Polymorphism of Cocoa Butter

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Abstract

Largely by x-ray diffraction six crystalline states, I–VI, in order of increasing melting point, have been identified for cocoa butter. Of these states II, IV, V and VI are pure and identifiable with previously (or presently) identified polymorphs of 2-oleoylpalmitoyl stearin (POS), namely α-2, β'-2, β-3 ("V") and β-3 ("VI"); V and VI representing distinct but very closely related crystalline structures. State I is a definite but fleeting and not readily characterized sub α state and may be a phase mixture, as state III may be also.

Melting points, heats of fusion and dilatometric data are reported for all states to the extent that their stability permits.

The normal state of cocoa butter in chocolate is apparently V, certainly β-3. While it is true that "bloom" has not been observed for pure V nor observed to exist in the absence of VI, it is premature to say that VI is specifically the phase of chocolate "bloom."

Introduction

AT LEAST FIVE POLYMORPHIC forms of cocoa butter are reported in the literature. In the most exhaustive study by Vaeck (1), substantiation for four forms with melting points at approximately 35, 28, 23 and 17C is based on microscopic studies of the appearance of crystals, melting point determinations, heating and cooling curves and dilatometric evidence. Duck (2) used viscosity to demonstrate two crystalline fractions of cocoa butter which would form at 29C, but only one of which was stable at 33C, thus indicating a possible fifth form. In another paper (3) Duck called the 33C melting form beta prime and the higher melting form beta, concluding that there are five forms. Few x-ray diffraction data have been reported. Chapman, Crossley and Davies (4) reported diffraction spacings for the stable form of cocoa butter and Lutton (5) reported diffraction spacings for the three forms of a "POS portion" of cocoa butter derived by fractional crystallization from acetone.

The polymorphism of the principal glycerides of cocoa butter has been studied thoroughly. Malkin and Wilson (6) reported five forms of 2-oleoyldipalmitin, including a vitreous form. Lutton and Jackson (7) found only four forms and disputed Malkin and Wilson's vitreous form and their association of melting points and diffraction spacings for the intermediate melting forms. Lutton (8) reported three forms for 2-oleoyldistearin, each with a triple-chain structure. Later a sub alpha-3 form (long spacing 80 Å, short spacings 4.22 VS and 2.82 M) was found and is reported in the present paper. Filer et al. (9) reported a beta prime-3 form for SOS obtainable only by crystallization from solvent. Lutton (10) reported five forms of 2-oleoylpalmitoyl stearin. The whole subject of polymorphism of glycerides has been reviewed by Chapman (11,12).

Terminology

Nomenclature in cases of polymorphism can be a great difficulty, certainly if there are several compounds showing both related and unrelated polymorphs and especially if a mixture of such compounds is being discussed. In the present paper, previously used phase designations are employed for the pure compounds, SOS, POP and POS, the same designations being used for what are judged to be related structures. For cocoa butter the distinguishable products of various treatments are referred to as products or states I–VI, I and III possibly being mixtures of phases, while II, IV, V and VI are clearly single phases related to known phases of SOS and POS. The relationships are indicated in Table II.

It is pertinent to state here the bases for phase designation. Beta signifies a phase with strong short spacing of 4.6 Å; sub beta, sometimes called X-3, is a phase melting several degrees below beta and with strong spacing greater than 4.6 Å, at about 4.7 Å; beta prime signifies an intermediate melting phase with short spacings near 4.2 Å and 3.8 Å; alpha signifies a phase with a single strong spacing near 4.2 Å; sub alpha signifies a low temperature phase with short spacings resembling those of beta prime. The designation, -3, implies a long spacing corresponding to triple-chain-length; while -2 implies a long spacing of double-chain-length. Intensity of the diffraction spacings is indicated by S, strong; M, medium; W, weak; V, very; and diff, diffused. Long spacings are abbreviated, L.S.; short spacings, S.S.

Experimental

The cocoa butter investigated in the present work was commercial material manufactured by the Hershey Chocolate Corporation. It had the analysis shown in Table I.

A small amount of suspended solid matter in cocoa butter causes the melted fat to be cloudy and unsuitable for precise melting point determinations. This difficulty was overcome by slurrying about 3% of a mixture of bleaching earth and kieselguhr in the melted fat and filtering under vacuum. The clear filtered fat was used for substantially all of the work in this investigation.

Melting points were obtained in special thin-wall and commercial 1 mm glass capillaries charged with approximately 1 cm columns of fat. Melting points of the lowest melting and intermediate melting products were obtained by "thrust in" technique in which capillaries containing the sample were plunged into a water bath at preadjusted temperature to find the smallest range at the limit of which the sample was observed either to melt or not melt. The midpoint of this range was taken as the melting point. The melting points of the two highest melting products were observed both by the "thrust in" method and

TABLE I
Cocoa Butter Analysis

Iodine value	36.9–37.5
Fatty acids, % (gas chromatography)	
$C_{16:0}$	25.5
$C_{18:0}$	36.5
$C_{18:1}$	35.0
$C_{18:2}$	2.0
$C_{18:3}$	1.0
$C_{18:1}$ *trans* isomer, % (infrared spectro.)	0.0
Saponification value	194
Free fatty acid as oleic, %	0.94
Specific heat, liquid 35–45C, cal/g	0.494
Specific heat, solid, stable phase 5–20C, cal/g	0.53

TABLE II

Polymorphs and "States" of Disaturated Triglycerides in Order of Decreasing Melting Point (or Range of Existence)

SOS[10]	POS[10]	POP[10][d]	Cocoa butter and 25% SOS, 50% POS, 25% SOO
β-3	β-3	"VI"	VI
		β-3	
		"V"	V
sub β-3 or X-3[a]			
β'-3[b]	β'-3		
	β'-2	β'-2	IV
		sub β'-2	III
α-3	α-2	α-2	II
sub α-3[c]	sub α-3	sub α-3[e]	I[f]

[a] Apparently variable in short spacings but regarded as one form.
[b] From rapidly cooled solvent only.
[c] Not previously reported: L.S.—80 Å; S.S.—4.22 VS, 3.82 M.
[d] A sub β-3 (β'') form has been reported only by Malkin ete al. (6).
[e] Not previously reported: L.S.—69 Å; S.S.—4.16 VS, 3.80 W.
[f] Long spacings difficult to intercept.

by the standard technique of observing the sample in a water bath as the bath temperature was increased slowly 0.2C per minute from a temperature some 5C below the expected melting point of the material.

Heating curves were obtained by observing time-temperature changes while heating 5 g of material in a test tube in an air chamber while maintaining a constant 5C temperature differential betweeen the sample and the heating medium. The heat input to the system was determined, and heats of fusion were calculated from these curves for the various preparations. Heats of fusion were also determined in a calorimeter made from a thermos bottle. Approximately 100 g of cocoa butter in the desired state was dumped into 250 g of hot water in the thermos bottle and temperature changes were noted. Corrections were made for heat losses to the atmosphere, sensible heat changes of the fat and the caloric value of the calorimeter.

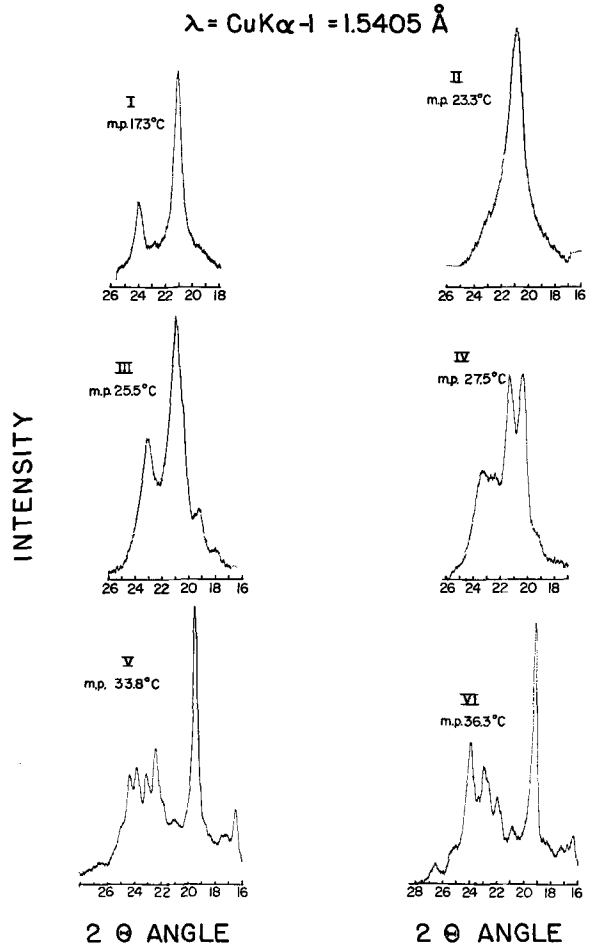

FIG. 1. Diffractometer short spacing patterns.

Solid Content Index (SCI) data were obtained by a minor modification of the dilatometric method described by Fulton et al. (13). The modification of the method involved changes in temperature manipulations necessary to make and preserve the various cocoa butter states.

The principal method for elucidating the polymorphism of cocoa butter was x-ray diffraction. Two different instruments were used: one, a Norelco Diffractometer, employing nickel-filtered CuK_α radiation, scanned the sample held in the slot of a metal sample holder and recorded results on chart paper; the other, a General Electric XRD-1 unit with nickel-filtered CuK_α radiation, handled samples prepared in thin-wall 1.0 mm O.D. Pyrex glass capillaries sealed on both ends. Diffraction patterns were recorded on film with a sample-to-film distance of 10 cm. The latter instrument was equipped for handling samples at controlled temperatures as low as −30C, but required several hours' exposure time. The former instrument had the advantage of speed, being able to scan a sample in a range of angles of interest and to give results within a matter of minutes after preparation. The problem of achieving low enough temperatures to avoid transformations during analysis by the diffractometer was solved by prechilling the sample-holding block and radiation shield of the instrument with crushed dry ice (solid CO_2) before running the samples. Duplication of results by two operators using the different instruments was achieved.

In attempting to understand the polymorphism of cocoa butter an effort was made to relate it to the polymorphism of (a) the major components, POS and SOS, (b) a binary system of the two and (c) a 3-component mixture, 50% POS, 25% SOS, 25% SOO, believed to approach reasonably closely to the reported composition of cocoa butter (52–57% POS, 19–22% SOS, 12–6% SOO, 9–7.5% POO, etc.) (14). These mixtures were subjected to treatments corresponding to those leading to the several cocoa butter states described herein. After treatment, samples were examined by melting point and x-ray diffraction.

Preparation and Detailed Examination of Products

Product I was the initial state obtained when melted cocoa butter was solidified at 0C and lower temperatures. In order to observe the melting point, it was necessary to prepare the material in small-diameter, thin-wall capillary tubes so that the fat would melt clear within one or two seconds after being thrust into a bath at the melting temperature. With larger samples, heat transfer through the material was slow enough that parts of the sample transformed to a higher melting state before all of the material came to the melting temperature. Consequently, with ordinary 1 mm I.D. glass melting point capillaries, for example, a clear, melted sample could not be observed.

The stability of product I was determined at several temperatures. Thin-wall capillary samples of cocoa butter were solidified and stored in ice water and in dry ice/acetone. Periodically, capillaries were taken from storage and plunged into a water bath at 18C to determine whether or not melting occurred.

If the sample melted, it was proved to have been stable for that length of time; if it did not melt, transformation was indicated. At very low temperatures stability was tested by x-ray diffraction. Results, given in Table III, show a very low order of stability for product I.

The possibility of a reversible transformation between I and II, the next higher melting product, was investigated by storing capillary samples of II at −70C for times ranging from 1 to 30 min and at −30C for 4 hr. No evidence of transformation from II to I was obtained either by melting point or x-ray diffraction techniques.

X-ray diffraction data for product I are given in Table IV and Figure 1. Although long spacings of unusual character were always found on film patterns, they were not always observed with the diffractometer. Cocoa butter that was solidified on a steel plate lying on dry ice and scanned immediately showed typical short spacings but only a smooth diffractometer base-line curve where long spacings normally should be observed. If the sample was stored on dry ice for a few minutes before scanning, long spacings and the usual short spacings were both observed. Possibly the crystals are, at first, very small or highly imperfect in the "long spacing" direction, but do develop with time.

Product II was obtained when melted cocoa butter was quick-frozen and stored for several minutes to an hour at 0C. Amounts of material as small as that held in a capillary melting point tube and as large as 150 g were prepared. The larger samples were obtained by pouring a thin layer of melted cocoa butter into an aluminum pan which had been packed in ice and water. Attempts to crystallize II directly from the melt at temperatures ranging from 5C to 18C invariably gave rise to higher melting forms. Preparation of II, therefore, appears to require initial formation of I and subsequent transformation to II, since the former has been demonstrated to be the initial state at 0C and lower temperatures, and direct crystallization of II from the melt could not be demonstrated.

The stability of product II was determined by means of x-ray diffraction of samples that had been stored at various temperatures. Results are given in Table III. At zero and 5C, II transformed to III. At 16C and 21C, II transformed to IV. At 25C, II melted almost completely and resolidified slowly in the shape of spherulites as V.

X-ray diffraction spacings and thermal data for product II are given in Table IV and Figures 1 and 2. Dilatometric data are shown in Figure 3.

Product III was obtained by solidification of the melt at 5 to 10C or by transformation of II by storage at 5 to 10C. Material for testing ordinarily was produced by storing II overnight at 5C. Thermal and diffraction data for the material are given in Table IV and Figures 1 and 2. SCI data are shown in Figure 3. Stability at various temperatures is indicated in Table III. At 10C III transformed directly to V in about 3 days. At 16C and 21C, III transformed to IV. At 26C, III partially melted and resolidified as V within 30 min.

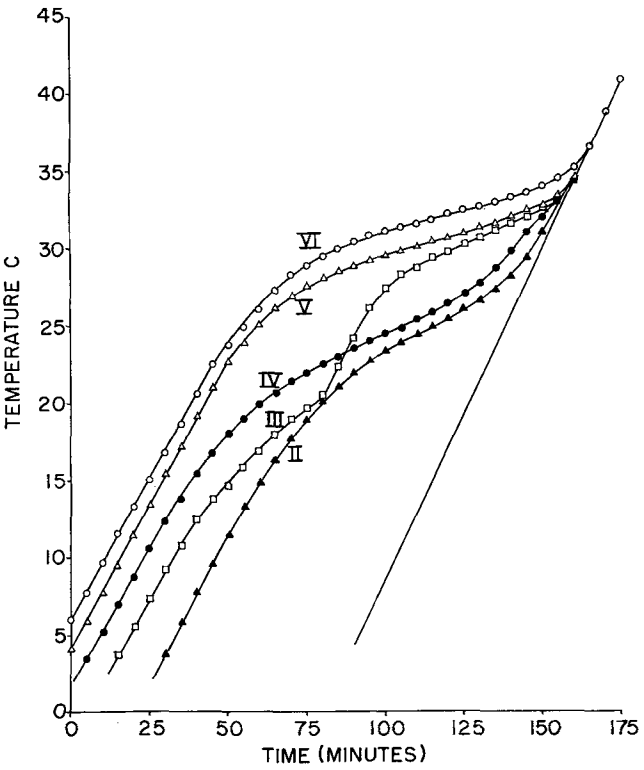

FIG. 2. Cocoa butter heating curves. Sample treatments: 5 g sample in 15 x 90 mm test tube. Melt 5 min at 55–60C. II Solidify sample 20 min in ice water. III Solidify sample 1 hr in ice water. Store 24 hr at 5C. IV Solidify sample 1 hr in ice water. Store overnight at 16C. V Solidify sample 15 min in ice water. Store overnight at 16C, three days at 21C. VI Solidify sample 15 min in ice water. Store two hr at 16C, 11 da at 28C, overnight at 21C. Prechill all samples except II one hr in ice water before running heating curve. Heat samples in air space maintaining 5C temperature differential.

Product IV was obtained by solidification of the melt at 16 to 21C or by transformation of a lower melting state by storage at 16 to 21C. Material for testing ordinarily was produced by solidification of the melt 4 to 8 hr at 16C. Thermal and diffraction data for product IV are given in Table IV and Figures 1 and 2. SCI data are shown in Figure 3. Stability at various temperatures is given in Table III. Transformation at every temperature was to V.

Product V was obtained by direct solidification of the melt, by transformation of lower melting products and by crystallization from solvents. A preparation simulating the tempering procedure used in

TABLE III

Stability of Cocoa Butter States

Temp C	I		II		III		IV		V		VI
	a	b	a	b	a	b	a	b	a	b	
−30	>4 hr										
0	15 sec	15 min	5 hr								
5			<2 hr	16 hr	5 da		>1 wk				
10					1 da	3 da [c]					
16	2 sec		<1 hr		<4 hr	4 hr	2 da	2 wk	>14 wk		
21							3 hr	1 da	7 wk	>18 wk	
26			Melted [d]		Melted [d]		<1 hr	1 hr	4 da	3 wk	Stable

[a] Approx. time at which transformation begins.
[b] Approx. time to complete transformation to next higher melting state.
[c] Transformed in solid state directly to V.
[d] Resolidified within 30 min as V.

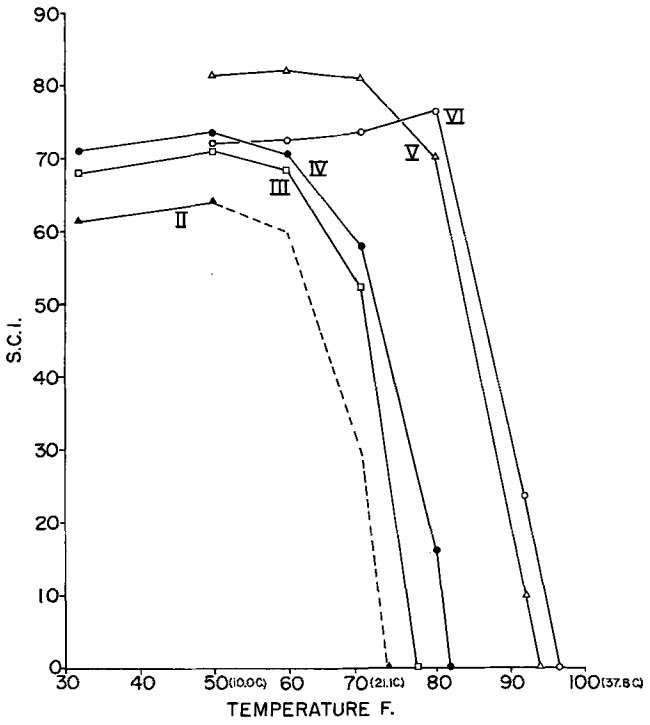

FIG. 3. Solid content index of cocoa butter. Sample treatments: 2 g sample. II Melt, chill 1 hr at 32F (0C). III Melt, chill 1 hr at 32F (0C), store 2 hr at 50F (10C). IV Melt, chill 1 hr at 32F (0C), store 2 hr at 60F (15.6C). V Melt, chill 1 hr at 32F (0C), store 1 da at 70F (21.1C), 1 da at 80F (26.7C), overnight at 50F (10C). VI Melt, chill 1 hr at 32F (0C), store 1 day at 70F (21.1C), 3 wk at 80F (26.7C), overnight at 50F (10C).

processing chocolate coatings before enrobing or molding gave V. In this preparation cocoa butter was agitated continuously at 25C until a creamy slurry of crystals had formed in about 30 min. The slurry was heated to 33C with agitation for 30 min and solidified at 5C or 21C. Transformation from lower melting states was accomplished in several ways. State V was obtained directly from II via melting at 25C, directly from III at 10C and directly from IV as previously described. Cocoa butter was successively transformed from I through all of the intermediate states to V by storage at progressively higher temperatures. In this experiment, melted cocoa butter was dripped into a beaker immersed in ice to form a thin layer of product I. After 15 min at 0C, I had transformed to II, mp 23.3C. Product III, mp 25.2C, was obtained after storing overnight at 5C. Product IV, mp 27.2C, was found after 5 hr at 16C. Transformation to V, mp 33.0C, was accomplished within 2 days at 24C. A final modification, mp 36.3C, was obtained after 2 months at room temperature (approximately 24–25C). All of these transformations were confirmed by x-ray. Crystallization of cocoa butter from acetone and petroleum ether (10 parts solvent:1 part fat, −13C) gave V, at least as indicated by x-ray. Melting points (36.0 and 37.4C, respectively) were high, no doubt because of the unavoidable fractionating effect of the crystallizations.

As indicated above, observation of V over a period of time showed a gradual increase in melting point from approximately 33–34C to 36C and some changes in x-ray diffraction. There were no significant changes in long spacings or in the beta characterizing 4.6 Å short spacing, but the strong spacing at 3.98 Å became weak, the medium intensity spacing at 3.87 Å became stronger, and the weak, diffuse doublet at 3.75 Å and 3.67 Å became a single strong spacing at 3.70 Å as illustrated in Figure 1. These changes occurred very slowly at 21C but were accelerated at higher temperatures as indicated in Table II. The final modification of V obtained by storage at 25C and higher temperatures below the melting point was called Product VI. VI was never obtained directly, but only by transformation of V. It is the product of highest stability.

We have no explanation for the abnormal character of that part of the SCI curve obtained for state VI at lower temperatures. Substantially identical values were obtained in two independently treated dilatometers several weeks apart.

Binary System SOS-POS

Since the two principal glycerides in cocoa butter are POS and SOS, an understanding of the SOS-POS binary system should contribute to an understanding of the crystallization of cocoa butter. It it clear from Table V that the stable state for this system is beta-3. Metastable states obtained by appropriate procedures exhibit a systematic but complex behavior. At 75% POS, the polymorphism is reasonably close to that exhibited by cocoa butter. Figure 4 shows a plot of the melting point data.

Ternary Mix 25% SOS—50% POS—25% SOO

In Table VI it is clear that treatments of the three-component system which approaches cocoa butter com-

TABLE IV

Thermal and X-Ray Diffraction Data for Cocoa Butter States

	I	II	III	IV	V	VI
Melting point, °C	17.3	23.3	25.5	27.5	33.8	36.3
Heat of fusion, cal/g at 11C						
Heating curve method		20.8	26.5	29.0	33.8	35.4
Calorimeter method		20.6	26.9	28.1	32.7	35.4
X-ray diffraction hkl						
Long spacings, Å 001	55.1 W	49.0 VS	49.0 VS	45.0 VS	63.1 M	63.1 VS
2	34.0 M, 26.8 W		24.6 VW	22.64 VW	32.2 VS	32.0
3		16.3 S	16.35 S, 15.24 W	14.87 S	21.02 W	21.25 VW
4					16.05 W	16.00 W
5	13.8 W	9.6 VW (diff)	9.82	8.93 W	12.80 S	12.76 S
6					10.64 M	10.62 W
7					9.40 VW	9.20 VW
8					8.04 M	7.96 M
9					7.10 W	7.08 M
Average d	68.5 and 54.5	49.0	49.1	45.0	64.1	63.8
Short spacings, Å	4.19 VS	4.24 VS	4.92 VW	4.35 VS	5.40 M	5.43 M
	3.70 S		4.62W	4.15 VS	5.15 W	5.15 W
			4.25 VS	3.97 M } diff	4.58 VS	4.59 VS
			3.86 S	3.81 M }	4.23 VVW	4.27 VW
					3.98 S	4.04 W
					3.87 M	3.86 M
					3.75 M	
					3.67 W	3.70 S
					3.39 VW	3.36 VW

position yield diffraction patterns closely approaching those of cocoa butter. It is particularly gratifying to find states I and II in the ternary system, I with its unusual long spacings and II with its alpha-2 character; although it is true that II for the ternary system shows some short spacing evidence of an additional form or forms. Likewise, the occurrence of state V and then VI on aging comports with cocoa butter behavior. An appearance similar to product III of cocoa butter was obtained but with enough differences to make complete identification uncertain. Again as with the 15.24 Å long spacing in cocoa butter III, Table IV, there is a suggestion that treatment to give III actually results in a mixture of II (alpha-2) and some higher melting state.

Discussion

Two "Alpha" Melting Points

State I (sub alpha type) and state II (alpha type) each has a melting point associated with it, the "alpha" melting point being some 6C higher than that of "sub alpha." This is unprecedented behavior and deserves discussion in view of statements that alpha phase, in pure triglycerides, permits little or no supercooling (15).

While alpha phase, as in tristearin, is so rapidly nucleated that it appears to crystallize without supercooling, when crystallized in appreciable bulk it does permit supercooling in a highly subdivided state as shown by the data of Skoda et al. (16) on emulsified samples. It is still believed that, for a pure triglyceride, no melting point lower than any properly observed alpha melting point is apt to be found, although alpha may show small variations in melting level. Conceivably, also, a lower true glassy melting point, lower than that of alpha, might yet be found in highly polymerized fatty or long chain molecules, but probably not in normal triglycerides.

The evidence on cocoa butter shows the possibility of different behavior by mixtures. The I and II melting points of cocoa butter are interpreted as follows. On quick chilling of a cocoa butter melt there is homogeneous crystallization in a low (17C) melting state I, with sub alpha-type short spacings and difficulty interpretable long spacings, some of which suggest sub alpha-3. However, on holding chilled cocoa butter at 0C some realignment of molecules results in state II, a pure alpha-2 phase; moreover, on subsequent lowering of temperature to the range for observation of I, state II remains as such, i.e. in the alpha-2 form.

Reversibility of Alpha and Sub Alpha

In several examples of alpha and sub alpha occurrence in glycerides the reversibility of transformation has been established (10,17). There are analogous changes in hydrocarbons, and, in all probability, such transformations occur in most relatively nonpolar long-chain compounds. The point has not been thoroughly explored for disaturated glycerides, but reversible alpha to sub alpha change is to be expected. However, when evidence has disclosed alpha-2 phase and sub alpha-3 phase as in the present case, alpha-2 $\rightleftarrows$ sub alpha-3 reversibility is not to be expected, and, experimentally, state II (alpha-2) could not be changed back to state I (sub alpha-3?).

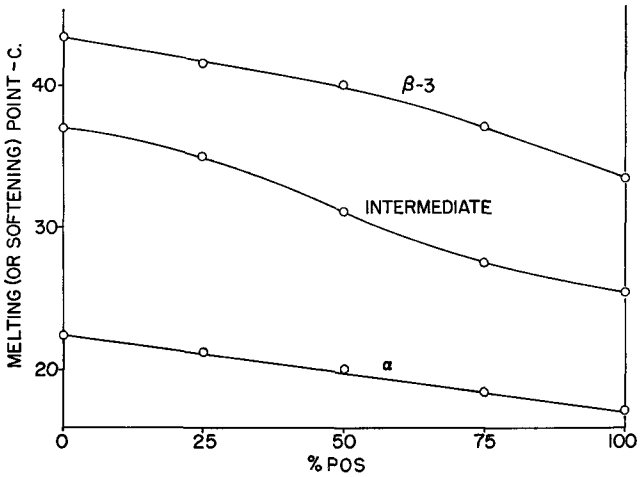

FIG. 4. Binary system SOS-POS.

Change of V to VI

The change from state V to VI, a real and reproducible change, must nevertheless involve only very minor change in the crystalline structure of cocoa butter, because there is no change in long spacings and only minor change in short spacings.

After the observation of a distinction between V and VI for cocoa butter, a reexamination of POS shows this pure glyceride to be subject to very similar changes. Thus POS, freshly prepared in beta phase obtained by melting, chilling, holding 1 day at 21C and 2 days at 27C, shows short spacings of 5.41 M, 5.09 W, 4.57 VS, 3.98 M, 3.86 W+, 3.73 VW, 3.65 W+ and, after 6 months at room temperature, shows 5.41 W+, 5.15 VW, 4.59 VS, 4.24 VW, 4.05 W+, 3.89 M, 3.70 S. These spacings correspond closely to those of cocoa butter states V and VI, respectively, as listed in Table IV, the data corresponding to VI agreeing with data earlier reported (10) for POS. We have continued in Table II to designate the two states of POS both as beta-3, realizing that they may be more properly regarded as two distinct but very similar polymorphs. It is of interest that the short

TABLE V

Phase Behavior of Binary System SOS-POS

% POS	Stable[a]			Intermediate[b]				Chilled, X-ray at Temp.		Chilled, X-ray at 0°C		
	X-Ray	L.S.[c] Å	M.P.[d] °C	Temp. °C	X-Ray	L.S. Å	M.P.[e] °C	Temp. °C	X-Ray	X-Ray	L.S. Å	M.P.[f] °C
0	β-3	64.7	43.5	23	sub β-3	70.5	37.0	17	α, sub β-3?	sub α-3	80	22.4
25	β-3	64.6	41.5	21.9	β'-3	69.5	35.0	17	α, sub β-3	sub α-3	79	21.2
50	β-3	64.3	40.0	20.8	β'-3	69.0	31.0	13	α-2	(sub α-2), sub α-3	79	20.0
75	β-3	64.2	37.0	19.4	β'-2	45.5	27.5	13	α-2	sub α-2, (sub α-3)	47.5	18.4
100	β-3	64.0	33.5[g]	17.5	β'-2	45.0	25.5		(α-2 assumed)	α-2	48.5	17.0

[a] Melt, chill, store 1 day at 21C, 2 days at 27C.
[b] Melt, hold 1 hr at temperature indicated.
[c] Long spacings.
[d] Complete melting point.
[e] Softening point when thrust in.
[f] Rapid complete melting point.
[g] After 6 months room temperature, mp 35.0C.

TABLE VI

Phase Behavior of 25% SOS—50% POS—25% SOO

Treatment	mp, °C	Short spacings, Å	Long spacing, Å	Most similar state of cocoa butter
Melt, chill, —30C	16.5	4.17 S, 3.71 W	55 M, 37 W	I
Melt, chill, 0C	20.4	4.21 S, 3.74 VW	47.5	II (modified)
Melt, chill, 5–10C	22.5	4.60 VW, 4.21 S, 3.82 W (diff.)	48, etc.	III (modified)
Melt, chill, 1 hr 18C	25.6	4.34 S, 4.13 S, 3.76 (diff.)	44.5	IV
Melt, chill, 1 day 21, 1 day 27C	37.0	5.45 M, 4.59 VS, 4.01 M, 3.89 W, 3.77 W, 3.67 M	64.5	V
Melt, chill, 4 mo. at 25C	37.0	5.45 W, 4.59 S, 4.06 W, 3.87 W+, 3.70 M	64.5	VI

spacings of state V of cocoa butter correspond also to those of beta-3 SOS, which has not been found to change to a state VI.

The nature of the change from V to VI is of particular interest because of implications concerning bloom development in chocolate coatings. The need for proper tempering in handling chocolate before enrobing or molding is well known in the confectionery industry. Normal procedure involves warming or holding the partially crystallized coating at a temperature sufficiently high (about 90F [32C]) to destroy low melting polymorphs, enrobing centers with the chocolate or casting molded shapes, and then chilling the material rapidly to solidify the coating. Inevitably during storage at ordinary temperatures the chocolate develops bloom, which appears to be a deposit of small fat crystals on the chocolate surface giving it a white or gray over-all appearance.

It is predictable from the present work that the initial crystalline state of cocoa butter in properly tempered chocolate is V, and this was confirmed by x-ray of fat from dark sweet chocolate coating from which sugar and cocoa particles were leached by extracting with a suitable solvent system at room temperature. (The solvent was 20% of a mixture of 2 parts methanol, 7 parts acetone and 80% water. Solid floating fat particles were skimmed from the solvent, filtered, dried and x-rayed). It is also predictable from the present work that during storage at 60F (16C) change from V to VI would be extremely slow, but at 80F (27C) change would occur within several weeks. This also was confirmed in actual coatings. After six and seven weeks, respectively, at 80F the cocoa butters recovered from two chocolate coatings were state VI, while the cocoa butters from other portions of the same coatings stored at 60F continued to be state V. Both coatings that had been stored at 80F had a slight bloom, but the 60F stored samples were bright and glossy.

It is not known at this time whether the change from V to VI is the cause of bloom or is just coincidental. We have never seen a bloomed sample that was not VI, nor a bright sample that was not V. However, it might well be that bloom is simply the growth of crystal agglomerates of VI from submicroscopic to macroscopic size brought about by digestion, migration and resolidification of fat molecules under the influence of small (or large) temperature variations, and has nothing to do with the internal crystal modification which gives rise to the change in x-ray diffraction pattern from V to VI.

Polymorphism of Components

Chapman (11) has reviewed several sets of data on disaturated triglycerides. The present authors' views are summarized in Table II in comparison with the behavior of cocoa butter. Deviations reported by Malkin et al. (6) are not shown, but his report of sub beta-3, which he called beta double prime, for POP is of interest, since it remains among the possibilities that state III of cocoa butter contains some sub beta-3 and since the solid glycerides of cottonseed oil stearin (chemically a mixture of POP and PLP, 2-linoleoyldipalmitin) obtained in the winterizing process is sub beta-3.

The polymorphism of SOO has been recently reported (18). It is believed to be of little relevance to the cocoa butter problem since the small SOO (and POO) content only slightly modifies POS-SOS polymorphism.

Asymmetry of Triglycerides

The present very limited evidence on naturally occurring triglycerides suggests that some naturally occurring asymmetric glycerides are racemic and some are not. Schlenk (19,20) has said, on the basis of x-ray diffraction and piezo-electric properties that the POS of cocoa butter is racemic; Morris (21) has said, however, on the basis of optical activity of a derivative, that the diunsaturated portion of cocoa butter is not racemic. (SOS, of course, is not isomeric.) At this time there is no adequate phase data on known mixtures of racemic vs. nonracemic glycerides to indicate the extent to which optical isomerism affects polymorphism.

The agreement in behavior of the present (racemic) 3-component synthetic sample with that of natural cocoa butter is rather good, considering the many difficulties in obtaining a match. The less than perfect agreement may indeed be due to the racemic character of the synthetic SOO; on the other hand it may be due to absence of POO or lack of perfect adjustment of POS-SOS proportions.

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[Received April 4, 1966]