unsaturated acid in the 2-position of one molecule would be adjacent to the saturated acids in the 1- and 3-positions of the next molecule. The stereochemistry would be such that close packing of the triglyceride molecules would not be possible. If, however, these triglycerides pack in the triple chain form or β-3, then the unsaturated chain in the 2-position of one molecule would lie adjacent to the unsaturated chain in the 2-position of the next molecule. It was long thought that they did this in such a way that the positions of the double bonds in the oleic acid chains were next to each other with the chains nesting together, almost like spoons. Recent work by Peschar *et al.* (2004) suggests that this is not the case, but that only the end parts of the oleic acid chain (from the double bond to the methyl end group) are actually adjacent to each other. This enables much closer triglyceride packing and hence much greater thermodynamic stability. It has been shown that in Forms III and IV cocoa butter the triglycerides pack in a double-chain system, whereas in Form V they pack in a triple-chain system. The stereochemical problem of SOS triglycerides packing in a double-chain system accounts for the much lower thermodynamic stability of Form IV relative to the triple-chain Form V.

7.2.3 Minor components

As well as the major triglycerides shown in Table 7.2, other triglycerides are present in cocoa butter in lower amounts. Trisaturated triglycerides can have an important effect in cocoa butter although they are generally present in low levels. The main ones in cocoa butter are PPP, PPSt, PStSt and StStSt. Typical levels in a normal cocoa butter are about 1.4% but these rose to 3.6% in a sample heated under vacuum to 250 °C (482 °F) for 1 h (Timms and Stewart, 1999). Foubert *et al.* (2004) measured levels of these four triglycerides in cocoa butter and found mean levels of 2.11% (SD = 0.57%). Davis and Dimick (1989) also measured the trisaturated triglyceride contents of whole cocoa butter and also of a high-melting fraction. The whole cocoa butter contained 4.47% of PPSt (and OOA), PStSt and StStSt in total, whereas the isolated high-melting fraction contained a total of 65.66% of these triglycerides. The importance of these trisaturated triglycerides and particularly of those found in a high-melting fraction is that, when chocolate is tempered, they can crystallise out early in the process and, in so doing, increase the viscosity of the chocolate without making any contribution to the state of temper of the chocolate.

As well as triglycerides, cocoa butter can contain varying amounts of partial glycerides (mainly diglycerides). It is known that diglycerides can affect crystallisation of fats (Siew and Ng, 1999; Tietz and Hartel, 2000), usually interfering with crystallisation, although Tietz and Hartel (2000) suggest that they can act as nucleation sites when present at low levels. Timms and Stewart (1999) suggest a maximum of 2.5% diglycerides as being acceptable in cocoa butter. Foubert *et al.* (2004) found a mean level of 0.92% in 20 different cocoa butters, with the highest diglyceride level being 2.2%.

Cocoa butter is one of the few oils used in food without refining to remove free fatty acids, pigments and flavours and odours. This is largely because the flavours naturally present in prime pressed cocoa butters enhance the flavour of chocolate. However, this does also mean that varying levels of free fatty acids can be present. Usually a maximum level of 1.75% free fatty acid is defined, often by legislation (Timms and Stewart, 1999; European Union, 2000; Folayan, 2010). As with partial glycerides, too high levels of free fatty acids can affect crystallisation. Foubert *et al.* (2004) found that, of 20 cocoa butters examined, four gave crystallisation problems. Of these four, three had free fatty acid levels above this maximum of 1.75%.

Although no maximum levels are specified, phospholipids are also present in varying amounts. Foubert *et al.* (2004) found levels between 0.006% and 0.16%, whereas Davis and Dimick (1989) found levels of 0.03% in whole cocoa butter and 6.56% in the high-melting seed fraction referred to earlier, suggesting that phospholipids may too have a part to play in early crystallisation during tempering.

Unsaponifiable matter can be present at levels of up to 0.35% in press cocoa butter, as defined by both the European Union (2000) and Codex Alimentarius (2001). In other types of cocoa butters the European Union (EU) permits up to 0.5% unsaponifiable matter and Codex Alimentarius permits up to 0.7% unsaponifiable matter. Foubert *et al.* (2004) found levels ranging between 0.31% and 0.53% in 20 different cocoa butters.

7.3 Cocoa butter equivalents

As defined earlier, cocoa butter equivalents (CBEs) are fats that have similar fatty acid and triglyceride compositions to cocoa butter and, as a result, also have similar physical characteristics. Research into the chemical properties of cocoa butter in the 1950s led to the conclusion that its triglycerides had the unique structure described in Section 7.2.1, and the realisation that, for the formulation of chocolate, any fat intended for use in blends with cocoa butter would need to have triglycerides of a similar structure. Unlike all animal fats, some vegetable oils contained triglycerides of the appropriate structure. This made possible the production of specific fat fractions which, when blended, had properties almost identical to those of cocoa butter itself.

A Unilever patent on the invention was filed in 1956, and CBEs were launched in the British market (Best *et al.*, 1956). They were immediately successful, and a partnership developed between the United Kingdom (UK) chocolate industry and Loders and Nucoline, the Unilever subsidiary specialising in the production and marketing of these new confectionery fats. At that time, and in fact until 1977, there was no official composition for chocolate in the UK, but the major manufacturers agreed to use a maximum of 5% CBE on the total weight of the chocolate.