

only about 25% of free amino acids (fermented, unroasted: 1–2%, dry weight) are used up and about 70% of the glucose and fructose (fermented, unroasted: 0.6% dry wt; Pinto and Chichester, 1966; Rohan and Stewart, 1966; Reineccius *et al.*, 1972a; Ziegler, 1991b; Mermet *et al.*, 1992). Reducing sugars as the minor component within the mixture of aroma precursors are converted to a greater extent, while free amino acids, due to their surplus concentration, are consumed to a smaller extent and are partially recycled as part of the chemical reactions. The Amadori compounds (fermented, unroasted: 0.08–0.27%) are highly reactive intermediates and are totally utilised and rapidly decompose into numerous flavour volatiles (Heinzler and Eichner, 1991; Ziegler and Oberparleiter, 1997a).

It has been speculated that a pre-treatment of unroasted cocoa nibs or mass with water or aqueous precursor solutions might increase flavour development. As reducing sugars have been identified as the flavour precursors that are totally used up, the addition of sugar solutions might promote the formation of desirable flavour components. The preparation of unroasted cocoa mass and the addition of sugar solutions to cocoa mass before thin-film processing was therefore investigated (Rapp, 1981). When cocoa mass is treated, however, the aqueous reagent solution must diffuse across the hydrophobic fat cover. Therefore, the treatment of cocoa nibs was recommended (Kleinert-Zollinger, 1986). After the infiltration of an aqueous solution of 1% glucose into cocoa nibs before roasting, an increased formation of volatile sugar degradation products was found within the roast flavour (Ziegler, 1993). A pre-treatment of raw cocoa nibs with 15% of water for 15 min at 40 °C (104 °F), followed by drying at 98 °C (208 °F) to 3.5% water content and roasting, brought a more intense cocoa taste and an increased level of roast flavour components compared to cocoa which had been roasted without water pre-treatment. As a consequence of the pre-treatment with water, the consumption of amino acids and reducing sugars was increased, and an increased level of Amadori compounds was temporarily reached (Ziegler and Oberparleiter, 1997a). Probably the added water temporarily dissolves amino acids and sugars and so supports their reaction.

8.4.3 Roast flavour

The pioneer work on cocoa flavour analysis was performed by Bainbridge and Davies (1912), who isolated about 20 g of an aroma oil by steam distillation of 2000 kg of cocoa beans. Since then several groups have analysed cocoa flavour volatiles and, to date, about 600 components have been found (Van Praag *et al.*, 1968; Keeney, 1972; Maniere and Dimick, 1979; Gill *et al.*, 1984; Hoskin and Dimick, 1984; Carlin *et al.*, 1986; Ziegler and Biehl, 1988; Ziegler, 1991a; Mermet *et al.*, 1992; Nijssen *et al.*, 1996; Schnermann and Schieberle, 1997; Jinap *et al.*, 1998; Bonvehí and Coll, 2002; Counet *et al.*, 2002; Luna *et al.*, 2002; Frauendorfer and Schieberle, 2006, 2008; Granvogl *et al.*, 2006; Ramli *et al.*, 2006; Afoakwa *et al.*, 2008; Owusu *et al.*, 2012). These flavour components occur only in traces, mainly at levels of few µg/kg or not more than few mg/kg. Among them, about 100 different pyrazines represent the predominant flavour fraction.

Other significant flavour fractions are aldehydes, ketones, acids, alcohols, amines, esters, sulphur compounds, phenols, pyrroles, pyridines, furans, pyrones, lactones, chinolines, chinoxalines, thiazoles and oxazoles.

Aldehydes and pyrazines are the major groups in cocoa flavour. The main aldehydes in fermented cocoa arise from Strecker degradation of hydrophobic amino acids. The amino acids react with the dicarbonyl part of sugars to form aldehydes and aminoketones (Figure 8.6a). So, the concentration of acetaldehyde, 2-methylpropanal, 3-methylbutanal, 2-methylbutanal and phenylacetaldehyde in fermented and roasted cocoa beans may be higher than 10 mg/kg and therefore greatly exceeds the threshold values (e.g. concentration for 3-methylbutanal 4 mg/kg, threshold value 0.008 mg/kg). The concentration of 3-methylbutanal is strongly increased during roasting and partly decreased due to evaporation together with the roasting gases or due to thin-layer treatment of cocoa mass (Mohr *et al.*, 1968; Mohr, 1978). Also, the level of aldehydes is reduced by every grinding step starting from cocoa beans through nibs to the liquefied masse (Ziegler, 1982b).

Pyrazines are heterocyclic compounds with two nitrogen atoms in a six-membered ring. Cocoa pyrazines have many different substituents, for example methyl-, ethyl-, propyl-, butyl-, 2-methyl-butyl-, isopropyl-, isobutyl-, vinyl-, isopropenyl-, isobutenyl-, furyl-, methoxy- and acetyl-groups. These alkyl pyrazines are generally considered to be important components contributing to the flavour of roasted cocoa. The odour threshold values of different pyrazines range from 10 to 0.000002 mg/kg depending upon the substitution. Their sensory attributes were varied: pungent, sweet, nutty, chocolate, cocoa, roasted nuts, green, potato-like, earthy, musty and beany (Misnawi and Ariza, 2011). The mechanism usually postulated for pyrazine formation, as shown in Figure 8.6b, is dimerisation of ketoamines to dihydropyrazines with a subsequent oxidation step (Rizzi, 1988; Cerny and Fay, 1995). The variety and quantity of the alkylpyrazine formation depends on the cocoa origin, fermentation, pH, and roasting procedure (Hwang *et al.*, 1995; Jinap *et al.*, 1998; Cremer and Eichner, 2000; Bonvehi and Coll, 2002; Huang and Barringer, 2010; Farah *et al.*, 2012). The total concentration of pyrazines in roasted beans varies according to variety. Ghanaian beans may have about 7 mg/kg, whereas traditionally low fermented Mexican beans may contain as little as 1.4 mg/kg (Reineccius *et al.*, 1972b). Only tetramethylpyrazine (TMP) occurs in large amounts (0.5–2.0 mg/kg) in fermented unroasted cocoa. During industrial roasting it may soon reach its maximum level as it is expelled to some extent with the roasting gases. The concentration of other pyrazines rises with increasing roasting time or temperature. Major quantitative differences involve primarily the dimethyl-, trimethyl- and tetramethylpyrazines whereas other alkylpyrazines appear only at minor level. While the trimethylpyrazine (TrMP) increases steadily, the 2,3-, 2,6- and 2,5-dimethylpyrazines do not increase until strong roasting conditions occur (Figure 8.8). This enables a correlation to be established between the sensorially