tical to the reported spectra for n-alkanes (12). It may be noted that nonacosane, hentriacontane and triacontane were not detected in amounts expected from plant sources where palmitic and stearic acids predominate. This would indicate that the hydrocarbon biosynthesis in palm fruits is unrelated to that for fatty acids.

The mass spectra of alkenes from palm fatty acid distillate are similar to those of n-alkanes except that the most abundant ion series is the C_nH_{2n-1} series (55, 69, 83, 97, 111, 125, 139, etc.), m/z 55 is always the base ion and molecular ions are always observed. The smooth curve of decreasing fragment intensities again indicated that there is no branching along the hydrocarbon chains. The position of double bond in the alkenes cannot be located by the mass spectra because of its facile migration in the mass spectrometer. However, proton NMR of the mixture revealed a triplet at 5.35 ppm (J 4.5 Hz), indicating that the double bond in the alkene is of a non-terminal type; no further attempt was made to locate the exact position or positions of the double bond in all the alkenes.

Small amounts of alkadienes (mainly $C_{23}H_{44}$ and $C_{26}H_{50}$) were obtained. The mass spectra of alkadienes are very similar to alkynes having m/z 67, 81, 95, 109, etc. as prominent peaks which are two masses lower than the corresponding alkenes or four masses lower than the alkanes. The assignment of alkadienes rather than the alkynes is made because we observed olefinic protons but no acetylenic or methylene protons allylic to the triple bonds in the proton NMR spectrum of the fraction containing di- and trienes. No further studies (such as micro-ozonolysis and oxidation) were carried out on these compounds. The mass spectra of the aromatic hydrocarbons (xylene, dimethylnaphthalene and ionene) were found to be identical to the reported spectra (12). Apart from squalene, the majority of the hydrocarbons (alkenes and diterpenes) in palm fatty acid distillate as discussed above contain degradation products from tocotrienols, carotenes, fatty acids and perhaps many other components.

ACKNOWLEDGMENTS

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Effect of Food Emulsifiers on Polymorphic Transitions of Cocoa Butter

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The polymorphic behavior of cocoa butter in the presence of several food emulsifiers serving as crystal structure modifiers was investigated. Emphasis was placed on transitions among the relatively stable forms IV, V and VI, which are significant for a confectionery industry.

As known from industry work, within the series of sorbitan esters and ethoxylated sorbitan esters, the solid emulsifiers were the most efficient in retarding transition of V form into VI modification. Blends of sorbitan monostearate (Span 60), ethoxylated sorbitan monostearate (Tween 60) and Span 60-Tween 65 used in the present study were particularly effective. Surprisingly, it was found that some combinations of emulsifiers accelerate the transition of form IV into form V. Transition of form V into form VI occurs via the solid state, and other transitions are known to take place via the liquid phase. Emulsifier was found to increase liquid fraction of the fat prior to its transition. Mechanistic considerations concerning these transitions are suggested.

As known from industry work, chocolate bloom is caused by separation of cocoa butter, the main fatty constituent, from the brown nonfat phase. This phenomenon, occurring more frequently in summer, is deleterious for many chocolate products and seems to be due to the complex polymorphic character of that fat. The phenomenon of polymorphism is known in triglycerides, and it has been studied from the crystallographic point of view (1-3) and with respect to its thermal behavior (4-8). Cocoa butter is a typical example of certain vegetable fats high in 2-oleo-disaturated triglycerides that exhibit complex polymorphism and conditions for isolating each polymorph have been described by other investigators (9,10).

Six polymorphs of cocoa butter are known, distinguishable by melting point, which rises with thermodynamic stability (9,10). Considering that during storage of chocolate, monotropic transition from the V form to the VI form was observed with simultaneous bloom occurrence (11), our study focused on the crystalline forms significant to the confectiner, i.e., forms IV, V and VI and the effect of emulsifiers on their stability and transformation rates. A blend of Span 60 and Tween 60 revealed itself to be a very good bloom inhibitor when added to chocolate (12), but the manner of fat protection is not completely understood.

In earlier publications, it was demonstrated that emulsifiers may be used as crystal structure modifiers in stearic acid; their presence retarded transformation from the unstable to the stable form in stearic acid crystallized from solvents (13,14). In another study we expanded the investigation of the effects of emulsifiers on polymorphic behavior to triglycerides crystallized from melt. Span 60 and Span 65 were found to be most effective in retarding transformation from α-= form to β-form in tristearin (15) and palm oil (16). Stabilization of intermediate forms in triglycerides by sorbitan esters is confirmed by Krog (17), who showed the effectiveness of sorbitan tristearate as a crystal habit modifier.

No definite mechanism has been proposed previously for the activity of emulsifiers as crystal structure modifiers. The purpose of the present study was to investigate their effect on polymorphic transformations in cocoa butter, using x-ray and differential scanning calorimetry (DSC) techniques, and to find correlation between physical properties of the emulsifier and polymorphic changes in cocoa butter.

EXPERIMENTAL PROCEDURES

Materials. Cocoa butter was purchased from Hamester (West Germany). The emulsifiers were available comercially from Atlas Europol A.p.S. (Italy), Grindsted Products (Denmark), Croda Chemicals (England) and Adumim Chemicals (Israel). Emulsifier types tested were sorbitan esters of fatty acids (Span 20, sorbitan monolaurate; Span 40, sorbitan monopalmitate; Span 60, sorbitan monostearate; Span 65, sorbitan tristearate; Span 80, sorbitan monooleate; and Span 85, sorbitan trioleate) and ethoxylated sorbitan esters of fatty acids (Tween 20, ethoxylated sorbitan monolaurate; Tween 40, ethoxylated sorbitan monopalmitate; Tween 60, ethoxylated sorbitan monostearate; Tween 65, ethoxylated sorbitan tristearate; Tween 80, ethoxylated sorbitan monooleate, and Tween 85, ethoxylated sorbitan trioleate).

The range of emulsifier concentrations was between one and 10 wt% of the cocoa butter. In each sample the emulsifier was added to the fat; the mixture was melted to a clear homogenous melt and mixed well before any thermal treatment.

Analytical Methods. X-ray powder data was obtained with a Philips diffractometer with Cu radiation, Ni-filtered.

Thermal data were obtained by a Mettler Differential Scanning Calorimeter (DSC TA3000). The instrument was calibrated with lauric acid and indium to ensure accuracy of the caloric data and with Pb and Zn to ensure accuracy of temperature readings. Cocoa butter (10-20 mg) was tested in a hermetically closed aluminum pan. A similarly closed empty pan was used as reference. The rate of heating was 2 C/min, within temperature ranges of 20-45 C.

Liquid fraction computation. The liquid fraction computed by the DSC processor is not an absolute value, being relative to an arbitrary temperature range. The principle of liquid fraction computation is shown in Figure 1.

Within the temperature range T_1-T_2 the overall enthalpy change, based on ΔH_f of indium, is recorded; this corresponds to the peak area between T_1 and T_2. The liquid fraction at T_A corresponds to the ratio between the darkened area (T_1-T_A) and the overall area (T_1-T_2). That computation is a useful means of comparison among various samples, if performed on the same crystalline modification and within identical temperature ranges.

Crystallization procedure and samples withdrawal. The three forms IV, V and VI were obtained using the following procedures: (a) Form VI was commercial cocoa butter as received. Attempts to obtain form VI directly from cooling of melt failed. (b) Form V was prepared by melting commercial cocoa butter at 50 C and cooling the melt to room temperature at a natural rate. (c) Form IV was obtained by cooling the melt to 16 C at a rate of 0.3 C/min.

The transformation of form V to VI takes ca. two mo at room temperature; to accelerate it, temperature fluctuations were performed between 20 C and 30 C, abbreviating the formation period to a few days. Before any thermal treatment, the emulsifier was blended in the liquid fat. Every emulsifier composition was blended at the liquid state and cooled before being added to the fat. Crystallization experiments were performed in 10 mm glass tubes, immersed in a water bath in which the temperature was monitored by an IBM computer (Series 1).

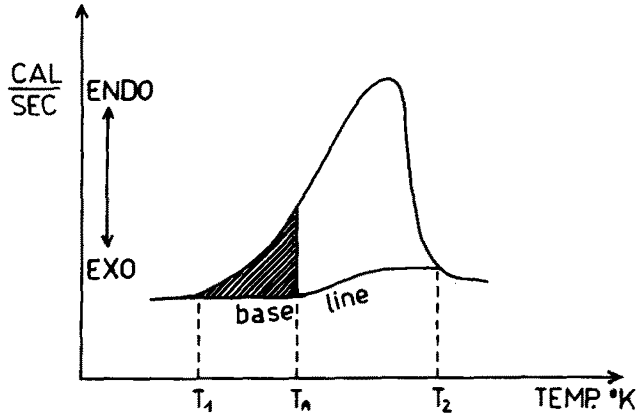

FIG. 1. DSC computation of liquid fraction at point T_A within the range T_1-T_A, corresponding to the ratio between the darkened area T_1-T_A and the overall area T_1-T_2.

RESULTS AND DISCUSSION

Polymorph identification. Figure 2 shows the characteristic diffractograms of the three forms. The range of diffraction angles that differentiates significantly between forms V and VI is within 2θ = 20-25°. Mixtures of the previously crystallized forms V and VI in various ratios were similarly analyzed by x-ray and gave distinctive diffractograms, which are shown in Figure 3. This measurement enables us to quantify the ratio between V and VI forms in each sample tested within satisfying error range of 10% because there is some overlapping between the peaks characteristic to each form. It can be seen from Figure 3 that progressive addition of form VI cocoa butter to form V cocoa butter causes the shape of the diffractogram to change gradually and become more similar to that of form VI.

The three crystalline forms were examined in the DSC and gave typical thermograms, which are presented in Figure 4. The enhancement of thermodynamic stability is associated with increase of endothermic value and enhancement of crystallinity, expressed by the narrower melting range; these phenomena result from more dense crystalline structure.

To examine the relative advantage of each method, comparison between x-ray and DSC determinations was carried out on one sample of cocoa butter during an experiment (Fig. 5). Both the diffractogram and the thermogram indicate that this sample is a mixture of forms V and VI. As the DSC screen is the superposition of all eventual curves, it was possible to draw two curves of which the DSC peak is the sum and compute their areas, according to standard procedure. The computed V-VI ratios according to the two tests are quite similar. In spite of that, DSC test could not be used for quantitative determination in each case, because the large part of the samples which were mixtures of forms V and VI showed a single peaked DSC curve rather than a split one, with the melting point situated between the melting temperatures of forms V and VI. However, the DSC screen permits us to distinguish low percentages of a certain polymorphic form (Fig. 6).

V-VI transformation. Each crystalline modification in cocoa butter except the VI form is obtainable directly from the melt,

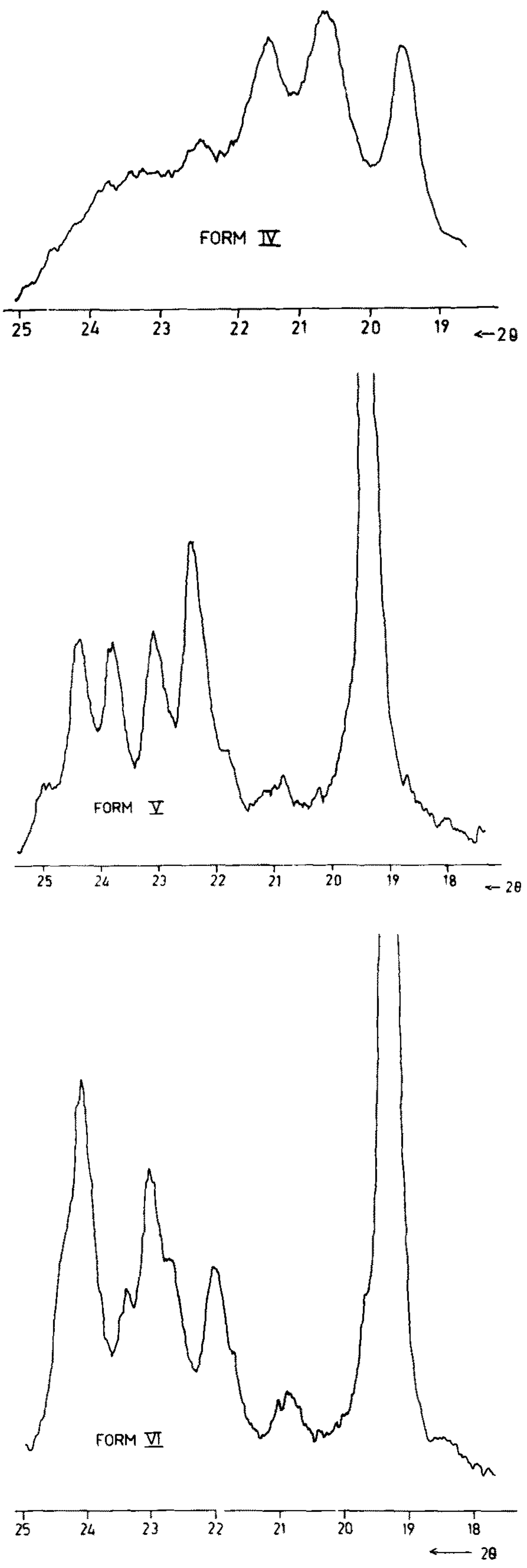

FIG. 2. X-ray diffraction powder patterns of form IV, V and VI in cocoa butter.

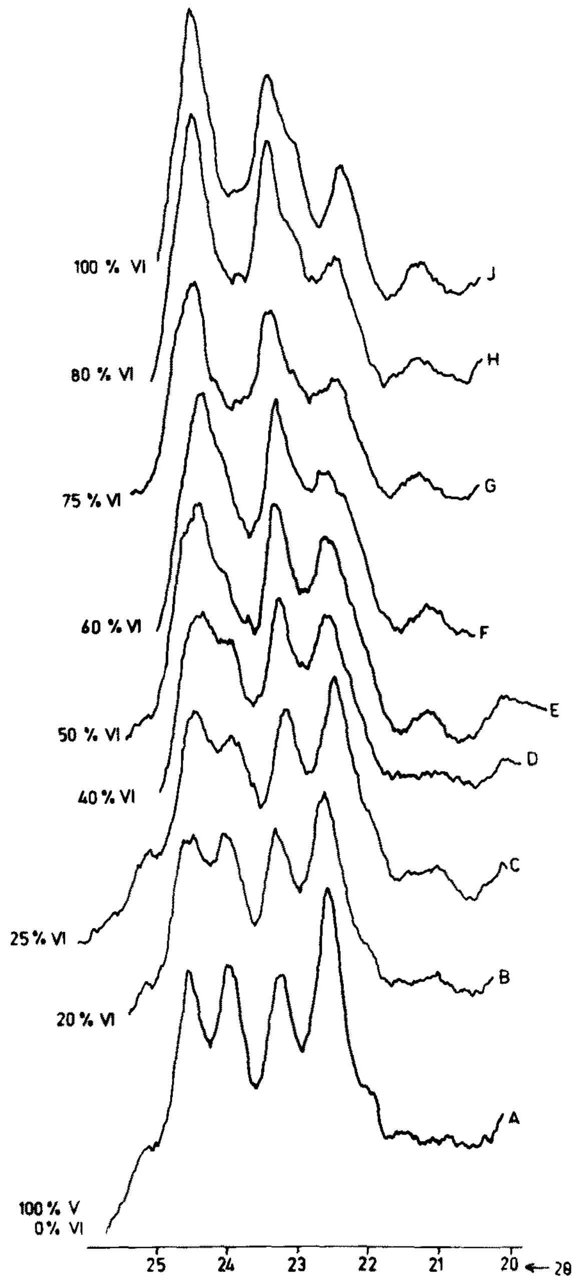

FIG. 3. X-ray diffraction powder patterns of form V-VI blends in cocoa butter.

either by appropriate cooling conditions or transformation of a lower modification. The fact that the VI form is not obtainable directly from the melt (9, 10) suggests that V-VI transformation is not liquid-mediated. At 30 C the nonliquid fat is not completely solid; however, it is plastic enough to allow slight modification of molecular configurations and organization in a more intricate and compact pattern. Such a structure seems attainable not from the state of entirely free molecules, but from molecules arranged in an already organized structure. According to laboratory results, if the temperature is higher than 30 C, a larger fraction of the fat will liquify; hence, the possibility of transformation to the VI form will decrease.

Effect of emulsifier on transformations. The addition of several emulsifiers was tested in order to investigate their influence on the extent of polymorphic transformations.

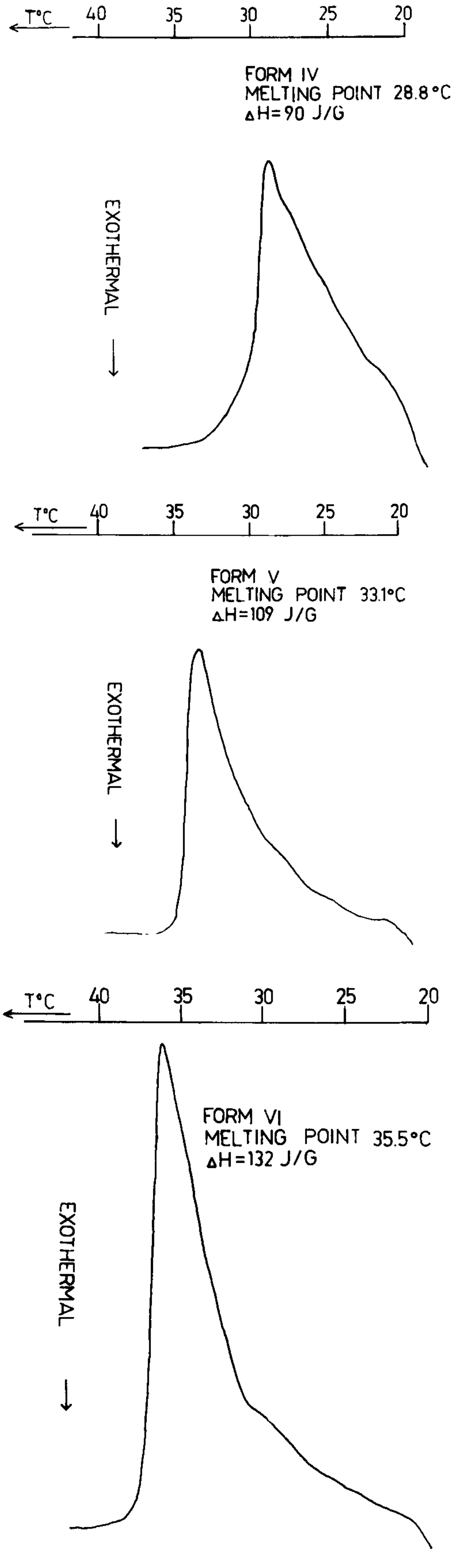

FIG. 4. DSC heating curves of forms IV, V and VI in cocoa butter.

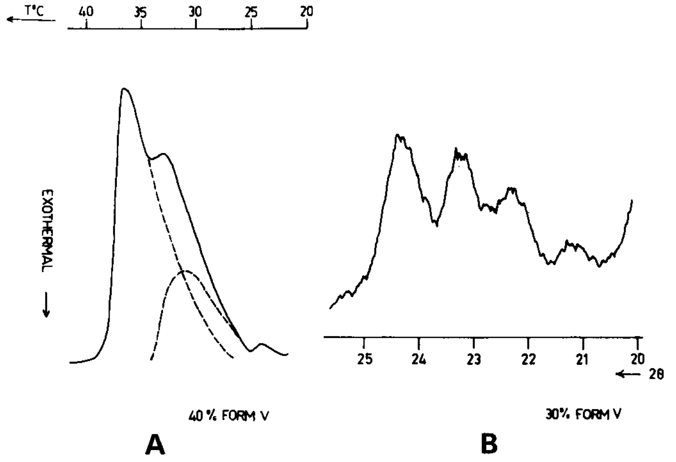

FIG. 5. A sample of cocoa butter containing 40% form V according to DSC heating curve (A) and 30% form V according to x-ray diffraction powder pattern (B).

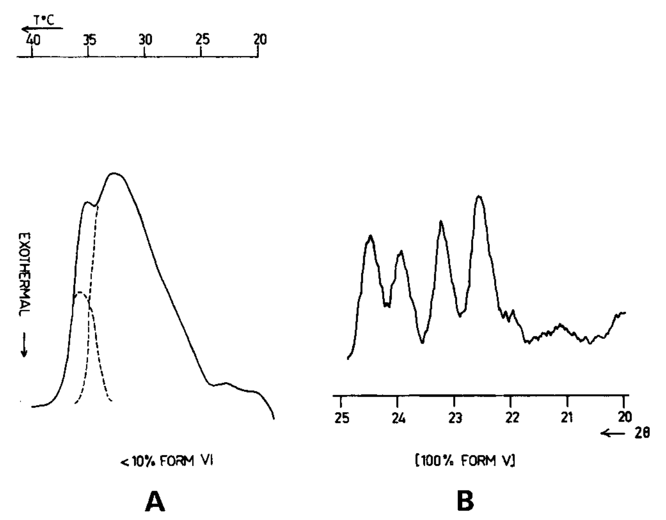

FIG. 6. A sample of cocoa butter containing 10% form VI according to DSC heating curve (A) and 0% form VI according to x-ray diffraction powder pattern (B).

Table 1 presents the percents of form V computed by x-rays, retained in the presence of 5 wt% emulsifier, in the same experimental conditions in which form V of pure cocoa butter was transformed fully to form VI. The melting point of each emulsifier is reported in the same table.

Among the Spans, the most effective for the preservation of the V form was Span 65, with melting point of 54 C. Span 60 and Span 40 (mp 48 C) were less effective than Span 65. The Tweens are liquid at room temperature and preserve form V only partially. Blends of Spans and Tweens in various ratios were tested similarly and results are shown in Table 2.

Two important results are: (a) correlation between the emulsifier melting point and its effectiveness in preserving form V, as seen from both tables, and (b) increase in melting point and effectiveness of Span 60 when blended with Tweens at certain ratios.

The first result suggests that to be an efficient crystal structure modifier, the emulsifier must be solids, in addition to having physical structural compatibility with the fat.

The second result seems very significant in relation to the mode of incorporation of the emulsifier into the fat. Combina-

TABLE 1

Effect of Emulsifiers on Polymorphic Transformation of Form V to Form VI Computed by X-rays

Emulsifier[a]	Percent of form V retention after temperature cyclings	Emulsifier melting point (C)
0	0	–
Span 20	40	Liquid at room temp.
Span 40	50	48
Span 60	60	48
Span 65	100	54
Span 80	30	Liquid at room temp.
Span 85	20	Liquid at room temp.
Tween 20	50	Liquid at room temp.
Tween 40	65	Liquid at room temp.
Tween 60	50	Liquid at room temp.
Tween 65	50	Liquid at room temp.
Tween 80	50	Liquid at room temp.
Tween 85	40	Liquid at room temp.

[a] See text for chemical identification.

TABLE 2

Effect of Emulsifier Combinations on Polymorphic Transformation of Form V to Form VI, Computed by X-ray Diffraction

Emulsifier	Percent of form V retention after temperature cyclings	Emulsifier melting point (C)
Span 60 + Tween 60 (25:75)	60	41
Span 60 + Tween 60 (50:50)	75	46
Span 60 + Tween 60 (75:25)	100	53
Span 60 + Tween 65 (25:75)	60	42
Span 60 + Tween 65 (50:50)	100	50
Span 60 + Tween 65 (75:25)	100	54
Span 65 + Tween 60 (25:75)	60	38
Span 65 + Tween 60 (50:50)	100	47
Span 65 + Tween 60 (75:25)	100	49
Span 65 + Tween 65 (25:75)	75	40
Span 65 + Tween 65 (50:50)	100	49
Span 65 + Tween 65 (75:25)	100	53

tion of lypophilic and hydrophilic emulsifiers in certain ratios is known in emulsion technology to form stable o/w emulsions. For a better, effective stabilization of an emulsion, the requirements from the emulsifier film are strength and elasticity. These features of the film depend on strong intermolecular forces and a high degree of organization between the emulsifier molecules. A blend of two different emulsifiers may be more active than each one of them; that is particularly true in blends of Span and Tween. Such a pattern is known as Sherman's model (18). With respect to the crystal modification activity, the same blends that show that particular feature also are quite effective in retarding transformation of form V. Relating to Table 1, only 60% of form V is retained in the presence of Span 60 after cyclings, while 100% of form V is retained in the presence of the blend Span 60-Tween 60 (3:1,v/v) (Table 2). The increase in activity of the blend can be viewed as synergism, as the activity of the blend is higher than the sum of the activities of the two emulsifiers would indicate.

A single emulsifier, Span 65, was added to cocoa butter to test its effect on the amount of transformation either from IV to V or V to VI forms, by means of DSC.

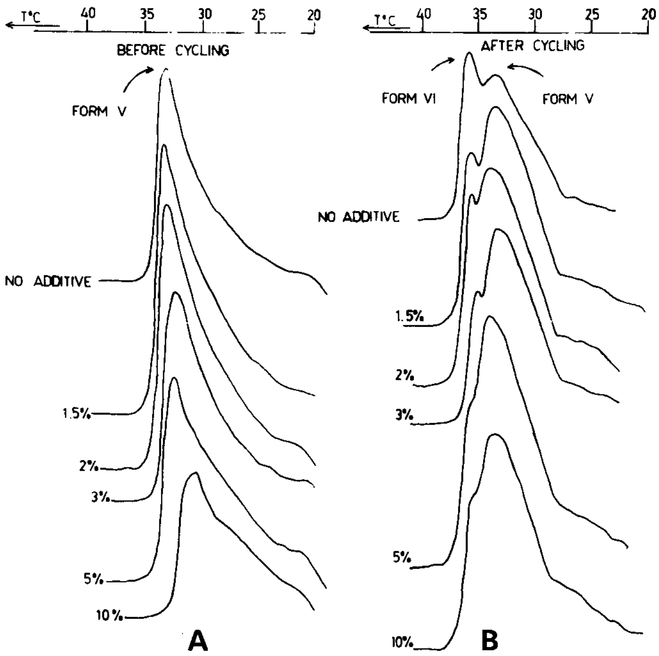

FIG. 7. Samples of cocoa butter crystallized from melt in presence of various percentages of Span 65. A, DSC heating curves, indicating presence of form V, before temperature cyclings between 20 C and 30 C; B, DSC heating curves after temperature cyclings, indicating presence of form V and VI in samples with low or no percentage of emulsifier.

Form V was crystallized in samples of cocoa butter with addition of Span 65. The thermograms are presented in Figure 7A. All the curves are characteristic for form V. However, as more emulsifier is present, the curve melting point decreases slightly and the shape of the curve becomes wider. Concurrently, the liquid fraction at a specific temperature rises as more emulsifier is present (Table 3). Increase in liquid fraction may be caused either by lowering of the melting point or by curve widening; both factors result from the emulsifier acting as an impurity in the sample.

Temperature cyclings were performed on the same samples and were analyzed again in the DSC (Fig. 7B). A change in curve patterns due to polymorphic transformation can be observed. In the sample of pure cocoa butter, the curve is split into two almost equivalent peaks, confirming that a significant amount of form VI is present. With the addition of 10% emulsifier, the amount of form VI is negligible (Table 3). The extent of form V retention is shown to be a function of emulsifier concentration.

Form IV was crystallized in cocoa butter samples with addition of Span 65 at various percentages. After a few hr of storage at room temperature, the samples were tested by DSC (Fig. 8). The thermograms show that as more emulsifier is present, the melting point of the sample is shifted toward that of form V. Hence, in this case, the emulsifier seems to accelerate the transformation of IV to V.

The experiments presented show the effect of emulsifiers on the degree of transformation within a given period. Consequently, it seems that the emulsifier kinetically stabilizes a given crystal modification; i.e., it cannot prevent transformation, but rather retards it through time.

To prove this point, the effect of the best blend of Span 60-Tween 60 (3:1,v/v) 2 wt% was tested as a function of time. Storage at 30 C accelerates V-VI transformation to a lower extent than the temperature cyclings. The presence of the emulsifier clearly retards transformation in both cases (Fig. 9).

TABLE 3

Effect of Span 65 on Liquid Fraction and V-VI Transition in Cocoa Butter

Sample	Melting point (C) before temperature cyclings	Liquid Fraction 29 C	31 C	33 C	% of form V after temperature cyclings
Cocoa butter	33.1	20.6	39.2	47	49
Cocoa butter + Span 65 1.5%	33.0	29.1	50.7	87.1	34
Cocoa butter + Span 65 2%	32.7	29.9	52.9	91.6	25
Cocoa butter + Span 65 3%	32.4	30.6	53.8	92.6	13
Cocoa butter + Span 65 5%	32.3	32.4	55.4	94.1	10
Cocoa butter + Span 65 10%	31.0	48.7	76.2	93.1	10

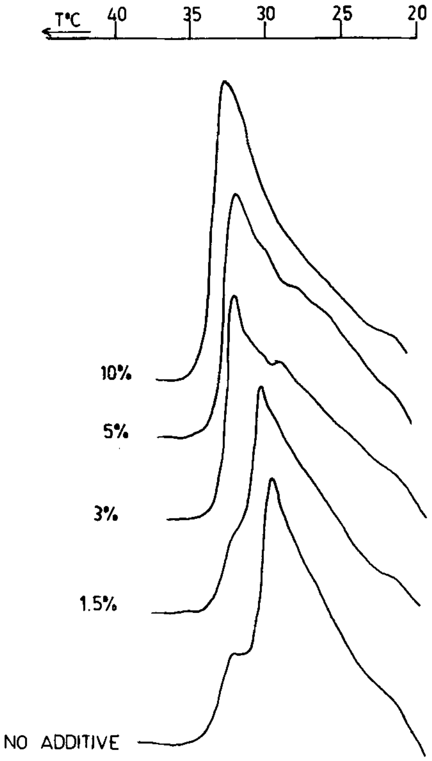

FIG. 8. Heating curves of cocoa butter samples in presence of various percentages of Span 65, cooled to 16 C at 30 C/min and stored 4 hr at room temperature.

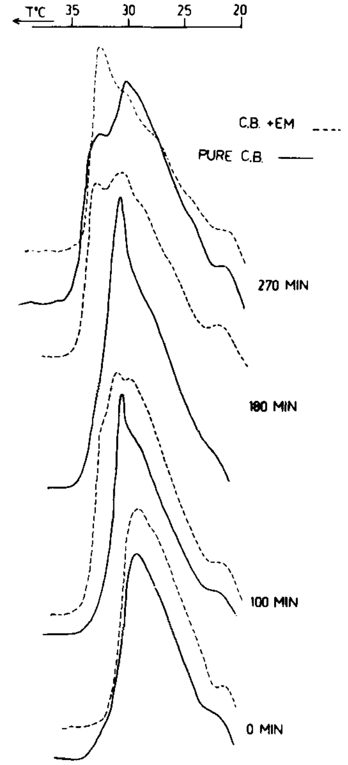

FIG. 10. DSC heating curves of pure cocoa butter (————) and in presence of 2 wt % emulsifier (EM) at various periods of storage at room temperature after being cooled to 16 at 0.3 C/min.

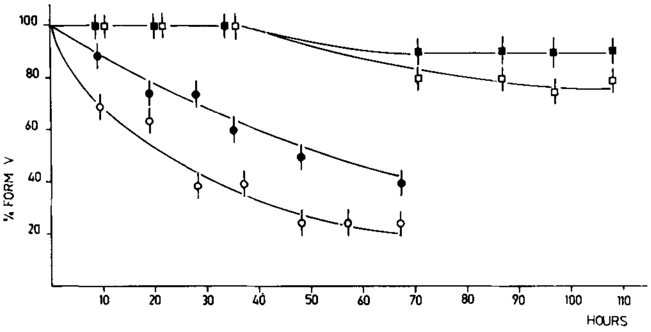

FIG. 9. Disappearance of form V during transformation to form VI. □, Temperature cyclings between 20 C and 30 C with no additives. ■, Temperature cyclings with 2 wt % Span 65. ○, Storage at 30 C with no additives. ●, Storage at 30 C with 2 wt % Span 65.

In Figure 10, the effect of emulsifier on the IV-V transformation is presented. It appears that in the presence of the emulsifier the transformation is expediated.

The conclusion is that the emulsifier oppositely influences the two polymorphic transitions investigated: the V-VI transition is retarded, and the IV-V transition is facilitated.

Mechanistic considerations and speculations. Some speculations are needed to explain these apparently contrasting phenomena. The two polymorphic transformations occur differently.

While IV-V transitions take place through liquid phase, the V-VI transitions occur through solid state only. Keeping in mind that the emulsifier increases the liquid fraction of V crystal modification in cocoa butter, it may be assumed that the same will occur with the IV modification. That effect will hence promote the IV-V transition and make the V-VI transition more difficult.

Synergism between Span 60 and Tween 60 may suggest that the emulsifiers do not function in a complete molecular dispersion, but are solubilized one into the other.

A relation between emulsifier structure and the ability to retard V-VI transformation has been demonstrated. It may be suggested that the effect on IV-V transition is due just to the increase in liquid fraction, but the effect on V-VI transition in addition is related closely to the emulsifier physical structure. We may imagine that a high melting point emulsifier will have its carbon chains tightly packaged, producing a rigid structure. Any polymorphic transition through solid phase, associated with slight movement of fat molecules will be hindered by the rigidity of that structure. Lack of rigidity will allow eventual undulation of the carbon chains, thus permitting the slight movement of the fat molecules.

Much work still must be performed to elucidate the action of the emulsifier; further results on the subject will be published later.

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Effects of Surfactants on Transition Kinetics of Stearic Acid Polymorphs

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The effects of some nonionic surfactants on the kinetics of the solution-mediated transition of stearic acid of B and C polymorphs were studied. Some surfactants were found to retard the transition of the thermodynamically unstable stearic acid modification to the stable form in methanol, n-hexane and decane solutions. The surfactants consisting of large hydrophilic moieties revealed a significant retardation effect. The effect also depends on the solvent; the lower the solubility of the surfactant in the solvents, the more the transition rate was decreased. Finally it should be noted that the C→B transition was more affected than the B→C transition with a given surfactant.

Surfactants have been known to be useful agents for controlling the polymorphic behaviors of fats and oils (1,2). The microscopic features of the surfactants' effects, however, have never been clarified. To elucidate this effect, we tried to examine the retardation of transition kinetics of different polymorphs of stearic acid crystals. As reported very shortly (3), two typical polymorphs, B and C, of stearic acid can transform to one another in the solution phase (solution-mediated transition). This transition occurs when the more stable polymorphs (C above 32 C, and B below 32 C) grow at the expense of the less stable ones (4). The rate of transition depends on temperature as well as on the solvent. The polarity of the solvent was found to be very important. The modification transitions were used as a model system to examine the effects of various surfactants, such as sorbitan esters, monoglycerides, polyglycerol esters and sucrose esters, on the kinetics of the polymorphic transition at low and high temperatures in polar and nonpolar solvents. By doing so, the effect of surfactant as a crystal-structure modifier could be examined in detail.

MATERIALS AND METHODS

Stearic acid of more than 99% purity from Ishizu Pharmacy was employed. The following solvents were utilized: nonpolar aprotic n-hexane (Yoneyama Pharmacy, 99.6%) and nonpolar aprotic decane (Tokyo Kasei Inc., 99%), and polar protic methanol (Yoneyama Pharmacy, 99.8%).

The transition rate was defined as the rate of change in fractional concentrations of C and B powdered crystals suspended in the solution. Stearic acid was crystallized in both forms, and the crude crystals were carefully ground for several hr prior to each experiment to obtain crystals of optimal small size. The particle size distribution was determined by optical microscope in the suspended solution of n-hexane at 10 C. As the solubility of stearic acid at this temperature is very low (0.1 g/100 g solvent), no appreciable dissolution occurred during the examination of the particle sizes, which was done within about 20 min. Thus, the average particle size was found to be about 30 μm for both polymorphs. The same samples were used throughout the experiments. A mixture of B and C powders was put into the solution, which had been saturated to the more stable form at a given temperature.

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