Journal of Oil Palm Research Vol. 12 No. 1, June 2000, p. 1-7

DIFFERENTIAL SCANNING THERMOGRAMS OF PALM OIL TRIGLYCERIDES IN THE PRESENCEOF DIGLYCERIDES

Keywords: Diglycerides, palm oil, melting, crystallization differential scanning calorimetry.

SIEW, W L* and NG, W L**

The melting and crystallization behaviour of palm oil triglycerides was characterized by differential scanning calorimetry (DSC). The influence that diglycerides have on the melting and cooling behaviour of palm oil is dependent on the concentration and nature of diglycerides. All the diglycerides (PP, PO and 00) and the palm diglyceride mixture (PDG) depressed the melting point of the oil. The 1,2 isomer was more effective than the 1,3 isomer. An excess of 1,3 PP elevated the meltingpoint. The crystallization behaviour is complicated if 1,3 PP is present in high concentrations. All the diglycerides studied can undergo co-crystallization with palm triglycerides, except for 1,3 PP at high concentration.

INTRODUCTION

Palm oil consists of four main triglycerides - POP and POO, together forming about 53%-57% of total triglycerides, POL 8%-11%, and PPP 5%-6% (Sassano and Jeffrey, 1993; Hamirin, 1981). In addition, it also contains about 4%-7.5% diglycerides (Jacobsberg, 1976; Goh and Timms, 1985; Siew and Ng, 1995). Under ambient conditions, palm oil appears as a heterogeneous slurry of crystals in a liquid oil. The two phases are distinct and can be clearly observed in their DSC crystallization and melting curves. The cooling thermogram of palm oil shows two exotherms which correspond to hard and soft components as discussed by Ng and Oh (1994). Fractionation of the oil gives a liquid fraction with one sharp exotherm and a solid fraction, stearin, with a complex crystallization thermogram.

The high diglyceride content in palm oil affects its crystallization properties (Okiy *et al.*, 1978; Okiy, 1978). In other oils, diglycerides retard their polymorphic change from one crys-

---

. Malaysian Palm Oil Board,
P.O. Box 10620, 50720 Kuala Lumpur. Malaysia.
** 15. Hujan Bubuk, Overseas Union Garden,
58200 Kuala Lumpur, Malaysia.

tal form to another (Hernquist et al., 1981; Hernquist and Anjou, 1983) with the saturated 1,2 isomer the more effective in doing so (Von Sabine Walnett et al., 1991). In this study, the melting and crystallization behaviour of palm oil under dynamic conditions was evaluated in the presence of different diglycerides.

MATERIALS AND METHODS

Sample Preparation

Palm oil was purified using column chromatography with a 2.5 cm diameter and 40 cm long column. About 30 g of oil were dissolved in 120 ml petroleum ether. Silica gel (30 g) was mixed with sufficient petroleum ether and the mixture transferred to the chromatographic column. The sample was eluted through the column with 1 litre petroleum ether-diethyl ether (95:5 v/v). The solvent was removed from the eluate under vacuum in a rotary evaporator. The purity of the triglycerides (PTG oil) was checked by HPLC using AOCS official Ce 5b-89 method.

Diglyceride from palm oil (PDG) was obtained from the same column after all the triglycerides had been eluted. The eluant (900 ml) consisting of petroleum ether-diethylether (85:15 v/v) was added to the column The solvent was removed by rotary evaporator from the PDG extract. The PDG consisted of62.3% palmitoyloleoyl-glycerol (PO), 23.2% dioleolylglycerol (OO) and 14.4% dipalmitoylglycerol (PP).

PTG oil was mixed with PDG in the proportions of 2.5%, 5% and 10% by weight. Individual diglycerides (> 99% pure) of 1,3 sn - PP and 1,2 PP from Sigma Chemicals, USA and rac 1,3 PO, 1,2 PO, 1,3 00 and 1,2 00 from Larodan Fine Chemicals, Sweden were mixed separately with the PTG oil. The concentrations prepared were 1% and 5% for 1,2 00 and 1,3 PP and 2.5%, 5% and 10% for the other standard diglycerides. For 1,2 00, only a 2.5% mixture was prepared. At the 5% and 10% levels, cloudy solutions formed.

Thermal Analysis by DSC

DSC analysis of the samples was performed with a Perkin Elmer DSC-7 instrument (Norwalk, CN, USA). The sample was completely melted at 80°C before being weighed (10 mg) into a aluminium pan which was -then sealed using a sample pan crimper. The thermal history of the sample was erased by heating it to 80°C in the DSC instrument and holding it for 10 min. The sample was then cooled to -30°C at a rate of 40°C min^{-1}. To obtain the heating thermogram, the sample was held at -30°C for 10 min and then heated to 80°C at the rate of 10°C min^{-1}. The reference cell used in the analysis was an empty aluminum pan. The temperature scale was calibrated with gallium and indium. For the cooling thermogram, the sample was held at 80°C for 10 min and then cooled to -30°C at the rate of 10°C min^{-1}.

RESULTS AND DISCUSSION

The melting and crystallization peaks of the pure diglycerides and PDG are given in Table *1.* While the pure diglycerides had only one endotherm and exotherm, indicative of their purity, PDG showed three fusion and crystal-

TABLE 1. MELTING AND CRYSTALLIZATION PEAKS OF DIGLYCERIDES BY DSC

Diglyceride	Fusion peak (°C)	Melting point (°C)	Crystallization peak (°C)	onset of crystallization (°C)
1,2 PP	50.7	52.5	47.4	50.0
1,3 PP	71.5	75.0	62.5	65.0
1,2 0 0	22.7	26.0	3.2	10.0
1,3 0 0	24.6	28.3	10.9	15.7
1,2 PO	51.5	54.0	47.5	49.8
1,3 PO	41.7	45.3	28.0	30.6
PDG	22.8, 30. 43	47.0	-15, 9. 26.7	32.0

lization peaks. This was expected since the mixture contained 62.3% PO, 23.2% 00 and 14.4% PP. The onset of crystallization was 32°C, close to that of 1,3 PO. Similarly, the first crystallization peak was at 26.7°C, being so close to that of 1,3 PO as to suggest that the exotherm represents the crystallization of the 1,3 PO, the main diglyceride in the mixture. The fusion peak also reflects that of the 1,3 PO. The various diglycerides showed a large range in melting and crystallization behaviour. The 1,2 and 1,3 positioning of the fatty acids in the diglycerides gave differences in the melting behaviour, indicative of polymorphism.

The DSC cooling thermograms showed differences caused by the diglycerides. In the thermogram of PTG oil, there are two exothermic peaks, the first at 14°C and the second at -0.3°C (Figure *1*). The first peak is sharp and represents the crystallization of the higher-melting triglycerides. The bulk of the triglycerides crystallizes out in the second exothermic peak. In the presence of PDG, the first peak becomes broader and shifts slightly to a lower temperature (*Figure 1*). In the case of added PO or 00, this exothermic peak shifts to 12.3°C and 11.9°C respectively (*Figures* 2 to 4). This shift to a lower temperature is in compliance with the melting point depression effected by the diglycerides. On the other hand, the broadening of this peak probably indicates that the high-melting component triglycerides which crystallize out together, had been affected to a different extent by the diglycerides. In the case of added PP, the effect is rather abnormal (Figure 5). For instance, in the presence of a low level (1%) of the 1,3 isomer, the highest exothermic peak is considerably reduced. At 5%, this peak diminishes in intensity and an additional peak is observed at a higher temperature of 27°C. This

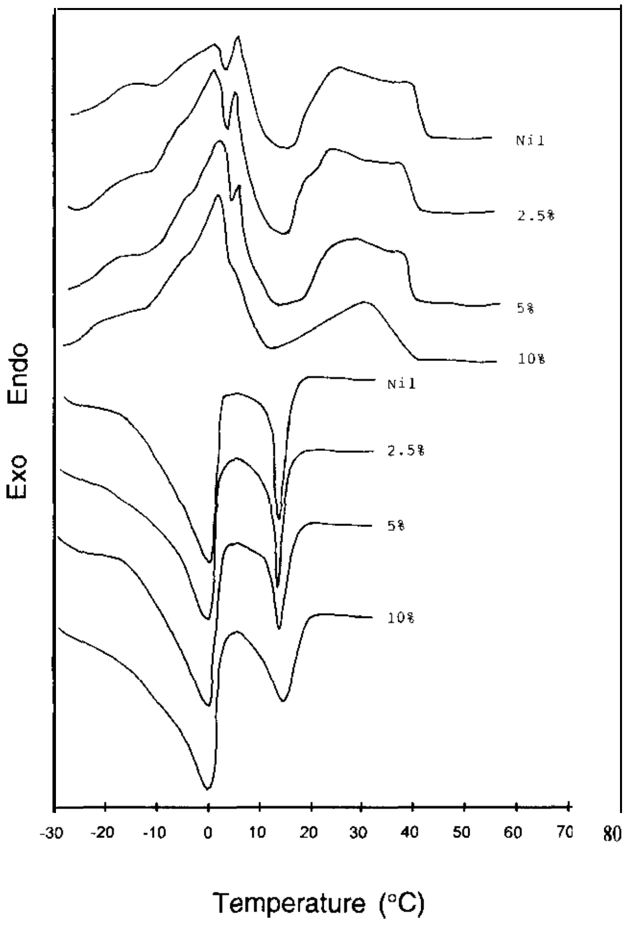

Figure 1. DSC thermograms of PTG oil with added PDG.

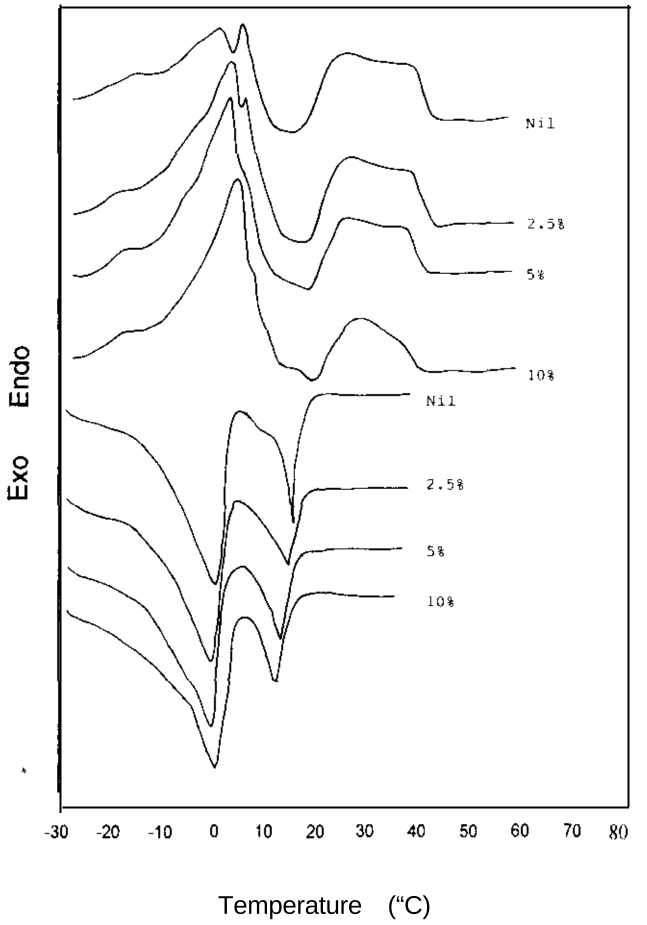

Figure 2. DSC thermograms of PTG oil with added 1,3 PO.

new peak can be attributed to the crystallization of excess 1,3 PP. Also, 1,3 PP has a much higher crystallization temperature than 1,2 PP (*Table 1*). In addition, it is probable that some of the high-melting triglycerides of palm oil may co-crystallize with the 1,3 PP. In contrast, the 1,2 isomer does not exhibit similar effects to those of the 1,3 isomer. It behaves just like the rest of the diglycerides studied. The above results show that all the diglycerides studied, with the exception of 1,3 PP at high concentration, can easily undergo co-crystallization with the PTG oil.

In the melting thermogram of PTG oil, there are two broad endotherms which are well separated from each other. The low-melting endotherm shows a sharp-peak at 4.9°C (Figure *1*). The melting characteristics of PTG oil are affected to a different extent by the different types of diglycerides, and the effect is more significant at higher concentrations. Because of the rapid cooling of the fat, it probably crystallized in the alpha form. During melting, polymorphic transition takes place as can be seen in the thermograms.

In the case of added PDG, the high-melting endotherm diminishes in intensity and shifts to a lower temperature, thus showing a distinct effect of melting point depression. In the low-melting endotherm, the sub-peak at 4.9°C diminishes in intensity and eventually disappears, causing the endotherm to be much sharper with the mean peak around 3°C (Figure *1*). Since PDG contains 62% PO, it is not surprising that the crystallization and melting thermograms are quite similar to those of 1,3 PO.

In the case of added palmitoyloleoyl diglyceride, there was a difference in the effect of 1,2 and 1,3 isomers. For 1,3 PO (*Figure 2*), the broad high-melting endotherm narrows down, with diminishing intensity, showing the effect of melting point depression. The low-melting endotherm also narrows down, with a concurrent increase in intensity resulting in the peak becoming very sharp. In the presence of the 1,2 isomer (Figure *3*), the high-melting endotherm shifts to a lower temperature which is indicative of the melting point depression. This peak also becomes narrower. The low-melting endotherm becomes narrower and sharper while a new peak emerges between the two endotherms. This peak, although small, is nevertheless distinct, with an intensity proportional to the concentration of 1,2 PO. This suggests that the endotherm is due to the melting of the diglyceride or its mixture with some palm triglycerides.

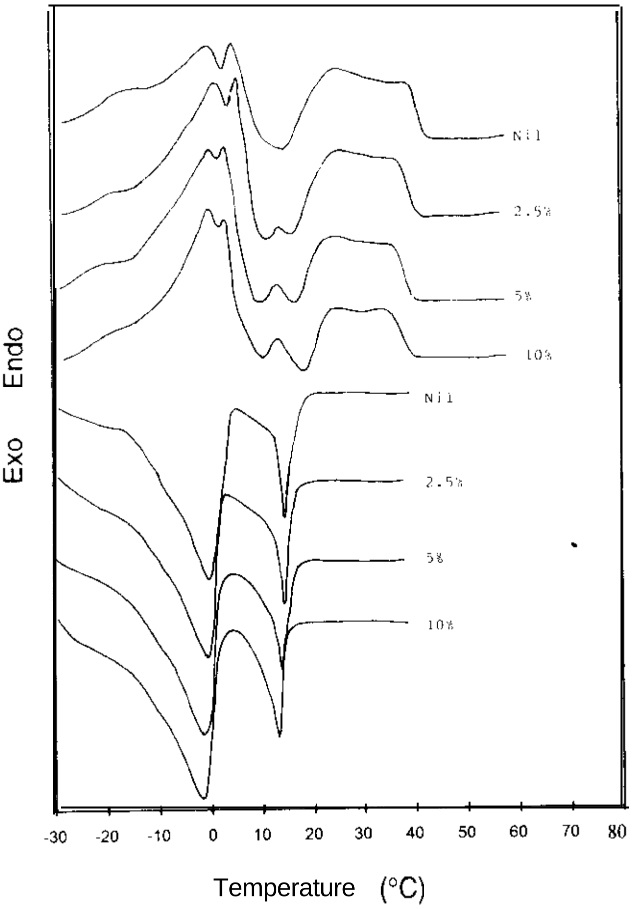

Figure 3. DSC thermograms of PTG oil with added 1,2 PO.

In the case of 1,3 00 (*Figure 4*), the effect is rather complex. The high-melting endotherm shifts to a lower temperature with a concurrent split into two peaks. The intensity of the low-temperature peak continues to increase while that of the high temperature peak diminishes, There is hardly any effect on the low-melting endotherm except that the peak at 4.9°C is shifted slightly higher and eventually merges with the low temperature peak of the high-melting endotherm. The 1,2 00 is unusual because of its low solubility in PTG. The presence of a small amount of dissolved 1,2 00 does not seem to have any significant effect except for the melting point depression.

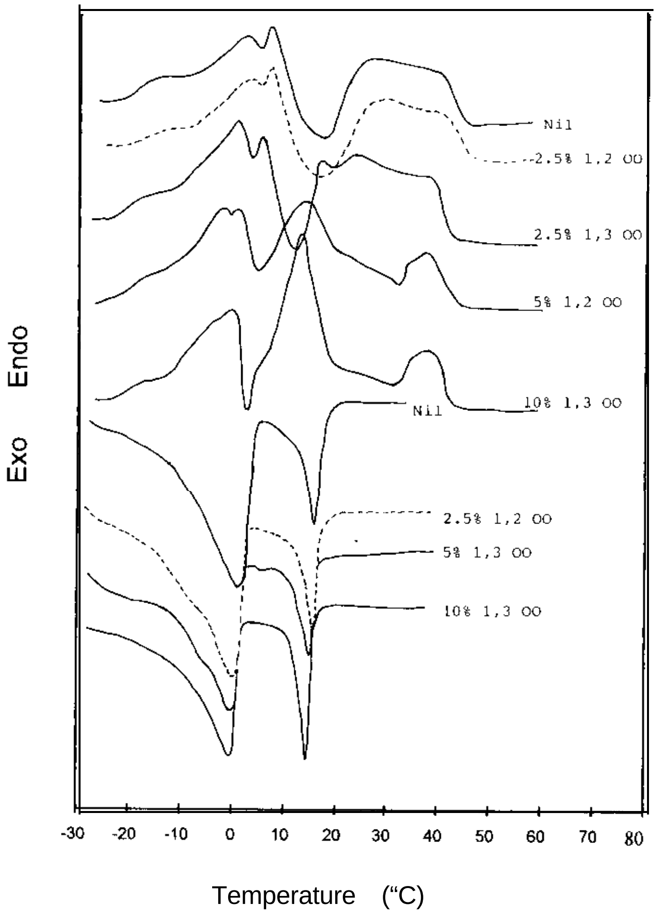

Figure 4. DSC thermograms of PTG oil with added OO.

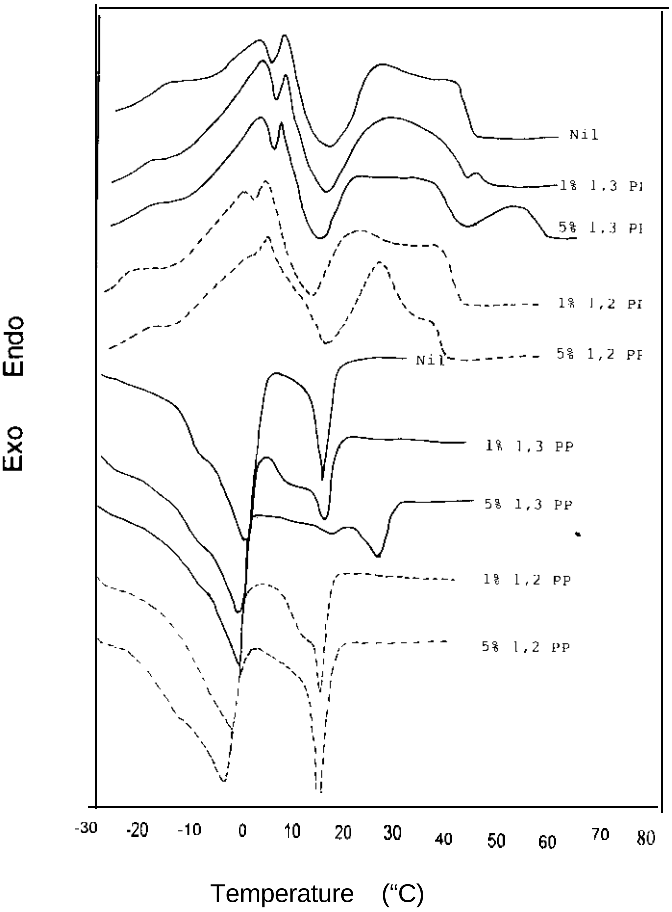

Figure 5. DSC thermograms of PTG oil with added PP.

The 1,2 and 1,3 *isomers* of PP exert different effects on the melting behaviour of PTG oil *(Figure 5). As* shown in *Table 1,* the 1,3 isomer melts and crystallizes at a much higher temperature than the 1,2 isomer. With added 1,3 PP, the high-melting endotherm narrows down with its higher end shifting to a lower temperature. However, a new peak then appears at the temperature just above the high-melting endotherm. This peak not only increases in intensity but also shifts to a high temperature as the concentration of 1,3 PP increases. This new peak is undoubtedly due to the diglyceride, and the fact that the peak position depends *on* the composition suggests intermolecular interactions between 1,3 PP and the saturated triglycerides in the PTG oil. In the case of the 1,2 isomer, the effect is mainly on the high-melting endotherm, which becomes much narrower and splits into two overlapping peaks of unequal intensity. Thus, while 1,2 PP forms an eutectic mixture with the PTG oil, this is not so for the 1,3 isomer of PP as it melts separately.

In conclusion, the melting and crystallization behaviour of palm oil is affected greatly by its diglyceride content. As the effect is concentration dependent, palm oil with more consistent properties can be produced if the variation in diglyceride composition can be minimized or better controlled.

The melting point of an oil is *an* important parameter as it determines its physical state at any temperature. It is one of the specifications normally required in the vegetable oil industry. In this study, the melting points of PTG oil and its fractions were determined from the DSC melting thermograms *(Table 2*). The melting point of PTG oil was 44.5°C, compared to the average slip melting point of palm oil at 36.0 (Tan and Oh, 1981). In general, all the indi-

TABLE 2. MELTING POINT OF PALM TRIGLYCERIDES IN THE PRESENCE OF DIGLYCERIDES

Diglyceride content	Melting point
Nil	44.5
1,3 PP	
1%	45.0
5%	54.5
1.2 PP	
1%	40.0
5%	38.0
1,3 00	
2.5%	44.0
5%	43.0
10%	42.0
1,200	
2.5%	44.0
1,3 PO	
2.5%	41.0
5%	40.0
10%	40.0
1,2 PO	
2.5%	39.5
5%	39.0
10%	38.5
PDG	
2.5%	39.5
5%	39.0
10%	39.0

vidual diglycerides, as well as PDG, depress the melting point of PTG oil. The 1,2 isomer is more effective than the 1,3 isomer in melting point depression. This effect of melting point depression has been attributed by other workers (Okiy *et* al., 1978; Okiy, 1978; Berger and Wright, 1976) to the formation of eutectic mixtures between diglycerides and triglycerides. However, 1,3 PP is an exception as it elevates the melting point of PTG oil. From the DSC melting thermograms, an additional peak at the highest temperature was observed. This peak is well separated from the endotherm of the PTG oil, implying that no eutectic mixture was formed between 1,3 PP and the component triglycerides in PTG oil.

The variable diglyceride contents of crude and refined palm oil and their fractions obviously have an effect on their melting points. This was observed in the slip melting point of palm oil which varied from 32°C to 39°C (Siew *et* al., 1993). There was no significant correlation between melting point and iodine value (Timms, 1985) for crude palm oil. This somewhat surprising observation can be attributed to the free fatty acids and diglyceride contents.

ACKNOWLEDGEMENTS

The authors thank the Director-General of MPOB for permission to publish this paper. Thanks are also due to the staff of the Analytical, Physics and Chemistry Groups for their technical support.

REFERENCES

BERGER, K G and WRIGHT, W B (1976). Crystallization behaviour of palm oil. Paper presented at ISF Conference, Marseilles.

GOH, E M and TIMMS, R E (1985). Determination of mono- and diglycerides in palm oil, olein and stearin, *J. Am. Oil Chem. Sm., 62:* 730-732.

HERNQUIST, L and ANJOU, K (1983). Diglycerides as stabilisers of the β' crystal form in margarines and fats. *Fette Seifen Anstrichm,* **85: 64-66**.

HERNQUIST, L; HERSLOF, B; LARSSON, K and PODLAHA, 0 (1981). Polymorphism of rapeseed oil with low content of erucic acid and possibilities to stabilise the β' crystal form in fats. *J. Sci. Food Agric, 32:* 1197.1202.

HAMIRIN, K (19811. Studies on palm oil with special reference to interesterification. Ph.D thesis, University of St. Andrews, U.K. p. 26.

JACOBSBERG, B and OH, C H (1976). Studies in palm oil crystallisation. *J. Am. Oil Chem Soc.,* **53: 609-617.**

NG, W L and OH, C H (1994). A kinetic study on isothermal crystallisation by solid fat content measurements. *J. Am. Oil Chem. Soc., 71:* 1135-1139.

OKIY, D A; WRIGHT, W B; BERGER, K G and MORTON, I D (1978). The physical properties of modified palm oil. *J. Sci. Food Agric., 29:* 1061-1068.

OKIY, D A (1978). Interaction of triglycerides and diglycerides of palm oil. *Oleagineux,* 33: *625-628.*

SASSANO, G H and JEFFREY, B S J (1993). Gas chromatography of triacylglycerols in palm oil fractions with medium polarity wide-bore columns. *J. Am. Oil Chem. Soc.,70:* 1111-1114.

SIEW, W L and NG, W L (1995). Diglyceride content and composition as indicators of palm oil quality. *J. Sci. Food Agric. 1995, 69: 73-79.*

SAMPLING and ANALYSIS of COMMERCIAL FATS and OILS. *AOCS Official Method Ce 5b-89 Triglycerides in Vegetable Oils* by HPLC.

SIEW, W L; CHONG, C L; TAN, Y A; TANG, T S and OH, C H (1993). Identity characteristics of Malaysian palm oil products: fatty acid and triglyceride composition and solid fat content. *Elaeis, 5: 38-46.*

TIMMS, R E (1985). Physical properties of oils and mixtures of oils. *J. Am. Oil Chem. Soc. 62:* 241-248.

TAN, B K and FLINGOH OH, C H (1981). Malaysian palm oil, chemical and physical characteristics. *PORZM Technology* No. 3, Palm Oil Research Insitute of Malaysia, Bangi.

VON SABINE WAHNELT; MANSEL, D and TULSNER, M (1991). Influence of isomeric diglycerides on phase transitions of cocoabutter Investigations by isothermal DSC. *Fat Sci. Tech. 93:* 174-178.