

FIG. 8. Capillary gas chromatograms of fat bloom and coating.

coconut oil whereas the SOS comes almost exclusively from cocoa butter. The small amount of diunsaturated compound is present in both cocoa butter and coconut oil, whereas the triunsaturated (OOO) is a component of cocoa butter. The ratio of SOS to SSS is approximately 1:1. In the fat bloom sample one can observe a rather changed ratio of SOS to SSS which is now close to 8:1, indicating a preferred migration of this fraction of cocoa butter to the surface area (15).

Lauric Fats for Medium-Chain Triglycerides

Lauric fats, in particular coconut oil, are an important starting material for the production of medium-chain triglycerides (MCTs). The MCTs have an important position

in the formulation of dietetic foods mainly for enteral and parenteral administration due to the fact that they are rapidly metabolized, thus being an excellent source of rapid energy. In cases of malabsorption of fats MCTs are the only fats which can be absorbed readily, which is most important for premature babies. MCTs are thus a valuable nutrient in infant feeding (16).

In view of the growing importance of MCTs for the food industry it may be interesting to look for palm kernel oil varieties containing higher amounts of caprylic and capric acids. These would be equally important as precursor of medium-chain triglycerides.

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Confectionery Fats from Palm Oil

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ABSTRACT

The influence of diglycerides (DG's) and trisaturated glycerides (P-P-P) on tempering and the hardness of confectionery products are described. Palm oil and its processed products in confectionery fats have been reported (1,2). Palm oil contains a symmetric triglyceride (P-O-P) as a main component which has polymorphic changes similar to those of cocoa butter, so a mixture of these is able to use a tempering process similar to that used for cocoa butter.

Details for fat crystals and polymorphism have been reported (3,4). Okada (5) used a mixture of tristearin and tripalmitin and studied the behavior of polymorphism using X-ray diffraction. The effects of DG's on polymorphic change in palm oil also have been reported (6,7), and Okiy (8) suggested that DG's have an inferior effect on the quality of palm oil when used in the solidified phase. However, there have not been many papers regarding how the above influence works in the production process or how it affects confectionery products.

Palm oil contains about 10% trisaturated glycerides together with a few percent of mono- and diglycerides as minor components, which have been produced during the maturation of palm fruits and processing of fats. It is very difficult to eliminate these completely during the refining process.

This paper reports a study of the influence of these minor com-

ponents on tempering and hardness of products by using a simulated tempering machine. We have found that DG's lower the temperature of tempering and soften the hardness of products and that P-P-P increased the viscosity of products during tempering process but increased the hardness of products very little.

INTRODUCTION

Cocoa butter is an important and expensive raw material used in the chocolate and related confectionery industries. Chocolate needs more cocoa butter than is present in cocoa beans. Today there are a number of fats suitable for total or partial replacement of cocoa butter components in confectionery products. When we consider the use of alternative fats, we have to study the properties and composition of cocoa butter.

Physico-chemical properties of cocoa butter have been reported. Kattenberg (9) pointed out that, according to their origin, cocoa butters have different properties that might have been caused by the content of symmetric glyceride (S-O-S), as shown on Table I and Figure 1. On the contrary, DG's and trisaturated glyceride contents of cocoa

TABLE I

Triglyceride Composition of Cocoa Butters from Different Origin

Origin	Trisaturated		Monounsaturated		Diunsaturated		Polyunsaturated SOL, etc.
	S3	SOS	SSO	S2L	SO2		
Ivory Coast	1.6	77.2	0.5	7.9	8.4	4.4	
Ghana	1.4	76.8	0.4	6.9	8.4	6.1	
Cameroon	1.3	75.2	0.5	7.1	11.0	4.9	
Brazil	1.0	63.7	0.5	8.9	17.9	8.0	

S = Saturated; O = Oleic; L = Linoleic acid.

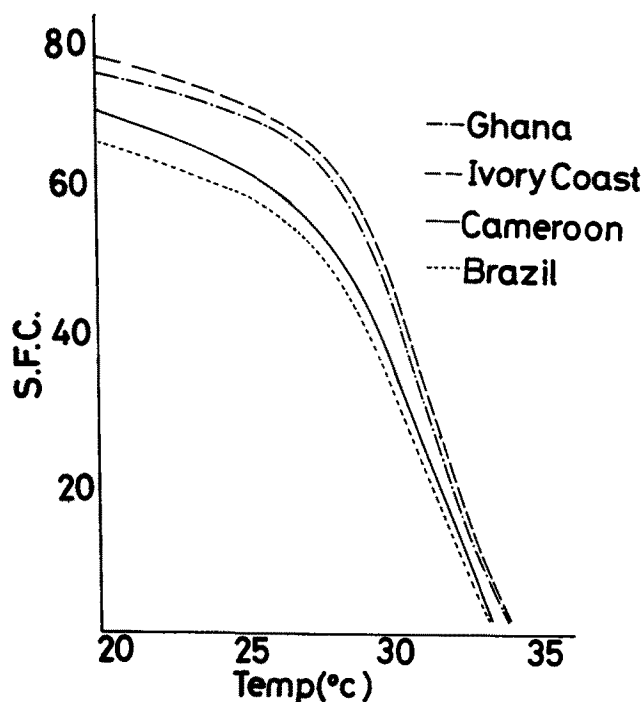


FIG. 1. Solid phase content as function of temperature of cocoa butter from different origin measured by pulsed NMR.

butter are very low, as in Table I: around 2% of DG's and 1% of trisaturated glycerides. The contents do not change much, in spite of different origins (10). At the moment, there are several kinds of cocoa butter alternative fats widely marketed. Cocoa butter equivalent (CBE) uses palm mid-fraction (PMF) as the main component (11,12). The necessary properties for CBE have been discussed (13,14). Hogenbirk (15) listed the physico-chemical properties of CBE according to their usage, enrobing, molding and panning.

Physico-chemical properties of palm oil and PMF have been reported by PORIM (16). PMF that may be used as part of CBE contains 2-4% of DG's and 3-5% of trisaturated glycerides as minor components. The influence of DG's on the properties of palm oil is reported by Okiy (17). We have added DG's and P-P-P to cocoa butter alternative fats and observed good workability and hardness of the products.

EXPERIMENTAL PROCEDURE

Materials

Standard sample. A standard sample was made by the mixture of PMF and shea stearin. PMF and shea stearin were made from Malaysian palm oil and Nigerian shea butter, by solvent fractionation according to British Patent Nos. 925 and 805. The mixture was purified by column chromatography.

Diglycerides. DG's were made from Malaysian palm oil

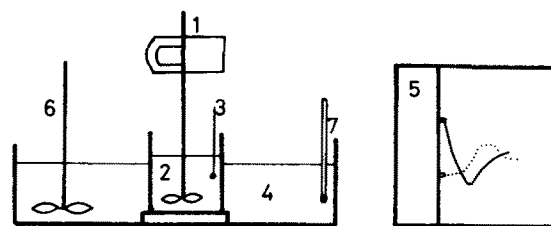


FIG. 2. Apparatus for simulation of tempering. 1. agitation motor with torque meter; 2. sample mixture; 3. thermo-sensor; 4. cooling water; 5. 2 pens recorder; 6. stirrer; 7. thermometer.

by using column chromatography.

Trisaturated glyceride (P-P-P). Tripalmitin from Wako Pure Chemical Industries Ltd. was used. Purity was approximately 99%.

Analysis Method

Column chromatography. Details followed Okiy's method (6) and used a 100 × 3 cm column packed with 200 gr Wakogel C-200 (100-200 mesh) and around 100 gr of sample at a time was applied in hexane.

Determination of glyceride composition. Glyceride compositions and degree of unsaturation in total glycerides were measured by thinchromography by Iatronscan manufactured by Iatron Co., Ltd. To determine glyceride composition (triglyceride, diglyceride, etc.), the sample was dissolved in CHCl_3 at 20-40 mg/ml solution; 1 μl of it was spotted on a microrod. The microrod was dried and developed by n-hexane,acetic acid 98:2 solution and dried at 100 C for 10 min., then set in thinchromography. Thinchromography was operated at 2000 ml/min. of hydrogen and 2000 ml/min. of air flow condition.

To determine degree of unsaturation the sample was dissolved in CHCl_3 made up to 30-60 mg/ml solution and 1 μl of sample solution was spotted on a microrod. Prior to spotting the sample, the microrod was washed four times with distilled water and dried at 100 C for 60 min., then immersed in 5% AgNO_3 solution for 2 min. so as to impregnate the rod, which was again dried at 110 C for 5 min. Development is done with n-hexane,benzene,ethyl-ether (50:50:1) and put on thinchromography after drying.

Differential scanning calorimetry (DSC). In this experiment, Daini-Seikosha Model SSC-560 amplifier was used. The sample was melted and placed in a weighed small aluminum pan and chilled in a methanol-carbon dioxide mixture. After it set firmly, the sample was conditioned at 20 C for 2, 4 and 24 hr.

The scanning rate was 5 C/min. For the determination of ratio between stable form of crystals and unstable form of crystals, the entire area under the DSC curve was traced, cut and weighed. The proportion of stable form of crystals was taken as the weight of the curve which was cut off at bottom of the peaks, where the temperature was nearly 20 C.

Simulation of tempering (Fig. 2). One kg of the mixture

TABLE II
Glyceride Compositions

Sample	Diglyceride (%)	Triglyceride		Melting point (°C)
		Trisaturated UO	Monounsaturated U1	
1. Control	0	1.7	82.6	34.1
2	2.0	1.7	81.3	33.0
3	5.0	1.7	80.0	32.1

of ingredients consisting of 15% cocoa mass, 44.5% sugar, 20% milk powder, 19.8% added fat and 0.5% lecithin at about 45 C was put into a stainless steel beaker and was set in cooling water at 15 C and stirred. The temperature of the mixture was recorded and the viscosity was measured by torque meter every minute after the temperature of the mixture reached 32 C. The temperature of the water was changed to 28 C when the temperature of the mixture reached a predetermined temperature. We continued to record the temperature and viscosity and stopped agitation when the temperature of the mixture became the same as that of the cooling water. The mixture was molded into 30 × 50 × 5 mm molds and kept in the refrigerator for 30 min.

RESULTS AND DISCUSSION

Effect of Diglycerides

Table II shows tri- and diglyceride contents and melting points of samples used in these experiments. Figure 3 shows cooling curves measured by the method of a Determination of Cooling Curve in British Standard Methods of Analysis of Fats and Fatty Oils. At no addition of DG, minimum and maximum temperature are 24.7 C and 30.6 C, respec-

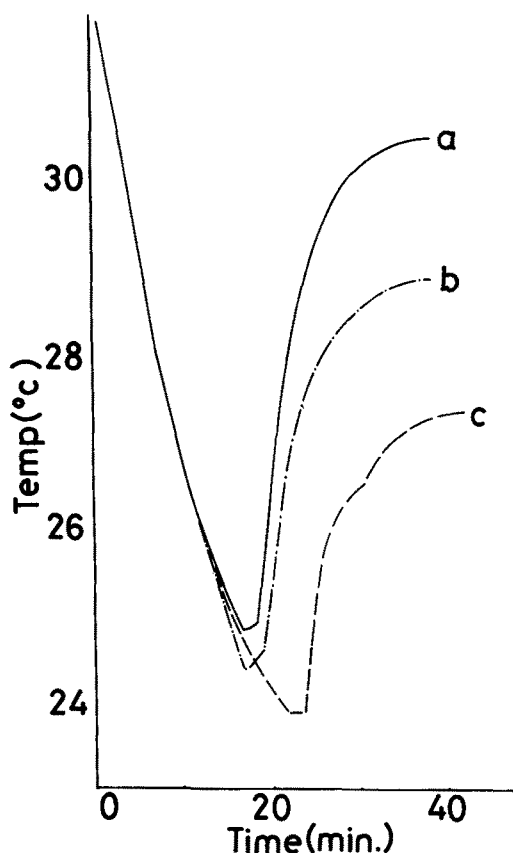


FIG. 3. Cooling curve. DG content for a = 0%; b = 2%; c = 5%.

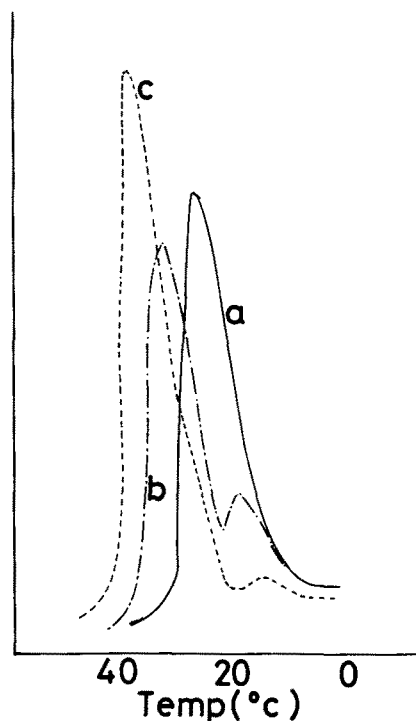


FIG. 4. Differential scanning calorimetric heating curves of standard sample. a. quick chilled; b. conditioned at 20 C for 2 hr; c. conditioned at 20 C for 24 hr.

tively, but the pattern was similar to that of cocoa butter. On the contrary, minimum and maximum temperatures went down according to the percentage of DG's. The results indicated a close relationship between DG content and pattern of cooling curve and that DG's prolong time of solidification of fats. The standard sample and the sample to which DG's were added were measured by DSC as shown in Figures 4 and 5. Only an unstable form of crystals, when the samples were quickly chilled at -20 C, was indicated. The form of crystals, however, changed to more stable form of crystals when a tempering process was applied. The longer the aging time at 20 C, the larger was the amount of stable form of crystals produced.

In the case of no addition of DG's, good coincidence was obtained with Lovegren's work, and polymorphic change to a stable form of crystals was nearly completed when aging was conducted at 20 C for 24 hr. On the other hand, the samples containing DG's at around 3-6% show that the ratio of stable form of crystals have increased when longer aging time was used. However, the ratio did not reach that of the standard sample.

Solid fat index (SFI) was measured by dilatometry in accordance with AOCS Tentative Method Cd 10-57, although 20 C for 24 hr of aging was used. In Figure 6, isodilatation curve at 30 C and 32.5 C are shown as contrasted with DG content. The results show good correlation with data measured by DSC. These results suggest that

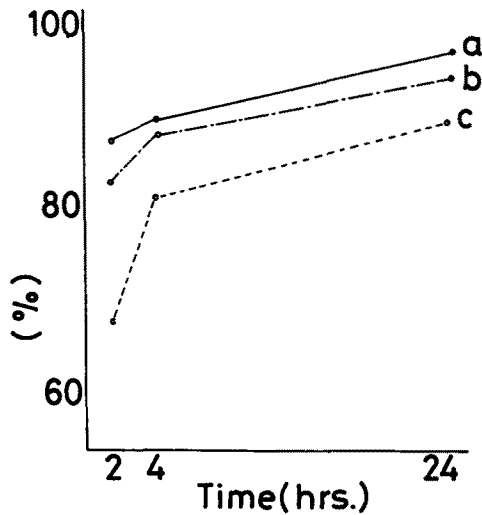


FIG. 5. Effect of DG content on the rate of polymorphic change of fats according to the time conditioned at 20 C which are measured by DSC. DG content is 0% for a and 2.2 and 5.9 for b and c, respectively.

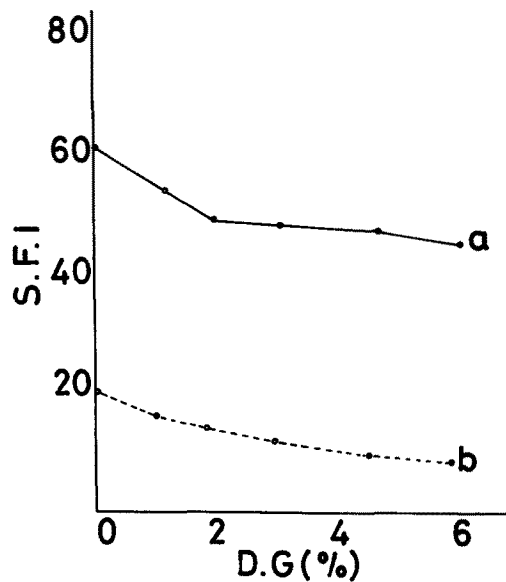


FIG. 6. Isodilatation curve measured by dilatometry. a. a value at 30 C; b. a value at 32.5 C.

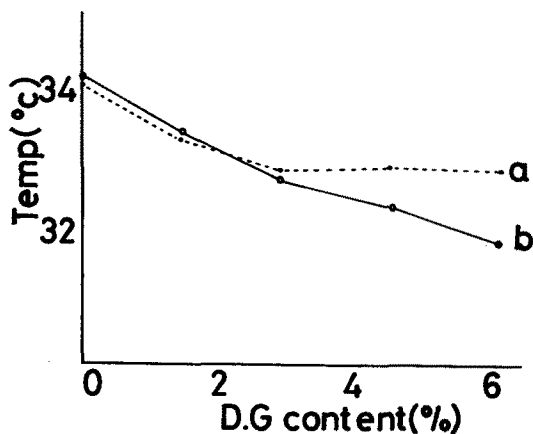


FIG. 7. Effect of DG content on melting points and the aging time. a. conditioned at 25 C for 7 days; b. conditioned at 20 C for 24 hr.

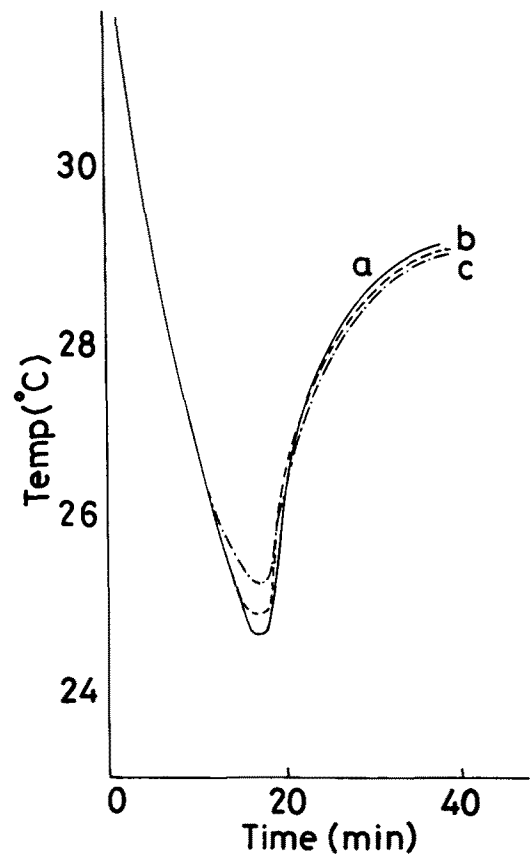


FIG. 8. Cooling curve. P-P-P content of a, b, c are 0%, 1%, 2% respectively.

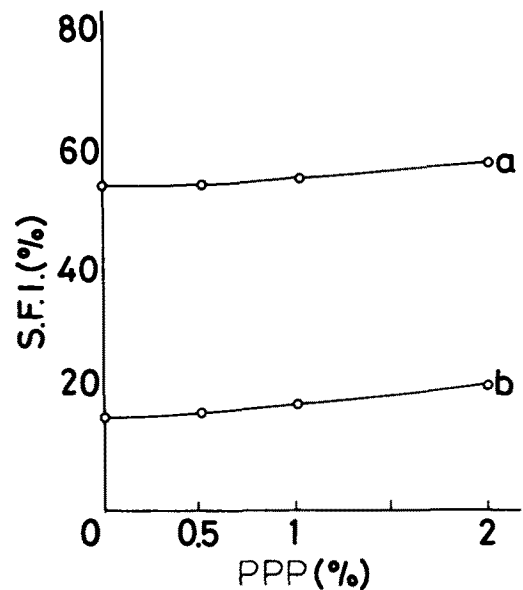


FIG. 9. Isodilatation curve measured by dilatometry. a. a value at 30 C; b. a value at 32.5 C.

DG's in fat disturb the polymorphic change of fat crystals and soften fats. Melting points measured by AOCS Cc 3-25 showed somewhat similar results to DSC and SFI. Melting points shown in Figure 7 dropped according to the content of DG's when conducted at 20 C for 24 hr of aging. At the same time, the melting point did not drop so much when applied for 25 C for 7 days of aging.

From these results we see that DG's disturb transformation of fat crystals when the aging condition is not long

TABLE III

Effect of P-P-P on Workabilities of Products

Sample numbers	P-P-P (%)	Tmin. ^a (°C)	ΔV^b (kg cm)	Heat resistance ^c		
				29 C	30 C	31 C
1	0	25.5	0.95	220	90	44
2	0.5	25.5	1.60	225	90	35
3	1.0	25.7	2.45	220	95	37
4	2.0	25.8	2.75	230	100	40

^aTmin.: minimum temperature of tempering.

^b ΔV (kg cm): increased viscosity from start of tempering to molding.

^cHeat resistance measured by rheometer.

TABLE IV

Effect of DG's on Workabilities of Products

Sample numbers	P-P-P (%)	Tmin. ^a (°C)	ΔV^b (kg cm)	Heat resistance ^c		
				29 C	30 C	31 C
1	0	25.9	0.75	230	108	44
2	2.0	25.2	1.30	220	80	30
3	5.0	24.4	2.00	150	46	20
Cocoa butter	1.3	26.6	0.45	310	99	40

^aTmin.: minimum temperature of tempering.

^b ΔV (kg cm): increased viscosity from start of tempering to molding.

^cHeat resistance measured by rheometer.

enough, and DG's may function to retard polymorphism at a certain condition of aging. The function is same as sorbitan tristearate in fats, as reported by Chapman (18).

Effect of P-P-P

We determined the relation between addition of P-P-P and properties of fats and chocolate products. Figure 8 shows that the minimum temperature of the cooling curve is elevated when P-P-P was added but maximum temperature did not change much. SFI value did not increase much when P-P-P was added to samples as shown in Figure 9, and the results show good correlation with data described in Table III, where we checked hardness of chocolate products. Therefore P-P-P acts as a seeding agent to solidify fats faster than in the case of fats with no P-P-P. On the other hand, hardness of products does not change much. This means that P-P-P functions as an accelerator for solidifying fats, and polymorphic change of fat crystals might have been disturbed.

Effect of Addition of DG's and P-P-P on Workability

Table IV shows temperature of tempering, viscosity and hardness of mixtures measured. Cocoa butter can be tempered at 26.6 C, which is comparable to around 29.5 C, by actual Automatic Tempering Machine of Aasted Chocolate Machine Co., and increased viscosity from start of tempering at 30 C to the stage of molding was 0.45 kg/cm. In addition, hardness of the products that have been stored at 20 C for 20 days were 310, 99, 40 for 29 C, 30 C and 31 C, respectively. Hardness of products was tested by a rheometer manufactured by Fudoh Kogyo Co., Ltd., and the unit of the values were dyn/cm².

As for completion of demolding the products to which DG's are added, low temperature for tempering was essential, and the viscosity increased due to low temperature. Further, hardness of products was rather low in comparison with cocoa butter. Products with 5.9% DG content showed nearly half the hardness of cocoa butter at 29 C, which indicated rather broad melting behavior.

This means that demolded products that have been made with fats containing DG's consist of some unstable forms of crystals together with stable forms of crystals. The unstable form of crystals has not sufficiently changed to a stable form of crystals under the condition of 20 C aging. Also, increased viscosity may be caused partly because unstable crystals in the products are rather bulky and sticky. Therefore, this disrupts the change of polymorphism.

Similar results were obtained by addition of P-P-P, with the exception of tempering temperature. This result indicates that, as mentioned before, although P-P-P works as an accelerator of solidifying fats, this cannot accelerate the polymorphic change of fat. Temperature range, then, becomes narrow, which does not influence hardness of products.

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