Cocoa Butter and Confectionery Fats. Studies Using Programmed Temperature X-Ray Diffraction and Differential Scanning Calorimetry

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Abstract

The polymorphic behavior and thermal properties of cocoa butter have been investigated by means of programmed temperature x-ray diffraction and differential scanning calorimetry. The relationship of this polymorphism to the technical problems of "tempering" and "bloom" development is discussed. Cocoa butter containing, respectively, milk fat and a bloom inhibitor, and some alternatives to cocoa butter have been studied. These results have provided information that will help determine process conditions for these particular fats.

Introduction

Cocoa Butter Polymorphism

The attainment of various requisites for finished chocolate, e.g., gloss, prevention of fat bloom and acceptable melting characteristics, has for a long time been associated with the ability of cocoa butter to solidify in various crystalline forms. These requirements have been met by determining conditions for the "tempering," cooling and storage of chocolate products; the conditions were first found empirically, but subsequently studies of the phase changes of cocoa butter have begun to give a more basic understanding of the physical processes involved.

Several papers have been published on the relationship between cocoa butter crystallization and tempering, cooling and "bloom" (1–8), but there has been controversy over the polymorphs involved and correlations of "melting points" with x-ray diffraction patterns have been confused. In Table I the correspondence of the various reported forms is outlined. The confusion is easily dispelled by the use of programmed temperature x-ray diffraction in which the diffraction pattern is obtained simultaneously with the temperature changes. This technique, together with differential scanning calorimetry, which supplies more detailed thermal information, is described below.

The polymorphism of glycerides has been reviewed by Chapman (13,14), who with the aid of IR spectroscopy reconciled the melting points and x-ray data for saturated glycerides. In his system the three main crystallographic forms for monoacid triglycerides were designated by the Greek letters α, β' and β in order of increasing melting point, heat of fusion and density.

The α-form had a sharp diffraction line at about 4.1 A, β', two strong lines at 3.8 and 4.2 A, and β, a strong line at 4.6 A. Larsson (15) has proposed a modified nomenclature which is applicable to mixtures of triglycerides; in this scheme x-ray diffraction patterns only are used. The α-form has one strong short spacing near 4.15 A, the β'-form has either two strong lines near 4.20 and 3.80 A or three strong lines near 4.27, 3.97 and 3.71 A, and the β-form is any polymorph which does not satisfy these criteria. If two or more crystal forms have the same designation they are distinguished by subscripts in order of decreasing melting-points.

For cocoa butter and its equivalents, the system of nomenclature used in this paper is that of Wille and Lutton (11), in which Roman numerals are used for the six forms of cocoa butter. The scheme of Larsson (15) is used for the other fats.

A detailed study of the polymorphism of cocoa butter was published by Wille and Lutton in 1966 (11), in which they described six crystalline forms. Form I they interpreted as a sub-α phase, although this is better referred to as β'_2 because the short spacings are characteristic of β' packing (10), and Form II corresponded to a normal α-form. Form III was possibly a mixture of phases. Form IV corresponded to a known state of 2-oleyl-palmitostearin (POS). These forms were related to the polymorphs of the principal glyceride constituents of cocoa butter, POS and 2-oleyldistearin (SOS), and a ternary mixture of 50% POS, 25% SOS and 25% 1-stearyldiolein (SOO) closely paralleled the behavior of cocoa butter.

Tempering

The object of tempering chocolate has been assumed to achieve a sufficient concentration of the stable crystalline form of cocoa butter so that on cooling the remaining liquid fat solidifies as this stable form with little supercooling. However, confusion has existed as to which is the stable crystalline form "β" or "β'," and during cooling it has been suggested that the solid phase is a mixture of "β" and "β'" (3,4). This confusion in the past has resulted from the controversy over glyceride polymorphs and from a failure to recognize a high melting β-form. By using Table I the earlier literature can be interpreted.

Bloom

Several theories have been suggested for the cause of fat bloom on chocolate, (1–6,16–20), and Wille and Lutton tentatively suggested it may be due to the formation of phase VI. There are obviously several types and causes of fat bloom and only the type that can occur in chocolate on its own is dealt with in this paper. The effect of one of the additives, claimed to be a bloom inhibitor, on the polymorphic changes of cocoa butter is described below.

Alternatives to Cocoa Butter

For economic and practical reasons, alternatives to cocoa butter which accurately reproduce its melting characteristics have been sought. The normal

TABLE I

The Correspondence of Reported Forms of Cocoa Butter

Wille and Lutton (11)		Witzel and Becker (8)	Vaeck (1)	Giddey and Clerc (2)	Riiner (9,10)	Duck (4)	Keil and Hettich (7)	Lovegren and Feuge (12)
I	γ		γ		β'_2			III
II	α	α	α		α	α	α	
III	β''	β_1'			Mixture of α and β'	β''		II
IV	β'	β_2'	β'	α	β'_1			
V	β	pre-β	β	β'	β	β'	β'	I
VI		β		β		β	β	

criteria for a cocoa butter equivalent are that it should have similar melting behavior and if it is to be used in conjunction with cocoa butter it should be "compatible." For a cocoa butter substitute that is not used in conjunction with cocoa butter, it is necessary to have similar melting behavior and the products should not be susceptible to bloom. The polymorphic behavior of two of these substitutes is outlined below. The fatty acid composition of the various fats is outlined in Table II.

Experimental

Programmed Temperature X-Ray Diffraction

The diffraction pattern temperature (DPT) camera was designed by S. Abrahamsson, Crystallography Group, Institute of Medical Biochemistry, University of Goteborg, Sweden, and was supplied by Incentive Research and Development, Sweden. It consists of a 3 cm internal diameter cylindrical specimen chamber mounted above a small furnace containing a heating coil. A stream of gas passing over the coil enters the specimen chamber axially below the specimen, which is mounted vertically. The x-ray beam is collimated by two vertical slits, and the diffracted rays pass out of the specimen chamber through a Mylar window. The diffraction pattern is recorded on film for 2θ is ca. 1.1 — 90° on one side of the central beam, and for 2θ is ca. 1.45 — 4° on the other. The film is carried on the inside of a quarter cylinder of 20 cm diameter, coaxial with the specimen, and moving vertically, normal to the x-ray beam, at a constant speed of 2.67 cm/hr. Only a narrow equatorial section of the diffraction pattern is allowed to fall on the film through an adjustable slit in a cylindrical screen.

Samples. Melted and sealed in thin walled glass capillary tubes, 0.7 mm. in diameter, the samples were either put through suitable thermal programs while recording their diffraction patterns, or were stored for two to three months in order to stabilize crystal forms and patterns then recorded.

Thermal Programs. Samples were heated and cooled by a stream of dry nitrogen, ca. 20 liters/min., obtained by boiling off liquid nitrogen and passing the gas over the heating coil in the camera furnace. The temperature of the gas was programmed by a Hewlett-Packard Model 240 reversible temperature programmer which was modified by the addition of a reference thermocouple held at 0 C to reduce program fluctuations due to changes in room temperature. The temperature of the specimen was sensed by a NiCr-NiAlC thermocouple placed as close as possible to the irradiated part of the specimen. The output from this thermocouple was recorded. This system enabled heating or cooling of specimens at rates of ca. 0.3 to 16 C/min or holding at any desired temperature while continuously recording pattern changes.

Pattern Recording, Measurement and Accuracy: Patterns were recorded on Ilford Industrial G fast x-ray film using Cu Kα Ni-filtered radiation from the line focus of a Philips x-ray tube (PW 2073/62) supplied by a Philips generator (PW 1011) operated at 20 ma and 40 kv.

Diffraction patterns were measured using a Joyce-Loebl Microdensitometer Mark III, with a trace to film ratio of 5:1, the long spacings recorded on each side of the direct beam being used to determine the center of the pattern. The accuracy attainable by this method is ca. ± 5 A at 70 A, ± 1 A at 35 A and ± 0.02 A at 4.5 A. Intensities of diffraction lines were estimated visually.

The accuracy with which melting points could be determined from disappearance of diffraction lines on the film was tested visually and by microdensitometry along the lengths of suitable lines for ice, gallium (99.9999% pure), laurie acid, β-naphthyl ethyl ether and thymol. Results (Table III) show that there is little difference in accuracy in the two methods of measurement, and as the visual method is quicker this was used in the present investigation.

The use of programmed temperature x-ray diffraction is a recent development. It has been used by Riiner (9,10) to study fats, and he made some observations on cocoa butter. The sample size is very small (ca. 1 mg) and the extrapolation from this to large scale operation requires caution.

Differential Scanning Calorimetry

The instrument used was a Perkin Elmer differential scanning calorimeter (DSC) 1B. The principles of differential scanning calorimetry and its

TABLE II

The Approximate Fatty Acid Composition of the Fats (GLC of Methylesters)

	Cocoa butter	Coberine	Cocoa butter with 30% milk fat	Nucoa S	A hydrogenated vegetable fat
C_{16}	.....	.....	0.7	2.7	5.5
C_{12}	.....	0.6	1.0	42.9	41.9
C_{14}	.....	0.5	2.4	19.0	16.0
C_{16}	24.4	28.8	25.2	10.3	10.2
C_{18}	35.0	26.3	25.4	12.7	17.6
C_{18}'	36.3	37.4	33.4	2.4	4.0
C_{18}''	2.8	4.4	4.3	.....	.....
C_{20}	1.0	0.6	1.3	.....	.....
Others	0.5	1.4	6.3	10.0	4.8

TABLE III

Comparison of Melting Points Determined by the Diffraction Pattern Temperature (DPT) Camera and Other Methods

Substance	mp From DPT film: Visual measurement, C	mp From DPT film: Micro densitometry, C	Determination in mp tube using NPL thermometer, C	Literature value, C
Ice	2.1	2.4		0
Gallium (99.999%)	28.3	.....		29.78
β-Naphthyl ethyl ether	35.6	36.3	36.0	35.0
Lauric acid	44.3	.....	44.0	44.0
Thymol	49.0	49.1	50.2	50.0

TABLE IV

The Phases of Cocoa Butter, Cocoa Butter Containing Milk Fat (CB/MF) and Coberine

Phases	Material	Melting point, C (DPT)[a]	Disappearance of form, C (DPT)	Appearance of form, C (DPT)	Heat of fusion, cal/g (DSC)	Formation on DSC	X-ray pattern: Long spacings, A		X-ray pattern: Short spacings, A	
	Cocoa Butter			ca. 5		Extremely rapid cooling (never observed pure)	54 27	S[b] M	4.17 3.87	S M
I	CB/MF			ca. 5	15.7	Rapid cooling of melt to 0 C	54 35 27	VS M M	4.18 3.80	VS MS
	Coberine			ca. 3		Rapid cooling of melt. Only observed as a shoulder on peak of Form II	51 28	VS W	4.18	VS
	Cocoa Butter				19.5	Cool the melt to 0 C, warm to 5 C and hold for 20 min	51 16.3	VS M	4.20	VS
II	CB/MF				18.8	Holding at 10 C for 100 min	52 16.2	VS M	4.21	VS
	Coberine				19.1	Rapid cooling of melt. Hold at 5 C for 5 min.	51 16.3	VS MS	4.20	S
	Cocoa Butter		20.7	14.5	21.5	Cool melt to 15 C	51 25 16.4	VS VW M	4.20 3.87	VS W
III	CB/MF		18.0	13.5	20.6	Warm II to 20 C. Hold for 20 min	52 16.1 15.2	VS M VW	4.61 4.23 3.86	VW VS W
	Coberine		20.9	14.6	22.3	Cool melt at 8 C/min to 10 C. Warm to 12 C. Hold for 10 min	50 24 16.6	VS VW M	4.20 3.89	VS VW
	Cocoa Butter	25.6			24.8	Slow warming of III to 26 C	49 14.8	VS W	4.32 4.13 3.88 3.75	S S W M
IV	CB/MF	21.9			24.0	Warm to 23 C. Hold for 10 min	46 14.9	VS M	4.34 4.12 3.83	S S W
	Coberine	23.6			.....	Unobtainable Pure	49 23 15.1	VS VW MS	4.30 4.15 3.92	S S M
	Cocoa Butter	30.8			28.1	Slow warming of IV to 29 C or holding at 25 C for 3 days	66 33 16.2 12.8 8.1 7.1 5.38 5.13	S S VW M M VW M VW	4.58 4.22 3.98 3.87 3.73 3.65	VS VW MS M M MS
V	CB/MF	27.2			27.5	Cool melt to 0 C. Warm to 25 C at 1 C/min. Hold for 30 min	67 33 16.2 12.9 8.1 7.1 5.40 5.16	S S VW VW M VW M VW	4.61 4.23 3.99 3.86 3.75 3.68	VS VW MS M M MS
	Coberine	30.2			26.8	Cool melt to 0 C. Warm to 23 C. Hold for 30 min	70 35 21 15.5 12.9 8.0 5.36	S S VW VW VW WM M	4.56 4.18 3.96 3.87 3.70	VS WM MS M MS

TABLE IV

The Phases of Cocoa Butter, Cocoa Butter Containing Milk Fat (CB/MF) and Coberine (Concluded)

Phases	Material	Melting point, C (DPT)[a]	(DPT) Disappearance of form, C	Appearance of form, C (DPT)	Heat of fusion, cal/g (DSC)	Formation on DSC	X-ray pattern: Long spacings, A		X-ray pattern: Short spacings, A	
	Cocoa Butter	32.3			32.9	Several months at 27 C (externally produced)	63 31 15.9 12.7 8.0 7.0 5.37 5.09	S S VW MW MW W M VW	4.53 4.21 4.01 3.84 3.67	VS VW W M S
VI	CB/MF	30.6			.....	Several months at 27 C	65 35 13.3 10.7 8.0 7.1 5.42 5.22	S S VW VW W VW M VW	4.88 4.60 4.25 4.02 3.87 3.68	VW VS VW W M S
	Coberine	30.5			28.2	One week at 27 C	70 33 23 12.8 7.9 7.0 5.42	S S VW VW VW VW M	4.61 4.22 4.01 3.86 3.68	VS WM WM M S

[a] Abbreviations: DPT, diffraction pattern temperature; DSC, differential scanning calorimetry.
[b] Intensities estimated visually as: VS, very strong; S, strong; MS, medium strong; M, medium; MW, medium to weak; WM, weak to medium; W, weak; VW, very weak.

application to fats have been described previously (21) and it has been used for investigating heats of fusion (22), fat solids (23) and the physical properties of chocolate (24). The DSC can also be used to provide complicated temperature programs to produce a particular polymorph or mixture of polymorphs and these can be investigated in situ.

Even at very slow heating rates the melting of one pure polymorph does not produce a sharp peak, but the solid melts over a range (21). For this reason melting points for fats by DSC are not reliable as indicators of the particular crystalline form involved, except where the melting range is sufficiently distinct to make assignment definite.

The DSC was calibrated for temperature and areas corresponding to enthalpy changes with gallium (99.9999% pure) and benzoic acid. The use of these standards requires care, since the liquid of the former dissolves the aluminium of the sample pans, and the latter is volatile around its melting point. Nevertheless they are the most convenient standards for measurements around the temperature range of fat melting.

Materials

The cocoa butter used for all these studies was from West Africa. Sorbitan tristearate was obtained from Croda Food Products Limited. Coberine, Nucoa S and the hydrogenated vegetable fat were supplied by Loders and Nucoline Limited.

Discussion

Cocoa Butter

The Six Phases. The six phases of cocoa butter are outlined in Table IV, and the data are similar to those of Wille and Lutton (11). However, temperatures of transformation or melting points of the phases were, on the whole, several degrees lower than theirs. Melting points determined for pure forms would be expected to have the same order of accuracy as those shown in Table II for gallium, lauric acid and β-naphthylethylether, but melting and transformation temperatures of mixed forms are more difficult to determine because of overlapping diffraction lines, and are likely to be less accurate. Although polymorphic forms were readily recognizable on the films, pure phases were rarely obtained. Consequently, estimated intensities of x-ray diffraction lines were modified by overlapping of patterns from different phases resulting in slightly different values from those reported by Wille and Lutton.

The heats of fusion were obtained by DSC, but none could be obtained for Form I, since this was never produced pure; it presumably has a heat of fusion less than Form II.

The six phases of cocoa butter are shown in Figure I as they were produced on the DPT camera. The scheme of presentation of this diagram is as follows. Time is marked off down the left-hand side, then the x-ray diffraction patterns are displayed; underneath the diffraction patterns the angles are marked out. Down the right hand side the temperature program is displayed.

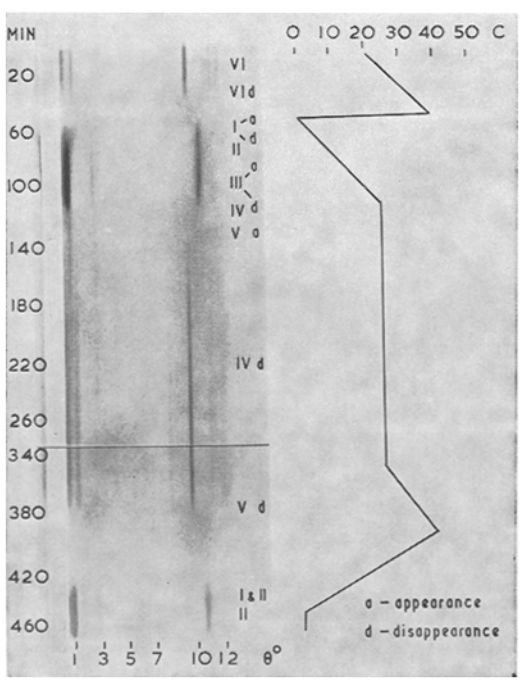

FIG. 1. The six phases of cocoa butter.

Form VI was produced externally and the sample was loaded in this form at room temperature. On heating, this melted at 32 C. Rapid cooling of the liquid produced Form I. On warming at 0.5 C/min the cocoa butter changed from Form I via II and III to Form IV. After holding at 25 C Form IV changed to Form V, being completely transformed after 100 min.

The interpretation of the diffraction patterns in terms of crystal structure has been outlined by Wille and Lutton (11) and the changes occurring during the transformation V → VI have been studied by Witzel and Becker (8).

Thermal Transformations. To the chocolate manufacturer, knowledge of the polymorphic forms with their respective stabilities is not sufficient to indicate practical conditions for tempering, cooling and storage. Information on the possible transformations and rate of transformations at various temperatures is also required. It is not just the higher melting forms that are of interest, since there are some processes concerned with manufacturing chocolate pieces that involve temperatures as low as −10 C.

The possible transformations of cocoa butter are outlined in Figure 2. All phases can transform to the higher melting one and all (except possibly Form I, which was not observed to melt) are able to melt. Evidence for the transformations to the higher melting phases is provided in Figure 1; rapid cooling of liquid cocoa butter produced Form I, which on slow warming (0.5 C/min) transformed through Forms II, III and IV to Form V.

It was found by DSC that slow cooling of the liquid (2 C/min) produced Form II, but it was difficult to determine whether rapid cooling of the melt produced a mixture of Forms I and II or pure Form I. A DSC scan of the solid produced always shows a mixture, but at least some of the Form II would have been generated during the scan. Wille and Lutton (11) achieved a complete melting of Form I by 18 C, but it has been suggested that this corresponds to a melting point for an incompletely developed Form II (10).

Form III could be produced either directly from the melt or by transformation of Form II. Form IV was produced from the liquid directly or it could be obtained by transformation of Form III.

The production of Form V directly from the melt was extremely slow; after cooling liquid cocoa butter to 30 C no solid was produced on holding at this temperature for one week (10 mg in a DSC sample pan). Form VI has only been produced by transformation from Form V.

A DSC trace of normal commercial chocolate indicates that the fat is present in Form V. Most tempering systems involve a final temperature of 29–31 C before setting and this is above the melting point of all polymorphs except Forms V and VI. Because of the time required to produce Form VI, the solid present in the tempered chocolate is presumably in Form V. On cooling the tempered chocolate it would then be expected that the remaining liquid crystallized as this polymorph.

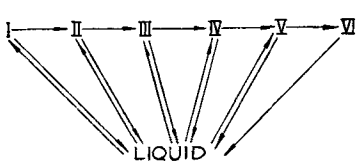

FIG. 2. The possible transformations of cocoa butter.

The tempering and cooling behavior of cocoa butter has been simulated on the DPT apparatus. A suitable program for preparing tempered cocoa butter evolved after several attempts but was not always reproducible; after rapid cooling of the melt the cocoa butter was slowly warmed to 25 C, at which temperature it was held for 2 to 2½ hr. It was then heated at 0.5 C/min to 29 C in order to destroy any Form IV.

At 29 C the cocoa butter then consisted of a mixture of Form V and liquid; on lowering the temperature at 0.5 C/min there was considerable supercooling until 16 C when Form II crystallized. When the tempered sample was cooled to 20 C and held at that temperature, a mixture of Forms IV and V solidified and the part in Form IV slowly transformed to Form V.

These results showed that liquid cocoa butter, in the presence of Form V, could crystallize partly as Form IV. These findings were supported by traces obtained from the DSC. When tempered cocoa butter (or chocolate) was rapidly cooled and subsequently scanned on warming, besides the presence of Form II a mixture of Forms IV and V was indicated; some of this Form IV was produced during the scan since a small exotherm was present but the larger part was formed during the cooling.

Bloom. Bloomed chocolate has been produced by cycling the temperature of finished chocolate between 9 C and 27 C over a period of months; this was the method used to produce Form VI in Figure 1. The chocolate was investigated by the DPT apparatus and the DSC. Because of the interference from the other x-ray lines of the other crystalline materials in chocolate, the small differences in x-ray spacings between Forms V and VI could not be discerned. By DSC it was shown that the fat was in a mixture of Forms V and VI.

Some of the actual bloomed portion was removed and compared with the normal dark colored chocolate for glyceride composition. Contrary to some claims (18) we have observed no significant differences between the fatty acid constituents of the bloomed and nonbloomed parts of chocolate (gas liquid chromatography of methyl esters), and the cause of this bloom is unlikely to be the separation of any particular glyceride or glycerides.

Other types of bloom can occur, particularly that associated with fat migration from a separate source such as where a center containing a liquid fat is surrounded by chocolate. In these cases the fatty acid constituents of the bloomed part could well be different, but this type of bloom is not dealt with in this paper.

Some types of bloom obviously consist of a fatty layer on the surface which can be wiped off, but the type produced by the temperature cycle above persists into the body of the material. On certain occasions the fat content of the bloomed chocolate was less than for the main body indicating that contraction of the fat had occurred into certain parts leaving others with less fat; a possible cause of this contraction could be the change of Form V to Form VI, with the subsequent stress produced causing breakup of the flat surfaces.

Cocoa Butter Containing Milk Fat

Most chocolate produced in Great Britain is milk chocolate, in which the fat is a mixture of cocoa butter and milk fat. The polymorphic behavior of this

mixture as shown in Table IV is very similar to that of cocoa butter; for these investigations the cow butter percentage was 30% of the total fat.

The melting points of all the phases are lower than for pure cocoa butter. The rate of transformation of each polymorph to the next higher melting one is slower, and pure Form I is obtainable giving a single melting peak on the DSC. Furthermore, the transformation of Form V to Form VI is slower; cocoa butter stored for five months at room temperature (23 C) showed considerably more Form VI than cocoa butter with milk fat after eight months at a similar temperature. This slow transition of Form V to VI may account for the observation that the addition of milk fat to cocoa butter retards bloom formation (6,18,25).

The six phases of cocoa butter containing milk fat have been prepared on the DPT apparatus. A tempering procedure similar to that for cocoa butter was used and cooling from 29 C of the mixture of Form V and liquid produced a mixture of Forms V and IV as with cocoa butter.

On some occasions after warming from 5 to 25 C, and holding at 25 C, there was a rapid development of Form V, whereas, on others the development was slow. Since the conditions were identical, it is presumably the randomness of chance nucleation that is the cause of the different rates of crystallization. However, it appeared that liquid cocoa butter containing milk fat was more willing to start crystallizing than cocoa butter alone at 25 C.

The ability of cocoa butter to dissolve up to 30% milk fat without significantly altering its polymorphism is surprising considering the very complex nature of the triglycerides of the animal fat. It may be this complexity that helps prevent glyceride separation. Milk fat is known to exist in the α, β' and β-modifications (26), which would tend to make it more compatible with cocoa butter.

Cocoa Butter With Sorbitan Tristearate

The addition of a variety of additives to chocolate to prevent fat bloom has been proposed, the most common being sorbitan tristearate sorbitan monostearate and polyoxyethylene sorbitan monostearate (6,16,24,25,27,28). The mechanism of the action of these bloom inhibitors is not known in detail, but for sorbitan tristearate only one crystal form has so far been observed with a single short spacing at 4.2 A (29). It was also shown that sorbitan tristearate stabilized the α-form of tripalmitin and it is possible that the action in cocoa butter is to retard any polymorphic changes.

Rapid cooling of molten sorbitan tristearate gave the same peak on the DSC as that produced by holding solid sorbitan tristearate 5 C below its melting point for two weeks (temperature and ΔH_f of the peaks were identical). This almost certainly rules out any polymorphic change in the material under these conditions, but it is recognized that this type of behavior does not necessarily extend to its action in cocoa butter.

The x-ray spacings for cocoa butter containing sorbitan tristearate (1.5%) were the same as for cocoa butter alone and only very small differences in the polymorphic behavior could be detected, one being the slower formation of Form VI.

Cocoa butter containing sorbitan tristearate has been tempered by the same procedure as for cocoa butter. With sorbitan tristearate present there was a very much smaller development of Form IV when the mixture of Form V and liquid was cooled from 29 C and held at 20 C. When the tempered mixture was cooled rapidly the polymorph that solidified with Form V was Form I.

The effect of sorbitan tristearate was the retardation of any polymorphic changes, once the crystal structure has been established, although it did not retard the initial development of solid. This would account for its action as a bloom inhibitor.

Other Confectionery Fats

Because of the comparative scarcity of cocoa butter, alternative coating fats have been sought for a long time, either for part or total replacement. The particular features of cocoa butter that need to be matched are its melting characteristics and its comparative freedom from bloom.

Three different types of cocoa butter alternatives have been distinguished: an equivalent, which can be mixed with cocoa butter in any proportion without altering the melting characteristics and which has itself similar melting properties; an extender which can be used as a part replacement for cocoa butter, but does not necessarily have similar melting properties over the whole range of addition; and a substitute, which alters the melting properties of cocoa butter, which may itself have different melting characteristics, but can be used as a coating fat. The crystal lattice, formed largely from a mixture of POS and SOS triglycerides in cocoa butter, can obviously accommodate large amounts of some fats (e.g., up to 30% butter fat) with only slight alteration to its polymorphic behavior. Some fats, such as those which contain a high proportion of long chain triglycerides, such as PSP, which do not have a β-form cannot be expected to fit into the crystal structure. The melting behavior of mixed triglycerides has been reviewed (30), but little is known of the complicated ternary mixtures involved.

Any substitute that is to be used in conjunction with cocoa butter, at levels up to 100%, must have a similar polymorphism to cocoa butter. Of those fats examined to date, the most successful attempt is the product marketed as Coberine (31).

Coberine (A Cocoa Butter Equivalent)

The data for the six polymorphic phases of Coberine are shown in Table IV.

The agreement with cocoa butter is very close with six comparable polymorphs melting at similar temperatures. The main difference between the behavior of Coberine and cocoa butter is the rate of transformation of one form into another. Form I (similar designations have been used for the polymorphs of Coberine) was unobtainable in the pure state and only appeared as a shoulder on the DSC peak of Form II; on the DPT camera very little Form I was visible. On the DSC, when the liquid was cooled at 8 C/min, the resulting solid was a mixture of Forms II and III. Coberine was also found to possess a more pronounced Form III than cocoa butter, since it had a more distinct x-ray pattern.

On the DPT, cooling of the tempered fat at 0.5 C/min produced Forms IV and V, although the amount of Form IV produced was less than for cocoa butter under similar conditions. In order to achieve the temper, the fat was held at 22 C instead of 25 C. There was also rapid development of Form VI with strong crystallinity, after six weeks' storage.

Nucoa S (A Cocoa Butter Substitute)

Nucoa S is a fat developed for high quality coatings, which contains added sorbitan tristearate.

Rapid cooling of liquid Nucoa S produced some α-phase with a trace of β'. After holding at 0 C the amount of β' increased, and on warming at 0.5 C/min all the α-phase disappeared by 16 C. Most of the β' melted at 33 C leaving a trace of crystallinity, and keeping the β' at 22 C produced no further polymorphic change.

From these results it can be seen that there is no advantage in tempering the fat to produce a stable polymorph provided the temperature remains above approximately 15 C, since the only polymorph that appears above this temperature during any reasonable processing time is β'.

A Hydrogenated Vegetable Fat (A Cocoa Butter Substitute)

This was a blend of hydrogenated vegetable fats used for some chocolate-type coatings. It existed predominantly in the β'-form but melted at three distinct temperatures, 24.5 C, 32.5 C and 38 C. These temperatures presumably correspond to the melting points of three inhomogenous constituent triglycerides. The addition of sorbitan tristearate (1.5%) and milk fat (30%) was investigated to find out if they influenced the polymorphic behavior. With both of these additives some α-phase was observed after rapid cooling and this α-pattern disappeared by 17 C; there was also very little difference in the melting points of the β'-phases from those of the fat without the additives.

After storage of the fat for three months a very weak β-pattern emerged.

As with Nucoa S, tempering of the fat produced no advantages in obtaining a stable polymorph and would not be of practical help.

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