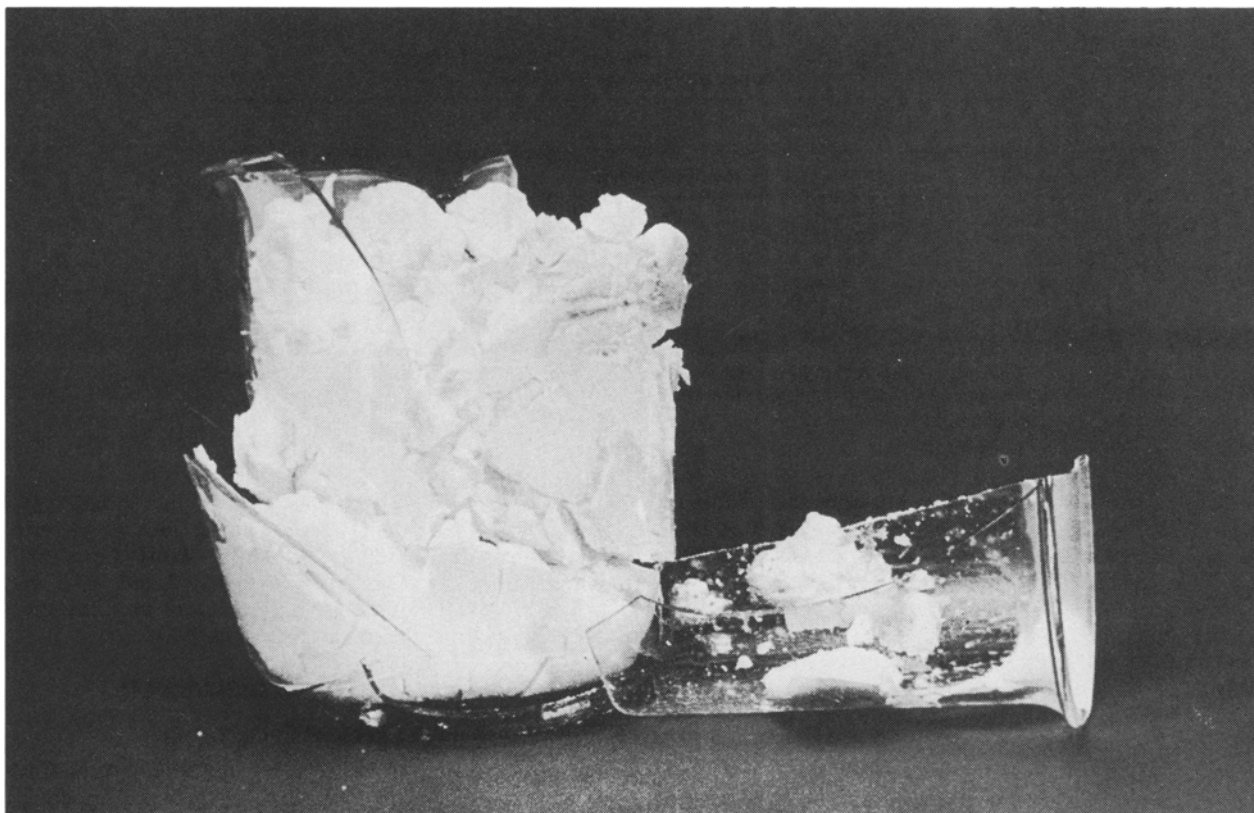


FIG. 2. A glass beaker broken to pieces caused by the expansion of solidifying fully hydrogenated soybean oil.

fractions, we have never observed solidification expansion of nonhydrogenated fats; nor have we observed solidification expansion with commercially available partially hydrogenated fats like hydrogenated soybean oil (mp = 28-41 C) and hydrogenated fish oil (mp = 31-55 C).

From the analytical data in Table II and the solidification results in Table III, it appears that all the saturated fats and triglycerides exhibiting solidification expansion are characterized chemically by being quantitatively dominated by one or two even fatty acids and by symmetrical triglycerides, e.g. tristearin and  $\beta$ -palmito-distearin (1, 9-13). The results of solidification experiments carried out with various mixtures of the individual fats mentioned in Table II also indicate that the expansion tendency is increased by increasing uniformity in chemical composition, e.g. it is more difficult to obtain expansion with a mixture of tripalmitin and tristearin than with these

triglycerides separately. For mixtures of liquid oils and expansion prone fats, it is surprisingly easy to obtain expansion, e.g. a mixture of nonhydrogenated soybean oil and fully hydrogenated soybean oil is able to expand in mixing ratios up to 1:1.

#### Dependence upon Crystalline Form

All solidified expanded fats were in the  $\beta$  form. All the solidified nonexpanded fats were in the  $\beta'$  form (Table III) (9-18). Abrupt cooling of expansion prone fats resulting in complete solidification in instable crystalline forms followed by tempering to transformation into the stable  $\beta$  crystals did not lead to expansion. Solidification of expansion prone fats at temperatures below the mp for the  $\beta$  form and well above the mp for the instable  $\beta'$  form results in undiminished expansion. Because of these facts, we conclude that the expansion can take place by direct transformation of the liquid into the stable  $\beta$  crystalline state (10). Seeding with powdered  $\beta$  crystals at temperatures below mp for the  $\beta$  crystals and well above mp for the  $\beta'$  crystals results in increased expansion tendency (19).

#### Dependence upon Cooling Conditions

In practice, e.g. voluntary cooling by standing, the expansion tendency increases with increasing bulk amount of fat (Fig. 1). However, it is possible to obtain expansion with any small amount of expansion prone fats by carefully controlled cooling. Thus, we easily have obtained expansion of 50 mg tripalmitin solidified at 60-63 C in a glass flask surrounded by still air of 59 C (mp for  $\beta$  form = 66 C, mp for the  $\beta'$  form = 56 C) (9).

The solidification expansion is avoidable by very rapid or very slow removal of the crystallization heat (10). Very rapid crystallization can be carried out by placing the solidifying fat in a metallic container surrounded by cold water and stirring the fat as long as the consistency permits. Very slow crystallization is obtainable by using heat insulating package material or by insulating the fat package and by placing it at a relatively high ambient temperature. A combination

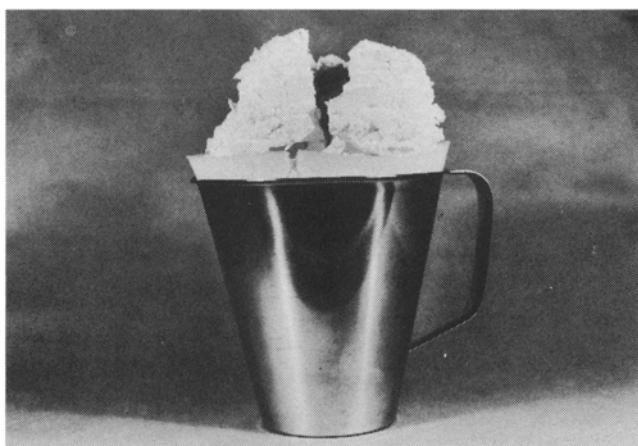


FIG. 3. Expanded solidified fully hydrogenated soybean oil in a 1000 ml conical steel pitcher. The pitcher was filled to the brim with liquid oil and the oil was voluntarily cooled by standing in still air at room temperature.

TABLE III

Solidification Properties of Saturated Fats and Triglycerides		
Fat	Expansion tendency <sup>a</sup>	Crystalline form <sup>b</sup>
Vegetable fats, fully hydrogenated		
Cocoa butter	Not expanding	$\beta'$
Coconut oil	Not expanding	$\beta'$
Corn Oil	Expanding	$\beta$
Cottonseed oil	Not expanding	$\beta'$
Linseed oil	Expanding	$\beta$
Olive oil	Not expanding	$\beta'$
Palm kernel oil	Not expanding	$\beta'$
Palm oil	Not expanding	$\beta'$
Peanut oil	Expanding	$\beta$
Rapeseed oil	Not expanding	$\beta'$
Sesame oil	Expanding	$\beta$
Shea butter	Expanding	$\beta$
Soybean oil	Expanding	$\beta$
Sunflowerseed oil	Expanding	$\beta$
Animal fats, fully hydrogenated		
Butterfat	Not expanding	$\beta'$
Lard	Expanding	$\beta$
Tallow	Not expanding	$\beta'$
Marine fats, fully hydrogenated		
Fish oil	Not expanding	$\beta'$
Seal oil	Not expanding	$\beta'$
Esterified triglycerides		
Trilaurin	Expanding	$\beta$
Trimyristin	Expanding	$\beta$
Tripalmitin	Expanding	$\beta$
Tristearin	Expanding	$\beta$
Tristearopalmitin	Not expanding	$\beta'$

<sup>a</sup>A fat is characterized as expanding if 250 ml of the melted fat in a conical steel pitcher surrounded by air (Fig. 3) expands significantly when left to solidify at 20, 40, or 50 C.

<sup>b</sup>Determined on sample taken from the upper center of the solidified fat.

of rapid and very slow crystallization can be practiced by stirring the solidifying fat as long as the consistency permits, i.e. removal of as much crystallization heat as possible without formation of crystallization and temperature gradients, followed by standing under slow crystallization conditions.

Since the expansion of fat in rigid walled containers normally takes place above the fat surface, the expansion is avoidable by removal of the crystallization heat totally through the bottom of the package, i.e. by insulating the sides and the top of the package and having the bottom of the package in direct contact with a cooling medium, e.g. a cool steel plate. Since the expansion of a solidifying fat results in cavities to a considerable extent in the solidified fat, it could be expected that the expansion would not take place by solidifying the fat in vacuum. However, our experiments have shown that it is impossible to prevent the expansion just by solidifying the fat in vacuum.

Our conclusion of the experiments carried out to elucidate the influence of cooling conditions on expansion tendency is that the expansion only takes place when the fat is crystallized with a moderate velocity. In the solidifying fat, the moderate crystallization velocity results in formation of temperature zones, where the crystallization takes place with a velocity so much higher in certain directions-planes than in other directions-planes (20,21) that columns of the solidified fat shoot up under the influence of the solidification of liquid fat continuously entering the lower sections of the column. In accordance with this tentative explanation, we found greater expansion tendency by solidification of a fat in a conical pitcher (the opening wider than the bottom, Fig. 3) than in a cylindrical container of same volume and construction material.

#### Avoidance of Solidification Expansion

The expansion of an expansion prone fat is naturally avoidable in practice by handling the fat in liquid, spray cooled, or flaked form. If moulding of an expansion prone

fat is necessary or desirable, the expansion is avoidable by using mechanically sufficiently strong package or by carefully controlled cooling, i.e. by very rapid or very slow cooling or by removal of the crystallization heat through the bottom of the rigid walled package. The possibility of avoiding the expansion by the aid of additives influencing the crystallization process has not been investigated.

#### ACKNOWLEDGMENTS

J. Sorensen assisted with experimental and analytical work. N. Krog, Grindsted Products Laboratory, Brabrand, determined crystalline forms in Table III. Permission for publication was granted by Dansk Sojakagefabrik.

#### REFERENCES

- Ferguson, R.H., and E.S. Lutton, *Chem. Rev.* 29:355 (1941).
- Bailey, A.E., and E.A. Kraemer, *Oil Soap* 21:251 (1944).
- Bailey, A.E., and W.S. Singleton, *Ibid.* 22:265 (1945).
- Bailey, A.E., "Melting and Solidification of Fats," Interscience Publishers, New York, N.Y. 1950, pp. 176-180.
- Craig, B.M., et al., *JAOCS* 29:128 (1952).
- Chapman, D., "The Structure of Lipids," Methuen and Co., London, England 1965, p. 266, 272-273.
- Hannewijk, J., et al., in "Analysis and Characterization of Oils, Fats, and Fat Products I," Edited by H.A. Boekennoogen, Interscience Publishers, New York, N.Y., 1964, p. 124.
- Joglekar, R.B., and H.E. Watson, *J. Indian Inst. Sci.*, A 13:119 (1930).
- Lutton, E.S., and A.J. Fehl, *Lipids* 5:90 (1970).
- Lutton, E.S., *JAOCS* 49:1 (1972).
- Imamura, M., et al., *Yukagaku* 17:610 (1968); *Chem. Abstr.* 70:27777r (1969).
- Imamura, M., et al., *Ibid.* 18:21 (1969); *Ibid.* 70:66933h (1969).
- Larsson, K., *Chem. Scripta* 1:21 (1971).
- Riiner, U., *Lebensm. Wiss. Technol.* 3:101 (1970).
- Lutton, E.S., *JAOCS* 44:303 (1967).
- Wiedermann, L.H., *Ibid.* 45:515A, 520A, 560A (1968).
- Hoerr, C.W., *Ibid.* 37:539 (1960).
- Swern, D., "Bailey's Industrial Oil and Fat Products," Inter-

- science Publishers, New York, N.Y., 1964, p. 307.
19. Bailey, A.E., "Melting and Solidification of Fats," Interscience Publishers, New York, N.Y., 1950, p. 47.
  20. Skoda, W., and M. van den Tempel, *J. Cryst. Growth* 1:207 (1967).
  21. Albon, N., et al., *Ibid.* 2:26 (1968).
  22. Charbonnet, G.H., and W.S. Singleton, *JAOCS* 24:140 (1947).
  23. Juriens, G., in "Analysis and Characterization of Oils, Fats, and Fat Products II," Edited by H.A. Boeckenoogen, Interscience Publishers, New York, N.Y., 1968, pp. 217-298.
  24. Coleman, H.M., *JAOCS* 38:685 (1961).
  25. Subbaram, M.R., and C.G. Youngs, *Ibid.* 41:595 (1964).
  26. Subbaram, M.R., and C.G. Youngs, *Ibid.* 44:425 (1967).
  27. Vereshchagin, A.G., and G.V. Novitskaya, *Ibid.* 42:970 (1965).

[Received September 10, 1973]