

Caramelization of maltose solution in presence of alanine

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Summary. Two solutions of maltose in water were used to prepare caramels. Alanine as a catalyst was added to one of these solutions. The caramelization was conducted at 130°C for total time period 90 minutes. Convenient samples were taken of each caramel solution every 30 min and subjected to sensory analysis and isolation of volatile components. The odour and colour sensory tests were evaluated according to the international standard methods (ISO). The results showed that, the presence of alanine gave rise to a high significant ($P < 0.01$) decrease in acid attributes and remarkable increase in the sweet and caramel attributes, which are the most important caramel notes. On the other hand the increase in heating time in presence of alanine as a catalyst resulted in a high significant ($P < 0.01$) increase in the browning rate of caramel solution. The new technique Solid Phase Micro Extraction (SPME) was used for trapping the volatile components in the headspace of each caramel samples followed by thermal desorption and GC and GC – MS analysis. The 5-hydroxymethyl-2-furfural (HMF), the main characteristic caramel product, showed its highest value in sample containing alanine after heating for 60 minutes. The best sensory results of the sample contains alanine were confirmed by the presence of high concentrations of the most potent odorants of caramel besides to the formation of some volatile compounds have caramel like flavours such as 2-acetyl pyrrole, 2-furanones and 1-(2-furanyl)1,2-propandione.

Keywords: Amino acids – Caramel – Maillard reaction – Maltose – Potent odorants – Sensory evaluation

Introduction

Caramels play important roles as colouring and flavouring agents in the manufacture of a divers range of foods (Chappel and Howell, 1992). Caramel colours have been in general use of more than 100 years, but only recently extensive effort has been made for characterize these colour additives to specify better the materials being marketed today (Myers and Howell, 1992; Coffey et al., 1997).

Caramels are formed by heating low molecular weight carbohydrates, such as dextrose or starch hydrolysate under a variety of reaction conditions to produce brown polymers. The exact reaction conditions and chemical reactants used are selected to give the caramel its desired characteristics. The influence of reaction conditions on the quality of caramels is continuously considered to be the problem of present interest. Composition of caramel from the qualitative point of view is independent of the sugar used but it is influenced by the method employed for its preparation (Palasinski et al., 1985). Several reports documented the effect on caramelization and its results of such parameters like temperature, mode of its application, time, pressure, atmosphere and catalyst added (Palasinski et al., 1985; Sikora et al., 1989; Ajandouz and Puigserver, 1999).

Aromatic caramel is generally obtained by heating sucrose in presence – or not – of acidic catalyst. Thermal treatment produces a large mixture of many species, which make up flavour, fragrance and colour (Adrian, 1987). 5-Hydroxymethyl furfural (HMF) is the principal degradation product in caramel (Theander, 1985). Pons et al. (1990) used an experimental device, which allows efficient analysis of volatile compounds in aromatic caramel without the solvent extraction step. Fifty-seven compounds were detected by this technique and also by solvent extraction and analysis of the vapour collected during caramelization process. Among these compounds 1-hydroxy-2-propanone, 2-furfuraldehyde, furfuryl alcohol and 2-furancarboxylic acid methyl ester were the predominants. More recently Pons et al. (1995) reported a correlation between the taste and aroma attributes of aromatic caramel and its volatile components.

Caramelization of various carbohydrates leads to a product with a high tinctorial strength provided by different additives catalyzing the process. As the caramel is a food additive, the catalysts for its manufacture under go regulations by food laws. Among legal catalysts ammonia and ammonium salts are listed. They provided the highest tinctorial strength of caramel (ammonia caramel), however these catalysts are responsible for the formation of 4(5)-methylimidazole, which has neurotoxic properties (Gaunt et al., 1977). The presence of this component in the caramel has evoked the tendency among relevant authorities toward absolute disqualification of all ammonia caramels (Sikora and Tomasik, 1989). On the other hand non – ammonia caramels do not satisfy demands of consumers needing a good food and pharmaceutical brown colourant. Therefore several attempts have been carried out to produce non – ammonia caramel that meet all consumer requirements by changing the reaction parameters. Sikora and Tomasik (1994) reported that using amino acids and their salts as catalysts in caramelization give high tinctorial strength and hence the organoleptic properties of the produced caramel.

It is well known that the generation of flavour and colour in thermally induced caramelization requires that sugar, normally monosaccharide structure should first undergo intramolecular rearrangement.

The developed colour and flavour depend on the conditions of reaction. A comparable Maillard reaction between D-glucose and glycine demonstrates

the very marked acceleration caused by the amino acid at same temperature (Kroh, 1994), a much more intense colour as well as a great range of flavour are produced within a few minutes. Although several studies demonstrated that using the amino acids as catalysts in the caramelization reaction improves the physical properties of the produced caramel (Sikora and Tomasik 1989, 1994). However as yet no reports could be found dealing with the effect of such parameter on the sensory attributes and volatile components of the obtained caramel. Therefore the present study was designed to evaluate the catalytic effect of the amino acid (alanine) on the sensory attributes of caramel obtained by heating maltose solution for different time intervals. The correlation between the sensory results and volatile components in the headspace of the caramel will be investigated.

Materials and methods

The caramelization was carried out with maltose DE 45.05 was kindly supplied by El-Nasr for Starch and Glucose Company, Cairo, Egypt with the following constituents: 26.5% water, 0.3% ash (on dry test), <5% glucose, approx. 50% maltose and approx. 20% maltotriose. L-alanine and the authentic compounds were purchased from Sigma – Aldrich (St. Louis, MN, USA) and Merck (Darmstadt, Germany).

Two samples of maltose solution (250 gm maltose with 5% w/w water) were prepared. Alanine (1% on the base of maltose weight) was added to one of these samples. Each sample was heated at 130°C in oil bath under efficient reflux system for a total time period 90 minutes. A convenient weight of each sample was taken every 30min. and subjected to sensory analysis, headspace extraction, gas chromatography (GC) and gas chromatography – mass spectrometry (GC – MS) analysis of the volatile components.

Sensory analysis

The sensory tests of odour and colour were investigated according to the international standards ISO 6658 (1985), ISO 8589 (1988), ISO 8586 (1989) and ISO 6564 (1985). The panel was carried out by 10 experienced assessors as follows: solutions of each caramel sample in distilled water were prepared to achieve concentration of 15% of dry matter in water (Pons et al., 1995), then the prepared solutions were subjected to panel test. The assessors were asked to identify the various smelling attributes of each caramel solution mentioned above. The attributes, which will be used to describe the olfactory sensations for caramel samples, were selected. This was done by individual evaluation followed by a common run. Then the individual panelist separately scored the intensity of the whole odour as well as those of each selected attribute on a scale consisting of 100 mm structured horizontal line anchored with descriptors at each ends (0.0 mm imperceptible – 100 mm very strong). The obtained results were represented in graphical profiles as shown in Fig. 1a,b and c. For the colour sensory test, the 10 assessors were asked to determine the intensity of each caramel sample by giving scores on a scale consisting of 100 mm structured horizontal line anchored with descriptors at each end (0.0 very light colour – 100 mm very dark colour).

Statistical analysis

For the results of the sensory tests, the statistical significance was determined by student's t-test. Each value was expressed as the mean of ten experiments \pm SD. Differences were considered significant at p-value <0.05.

Extraction of volatiles

The volatile components in the headspace of each caramel solution sample were isolated by using the Solid Phase Micro Extraction (SPME) technique, which is a powerful adsorption/desorption method newly accepted in isolation of volatile components (Pawliszyn, 1997).

A 65 μm CarbowaxTM – Divinylbenzene (CW/DVB) coating fiber for a Manual Holder (Orange Label) produced by Supelco (Bellefonte, USA) was used. The extraction was performed at 80°C for 1 hour. Then SPME fiber was inserted into the injector of GC and GC – MS instruments. Desorption of the volatiles were performed at 220°C for 2 minutes.

Analysis of volatiles

Gas chromatographic (GC) analysis: An apparatus GC 8000 series gas chromatograph (Fisons Instrument, Milan, Italy) was equipped with an autosampler HS 800 (Fisons Instrument, Milan, Italy). The capillary column (60m \times 0.32mm) coated with Supelcowax 10, film thickness 0.25 μm (Supelco, Bellefonte, USA) was used. The column temperature was programmed as follows: 50°C for 2min isothermally, then heating by 2°C/min to 220°C, and isothermally for 30min at 220°C. The carrier gas was helium, at the initial pressure of 100kPa; the inject: split ratio was 1:25; FID detector; injection and detector temperature was 220°C.

Gas chromatographic – mass spectrometry (GC – MS) analysis: A Fisons MSD 8000 mass spectrometer (Fisons Instrument, Milan, Italy) was used. The MS instrument was operated in electron impact mode (70eV). Temperature of the source and interface was 250°C. The capillary column and temperature program were the same as those in GC analysis. Identifications were based on comparison with the respective retention indices, MS computer library (NIST – MassLab software package, Fisons, Milan, Italy), and on the experimental linear retention indices calculated with reference to the retention times of a series of C7–C26 n-paraffin standard (Alltech Associates, USA) run under the same conditions.

Results

Figure 1 demonstrates the effect of adding alanine as a catalyst and heating time on the sensory profile of the caramel aroma. A trained panel using a scaling procedure quantified the whole flavour as well as the intensity of eight part qualities (sensory notes). Three-fold repetition and use of standard gave reproducibility of the tests. The figure shows the graphical profile of the obtained results. Figure 2 shows the effect of using alanine as a catalyst on the intensity of the developed brown colour; the influence of heating time is also given in the figure.

Figure 3 shows the whole GC – MS chromatograms of the volatile components present in the headspace of maltose solution heated for 30, 60 and 90 minutes, respectively. Figure 4a shows the GC – MS chromatogram of the volatile components isolated from the headspace of maltose – alanine solution heated for 30, 60 and 90 minutes. However, because the components separated at retention time from 10min to 37min are present in trace concentrations relative to the hydroxymethyl furfural (HMF), so this area was enlarged as shown in Fig. 4b. More than 300 volatile compounds were identified including hydrocarbons, aliphatic aldehydes, ketones, alcohols and acids, furans and

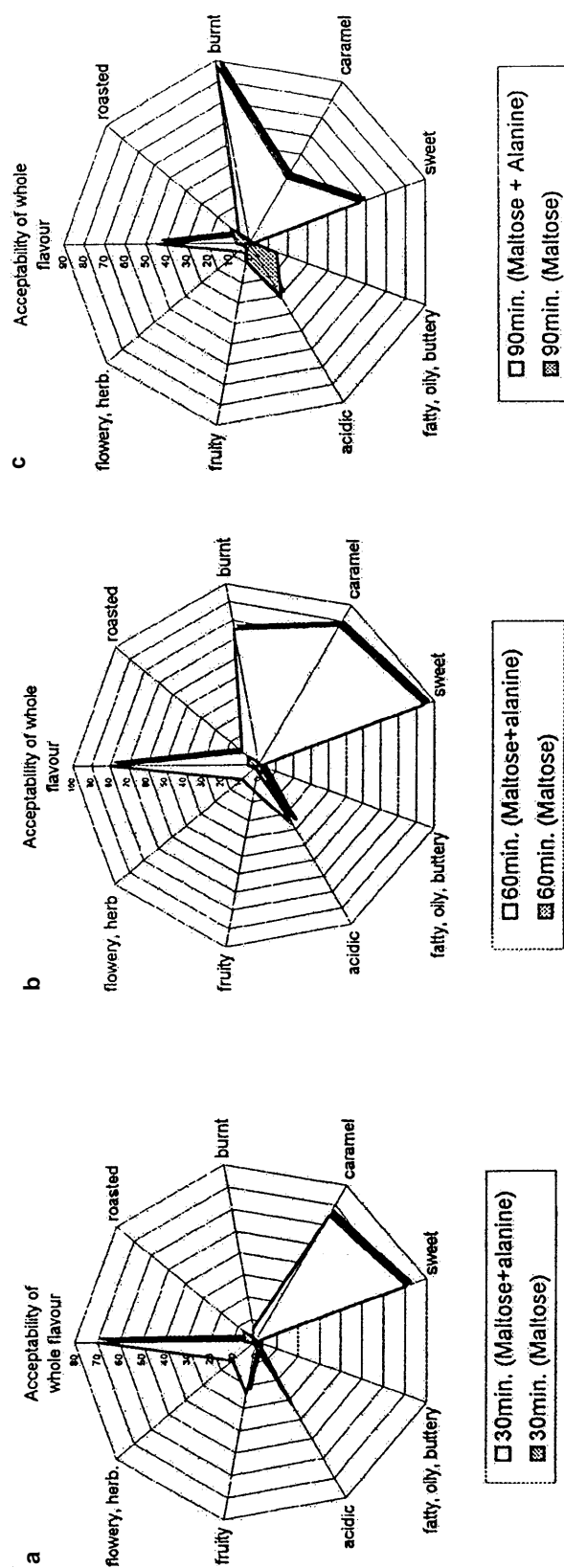


Fig. 1. Effect of adding alanine as a catalyst on the sensory profile of caramel produced by heating solutions of maltose in water (values are the mean of 10 determinations, SD not more than ± 1)

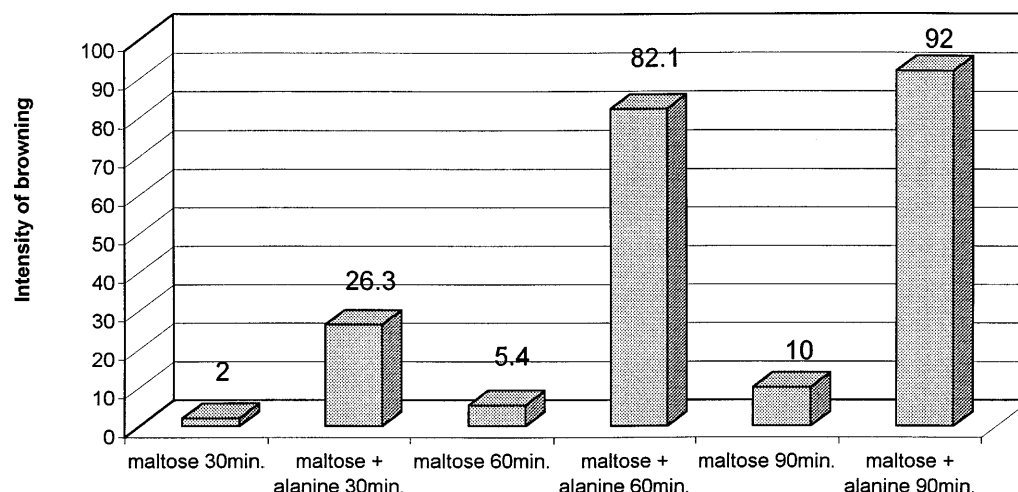


Fig. 2. Effect of using alanine as a catalyst in caramelization reaction of maltose in water heated at 30 min, 60 min and 90 min on the browning intensity (Values are the mean of ten determinations, SD not more than ± 1)

furanones, pyrroles and carbocyclics. The most potent components for caramel aroma along with their relative area percentages were only reported in Table 1.

Discussion

Sensory properties

A detail sensory profile analysis was carried out with the two caramel solutions under investigation (maltose in water and maltose in water with alanine as a catalyst) to study the effect of amino acid as well as duration of heating time on the developed aroma and colour.

It is obvious that using alanine as a catalyst in the caramelization reaction resulted in high quality product. Concerning the individual aroma attributes, it is clear that maltose solution has high acidic character whereas the presence of alanine gave rise to a highly significant ($P < 0.01$) decrease in the acidic attribute and remarkable increase in the caramel and sweet notes (Fig. 1a). These results are in accordance with Baczkowicz (1991) who reported that the involvement of alanine and polysaccharide in Maillard reaction resulted in caramel aroma. The effect of duration of reaction on the graphical profiles of the aroma notes is illustrated in Fig. 1a,b and c. The aroma sensory notes of the two samples under investigation are highly varied by increasing time of reaction. Heating the samples for 60 min. resulted in a high quality flavour caramel. This may be attributed to the high intensity of the sweet and caramel notes with relatively high burnt note. These attributes are the most favour for high quality flavour caramel (Pons et al., 1995).

Ammonia caramel, which is known as colour caramel (Hardt and Baltes, 1987), is the most widely used colouring agent in foods and beverages, how-

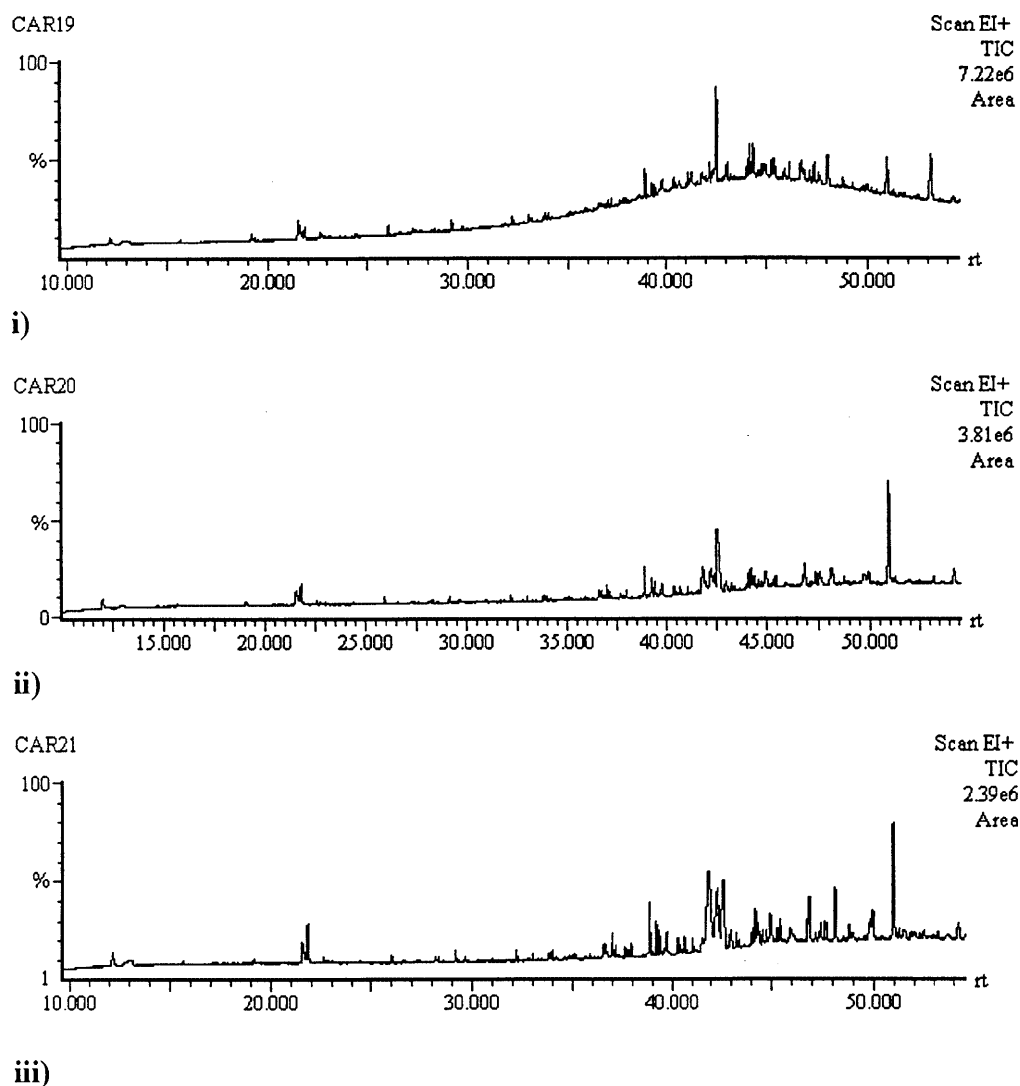


Fig. 3. GC-MS Chromatogram of caramelized maltose in water for i) 30 min, ii) 60 min and iii) 90 min

ever it does not satisfy all the consumer requirements. Thus many attempts have been carried out to use the amino acids as catalysts to prepare caramel with reasonable colour and flavour (Baczkowicz, 1991; Sikora and Tomasik, 1989, 1994). High significant ($P < 0.01$) increase in the browning rate of caramel solution was observed by adding alanine as a catalyst under similar conditions. It is obvious that the increase of heating time was accompanied by gradual increase in colour formation in the two present caramel samples however after heating for 90 min the colour intensity in caramel solution containing alanine was more than twelve times that in its absence. It was documented that the major products of amino acid – sugar degradation reaction are high molecular weight melanoidins, which are largely responsible for

Table 1. Effect of adding alanine as a catalyst on the volatile components developed by heating solution of maltose in water for 30, 60 and 90 min
(Values expressed as relative area percentages to the total identified compounds)

No.	Structure	30 min		60 min		90 min		Retention time	Retention index
		Maltose in water	Maltose/alanine in water	Maltose in water	Maltose/alanine in water	Maltose in water	Maltose/alanine in water		
1	Carbon dioxide				0.21146		1.110000	3,586	
2	Acetaldehyde		4.591384		7.664268		7.111644	3,953	
3	Formic acid, ethyl ester		7.742927		15.24791		11.35007	5,779	
4	1-Butanol, 3-methyl-				0.032447			13,042	
5	Furan, 2-pentyl-	0.06768		0.224895	0.026108	0.115427	0.008029	13,392	1,210
6	1,2-Cyclopentandiol				0.034728			15,610	
7	2-Butanone, 3-hydroxy-	0.551766	0.022169	0.729617	0.042405	9.625343	0.044146	15,935	
8	Acetic acid, methyl ester		0.009928		0.064331		0.073375	16,477	1,298
9	Acetic acid*	5.251102	0.044367	6.971748	1.390053	5.216987	0.947593	21,589	1,448
10	2-Furancarboxaldehyde*	2.022071	0.101049	6.170338	0.478496	6.149382	0.606525	21,972	1,461
11	2-Butanone*				0.022466			22,264	
12	Decanal	0.186641	0.044618	0.697256	0.307319	0.288087	0.10256	22,940	
13	Ethanone, 1-(2-furanyl)-*				0.161121		0.32434	23,348	1,494
14	Furfuryl ethanoate						0.004629	23,849	1,525
15	2,3-Butanediol, S-(R,R)-*		0.109253		0.108109		0.310295	24,307	
16	Propanoic acid			0.982522		0.432371	0.118393	25,291	
17	2-Furancarboxaldehyde, 5-methyl-				0.18642		0.066018	25,624	1,562
18	1-Propanone, 1-(2-furanyl)-		0.007174		0.14854		0.349969	25,666	1,564
19	Ethanone, 1-(2-methyl-1-cyclopenten-1-yl)-						0.010511	26,592	

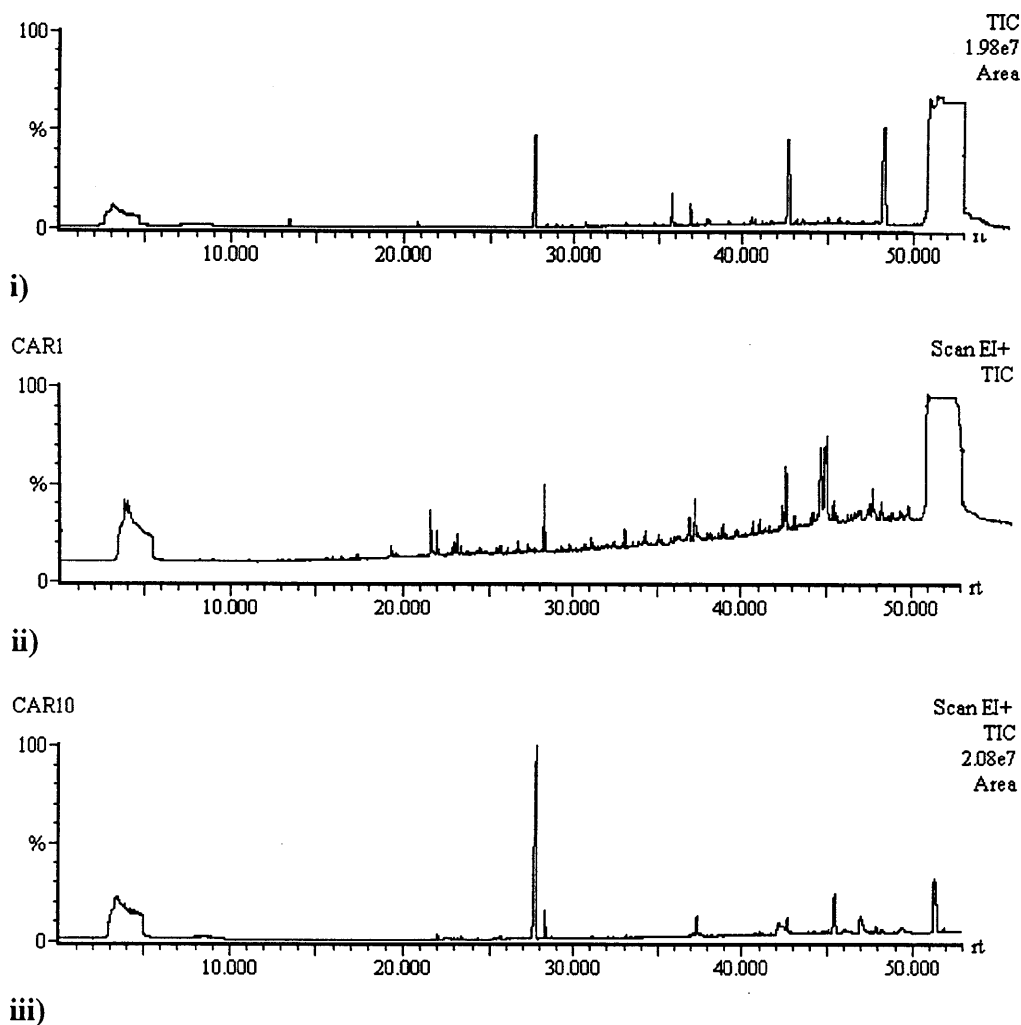
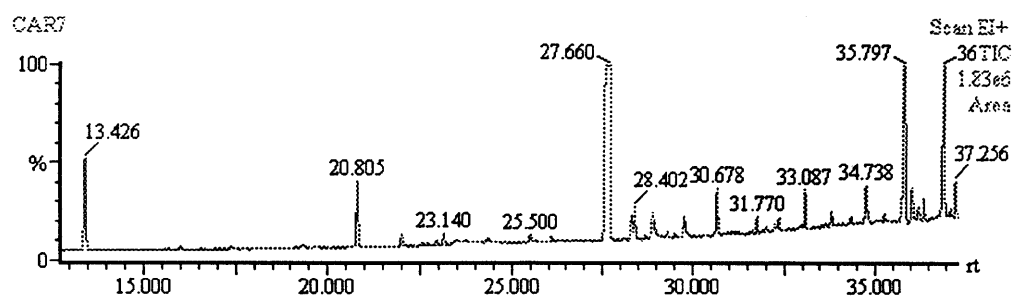


Fig. 4a,b. GC-MS Chromatogram of caramelized maltose and alanine in water for i) 30 min, ii) 60 min and iii) 90 min

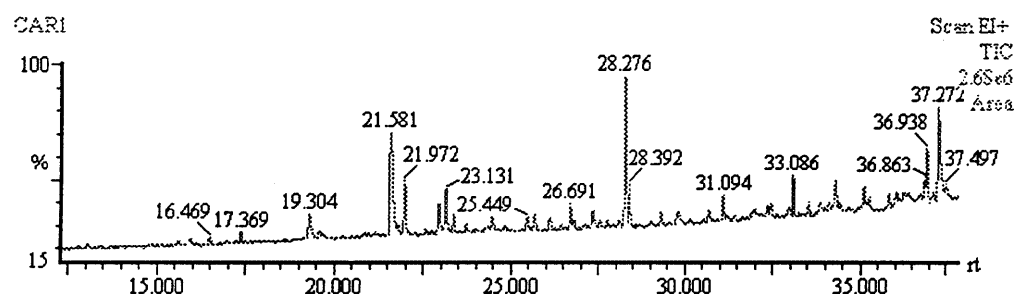
the characteristic brown colour that developed in such type of reactions (Hodge, 1953).

Effect of adding alanine as a catalyst and heating time on the volatiles of caramel solutions

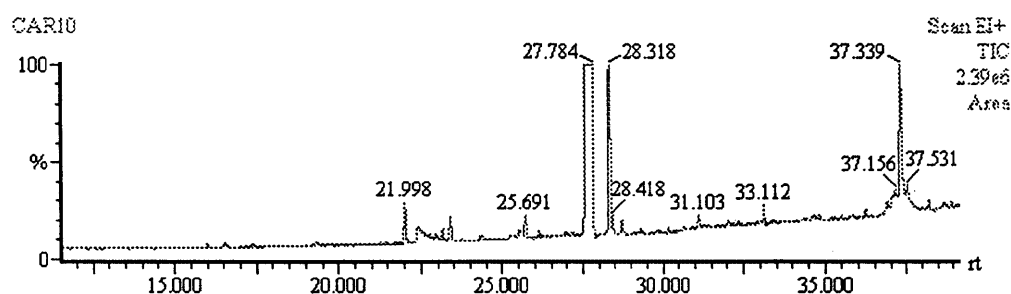
For modern food processing the only use of sensory methods is not sufficient, thus instrumental analysis must be carried out for flavour evaluation. The advanced GC – MS analysis is the only suitable method for volatile analysis. It is clear that the increase in duration of reaction as well as using alanine as a catalyst gave rise to remarkable increase in the number and concentrations of the most potent odorants for caramel aroma (Figs. 3, 4 and Table 1).



i)



ii)



iii)

b

Fig. 4b

As expected for maltose caramel, most of the identified volatiles were furan derivatives besides to some lipid degradation products, which may be present due to lack in the processing of maltose preparation (Commerford, 1974). 2-Furfural is the major compound in this caramel solution, its concentration increased steeply by increasing heating time. Pons et al. (1991) reported this compound among the major components in the volatiles of industrial caramel. 2-Furfural is documented as a typical caramelization product of sugar; it has a characteristic toasted penetrating odour and hence extensively used as flavour ingredient (Flament, 1989). Acetic acid, the second

major component in maltose caramel, reached its highest value after 60 min. then it showed noticeable decrease by continuous heating, which may be attributed to its reaction with other sugar aliphatic degradation products to produce oxygen heterocyclic compounds (Ledl and Schleicher, 1991; Kroh, 1994). These results confirm those of acidic attribute of maltose caramel cited in Fig. 1.

5-Hydroxymethyl-2-furfural (HMF), the main characteristic caramelization product (Kroh, 1994), showed its highest value after heating for 60 min. followed by highly remarkable decrease at the end of heating period. Previous studies related the decrease of HMF to the possibility of its incorporation into the brown caramel colouring matter or it could be the precursor for the formation of various furan derivatives (Luijckx et al., 1993). Further more it was reported that although HMF is relatively stable compound and its concentration increases with time within certain limits of temperature, it polymerizes regularly giving rise to more intense in caramel colour (Tomasik et al., 1989; Kroh, 1994). These results are in agreement with those of colour sensory test of maltose caramel (Fig. 2).

Table 1 shows that addition of alanine as a catalyst to caramel solution gave rise to an increase in the number of the separated volatile compounds as well as in concentrations of some typical components of caramel flavour such as furanones, HMF and maltol. This confirm the reported facts that, the rate of caramelization reaction and the range of low and high molecular weight reaction products which are formed can significantly increased by adding nitrogen – containing compounds such as amino acids and proteins. In such a situation the process taking place is the Maillard reaction (Kroh, 1994). However in the present study because of the excess of sugar (maltose) in the reaction mixtures, the oxygen containing heterocyclic compounds were predominately formed.

Acetaldehyde the main Strecker degradation product of alanine (Shu, 1998) was detected in considerable high concentration in the volatiles of maltose – alanine caramel heated for 60 min, however continuous heating for 90 min resulted in a decrease in its concentration. This active Strecker aldehyde may undergo further reactions during heating of caramel solution. On the other hand the total yield of carbon dioxide (CO_2) was significantly increased after 90 min. It is well documented that CO_2 is formed via Strecker degradation of amino acids (Olsson et al., 1981). Decarboxylation of amino acids on heating with sugars has been known for many years (Eichner and Ciner-Doruk, 1981). The significant of Strecker degradation lies in the fact that the amino acids furnish ammonia and reactive aldehydes that can undergo further condensation reactions to produce furans which in presence of ammonia favourably convert into pyrrole.

In the present study four pyrrole derivatives were identified in the volatiles of maltose – alanine caramel. Baltes and Bochmann (1987a), have described the fragmentation pattern of these pyrroles. 2-Acetyl pyrrole and methyl pyrrolealdehyde were identified in many aroma complexes (Flament, 1989). The first named compound was described to have slightly caramel like and burnt like aroma (Watanabe and Sato, 1972).

Maltol and cyclotene were identified only in the volatiles of caramel solutions containing alanine. Their concentration showed the highest values after heating 90 min. These two compounds are of great interest for the aroma intensity because they carry pleasant caramel tastes and have enhancing properties (Ziegleder, 1991). Maltol is the main degradation product of maltose (Ledl and Schleicher, 1990).

Two furan ketones and one diketone were only detected in the volatiles of caramel solution containing alanine; they have caramel like and nutty burnt notes (Flament, 1989). The fragmentation patterns of these compounds have been discussed (Baltes and Bochmann, 1987b).

Four furanones are recorded among the volatile components present in caramel solution containing alanine (Table 1). Furanones isolated from browned flavour was described to have caramel like, sweet nutty and burnt odour impression (Flament, 1989). 2(5H)-Furanone, which comprised the highest yield in pyrolysis of maltose at 300°C was detected in low concentration in the present study. Kroh (1994), gave the mechanism of its formation. The above-mentioned results confirm those concerning the catalytic effect of alanine on the flavour attributes (Fig. 1). Furans, furanones and maltol are well known to be sugar degradation products after pyrolysis and after Maillard reaction however their formation is not specific for amino acids (Baltes, 1979).

5-Hydroxymethyl furfural (HMF), the last recorded components in Table 1, possessed the highest area percentages in the volatiles of caramel solution containing alanine heated for 30 and 60 min. It was greatly decreased at the end of reacting period. The reason of this decrease was explained above concerning the volatiles of caramel solution of maltose.

In view of the fact that during sugar degradation via Maillard reaction, many important reactions take place via degradation of 3-deoxydiketoses and 1-deoxyaldoketoses. These last named compounds are important intermediates that can under go further reaction in presence of nitrogen – containing compounds to produce volatiles related to different chemical classes (Ledl and Schleicher, 1990). Although HMF is the largest degradation product of 3-deoxyaldoketose, it is largely suppressed in presence of primary amine to produce pyrrolealdehyde (Ledl and Schleicher, 1990). On the other hand, 2-furfuryl alcohol and 2-tetrahydrofuranone showed significant increase by prolonged heating time (Table 1); heating 3-deoxyaldoketose under Maillard reaction conditions yields furfuryl alcohol amongst other products. As shown in Table 1, maltol showed remarkable increase at the end of heating period. Maltol is documented as main degradation product of 1-deoxydiketose (Ledl and Schleicher, 1990; Kroh, 1994). Thus the total yield of HMF is highly affected by the overall reaction pathways that take place during preparation of caramel and hence the measurement of its concentration could be introduced into the control of caramel processing operation (Lee and Nagy, 1988).

From the aforementioned results it is clear that the involvement of alanine as a catalyst in the caramelization reaction improved the sensory attributes of the obtained caramel that may be correlated to the increase in the concentrations of the potent odorants of caramel besides to the formation of some

volatile compounds have caramel flavour. Therefore our study will be continued with amino acids other than alanine.

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