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POLYMORPHIC TRANSFORMATIONS OF COCOA BUTTER IN THE PRESENCE OF EMULSIFIER, STUDIED BY THE DSC.

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ABSTRACT

The DSC technique was used to investigate the extent of polymorphic transformations in pure cocoa butter and in the presence of a food emulsifier. The spontaneous transformation from the low to the high polymorph was accelerated by low percentages of emulsifier, but the transformation to the most stable VI form was retarded. The available liquid fraction program was used to explain this apparent controversy.

INTRODUCTION

The differential scanning calorimeter provides an efficient technique for analyzing the polymorphic behaviour of fat crystals.

Cocoa butter may solidify in six forms, differing in thermodynamic stability. Each polymorphic form can be solidified from the melt, except the VI form, which is reported to be obtained only from the transformation of the V form. Each unstable form transforms spontaneously into a more stable one.

The rate of transition can be affected by the incorporation of solid emulsifiers at low percentages. In most cases, the emulsifier has been found to retard crystal modification in fats (ref.1), in tristearine (ref.2), in palm oil (ref.3).

In the present work the DSC technique has been used to observe the effects of an emulsifier on the strongly polymorphic behaviour of cocoa butter.

MATERIALS AND METHODS

Cocoa butter was purchased from Hamester, West Germany. The emulsifier tested was sorbitan ester of stearic acid (sorbitan tristearate, Span 65), commercially available from Atlas Europol A.p.S., Italy.

The range of emulsifier concentration was between 1 and 10 wt % of the cocoa butter.

The crystallization procedures used: the III form was crystallized in the DSC, by cooling from 50°C to 15°C at a rate of 0.3°C/min, aged for 45 minutes at 15°C; the IV form was obtained by cooling the melted fat from 50°C to 16°C

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at a rate of 0.3°C/min; the V form was obtained by aging the IV form at room temperature. The aging of the V form for transformation to the VI form was accelerated by temperature fluctuations between 20°C and 30°C. The thermal data were obtained by a Mettler Differential Scanning Calorimeter (DSC TA3000). The instrument was calibrated with lauric acid and indium. The weight of cocoa butter tested was within the range of 10-20 mg; the sample was introduced in an aluminum pan hermetically closed. A similar empty pan was used as reference.

RESULTS

The polymorphic forms III, IV, V and VI were isolated and characterized in the DSC. The melting point of the fat increases and the peaks become narrower as the stability of the polymorph is higher, the VI form being the most stable one.

The V form of cocoa butter crystallized in the presence of the emulsifier at various concentrations was tested in the DSC (Fig.1A). As the emulsifier concentration increases, the melting point of the curve decreases and the shape is broadened. The liquid fraction was computed in a built-in computer program, at a given temperature (Table 1). As the emulsifier concentration increases, a greater portion of the fat is liquid at a pre-determined temperature. The samples of cocoa butter crystallized in the V form for this experiment were aged for a few days in order to allow the transformation of the VI form and tested again in the DSC (FIG.1B). The split curves indicate that a considerable part of the fat has transformed to the VI form. As more emulsifier is present in the sample, a greater part of the V form remains unchanged. The addition of 10% emulsifier prevents almost completely the transformation of the V form to the VI form.

The IV form of cocoa butter crystallized with emulsifier was aged at room temperature for a few hours and tested in the DSC (Fig.2). The heating curve of pure cocoa butter shows that most of the fat is in the IV form and only a small part of it has transformed into a more stable intermediate polymorph. As more emulsifier is present, a higher polymorph is developed; with 10% emulsifier, transformation of the V form occurs.

The III form was conveniently solidified in the DSC and the liquid fraction was computed (Table 1) at 26°C. The effect of the emulsifier on the III form is the same as that on the V form shown above: the addition of the emulsifier increases the liquid fraction of the fat at a determined temperature. The III form was solidified again in the DSC, using the same procedure, aged for 270 minutes at 25°C, for allowing the transformation to the IV form, and scanned immediately (Fig.3). The extent of transformation III-IV is affected by the emulsifier as in the IV-V transformation, i.e. the addition of the emulsifier

increases the fraction of the fat which transforms from the III to the IV form.

DISCUSSION

The results presented indicated inhibition and enhancement of the polymorphic transformation by the emulsifier. However, more detailed experiments not reported here show that the emulsifier does not prevent transformation, but it can either retard or accelerate it. The V-VI transformation is retarded when the emulsifier is added, while the III-IV and IV-V transformations are accelerated in the presence of the same emulsifier. Both in the III form and

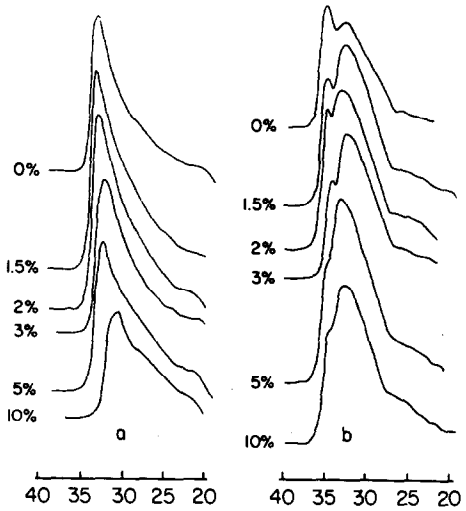

Fig. 1. A) Heating curves of form V with various concentrations of emulsifier. B) Heating curves of the same samples after aging.

TABLE 1

Melting point (mp) and liquid fraction (lf) of polymorph V and polymorph III in cocoa butter (CB) with increasing emulsifier concentration.

Emulsifier concentration (%)	Polymorph V (mp 33.1°C)		Polymorph III (mp 25.7°C)	
	mp(°C)	lf at 31°C (%)	mp(°C)	lf at 23°C (%)
CB	33.1	39.2	25.7	36.4
1	33.0	50.7		
2	32.7	52.9	25.6	36.4
4			25.2	43.5
5	32.3	55.4		
7			23.9	59.1

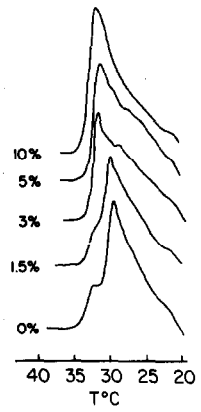

Fig.2. Heating curves of cocoa butter crystallized in the IV form and aged, in the presence of emulsifier.

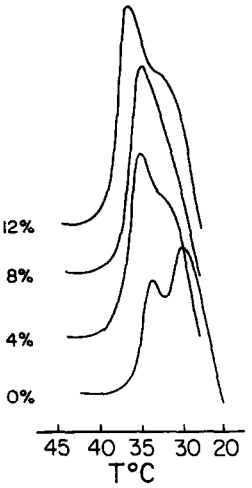

Fig.3. Heating curves of cocoa butter crystallized in the III form and aged, in the presence of emulsifier.

in the V form, the liquid fraction increases when the emulsifier is added. It has been demonstrated in our laboratory that the transformation of the thermodynamically unstable form can take place through the liquid phase while the V-VI transformation occurs through the solid state only.

The assumption that all transformations occur through the liquid state except the V-VI transformation which occurs through the solid state can be supported by the opposite effects of the emulsifier on these transformations: the augmentation of the liquid fraction may cause a retardation of the transformation which occurs through a solid state and an accelerating effect when it occurs through liquid state.

A better understanding of the causes affecting transformations in fats may allow to control their occurrence by adding selected emulsifiers.

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