The identification of some furan derivatives in glucose-lysine model system by gas chromatography/ mass spectrometry

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Abstract
Colour, taste and flavour are among the most important factors in accepting food products on market. Furan derivatives, beside other flavour compounds, are important for the aroma of thermic processed food. This study presents the results of the separation, identification and quantification of some furan derivatives generated in the glucose-lysine model system. The volatile compounds, extracted with ethyl ether-pentane were separated by Gas-Chromatography and identified by GC-MS method. The system revealed a pH decreasing during the heat treatment at the same time with the arising of the volatile compounds. Eight furan derivatives having caramel flavor were identified in glucose-lysine system. The quantity of separated furans from all systems generally increases relating to the heating time. The addition of D-glucose increases the production of furan derivatives. The addition of amino acid doesn’t substantially influences the quantities of furan derivatives.

Keywords: furan derivatives, glucose-lysine model system, Gas Chromatography-Mass Spectrometry method.

1. Introduction

The aroma can be determined by certain substances or it can be the result of combining some chemical substances in the food products, this being one of the most important qualities attributed to the food products. It is known that the taste and smell play an important role in accepting a food product. Many volatile compounds which are responsible for the aroma characteristic to food products are generated through frying and baking the food.

It is known that Maillard reaction or the browning reaction has a special importance in obtaining the aromas during the technological processes of food (Hurerell, 1985).

The qualitative and quantitative analysis of the chemical compounds formed by food processing is very difficult even in the conditions of using the most modern equipment and analytical means.

For this reason, in the study of aroma compounds, the food products were replaced by model systems formed from representative substances for food products (Bemelmans, 1979).

In the model experiments, the reactants (for example: sugars, amino acids, water, starch) are heated for certain periods of time and certain conditions of temperature, humidity, pH, and catalysers.

Most of the reactions that take place in the thermal processing of food products were explained on the basis of model systems and reactions. Recent studies present the identification of many aroma substances in the model systems and in the food products (Farníková, 1997; Farouk, 2000).

This paper presents a study performed on the glucose-lysine model system, regarding the isolation, separation and identification of aroma volatile compounds.
It is known that furan and its derivatives have an important contribution on bread aroma and on bakery products in general (Apriyantono, 1993; Mastrocola, 2000; Farouk, 2001). For this reason, this study was oriented on the identification and characterisation of some furan derivatives, generated in the glucose-lysine model system.

2. Materials and methods

Materials. In experiments were used lysine monochloride (Sigma Italy), D (+)- glucose anhidrous (RPE-ACS REAGENT, CARLO-ERBA, Milano, Italy), pentane, ethylic ether (BAKER ANALYZED-REAGENT, Holland).

Extract of volatile compounds. Solutions of glucose and lysine monochloride (1:1, 1:2 mole ratios) in deionized water were refluxed in a distiller/extractor of type LIKENS-NICKERSON (Apriyantono, 1993). The extraction solvent was a mixture of pentane: ethylic ether of ratio 9:1. The systems were heated to 100°C without pH control. The extracts obtained were concentrated into a volume of 0.5-1mL by using a VIGREUX column. Further, the extract was brought a final volume of 0.02-0.05mL using KUDERNA-DANISCH apparatus. The samples thus obtained were kept in a refrigerator until the analyses were performed.

The chromatographic analysis of gases using a capillary column.

The extracts of volatile compounds were subjected to gas chromatography using a capillary column of type DB-5 (30m x 0.32mm d.i.; the thickness of the film: 0.25µm) (J&W USA).

The gas chromatograph of type VARIAN Model 3300 (USA) was equipped with a flame ionization detector (FID).

The retention times and the quantitative data were obtained with an integrator of type CARLO-ERBA (IT), model MEGA SERIES.

The chromatographic analysis of gases and the mass spectrometry (CG-SM).

The CG-SM analysis was performed by means of a gas chromatograph VARIAN model 3400 connected with a mass spectrometer VARIAN SATURN (IT DMS).

The separation of volatile compound was achieved by using the same capillary column DB-5. The conveying gas was He, with a flow of 1.5 mL/min. The instrument was fitted with a Filter Karnak personal computer and an EPSON LX – 400 printer.

The program of temperature for the capillary column was: 40°C (5min), 2°C/min, 80°C (0 min.), 8°C/min., 200°C 20min). The components were identified with the standard substances (existing in laboratory) and with the data bank (WILEY 5 MS) from the mass spectrometer endowment.

3. Results and discussion

The volatile compounds were separated from the extract by gas chromatographic analysis with capillary column.

The linear retention indices for each component were calculated using the internal standard method. The furan derivatives were identified in the volatile compounds extract using the results regarding the retention intervals of the standard substances.

In table 1, there are given the values of the linear retention indices for the furan derivatives found in our mixture.

In order to identify the furan derivatives in the volatile compound extract separated from the glucose-lysine mixture it has been used GC-MS method.

In table 2, there are the main fragments resulted from the electronic impact of these molecules in decreasing order of the relative intensity.
Table 1. The furan derivatives identified in the glucose-lysine model system

<table>
<thead>
<tr>
<th>No.</th>
<th>The volatile compound name</th>
<th>Experimental column</th>
<th>Literature**</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2-methyl-tetrahydro-furan-3-one</td>
<td>689</td>
<td>690(I)</td>
</tr>
<tr>
<td>2</td>
<td>Furanaldehyde, (2-Furylmethanal)</td>
<td>732</td>
<td>804(II), 783(III)</td>
</tr>
<tr>
<td>3</td>
<td>5-methyl-2(3H)-furanone</td>
<td>754</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>2-hydroxy-methylfurane</td>
<td>766</td>
<td>823(II)</td>
</tr>
<tr>
<td>5</td>
<td>2-acetylfuran</td>
<td>814</td>
<td>883(II)</td>
</tr>
<tr>
<td>6</td>
<td>5-Methylfuranaldehyde</td>
<td>879</td>
<td>937(II)</td>
</tr>
<tr>
<td>7</td>
<td>2-acetylfuranaldehyde</td>
<td>928</td>
<td>970(I)</td>
</tr>
<tr>
<td>8</td>
<td>bis-(5-methyl-2-furyl)-methane</td>
<td>1191</td>
<td>1750(I)</td>
</tr>
</tbody>
</table>

** The meaning of the symbols I-III is the same to the ILR comparison corresponding to the DB-5 column with the data from literature. (I)– Baltes (1993); (II) – Hwang (1994); (III) – Lu (1997).

Table 2. The mass spectrometers of the furan derivatives separated and identified from the glucose-lysine mixture.

<table>
<thead>
<tr>
<th>No.</th>
<th>Structural formula</th>
<th>Name</th>
<th>Main fragments(m/e)**</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>2-Methyl-tetrahydro-furan-3 one</td>
<td>43, 72, 100, 45</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>2-Furanaldehyde</td>
<td>96, 95, 39, 38, 67</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>5-Methyl-2(3H)-furanone</td>
<td>55, 98, 43, 27, 39</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>2-Furyl-methanol (furfuryl alcohol)</td>
<td>98, 43, 55, 70, 81</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>2-Acetylfuran</td>
<td>95, 110, 39, 43, 67</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>5-Methylfuranaldehyde</td>
<td>110, 109, 53, 81, 95</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>2-Acetylfuranaldehyde</td>
<td>109, 124, 43, 53, 81</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td>Bis-(5-methyl-2-furyl)-methane</td>
<td>176, 43, 105, 161, 133</td>
</tr>
</tbody>
</table>

**The molecular fragments are arranged in decreasing order of the relative intensity. The first fragment is the base peak. The underlined peak is the molecular peak.
The structure of furan derivatives was provided on the basis of mass spectrums. Their identification was also made on the basis of the existent standards in the laboratory (for furfural, furfurilic alcohol, 2-acetylfururan, 5-methyl-furfural, 2-acetyl-5-methyl-furan) and the information existing in the computer’s data bank from the mass spectrometer equipment were taken into account.

In order to characterize the influence of either glucose or amino acid on the composition of volatile compounds in Maillard reaction two different aqueous glucose-lysine model systems were analyzed: the first one with 50% D-glucose and 50% L-lysine, the second system with 66.66% D-glucose and 33.33% L-lysine. The results regarding the quantity of furans identified from the first system are pointed out in the figures 1a and 1b.

The 2-Furylmethanal is a major compound in the all period of thermal treatment. The quantity of 2-Furylmethanal increase with the increasing of heating time(Fig. 1b). These results are in accord to the literature, i.e. Apriyantono et al. (1993) have studied on xylose lysine model system).

The quantities of 2-Acetylfurane and 5-Methyl-furanaldehyde increase during the heating of the system. Though bis-(5-methyl-2-furyl)-methane is in low quantity however it is an important volatile compound that is generated in interaction of furfural with glucose (Baltes, 1993).

In the figures 2a and 2b there are pointed out the quantities of furan derivatives produced on glucose-lysine system (2:1 molar ratio). The quantities of each compounds are increasing as the same way as in the case of glucose-lysine (1:1 molar ratio); their quantities are almost twice. The bigger quantity of glucose into system there is the bigger amounts of furans there are. It’s not necessary to increase the amount of lysine in order to increasing the rate of reaction so to increase the amounts of furan derivatives.

The quantity of furan derivatives as 2-acetyl-5-methylfurane and bis-(5-methyl-2-furyl) ethane slowly decreases during of the thermal processing of systems because of their high reactivity and interaction with other compounds in the advanced stage of Maillard reaction.

![Figure 1a. The effect of heating time on furan derivatives generated in glucose-lysine system (1:1 molar ratio).](image-url)
Figure 1b. The effect of heating time on furan derivatives in glucose-lysine system (1:1 mole ratio).

Figure 2a. The effect of heating time on furan derivatives generated in glucose-lysine system (2:1 molar ratio).

Figure 2b. The effect of heating time on furan derivatives generated in glucose-lysine system (2:1 molar ratio).
4. Conclusion

In the volatile compound extract separated from the glucose and lysine mixture in aqueous solution, only eight furan derivatives were identified in the above presented working conditions.

The amounts of furan derivatives produced into model system depend of how long is heated the system. The addition of glucose increases the production of furan derivatives. The odor intensity increased with the heating time and with addition of glucose in the model system. The addition of lysine don’t visible modify the amounts of furans, but increases the pyrazines content (experimental results aren’t point out in this work).

The relationship between the amount of furans and the heating time can be a good key for evaluation of advanced glycation in processed food. The 2-furyl-methanal is a representative furan derivative because of its great amount and its importance in odor can be used as a marker for excessive thermal processed foods.

References


Baltes, W., Knoch, E, (1993). “Model reactions on roast aroma formation XIII. The formation of some uncommon N-heterocyclic compounds and furans after roasting of tryptophan with reducing sugars and sugar degradation products “, Food Chemistry, 46, 343-349.
