3 Basic chemistry and process conditions for reaction flavours with particular focus on Maillard-type reactions

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3.1 INTRODUCTION

Maillard reaction technology is used by the flavour and food industry for the production of process/reaction flavours or generating flavour upon food processing (in-process flavour generation). Process flavours are complex building blocks that provide similar aroma and taste properties to those found in thermally treated foodstuffs such as meat, chocolate, coffee, caramel, popcorn and bread. The Maillard reaction between a reducing sugar and a food-grade nitrogen source is the principal underlying reaction, which is responsible for flavour and colour development. However, Maillard-type reactions may also give rise to undesirable molecules that need to be limited using mitigation concepts. This review provides a summary of general aspects of the Maillard reaction in flavour formation in view of reinforcing distinct desirable flavour notes. An overview of important aroma compounds of thermally treated foodstuffs and process flavours is given. In addition, the patent literature and other publications relating to reaction flavour production and their process conditions are discussed. This chapter focuses on Maillard-type reactions and only partially deals with other reactions occurring during process flavour preparation (e.g. lipid oxidation).

3.2 GENERAL ASPECTS OF THE MAILLARD REACTION CASCADE

The ‘Maillard reaction’ is of great importance for flavour and colour formation of thermally treated foodstuffs. It is a complex cascade of many different types of reactions rather than one single reaction type, even though it is initiated by an amino-carbonyl reaction step. The thermal generation of flavours in foods, process flavours and model systems has accordingly been the subject of many symposia and reviews (e.g. Parliment et al., 1989, 1994; Weenen et al., 1997; Reineccius, 1998; Tressl and Rewicki, 1999; Cerny, 2007; Yeretzian et al., 2007). A first milestone in the history of Maillard chemistry was the publication of the well-known Hodge scheme (Hodge, 1953). Although Hodge’s studies focused only on Maillard browning, this scheme provided a framework that also covered important reaction routes for the formation of aroma compounds. The work of Hodge triggered a large number of studies on the elucidation of important intermediates and pathways of the Maillard reaction (see reviews by Ledl and Schleicher, 1990; Tressl and Rewicki, 1999). Isotopic labelling of sugars and/or amino acids in conjunction with GC-MS (gas chromatography–mass spectrometry) analysis (Tressl et al., 1993; Gi and Baltes, 1995; Keyhani and Yaylayan, 1996) and trapping of
reactive intermediates (Nedvidek et al., 1992; Hofmann, 1999) are key techniques for the improved understanding of Maillard reaction pathways.

Improvements and refinements of the Hodge scheme were presented by Tressl et al. (1995). Their scheme provides an excellent overview of Maillard reaction pathways leading to the formation of volatile compounds. For the optimisation of reaction flavours, however, a strong emphasis is required on those routes that are involved in the generation of key aroma compounds. This can be achieved by first evaluating the character-impact compounds of a process flavour or model system using a combination of sensorial and instrumental analysis on the basis of the odour activity value concept (Grosch, 1994). The mechanistic studies can then be focused on the key substances only. The work of Hofmann (1995) is an excellent example of such an approach.

Figure 3.1 gives an overview of the pathways that are involved in the formation of important aroma compounds during Maillard reaction. There are three main routes involved in flavour generation. All three routes start with imine formation between a reducing sugar and an amino acid. The Amadori (derived from aldoses) or Heyns (derived from ketoses) rearrangement products are important intermediates of the early phase of the Maillard reaction. Route A (see also Section 3.2.1) leads to the formation of 1- and 3-deoxyosones, which on cyclisation, reduction, dehydration and/or reaction with hydrogen sulfide result in heterocyclic aroma compounds. Route B (see also Section 3.2.2) is characterised by fragmentation of the sugar chain through retro-aldolisation or α-β-cleavage. By aldol-condensation of two sugar fragments or a sugar fragment and an amino acid fragment, heterocyclic aroma compounds are generated on cyclisation, dehydration and/or oxidation reactions. Alternatively, the fragments can react with hydrogen sulfide and form very potent alicyclic flavour substances. Route C (see also Section 3.3) involves the so-called Strecker degradation of amino acids, which is catalysed by dicarbonyl or hydroxycarbonyl compounds. The reaction

**Fig. 3.1** Major pathways for the formation of flavour substances during Maillard reaction. A, B and C denote the three key pathways.
is a ‘decarboxylating transamination’ and the resulting Strecker aldehydes are potent flavour compounds. Strecker aldehydes can also be formed directly from Amadori rearrangement products (ARPs) or Heyns rearrangement products (HRPs).

A more detailed, but still simplified scheme is depicted in Fig. 3.2 (Davidek et al., 2002) showing the formation of Amadori compounds, N-substituted 1-amino-1-deoxy-ketoses (V) representing an important class of Maillard intermediates (Ledl and Schleicher, 1990). They are formed in the initial phase of the Maillard reaction by Amadori rearrangement of the corresponding N-glycosylamines (II), the latter obtained by condensation of amino acids and aldoses such as glucose (I) as shown in pathway A. The importance of Amadori compounds stems from the fact that their formation as well as decomposition can be initiated under mild conditions. Thus, the formation of Amadori compounds represents a low-energy pathway of sugar degradation. The chemistry of Amadori compounds has recently been reviewed (Yaylayan and Huyghues-Despointes, 1994). Degradation of the Amadori compound V by 1,2-enolisation (pathway B) and 2,3-enolisation (pathway D) leads to the formation of 3-deoxy-2-hexosulose (VII) and 1-deoxy-2,3-hexodiulose (XII), respectively, as already suggested by
Hodge (1953). In parallel to these pathways, other α-dicarbonyls can be formed by enolisation. For example, transition metal-catalysed oxidation of 1,2-enaminol IV can lead via pathway C to osones such as glucosone (IX). Pathway E gives rise to the 1-amino-1,4-dideoxy-2,3-diulose (XIII) by elimination of the C4-OH group of the 2,3-endiol (VI). If the iminoketone (VIII) formed by oxidation of 1,2-enaminol (IV) is not hydrolysed, then Strecker aldehydes can be formed in the course of pathway C by direct oxidative degradation of the Amadori compound and decarboxylation of X, as proposed by Hofmann and Schieberle (2000a).

The so-called carbon module labelling (CAMOLA) technique (Schieberle et al., 2003; Schieberle, 2005) has been introduced as an advanced tool to quantify the relative contribution of carbohydrate fragments (e.g. C1–C4 fragments derived from Route B in Fig. 3.1) in comparison with transient intermediates with intact carbon chain configuration (e.g. deoxyosones; formed via Route A in Fig. 3.1) in the generation of Maillard-derived aroma compounds. The authors used a model system containing 1:1 mixtures of unlabelled and 13C6-labelled glucose as well as unlabelled proline and then measured the labelling pattern (12C6, 13C3 and 13C6) of the caramel-like odourant 4-hydroxy-2,5-dimethyl-3(2H)-furanone (Furaneol®) by GC-MS. The study revealed that, under dry heating conditions, Furaneol was generated entirely via the intact sugar skeleton, whereas in aqueous solution, 63% of the furanone was derived from the recombination of two C3-fragments. This work can be considered as another milestone in the history of research on Maillard chemistry. The CAMOLA technique has recently also been applied for studying the formation of furan in both model systems and foodstuffs (Limacher et al., 2008).

### 3.2.1 Intermediates as flavour precursors

ARPs and HRPs are relatively stable intermediates and have been detected in various heat-processed foods (Eichner et al., 1994). Since ARPs and HRPs can easily be synthesised (Van den Ouweland and Peer, 1970; Yaylayan and Sporns, 1987), their potential as flavour precursors has been evaluated in several studies. Doornbos et al. (1981), for example, found that the ARP derived from rhamnose and proline is a useful precursor for the generation of the potent caramel-like odourant 4-hydroxy-2,5-dimethyl-3(2H)-furanone. ARPs and HRPs have also been reported to be good precursors for Strecker aldehydes and, in the absence of oxygen, also for 1- and 3-deoxyosones (Hofmann and Schieberle, 2000a). At higher pH values, ARPs and HRPs easily undergo cleavage of the carbohydrate chain, yielding fission products such as 2,3-butanedione and pyruvaldehyde (Weenen and Apeldoorn, 1996).

When cysteine is heated with reducing sugars, thiazolidine carboxylic acids (TCAs) are formed instead of ARPs or HRPs (de Roos, 1992). TCAs are relatively stable in anionic form, which is probably the main reason for the inhibitory effect of cysteine in Maillard reactions, especially at higher pH. This can also explain the more efficient formation of important meat sulfur compounds at low pH (Hofmann and Schieberle, 1998a). A research disclosure (Anonymous, 1979), however, describes the use of TCAs as precursors for meat flavours. TCAs of glyceraldehyde, fructose or xylene were reacted as such or in conjunction with organic acids (e.g. succinic acid, malic acid and citric acid) or fatty acids (e.g. oleic acid and linoleic acid). Using a pH of 6–7 and temperatures between 50 and 100 °C, the TCA of glyceraldehyde and cysteine was reported to result in a beef-like aroma, whereas TCAs of fructose or xylene and cysteine yielded ‘meaty/savoury’ flavours.

Other important Maillard reaction intermediates are the deoxyosones. In general, 1-deoxyosones are more important flavour precursors than 3-deoxyosones, whose formation is favoured under neutral/slightly basic and acidic pH, respectively. Although 1-deoxyglucosone has been synthesised by Ishizu et al. (1967), 1-deoxyosones are too
unstable to be used as precursors. 3-Deoxyosones, however, are more stable and are easily obtainable from compounds such as difructoseglycine (Anet, 1960). The structure and reactivity of various 3-deoxyosones have been extensively studied by Weenen and Tjan (1992, 1994) and Weenen et al. (1998). By using various $^1$H NMR and $^{13}$C NMR techniques, the authors showed that 3-deoxypentosone and 3-deoxyglucosone consist almost exclusively of monocyclic and bicyclic (hemi)acetal/(hemi)ketal structures. 3-Deoxypentosones and 3-deoxyhexosones are good precursors for furfural and (5-hydroxymethyl)furfural under acidic conditions. Under basic conditions, they undergo cleavage of the carbohydrate chain and can form pyrazines in the presence of an N-source.

Hofmann and Schieberle (2000b) showed that acetylformoin, which is formed from 1-deoxyhexosone, is an effective precursor for 4-hydroxy-2,5-dimethyl-3(2$H$)-furanone (Furaneol). The amounts of Furaneol obtained from acetylformoin were significantly enhanced in the presence of reductones such as ascorbic acid or methylene reductinic acid as well as the Strecker-active amino acid proline. The reaction between acetylformoin and proline also resulted in high amounts of the cracker-like odourant 6-acetyltetrahydropyridine (ACTP).

A number of articles and patents report the production of meat-like aromas by reacting 4-hydroxy-5-methyl-3(2$H$)-furanone (norfuraneol) with hydrogen sulfide or cysteine. Van den Ouweland and Peer (1968) were first to file a patent on the use of this precursor system to prepare 3-mercaptomethylfurans, which exhibit meat-like character. Later, several studies identified sulfur-containing aroma compounds derived from the reaction of norfuranoe and hydrogen sulfide (e.g. Van den Ouweland and Peer, 1975; Whitfield and Mottram, 1999). The latter authors showed that this precursor system is capable of producing compounds such as 2-methyl-3-furanthiol (MFT) and 2/3-mercapto-3/2-pentanone in relatively high amounts. These thiols are also key aroma compounds of heated meat (Kerscher and Grosch, 1998).

Shu and Ho (1989) and Zheng et al. (1997) studied the reaction of the methyl homologue 4-hydroxy-2,5-dimethyl-3(2$H$)-furanone (Furaneol) with hydrogen sulfide or cysteine, which also gave rise to meat-like aromas. Among the identified sulfur-containing volatiles, however, the methyl homologue of MFT (2,5-dimethyl-3-furanthiol) was not found in the reaction mixtures.

Unilever patented processes for the preparation of savoury flavours using the precursor systems and reaction conditions shown in Fig. 3.3 (Turksma, 1993; Rosing and Turksma, 1997). When 2,5-dimethyl-2-(2-hydroxy-3-oxo-2-butyl)-3(2$H$)-furanone (diacetyloligomer; R and $R'$ = CH$_3$; process A in Fig. 3.3), which can be obtained by heating 2,3-butanedione under acidic conditions (Doornbos et al., 1991), is reacted with cysteine and hydrogen sulfide, high amounts of 2,5-dimethyl-3-furanthiol (DMFT) are generated (Turksma, 1993). For example, almost 40% yield of DMFT was obtained after 1 hour at 120$^\circ$C using a polar organic solvent, acidic conditions and super-atmospheric pressure (100–2500 kPa). DMFT, which was found to have a ‘meaty taste and roasted meat aroma’ was also formed from 2,5-dimethyl-3(2$H$)-furanone. Using similar conditions as for the diacetyloligomer, Rosing and Turksma (1997) reacted 4-hydroxy-2,5-dimethyl-(2-hydroxy-3-oxo-2-butyl)-3(2$H$)-furanone (Fig. 3.3; $R^1 = R^3 = CH_3$, $R^2 = $ acetyl; process B) with cysteine and hydrogen sulfide. This process resulted in a flavouring with sweet, onion-like, meaty aroma, odours attributed to high amounts of 2,5-dimethyl-4-mercapto-3(2$H$)-furanone and 2,5-dimethyl-4-mercapto-3(2$H$)-thiophenone. However, these two sulfur compounds were not found to significantly contribute to the flavour of heated meat.

Mottram et al. (1998) filed a patent on flavouring agents that serve as precursors for generating cooked (e.g. cooked meat) flavours in foodstuffs in situ. The authors claim
Fig. 3.3 Precursors, reaction conditions and main aroma compounds of two savoury process flavours (according to Turksma, 1993 [A], and Rosing and Turksma, 1997 [B]).

a long list of precursor substances that are capable of developing flavour during microwave cooking or conventional oven cooking with reduced cooking times. This list comprises several sulfur compounds such as hydrogen/ammonium/sodium sulfides, cysteine, thiamine, onion and garlic as well as ‘non-sulfur-containing post-rearrangement Maillard products such as furanones (e.g. 4-hydroxy-5-methyl-3(2H)-furanone, 4-hydroxy-2,5-dimethyl-3(2H)-furanone, 2-methyl-4,5-dihydro-3(2H)-furanone), pyranones (e.g. maltol, 5-hydroxy-5,6-dihydromaltol), 3-deoxyglucosone, ketones (e.g. cyclotene) and aldehydes. The precursor mixtures were encapsulated or spray-dried and applied to the foodstuffs through dusting or inclusion prior to the heat treatment. In two other studies, a similar precursor system consisting of unsaturated aldehydes and hydrogen sulfide resulted in aroma blocks with deep-fried notes (Van den Ouweland, 1989; Zhang and Ho, 1989).

As shown in this chapter, meat-like flavours can be obtained from the reaction of intermediate precursor systems such as 4-hydroxy-5-methyl-3(2H)-furanone (norfuranone) and cysteine. Cerny and Davidek (2003) investigated the efficiency of this precursor system in the generation of the meat-like odourants 2-methyl-3-furanthiol (MFT) and 3-mercapto-2-pentanone (MP) relative to their formation from ribose/cysteine. Reacting $^{13}$C$_5$-labelled ribose together with unlabelled norfuranone and cysteine under aqueous conditions (pH 5, 95°C for 4 hours), the authors showed that mainly $^{13}$C$_5$-labelled MFT was formed, suggesting that norfuranone is less important as intermediate of MFT. In contrast, MP was found unlabelled and hence originated from norfuranone. On the basis of these results, as well as additional mechanistic studies using the CAMOLA technique (heating of ribose and [13C$_5$]-ribose (1 + 1) with cysteine under above-mentioned conditions), a new reaction pathway for the formation of MFT and MP from ribose via 1,4-dideoxyosone was proposed (Fig. 3.4).
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Fig. 3.4 Proposed formation pathway for 3-mercapto-2-pentanone and 2-methyl-3-furanthiol from ribose and cysteine via the 1,4-dideoxyosone route (adapted from Cerny and Davidek, 2003).
3.2.2 Carbohydrate fragmentation

Carbohydrate fragments have been found to originate from deoxyosones, ARPs or HRPs, as well as from the sugar directly (Ledl and Schleicher, 1990; Weenen, 1998) (Fig. 3.1). The extent of the sugar cleavage reactions depends on the pH and on the reaction medium, with fragmentation favoured at higher pH values (pH ≥ 7) and in aqueous systems. Using isotopic labelling of the sugar molecule in conjunction with GC-MS analysis, C₅/C₁, C₄/C₂ and C₃/C₃ fission reactions were established (review by Tressl et al., 1995). The proposed cleavage routes involve retro-aldolisation, vinylogous retro-aldolisation, α- and β-dicarbonyl cleavage (reviewed by Weenen, 1998; Tressl and Rewicki, 1999). Retro-aldolisation is by far the most accepted fragmentation route.

Studying the generation of acetic acid (which is a major carbohydrate fragmentation product and also a good marker for the 2,3-enolisation pathway, as exclusively formed from 1-deoxy-2,3-diuloses) during Maillard reaction of glucose and glycine under aqueous conditions (90–120°C, pH 6–8), Davidek et al. (2006a) revealed that the organic acid is mainly formed through a hydrolytic β-dicarbonyl cleavage pathway (Fig. 3.5). The authors also evidenced that β-dicarbonyl cleavage, which can be seen as an acyloin cleavage or a reverse Claisen-type reaction, represents a general cleavage route for diacylcarbinol intermediates of the Maillard reaction under aqueous conditions and that the frequently reported hydrolytic α-dicarbonyl cleavage can be ruled out as a sugar fragmentation mechanism. Furthermore, a new sugar fragmentation pathway has been suggested to occur under oxidative conditions (Davidek et al., 2006b) by oxidative α-dicarbonyl cleavage with a Baeyer–Villiger-type rearrangement as key steps. The sugar degradation pathway will mainly depend on the reaction conditions (Fig. 3.6).

Carbohydrate cleavage products have been analysed by several authors (Nedvidek et al., 1992; Weenen and Apeldoorn, 1996; Hofmann, 1999). Since these intermediates are reactive dicarbonyl and hydroxycarbonyl compounds, trapping agents such as 1,2-diaminobenzene and ethoxamine hydrochloride were used to transform them into stable quinoxaline and O-ethyloxime derivatives, respectively. Weenen and Apeldoorn (1996) studied the formation of glyoxal, methylglyoxal, 2,3-butanedione and 2,3-pentanedione in both Maillard and caramelisation reactions. The results are shown in Table 3.1. The study revealed that sugar fragmentation is highest in the presence of a Strecker-inactive amine functionality (cyclohexylamine), followed by a Strecker-active amino acid (alanine). Without amine (caramelisation reaction), the extent of fragmentation was even lower and no detectable amounts of 2,3-butanedione and 2,3-pentanedione were observed. The yields of the pentanedione were relatively high in alanine model systems, indicating that the Strecker aldehyde, acetaldehyde, is involved in its formation. In addition, the ARP of glucose and alanine was found to be an efficient α-dicarbonyl precursor, whereas the 3-deoxyglucosone/alanine reaction mixture yielded only low concentrations of fission products (Table 3.1). The latter result is in good agreement with the finding that 3-deoxyglucosone is also a poor pyrazine precursor (Weenen and Tjan, 1994).

Hofmann (1999) studied the time course of the formation of carbohydrate degradation products in thermally treated solutions of either xylose or glucose with alanine. The author showed that during the first 10 minutes of the Maillard reaction, glyoxal is the most abundant fragmentation product from both xylose and glucose. Its formation can be explained by retroaldol cleavage of 2-xylosulose or 2-glucosulose. After 20 minutes of the Maillard reaction, the main fission products were found to be methyl glyoxal and hydroxy-2-propanone, with xylose yielding higher amounts than glucose. One year later, Yaylayan and Keyhani (2000)
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Fig. 3.5 Formation of acetic acid from glucose via 1-deoxy-2,3-hexodiulose as the key intermediate by the hydrolytic β-dicarbonyl cleavage mechanism, indicating the various possible degradation pathways (adapted from Davidek et al., 2006a).
performed a mechanistic study to determine the origin of Maillard intermediates such as glycolaldehyde, methylglyoxal, hydroxy-2-propanone and 3-hydroxy-2-butanone.

2,3-Butanedione (diacetyl) and 2,3-pentanedione are aroma-active carbohydrate cleavage products, contributing to a sweet-caramel odour of coffee (Grosch, 2001), and, for example, in the presence of hydrogen sulfide or cysteine, they are precursors of important sulfur aroma compounds such as 2-mercapto-3-butanol and 2/3-mercapto-3/2-pentanone (Hofmann, 1995). Yaylayan and Keyhani (1999) investigated the origin of these two dicarbonyl compounds in glucose/alanine Maillard model systems under pyrolytic conditions. Using labelled glucose or alanine, the authors showed that 90% of the formed pentanedione requires the participation of the C2/C3 atoms of alanine, whereas diacetyl was derived from the sugar chain only. This result is supported by the finding of Hofmann (1995) that
Table 3.1  Formation of α-dicarbonyl products (according to Weenen and Apeldoorn, 1996).

<table>
<thead>
<tr>
<th>Amine</th>
<th>Carbohydrate</th>
<th>Glyoxal</th>
<th>Methylglyoxal</th>
<th>2,3-Butanedione</th>
<th>2,3-Penta-nedione</th>
</tr>
</thead>
<tbody>
<tr>
<td>No</td>
<td>Glucose</td>
<td>26</td>
<td>11</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>No</td>
<td>Fructose</td>
<td>28</td>
<td>15</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>No</td>
<td>Xylose</td>
<td>62</td>
<td>17</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>No</td>
<td>3-Deoxyglucose</td>
<td>23</td>
<td>57</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>No</td>
<td>Fru-Ala&lt;sup&gt;a&lt;/sup&gt;</td>
<td>103</td>
<td>101</td>
<td>98</td>
<td>18</td>
</tr>
<tr>
<td>Alanine</td>
<td>Glucose</td>
<td>58</td>
<td>43</td>
<td>41</td>
<td>38</td>
</tr>
<tr>
<td>Alanine</td>
<td>Fructose</td>
<td>45</td>
<td>28</td>
<td>22</td>
<td>25</td>
</tr>
<tr>
<td>Alanine</td>
<td>Xylose</td>
<td>27</td>
<td>81</td>
<td>28</td>
<td>42</td>
</tr>
<tr>
<td>Alanine</td>
<td>3-Deoxyglucose</td>
<td>16</td>
<td>56</td>
<td>11</td>
<td>21</td>
</tr>
<tr>
<td>Alanine</td>
<td>Fru-Ala&lt;sup&gt;a&lt;/sup&gt;</td>
<td>81</td>
<td>67</td>
<td>81</td>
<td>22</td>
</tr>
<tr>
<td>Cyclohexylamine</td>
<td>Glucose</td>
<td>618</td>
<td>865</td>
<td>227</td>
<td>39</td>
</tr>
<tr>
<td>Cyclohexylamine</td>
<td>Fructose</td>
<td>691</td>
<td>1104</td>
<td>265</td>
<td>89</td>
</tr>
<tr>
<td>Cyclohexylamine</td>
<td>Xylose</td>
<td>591</td>
<td>925</td>
<td>614</td>
<td>101</td>
</tr>
<tr>
<td>Cyclohexylamine</td>
<td>3-Deoxyglucose</td>
<td>317</td>
<td>583</td>
<td>146</td>
<td>25</td>
</tr>
<tr>
<td>Cyclohexylamine</td>
<td>Fru-Ala&lt;sup&gt;a&lt;/sup&gt;</td>
<td>509</td>
<td>454</td>
<td>232</td>
<td>39</td>
</tr>
</tbody>
</table>

<sup>a</sup> N-1-(deoxy-d-fructosyl)-l-alanine (Amadori rearrangement product of glucose and alanine).

2,3-pentanedione is formed by reacting acetaldehyde and hydroxy-2-propanone. Schieberle <i>et al.</i> (2003) applied the CAMOLA technique to a Maillard model system of glucose ($^{13}$C<sub>6</sub> + $^{12}$C<sub>6</sub> = 1 + 1) and proline and showed that 2,3-butanedione was formed by 87 and 13% through the recombination of C3 + C1 and C2 + C2 fragments (Route B in Fig. 3.1), respectively. As a result, no diacetyl is generated from the intact carbon chain (Route A in Fig. 3.1).

### 3.2.3 Strecker degradation

In the presence of α- or vinylogous dicarbonyl compounds, α-amino acids can undergo a 'decarboxylating transamination', which results in the formation of aldehydes with one carbon atom less than the amino acid (Strecker aldehydes) (Schönberg and Moubacher, 1952). The Strecker degradation of amino acids is a key reaction in the generation of potent aroma compounds during Maillard-type processes (Ledl and Schleicher, 1990) (see also Fig. 3.1). Certain amino acids (leucine, valine, methionine or phenylalanine) are known to produce Strecker aldehydes with significant odour strength such as 3-methylbutanal, methylpropanal, methional or phenylacetalddehyde. These aldehydes have been confirmed as key contributors to many thermally processed foods (Hofmann <i>et al.</i>, 2000). Besides aldehyde formation, Strecker degradation also contributes to flavour formation during Maillard reaction by reducing dicarboxyls to hydroxycarbonyls (e.g. formation of 1,4-dideoxyosone from 1-deoxyosone) (Nedvidek <i>et al.</i>, 1992) or by generating α-aminocarbonyl compounds, which are pyrazine precursors (Weenen and Tjan, 1994).

Weenen and van der Ven (1999) studied the formation of phenylacetalddehyde in Maillard model systems, including reactions of phenylalanine with various sugars, α-dicarbonyl and hydroxycarbonyl compounds as well as ARPs. The authors found that methyl glyoxal was the most efficient dicarbonyl compound for the formation of phenylacetalddehyde, followed by 3-deoxyerythrose, glyoxal, 3-deoxyxyllose and 3-deoxyglucosone. Hydroxycarbonyl compounds such as dihydroxyacetone and glyceraldehyde also yielded high amounts of the...
Fig. 3.7 Formation of phenylacetaldehyde via an oxidative degradation of N-(1-deoxy-D-fructosyl)-L-phenylalanine (Fru-Phe) (adapted from Hofmann and Schieberle, 2000a).

Strecker aldehyde. Sugars were less reactive, with the reactivity decreasing in the order erythrose, xylose, fructose and glucose. In addition, the authors showed that the Amadori compound Fru-Phe is a superior phenylacetaldehyde precursor to the corresponding sugar/amino acid mixture. This finding was also confirmed by Hofmann and Schieberle (2000a).

In addition, Hofmann and Schieberle (2000a) revealed that the yields of phenylacetaldehyde formed from the Amadori compound Fru-Phe were significantly increased in the presence of oxygen and copper (II) ions. On the basis of the observation that 1,2-hexodiolose is also generated in high amounts under these conditions, they proposed a mechanism for the formation of phenylacetaldehyde from Fru-Phe (Fig. 3.7). Hofmann et al. (2000) additionally found that in the reaction of phenylalanine and glucose, considerable amounts of phenylacetic acid were generated. While the formation of phenylacetaldehyde showed an optimum pH of 5 and was not influenced by oxygen, the acid was most abundant at pH 9 in the presence of oxygen and copper (II) ions. The authors proposed a mechanism for the generation of phenylacetic acid that involves a similar oxidation step to that shown in Fig. 3.7.

Cremer and Eichner (2000) studied the influence of the pH on the formation of 3-methylbutanal during Maillard reaction of glucose and leucine. They showed that the formation rate of the aldehyde was higher at pH 7 than at pH 5 or 3. This was consistent with the high degradation rate of the Amadori compound Fru-Leu at pH 7, suggesting that the ARP was a good precursor for 3-methylbutanal. However, Chan and Reineccius (1994) showed that the optimal reaction conditions of different Strecker aldehydes vary, owing to differences in stability of the aldehydes.

3.2.4 Interactions with lipids

In addition to the Maillard reaction, lipid oxidation is another major reaction occurring in process flavour production and food systems. Both reaction cascades include a whole network of different reactions in which extraordinary complex mixtures of compounds are obtained, triggering important changes in food flavour, colour, texture and nutritional value, with desirable and undesirable consequences. In addition, both reactions are intimately interrelated as shown in Fig. 3.8 (Zamora and Hidalgo, 2005) and the products of each reaction influence the other. Furthermore, there are common intermediates and products in both pathways. The existing data suggest that both Maillard reaction and lipid peroxidation are so closely interrelated that they should be considered simultaneously to understand the
Fig. 3.8 Known interactions between Maillard reaction and lipid oxidation pathways in nonenzymatic browning development (adapted from Zamora and Hidalgo, 2005).

reaction mechanisms, kinetics, and products in the complex mixtures of carbohydrates, lipids and proteins occurring in food systems and process flavours. In these systems, lipids and carbohydrates are competing in the chemical modification of amino compounds (e.g. proteins and phospholipids). Therefore, although there are significant differences between Maillard reaction and lipid peroxidation, many aspects of both reactions can be better understood if they are included in only one general carbonyl pathway that can be initiated by both lipids and carbohydrates (Hidalgo and Zamora, 2005).

As an example, 2-pentylpyridine has been reported (Henderson and Nawar, 1981) as an interaction product of linoleic acid and valine, with 2,4-decadienal and ammonia being the key intermediates (Fig. 3.9). Its formation was studied by Kim et al. (1996) in model systems.

Fig. 3.9 Formation of 2-pentylpyridine from 2,4-decadienal and an amino acid (adapted from Henderson and Nawar, 1981).
by reacting 2,4-decadienal with amino acids (glycine, aspartic acid, asparagine, glutamic acid and glutamine) at 180°C for 1 hour (pH 7.5). The relative yields of alkylpyridine formation from the reactions were asparagine > glutamine > aspartic acid > glutamic acid > glycine. When amide-15N-labelled glutamine and asparagine were heated with 2,4-decadienal, the relative contribution of amide nitrogens to the formation of alkylpyridine was determined. Approximately half the nitrogen atoms in 2-pentylpyridine formed from asparagine, originated from the amide nitrogens of asparagine, whereas when glutamine was the reactant, almost all the nitrogen atoms came from the amide nitrogens in glutamine. The above-mentioned results may indicate that both free ammonia and α-amino groups bound in amino acids can contribute to the formation of alkylpyridines, but free ammonia does so more effectively.

The formation of Strecker aldehydes in the presence of lipid oxidation products is another example, illustrating the interactions between Maillard and lipid intermediates. Strecker degradation of amino acids is one of the most important reactions leading to final aroma compounds in the Maillard reaction. Hidalgo and Zamora (2004) have studied the reaction of 4,5-epoxy-2-alkenals with phenylalanine. In addition to N-substituted 2-(1-hydroxyalkyl)pyrroles and N-substituted pyrroles, which are major products of the reaction, the formation of both the Strecker aldehyde, phenylacetaldehyde, and 2-alkylpyridines was also observed. The aldehyde was only produced from the free amino acid (not esterified), suggested to be produced through imine formation, which is then decarboxylated and hydrolysed (Fig. 3.10). This reaction also produces a hydroxyl amino derivative, which is the origin of the 2-alkylpyridines. These data indicate that Strecker-type degradation of amino acids occurs at low temperature by some lipid oxidation products. This is a proof of the interrelations between lipid oxidation and Maillard reaction, which are able to produce common products by analogous mechanisms. However, recent results suggest that, analogously to carbohydrates, certain lipid oxidation products may also degrade certain amino acids to

![Fig. 3.10](image-url)  
Strecker-type degradation of phenylalanine produced by 4,5-epoxy-2-alkenals (adapted from Hidalgo and Zamora, 2004).
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undesirable compounds, e.g. vinylogous derivatives such as styrene (Hidalgo and Zamora, 2007).

Simulating food flavours by the process flavour approach requires precursors and recipes that are close to food or which well represent the composition of food. Therefore, lipids are key ingredients in the reaction flavour system to obtain boiled chicken notes. Similarly, polyphenols play an important role in generating cocoa flavour. The role of these specific components (lipids, polyphenols, vitamins) may be (i) generating new specific flavour compounds (Whitfield, 1992) as compared to the pure Maillard system (e.g. 2-pentylpyridine) or (ii) intervening in the Maillard reaction cascade and thus alerting the overall flavour composition. The latter is probably of higher relevance.

3.3 IMPORTANT AROMA COMPOUNDS DERIVED FROM MAILLARD REACTION IN FOOD AND PROCESS FLAVOURS

In the flavour industry, process flavours are often developed by empirical means, i.e. the reaction conditions are optimised using organoleptic evaluation. However, this approach should be accompanied by analytical evaluation of the products. Knowledge of the important aroma compounds derived from the Maillard reaction in food and process flavours is essential in order to focus investigations into reaction mechanisms enhancing the key aroma compounds. In addition, the knowledge of their formation pathways and key intermediates allows the development of multi-step approaches (e.g. two-step reactions), which aim at optimising reaction conditions of each of the flavour generation stages (e.g. from sugar/aminoo acid mixture to deoxyosones, from deoxyosones to target flavour compounds). One of these steps (often the first step) can also be a biotransformation that yields an intermediate that, on thermal treatment, releases the key aroma compound. An example for such an approach is the biogeneration of 2-(1-hydroxyethyl)-4,5-dihydrothiazole through yeast fermentation, which releases 2-acetylthiazoline on microwave heating (Bel Rhild et al., 2002).

It is recommended that the evaluation of character-impact aroma compounds should be based on a combination of instrumental and sensorial analysis. A well-established approach involves the determination of the odour activity values (ratio of concentration and odour threshold values) of aroma compounds (Grosch, 1994). This requires quantitative analysis of a selected number of aroma compounds, the importance of which has been screened by GC-olfactometry (GC-O). Suitable screening techniques such as aroma extract dilution analysis or headspace dilution analysis are available (Ullrich and Grosch, 1987; Guth and Grosch, 1993a, b). As these methods do not consider interactions of different aroma compounds, they should be combined with organoleptic evaluations of reconstituted model mixtures.

Our selection of important Maillard-derived aroma compounds (see Sections 3.3.1 and 3.3.2) is primarily based on results of GC-O techniques or other sensory evaluations or on quantitative data.

3.3.1 Character-impact compounds of thermally treated foods

Character-impact compounds of thermally treated foods that are formed during Maillard reaction are summarised in Table 3.2. Their identification in foodstuffs such as meat, bread,
<table>
<thead>
<tr>
<th>No.</th>
<th>Compound</th>
<th>Odour description</th>
<th>Odour threshold in water (µg/kg)$^b$</th>
<th>Detected in$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A: Compounds containing sulfur</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>2-Methyl-3-furanthiol</td>
<td>Meaty, sweet, sulfury</td>
<td>0.007 (1)</td>
<td>Meat (2–6), yeast (20, 40), coffee (7, 8)</td>
</tr>
<tr>
<td>2</td>
<td>2-Furfurylthiol</td>
<td>Roasty, sulfury</td>
<td>0.01 (1)</td>
<td>Meat (3–6, 9), yeast (40), coffee (7, 8), sesame (10), popcorn (11)</td>
</tr>
<tr>
<td>3</td>
<td>3-Mercapto-2-butanone</td>
<td>Sulfury, catty</td>
<td>3.0 (1)</td>
<td>Beef (12)</td>
</tr>
<tr>
<td>4</td>
<td>3-Mercapto-2-pentanone</td>
<td>Sulfury, catty</td>
<td>0.7 (1)</td>
<td>Beef (3, 4, 13), chicken (3, 14), yeast (40)</td>
</tr>
<tr>
<td>5</td>
<td>2,5-Dimethyl-3-furanthiol</td>
<td>Meaty, sweet, sulfury</td>
<td>0.018 (1)</td>
<td>Chicken (4)</td>
</tr>
<tr>
<td>6</td>
<td>2-Methyl-3-(methylthio)furan</td>
<td>Meaty, thiamine-like</td>
<td>0.05 (15)</td>
<td>Yeast (15)</td>
</tr>
<tr>
<td>7</td>
<td>2-Methyl-3-(methylthio)furan</td>
<td>Cooked meat-like</td>
<td>0.004 (16)</td>
<td>Cocoa (17), chocolate (17), meat (41)</td>
</tr>
<tr>
<td>8</td>
<td>2-Methyl-3-(methyldithio)furan</td>
<td>Cooked meat-like</td>
<td>—</td>
<td>Beef (12)</td>
</tr>
<tr>
<td>9</td>
<td>2-Furfurylmethyl disulfide</td>
<td>Roasty, brothy</td>
<td>—</td>
<td>Beef (12)</td>
</tr>
<tr>
<td>10</td>
<td>2-Methyl-3-furythioacetate</td>
<td>Meaty, onion-like, coffee-like</td>
<td>—</td>
<td>Yeast (20)</td>
</tr>
<tr>
<td>11</td>
<td>1-(2-Methyl-3-furyl)ethanethiol</td>
<td>Meaty, roast beef</td>
<td>—</td>
<td>Yeast (20)</td>
</tr>
<tr>
<td>12</td>
<td>4-Hydroxy-2,5-dimethyl-3(2H)-thiophenone</td>
<td>Caramel-like, fruity</td>
<td>0.05 (20)</td>
<td>Yeast (20)</td>
</tr>
<tr>
<td>13</td>
<td>Methional</td>
<td>Cooked potato-like</td>
<td>0.2 (18)</td>
<td>Beef (3, 9, 19), chicken (4, 5), pork (6), coffee (7), French fries (21), potato chip (18), fish (22, 23), bread (24), yeast (40)</td>
</tr>
<tr>
<td>14</td>
<td>2-Acetyl-2-thiazoline</td>
<td>Roasty, popcorn-like, burnt</td>
<td>1.0 (25)</td>
<td>Beef (3, 9), chicken (4, 5), sesame (10), fish (22)</td>
</tr>
<tr>
<td>B: Compounds containing oxygen</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>4-Hydroxy-2,5-dimethyl-3(2H)-furanone</td>
<td>Caramel-like, strawberry-like</td>
<td>10 (26)</td>
<td>Beef (3, 9, 19), chicken (6), coffee (7), beer (27), popcorn (27), bread (24), chocolate (17), sesame (28), French fries (21), tea (29), yeast (40)</td>
</tr>
<tr>
<td>16</td>
<td>3-Hydroxy-4,5-dimethyl-2(5H)-furanone (sotolon)</td>
<td>Seasoning-like</td>
<td>0.3 (5)</td>
<td>Beef (3, 9, 19), chicken (5), coffee (7), French fries (21), tea (29), chocolate (17), cocoa (17), yeast (40)</td>
</tr>
<tr>
<td>17</td>
<td>2-Ethyl-4-hydroxy-5-methyl-3(2H)-furanone</td>
<td>Caramel-like, sweet</td>
<td>1.15 (26)</td>
<td>Coffee (7)</td>
</tr>
<tr>
<td>18</td>
<td>3-Hydroxy-4-methyl-5-ethyl-2(5H)-furanone (abhexon)</td>
<td>Seasoning-like</td>
<td>7.5 (26)</td>
<td>Coffee (26), chocolate (17), cocoa (17)</td>
</tr>
<tr>
<td>No.</td>
<td>Compounds含氮化合物</td>
<td>Sensory description</td>
<td>Concentration (μg/kg)</td>
<td></td>
</tr>
<tr>
<td>-----</td>
<td>--------------------</td>
<td>---------------------</td>
<td>----------------------</td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>2/3-Methylbutanal</td>
<td>Malty, cocoa-like</td>
<td>0.35 (5)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Meat (3, 5), yeast (40), chocolate (17), cocoa (17), coffee (7), French fries (21), bread (24), tea (29), beer (30)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>Methylpropanal</td>
<td>Malty, fruity, pungent</td>
<td>0.7 (23)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Beef (19), chicken (5), bread (24), chocolate (17), coffee (7), French fries (20), tea (29)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>Phenylacetalddehyde</td>
<td>Honey-like, sweet, flowery</td>
<td>4 (18)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Beef (2, 19), cocoa (17), chocolate (17), bread (24), French fries (21), coffee (7), tea (29), yeast (40)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>Acetaldehyde</td>
<td>Solvent-like</td>
<td>25 (9)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Beef (9), chicken (5), coffee (8), French fries (21), fish (31)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>2,3-Butanedione</td>
<td>Buttery</td>
<td>15 (32)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Beef (3, 9), bread (24), coffee (7), fish (22, 23), Chocolate (17), cocoa (17), yeast (40)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>2,3-Pentanedione</td>
<td>Buttery, green</td>
<td>30 (32)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fish (22, 23), coffee (7), bread (24)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C: Compounds containing nitrogen</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>2-Acetyl-1-pyrroline</td>
<td>Roasty, popcorn, bread-like</td>
<td>0.1 (33)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bread (24), rice (34), popcorn (11), sesame (10), beef (2, 3), French fries (21), yeast (40)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>6-Acetyltetrahydropyridine</td>
<td>Roasty, cracker-like</td>
<td>1.6 (35)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bread (24), popcorn (11)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>27</td>
<td>2-Ethyl-3,5-dimethylpyrazine</td>
<td>Earthy, roasty</td>
<td>0.16 (7)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Beef (19, 25), chicken (14), coffee (7), sesame (10), bread (24), French fries (21), cocoa (17), chocolate (17), popcorn (36)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>2-Ethyl-3,6-dimethylpyrazine</td>
<td>Earthy, roasty</td>
<td>0.4 (18)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bread (24), French fries (21), cocoa (17), chocolate (17), popcorn (36)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>29</td>
<td>2,3-Diethyl-5-methylpyrazine</td>
<td>Earthy, roasty</td>
<td>0.09 (7)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Beef (19, 25), chicken (14), coffee (7), French fries (21), cocoa (17), chocolate (17), sesame (10), popcorn (36), bread (37), yeast (40)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>2-Ethenyl-3,5-dimethylpyrazine</td>
<td>Earthy, roasty</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Coffee (7)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>31</td>
<td>2-Ethenyl-3-ethyl-5-methylpyrazine</td>
<td>Earthy, roasty</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Coffee (7), French fries (21)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>2-Acetylpyrazine</td>
<td>Roasty, sweet, nutty</td>
<td>62 (38)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sesame (28), popcorn (39), bread (36)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*A: The sensory significance of the aroma compounds was assessed by quantitative data or by GC-O techniques.**

coffee, cocoa, chocolate, sesame, popcorn, French fries, tea, fish and yeast, as well as odour description and odour thresholds of the aroma substances, is covered. In the following discussion of Table 3.2, emphasis is given to important aroma compounds of meat, yeast, coffee and bread.

The meaty character of boiled beef, pork or chicken is mainly due to sulfur compounds such as MFT, 2-furfurylthiol, 3-mercapto-2-butanone, 2/3-mercapto-3/2-pentanone, DMFT, methanethiol, hydrogen sulfide and methional (Gasser and Grosch, 1988, 1990; Mottram and Madruga, 1994; Kerscher, 2000). The precursors of these aroma substances in meat are known to be free or bound C5-sugars such as ribose, ribose phosphate and inosine monophosphate as well as sulfur-containing compounds such as thiamine, cysteine, glutathione and methionine. After the publication of the patent of Morton et al. (1960), in which meat aroma formation established from the reaction of cysteine and ribose was described, a great number of patents and publication on meat-like process flavours followed (see Section 3.4.3).

It is well known that species-specific differences in the aroma of cooked meats such as beef and chicken are mainly due to concentration and composition differences in lipid-derived flavour substances. Kerscher and Grosch (1998) and Kerscher (2000) confirmed these findings and showed that significant differences also exist for Maillard-derived aroma compounds. Cooked beef, for example, was found to contain higher amounts of the sulfur compounds MFT and 2-furfurylthiol as well as the caramel-like 4-hydroxy-2,5-dimethyl-3(2H)-furanone, whereas MP and methional were more important in cooked chicken.

The character-impact compounds of yeast extracts were found to be very similar to those of cooked meat, which is due to similar pools of Maillard precursors. Münch and Schieberle (1998) reported high odour activity values for the sulfur compounds MFT, 2-furfurylthiol, MP and methional, the Strecker aldehydes 3-methylbutanal and phenylacetaldehyde, as well as the furanones 4-hydroxy-2,5-dimethyl-3(2H)-furanone (Furaneol) and 3-hydroxy-4,5-dimethyl-2(5H)-furanone (sotolon). Werkhoff et al. (1991) additionally identified 2-methyl-3-(methylthio)furan, 2-methyl-3-furylthioacetate, 1-(2-methyl-3-furylthio)ethanethiol and 4-hydroxy-2,5-dimethyl-3(2H)-thiophenone (thiofuraneol) in yeast. The authors claimed that these sulfur compounds contribute significantly to the meaty character of yeast. Besides yeast, onion extracts are also used in process flavourings. Widder et al. (2000) have identified 3-mercapto-2-methylpentan-1-ol as new powerful aroma compounds in both process flavourings (containing onion extract) and raw onions. This odourant that exhibits a pleasant meat broth, sweetish, onion and leek-like character (at a low concentration of 0.5 ppb in water), is suggested to be formed by aldol condensation of two molecules of propanal, followed by hydrogen sulfide addition at the double bond to yield 3-mercapto-2-methylpentanal. The aldehydes are finally reduced enzymatically to the corresponding alcohol.

The Maillard reaction is also a key reaction in flavour formation during roasting of coffee. The precursor pool in green coffee comprises a complex mixture of various soluble sugars such as glucose, fructose, galactose and sucrose. In addition, the amount of polymeric arabinose and rhamnose was found to decrease during roasting, which indicates that these sugars are also involved in caramelisation and Maillard processes (Tressl, 1989). The total amino acid content drops by about 30% during roasting. Especially, the amino acids – lysine, serine, threonine, arginine, histidine, methionine and cystine – are degraded to a high extent during the roasting process (Belitz et al., 2008). Semmelroch and Grosch (1995) reported the simulation of the aroma of Arabica and Robusta coffee brews using reconstituted mixtures of 23 aroma compounds. The authors showed that the Maillard products – 2-furfurylthiol, Furaneol, sotolon, methanethiol, 2,3-butanedione, 2,3-pentanedione, 2-ethyl-3,5-dimethylpyrazine (EDMP), 2,3-diethyl-5-methylpyrazine (DEMP), methylpropanal and
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3-methylbutanal – contribute to the flavour of coffee brews. They also investigated the aroma differences between Arabica and Robusta coffee. The more earthy/roasty and less caramel character of Robusta was found to be due to higher concentrations of the pyrazines EDPM and DEMP as well as to lower amounts of Furaneol and sotolon, respectively.

The flavour of cereal products, especially of bread, has been studied extensively, and the results have been reviewed (Grosch and Schieberle, 1997). 2-Acetyl-1-pyrroline (ACP) and 6-acetyltetrahydropyridine (ACTP) are responsible for the pleasant roasty character of wheat bread crust and popcorn. However, these compounds are not important in wheat bread crumb and rye bread. Both ACP and ACTP are generated by a reaction of proline with reducing sugars or sugar breakdown products (Schieberle, 1990). When ornithine instead of proline was reacted, only ACP was formed. The fact that yeast contains relatively high amounts of ornithine explains why ACP concentrations in bread are strongly dependent on the amount of yeast used in the baking process (Grosch and Schieberle, 1997). Other important Maillard-derived aroma compounds of wheat and rye bread are Furaneol and the Strecker aldehydes methional, 3-methylbutanal and methylpropanal. They contribute to the caramel-like and malty aroma of bread.

Another breakthrough has been the identification of new taste-active molecules and taste modifiers as result of Maillard-type reactions (Fig. 3.11), which contribute to the overall flavour perception (Hofmann, 2005). As an example, Alapyridaine has been identified in Maillard model systems containing hexose sugars and alanine as well as in beef broth as an essential compound enhancing the sweet taste and umami character in beef broth (Ottinger and Hofmann, 2003; Soldo et al., 2003). Glycoconjugates of glutamic acid, namely the N-glycoside dipotassium N-(d-glucos-1-yl)-L-glutamate and the corresponding Amadori compound N-(1-deoxy-d-fructos-1-yl)-L-glutamic acid (Fru-Glu), were found by systematic sensory studies to exhibit a pronounced umami-like taste, with recognition taste thresholds of 1–2 mmol/L, close to that of monosodium glutamate (MSG) (Beksan et al., 2003). Contrary to MSG, they do not show the sweetish and slightly soapy by-note, but evoke an intense umami, seasoning, and bouillon-like taste. Added to a bouillon base, which did not contain any taste enhancers, both glycoconjugates imparted a distinct umami character similar to the control sample containing the same amount of MSG on a molar basis (Schlichtherle-Cerny et al., 2002). The Amadori compound Fru-Glu has been reported in dried tomatoes as an example (Eichner et al., 1994). Furthermore, thermal treatment of aqueous solutions of xylose,
rhamnose and L-alanine led to a rapid development of a bitter taste of the reaction mixture (Frank et al., 2003). Liquid chromatography/mass spectrometry (LC/MS) and nuclear magnetic resonance (NMR) spectroscopy revealed 1-oxo-2,3-dihydro-1H-indolizinium-6-olates as the key compounds and most significant contributors to the intense bitter taste of this process flavour mixture. Thermally treated glucose/L-proline mixtures that contain 'cooling' compounds were recently reported. These Maillard systems generate 5-methyl-2-(1-pyrrolidinyl)-2-cyclopenten-1-one (5-MPC) and 5-methyl-4-(1-pyrrolidinyl)-3(2H)-furanone (MPF) as key compounds contributing to the cooling sensation without imparting aroma notes (Hofmann et al., 2001; Ottinger et al., 2001a). They have also been found in dark malt (10–100 µg/kg) (Ottinger et al., 2001b).

### 3.3.2 Character-impact compounds of process flavours

Meat-like process flavours are often prepared by reacting cysteine and/or thiamine with sugars, although pentoses such as xylose and ribose are preferably used. There is a range of additional precursor sources such as pectin hydrolysates (C-source), hydrolysed vegetable proteins and wheat protein hydrolysates (N-sources) as well as hydrogen sulfide, inorganic sulfides, onion, garlic and cabbage (S-sources). The products serve as building blocks in the creation of meat flavours (see also Section 3.4.3). They can also be described as middle notes that are combined with base notes (mainly taste compounds and taste enhancers) and top notes (mainly compounded flavourings) (savoury flavour pyramid according to Yeretzian et al., 2007). The important sulfur-containing compounds in process flavourings derived from either cysteine/ribose or thiamine reaction systems are quite similar (Table 3.3). The aroma of both cysteine- and thiamine-based process flavours is determined by MFT, 3-mercapto-2-butanone, 2/3-mercapto-3/2-pentanone, 2-methyl-3-thiophenethiol and 2-thienylthiol (Güntert et al., 1992, 1996; Hofmann and Schieberle, 1995, 1997). The same compounds are also responsible for the meaty character of process flavours that are based on 5′-inosine monophosphate (5′-IMP) and cysteine (Zhang and Ho, 1991; Madruga and Mottram, 1998). Although 5′-IMP is more abundant than ribose in raw meat, it is a much poorer precursor for these sulfur compounds than ribose, when reacted with cysteine (Mottram and Nobrega, 1998). Other character-impact compounds that are formed primarily in thiamine or thiamine/cysteine reaction systems are 2-methyl-4,5-dihydro-3-furantal, 1-(methylthio)ethanethiol, mercaptoacetaldehyde and 2-methyl-1,3-dithiolane (Güntert et al., 1996).

Many of the thiols mentioned above are also important aroma substances in glucose/cysteine or rhamnose/cysteine process flavourings (Hofmann and Schieberle, 1997). However, both reaction systems contain other characteristic aroma compounds. For example, 2-(1-mercaptoethyl)furane and its thiophene derivative are only formed from glucose and cysteine, whereas 4-hydroxy-2,5-dimethyl-3(2H)-furanone (Furaneol) and 3-hydroxy-6-methyl-2(2H)-pyranone belong to key odourants of the rhamnose system. The latter two substances are responsible for the strong caramel and seasoning-like character of rhamnose/cysteine process blocks, which render them very suitable for application in beef flavours. Another compound having seasoning-like character is 3-hydroxy-4,5-dimethyl-2(5H)-furanone (sotolon). Sotolon was found to contribute to the aroma of various cysteine-derived reaction flavours (Hofmann and Schieberle, 1995, 1997). In contrast to the other compounds mentioned above, the formation of sotolon is less influenced by the type of sugar.
Table 3.3  Character-impact compounds of process flavourings.

<table>
<thead>
<tr>
<th>No.</th>
<th>Compound</th>
<th>Odour description</th>
<th>Odour threshold (µg/kg) in water</th>
<th>Detected in</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A:</td>
<td>Compounds containing sulfur</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>2-Methyl-3-furanthiol</td>
<td>Meaty, sulfury, sweet</td>
<td>0.007 (1)</td>
<td>Cysteine/ribose [2, 3, 6], cysteine/glucose [4], cysteine/rhamnose [4], glutathione/ribose [3], thiamine [3, 5], thiamine/cysteine [5], cysteine/IMP [6, 7], cysteine/ribose-5-P [6]</td>
</tr>
<tr>
<td>2</td>
<td>2-Furfurylthiol</td>
<td>Sulfury, roasty, coffee-like</td>
<td>0.01 (1)</td>
<td>Cysteine/ribose [2, 3, 6], cysteine/glucose [4], cysteine/rhamnose [4], glutathione/ribose [3], thiamine [3, 5], cysteine/IMP [6, 7], cysteine/ribose-5-P [6]</td>
</tr>
<tr>
<td>3</td>
<td>Mercaptoacetaldehyde</td>
<td>Cabbage-like</td>
<td>—</td>
<td>Thiamine/cysteine [5]</td>
</tr>
<tr>
<td>4</td>
<td>Mercapta-2-propanone</td>
<td>Sulfury, putrid</td>
<td>—</td>
<td>Cysteine/IMP [7]</td>
</tr>
<tr>
<td>5</td>
<td>3-Mercapto-2-butanone</td>
<td>Sulfury, catty</td>
<td>3.0 (1)</td>
<td>Cysteine/ribose [2, 6], cysteine/glucose [4], cysteine/rhamnose [4], thiamine/cysteine [5], cysteine/IMP [6, 7], cysteine/ribose-5-P [6]</td>
</tr>
<tr>
<td>6</td>
<td>3/2-Mercapto-2/3-pentanone</td>
<td>Sulfury, catty</td>
<td>0.7 (1)</td>
<td>Cysteine/ribose [2, 3, 6], cysteine/glucose [4], cysteine/rhamnose [4], glutathione/ribose [3], thiamine [3, 5], thiamine/cysteine [5], cysteine/IMP [6], cysteine/ribose-5-P [6]</td>
</tr>
<tr>
<td>7</td>
<td>Methional</td>
<td>Cooked potato-like</td>
<td>0.2 (8)</td>
<td>Methionine/ribose [9], thiamine/methionine [5]</td>
</tr>
<tr>
<td>8</td>
<td>2-Methyl-3-thiophenethiol</td>
<td>Meaty, sulfury</td>
<td>0.02 (1)</td>
<td>Cysteine/ribose [2, 6], cysteine/IMP [6], cysteine/ribose-5-P [6], thiamine/methionine [5]</td>
</tr>
<tr>
<td>9</td>
<td>2-Methyl-4,5-dihydro-3-furanthiol</td>
<td>Meaty, sulfury</td>
<td>—</td>
<td>Thiamine [3, 5], thiamine/cysteine [5]</td>
</tr>
<tr>
<td>10</td>
<td>Bis(2-methyl-3-fury) disulfide</td>
<td>Meaty, sulfury</td>
<td>0.00002 (10)</td>
<td>Cysteine/ribose [2, 3, 6], glutathione/ribose [3], thiamine [5], cysteine/IMP [6], cysteine/ribose-5-P [6]</td>
</tr>
<tr>
<td>11</td>
<td>2-Thenylthiol</td>
<td>Sulfury, roasty</td>
<td>0.042 (1)</td>
<td>Cysteine/ribose [2, 6], cysteine/glucose [4], thiamine/cysteine [5], cysteine/IMP [6, 7], cysteine/ribose-5-P [6]</td>
</tr>
</tbody>
</table>

(Continued)
Table 3.3 (Continued)

<table>
<thead>
<tr>
<th>No.</th>
<th>Compound</th>
<th>Odour description</th>
<th>Odour threshold (µg/kg) in water&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Detected in&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>5-Methyl-2-furfurylthiol</td>
<td>Sulfury, roasty</td>
<td>0.048 (1)</td>
<td>Cysteine/rhamnose (4)</td>
</tr>
<tr>
<td>13</td>
<td>5-Methyl-2-thienylthiol</td>
<td>Sulfury, roasty</td>
<td>0.049 (1)</td>
<td>Cysteine/rhamnose (4)</td>
</tr>
<tr>
<td>14</td>
<td>2-(1-Mercaptoethyl)furane</td>
<td>Sulfury, burnt</td>
<td>0.022 (1)</td>
<td>Cysteine/glucose (4)</td>
</tr>
<tr>
<td>15</td>
<td>2-(1-Mercaptoethyl)thiophene</td>
<td>Sulfury, burnt</td>
<td>0.038 (1)</td>
<td>Cysteine/glucose (4)</td>
</tr>
<tr>
<td>16</td>
<td>2-Methyltetrahydrothiophen-3-one</td>
<td>Sulfury, burnt</td>
<td>—</td>
<td>Cysteine/ribose (2, 3), thiamine (5), thiamine/cysteine (5), cysteine/IMP (6, 7), cysteine/ribose-5-P (6)</td>
</tr>
<tr>
<td>17</td>
<td>1-(Methylthio)ethanethiol</td>
<td>Thiamine-like, meaty</td>
<td>—</td>
<td>Thiamine/cysteine (5), thiamine/methionine (5)</td>
</tr>
<tr>
<td>18</td>
<td>2-Methyl-1,3-dithiolane</td>
<td>Sulfury</td>
<td>—</td>
<td>Thiamine/cysteine (5)</td>
</tr>
<tr>
<td>19</td>
<td>Hydrogen sulfide</td>
<td>Sulfury, egg-like</td>
<td>10 (11)</td>
<td>Cysteine/ribose (2), cysteine/glucose (4), cysteine/rhamnose (4)</td>
</tr>
<tr>
<td>20</td>
<td>Methanethiol</td>
<td>Sulfury, putrid</td>
<td>0.2 (12)</td>
<td>Cysteine/ribose (2), cysteine/glucose (4), cysteine/rhamnose (4)</td>
</tr>
<tr>
<td>21</td>
<td>Ethanethiol</td>
<td>Sulfury, putrid</td>
<td>—</td>
<td>Cysteine/ribose (2), cysteine/glucose (4), cysteine/rhamnose (4)</td>
</tr>
<tr>
<td>22</td>
<td>2-Acetyl-2-thiazoline</td>
<td>Roasty, popcorn-like</td>
<td>1.0 (13)</td>
<td>Cysteine/ribose (2), cysteine/glucose (4), cysteine/rhamnose (4)</td>
</tr>
<tr>
<td>23</td>
<td>5-Acetyl-2,3-dihydro-1,4-thiazine</td>
<td>Roasty, popcorn-like</td>
<td>1.25 (1)</td>
<td>Cysteine/ribose (2), cysteine/glucose (4), cysteine/rhamnose (4)</td>
</tr>
<tr>
<td>24</td>
<td>4-Hydroxy-2,5-methyl-3(2H)-thiophenone</td>
<td>Caramel-like, sweet, meaty</td>
<td>24.0 (1)</td>
<td>Cysteine/glucose (4)</td>
</tr>
</tbody>
</table>
### B: Compounds containing oxygen

<table>
<thead>
<tr>
<th>No.</th>
<th>Compound Name</th>
<th>Description</th>
<th>Concentration</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>4-Hydroxy-2,5-dimethyl-3(2H)-furanone</td>
<td>Caramel, strawberry-like</td>
<td>10 (14)</td>
<td>Hofmann (1995); Gasser (1990); Guth and Grosch (1994); Cerny and Grosch (1993); Decnop et al. (1990); Pittet et al. (1970); Fickert (1999); Kerler and Grosch (1997); Grosh (2001); Buttery et al. (1983); Buttery and Ling (1995); Teranishi et al. (1975).</td>
</tr>
<tr>
<td>26</td>
<td>4-Hydroxy-5-methyl-3(2H)-furanone (norfuranone)</td>
<td>Caramel-like, burnt chicory</td>
<td>8.500 (1)</td>
<td>Gantar et al. (1996); Mottram and Nobrega (1998); Guth and Grosch (1994); Buttery and Ling (1995); Buttery et al. (1983); Buttery et al. (1984); Pippen and Mecchi (1969); Meynier and Mottram (1995); Zhang and Ho (1991); Guadagnini et al. (1972); Teranishi et al. (1975); Roberts and Acree (1994); Dencop et al. (1990); Pittet et al. (1970); Semmelroch et al. (1995); Decnop et al. (1990); Buttery et al. (1984); Buttery and Ling (1995); Teranishi et al. (1975).</td>
</tr>
<tr>
<td>27</td>
<td>2-Ethyl-4-hydroxy-5-methyl-3(2H)-furanone (homofuranone)</td>
<td>Caramel-like, sweet</td>
<td>1.15 (14)</td>
<td>Hofmann (1995); Gasser (1990); Guth and Grosch (1994); Cerny and Grosch (1993); Decnop et al. (1990); Pittet et al. (1970); Fickert (1999); Kerler and Grosch (1997); Grosh (2001); Buttery et al. (1983); Buttery and Ling (1995); Teranishi et al. (1975).</td>
</tr>
<tr>
<td>28</td>
<td>3-Hydroxy-2-methyl-4(4H)-pyranone (maltol)</td>
<td>Caramel-like</td>
<td>35.000 (17)</td>
<td>Gantar et al. (1996); Mottram and Nobrega (1998); Guth and Grosch (1994); Buttery and Ling (1995); Buttery et al. (1983); Buttery et al. (1984); Pippen and Mecchi (1969); Meynier and Mottram (1995); Zhang and Ho (1991); Guadagnini et al. (1972); Teranishi et al. (1975); Roberts and Acree (1994); Dencop et al. (1990); Pittet et al. (1970); Semmelroch et al. (1995); Decnop et al. (1990); Buttery et al. (1984); Buttery and Ling (1995); Teranishi et al. (1975).</td>
</tr>
<tr>
<td>29</td>
<td>3-Hydroxy-4,5-dimethyl-2(5H)-furanone (sotolon)</td>
<td>Seasoning-like</td>
<td>0.3 (19)</td>
<td>Gantar et al. (1996); Mottram and Nobrega (1998); Guth and Grosch (1994); Buttery and Ling (1995); Buttery et al. (1983); Buttery et al. (1984); Pippen and Mecchi (1969); Meynier and Mottram (1995); Zhang and Ho (1991); Guadagnini et al. (1972); Teranishi et al. (1975); Roberts and Acree (1994); Dencop et al. (1990); Pittet et al. (1970); Semmelroch et al. (1995); Decnop et al. (1990); Buttery et al. (1984); Buttery and Ling (1995); Teranishi et al. (1975).</td>
</tr>
<tr>
<td>30</td>
<td>3-Hydroxy-6-methyl-2(2H)-pyranone</td>
<td>Seasoning-like</td>
<td>15.0 (1)</td>
<td>Gantar et al. (1996); Mottram and Nobrega (1998); Guth and Grosch (1994); Buttery and Ling (1995); Buttery et al. (1983); Buttery et al. (1984); Pippen and Mecchi (1969); Meynier and Mottram (1995); Zhang and Ho (1991); Guadagnini et al. (1972); Teranishi et al. (1975); Roberts and Acree (1994); Dencop et al. (1990); Pittet et al. (1970); Semmelroch et al. (1995); Decnop et al. (1990); Buttery et al. (1984); Buttery and Ling (1995); Teranishi et al. (1975).</td>
</tr>
</tbody>
</table>

### C: Compounds containing nitrogen

<table>
<thead>
<tr>
<th>No.</th>
<th>Compound Name</th>
<th>Description</th>
<th>Concentration</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>31</td>
<td>2,3-Diethyl-5-methylpyrazine</td>
<td>Earthy, roasty</td>
<td>0.09 (20)</td>
<td>Grosh (2001); Buttery et al. (1983); Buttery and Ling (1995); Teranishi et al. (1975).</td>
</tr>
<tr>
<td>32</td>
<td>2-Acetyl-1-pyrroline</td>
<td>Roasty, popcorn-like</td>
<td>0.1 (21)</td>
<td>Grosh (2001); Buttery et al. (1983); Buttery and Ling (1995); Teranishi et al. (1975).</td>
</tr>
<tr>
<td>33</td>
<td>6-Acetyltetrahydropyridine</td>
<td>Roasty, burnt, caramel-like</td>
<td>1.6 (22)</td>
<td>Grosh (2001); Buttery et al. (1983); Buttery and Ling (1995); Teranishi et al. (1975).</td>
</tr>
<tr>
<td>34</td>
<td>2-Acetylpyridine</td>
<td>Roasty, caramel-like</td>
<td>19 (23)</td>
<td>Grosh (2001); Buttery et al. (1983); Buttery and Ling (1995); Teranishi et al. (1975).</td>
</tr>
</tbody>
</table>

The sensory significance of the aroma compounds was assessed by quantitative data or by GC-O techniques.

Food Flavour Technology

Furaneol, which is also a key ingredient of caramel-like process flavours, can be efficiently prepared by reacting rhamnose or other 6-deoxyhexoses with lysine, proline or hydroxyproline (Decnop et al., 1990). Another important caramel-like aroma compound, 3-hydroxy-2-methyl-4(4H)-pyranone (maltol), is a key substance of process flavours that are prepared from disaccharides (maltose or lactose) and proline or serine (Fickert, 1999).

In thermally treated solutions of proline and glucose or fructose, ACP and ACTP have been evaluated as important aroma compounds, contributing a roasty, popcorn-like odour to these process flavours (Roberts and Acree, 1994; Schieberle, 1995). ACP and ACTP have also been reported to be character-impact compounds of various thermally treated cereal products (see also Section 3.3.1). In addition, Roberts and Acree (1994) showed that Furaneol and 2-acetylpyridine contribute to the flavour of the proline/glucose model system.

3.4 PREPARATION OF PROCESS FLAVOURS

3.4.1 General aspects

In Europe, flavourings that are obtained by thermal treatment of a reducing sugar and a food-grade nitrogen source such as amino acids, peptides, food proteins, hydrolysed vegetable proteins (HVPs) and yeasts are referred to as thermal process flavourings (official terminology revised by EU in 2008; see Chapter 2 for more details). These products have been designated as a separate class of flavours and are identified as complex mixtures that have been converted to flavours by heat processing. In the US, the term ‘process flavours’ does not exist in regulatory terms. Maillard reaction flavours are considered natural or artificial flavours, depending on whether the starting materials and process are considered natural. The International Organisation of the Flavour Industry (IOFI) has established a guideline for manufacturers of process flavours. This guideline is part of the IOFI’s Code of Practice and defines the types of raw materials and general reaction conditions (for instance, a maximum temperature/time treatment of 180°C/15 minutes, pH ≤8) (reviewed by Manley, 1995). The US Department of Agriculture, however, did not set a guideline for manufacture but established labelling criteria for materials used to produce a process flavour (Lin, 1995). Although processed flavours that are prepared according to the IOFI guidelines were considered GRAS (generally recognised as safe) in the US in 1995, the regulatory status of Maillard reaction flavours still lacks clarity with respect to the GRAS specification. This is due to lack of information on whether processed flavours contain heterocyclic amines in amounts sufficient to affect their safe use in foods.

Maillard reaction technology is commonly used by the flavour industry to produce complex building blocks that provide similar aroma and taste properties to thermally treated foodstuffs such as meat, chocolate, coffee, caramel, popcorn or bread. Although flavour formation during the Maillard reaction is quantitatively a minor pathway, process flavours are very important to the flavour industry. This is because these complex blocks exhibit unique flavour qualities, are difficult to copy and are relatively cheap, being based on low production costs and high flavour potency of the aroma compounds formed.

3.4.2 Factors influencing flavour formation

The factors that influence flavour formation and, thus, the sensory properties of process flavours, are the type of sugar and amino acid, pH, reaction media, water activity as well as...
Basic chemistry and process conditions for reaction flavours

Table 3.4 Flavour types of processed sugar–amino acid model mixtures.

<table>
<thead>
<tr>
<th>Sugar</th>
<th>Amino acid</th>
<th>Temperature (°C)</th>
<th>Flavour description</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glucose</td>
<td>Cysteine</td>
<td>100–140</td>
<td>Meaty, beefy</td>
<td>1, 6</td>
</tr>
<tr>
<td>Ribose</td>
<td>Cysteine</td>
<td>100</td>
<td>Meaty, roast beef</td>
<td>1, 2, 6</td>
</tr>
<tr>
<td>Ascorbic acid</td>
<td>Threonine</td>
<td>140</td>
<td>Beef extract, meaty</td>
<td>1</td>
</tr>
<tr>
<td>Ascorbic acid</td>
<td>Cysteine</td>
<td>140</td>
<td>Chicken</td>
<td>1</td>
</tr>
<tr>
<td>Glucose</td>
<td>Serine or glutamine or tyrosine</td>
<td>100–220</td>
<td>Chocolate</td>
<td>1</td>
</tr>
<tr>
<td>Glucose</td>
<td>Leucine</td>
<td>100</td>
<td>Chocolate</td>
<td>3</td>
</tr>
<tr>
<td>Glucose</td>
<td>Threonine</td>
<td>100</td>
<td>Chocolate</td>
<td>3</td>
</tr>
<tr>
<td>Glucose</td>
<td>Phenylalanine</td>
<td>100–140</td>
<td>Floral, chocolate</td>
<td>1</td>
</tr>
<tr>
<td>Ribose or xylose</td>
<td>Threonine</td>
<td>140</td>
<td>Almond, marzipan</td>
<td>1</td>
</tr>
<tr>
<td>Glucose</td>
<td>Proline</td>
<td>100–140</td>
<td>Nutty</td>
<td>1</td>
</tr>
<tr>
<td>Glucose</td>
<td>Proline or hydroxyproline</td>
<td>180</td>
<td>Bread, baked</td>
<td>3, 6</td>
</tr>
<tr>
<td>Glucose</td>
<td>Alanine</td>
<td>100–220</td>
<td>Caramel</td>
<td>1, 6</td>
</tr>
<tr>
<td>Glucose</td>
<td>Lysine</td>
<td>110–120</td>
<td>Caramel</td>
<td>4</td>
</tr>
<tr>
<td>Xylose</td>
<td>Lysine</td>
<td>100</td>
<td>Caramel, buttery</td>
<td>5</td>
</tr>
<tr>
<td>Ribose</td>
<td>Lysine</td>
<td>140</td>
<td>Toast</td>
<td>1</td>
</tr>
<tr>
<td>Glucose</td>
<td>Valine</td>
<td>100</td>
<td>Rye bread</td>
<td>3</td>
</tr>
<tr>
<td>Glucose</td>
<td>Arginine</td>
<td>100</td>
<td>Popcorn</td>
<td>3</td>
</tr>
<tr>
<td>Glucose</td>
<td>Methionine</td>
<td>100–140</td>
<td>Cooked potatoes</td>
<td>1, 3</td>
</tr>
<tr>
<td>Glucose</td>
<td>Isoleucine</td>
<td>100</td>
<td>Celery</td>
<td>1</td>
</tr>
<tr>
<td>Glucose</td>
<td>Glutamine or asparagine</td>
<td>—b</td>
<td>Nutty</td>
<td>6</td>
</tr>
</tbody>
</table>

References:

1, Lane and Nursten (1983); 2, Morton et al. (1960); 3, Herz and Schallenberger (1960); 4, McKenna (1988); 5, Apriyantono and Ames (1990); 6, Yaylayan et al. (1994).

Microwave heating (640 W for 2–4 minutes).

In general, the sensory quality of a process flavour is less influenced by the type of sugar than by the amino acid. Several authors (Herz and Schallenberger, 1960; Lane and Nursten, 1983; Yaylayan et al., 1994) studied the variety of odours produced in Maillard model systems, comprising two or more components in reaction systems containing various sugars (or ascorbic acid) with each of the protein-derived amino acids. The flavour characters of some of these processed sugar–amino acid model mixtures are summarised in Table 3.4.

Glucose and cysteine are the preferred amino acids to produce meat-like flavours, both on heating with reducing sugars or alone (Lane and Nursten, 1983). These authors also obtained chicken and beef aromas by reacting, respectively, cysteine and threonine with ascorbic acid. Chocolate flavours can be prepared by heating glucose with amino acids such as serine, glutamine, tyrosine, leucine, threonine or phenylalanine (Herz and Schallenberger, 1960; Lane and Nursten, 1983). Phenylalanine also gives rise to a floral aroma (in reaction with glucose or alone), whereas threonine yields nutty aromas when reacted with ribose or xylose. Proline is the favoured amino acid for the production of bread-like and baked flavours (Lane and Nursten, 1983; Yaylayan et al., 1994). However, Schieberle (1992a) showed that the yeast-derived amino acids ornithine and citrulline are even more effective precursors for ACP, which is a key aroma compound of bread crust. Herz and Schallenberger (1960) reported the generation of rye bread and popcorn aromas by heating valine or arginine with glucose.
addition, alanine and lysine were found to give caramel flavours, and glutamine and arginine, nutty flavours.

Besides the type of sugar and amino acid, pH is another important factor determining aroma of process flavours. It is well known to the flavour industry that meat flavours are preferably prepared at low pH (4–5.5), whereas roast and caramel flavours are obtained under neutral or slightly basic conditions. Madruga and Mottram (1995) as well as Hofmann and Schieberle (1998a) showed that important sulfur-containing compounds in meat, such as MFT, 2-furfurylthiol and 2-methyl-3-(methylthio)furan, are preferably formed at a pH of 3–4. Sensorial evaluations of thermally treated model mixtures of ribose or 5′-IMP and cysteine revealed that the highest scores for boiled meat character were obtained when the reactions were carried out at pH 4.5 (ribose) and 3 (5′-IMP) (Madruga and Mottram, 1998).

Reaction media and water activity of the Maillard reaction systems are additional factors that influence aroma generation. Besides buffered aqueous solutions, solvents such as propylene glycol, glycerol, triacetin or fats and oils, as well as their emulsions or mixtures with water, are used. Vauthey et al. (1998), for example, filed a patent on the generation of roast chicken aroma using a cubic phase system. This system was prepared by introducing a melted monoglyceride (saturated in C\textsubscript{16} and C\textsubscript{18}) into an aqueous phosphate buffer solution. Compared to the same reaction in phosphate buffer, the flavour formed in the cubic system was more intense, corresponding to higher amounts of sulfur compounds such as MFT. Shu and Ho (1989) investigated the reaction of cysteine and 4-hydroxy-2,5-dimethyl-3(2H)-furanone in varying proportions of water and glycerol. They found that a superior roasted/meaty character was obtained in the aqueous system. The influence of the water activity on pyrazine formation during Maillard reaction was studied by Leathy and Reineccius (1989a). The authors observed that pyrazine formation was optimal at an A\textsubscript{w} of about 0.75.

Schieberle and Hofmann (1998) compared the character-impact compounds of cysteine-based process flavours formed in aqueous solution and under dry heating conditions. In a cysteine/ribose model system, dry heating yielded higher amounts of key odourants with roasty notes such as 2-furfurylthiol, 2-acetyl-2-thiazoline and 2-propionyl-2-thiazoline as well as 2-ethyl- and 2-ethenyl-3,5-dimethylpyrazine, whereas the meat-like sulfur compounds MFT and MP were found in comparable or lower concentrations, respectively. Their study also revealed that the amounts of the 3-deoxyosone-derived compounds 2-fural and 5-methylfuran-2-aldehyde were significantly higher in the dry-heated model systems, whereas the formation of the 1-deoxyosone-derived 4-hydroxy-2,5-dimethyl-3(2H)-furanone (Furaneol) was enhanced in aqueous solution. An explanation for this finding could be that, under dry heating conditions, caramelisation processes are favoured relative to Maillard reaction. In caramelisation processes, 1,2-enolisation of the sugar molecule is preferred over 2,3-enolisation, leading to the formation of high amounts of 3-deoxyosones (Kroh, 1994).

Apart from the precursor composition (e.g. availability of amino acids as reactants), pH and the reaction medium, other reaction parameters such as the presence of catalysts (e.g. phosphates) as well as temperature and time have a major effect on the sensory properties of process flavourings. Many of these parameters have extensively been studied for the generation of the caramel-like smelling Furaneol from 6-deoxyhexoses (Schieberle, 1992b; Havela-Toledo et al., 1997, 1999; Hofmann and Schieberle, 1997, 1998b; Schieberle and Hofmann, 2002). For example, the yield of Furaneol from rhamnose (pH 7, 150°C, 45 minutes) was increased about 40 times when the malonate buffer was replaced with phosphate buffer (Schieberle, 1992b). Even a higher increase of its yield (70-fold) was observed when the pH of rhamnose/cysteine system (145°C, 20 minutes) was increased from 3 to 7.
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(Schieberle and Hofmann, 2002). Recently, Illmann et al. (2009) used a fractional factorial design to identify critical reaction parameters affecting kinetics of Furaneol generation from rhamnose under cooking conditions (120°C). The importance of the reaction parameters was found to decrease in the following order: phosphate concentration > concentration of precursors > pH > rhamnose to lysine ratio. The experimental design approach achieved very high yields of Furaneol (about 40 mol%). The type of amino acid was also shown to affect the yield of Furaneol from rhamnose. Lysine was most efficient in generating the caramel-like odourant, followed by alanine, serine, glycine and threonine. On the other hand, much lower yields were obtained in the presence of proline and especially cysteine (Davidek et al., 2009).

The generation of 3-hydroxy-2-methyl-4(4H)-pyranone (maltol), another important caramel-like aroma compound, was shown to strongly depend on the reaction media. Rather low yields of maltol were obtained when lactose was heated with proline in aqueous systems (13.5 mmol/mol lactose) or when the precursors were dry heated (7.2 mmol/mol lactose). However, the yield of maltol increased significantly when water was replaced by propylene glycol (70 mmol/mol lactose; Černý, 2003).

In addition, the knowledge of the reaction kinetics of aroma compounds helps to explain the influence of temperature and time on their formation (Reineccius, 1990). Although flavour formation is a multi-step reaction sequence, Arrhenius kinetics have been found to describe flavour formation well in model and real food systems. Stahl and Parliment (1994) used an ingenious device to obtain clear time/temperature conditions for model systems and determined the activation energies of flavour compounds. Leathy and Reineccius (1989b) showed that the sensory quality of a product is less influenced by temperature/time in a model system that is designed to result in similar key aroma compounds (e.g. pyrazines). This can be explained by the fact that these compounds have similar activation energies. However, their study focused on dialkylpyrazines and did not consider the more potent trialkylpyrazines, which were suggested to have different formation pathways (Amrani-Hemaimi et al., 1995; Schieberle and Hofmann, 1998). As a result, flavour generation during Maillard reaction is in most cases strongly influenced by temperature and time, also because Maillard reaction flavours are complex mixtures of different classes of key aroma compounds. Lee (1995) proposed a different approach, on the basis of differential equations, to describe Maillard kinetics. The model produced was able to simulate the Maillard reaction not just as a function of time and temperature but also as a function of reactant concentrations and pH. From this simulation, the relative amounts of reactants could be plotted against time. Examples given include the concentrations of aldose and Amadori compounds over a 10-hour reaction and the time profiles of enolisation compounds from both the 1,2- and 2,3-pathways under defined pH conditions.

The use of stable intermediates as flavour precursors and/or the application of multi-step reactions are another way of optimising processing conditions on the basis of the required application. Blank et al. (2003a,b) compared the generation of odourants in Maillard reaction systems containing glucose and proline (Glc/Pro) or the corresponding Amadori compound fructosyl-proline (Fru-Pro). The major odourants found in both systems were similar and included ACP, 4-hydroxy-2,5-dimethyl-3(2H)furanone (Furaneol), acetic acid, 3-hydroxy-4,5-dimethyl-2(5H)furanone (sotolon), 2,3-butanedione and ACTP. However, their concentrations as well as their contributions to the final flavour differed. For example, the formation of Furaneol was favoured from Fru-Pro, namely at pH 6 and 7. On the other hand, the reaction system Glc/Pro gave rise to relative high yields of ACP and ACTP. Although both roasted-smelling popcorn odourants showed high sensory relevance in both reaction systems,
they dominated especially the aroma of the Glc/Pro process flavouring. These results also indicate that there is no benefit in using Amadori compound for the formation ACTP and ACP.

The following sections give a survey of the patent literature in the area of savoury and sweet process flavours. Emphasis is given to meat-like process flavours.

### 3.4.3 Savoury process flavours

The great majority of patents based on Maillard reaction technology have been directed to the production of meat-like process flavours. Most of these reaction flavours indicate cysteine and thiamine as the essential sulfur-containing precursor compounds. In 1960, the basic concept of Maillard flavour technology was beginning to emerge with the Unilever patent of Morton et al. (1960). The authors disclosed Maillard processes for the production of cooked beef and pork flavours by reacting ribose or mixtures of ribose and glucose with cysteine and other additional amino acids or deflavoured protein hydrolysates from cod fish flesh, casein, groundnut or soya. The group of additional amino acids was consisted of β-alanine, glutamic acid, glycine, α-alanine, threonine, histidine, lysine, leucine, serine and valine. All flavours were prepared in water at a pH between 3 and 6 and a temperature around 130°C. Using similar reaction conditions, May and Morton (1960) and May (1961) also prepared meat flavours through reacting cysteine with glycerolaldehyde or furfural in combination with deflavoured cod fish hydrolysates or amino acid mixtures.

Jaeggi (1973) patented processes for boiled and roasted beef flavours, which were also based on the reaction of ribose and cysteine. However, the inventor used methionine and proline as additional amino acids and carried out the reaction in glycerol or groundnut oil instead of water. Methionine as the sole sulfur source was also reported to result in beef flavourings when reacted with xylose and cysteine-free hydrolysed plant protein (Van Pottelsberghe de la Potterie, 1973). Tandy (1985) prepared process flavourings with white chicken meat character using leucine and cysteine in combination with the reducing sugars arabinose and glucose. In addition, he found that the use of rhamnose instead of glucose (as well as the addition of serine) provided a more aromatic, characteristic white meat chicken flavour.

International Flavors and Fragrances (IFF) filed a number of patents on the preparation of chicken, beef and pork flavours using cysteine in combination with thiamine, often in carbohydrate-free systems. This demonstrates that thiamine is capable of replacing carbohydrates by providing similar intermediates and aroma compounds as found in Maillard systems. Intense beef flavours, for example, were obtained by refluxing cysteine, thiamine and carbohydrate-free vegetable protein hydrolysate (HVP) in water or water–ethanol mixtures (IFF, 1965). The addition of beef tallow was found to result in a beef flavour with a ‘pan-dripping’ character. In addition, chicken flavourings were prepared by heating cysteine, thiamine and HVP in combination with other ingredients such as β-alanine, glycine and ascorbic acid, whereas pork flavours required the addition of methionine and lard. Similar processes for chicken, beef and pork flavours were disclosed in other IFF patents (IFF, 1967; Giacino, 1968a, 1969; Katz and Evers, 1973). Chicken aroma was found to be improved, for example, by adding diacetyl and hexanal (Giacino, 1968a) or mercaptoalkanones (Katz and Evers, 1973) to the processed flavours. Dihydroxyacetone, pyruvic acid or pyruvic aldehyde in combination with thiamine and HVPs were claimed to result in beef flavourings with improved cooked note (Giacino, 1968b).

Kerscher (2000) investigated the analytical assessment of the species-specific character of beef, chicken and pork. His results (see Section 3.3.1) cannot explain the choice of the
ingredients for the preparation of chicken, beef and pork flavours that are disclosed in the IFF patents mentioned above, but are in agreement with the findings of Chen and Tandy (1988). The authors developed species-specific beef and chicken flavourings through oxidation of oleic and linoleic acids, respectively. Their processes involved heat treatment of oleic or linoleic acid in the presence of air at high temperatures of about 300°C as well as trapping of the resulting aroma fraction in cold traps. The authors also claimed flavour blocks that resembled roast, grilled, bloody and braised beef in different fractions of the distillate of oxidised oleic acid.

In terms of alternative sulfur sources to cysteine and thiamine, Giacino (1970) found that process flavours with similar characters were obtained when cysteine was replaced by taurine. Patents of the Corn Products Company also describe the production of Maillard reaction flavours using taurine in combination with HVPs and xylose (Corn Products Company, 1969; Hack and Konigsdorfg, 1969). From a scientific point of view, however, the finding that cysteine can be replaced by taurine has to be questioned, because there are no studies that report the generation of important meat aroma compounds from taurine. In addition, Tai and Ho (1997) could detect only trace amounts of volatile sulfur compounds in a Maillard model system containing cysteinesulfinic acid and glucose. Broderick and Linteris (1960) used derivatives of mercaptoacetaldehyde such as 2,5-dihydroxy-1,4-dithiane, diethyl- or dithiaoacetals and hemimercaptals as precursors to impart meat-like flavour to canned simulated meat and vegetable products on sterilisation. The patent of Heyland (1977) involved the use of hydrolysed onion, garlic and cabbage in combination with HVP, ribose and beef fat for the preparation of beef flavours. Other flavour companies developed meat flavourings with sulfur sources such as hydrogen, sodium or ammonium sulfides (Godman and Osborne, 1972; Gunther, 1972), methionine (Van Pottelsbergh de la Potterie, 1972) or egg white (Theron et al., 1975).

Yeast extracts or yeast hydrolysates have traditionally been used either as precursors for the thermal generation of meat flavourings or as taste-enhancing ingredients, in blends with process flavours. The advantage of yeast extracts is that they are a relatively cheap, natural source of amino acids and thiamine. In addition, their high content of glutamate and 5′-ribonucleotides, particularly inosine 5′-monophosphate and guanosine 5′-monophosphate, provides complexity, body and flavour enhancement. Nestlé, for example, filed several patents in which the preparation of beef and chicken process flavours using yeast extracts was disclosed (Nestlé, 1966; Rolli et al., 1988; Cerny, 1995). Cerny (1995) also developed bouillon flavours using yeast cream, which is enriched in hydrogen sulfide. Such a yeast cream was obtained by incubating baker’s yeast with elemental sulfur.

In order to obtain complete meat flavouring products, process flavours are blended with several other ingredients, which provide aroma (e.g. compounded aroma blocks referred to as top notes or topnote flavours), taste, taste enhancement, mouth feel and body (referred to as base notes). Besides topnote flavours, yeast extracts, hydrolysed vegetable proteins and the monosodium salts of glutamate, inosinate and guanylate, ingredients such as onion, garlic, celery and/or caramel powder, animal or vegetable fats, gelatine and spices are often used in meat flavour compositions. The use of some yeast extracts, however, is limited owing to their undesirable ‘yeasty’ character. Therefore, research groups have developed processes for manufacturing yeast hydrolysates with improved meat-like taste, in which the yeasty notes are absent. De Rooij and Hakkaart (1992), for example, improved the meaty character of yeast hydrolysates prepared from several yeast species by combining the enzymatic degradation of yeast cells with an additional fermentation step, which was carried out using lactic acid-producing micro-organisms or additional yeasts. Hyöky et al.
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(1996) developed a method for the production of yeast extracts in which undesirable bitter and yeasty flavour notes were removed. The authors evaluated several non-ionic and slightly basic macroporous polymeric adsorbents as well as activated carbon for their ability to bind bitter and other undesirable flavouring substances of yeast hydrolysates, without binding yeast peptides, amino acids or nucleotides. The best results were obtained with Amberlite XAD-16 and Amberlite XAD-765, which are a non-ionic styrene/divinylbenzene copolymer and a weakly basic phenolformaldehyde polymer, respectively.

3.4.4 Sweet process flavours

A few patents and articles on the generation of chocolate and caramel flavours are discussed here. Rusoff (1958) prepared artificial chocolate flavours by heating partially hydrolysed proteins with sugars. The Maillard reactions were performed between protein hydrolysates derived from casein, soy, wheat gluten or gelatine and mixtures of pentoses and hexoses. The reaction medium contained 30% water and the reaction temperature ranged between 130 and 150°C. These ‘base chocolate flavours’ were rounded off by adding ingredients such as caffeine, theobromine and tannins before or after the heating process.

The need for hydrolysed proteins to generate chocolate flavours through Maillard reaction was stressed by Rödel et al. (1988). The authors based their investigations on precursor studies of Mohr et al. (1971, 1976), who found that only mixtures of peptide and free amino acid fractions isolated from fermented raw cocoa beans developed cocoa aroma on thermal treatment. The study of Rödel et al. (1988) covered a complete range of parameters such as source of protein, rate of hydrolysis, source of enzyme, amount of sugar, water content as well as temperature and time. The Maillard reaction flavours obtained were evaluated organoleptically and analytically. The authors revealed that gelatine that is enzymatically hydrolysed by more than 20% is an appropriate protein source for producing cocoa flavours through Maillard reaction. The quality of the cocoa aroma was further affected by water and sugar contents, whereas the source of enzyme had no influence. A water content of at least 5% and a sugar content of 20 g per 100 g hydrolysed protein gave a positive effect on flavour. In addition, temperature and time, which were the most sensitive parameters, were optimised at 144°C and 21 minutes.

Pittet and Seitz (1974) disclosed processes for the preparation of various flavours resembling chocolate, sweet corn, popcorn, bread, cracker and caramel toffee. The flavours were prepared by heating cyclic enolones such as Furaneol, maltol or cyclotene with amino acids in propylene glycol or glycerol. The temperatures ranged between 120 and 205°C. Chocolate flavours, for example, were obtained when valine or leucine was reacted with maltol or Furaneol, whereas proline (in combination with Furaneol or maltol) yielded cracker-like, popcorn, sweet corn and bread aromas. In addition, caramel toffee and burnt sugar flavours were established from proline and cyclotene or ethyl cyclotene. Gilmore (1988) also developed a caramel butterscotch flavour by heating a mixture of sugar syrup and butter in the presence of ammonia at a pH of 7 and a temperature of about 100°C.

3.5 OUTLOOK

Flavour formation is a minor but important pathway within the complex cascade of chemical reactions occurring during Maillard processes. A strong focus on the key flavour compounds (aroma and taste-active molecules), their precursors and reaction routes is required for the
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optimisation of process flavours. In addition, the formation of undesirable molecules needs to be taken into account when it comes to the optimisation of processing parameters. The better understanding of the influence of various process parameters on the formation of both the key aroma compounds and their precursors is still a challenge for future research.

Experimental design and kinetic parameter estimations are good tools for limiting the amount of experiment required. In addition, the evaluation of important taste compounds derived from the Maillard reaction, the elucidation of their formation pathways as well as the understanding of how the interaction of aroma and taste compounds affects the sensorial quality of the flavours are certainly research areas that are worth investigating.

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