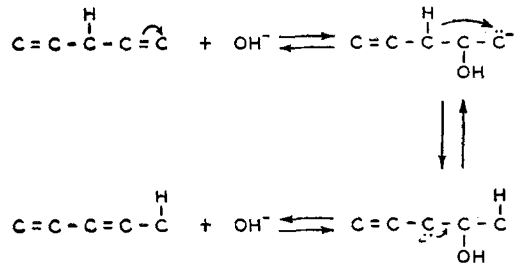

Summary

Attempts to obtain 1,3-pentadiene from the uncatalyzed or catalyzed isomerization of 1,4-pentadiene at 200–250° were not successful. Dimers and higher polymers were formed, presumably by conjugation and addition reactions. The activity of several catalysts was measured by the yields of polymer. Sodium hydroxide was most effective, followed by sulfur dioxide, *beta*-chloroanthraquinone, anthraquinone-*beta*-carboxylic acid, and anthraquinone in order of decreasing activity. In 1,4 and 1,3-pentadiene mixtures, anthraquinone and sulfur dioxide catalyze slightly the formation of high polymers, but sodium hydroxide catalyzes both total polymer and dimer. The quinones are believed to function in 1,4 to 1,3-diene isomerization by a free radical mechanism, sulfur dioxide and sodium hydroxide by polar mechanisms. These results are related to the polymerization of non-conjugated drying oils.

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[Received March 8, 1955]

Dilatometric Investigations of Fatty Acid Methyl Esters[1]

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DILATOMETRY or the measurement of volume change with temperature is a means of studying physical changes in solid and liquid states in which adequate time may be allowed for attaining equilibrium. The melting dilations and coefficients of expansion of liquid and solid states have been reported for a number of glycerides (3, 5, 10, 11) and fatty acids (8, 9, 13).

A linear volume-temperature relationship has been found for the liquid state of all fatty acids and glycerides. However the same relation does not appear to be valid for the solid state of the same materials. Bailey and Singleton (3) used the temperature interval from —38°C. to —20°C. to calculate the coefficient of expansion of the solid state of a number of saturated glycerides. The validity of this temperature interval for the solid state was corroborated by calorimetric data and the coefficients varied in magnitude from 0.00019 to 0.00030 ml. per gram per degree. A number of unsaturated fatty acids were found to have coefficients greater than 0.00030 ml. per gram per degree in the temperature region above —38.87°C. On the basis of calorimetric data (where temperatures below the melting point of mercury could be used) and the large observed coefficients of expansion, these materials were not in a completely solid state even at —38°C., and an arbitrary coefficient of 0.00030 ml. per gram per degree was used to calculate the melting dilation.

An examination of existing dilatometric data on fatty acids and glycerides shows that there is a curvilinear relation between volume and temperature within a few degrees of the melting point. The relation between volume and temperature in the temperature interval from that of the completely solid state to the melting temperature has not been thoroughly investigated. Vaeck (12) reported an inflection point in the solidus line for cocoa butter at around —20°C. and a linear relation for volume-temperature from —20°C. to 14°C. Craig, Lundberg, and Geddes (5) reported two coefficients of expansion for the solid state of a number of saturated glycerides and indicated that the "break-point" might be related to the melting point of the particular glyceride.

The present work on methyl esters of fatty acids was undertaken to provide additional data on melting dilations and the coefficients of expansion of solid and liquid states. The methyl esters appeared to be especially appropriate for this type of study since they may be obtained easily in a state of high purity. Particular attention was directed to a study of the volume-temperature relation in the solid state.

Experimental

Methyl palmitate, methyl stearate, methyl arachidate, methyl behenate, and methyl oleate were purified by fractional distillation and fractional crystallization and their properties have been described elsewhere (4). The esters were thoroughly degassed under vacuum by agitation during repeated melting and solidification, and the saturated methyl esters were formed under vacuum into solid rods of 4 mm. diameter.

The gravimetric dilatometer described by Bailey and Kraemer (2) was modified for use in this study.

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[1] Presented at the fall meeting, American Oil Chemists' Society, Mnneapolis, Minn., October 11, 1954. Issued as Paper No. 196 on the "Uses of Plant Products" and as N.R.C. No. 3671.

The capillary section sealed to the bottom of the dilatometer bulb (volume approximately 15 ml.) was 0.5 mm. in diameter to make "stem-emergence" corrections negligible. A short section of 6 mm. glas tubing, sealed to the top of the dilatometer bulb, facilitated admission of the samples and evacuation of air from the solid sample and bulb. Mercury was admitted from the capillary end during the filling procedure, and the 6-mm. tubing was drawn off before filling was completed to give a sealed unit. Volume corrections for the glass container and mercury were applied to all measurements.

A temperature variation of ± 0.005°C. was maintained in a water bath operated between 10°C. and 70°C. and in a low temperature methanol bath by an electronic temperature controller.

The melting dilations and coefficients of expansion for the solid and liquid states are given in Table I. The coefficients of expansion for the solid state were calculated for the temperature interval from —38°C. to —20°C. Methyl oleate (dilatometric m.p. —19.8° C.) had a coefficient of expansion of 0.00036 ml. per gram per °C. from —38°C. to —26°C. The coefficient 0.00030 ml. per gram per °C. was used to calculate the melting dilation. The melting dilation of methyl oleate is considerably greater than reported for triolein (3, 5) but is of the same magnitude as oleic acid (13). The melting dilations of methyl palmitate and methyl stearate are similar to those reported for tripalmitin and tristearin (3, 5). The melting dilations of the methyl esters of saturated acids on a ml. per gram basis should be similar to the saturated triglycerides because of the similarity in the molecules.

TABLE I

Melting Dilations and Expansivities of Methyl Esters

Methyl ester	Expansivity ml./g./°C.		Melting dilation	
	Solid	Liquid	Ml./g.	Ml./mole
Methyl palmitate	0.00025	0.00099	0.1698	45.92
Methyl stearate	0.00022	0.00100	0.1726	51.52
Methyl arachidate	0.00025	0.00101	0.1769	57.76
Methyl behenate	0.00022	0.00100	0.1821	64.57
Methyl oleate	0.00036[a]	0.00090	0.1187	35.19

[a] 0.00036 found between —38°C. and —25°C., and the coefficient 0.00030 ml. per gram per °C. was used to calculate the melting dilation.

A careful study of the volume-temperature relationship from —38°C. to the melting point was made for methyl palmitate and methyl stearate. The heating and cooling cycles of three samples of methyl palmitate were studied in the following sequence:

1. Dilatometers were equilibrated at 29°C. to produce the stable polymorphic form. Equilibration was assumed to be complete when successive weighings at 8-hr. intervals agreed to within one mg. The temperature of the bath was lowered to —38°C. over a period of 6 hrs. After equilibration at —38°C. the heating cycle curve from —38°C. to 29°C. was obtained by taking measurements at 2-degree intervals to 20°C. and at 1-degree intervals to 29°C. Fifty minutes were allowed for equilibration at each temperature except when the samples were allowed to stand overnight. "After-contractions" appeared at a temperature of 22°C., and adequate time was allowed for equilibration at subsequent temperatures to 29°C.
2. The cooling cycle curve was then obtained. Measurements were made at 1-degree intervals to 20°C. and 3-degree intervals below 20°C. As much time as required was allowed for equilibration at temperatures above 20°C. Except when the samples stood over night, 50 min. were used for equilibration at temperatures from 20°C. to —38°C. The heating cycle was repeated as in 1.
3. The cooling cycle curve was repeated as in 2. The dilatometers were equilibrated at —38°C. and then were immersed at —70°C. for 1 hr. After re-equilibration at —38°C. the heating cycle was repeated as in 1.
4. The cooling and heating cycles were repeated as in 3, but sufficient time was allowed for complete equilibration at each temperature as judged by successive weighings at 8-hr. intervals.

The same sequence was used with four samples of methyl stearate between the temperatures —38°C. and 37.5°C. with a preliminary equilibration at 37.5°C. to establish the most stable polymorphic form.

The data for individual heating and cooling cycles were plotted on large scale graphs. Individual heating cycle curves were slightly different and were all higher than individual cooling cycle curves. The variation in volume between individual heating cycle curves in the temperature region from —25°C. to 25°C. was about 0.0003 ml. per gram. A similar variation was found in individual cooling cycle curves, but no regular variation was found in heating cycles which could be ascribed to different cooling treatments. Accordingly the cooling and heating data for all dilatometers and all determinations were averaged and are presented in Figures 1 and 2. The combined data were a more accurate representation of the volume-temperature relationship and were used to obtain a reliable estimation of the "break-point."

The "break-point" for methyl palmitate (m.p. 30.1°C.) occurred at —19°C. and for methyl stearate (m.p. 39.1°C.) at —10°C., or 49 degrees below the melting point of the respective ester. The curve for the volume expansion of the solid state was composed of two sections, a linear section followed by a curvilinear section to the melting point. The cooling cycle curve was curvilinear over the complete temperature interval. The difference in heating and cooling cycle curves was not reflected by a difference in the total volume change between —38°C. and 29°C. for methyl palmitate and between —38°C. and 37.5°C. for methyl stearate.

No explanation can be offered for the curvilinearity of the cooling cycle curve in the temperature range from —38°C. to —20°C. where the heating cycle curve is linear. The data obtained by Craig *et al.* (5) for triglycerides may have followed a similar pattern but were insufficient to allow for a reliable determination of the linearity of the second section for volume expansion in the solid state. Subsequent experience

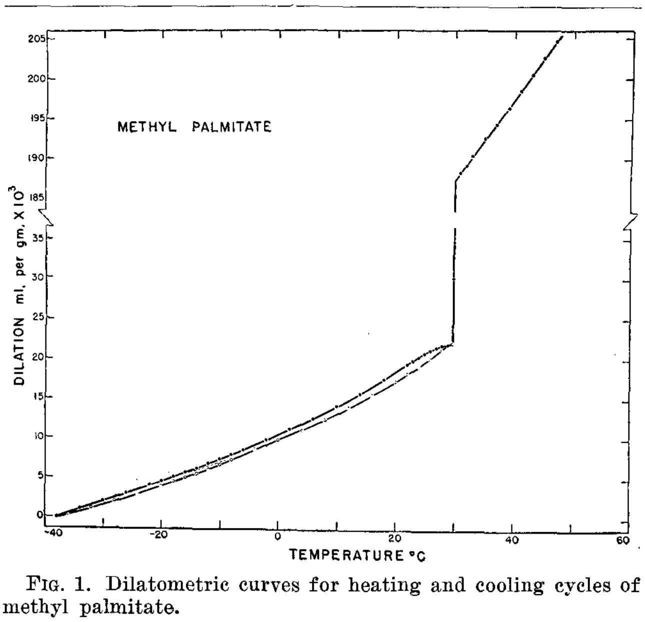

Fig. 1. Dilatometric curves for heating and cooling cycles of methyl palmitate.

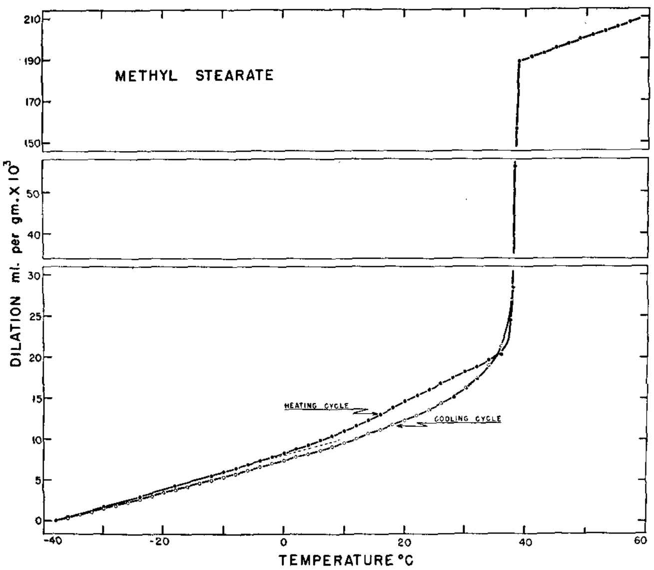

FIG. 2. Dilatometric curves for heating and cooling cycles of methyl stearate.

by the author has shown that precise temperature control is required and that dilatometer bulbs which are made of Pyrex glass do not show linear and reproducible volume contractions and expansions. Variations of ± 0.0001 ml. have been found in the measurement of the volume of dilatometer bulbs of 15-ml. capacity.

The heating cycle curves showed "after-contractions" from 22°C. to 29°C. for methyl palmitate and 26°C. to 37.5°C. for methyl stearate. These are shown in Figures 1 and 2 by the change of slope in these temperature regions. Dilatometric measurements in these temperature regions showed that an increase of temperature resulted in an immediate increase in volume (measured after 50 min. for equilibration). Further equilibration at this temperature showed volume decreases which were reduced in magnitude over intervals of time to final equilibration. These results might be attributed to an unstable polymorphic form. X-ray data were not obtained to prove conclusively that only the stable modification was obtained, but the length of time allowed for equilibration at temperatures slightly below the melting point of the stable form should have produced the stable form. The results may also have been due to vacuoles or voids in the system, but formation of the samples in the form of solid rods was expected to eliminate most of this difficulty.

The dilatometric method has been suggested for the accurate determination of melting points (1). The intersection of lines representing melting of the solid and volume expansion of the liquid will give the melting point to the second decimal place. From the curvilinearity of the melting section shown in Figure 2 it is obvious that points on this section must be chosen with care, and more than two points are required to assess the linearity of the chosen section. In addition, the control of temperature must be very precise since the volume change per unit of temperature is very large in the melting region. Equilibrated volumes were obtained at 38.7°C., 38.9°C., and 39.0° C. for methyl stearate. Liquid methyl stearate was visibly present in the dilatometer bulb at 39.0°C., and equilibration for a further period of three days gave no measurable increase in volume. Increasing the bath temperature to 39.1°C. resulted in complete melting of the sample within an hour. These equilibrated points in the melting section within 0.5 degree of the final melting temperature represent stable states which may or may not have been true equilibria.

A separate investigation has shown that the shape of the dilatometer bulb has an effect on the rate of melting. A cylindrical bulb of 1.5-cm. diameter was compared to one of comparable volume but with a diameter of 5.0 cm. A sample of methyl palmitate required 24 hrs. to melt in the former and 4 hrs. to melt in the latter when both samples were immersed in the same bath at the same time, and it was deduced that the heat transfer characteristics of the two bulbs were different. The smaller diameter bulbs were used in the present investigation, but the time allowed for equilibrium would have compensated for the heat transfer problem. If the equilibrated points were accepted as representing states of true equilibria, methyl stearate must melt over a range of temperature and 39.1°C. represents the final melting temperature.

The variation of dielectric constant with temperature has been studied by Müller (7), Smyth and coworkers (6), and others for a number of long chain molecules, and a curvilinear relation has been observed in the temperature region 15 to 20 degrees below the melting point. Müller (7) and Smyth and coworkers (6) have interpreted the results as due to rotational oscillations of the molecules in the lattice structure. Changes in volume would be expected to accompany this phenomenon, and there is a striking similarity between the dielectric constant relation with temperature and the dilatometric relation, both measurements showing curvilinearity in the temperature region preceding the final melting temperature.

Summary

The coefficients of expansion and melting dilations were measured for methyl palmitate, methyl stearate, methyl arachidate, methyl behenate, and methyl oleate. The dilatometric curve for the heating cycle of methyl palmitate and methyl stearate in the solid state was composed of a linear section to 49 degrees below the melting point, followed by a curvilinear section to the melting point. The heating and cooling cycle curves for methyl palmitate show the same volume change from —38°C. to 29°C., but the shape of the curves is different. The same relation holds for methyl stearate from —38°C. to 37.5°C. "After-contractions" were found in volume measurements within a few degrees of the melting point of both esters. Equilibrated points were found within 0.5 degrees of the final melting temperature of methyl stearate. A striking similarity exists between curves for variation of the dielectric constant with temperature for long chain linear molecules and the dilatometric data.

Acknowledgment

The author wishes to acknowledge with thanks the work of T. M. Mallard, who built the electronic temperature controller and assisted in the measurements and calculations.

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[Received February 7, 1955]

ABSTRACTS . . . . R. A. Reiners, Editor

• Oils and Fats

Ralph W. Planck, Abstractor
Dorothy M. Rathmann, Abstractor
Sin'itiro Kawamura, Abstractor

Loss of weight during oil-seed processing. F. Wittka. *Olearia* **9**, 55–64(1955). The losses in weight occurring during oilseed processing are practically constant in all oil-mills (antiquated or ultra-modern) and cannot result, therefore, from the methods of handling the seeds. Data are given to show that the weight changes cannot be accounted for on the basis of errors in weighing or analysis or losses or decomposition of fatty materials or carbohydrates. The most widely accepted theory used to account for the phenomenon is that water is formed and lost through an inter-molecular reaction of the proteins in the seeds. In support of this theory it is shown that seeds rich in protein such as peanuts (30% protein) and castor beans (20% protein) suffer about five times more loss in weight during processing than low protein content seeds such as olives (7% protein).

Wool scouring products and lanolin. The current point of view on this question. J. Vallee. *Revue Francaise des Corps Gras.* **2**, 323–336(1955). The commercial applications of lanolin and lanolin by-products as well as methods of recovering and refining crude wool fats and lanolin are reviewed. The 134 references cited are numbered to supplement and bring up to date the bibliography from a previous review on wool wax by D. T. C. Gillespie in the Journal of the Textile Institute, February, 1948.

Preparation of acetoglycerides. M. T. Mellier. *Oleagineux* **10**, 335–336(1955). Hydrogenated or distilled methyl esters prepared from palm oil were reacted with four times the theoretical quantity of triacetin required to form the diacetoglycerides in the presence of sodium or sodium methoxide as the catalyst. Xylene was used as the solvent in the sodium catalyzed reactions while no solvent was used in the sodium methoxide procedures. When the reaction was completed the xylene solutions were water washed to remove the resulting methyl acetate, the solvent stripped and the excess triacetin and unreacted methyl esters removed by vacuum distillation. In the sodium methoxide procedure the methyl acetate was distilled off and the triacetin and unreacted methyl esters removed as before. In all cases mixtures of diacetoglycerides (60–70%) and monoacetoglycerides (30–40%) were obtained. Possible commercial uses of the products are discussed.

Note on the economic refining and decolorization of acidic oils. M. Loury. *Revue Francaise des Corps Gras* **2**, 150–158(1955). Very impure acidic oils resulting from the acidification of the foots obtained in the alkali refining of soya, linseed, corn, and rapeseed oils were studied in order to determine whether a more economical method than low pressure distillation could be found to purify and decolorize them for use in the manufacture of soft soaps. Preliminary purification involved the removal of metallic impurities. Phosphoric acid was found to be superior to sulfuric, hydrochloric, nitric, acetic, and oxalic acids or acid salts for this purpose. Furthermore, the use of phosphoric acid resulted in the ready flocculation and separation of the mucilages in the oil. Nitric acid afforded good decolorization but the soaps obtained were hard presumably because of elaidinization during the treatment. Classical oxidizing agents such as potassium permanganate, bichromate, chlorate, and hypochlorite were used in the presence of mineral acids but the results were not very satisfactory. The use of potassium perchlorate and hydrochloric acid gave considerably better results but the use of such a mixture on a commercial scale would not be without hazard. Benzoyl peroxide gave much better decolorization than did hydrogen peroxide or the peroxides of sodium, magnesium, or urea. Ammonium and potassium persulfate gave good decolorization. When soaps were decolorized with the peroxides the clarity of the soaps was reduced considerably by the presence of gas bubbles. Sodium chlorite was found to be superior to chlorine dioxide since it did not require special equipment for processing, gave more constant results and was less sensitive to operating conditions. The best procedure found from all these tests involved the room temperature separation of mucilages by stirring a mixture of oil with 0.2 to 0.5% of 60° Bé phosphoric acid diluted with three volumes of water followed by centrifuging and filtration with the aid of clay. The resulting product was decolorized with 0.2 to 1.0% of sodium chlorite.

Upgrading of methyl esters—a by-product of carotene extraction from palm oil. J. Jorand. *Oleagineux* **10**, 99–105, 193–196, 264–274(1955). Standard methods of converting the methyl esters from palm oil processing into valuable commercial products by means of saponification, glycerolysis, hydrogenation to give saturated compounds, and reduction of the esters to alcohols are discussed. Conversions of the methyl esters into amides, hydroxy acids, acetostearins, and aceto-oleins are considered briefly. 65 references.

Epoxidation and hydroxylation of unsaturated derivatives. P. Blaizot. *Oleagineux* **10**, 311–317(1955). Methods for preparing epoxides and hydroxy compounds from unsaturated fatty acids and vegetable oils are reviewed. Commercial uses of such derivatives are discussed.

Tall oils. II. Urea adduct of tall oil. Taro Matsumoto and Toshitake Tamura (Nihon Univ., Tokyo). *J. Japan Oil Chemists' Soc.* **4**, 23–5(1955). Japanese tall oil (containing 40% fatty acids) reacted with urea gave urea adducts consisting of most of fatty acids leaving nonadducts containing much resin acids and a lesser amount of fatty acids (a part of linoleic acid, oxidized, and polymerized acids). When 1 part of tall oil was treated with 4 parts urea, 12 methanol, and 10 benzene for washing, 27% of urea adducts consisting of 90% fatty acids, 4% resin acids, and 6% unsaponifiable matter, and 73% of nonadducts consisting of 21% fatty acids, 63% resin acids, and 16% unsaponifiable matter were obtained. Partially hydrogenated tall oil, methyl ester, and Na salt of tall oil were also treated with urea and similar results were obtained.

The color and flavor of fats and oils. Yataro Obata (Hokkaido Univ., Sapporo). *J. Japan Oil Chemists' Soc.* **4**, 115–24(1955). A review with 113 references.

Wool fat. Eiichi Kawahara. *J. Japan Oil Chemists' Soc.* **4**, 134–42(1955). A lecture on wool fat and lanolin.

Volatile substances formed by the decomposition of peroxides of methyl esters of highly unsaturated acids. Yoshiyuki Toyama and Katsuhito Suzuki (Nagoya Univ.). *J. Chem. Soc. Japan, Ind. Chem. Sect.* **58**, 52–4(1955). The methyl esters of a fraction of highly unsaturated acids of sardine oil were oxidized at 0–25° by oxygen absorption. The oxidized product was decomposed by heating at 90–100° in nitrogen. The volatile acids thus obtained were identified by paper chromatography of hydroxamic acids to be formic, acetic, and propionic acids. The volatile carbonyl compounds were precipitated as 2,4-dinitrophenylhydrazones and were identified by their m.p., N content, and absorption spectra to be *n*-butyraldehyde, *n*-hexanal, mixture of lower saturated aldehydes, crotonaldehyde, 2-pentenal, and 2-hexenal.

Plasticizers from fatty oils. II. Plasticizers from coconut-oil lower fatty alcohols, sperm alcohols, phthalic acid, and aliphatic dibasic acids. Koichi Murai, Giichi Akazome, Naraichi Tsujisaka, and Mahisa Sakurai (Nihon Yushi Co., Osaka). *J. Oil Chemists' Soc., Japan* **3**, 200–3(1954). Phthalic acid esters were synthesized and examined as plasticizers for polyvinyl chloride by similar technique described in Part I. The esters synthesized included di-*n*-octyl phthalate (DOP), di-*n*-decyl phthalate, di-*n*-lauryl phthalate, butyl decyl phthalate, methyl oleyl phthalate, di-(2-ethylhexyl)phthalate, di-(*sec*-octyl) phthalate, di-isooctyl)phthalate, di-(3,5,5-trimethylhexyl) phthalate, di-(diethyleneglycolmonoethylether) phthalate, butyl cetyl phthalate, and methyl cetyl phthalate. Among them the last 2 were more or less nonmiscible with polyvinyl chloride,