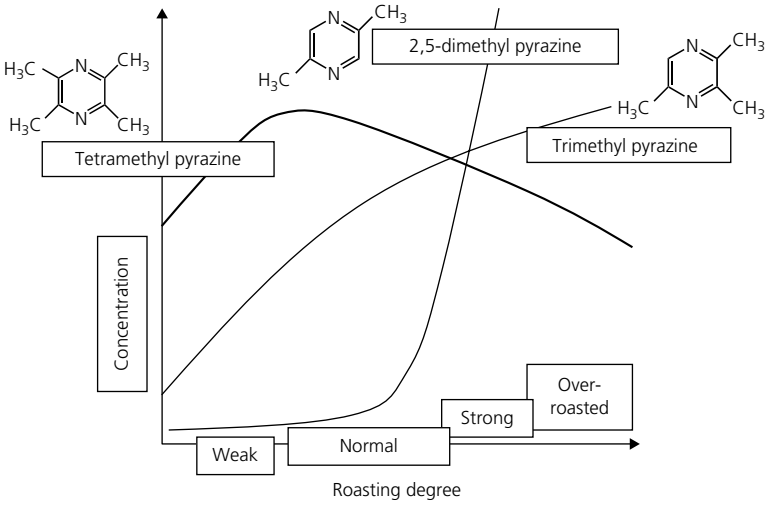

Figure 8.8 Influence of roasting on the formation of selected alkylpyrazines and on the sensorial roasting degree (Ziegleder, 1982b).

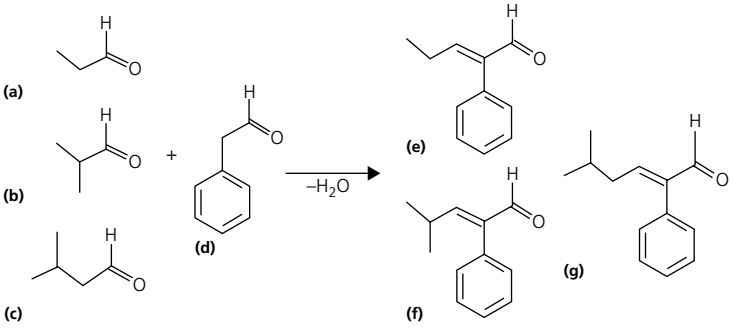

Figure 8.9 Aldol condensation of aldehydes with phenylacetaldehyde to form 2-phenyl-alk-2-enals: (a) acetaldehyde, (b) 2-methyl-propanal, (c) 3-methyl-butanal, (d) phenylacetaldehyde, (e) 2-phenyl-but-2-enal, (f) 2-phenyl-4-methyl-pent-2-enal, (g) 2-phenyl-5-methyl-hex-2-enal.

perceptible roasting degree of cocoa and selected components of the methylpyrazine fraction (Ziegleder, 1982b; Ziegleder and Sandmeier, 1983). The sensory evaluation of different roasted cocoa beans showed that a concentration ratio of TMP/TrMP between about 1.5 and 2.5 was obtained when the degree of roasting was normal. Over-roasted samples have a burnt, coffee-like taste and show significant concentration levels of 2,5-dimethylpyrazine and have TMP/TrMP ratios below 1.0 (Ziegleder, 1982b).

Due to their chemical reactivity aldehydes may be converted during certain secondary reactions. In this way acetaldehyde, 3-methylbutanal and 2-methylpropanal undergo aldol condensation with phenylacetaldehyde to form 2-phenylbut-2-enal, 2-phenyl-4-methyl-pent-2-enal and 2-phenyl-5-methyl-hex-2-enal (Figure 8.9), which carry an odour faintly reminiscent of

chocolate (Van Praag *et al.*, 1968) and which significantly increase with roasting time (Meili, 1985; Ziegleder and Biehl, 1988). As intermediates, aldehydes are involved in the formation of pyrazines and further heterocyclic compounds, which are dominant in the flavour of cocoa. Methods for evaluating cocoa bean quality by headspace measurements of 2-methylpropanal and 2-/3-methylbutanal have been suggested (Keeney, 1972; Ziegleder, 1982a).

As demonstrated by Granvogl *et al.*, 2006, a Strecker-type degradation of amino acids may lead to amines as well as to aldehydes. The authors found several amines in cocoa for the first time, such as 2-methylpropyl-, 2-methylbutyl-, 2-methylbutyl-, 2-phenylethyl- and 3-(methylthio)propyl-amine, which derive from the amino acids valine, leucine, isoleucine, phenylalanine and methionine. Only 2-phenylethylamine was already known in cocoa before, and of special interest due to its influence on human physiology (Chaytor *et al.*, 1975). Also, 3-aminopropionamide, a further biogenic amine, was found in roasted cocoa (Granvogl and Schieberle, 2007). Fermentation of cocoa led to amine levels of about 1 mg/kg and subsequent roasting up to 10 mg/kg (Granvogl *et al.*, 2006). While the corresponding aldehydes are potent odorants, the amines have less contribution to the aroma of cocoa. Their reported odour thresholds in oil are comparably high, between 0.3 mg/l for 3-(methylthio)-propylamine and 90 mg/l for 2-phenylethylamine.

Besides amino acids and sugars, other compounds such as peptides, proteins, vitamins, polyphenols and lipids and their oxidation products can enter the roasting reactions and influence the final flavour. In this way, heat treatment may generate specific flavour compounds: 1,2-benzendiol (pyrocatechol) is formed in cocoa by thermal decomposition of catechin, as well as thiazoles by thermal decomposition of the vitamin thiamine. Several pyrones, such as maltol, dihydro-hydroxymaltol, hydroxymethylfurfural and furaneol stem from the degradation of sugar precursors in cocoa (Ziegleder, 1991a). Some of the furaneol and 2,3-dihydro-6-methyl-4H-pyran-4-one has already been formed at earlier moderate temperatures and relatively high humidities (Figure 8.10). This makes these volatiles a useful indicator, whose level can be used for monitoring drying processes or the early stages of roasting (Schnee and Eichner, 1985; Ziegleder, 1991a, b). These compounds decrease slightly during extended roasting, probably as a result of their chemical reactivity. Furaneol has a pleasant caramel taste and may also have a flavour-enhancing effect.

Diketopiperazines, cyclic dipeptides, are generated by the intramolecular breakdown of peptides (Figure 8.11). In cocoa several diketopiperazines [e.g. Cyclo(ALA-VAL), Cyclo(ALA-Gly), Cyclo(LEU-PRO), Cyclo(ALA-LEU), Cyclo(ALA-PHE), Cyclo(PRO-GLY)] have been identified (Pickenhagen *et al.*, 1975; Rizzi, 1989; Bonvehi and Coll, 2000). Model experiments demonstrated that these diketopiperazines, when mixed with theobromine in a 2:1 mole ratio, induce a bitter taste sensation similar to that perceived from an aqueous suspension of cocoa powder (Pickenhagen *et al.*, 1975). Comparison of quantitative data of diketopiperazines