

SFI at 50F =	72.69-6.143 NMR value
SFI at 70F =	87.27-7.880 NMR value
SFI at 80F =	104.03-9.431 NMR value
SFI at 92F =	111.09-10.079 NMR value
SFI at 100F =	104.35-9.463 NMR value

The common (over-all) regression equation is: SFI = 83.05-7.365 NMR value.

The relationship between SFI and NMR values was excellent. Using the regression equations or a graph for each temp, the SFI value can be estimated within  $\pm 1.5$  when the SFI value is less than 30 and within  $\pm 3$  if the common (over-all) regression equation is used. The data obtained using the regression equations for each temp are shown in Figure 9.

### Discussion

The low resolution NMR spectrometer has been shown to determine the solids content of fats accurately over the entire range. The solids content

of the sample can be determined as received or after any conditioning or storage sequence or period. This would be of particular advantage in studying degree of crystallization occurring under different tempering and storage conditions and the amount of solids at any given time. The determination of the solids content of a sample as received in the laboratory is not possible by conventional techniques, so NMR opens new potentials to the analyst as well as taking less time.

The limited data collected on consistency indicate that the % solids in a sample can be related to a given consistency test, and that once the relationship is established the % solids can be used to predict consistency.

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## The Oxidized-Metallic and Grassy Flavor Components of Autoxidized Milk Fat<sup>1</sup>

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### Abstract

Oct-1-en-3-one accounts for the metallic flavor of autoxidized milk fat. In combination with small amounts of aldehydes it gives an oxidized flavor to milk. The grassy flavor component observed in autoxidized milk fat is shown to be *trans-cis*-2,6-nonadienal. Mechanisms are proposed for the production of oct-1-en-3-one from linoleate and 2,6-nonadienal from linolenate.

### Introduction

STUDIES ON THE volatile components of autoxidized milk fat, using gas chromatography, indicated that a single fraction could reproduce the oxidized flavor found in dairy products during the early stages of autoxidation (7). This fraction migrated close to octanal during gas chromatography on both polar and non-polar columns. Other experiments indicated that the tallowy flavor found in the later stages of autoxidation in dairy products was a blend of the oxidized component with 2,4-decadienal and a grassy-flavored component (8). The oxidized component and 2,4-decadienal were found among autoxidation products of methyl linoleate.

Forss et al. have reported a number of studies on the flavors of autoxidized dairy products (9,10,11,13,14,22). Although they concluded that the oxidized flavor of dairy products was caused by a series of 2-enals and 2,4-dienals, they found a single compound which caused the metallic flavor sometimes found in autoxidized dairy products. This compound was eventually found to be the same component that we had called oxidized (8).

Recently Stark and Forss succeeded in identifying the metallic flavored compound as oct-1-en-3-one (vinyl amyl ketone) by using mass spec-

trometry in conjunction with gas chromatography (24). They found that previous attempts to isolate this compound as the 2,4-dinitrophenylhydrazone (2,4-DNPH) were vitiated by the poor yields obtained when vinyl ketones are reacted with the usual 2,4-DNPH reagents. They were able to isolate the vinyl amyl ketone-2,4-DNPH from autoxidized butter oil and safflower oil by suitably altered procedures.

The grassy flavored component which we had previously found to be an important flavor constituent in autoxidized milk fat was not produced during the autoxidation of oil which contained no linolenic acid, nor was this flavor found among the autoxidation products of highly purified methyl linoleate (8). When highly purified methyl linolenate was autoxidized at room temperature, it had a strong beany flavor. This flavor was isolated and fractionated by gas chromatography. The beany flavor was found to be a blend of short chain compounds with the same grassy component found in autoxidized milk fat. This grassy flavor had gas chromatographic properties similar to that of a cucumber-flavored component found in autoxidized milk fat by Forss et al. (9,10,11). They concluded that this flavor was caused by 2-nonenal.

This paper contains a report of efforts to identify the oxidized-metallic and grassy compounds. The properties of vinyl amyl ketone were found to account for observations on the oxidized-metallic compound isolated from an autoxidized trilinolein concentrate, thus confirming the discovery of Stark and Forss. The grassy compound was found to be *trans-cis*-2,6-nonadienal rather than 2-nonenal.

### Procedures

Methyl linoleate was prepared from safflower oil (20), and transesterified with triacetin under reduced pressure with a sodium methoxide catalyst. Methyl

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TABLE I  
Comparison of Properties of Compounds Isolated from Oxidized-metallic Fraction with Those of Known Compounds.

Compound	Relative retention time <sup>a</sup>			Properties of the 2,4-DNPH's					
	Butanediol succinate 150C	Silicone grease 150C	Tide 102C	Class by paper chromatogram	R <sub>f</sub>				
					Vaseline <sup>b</sup> system	Heptane-ether	Heptane-nitromethane-chloroform	λ Max. <sup>c</sup> mμ	Aroma on regeneration
Isolated									
Sat. monocarbonyl I.....	98	102	100	Ketone	0.58	.....	.....	361	Metallic
Sat. monocarbonyl II.....				Aldehyde	0.65	.....	.....	.....	Like octanal
Polar carbonyl.....				Polar carbonyl	.....	0.47	0.84	352	None
2-Enal.....				2-Enal	0.75	.....	.....	.....	None
Known compounds									
Oct-1-en-3-one.....	100	100	100						
Derivatives									
Mono-2,4-DNPH.....				Ketone	0.59	.....	.....	368	Metallic
Form I.....				Polar carbonyl	.....	0.00	0.81	352	None
Form II.....				Polar carbonyl	.....	0.50 <sup>d</sup>	0.88	358	None
Form III.....				Polar carbonyl	.....	0.48	0.85	352	None
Octanal.....	98	109	146	Aldehyde	0.65	.....	.....	357	Like octanal
2-Octanone.....	98	104	116	Ketone	0.58	.....	.....	360	Like 2-octanone
2-Heptenal.....	118	96	114	2-Enal	0.80	.....	.....	373	Like 2-heptenal

<sup>a</sup> Based on vinyl amyl ketone as 100.

<sup>b</sup> The mobile phase was methanol-ethanol-water (10:10:5 v/v/v).

<sup>c</sup> In ethanol.

<sup>d</sup> This compound was barely soluble in heptane-ether and only a faint spot could be obtained. This contrasted with Form III and the unknown which were quite soluble.

linolenate was prepared from linseed oil by the same method used for methyl linoleate. This yielded a concentrate containing 71.8% linolenic acid, 20.1% linoleic acid, and 8.1% oleic acid, determined by gas phase chromatography on butanediol succinate (4). This was converted to "trilinolenin" by transesterification as before. The triglycerides were autoxidized at room temperature, with stirring, until they developed a strong aroma. The volatile products were isolated by high vacuum distillation (7). The deodorized triglycerides were allowed to oxidize again to yield additional volatile products as needed.

About 1 ml of volatile material was obtained from each distillation of 500 g of the trilinolein or 200 g of trilinolenin. This was fractionated by gas phase chromatography using a 6 ft column  $\frac{3}{8}$  in. diam filled with butanediol succinate on Chromasorb (4). The sample was injected in 0.1 ml portions. When the desired flavor component emerged from the column, it was collected in a U-tube cooled with liquid nitrogen. The oxidized-metallic flavor collected in this way from the trilinolein was dissolved in 0.3 ml of petroleum ether and extracted several times with 1% sodium bicarbonate solution to remove certain contaminants. The grassy flavor collected from trilinolenin was too soluble in water to be washed in this way. The flavor compounds were further purified by rechromatography, either again on butanediol succinate or on silicone grease or Tide (6). The flavor components were converted to 2,4-DNPH's as they emerged from the column by bubbling the carrier gas through a saturated aqueous solution of 2,4-DNPH in 2N HCl. The 2,4-DNPH's were recovered by filtering the reaction mixture through a fritted glass filter.

The 2,4-DNPH's were separated into classes by paper chromatography in pentane, and the classes were further separated by paper chromatography on vaseline impregnated paper (7). Compounds which had a zero R<sub>f</sub> in the class separation were designated "polar carbonyls." They were separated by chromatography on Whatman No. 1 paper strips (17 x 2 cm) with heptane-ether 2:3 v/v or heptane-nitromethane-chloroform 20:9:4 v/v/v (15). Liquid column partition chromatography was carried out according to Day et al. (5). Thin-layer chromatography plates were covered with silica gel G according to Stahl (19) and developed with 7% ethyl ether in Skellysolve B.

The 2,4-DNPH's were regenerated to the free carbonyl compounds for organoleptic evaluation with levulinic acid (18).

Vinyl amyl carbinol was prepared according to Crabolona (3) and oxidized to vinyl amyl ketone according to Brown and Garg (2). The ketone 2,4-DNPH was prepared according to Shine (23), using tetrahydrofuran as solvent and acetic acid as catalyst. It was crystallized from ethyl ether and melted at 81C. Stark and Forss (24) have reported that several mono-2,4-DNPH's can be made from this ketone. When vinyl amyl ketone reacts with aqueous 2,4-DNPH in 2N HCl, at least three additional derivatives are formed along with some of the regular ketone-mono-2,4-DNPH's. These probably involve the addition of 2,4-DNPH to the double bond of the vinyl amyl ketone. To fractionate this complex mixture, the reaction product was dissolved in chloroform and deposited on celite. The chloroform was evaporated, and the celite was extracted with petroleum ether, ethyl ether, and ethanol in that order. The ethanol insoluble material was recovered from the celite and crystallized from ethyl acetate to yield yellow crystals of Form I (transition 160C, mp 192C, C 50.18, H 5.22, N 20.18). The ether soluble fraction was crystallized from methanol and then ethyl acetate to yield Form II (mp 170C, C 48.91, N 21.65). The material from the mother liquor of Form II was crystallized from ethanol-ethyl acetate (1:1) to yield Form III (mp 127C). The petroleum ether soluble fraction contained the ketone-mono-2,4-DNPH's.

The 2,4-heptadienal was prepared according to Pippen and Nonaka (21). The other known compounds were commercial preparations.

For flavor evaluation the synthetic compounds were purified by gas chromatography. The compounds were collected as they emerged from the gas chromatograph by bubbling the effluent gas through 50 ml of milk. The milk was tasted at appropriate dilutions by a trained flavor panel. The compounds produced by the autoxidation of the synthetic glycerides were collected for comparison in a similar manner.

## Results

### The Oxidized-Metallic Flavor

The oxidized-metallic flavor compound had a retention time close to octanal on both butanediol succinate and silicone grease columns. It emerged just before octanal on Tide.

During the gas phase chromatography of the trilinolein distillate on butanediol succinate, one of the

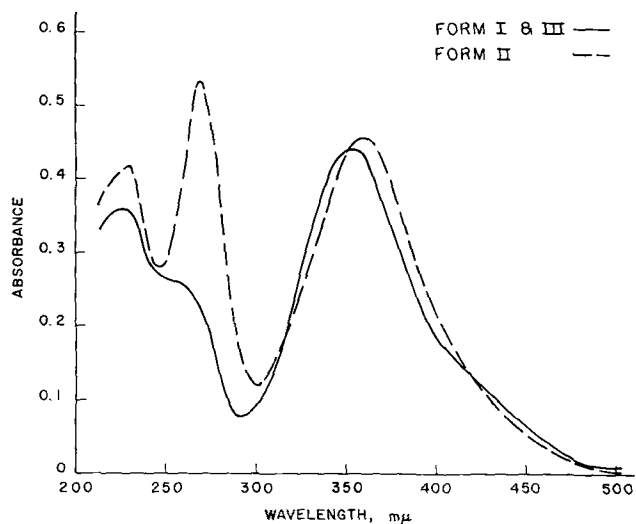


FIG. 1. The ultraviolet spectrum of the Form I, II, and III 2,4-DNPH derivatives of vinyl amyl ketone.

components was found to have a retention time which varied considerably with the amount of sample put on the column. The more sample injected, the shorter the retention time. At the high sample loads used, this compound had the same retention time as the oxidized-metallic compound; however, it was eliminated in the washing procedure.

2,4-DNPH's were obtained from the oxidized-metallic fraction after it had been purified by gas chromatography on butanediol succinate and silicone grease or Tide. Paper chromatography revealed that saturated monocarbonyl, 2-enal, and polar carbonyl were present. In all cases, a polar carbonyl was present which had an  $R_f$  of about 0.5 in the heptane-ether system. Since this polar carbonyl traveled with the oxidized-metallic flavor on both polar and non-polar gas chromatography columns and was not removed by the water washing, it seemed likely that it did not gain its polar, dicarbonyl-like nature until after its reaction with 2,4-DNPH.

When the 2,4-DNPH's from the oxidized-metallic fraction were regenerated with levulinic acid, a faint metallic aroma was observed. When the regeneration procedure was used on the 2,4-DNPH's after class separation, the metallic aroma was found to come from the saturated monocarbonyl fraction. The saturated monocarbonyl fraction was separated into two compounds by liquid partition chromatography. One of these compounds, which had an ultraviolet spectrum like a ketone, was found to give the metallic aroma.

After Stark and Forss identified their metallic compound as vinyl amyl ketone, this compound was prepared and compared with the oxidized-metallic compound. This comparison is shown in Table I.

The ketone-2,4-DNPH that gave the metallic flavor is evidently an impure vinyl amyl ketone-mono-2,4-DNPH, and the polar carbonyl is evidently the Form III derivative. IR and UV spectra of the polar carbonyls derived from vinyl amyl ketone are given in Figures 1 and 2.

When vinyl amyl ketone was tasted in homogenized milk, it had a metallic flavor. A typical oxidized flavor could not be obtained consistently at any dilution. However, when the vinyl amyl ketone was mixed with small amounts of octanal, 2-heptenal, or 2,4-heptadienal, it gave a typical oxidized flavor. 2-Octanone would not give an oxidized flavor with vinyl amyl ketone. The concentrations used in these experiments

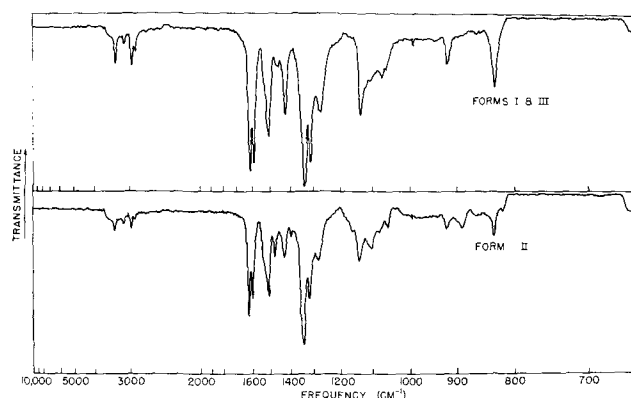


FIG. 2. The infrared spectrum of the Form I, II, and III 2,4-DNPH derivatives of vinyl amyl ketone.

were of the order of 10 parts per billion, but this cannot be taken as an absolute level as the flavors fade rapidly and at different rates in fresh pasteurized homogenized milk. Oxidized flavors could sometimes be obtained with vinyl amyl ketone alone, if it was left in the milk for an hour or two.

#### The Grassy Flavor

On butanediol succinate, the grassy component from the trilinolenin had a retention time close to undecanal. On Tide columns, it came out between nonanal and decanal. This is the behavior to be expected of a  $C_9$  2-enal.

The 2,4-DNPH obtained from the grassy component, after it had been fractionated on both butanediol succinate and Tide columns, was examined by paper chromatography. The class separation showed only 2-enal to be present; however, the peak which emerged from the gas chromatograph just before the grassy fraction was found to contain a 2,4-dienal, and this 2,4-dienal behaved like a 2-enal in the class separation. Paper chromatography in the vaseline system showed that the grassy fraction contained both 2-enal and the 2,4-dienal. These compounds could not be separated by nitromethane-petroleum ether liquid column partition chromatography. They were separated by TLC on silica gel, the 2,4-dienal having the greater  $R_f$ .

When regenerated from its 2,4-DNPH, the 2-enal from the grassy fraction had an aroma like cucumbers. The 2,4-dienal could not be regenerated to give an aroma. Forss et al. have described 2-nonenal as having a cucumber flavor and as accounting for this flavor in autoxidized milkfat (9,10,11). However, the 2-enal-2,4-DNPH from the grassy fraction did not migrate with 2-nonenal-2,4-DNPH during paper chromatography in the vaseline system, and a large majority of our judges who examined 2-nonenal did not think it resembled cucumbers or the grassy flavor. In their examination of the flavors actually isolated from cucumbers, Forss et al. concluded that *trans-cis*-2,6-nonadienal was important in the flavor of cucumbers and tasted more typical of cucumbers than 2-nonenal. Since the grassy flavor arises from linolenate and not linoleate, one would expect it to have a *cis* double bond 3 carbons from the methyl end. Therefore, both *trans-cis*, and *trans-trans*-2,6-nonadienal were examined. Their properties are compared with the grassy 2-enal in Table II. The *trans-cis*-2,6-nonadienal accounts for the observed properties of the isolated 2-enal. Both the *trans-cis* and the *trans-trans*-isomers gave grassy flavors in milk which were like the flavors

TABLE II  
 Comparison of Properties of Compounds Isolated from Grassy Fraction with Those of Known Compounds.

Compound	Relative retention time <sup>a</sup>		Properties of 2,4-DNPH's				
	Butanediol succinate 168C	Tide 164C	Class by paper chromatogram	R <sub>f</sub> Vaseline <sup>b</sup> system	λ Max. <sup>c</sup> mμ	Aroma on regeneration	mp °C
Isolated							
2-Enal.....	98	107 <sup>d</sup>	2-Enal	0.61	373	Cucumber-like	118 <sup>e</sup>
2,4-Dienal.....	76?	91	2-Enal	0.48	388	None	186
Known compounds							
2,6- <i>trans-cis</i> -nonadienal.....	100	100	2-Enal	0.61	373	Cucumber-like	118
2,6- <i>trans-trans</i> -nonadienal.....	90	97	2-Enal	0.58	373	Cucumber-like	140
2,4- <i>trans-trans</i> -heptadienal.....	78	73	2,4-Dienal	0.71	389	Oily	156
2-nonenal.....	82	102	2-Enal	0.49	373	Like 2-nonenal	130

<sup>a</sup> Based on 2,6-*trans-cis*-nonadienal as 100.

<sup>b</sup> The mobile phase was methanol-ethanol-water (10:10:5 v/v/v).

<sup>c</sup> In ethanol.

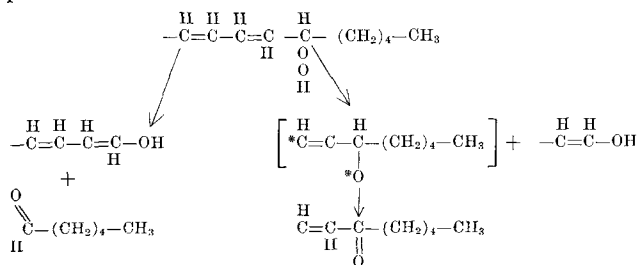
<sup>d</sup> This value deviates from 100 more than expected. This may be because the unknown and known values were determined on separate columns or because there was some impurity in the unknown.

<sup>e</sup> The unknown 2-enal-2,4-DNPH did not depress the mp of 2,6-*trans-cis*-nonadienal-2,4-DNPH. The infrared spectrum of the unknown 2-enal-2,4-DNPH agreed closely with that of the *trans-cis*-2,6-nonadienal. It differed from that of the *trans-trans*-isomer.

isolated from autoxidized linolenate. As Forss et al. have reported, the *trans-cis*-2,6-nonadienal tasted distinctly like cucumbers under certain conditions.

### Discussion

The vinyl amyl ketone responsible for the oxidized-metallic flavor has been shown to come from linoleate (7,8). The following mechanism might explain its production:



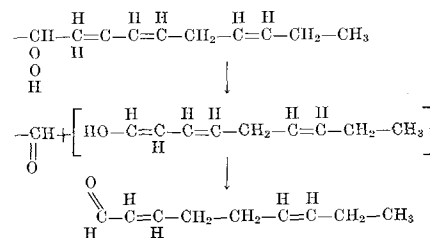
The di-free radical could theoretically cyclize to oxytene, but such compounds probably have too much ring strain to be stable (1). The particular path of breakdown of the peroxide probably depends on the environmental conditions. Linolenate should yield oct-1,5-*cis*-dien-3-one by a similar mechanism. This might account for the trace of oxidized-metallic flavor found when very pure methyl linolenate was autoxidized (8).

The flavor of the vinyl amyl ketone seems to depend on the presence of other aldehydes. When put in milk by itself, it usually tastes metallic; but, in the presence of small amounts of various aldehydes, it tastes oxidized. The role of the aldehydes themselves is not clear. The three aldehydes tested, octanal, 2-heptenal, and 2,4-heptadienal, all have quite different flavors, but all of them gave typical oxidized flavors with the vinyl amyl ketone. One effect which all had in common was to destroy the heated flavor of the pasteurized milk. However, even in raw milk, the presence of an aldehyde was necessary for vinyl amyl ketone to give an oxidized flavor. The development of an oxidized flavor in milk which contains only vinyl amyl ketone after an hour or two is also difficult to explain. It may be that the vinyl amyl ketone induces autoxidation of the milk fat, producing aldehydes which blend with the vinyl amyl ketone to give the observed flavor. Or it may be that the milk already contains aldehydes in sub-threshold levels and that the flavor of the vinyl amyl ketone fades in the milk until it is in the right ratio with the other aldehydes to give an oxidized sensation.

It has been suggested that the pasteurization of milk protects it against oxidized flavor by virtue of

the sulfhydryl groups which are formed in the milk on heating. These sulfhydryl groups are thought to act as antioxidants and also to cause the heated flavor (16). However, the fading of the flavor of carbonyl compounds added to pasteurized milk, along with the simultaneous disappearance of the heated flavor of the milk, suggest that there may be a direct reaction between sulfhydryl compounds in the milk and the flavor compounds. It is well known that milk from different cows may vary greatly in its resistance to oxidized flavor development (16). This may represent a variation in sulfhydryl groups or other compounds which react with the oxidized flavor compounds rather than a variation in the stability of the milk towards autoxidation. These same considerations may be important in the stability of foods other than milk to autoxidation.

The *trans-cis*-2,6-nonadienal which is responsible for the grassy flavor is known to arise from linolenate (8). The following mechanism might explain its production:



Such a conjugated enol should rearrange easily to a 2-enal (25).

The grassy flavor of 2,6-nonadienal is quite intense compared with the other autoxidation products of linolenic acid. It was shown previously that it would blend with short chain carbonyls to give a beany flavor (8), and it is probably important in the flavor of reverted oils.

### ACKNOWLEDGMENT

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# The Temperature Dependence of the Expansion Coefficient of Liquid Glycerides

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## Abstract

The temperature dependence of the expansion per degree C,  $E$ , has been determined for a number of simple triglycerides and for natural oils and fats. This dependence could be expressed as a straight line:

$$E = E_0 + kt$$

The  $E$ -values found for simple triglycerides indicate that:

- 1) The  $E$ -value for the trisaturated glycerides is independent of the chain length;
- 2) the  $E$ -lines for triolein and the trisaturated glycerides run parallel, thus enabling the  $E$  for a mixed triglyceride as 2-oleoyl-distearoyl glycerol to be calculated from those for triolein and tristearin;
- 3) the  $E$ -line for trielaidin has a different slope from that of triolein.

In calculating dilatations for practical purposes, the  $E$ -values for natural oils and fats can be rounded off to  $20.5 + 0.02t$ .

When we have to correct for the expansion of the liquid fat phase, the equation:  $U_x = E \cdot (t_e - t_x)$  has to be changed into the more accurate expression:

$$U_x = \left[ E_0 + k \cdot \frac{t_e + t_x}{2} \right] (t_e - t_x).$$

## Introduction

TO DETERMINE the dilatation of a fat from changes in volume between two temperatures, a number of corrections must be applied. Among these are corrections for the expansion of the glass, the sealing liquid and the liquid phase of the glyceride. In order to check the usual correction for the expansion of the liquid phase, we measured this value accurately for several pure triglycerides, as well as for many oils and fats.

When dilatation is expressed in the usual ml/g values, the small numbers which result are difficult to handle. Even the expression in ml/kg (according to practice in the U.S.A.) gives unwieldy small values. We have, therefore, used the expression more usual in Europe, in  $\text{mm}^3/25 \text{ g fat}$ .

## Procedures

### Calculation of the Dilatation

The dilatation (1-6) is calculated from two volume

readings (Fig. 1). The first reading is made at  $t_e$  degree C, a temperature at which the fat is completely liquid. A second reading is made at temperature  $t_x$ , the temperature at which the dilatation is to be determined. If these volume readings, after correction for the expansion of the glass and the sealing liquid, are  $V_e$  and  $V_x$ , respectively, then  $(V_e - V_x)$  represents the increase in volume on heating from  $t_x$  to  $t_e$  degrees C. Finally the correction for the expansion,  $U_x$ , of the liquid fat at  $t_x$ , has to be made.

The dilatation can then be expressed as:

$$D_x = (V_e - V_x) - U_x \quad [1]$$

This correction for the expansion of the liquid phase of the fat  $U_x$  can, in practice, be calculated from the equation:

$$U_x = E (t_e - t_x), \quad [2]$$

where  $E$  is the expansion of the liquid phase per degree C (in  $\text{mm}^3/25 \text{ g}$ ), a constant.

### Temperature Dependence of the Expansion per Degree C

*Expansion of a liquid.* The volume of a liquid on heating from 0 to  $t$  degree C is expressed as:

$$V_t = V_0 (1 + at + bt^2 + ct^3 + \dots) \quad [3]$$

The coefficient of expansion at  $t$  degree C is given by:

$$\frac{1}{V_0} \frac{dV}{dt} = a + 2bt + 3ct^2 + \dots \quad [4]$$

Partington (7) gives for olive oil:

$$\begin{aligned} a \times 10^3 &= 0.68215 \text{ ml/g degree C} \\ b \times 10^6 &= 1.14053 \text{ ml/g degree C} \\ c \times 10^8 &= -0.539 \text{ ml/g degree C} \\ a &= 17.05 \text{ mm}^3/25 \text{ g degree C} \\ b &= 0.06 \text{ mm}^3/25 \text{ g degree C} \\ c &= -0.0004 \text{ mm}^3/25 \text{ g degree C} \end{aligned}$$

As the constant  $a = 17.05$  strongly deviates from the values for the fats according to Bailey (3), and other data are not given in the literature, our measurements were carried out with pure triglycerides.

From such measurements with a number of simple triglycerides, we found that the temperature dependence of the expansion per degree C,  $E$ , can best be expressed as:

$$E = E_0 + kt \quad [5]$$

in which:

$E_0$  = expansion per degree C in  $\text{mm}^3/25 \text{ g}$  at  $t = 0\text{C}$ ,  
a constant

$k$  = slope of the line