INVESTIGATION OF THE THERMAL STABILITY OF THE TOTAL LIPIDS ISOLATED FROM SMOKED ZLATIBOR BACON

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Thermal stability of total lipids extracted from Zlatibor smoked bacon was analyzed applying TG (thermogravimetric) analysis performed in air and nitrogen atmosphere. The total lipids were extracted using the procedure described by Folch. About 10 mg (10%) of total lipids was usually the initial sample weight in a TGS-2-Perkin Elmer thermobalance; it was heated from 30-220 °C using 2.5 and 5 K/min with constant nitrogen or air flow rate (25 cc/min).

The main goal of this investigation was to show if there were any differences in the total lipids thermal stability, by analyzing samples extracted from Zlatibor bacon originating from different times of its manufacture. The above analysis was performed using lipids extracted from: an initial sample of the bacon (A), samples of bacon after 10 and 30 days of the smoking process (B and C, respectively), as well as a sample of bacon after the smoking process was finished and 30 after days of maturing and storage (D).

Thermal analysis can be applied as a standard method for the investigation and control of the quality of starting raw materials and final products. It can also serve not only to determine the thermal stability of different materials, but also to detect the optimal conditions of a specific technology and the storage procedure of different pharmaceutical products, as well as food stuffs. According to the results published by Hassel (1976), thermogravimetric analysis (TGA) is a very promising method for the determination of oil stability. Buzas and Kurucz (1979) developed a very simple and fast method, applicable to routine determination of the storage time, i.e. the prediction of the oxidative stability and oxidative status of edible oils. Hageman and Rothfus (1979) concluded on the basis of their own experimental results that TGA is very promising for the determination of oxidative change of whales fat, as well as some natural and synthetic esters of different waxes. Lj. Bastic (1987, 1992) analyzed the rate of oxidation and formation of volatile compounds from the intramuscular lipids of white meaty hog. TG results were used not only for the determination of the oxidation rate, but also for the identification of changes obtained during lipids storage and thermal treatment. TGA could also be used as useful method for the fast determination of the lipids originating from different hog and cattle tissues, and also to determine the relationship of the kinetic parameters of lipid oxidation and total lipids composition (Skala et al, 1991).

The main goal of this investigation was to show if there were any differences in the total lipids thermal stability. The lipids were extracted from Zlatibor bacon originating from different times of its manufacture. Four samples of lipids prepared from different stages of the smoked bacon preparation gave enough information to conclude about changes in the lipids composition caused by the aging process. The analysis was performed using lipids extracted from: the initial bacon sample (A), bacon samples after 10 and 30 days of smoking process (B and C, respectively), as well as a sample of bacon after the smoking process was finished and after 30 days of maturing and storage (D). According to literature data (Lj. Bastic, 1986), non isothermal TGA performed in an oxidizing atmosphere (air or oxygen) caused a smaller increase of the weight of the lipids sample at the beginning of heating compared to the weight loss in nitrogen atmosphere as a result of the initiation of oxidation followed by rapid lipids decomposition and the formation of volatile compounds at higher temperature. With the aim of determing the oxidative stability of the extracted lipids from Zlatibor bacon, TGA was performed in nitrogen and air atmosphere. The oxidative stability was determined according to the values of the kinetic parameters calculated from the non-isothermal TG data.

EXPERIMENTAL METHODS

The samples of total lipids used for TGA were obtained according to the procedure described by Folch et al (1957). The prepared samples were preserved in closed vials under nitrogen and stored at -24 °C for about 6 months before analysis. The Perkin-Elmer thermobalance (TGS-2) used for the analysis, performed always with a sample weighted 10 mg 10%, in temperature range 30-220 °C , using nitrogen or air as the carrier gas (25 cm^3/min). The samples originated from different stages of Zlatibor bacon production as decribed above (samples A, B, C and D). Probably, the last two stages (C and D) represented the most significant and characteristic samples for TGA from the standpoint that they passed through the whole technological route of Zlatibor bacon manufacture and, probably, increased oxidation of the total lipids in these samples can be expected.

RESULTS AND DISCUSSION

All TG curves express that increased mass change appears if a slower heating rate was applied. Namely, the beginning of the mass change (heating rate 2.5 K/min) started almost at 80 °C, while at 5 K/min it was above 100 °C. This observation supported the results given by Lj. Bastic (1986) that the characteristic temperature at which degradation can occur shifts towards higher temperatures if a faster heating rate is applied.
Figure 1 (a, b, c and d) represents the comparative mass change of total lipids (samples A, B, C and D) determined during non-isothermal analysis (2.5 K/min) performed in nitrogen or air atmosphere. Obviously, a greater mass change was detected for samples A (lipids extracted from raw material - bacon) compared to the three other present in this paper.

Figure 1. TG plots for samples A (upper left); B (upper right); C (down left) and D (down right); symbols used on the plots: B-TGA performed in air and C-TGA performed in nitrogen.

Probably salting, as well as smoking, have some anti-oxidative influences, so the rate of lipids oxidation was suppressed not allowing effective contact of the oxygen with the most reactive components of the total lipids. Namely samples A, did not contain any amount of components which can function as a conservance suppressing the oxidation process.
Figure 1 also shows that the mass change of total lipids is greater when TGA was done in air, which was expected because the thermal degradation of total lipids in air, probably induced by a chain auto-oxidative reaction and the formation of hydroperoxide which can easily degraded in a further step producing components with 3-4 C atoms of the aldehyde type, ketones, acids as well as CO_2. The effect of the thermal degradation of total lipids (samples A, B, C and D) was compared to the determined fatty acids composition of the lipids determined by GC analysis. In Table 1, the ratios of the saturated (S) and monounsaturated (M), the saturated and polyunsaturated (P), as well as the mono and polyunsaturated fatty acids were used for the explanation of some of the effects observed during the TGA of sample C in air (Figure 1c).

The ratio of monounsaturated fatty acids (M) for samples B, C and D compared to sample A are : B/A=0.98; C/A=0.97 and D/A=0.96, indicating only a small change of M during the production of Zlatibor bacon. A similar analysis can be drawn taking into account the polyunsaturated fatty acids (P) content for samples B, C, D and A and calculating their ratio: B/A=1.03; C/A=0.98 and D/A=0.96. This reduction of the ratio of the P content probably caused some oxidative changes during smoking and storing in Zlatibor bacon manufacture. The analysis of fatty acids composition in samples A-D, and, especially, the content of free fatty acids (predominantly of the M type) in neutral lipids showed that the maximum presence existed in the sample C. This fact can be used for the explanation that the reaction with oxygen from air was more pronounced for this sample (see Figure 1c) which is the main reason why in one temperature range the increased sample mass was detected.

Kinetic parameters determination

The experimental results indicated that greater mass change of total lipids can be expected for temperatures above 100°C in nitrogen and 80°C in air atmosphere. This is the reason why only mass changes above the indicated temperature were used for the kinetic analysis of the thermal degradation process. The rate of oxidation and formation of volatile compounds (R) at higher temperature can be defined by a simple rate expression:

$$r_R = k.m = k.m_o\,(1-X) \qquad (1)$$

where: m is the actual and mo the initial mass of the sample; k=A.exp(-E/RT) min^{-1}, the reaction rate constant determined by the frequency factor A (min^{-1}) and the activation energy E (kJ/mol); X- is the degree of total lipids conversion ($X=(m_o-m)/m_o$); T (K)- temperature, and R=8.314 kJ/mol.K the gas constant.
The rate of thermal degradation was based in analogy with a first order chemical reaction in the gas or liquid phase. For the non-isothermal process performed in a TG thermobalance, the following mass balance can be written:

$$r_R = -dm/dt = k.m \qquad (2)$$

or taking into account the constant heating rate of sample q (K/min), as well as the degree of sample conversion X, equation (2) can be expressed by the relation:

$$q(dX/dT) = A.(1-X)\exp(-E/RT) \qquad (3)$$

One form of the solution of equation (3) was given by Doyle (1961) and Gorbachev (1975) which can be effectively used for the kinetic parameter calculation of the thermal degradation process:

$$-\ln(-\ln(1-X)/T^2) = k_o + E/(RT) \qquad (4)$$

where: $k_o = -\ln((A/q)(R/(E+2RT))$

Figure 2 shows an analysis of the kinetic parameters of the thermal degradation of sample A (in air) based on equation (4). Similar analyses were done for the other samples and the thermal degradation processes performed in nitrogen and air atmosphere, and the obtained results are presented in Table 2.

The values of the determined activation energy are a little bit higher compared to those calculated from the experiments performed in nitrogen. This fact indicates the higher sensitivity of the thermal degradation process if TGA performed in air. However, all the results indicated that the total lipids extracted from Zlatibor bacon are more stable compared to the results recently published by Lj. Bastic (1986) using TG analysis of the total intramuscular lipids from boars was analyzed (57.9 and 61.5 kJ/mol for nitrogen and air atmosphere). Also this author showed that above 130 °C very fast thermal degradation followed by auto-oxidation (in air atmosphere) exists, which also indicates a higher value of the activation energy. The results of this investigation also confirm the published ones, because the activation energy of the non-isothermal thermal degradation process in air are in the range 42-50 kJ/mol, and for degradation in nitrogen they are lower and in the range 35-47 kJ/mol.
An increase of the activation energy with the age of the sample (A-D, from 0 to 80 weeks, Table 2) is a logical consequence of the increased instability to thermal processes more expressed if the period of final product maturing and storage is more pronounced. This is also more expressed if non-desired conditions are favored, e.g. contact of bacon with light, increased temperature and humidity during storage, etc.
Only a 25% increase of the activation energy with sample age, which is a measure of the thermal stability of total lipids on thermal degradation, as well as other data obtained by TGA, indicate that only minor changes of the total lipids composition obviously existed. This was also confirmed by the results of another investigation (fatty acids composition) which showed that the final product, Zlatibor bacon, after 80 weeks of production practically has the same composition as the starting bacon, followed by very good sensor analysis.

CONCLUSION

In order to obtain a more complete picture of the state of lipids in Zlatibor bacon and to confirm the results obtained by the analysis of the fatty acids composition, TGA was performed. The TGA of the total lipids of Zlatibor bacon in nitrogen and air flow under non-isothermal conditions (30-220 °C) are presented. The TG curves of samples heated under nitrogen at various heating rates (2.5 and 5 K/min), as well as the TG curves of samples heated in air (2.5 K/min) are presented. The TG curves were found to depend on the fatty acid content, especially the unsaturated fatty acids. By using the integral method, the kinetic parameters (A-frequency factor, E-the activation energy) were determined. The rates of oxidation and/or thermal degradation of the total lipids of Zlatibor bacon in air or nitrogen were defined by the kinetic parameters. A moderate increase in the

activation energy with production and maturing time indicates that there are no relevant changes in the lipids of Zlatibor bacon also confirming the results obtained by sensor analysis.

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