SPECIFIC HEAT CAPACITIES OF PURE TRIGLYCERIDES BY HEAT-FLUX DIFFERENTIAL SCANNING CALORIMETRY

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Abstract

The specific heat capacities of some triglycerides commonly found in palm oil were determined with a heat-flux differential scanning calorimeter. The specific heat capacity measurements were made under the optimum operating conditions determined earlier: scan rate 17 deg·min^{-1}, sample mass 21 mg and purge gas (nitrogen) flow rate 50 ml/min. Pure triglycerides (four simple and four mixed) were used in the experiments. The four simple triglycerides were trilaurin, trimyristin, tripalmitin and tristearin, and the mixed triglycerides were 1,2-dimyristoyl-3-oleoyl, 1,2-dimyristoyl-3-palmitoyl, 1,2-dipalmitoyl-3-oleoyl and 1,2-di-oleoyl-3-palmitoyl. The results of this study are compared with literature values and also with values obtained by using estimation methods. The experimental specific heat capacities are within ±1% precision with a 95% confidence level.

Keywords: DSC, specific heat capacity, triglycerides

Introduction

Malaysia is the world's leading exporter of palm oil. The growth of the industry is greatly dependent upon effective and productive research and development to meet the requirements and demands in the ever competitive fields of oils and fats. Research efforts are geared to solving existing problems in the oil palm industry and also to developing new technologies in downstream products such as fatty acids and fatty acid methyl esters. This requires a comprehensive database of the physical properties of palm oil and its related compounds.

The data on the physical properties of pure triglycerides are considerably deficient: the specific heat capacities of some simple triglycerides in the temperature range up to 100°C have been reported in the literature, but no such data are known for mixed triglycerides. The specific heat capacities of triglycerides, like other physical properties at elevated temperatures, are necessary for the realistic

design of process equipment used in the palm oil industry. Even now, certain processes in palm oil physical refining plants, such as deodorization, operate at elevated temperatures in the range 250–270°C at 1 mmHg.

Most of the empirical methods for estimating the specific heat capacities of liquids have limited engineering applicability: either the values are estimated only at room temperature or the methods are not suitable when applied to fairly large and complicated molecules such as triglycerides. However, Phillips and Mattamal [1] developed a group contribution method for carboxylic esters (including triglyceride series) covering the temperature range 20–180°C. This method estimates the specific heat capacities of carboxylic esters to within ±5% variation of their own experimental results. There are methods [2, 3] which have not been specifically developed for estimation of the specific heat capacities of triglycerides, but which are applied to triglycerides for comparison purposes.

Sakiadis and Coates [2] derived a correlation base on the semi-empirical application of the theory of corresponding states, in order to predict the specific heat capacities of hydrocarbons as a function of temperature. The method incorporates chain length, different types of branching, and unsaturation in its calculation of specific heat. The average deviation of the calculated from the observed specific heat capacities of hydrocarbons was found to be ±0.9%. The method is applicable from the melting point to the boiling temperature of the liquid.

Bondi [3] developed a method of estimation of specific heat capacity for a wide range of large and long-chain molecules. The method takes into account molecular structure and related parameters such as flexibility, number of carbon atoms and skeletal atoms, polarity and internal rotation within the molecule. The method requires experimental data such as liquid density for use in the calculations. The heats of vibration of the various groups to be used in the Bondi estimation method are reported by Rihani and Doraisamy [4].

The methods of Sakiadis and Coates [2] and Bondi [3] may both give useful approximations to high molecular weight liquids such as triglycerides. Robiah [5] has claimed to have successfully applied the methods of Sakiadis and Coates [2] and Bondi [3] for the estimation of specific heat capacities of palm oil mixtures.

Since the mid-1960-s, the use of DSC in the measurement of specific heat capacity and phase transitions is being favoured and is fast replacing all other routine methods of measurement. The handling of the equipment is easy and large numbers of data points of high accuracy can be obtained in a relatively short period.

The present investigation reports on the measurement of the specific heat capacities of four simple and four mixed triglycerides by using DSC within the

temperature range from the melting point (25–80°C) to 250°C. The eight triglycerides chosen for this study, with carbon numbers ranging from C36 to C54, are common in most vegetable oils. The experimental results are compared with the specific heat capacities estimated from the methods of Phillips and Mattamal [1], Sakiadis and Coates [2] and Bondi [3], and also the values reported by Phillips and Mattamal [1], Charbonnet and Singleton [6] and Hampson and Rothbart [7].
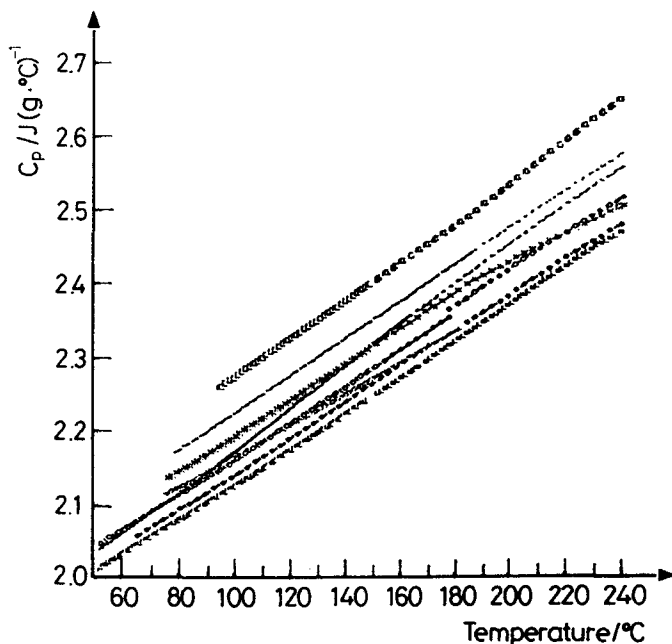

Fig. 1 Specific heat capacity of triglycerides as a function of temperature
(scan rate = 17 deg·min^{-1}, sample weight = 21 mg and N$_2$ flow = 50 ml/min; C_p of simple triglycerides increases with carbon number);
(—) trilaurin–C36; (—) trimyristin–C42; (—) tripalmitin–C48; (—) tristearin–C54; (—) MMO–C46; (—) MMP–C44; (—) PPO–C50; (—) OOP–C52

Experimental

Samples

The samples of simple triglycerides (trilaurin, trimyristin, tripalmitin and tristearin) and mixed triglycerides (1,2-dimyristoyl-3-oleoyl (MMO), 1,2-dimyristoyl-3-palmitoyl (MMP), 1,2-dipalmitoyl-3-oleoyl (PPO) and 1,2-dioleoyl-3-palmitoyl (OOP)) were obtained from Sigma Chemical Co., Dorset, England, with purities higher than 99%. The sapphire used as a standard was a single-crystal synthetic sapphire supplied by Seiko Instrumentation Inc., Japan.

Apparatus

A Seiko DSC 220 heat-flux type DSC instrument connected to a Seiko SSC 5200 thermal analysis system was used for the experiments.

Procedure

The round robin test described earlier [8–10] was used for specific heat capacity measurements on DSC.

The melting points of triglycerides are required in order to ensure that the specific heat capacity measurements are conducted in the liquid phase only. The melting points of triglycerides obtained by DSC measurement are only approximate. Two sample pans of approximately equal masses were used. One of the sample pans was filled with 20 mg triglyceride sample. The empty pan was then placed on the reference side of the holder and the triglyceride sample on the sample holder in the DSC cell. The sample was scanned at 10 deg·min^{-1} from 30 to 90°C with isotherms of 3 minutes at the starting and final temperatures.

Results and discussion

Experimental results

The optimum conditions for the determination of specific heat capacities of triglycerides were described previously [10]: scan rate 17 deg·min^{-1}; sample weight 21 mg; and purge gas flow rate 50 ml/min, with triglyceride specific heat capacity determinations up to 250°C.

Experimental data on the physical properties are usually available for the four simple triglycerides chosen. These enable comparison between experimental and reported values. The major components of palm oil, however, are mixed triglycerides, PPO and OOP. All the triglycerides except MMO and OOP exist in the solid state at room temperature (between 20 and 30°C). In most cases, more than one melting point (polymorphism) is reported [11].

Triglycerides occur in one of the three basic polymorphs, designated α, β′ and β. β′ is the least stable and has the lowest melting point; β is the most stable and has the highest melting point. During melting, transformation takes place from α to β′ and then to β and the process is irreversible [11].

Table 1 shows the melting points of these triglycerides; the values correspond to the β form. The Table also shows the approximate temperatures at the onset of degradation. The onset of degradation of the triglycerides was ascertained by specific heat measurements by means of DSC, described earlier [10]. The specific heat capacities of the samples were observed to drop suddenly above 150°C when no purge gas was used in the apparatus. This point was taken as a rough indicator of the onset of degradation.

Figure 1 depicts the specific heat capacities of the triglycerides as a function of temperature; these form a family of straight lines (solid lines with symbols). It is observed that the specific heat capacities are higher for larger molecules (high carbon number) among the simple trigliceride. Thus, tristearin, with carbon number 54 (C54), has the highest specific heat capacity, followed by tripalmitin (C48), trimyristin (C42) and trilaurin (C36).

Table 1 Onset of melting and degradation of pure triglycerides in a DSC

Triglyceride	C No.	T_{melt} / °C	T_{deg} / °C
Trilaurin	C36	44	170
Trimyristin	C42	52.2	181
Tripalmitin	C48	63	184
Tristearin	C54	70	187
1,2-dimyristoyl-3-palmytoyl (MMP)	C44	51.5	181
1,2-dimyristoyl-3-oleoyl (MMO)	C46	<27	170
1,2-dipalmitoyl-3-oleoyl (PPO)	C50	34.9	180
1,2-dioleoyl-3-palmitoyl (OOP)	C52	<27	162

The values of the melting point are those for the β polymorph (the highest melting point)

For mixed triglycerides, no such pattern between specific heat capacity and carbon number is observed. It is found that the specific heat capacities of the mixed triglycerides are lower than those of the simple triglycerides. A further reduction in the specific heat capacities of MMO and OOP may be attributed to the presence of double bonds.

The specific heat capacities in the higher temperature region (from about 160 to 250°C) are obtained only through nitrogen gas purging, and are also illustrated in Fig. 1 (dotted lines). Tristearin (C54) has the highest specific heat capacity, followed by tripalmitin (C48), trimyristin (C42) and trilaurin (C36). The specific heat capacities for the mixed triglycerides are in general lower and the degree of unsaturation decreases the values further, as observed in the lower temperature range.

In general, the specific heat capacities of the triglycerides are given by the following relations:

$$C_p \ (J \cdot g^{-1} \cdot deg^{-1}) = A \cdot T \ (°C) + B \qquad (1)$$

in the lower temperature range (before degradation) and

$$C_p \ (J \cdot g^{-1} \cdot deg^{-1}) = C \cdot T \ (°C) + D \qquad (2)$$

in the higher temperature range (after degradation). The values of the constants A, B, C and D in the above equations, together with the temperature range in which they are valid, are given in Table 2.

Comparison of experimental specific heat capacities with reported data and correlation

Use of the DSC technique for determination of the specific heat capacities of simple triglycerides in the temperature range 50–180°C was first reported by Phillips and Mattamal [1]. Hampson and Rothbart [7] carried out specific heat capacity determinations for all three polymorphic forms between −90 and 100°C. The earliest reported values for the specific heat capacities of triglycerides were probably those of Charbonnet and Singleton [6], who used calorimetric methods in the temperature range -183 to 100°C. (Subambient temperatures were used to study the specific heats of the respective crystals of the different polymorphs.)

All three reported experimental specific heat capacities related to only a few selected temperatures in a very narrow range. These are the only available experimental values for comparison with the results of the present work. The results are also compared with the values estimated by using the methods of Phillips and Mattama [1], Sakiadis and Coates [2] and Bondi [3] over a wider temperature range, from the melting point up to about 250°C.

Comparisons of experimental specific heat capacities with reported and estimated values are shown in Figs 2–5 for the simple triglycerides trilaurin, trimyristin, tripalmitin and tristearin, respectively and those of the mixed triglycerides MMP, MMO, PPO and OOP in Figs 6–9, respectively. The experimental values in this work agree best with the values reported by Charbonnet and Singleton [6]. The agreement was found to be best for tristearin (C54), the remaining experimental values all being lower than those reported earlier, the maximum deviation being about 4%.

Comparison with the results of Phillips and Mattamal [1] and Hampson and Rothbart [7] is difficult because their experimental data are sporadic in nature. Phillips and Mattamal [1] themselves gave a 5% deviation from the experimental results. The individual data points of Hampson and Rothbart [7] show a 2–4% deviation, except for tristearin, where the result is lower by 5–10% as compared with the values in this work. It may be noted that both Phillips and Mattamal [1] and Hampson and Rothbart [7] used power-compensated DSC and not heat-flux DSC as in this study.

The specific heat capacity of trilaurin is also compared with the estimated value obtained by the method of Sakiadis and Coates [2]. This deviates appreciably from the experimental values and also from the reported specific heat capacity. The method involves a tedious calculation procedure and requires certain parameters (thermal expansion, and the velocity of sound in the liquid), which are not available for trilaurin. Approximation of these values with the known data for other vegetable oils might have introduced large errors in the final results. Therefore, this method was not used for estimation of the specific

Table 2 Constants for the specific heat capacity Eqs (1) and (2)

Triglyceride	Temp. range /°C	A	B	Temp. range /°C	C	D
Trilaurin	55–170	0.002443	1.8991	170–250	0.001990	1.9756
Trimyristin	65–181	0.002390	1.9565	181–250	0.001908	2.0460
Tripalmitin	75–184	0.002474	1.9793	184–250	0.002501	1.9750
Tristearin	80–187	0.002530	2.0208	187–250	0.002916	1.9588
1,2-dimyristoyl-3-palmytoyl	60–181	0.002078	1.9603	181–250	0.002408	1.9000
1,2-dimyristoyl-3-oleoyl	35–170	0.002390	1.8885	070–250	0.002498	1.8700
1,2 dipalmitoyl-3-oleoyl	50–180	0.002427	1.9213	180–250	0.002452	1.9276
1,2-dioleoyl-3-palmitoyl	35–162	0.002842	1.8916	162–250	0.002649	1.9230

The specific heat capacity is given by the equations:

C_p (J·g^{-1}·deg^{-1}) = $A \cdot T$ (°C) + B (1) for lower temperature range and

C_p (J·g^{-1}·deg^{-1}) = $C \cdot T$ (°C) + D (2) for higher temperature range

heat capacities of the other triglycerides. In fact, this method is more suitable for hydrocarbons [2].

Comparisons were also made with specific heat capacities of triglycerides estimated by using the methods of Phillips and Mattamal [1] and Bondi [3] and are shown in Figs 2–9. Both of these methods estimate specific heat capacities lower than the experimental values in this work; the Phillips and Mattamal [1] method gives estimates closer to the experimental values. The deviation ranges from 1.5% for trilaurin to 6% for tristearin.

The best estimate is given for trilaurin, followed by MMP, trimyristin, tripalmitin and tristearin. However, the method gives large deviations for the unsaturated triglycerides, MMO, PPO and OOP. The method may not be used for estimation of the specific heat capacities of unsaturated triglycerides. This method does not consider the presence of double bonds in the triglycerides (but takes into account merely the types and numbers of alkyl groups present and the number of carboxyl groups). This might be the cause of the large deviations observed.

The method of Bondi [3] when applied to triglycerides does not give a satisfactory estimate of the specific heat capacity, as can be seen in all the Figures. When used to estimate the specific heat capacities of triglycerides, Bondi's
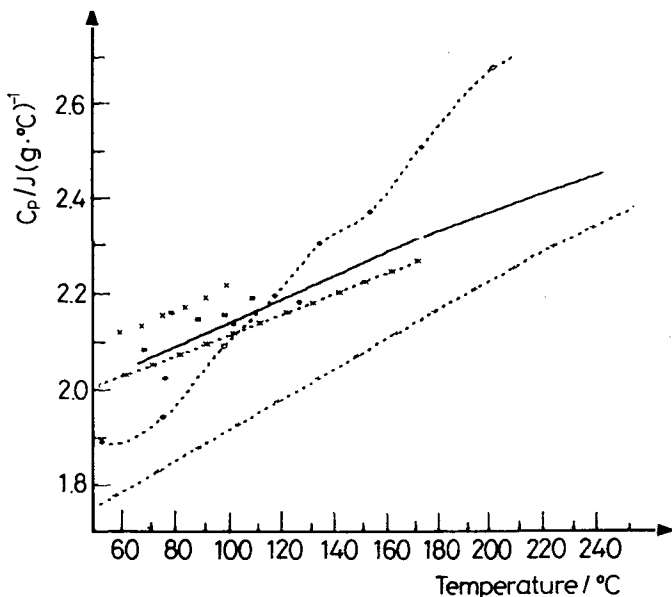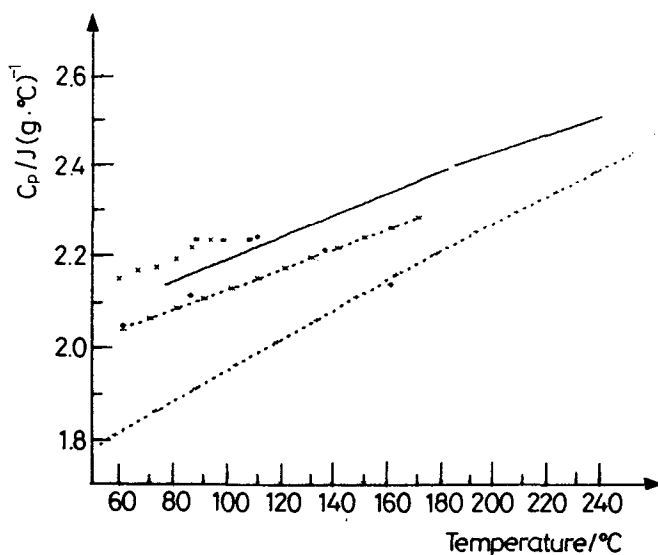

Fig. 2 Specific heat capacity of trilaurin as a function of temperature (scan rate = 17 deg·min^{-1}, sample weight=21 mg and purge gas=50 ml/min); Comparison of experimental C_p (solid line) with estimated values of (⇢) Bondi [3], (⇢) Phillips et al. [1], ( ) Sakiadis et al. [2] and reported values of (•) Phillips et al. [1], (×) Charbonnet et al. [6], (▪) Hampson et al. [7]

Fig. 3 Specific heat capacity of trimyristin as a function of temperature (scan rate=
17 deg·min⁻¹, sample weight=21mg and purge gas=50 ml/min); Comparison of ex-
perimental C_p (solid line) with estimated values of (⁻⁺) Bondi [3], (⁻⁺) Phillips *et
al.* [1] and reported values of (•) Phillips *et al.* [1], (×) Charbonnet *et al.* [6],
(■) Hampson *et al.* [7]

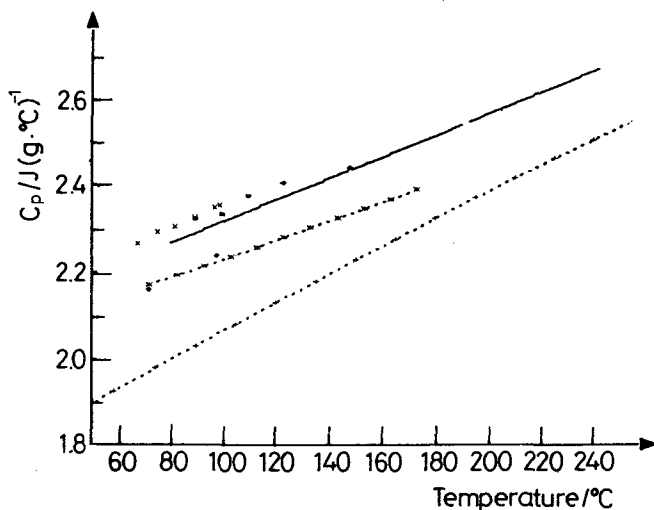**Fig. 4** Specific heat capacity of tripalmitin as a function of temperature (scan rate=
17 deg·min⁻¹, sample weight=21 mg and purge gas=50 ml/min); Comparison of ex-
perimental C_p (solid line) with estimated values of (⁻⁺) Bondi [3], (⁻⁺) Phillips *et
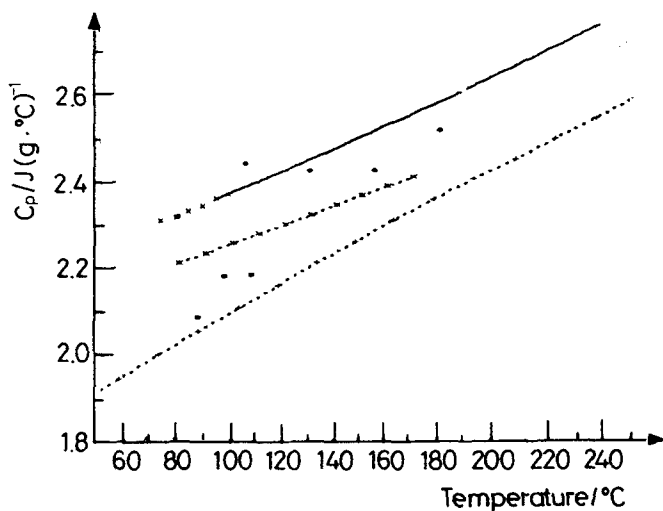al.* [1] and reported values of (•) Phillips *et al.* [1], (×) Charbonnet *et al.* [6],
(■) Hampson *et al.* [7]

Fig. 5 Specific heat capacity of tristearin as a function of temperature (scan rate= 17 deg·min^{-1}, sample weight=21 mg and purge gas=50 ml/min); Comparison of experimental C_p (solid line) with estimated values of (⟶) Bondi [3], (⟶) Phillips *et al.* [1] and reported values of (•) Phillips *et al.* [1], × Charbonnet *et al.* [6], (■) Hampson *et al.* [7]

method gives a linear relationship with temperature, with a maximum deviation of 12%. The large deviation is probably due to an accumulation of errors caused by the many assumptions made throughout the calculation procedure, many of which may not be valid. Bondi's method is a group contribution method developed on the basis of the principles of corresponding states. This involves assumptions when theoretical parameters such as ideal specific heat capacity at constant volume (C_V^0), vibrational contributions to the specific heat capacity of a liquid, and reduced density ($r*$) have to be calculated.

Conclusions

1. The dependence of the specific heat capacities of triglycerides on temperature in the experimental range (T_m to 250°C) can be described by a straight line relationship.

2. For simple triglycerides, the values reported by Charbonnet and Singleton [6] give the best agreement, within 4% of the experimental results found in this work.

3. The best estimated specific heat capacities of triglycerides were found to be those obtained with the method developed by Phillips and Mattamal [1]; however, this applies only to saturated triglycerides. The deviation of the estimated values from the experimental values varies between 1.5 and 6%.
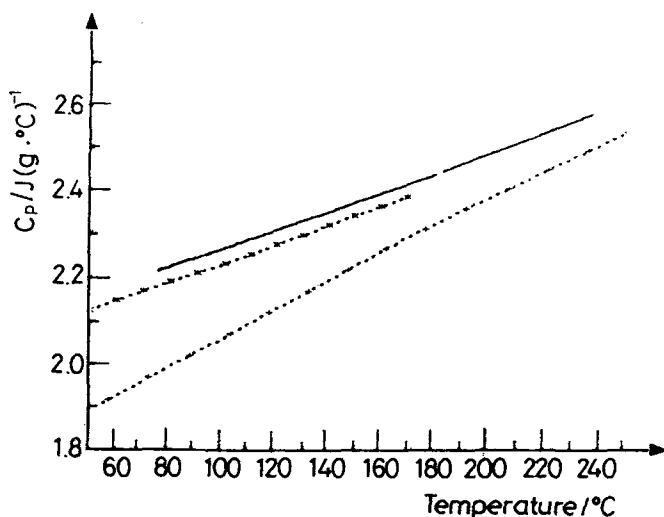
Fig. 6 Specific heat capacity of 1,2-myristoyl-3-palmitoyl triglyceride (MMP) as a function
of temperature (scan rate = 17 deg·min^{-1}, sample weight = 21 mg and purge
gas = 50 ml/min); Comparison of experimental C_p (solid line) with estimated values
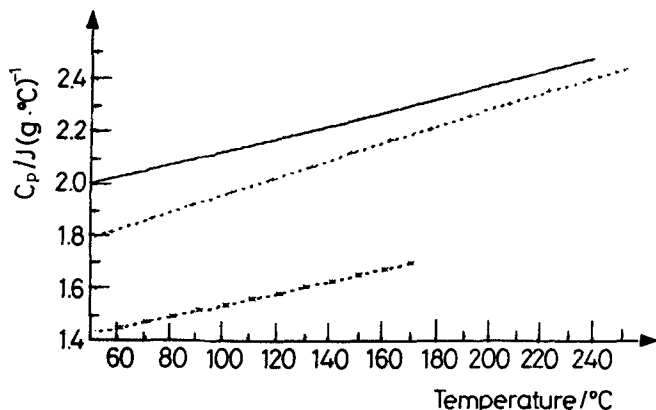of (→) Bondi [3] and (–✶) Phillips *et al.* [1]

Fig. 7 Specific heat capacity of 1,2-dimyristoyl-3-oleoyl triglyceride (MMO) as a function
of temperature (scan rate = 17 deg·min^{-1}, sample weight = 21 mg and purge
gas = 50 ml/min); Comparison of experimental C_p (solid line) with estimated values
of (→) Bondi [3] and (–✶) Phillips *et al.* [1]

4. DSC was found to be a satisfactory method for measurement of specific
heat capacity, despite the limitations, e.g. determination of optimum conditions
prior to experimental runs, and repeated runs for a given sample. DSC experi-
ments yield a large number of data for a given set of runs and are especially
suitable for expensive samples such as triglycerides, since only a small amount
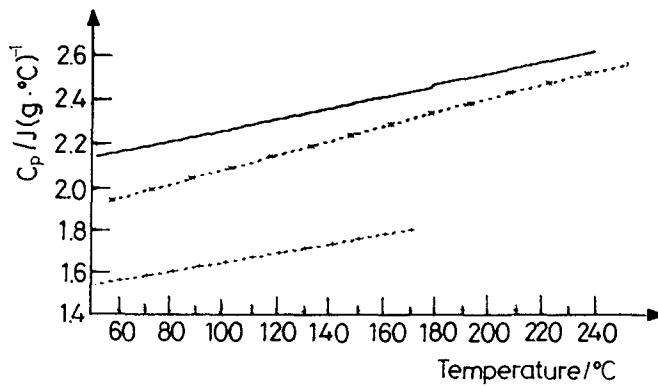of sample is required.

Fig. 8 Specific heat capacity of 1,2-palmitoyl-3-oleoyl triglyceride (PPO) as a function of temperature (scan rate=17 deg·min^{-1}, sample weight=21 mg and purge gas=50 ml/min); Comparison of experimental C_p (solid line) with estimated values of (-•-) Bondi [3] and (-•-) Phillips et al. [1]
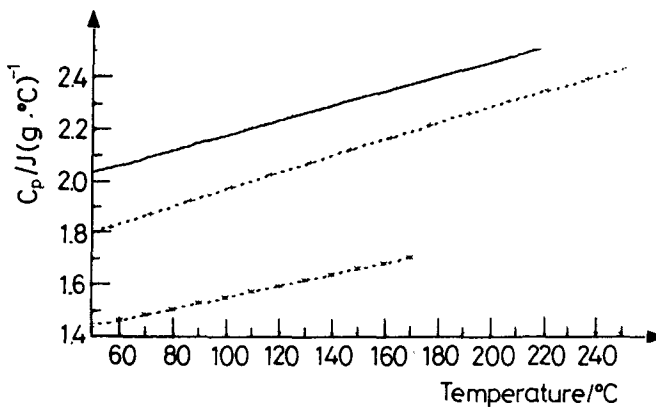

Fig. 9 Specific heat capacity of 1,2-dioleoyl-3-palmitoyl triglyceride (OOP) as a function of temperature (scan rate=17 deg·min^{-1}, sample weight=21 mg and purge gas=50 ml/min); Comparison of experimental C_p (solid line) with estimated values of (-•-) Bondi [3] and (-•-) Phillips et al. [1]

5. The experimental specific heat capacities measured for the eight triglycerides are accurate within ±1% and are reproducible within the optimum conditions used.

*   *   *

Nomenclature

C – carbon number, e. g. C36 indicates a carbon number of 36
C_p – specific heat capacity at constant pressure, $J \cdot g^{-1} \cdot deg^{-1}$
C_V – specific heat capacity at constant volume, $J \cdot mol^{-1} \cdot deg^{-1}$
C_V^o – ideal specific heat capacity at constant volume, $J \cdot mol^{-1} \cdot deg^{-1}$
MMO – 1,2-dimyristoyl-3-oleoyl, a triglyceride
MMP – 1,2-dimyristoyl-3-palmitoyl, a triglyceride
OOP – 1,2-dioleoyl-3-palmitoyl, a triglyceride
P – pressure
PPO – 1,2-dipalmitoyl-3-oleoyl, a triglyceride
T – temperature, °C
T_m – melting point, °C
Greek letters
α – the unstable phase in the triglyceride
β – the most stable phase in the triglyceride polymorph
β' – the most unstable phase and intermediate phase in the triglyceride polymorph
r^* – reduced density used the estimation method of Bondi (1968)

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Zusammenfassung — Mittels eines Wärmefluß-Differential-Scanningkalorimeters wurde die spezifische Wärmekapazität einiger, für gewöhnlich in Palmöl vorkommender Triglyceride bestimmt. Die Messungen der spezifischen Wärmekapazität wurden unter den bereits zuvor ermittelten optimalen Versuchsbedingungen durchgeführt: Scangeschwindigkeit 17 deg/min, Probenmasse 21 mg und Spülgasgeschwindigkeit(Stickstoff) 50 mL/min. In den Experimenten wurden reine Triglyceride (vier einfache und vier gemischte) verwendet. Die vier einfachen Triglyceride waren Trilaurin, Trimyristin, Tripalmitin und Tristearin, die gemischten Triglyceride waren 1,2-Dimyristol-3-oleoyl, 1,2-Dimyristol-3-palmitoyl, 1,2-Dipalmitoyl- 3-oleoyl und 1,2-Dioleoyl-3-palmitoyl. Die Ergebnisse dieser Untersuchung wurden mit Literaturwerten und auch mit Werten verglichen, die anhand von Schätzungsmethoden erhalten wurden. Die experimentellen spezifischen Wärmekapazitäten lagen bei einem Konfidenzintervall von 95% innerhalb von 1%.