Table 7.4 Polymorphic forms of cocoa butter.

Wille and Lutton (1966)	Larsson (1966)	Van Malssen *et al.* (1999)	Chain packing
Form I	β'_2	γ or sub-α	Double
Form II	α	α	Double
Form III	mixed	β′ range	Double
Form IV	β'_1		Double
Form V	β_2	β_V	Triple
Form VI	β_1	β_{VI}	Triple

Table 7.5 Melting points (°C; °F in parentheses) of polymorphic forms of cocoa butter.

Polymorphic form	Wille and Lutton (1966)	Van Malssen *et al.* (1999)
Form I/sub-α	17.3 (63)	–5 to +5 (23–41)
Form II/α	23.3 (74)	17–22 (63–72)
Form III/β′	25.5 (78)	20–27 (68–81)
Form IV/β′	27.5 (82)	
Form V/β_V	33.8 (93)	29–34 (84–93)
Form VI/β_{VI}	36.3 (97)	

defined for each individual polymorphic form. Van Malssen *et al.* (1999) found only five polymorphic forms in cocoa butter. The assignments of each form by these three groups of researchers are shown in Table 7.4.

The difference between the "traditional" polymorphic assignments and those of van Malssen *et al* is that the latter group found not two β′ forms but a range of these indicating the presence of either five forms (if the range is treated as a single form) or many forms (if the polymorphic forms in the range are treated individually).

Van Malssen *et al.* (1999) also found that the melting points of each of the polymorphic forms had been wrongly assigned by Wille and Lutton and that the melting point of the lowest stability form (Form I or γ/sub-α) was significantly lower than that measured by Wille and Lutton, mainly because this form very quickly transforms into the α form making determination of its melting point quite difficult. For comparison, the melting points assigned to each of these polymorphs by both groups (Wille and Lutton and van Malssen *et al.*) are shown in Table 7.5.

Because of the familiarity in the confectionery industry with the Wille and Lutton convention this will be used in the rest of this chapter interchangeably with the new convention defined by van Malssen *et al*. To allow for the presence of a range of β′ forms as defined by van Malssen *et al.*, Forms III and IV will be treated as a single form when using the Wille and Lutton convention.

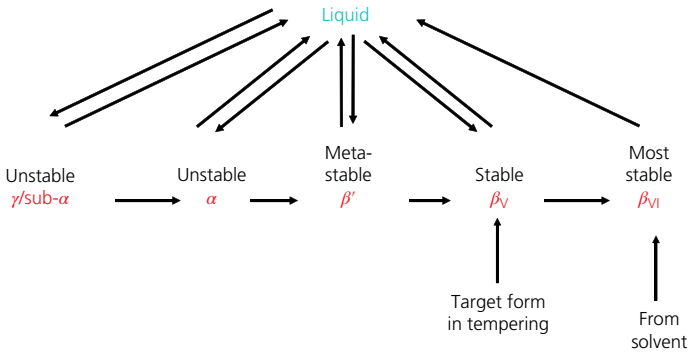

Figure 7.1 Polymorphic changes in cocoa butter. Reproduced with permission of Loders Croklaan.

Form I (sub-α) is produced by rapid cooling at low temperatures. It is very unstable and rapidly transforms into Form II (α). This form will change more slowly into Forms III and IV (β′).

β′ is the polymorphic form which would generally be produced if un-tempered or extremely poorly tempered chocolate were then cooled in a cooling tunnel, as though it were properly tempered. This form will also fairly rapidly (sometimes even before leaving the cooling tunnel) transform into Form V (β).

Forms V and VI or the β forms are the most stable forms of cocoa butter. Form V is the state which is produced in a well-tempered chocolate. On lengthy storage this can very slowly transform into Form Vl, a change which is often accompanied by the formation of fat bloom. It is difficult to generate Form Vl cocoa butter quickly and directly, although this has been observed when cocoa butter is allowed to crystallise from a solvent (Figure 7.1)

These different polymorphic forms or packing configurations are characterised by differences in the distances between the glyceride chains and in the "angle of tilt" relative to the plane of the end methyl group of the chain (see Figure 7.2).

The three main polymorphic forms found in fats (not only in cocoa butter): α, β′ and β have crystal packing configurations as shown in Figure 7.2. The α configuration has alkyl (fatty acid) chains which are both straight and parallel to each other, but which are also perpendicular to the end planes of the molecules. If we were to look end-on at the chains they would appear to have a cross-section of hexagonal symmetry reminiscent of looking end-on at a clump of pencils.

The β′ and β polymorphs show considerably more order in their crystal packing. Both display an angle of tilt relative to the end plane of the molecules. This angle is slightly greater (i.e. closer to perpendicular) in the β′ form than in the β form. In the β′ form the chains pack in an orthorhombic sub-cell in which adjacent zigzag fatty acid planes are mutually perpendicular when viewed end-on. In the β form the chains pack in a triclinic sub-cell with all the zigzag fatty acid chains being parallel to each other.