

8.2.2 Chemical changes and development of flavour precursors

8.2.2.1 Polyphenols

Cocoa is rich in polyphenols, specifically catechins and procyanidins. They cause astringency and bitterness and may mask fruity flavours (Luna *et al.*, 2002). Polyphenols consist of anthocyanins, causing the characteristic purple colour of unfermented cocoas, colourless catechin and epicatechin, and their dimers, trimers, tetramers and higher oligomers, called procyanidins, as well as polymers. Epicatechin tends to polymerise under the influence of oxygen. Figure 8.2 shows the molecular structure of selected polyphenols, the monomer epicatechin, a dimer procyanidin built up of two epicatechin subunits and a tetramer procyanidin built up of four subunits. Epicatechin and the smaller procyanidins up to three subunits are soluble and therefore cause the astringent taste sensation of cocoa. Molecules, built up of more than three subunits, are insoluble and cause no astringency. During the whole fermentation 50% of the soluble polyphenols are lost by oxidation and polymerisation or by “bleeding” out of seeds (Wollgast and Anklam, 2000; Camu *et al.*, 2008; Payne *et al.* 2010). So, astringency of cocoa is reduced and the colour changes from purple to brown. As expected, a negative correlation between the levels of remaining procyanidins and the flavour potential was found for cocoas from different origins (Counet *et al.*, 2004).

8.2.2.2 Free amino acids

The major nitrogen-containing precursors are the numerous amino acids and peptides (Timbie and Keeney, 1997). Ripe cocoa seeds contain between 10 and 16% (dry wt) of protein and a low level of free amino acids. During fermentation

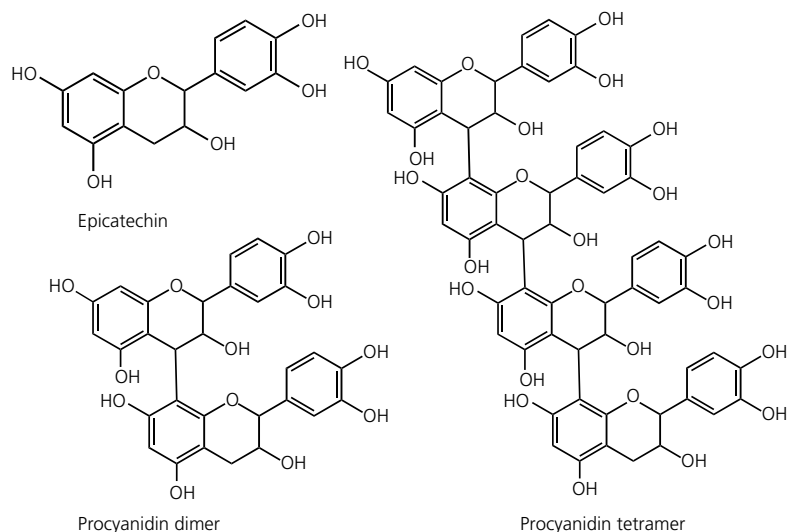


Figure 8.2 Molecular structure of some selected polyphenols in cocoa.

Table 8.1 Hydrophobic free amino acids [alanine (Ala), valine (Val), leucine (Leu), isoleucine (Ile), phenylalanine (Phe)] as precursors of volatile aldehydes, acids, alcohols, esters.

Amino acid	Aldehyde	Acid	Alcohol	Ester
Ala	Acetaldehyde	Acetic acid	Ethanol	Ethyl acetate
Val	2-Methyl-propanal	2-Methyl propanoic acid	2-Methyl-1-propanol	2-Methylpropyl acetate, ethyl 2-methylpropionate
Leu	3-Methyl-butanal	3-Methyl-butanoic acid	3-Methyl-1-butanol	3-Methylbutyl acetate, ethyl 3-methyl butanoate
Ile	2-Methyl-butanal	2-Methyl-butanoic acid	2-Methyl-1-butanol	2-Methylbutyl acetate, ethyl 2-methyl butanoate
Phe	Phenylacetaldehyde, benzaldehyde acetophenone ^a	Phenylacetic acid, benzoic acid	2-Phenylethanol, 1-phenylethanol, benzyl alcohol	Phenylethyl acetate, benzyl acetate, ethyl benzoate

^a Ketone.

seed proteins are degraded by post-mortem enzymatic hydrolysis giving rise to 1–2% (dry wt) of free amino acids. Proteolysis in the seeds mainly takes place within about 24 h after destruction of the cells and acidification by acetic acid. As mainly hydrophobic amino acids are set free, there is a clear difference between the compositions of the protein-bound free amino acids and resulting free amino acids (Kirchhoff *et al.*, 1989; Voigt *et al.*, 1994; Voigt, 2013). Hydrophobic amino acids, especially leucine, valine, alanine, isoleucine, phenylalanine, and hydrophobic peptides are of major importance as precursors for the formation of cocoa flavour (Biehl and Ziegler, 2003). Table 8.1 shows some examples of volatile derivatives of hydrophobic amino acids.

8.2.2.3 Sugars

Fresh cocoa beans contain 5–9% (dry wt) of starch and 2–4% (dry wt) of free sugars. In early fermentation the major sugar is sucrose; however, it is soon hydrolysed into glucose and fructose as fermentation progresses (Berbert, 1978; Reineccius *et al.*, 1972a). In Sanchez or Arriba cocoas, which are traditionally weakly fermented, up to 1% sucrose is found (Keeney, 1972). The sucrose content in well-fermented raw cocoas, however, is near to zero, but fructose and glucose levels increase up to about 0.6% (dry wt). As the amount of fructose and glucose formed is considerably lower than the decrease of sucrose, it would appear that a substantial proportion must exude from the pulp.

8.2.2.4 Acids

Acetic acid and lactic acid, which are produced in the pulp during fermentation, are assumed to cause the acid and sour taste of raw cocoa. During