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Caramelisation in food and beverages

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The decomposition of sugars leads to the formation of volatile (caramel aroma) and brown-coloured compounds (caramel colours). The reaction can be effected by heat and is catalysed by acids and bases. The colours and aromas depend on the sugar used (i.e. whether mono-, oligo- or polysaccharide) and are formed mostly through deoxyosuloses, *O*-heterocyclic and carbocyclic intermediates as well as low-molecular-weight sugar fragments. The typical caramel aromas are traced back to cyclopentanone (cyclotene) and hydroxymethylfuranone (furaneol) and their formation and analysis, discussed. The structures of coloured products of caramelisation are still not fully understood. The formation of brown products of caramelisation in dessert wine is discussed.

INTRODUCTION

One of the oldest methods of causing colour and flavour in food is the heating of sugar and sugar-rich foods. The reactions which occur are responsible for the caramel-like flavour and the development of a brown colour.

The rate of the reaction and the range of the low- and high-molecular-weight reaction products which are formed can be significantly increased by adding amino compounds such as amino acids and proteins. In such a situation the process taking place is the Maillard reaction.

Caramelisation requires temperatures $>120°C$ or $9<pH<3$. On the other hand, the Maillard reaction proceeds effectively at temperatures $>50°C$ and is favoured at pH 4–7, i.e. in the pH range of food. Caramelisation occurs in food, when food surfaces are heated strongly, e.g. the baking and roasting processes, the processing of foods with high sugar content such as jams and certain fruit juices (Ledl, 1987), or in wine production (Russev & Kroh, 1993). Caramelisation is encouraged in the production of sweets (e.g. Gotsch, 1979) but is undesirable during the crystallisation of sugar, e.g. in the production of sucrose (Chen & Yu, 1992). Caramel colours, i.e. ammonia caramel, ammonia sulphite caramel, and caustic caramel are the most widely used food additives and are found as colouring agents in a wide range of foods and beverages (Hardt & Baltes, 1987).

The apparently 'natural' process of generating colour and flavour by the heating of food is not without controversy; much work on the mutagenetic properties of caramelisation products has been published (Tomasik *et al.*, 1989).

The products of caramelisation also have secondary uses in food. One example is that antioxidant activity accompanies the caramelising reaction; such products are likely to be colourless, low-molecular-weight reductones (Rhee & Kim, 1975).

GENERATION OF REACTIVE SUGAR-DEGRADATION PRODUCTS IN THERMALLY INDUCED CARAMELISATION

The generation of flavours and colours in thermally induced caramelisation requires that sugars, normally monosaccharide structures, should first undergo intramolecular rearrangements. Depending on the time and temperature, yellow and brown shades are obtained when solid glucose or solutions of glucose are heated on their own. The flavour so produced changes from mild, caramel-like and sweet to burning bitter. The reaction causes the release of H^+. Thus the pH of the solution undergoing caramelisation falls with time, eventually into the slightly sour region of pH 4–5.

A comparable Maillard reaction between D-glucose and glycine demonstrates the very marked acceleration caused by the amino acid; at the same temperature, a much more intense colour as well as a greater range of flavour are produced within a few minutes.

Figure 1 shows a sequence of sugar degradation reactions which are characterised by the initial enolisation known as the de Bruijn van Eckenstein rearrangement, and is followed by dehydration or β-elimination, dicarboxylic cleaving, retro-aldol reaction and later, aldol condensation and, finally, a radical reaction (after Bruijn *et al.*, 1986). The enolisation reaction is of particular importance because it initiates the subsequent chain of events. These reactions give rise to aliphatic sugar degradation products which can react further to

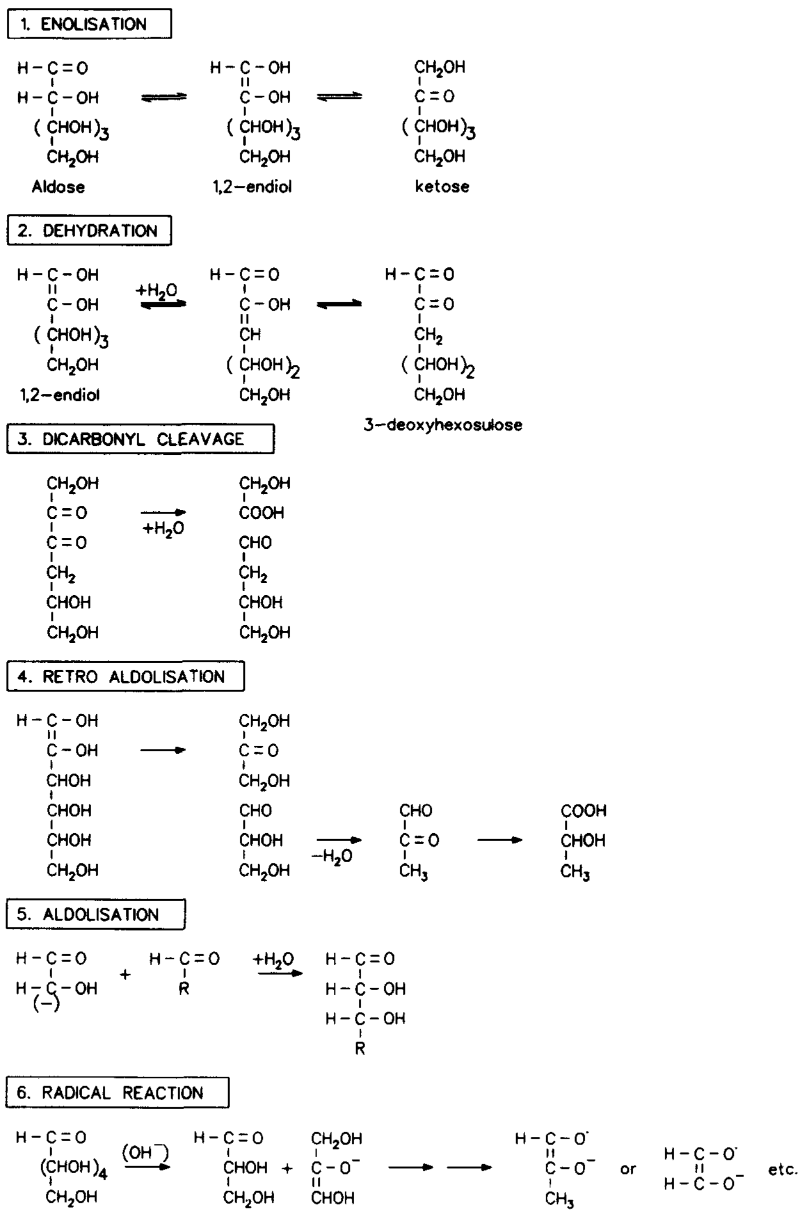

Fig. 1. Selected sugar degradation reactions.

produce oxygen heterocyclic and carbocyclic compounds via aldol condensation.

From these principal sugar-degradation reactions, we can see that key intermediates of the thermal caramelisation are the osuloses, which are α-dicarbonyl compounds such as 3-deoxyhexosulose. These not only lead to the formation of caramel colour but give rise to the important volatile products which are typical of caramel flavour.

Some typical components of caramel flavour are shown in Fig. 2. The relative proportions of these compounds can be influenced by the temperature and whether the conditions, are acidic or basic. While the thermally and/or acid-induced dehydration and cyclisation reactions dominate, there is an increased tendency for cleavage of the carbon chain of the sugar under basic conditions. Thus, depending on the reaction conditions, one finds derivatives of furan, such as hydroxymethylfurfural (HMF) and hydroxyacetylfuran (HAF), furanones such as hydroxydimethylfuranone (HDF), dihydroxydimethylfuranone (DDF) and the pyranones 'maltol' from disaccharides and 'hydroxymaltol' from monosaccharides. Derivatives of cyclopentenone are examples of carbocyclic products. All these components have different odour threshold values.

It is probable that a structure of the type $CH_3–CH=CH–CH(OH)–C=O$ (Hodge, 1965) is responsible for the characteristic caramel flavour, and this moiety is part of the structure of HDF. All of these compounds can also be detected in the amino-carbonyl (Maillard) reaction.

Figure 3 shows detail of the relationship of osuloses to the formation of three typical *O*-heterocyclic products: HMF, HDF and HAF from D-glucose. Thus, the reaction proceeds principally via 1,2- or 2,3-enolisation of the sugar and β-elimination of water leading to the formation of the 1-, 3- and 4-hexosuloses. In fact, the intramolecular cyclisation and further dehydration gives rise to an extensive range of *O*-heterocycles of the furan and pyran types with HMF, HDF and HAF pre-

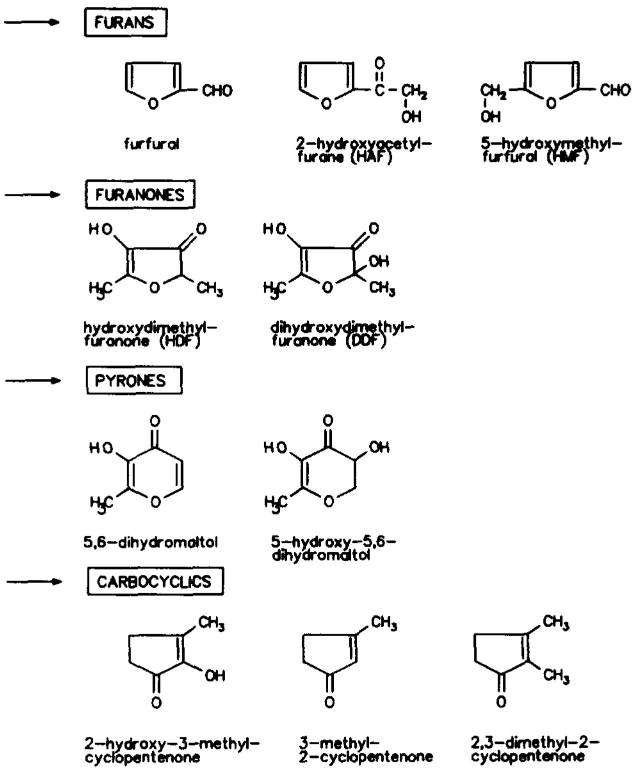

Fig. 2. Typical caramel aromatics.

dominating. The dehydration of the sugar via β-elimination is central in thermally induced sugar degradation under almost anhydrous conditions. One should be aware of the fact that approximately 40% by weight of water is formed as a primary reaction product of caramelisation during the thermal decomposition of D-glucose (Heyns *et al.*, 1966) at 300°C by Curie-Point-Pyrolysis.

The elucidation of this reaction mechanism for the formation of volatiles in caramelisation has been made possible by the use of GC and HPLC for their separation and especially by GC–MS or GC–IR as well as ^{1}H- and ^{13}C-NMR.

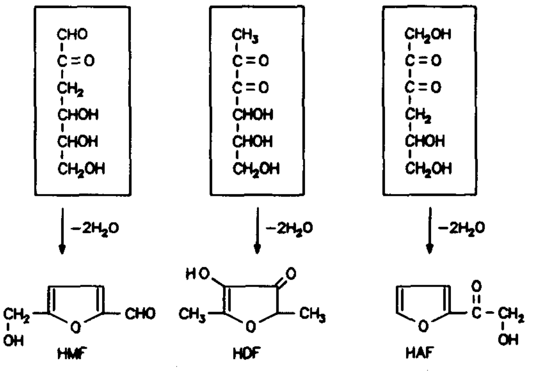

Fig. 3. 1,2- and 2,3-enolisation of D-glucose and formation of HMF, HDF and HAF via 3-, and 4-deoxyhexosulose.

LOW-MOLECULAR REACTION PRODUCTS OF CARAMELISATION

Significant concentrations of HMF can be measured after thermal and/or acid-catalysed caramelisation of D-glucose at 200°C (2 h). The corresponding reaction of D-fructose leads to markedly increased concentrations of HMF (Telegdy-Kovats & Örsi, 1973). The HMF concentration measured in solvent extracts of caramel colours (Pous *et al.*, 1991) is also significantly greater than that of the comparable volatile compounds, as the reaction proceeds. Thus, the caramelisation reaction could be followed kinetically by the measurement of HMF concentration and such measurement could be introduced into the control of food processing operations (Lee & Nagy, 1988). However, a problem with this approach is that HMF could be incorporated into the brown caramel colouring matter or it could be a precursor for the formation of various furans, and 1,2,4-benzenetriol (Luijkx *et al.*, 1993). Hence, the yield of HMF would depend on the rates of these subsequent reactions. Studies of the decomposition of glucose, ^{13}C-labelled in positions 1 and 6, under Curie-Point-Pyrolysis conditions at 300°C, allow the specific incorporation of the label into 2,5-furandialdehyde, HMF and furfural to be established by mass spectrometry (Schrödter, 1992). Possible reaction schemes are shown in Fig. 4.

The temperature of 300°C permits thermally induced caramelisation rather than pyrolysis and the reaction products are the result of HMF degradation. Furfural is a thermodynamically stable degradation product of HMF and can, under these condition, be traced back to the splitting off of the $^{13}C_6$-atom (80%) and the $^{13}C_1$-atom (20%) from HMF. In addition, formaldehyde is

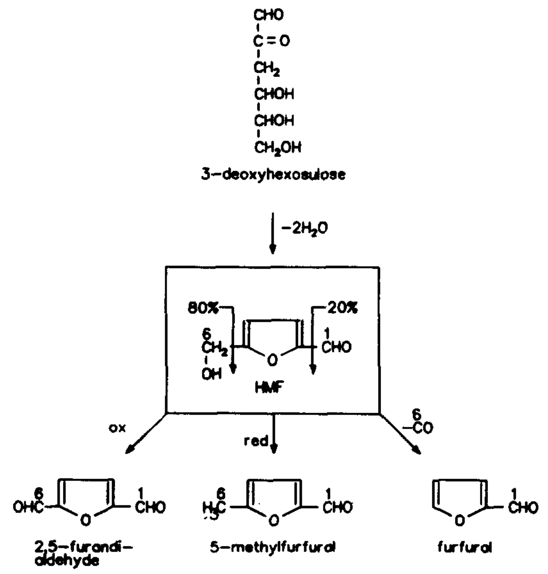

Fig. 4. Thermal decomposition of hydroxymethylfurfural, (Schrödter, 1992).

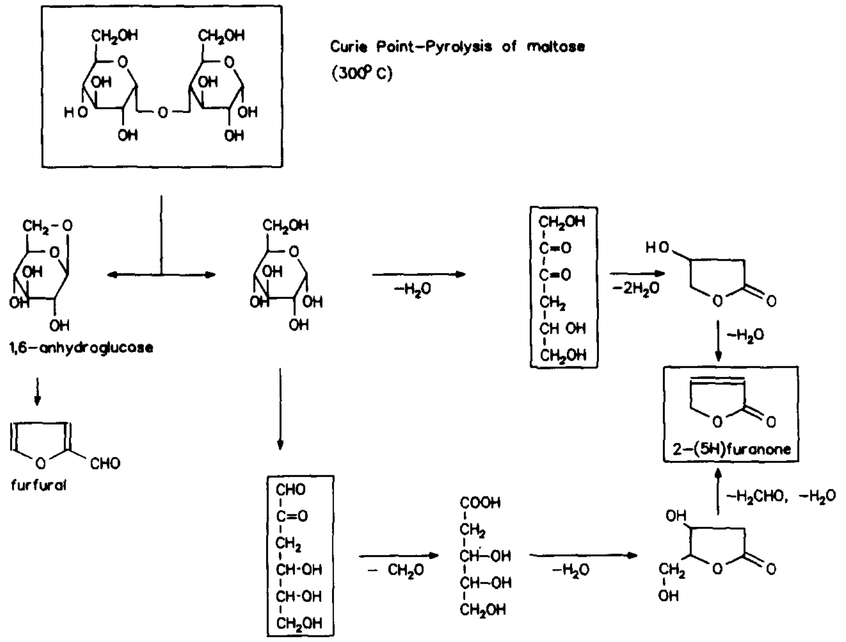

Fig. 5. Formation of 2(5H)-furanone from maltose.

produced mainly from the $^{13}C_6$- and formic acid from the $^{13}C_1$-atom (Schrödter, 1992).

The importance of furanones as volatile products of thermally induced caramelisation has, so far, been given less consideration. The 2[5H]-furanone, which was discovered in the Curie-Point-Pyrolysis of maltose at 300°C (Kroh *et al.*, 1992), has been investigated in the thermal degradation of maltulosyl and fructosyl-Amadori compounds of the Maillard reaction; the mechanism of its formation is given in Fig. 5.

2[5H]-furanone is the product formed in highest yield, amongst those given in the scheme. There are two reactions pathways for the formation of this compound, the reaction can proceed either via the 3-deoxyhexosulose or the 4-deoxyhexosulose. The question is still open as to the sensory relevance of the 2[5H]-furanone or if it plays any role in the formation of brown colouring matter.

One should not be led to believe that the sugar molecules are only degraded. During thermally induced caramelisation, transglycosidation and the formation of oligomers by polymerisation are important. The formation of anhydro sugars via intramolecular dehydration is known. While it is the higher oligomers from D-glucose that are found, dimers from D-fructose are very well known. The degree of polymerisation, measured by gel

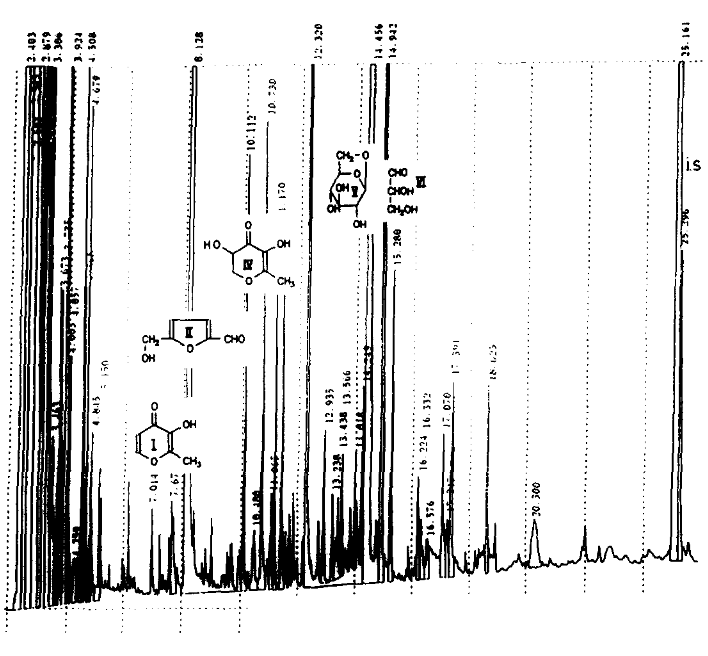

Fig. 6. Gas chromatogram (OV1, 25 m × 0·25 mm, 100°C–280°C, 8°/min) of silylated products from the caramelisation of maltose; I: maltol, II: hydroxymethylfurfural, IV: hydroxymaltol, V: 1,6-anhydroglucose, VI: glyceraldehyde.

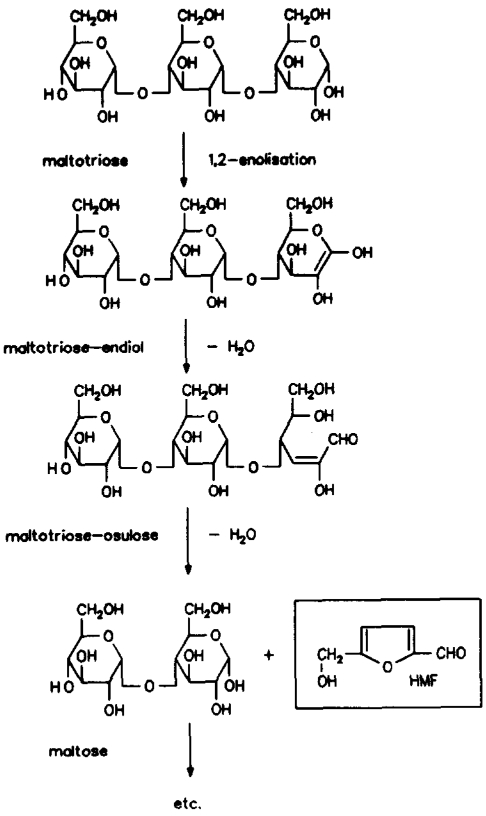

Fig. 7. Proposal for a reaction pathway, forming hydroxymethylfurfural from maltotriose.

permeation chromatography, is about 25 for sucrose caramelisation and is explained by the reaction of the fructose or glucose carbonium ions (Manley-Harris & Richards, 1993).

In addition to D-glucose and D-fructose, the disaccharides trehalose, maltose, isomaltose and gentiobiose may be found in a sucrose caramel, when analysed by gas chromatography of permethylated reaction products (Tschiersky & Baltes, 1989). Moreover the anhydro sugars 1,6-anhydroglucofuranose, 1,6-anhydroglucopyranose as well as difructosedianhydride also occur in sucrose caramel.

In the caramelisation of maltose under almost anhydrous conditions at 200°C, a relatively high concentration of 1,6-anhydroglucose may be detected by gas chromatography of the silylated mixture, as illustrated in Fig. 6. This also shows the expected high concentrations of HMF and glyceraldehyde. Peak 4, identified as 3,5-dihydroxy-2-methyl-4-pyranone ('hydroxymaltol'), is, however, a typical sugar-degradation product of monosaccharides (Ledl, 1987). The presence of this can only be explained by the splitting off of D-glucose from maltose by cleavage of the glycosidic bond between the D-glucose molecules and/or by intramolecular reaction to 1,6-anhydroglucose (lævoglucosan).

If 4 grams of D-glucose, maltose and maltotriose are caramelised at 200°C for 120 min, the amount of HMF formed is 10, 30 and 400 mg, respectively. An explanation for this effect is an intramolecular formation of osuloses at the reducing end of the oligosaccharides which, at position-4, prefer to cleave the glycosidic bond between the monosaccharide residues in the same way as glucose eliminates water, but more efficiently, to give HMF as illustrated in Fig. 7.

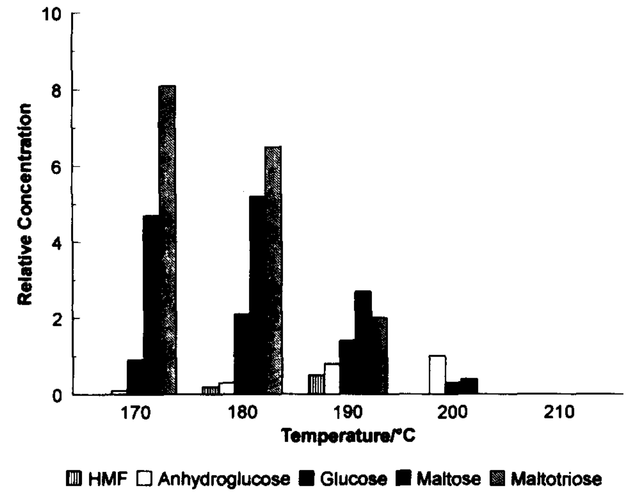

Fig. 8. Relative yields of maltrotroise pyrolysis products after 120 min at the temperatures shown.

The nonvolatile residue after the caramelisation of maltotriose contains D-glucose, 1,6-anhydroglucose, maltose, unreacted maltotriose. The relative concentrations of these compounds, and that of HMF, are shown for caramelisation reactions carried out at different temperatures in the range 170–210°C, in Fig. 8. The maltotriose concentration is seen to decrease in favour of the formation of the cleavage products, i.e. maltose and, to some extent, D-glucose. The amount of 1,6-anhydroglucose, however, steadily increases with temperature. The role that the oligosaccharides play in non-enzymic browning, and subsequent formation of volatile compounds and colouring agents has, to date, been given less attention, and must be investigated further (Kroh & Neye, 1992).

POLYMERIC PRODUCTS OF CARAMELISATION

The visible sign of a caramelisation reaction is the formation of a brown product which, to most people, is caramel. While the analysis and mechanism of the formation of the low-molecular-weight reaction products have generally been reliable, published work on the structure of the polymeric products and the stage at which they are formed is relatively unsatisfactory. This is similar to the situation which exists in relation to the Maillard reaction.

Although the number of reactive intermediates in caramelisation is limited in comparison to those expected in the Maillard reaction, one can, at this stage, only assume structures for the brown colouring agent. Examples are shown in Fig. 9.

HMF, furfural and HAF are considered to be precursors of such regular polymers (Tomasik *et al.*, 1989). There are, however, various arguments against such structures. A regular structure of this type would be

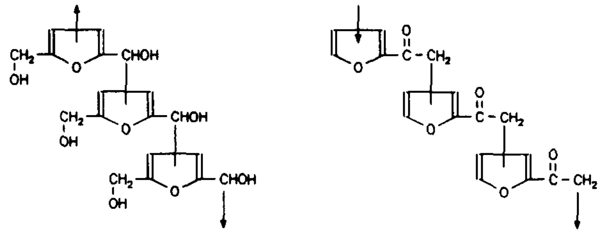

Fig. 9. Selected hypothetical polymer structure of sugar caramel.

relatively easy to confirm by means of high resolution ^{1}H- and ^{13}C-NMR. One might ask the question as to why should HMF, a relatively stable compound whose concentration increases with time, within certain limits of temperature, polymerise regularly when its precursors, such as deoxyhexosuloses, are much more reactive and better suited for forming such polymers. It is suggested that the osuloses are of much greater importance for the formation of these polymers.

Only studies of the structures and reactivities of the caramelisation products themselves can throw light onto the nature of the caramel colouring agents.

NON-ENZYMIC BROWNING IN DESSERT WINE

A model dessert wine system offers an opportunity to study caramelisation reactions in a relatively simple real food situation, and particularly to evaluate the relative importance of Maillard browning and caramelisation (Russev & Kroh, 1993). It is shown (Olano *et al.*, 1992) that browning of lactose via caramelisation (enolisation, dehydration, etc.) is favoured in comparison with browning via the Maillard reaction of lactose-Amadori compounds. But it is generally known and accepted that the Maillard reaction is kinetically favoured; therefore it is necessary to investigate and to compare the contributions of both these reactions to non-enzymic browning.

Aqueous solutions of D-glucose and D-fructose (concentration) were adjusted to pH 3·5 with different acids (mixture of tartaric acid, citric acid and malic acid) ethanol (16%) was added and some contained a typical mixture of three wine amino acids at concentrations of 0·1% (D,L-alanine, L-arginine, L-proline). The test solutions were stored for a few weeks at 75°C and were analysed at intervals, for absorbance (290 and 420 nm), sugar concentration and HMF. The results are illustrated in Figs. 10 and 11.

Reaction mixtures containing fructose gave highest absorbance at both wavelengths. Data at 280 nm correspond to absorbances due to both intermediates (e.g. conjugated carbonyl compounds) and the brown products, whereas 420 nm is the wavelength often used to determine 'browning'. It is clear that the absorbances in amino acid-containing mixtures are either equal to those containing no amino acid or are lower.

At pH 3·5 the amino groups of the amino acids are largely protonated and the amount of free amino compound available for participation in the Maillard reaction is small. The conversion of D-fructose to a reactive intermediate in browning does not require the involvement of an amino compound and this explains why the browning of D-fructose is so favoured at low pH (Swales & Wedzicha, 1992). These results are reflected in the formation of HMF shown in Fig. 12.

Only the reaction between D-glucose and the amino acids in the presence of 16% ethanol can attain approximately the same HMF concentration as the D-fructose-containing reactions. We have shown that, in these model systems, the HMF concentration was very similar to that found in Madeira wine.

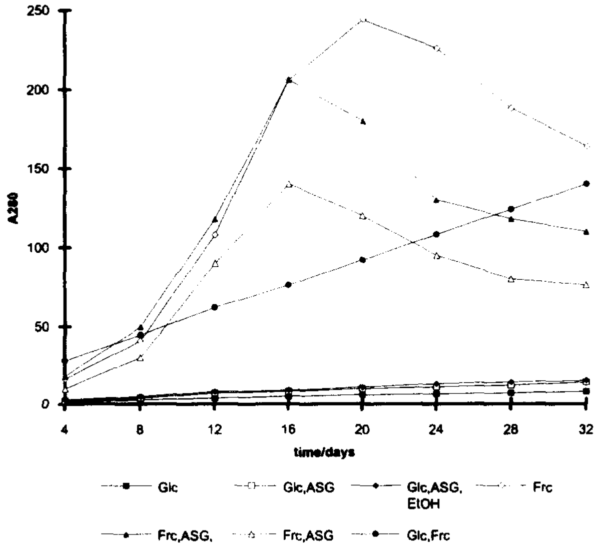

Fig. 10. Kinetics of browning in a model caramelisation system in dessert wine at 280 nm (where Glc:D-glucose, Frc: D-fructose, ASG: D,L-alanine/L-arginine/L-proline-mixture, EtOH: ethanol).

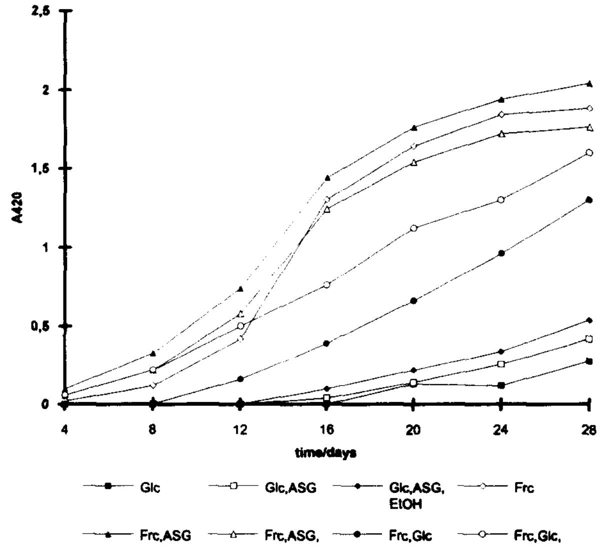

Fig. 11. Kinetics of browning in a model caramelisation system in dessert wine at 420 nm (where Glc:D-glucose, Frc: D-fructose, ASG: D,L-alanine/L-arginine/L-proline-mixture, EtOH: ethanol).

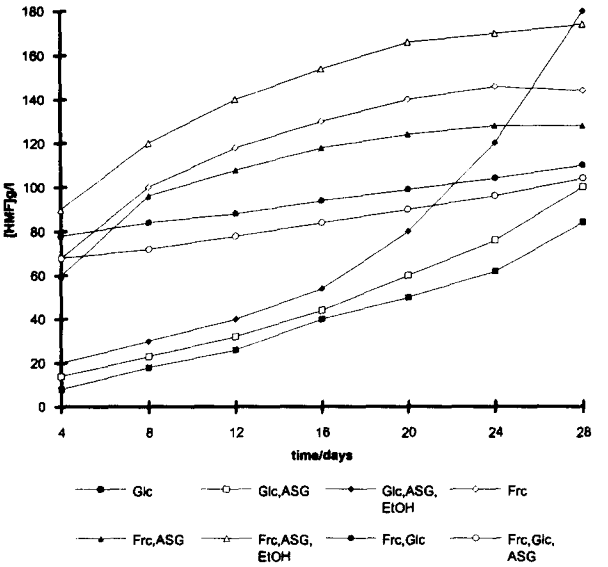

Fig. 12. Kinetics of formation of hydroxymethylfurfural in a model dessert wine (where Glc:D-glucose, Frc: D-fructose, ASG: D,L-alanine/L-arginine/L-proline-mixture, EtOH: ethanol).

The influence on non-enzymic browning of the structure and concentration of the reactive compounds and the external factors of reaction environment is an object for further research on this topic.

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