

Figure 8.4 Formation of Amadori compounds from glucose and amino acids.

cocoa beans (Heinzler and Eichner, 1991; Oberparleiter and Ziegler, 1997a). They are the first intermediates of the reaction of free amino acid and glucose. Although the formation of these Amadori compounds is not detectable by colour or odour and may even be reversible at this stage, these initial reactions are important because Amadori intermediates will, during subsequent roasting, decompose into numerous volatile components. The reaction of phenylalanine (Phe) and glucose (Glc), as an example, delivers the Amadori compound fructose-phenylalanine (Fru-Phe). In course of the so-called Amadori rearrangement, the structure of glucose is turned into fructose (see Figure 8.4). It was shown that Fru-Phe after heating produces much more cocoa-like flavour components than the simple mixture of Phe and Glc (Oberparleiter and Ziegler, 1997a). The Amadori compounds Fru-Thr, Fru-Ser, Fru-Gly, Fru-Ala, Fru-Val, Fru-Ile, Fru-Leu, Fru-Phe and Fru-Abu have been found in dried cocoa, being generated by the reaction of the amino acids threonine, serine, alanine, valine, *i*-leucine, leucine, phenylalanine and α -amino butyric acid with glucose. The concentrations of single Amadori compounds are between 20 and 70 mg/100 g (dry wt) in dry raw cocoa, which means a conversion of about 10% of the single free amino acids into the corresponding Amadori compound. Owing to the high thermal reactivity of Amadori compounds, cocoa flavour may be generated at increased drying or low roasting temperatures. Figure 8.5 illustrates the formation of flavour precursors and flavour components during cocoa processing.

8.3.2 Flavour of unroasted, fermented cocoa beans

The first flavour compounds are developed during fermentation and drying and are predominantly aldehydes, alcohols, acids and acetates (Table 8.1). They derive from the hydrophobic amino acids alanine, valine, leucine, isoleucine and phenylalanine, starting with aldehydes from Strecker degradation (see also Figure 8.6a) and their partial conversion into alcohols and acids. Model reactions confirmed that Strecker aldehydes may be already formed under mild conditions (Pripis-Nicolau *et al.*, 2000). Alcohols were partly esterified by acetic acid to form acetates. In addition, methylbutanoic acids and benzoic acid are esterified by ethanol to form ethyl-methyl-butanoates and ethylbenzoate. In unroasted cocoa beans, quite high

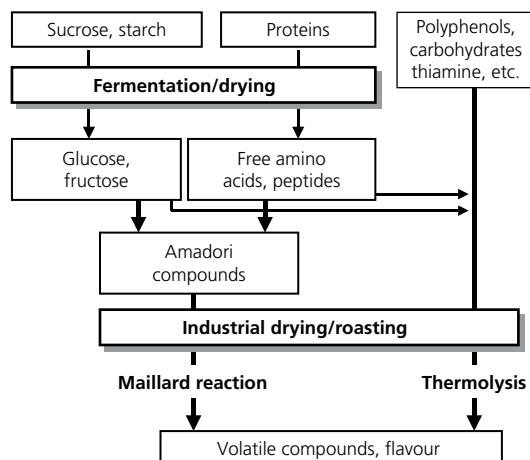


Figure 8.5 Influence of cocoa processing on development of flavour precursors and flavour compounds (schematic).

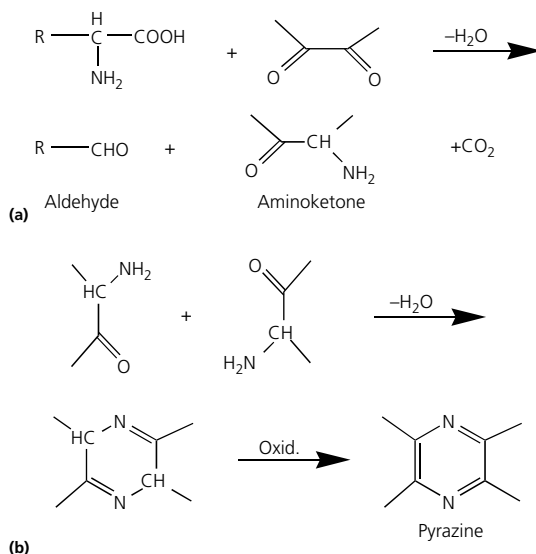


Figure 8.6 (a) Formation of aldehydes and aminoketones via Strecker degradation of amino acids. (b) Conversion of aminoketones into alkylpyrazines.

concentrations were found for 3-methylbutanal (16 mg/kg), 2-phenylethanol (3.5 mg/kg), as well as methylpropanoic acid (9.7 mg/kg), 3-methylbutanoic acid (9.3 mg/kg) and 2-phenylacetic acid with 5.1 mg/kg (Frauendorfer and Schieberle, 2008). Due to their very low odour thresholds between about 10 and 300 µg/kg (according to data of Frauendorfer and Schieberle, 2006), all these volatiles have a high odour activity and contribute to cocoa flavour. Tetramethylpyrazine occurs in relatively high concentrations in fermented unroasted cocoa and is produced