ELSEVIER

Food Chemistry 71 (2000) 37–43

Food Chemistry

www.elsevier.com/locate/foodchem

The reaction kinetics for the formation of Strecker aldehydes in low moisture model systems and in plant powders

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Received 30 November 1999; accepted 29 February 2000

Abstract

The Strecker aldehydes, acetaldehyde (AA), 2-methylpropanal (2-MP), 2-methylbutanal (2-MB) and 3-methylbutanal (3-MB), are regularly found in processed foods of plant origin. They are produced by Strecker degradation of the amino acids, alanine, valine, isoleucine and leucine. The observed reaction of their formation in a low moisture model system and in commercially available plant powders turned out to be pseudo zero order. The activation energies for their formation, in a low moisture model system containing glucose and alanine, valine, isoleucine and leucine, ranged from 115 to 124 kJ/mol. Using a model system containing glucose and leucine it became possible to interpret the kinetics of the formation of Strecker aldehydes in relation to the formation of Amadori rearrangement products (ARP), the decrease of leucine and the formation of brown pigments as a function of heating time.

Keywords: Strecker aldehydes; Activation energy; Maillard reaction; Kinetics; Plants

1. Introduction

The Strecker aldehydes, acetaldehyde (AA), 2-methylpropanal (2-MP), 2-methylbutanal (2-MB) and 3-methylbutanal (3-MB), are regularly found in the low-boiling fraction of volatile compounds of processed plant foods (Buttery, Stern & Ling, 1994; Collin, Vanhavre, Bodart & Bouseta, 1995; Heatherbell, Wrolstad & Libbey, 1971; Herrmann, 1979; Sapers, 1970; Self, Casey & Swain, 1963; Van Ruth, Roozen & Cozijnsen, 1995), indicating that the Maillard reaction has occurred during processing operations such as drying and grinding of the dried products. These volatile compounds have low odour thresholds (Rychlik, Schieberle & Grosch, 1998) and contribute to undesirable flavours of processed plant foods. The above-mentioned Strecker aldehydes are formed by the Strecker degradation of alanine, valine, isoleucine and leucine. The Strecker degradation, which is a minor pathway of the Maillard reaction, involves the oxidative deamination and decarboxylation of α-amino acids in the presence of α-dicarbonyl compounds which are formed during the Maillard reaction. The Strecker degradation products (Strecker aldehydes) contain one less carbon than the original amino acid. A literature review showed that the formation of Strecker aldehydes in foods and food-related model systems had been thoroughly studied (Blockmans & Dujardin, 1973; Collin et al., 1995; Hall, Andersson, Lingnert & Olofsson, 1985; Hartman, Scheide & Ho, 1983/1984; Pokorny, 1980; Seck & Crouzet, 1982; Velisek, Davidek, Pokorny, Grundova & Janicek, 1972); however, little work had been published with respect to the kinetic of their formation. Chan and Reineccius (1994) were probably the first who determined the activation energies for the formation of the Strecker aldehydes 3-MB and phenylacetaldehyde in aqueous glucose/amino acid model systems. The activation energy of a chemical reaction can be calculated from the temperature dependence of its reaction rate constant using the Arrhenius equation. The present paper deals with the formation of the above mentioned four aldehydes by Strecker degradation of the pertinent amino acids, which have nearly the same pK_1- and pK_2-values. The Strecker aldehydes were determined by headspace gaschromatography (headspace-GC). The investigations were carried out in two low moisture model systems and in five different commercially-dried plant powders. One model system, abbreviated as G/L, contained glucose and leucine at a molar ratio of 20:1; another, abbreviated as G/AVIL,

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0308-8146/00/$ - see front matter
PII: S0308-8146(00)00122-9

had glucose and the above-mentioned four amino acids at a molar ratio of 20:1:1:1:1, which was used for the determination of the activation energies of Strecker aldehyde formation. In order to interpret the kinetics of Strecker aldehyde formation in the course of the complex Maillard reaction, the model system G/L was heated and analyzed with respect to the Strecker aldehyde formation as well as to the formation of the Amadori rearrangement product fructose-leucine (Fru-Leu) as a Maillard reaction intermediate, and the decrease of leucine and the production of brown pigments.

2. Materials and methods

2.1. Materials

Glucose, L-alanine, L-valine, L-isoleucine, L-leucine, acetaldehyde, 2-methylpropanal, 2-methylbutanal and 3-methylbutanal, diethylene glycol dimethyl ether, and magnesium nitrate hexahydrate were purchased from Fluka, Buchs, Switzerland; citric acid monohydrate, hydrochloric acid (0.1 M) and sodium hydroxide (0.1 and 1 M) from Grüssing, Filsum, Germany; microcrystalline cellulose 0.020 mm (Avicel) was purchased from Serva, Heidelberg, Germany. The ARP fructose-leucine was prepared and its purity (~99% purity) controlled by ion-exchange chromatography, applying the method described by Schräder and Eichner (1996). Headspace vials (22 ml) were obtained from Perkin-Elmer, Ueberlingen, Germany.

2.2. Reagents

0.1 M citrate buffers were prepared as follows: Solution A: 21.01 g citric acid monohydrate were dissolved in distilled water, mixed with 200 ml 1 M sodium hydroxide and the volume brought to 1000 ml. Solution B: 0.1 M sodium hydroxide. Mixing of 96.4 ml A and 3.6 ml B yields a buffer solution of pH 5. After mixing, the pH was adjusted at 5.0 using 0.1 M sodium hydroxide or 0.1 M hydrochloric acid. 0.1 M amino acid solutions were prepared using ultra sonication and as much hydrochloric acid as necessary.

2.3. Preparing the model systems and plant powders

- Model G/AVIL: 1.80 g glucose and 5.0 ml of each of the 0.1 M amino acid solutions (containing 44.5 mg Ala, 58.5 mg Val, 65.6 mg Leu, 65.6 mg Ile; sum of amino acids: 234 mg), 20 ml buffer (pH 5.0; 0.56 g dry matter), 20 ml distilled water and (10.0−1.80−0.56−0.234 g=) 7.406 g microcrystalline cellulose were mixed, the pH corrected, using sodium hydroxide solution and/or hydrochloric acid, the mixture deep-frozen and freeze-dried. The model system contained 1.0 mol/kg glucose and 50 mmol/kg of each of the four amino acids.
- Model G/L: This model was prepared using the same procedure as for the model described above. It contained 1.0 mol/kg glucose and 50 mmol/kg leucine.

200 mg aliquots of the freeze-dried model systems and 500 mg aliquots of the plant powders (cauliflower, spice paprika, asparagus, tomato, onion) were adjusted to an a_w-value of 0.52 by storing them for four days in a headspace vial placed in a desiccator over a saturated magnesium nitrate hexahydrate solution.

2.4. Quantitative headspace-GC determination of Strecker aldehydes

A stock solution of the above-mentioned aldehydes (AA, 2-MP, 2-MB, 3-MB) was prepared as a standard for headspace-GC by adding 100 mg of each of the aldehydes to 100 ml diethylene gycol dimethyl ether.

The quantitative determination of the aldehydes in the model systems and in the plant powders was carried out according to the standard addition method. 10, 20 and 30 μl of the aldehyde stock solution were added to aliquots of the model systems and to the plant powders in the headspace vials. The vials were sealed immediately with a septum and the samples mixed with a reaction tube mixer (vibro fix). Samples and standard addition samples were analysed by headspace-GC.

2.5. Headspace-GC-analysis

The prepared sample aliquots were heated (thermostatted) for 3 to 120 min in the headspace oven at 70 to 110°C. A Perkin-Elmer Headspace-GC 8410 equipped with the autosampler system HS-101, a FID and a 60 m×0.32 mm×1.0 μm fused silica Stabilwax® capillary column was used. The oven temperature was held at 40°C for 5 min and then programmed to 70°C at 2°C/min; the temperature was held for 5 min. The injector and detector temperatures were, respectively 130 and 230°C. Carrier gas (helium), hydrogen, air and make-up gas (nitrogen) pressures were 200, 140, 140 and 75 KPa, respectively. FID-sensitivity was high. Peak areas were integrated with a Merck-Hitachi D 2000 integrator. The autosampler parameters were: needle temperature, 120°C; sample temperature, 70–110°C; thermostatting time, 3–120 min; transferline temperature, 130°C; pressurisation time, 0.8 min; injection time, 0.06 min; injection per vial; 1; withdrawal time, 0.2 min.

2.6. Analysis of Fru-Leu and Leu

After headspace-GC analysis, the samples of the model system G/L were extracted with 1.0 ml of distilled

water, centrifuged and an aliquot of the supernatant analyzed using a Biotronic LC 5001 Automated Amino Acid Analyzer and applying the method described by Schräder and Eichner (1996). External calibration curves were used for quantitative determination.

2.7. Spectrometry

The Maillard browning of the samples of the model system G/L was measured in a 1.00 cm cell in the aqueous extract described above. When necessary, appropriate dilutions were made in order to have an optical density of less than 0.8. A Perkin-Elmer Spectrometer Lambda 40 was used.

3. Results and discussion

3.1. Strecker aldehyde formation in plant powders

Figs. 1 and 2 show the formation of the sum of 2-MP, 2-MB and 3-MB, as well as the formation of AA in plant powders as a function of heating time at 90°C. Since the characteristics of the formation of the aldehydes 2-MP, 2-MB and 3-MB were very similar, their formation was presented as the sum. Additionally Fig. 3 shows the amounts of the four aldehydes produced after the plant powder samples had been heated 60 min at 90°C.

As can be seen from Figs. 1 and 2, the formation of the Strecker aldehydes, except AA, followed a zero order kinetic, irrespective of the kind of plant powder heated. The formation of AA followed a parabolic function in some cases. This is possibly due to the fact that AA formation can not only occur via Maillard reaction but also for example during heat-induced lipid and carotenoid oxidation (Baltes, 1983; Josephson & Glinka, 1989; Yasuhara & Shibamoto, 1991).

As can be seen from Fig. 3 the amounts of aldehydes produced in the plant powders differed from sample to sample. It can be assumed that the amounts of aldehydes produced are correlated to the concentrations of the corresponding free amino acids present in the powders, as can be seen in Fig. 4, for the spice paprika sample. This assumption was also found to be true for tomato while it could not be proved for the other plant powders since their free amino acid compositions were unknown. The mean free amino acid compositions of tomato and spice paprika was taken from Souci, Fachmann and Kraut (1989) and Cremer (1999). It is striking that even though the rates of the formation of AA are comparable to the rates of the formation of the other Strecker aldehydes, the concentration level of AA exceeds the level of the other aldehydes abundantly. This observation has already been described in the literature for the volatiles of tomato, for example by Nelson and Hoff (1969) and Kazeniak and Hall (1979). According to Kazeniac and Hall and Miyake and Shibamoto (1993), it can be assumed that, due to the biochemical production of AA in the plants — AA is an intermediate product in the respiration of higher plants (Fishbein, 1979), part of the amount of AA determined was already present in the plant powder samples, while the other part was produced during the heating process we applied.

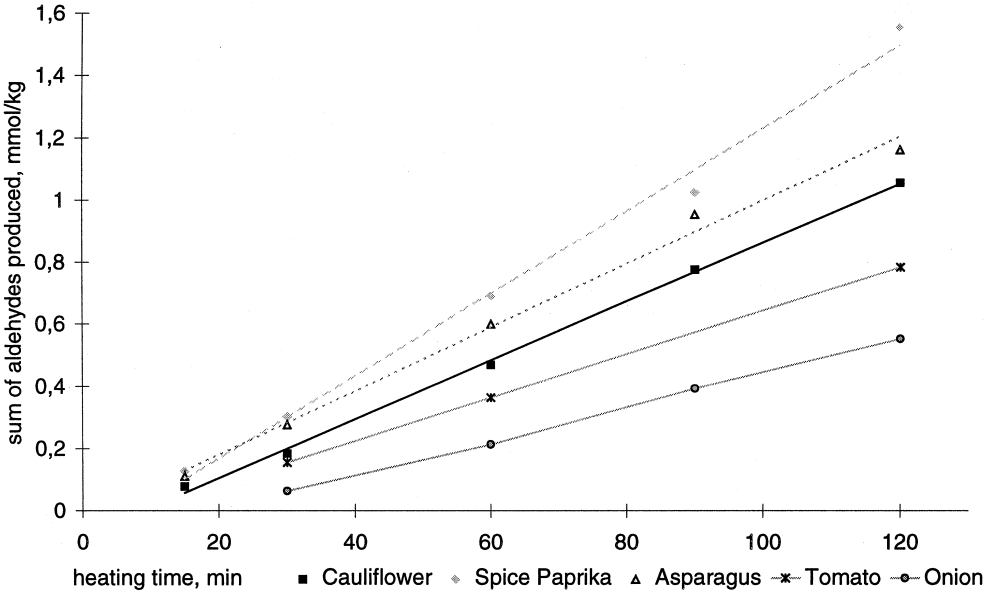

Fig. 1. Formation of the Strecker aldehydes 2-methylpropanal (2-MP), 2-methylbutanal (2-MB) and 3-methylbutanal (3-MB) as a function of heating time at 90°C in commercially dried plant powders (a_w-value 0.52).

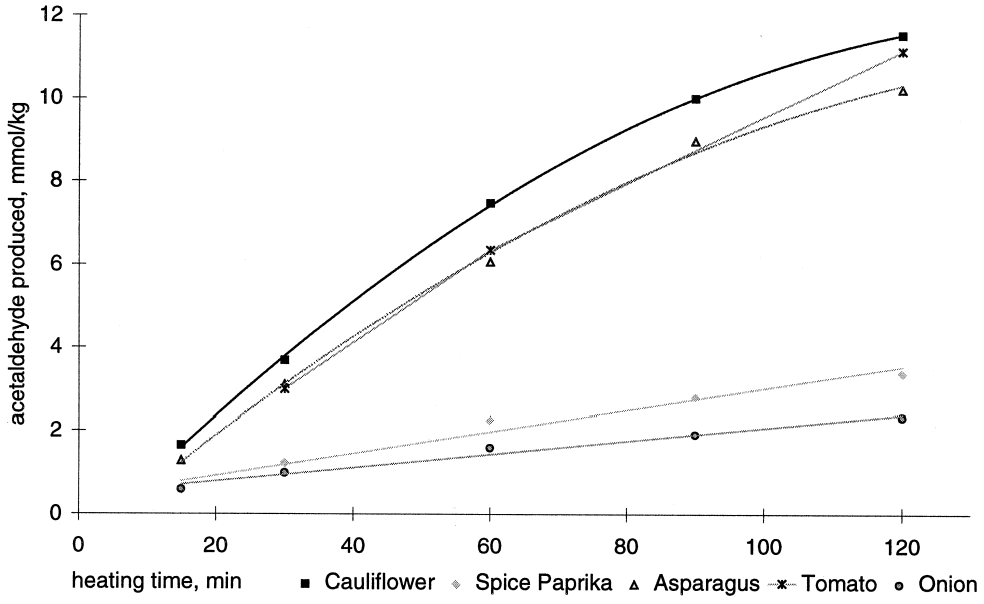

Fig. 2. Formation of the Strecker aldehyde acetaldehyde (AA) as a function of heating time at 90°C in commercially dried plant powders (a_w-value 0.52).

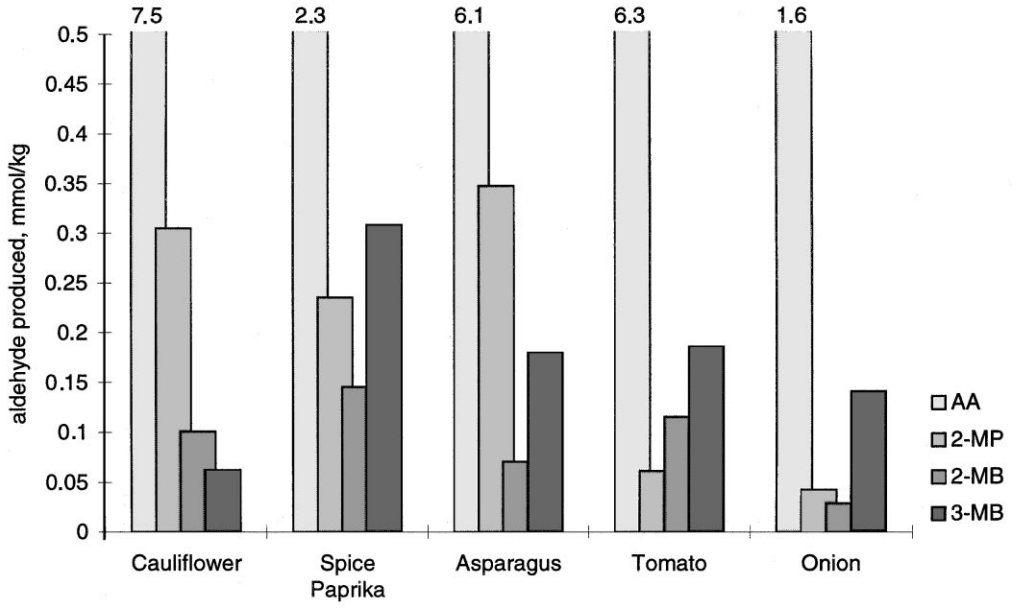

Fig. 3. Amounts of Strecker aldehydes produced after heating commercially dried plant powders (a_w-value 0.52) for 60 min at 9°C.

3.2. Interpreting Strecker aldehyde formation in the model system G/L with respect to other parameters of the Maillard reaction

Since numerous different reactions contribute to the overall Maillard reaction it is interesting to relate a particular sub-reaction, such as the Strecker degradation, to others, which may provide additional information for the understanding of the overall reaction.

Fig. 5 shows the formation of 3-MB and Fru-Leu as well as the decrease of Leu and the formation of browning pigments in the model system G/L containing glucose and leucine as a function of heating time. As can be seen, the Strecker aldehyde formation followed a sigmoid curve characteristic. The inflection point is reached after about 180 min. The induction period for the aldehyde formation at the beginning of heating resulted from the fact that, at first, the Maillard reaction intermediate Fru-Leu must be formed; the reactive α-dicarbonyl compounds undergoing the Strecker reaction are formed by decomposition of Fru-Leu at a later stage.

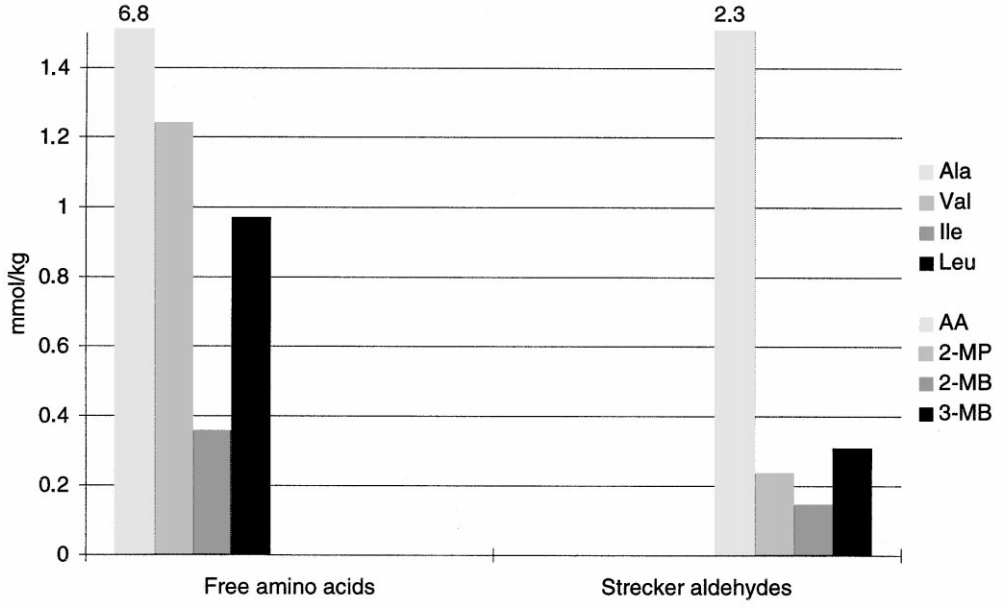

Fig. 4. Concentration levels of some free amino acids present in a commercially available spice paprika powder and amounts of related Strecker aldehydes that had been produced after heating the powder for 60 min at 90°C.

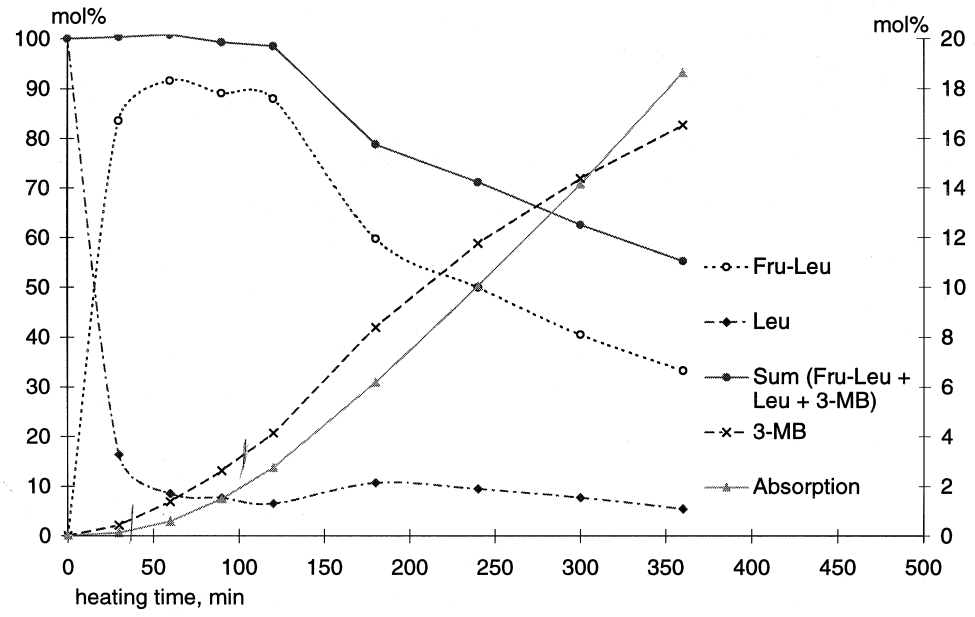

Fig. 5. Formation of Maillard reaction products as a function of heating time at 90°C in a low moisture model system (a_w-value 0.52) containing glucose and leucine at a molar ratio of 20:1; formation of 3-MB (mol%) and normalized absorption at 420 nm: right y-axis.

As can also be seen from Fig. 5, at the beginning, the decrease of Leu corresponded with the increase of Fru-Leu, indicating an equimolar reaction of Leu with glucose. The 100% level is related to the initial molar amount of leucine. After about 40 min the concentration of Fru-Leu reached a steady state level where its rate of formation and decomposition were apparently equal; this is also the case with the concentration of Leu because part of it was set free during decomposition of Fru-Leu and part of it may have reacted with glucose. After 120 min, the decomposition of Fru-Leu prevailed, connected with a slight increase of Leu which was set free during decomposition of Fru-Leu. During the steady state period, the sum of the molar amounts of Leu, Fru-Leu and the related Strecker aldehyde 3-MB remained approximately at the 100 mol% level; therefore, during that reaction period, the amount of leucine incorporated into browning pigments and other Maillard products must have been very small. After 120 min, this sum declined steeply, indicating that Leu was increasingly incorporated into other Maillard products.

With respect to the Strecker degradation, it is noteworthy that, in the period of the steady state concentration of Fru-Leu (30–120 min), the formation of the corresponding Strecker aldehyde fits the zero order kinetic very well ($r^2 = 0.99$). Therefore, for calculation of the activation energies in the model system G/AVIL (see below), the rate constants for the Strecker aldehyde formation were determined on the basis of this linear section.

3.3. Determination of activation energies for the formation of Strecker aldehydes in the model system G/AVIL

The activation energies for the formation of Strecker aldehydes were determined in the low moisture model system G/AVIL, which contained glucose, Ala, Val, Ile and Leu at a molar ratio of 20:1:1:1:1. According to the results shown in Figs. 1, 2 and 6 the Strecker aldehyde

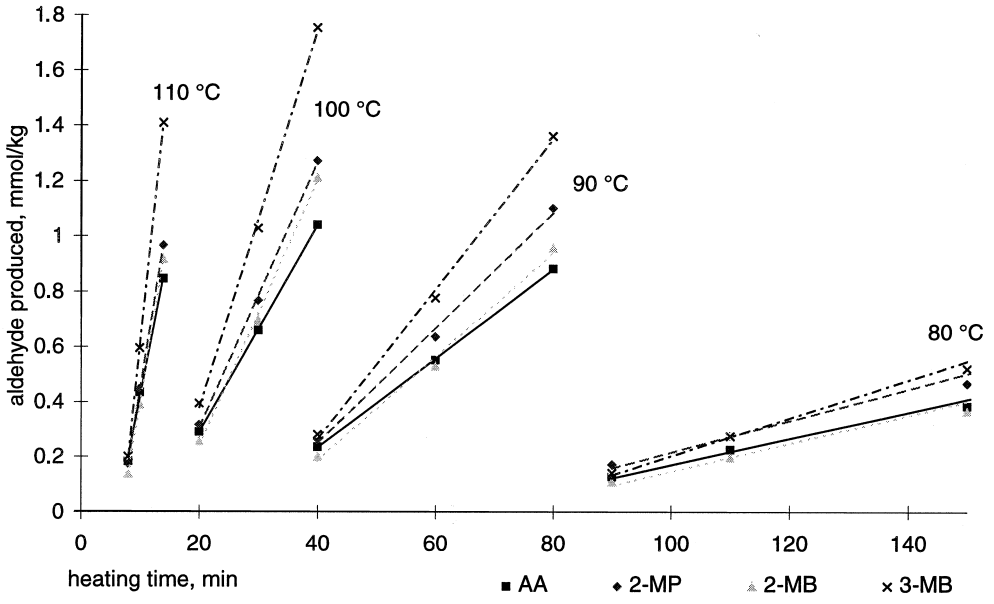

Fig. 6. Formation of Strecker aldehydes in a low moisture model system (a_w-value 0.52) containing glucose, alanine, valine, isoleucine, and leucine at a molar ratio of 20:1:1:1:1.

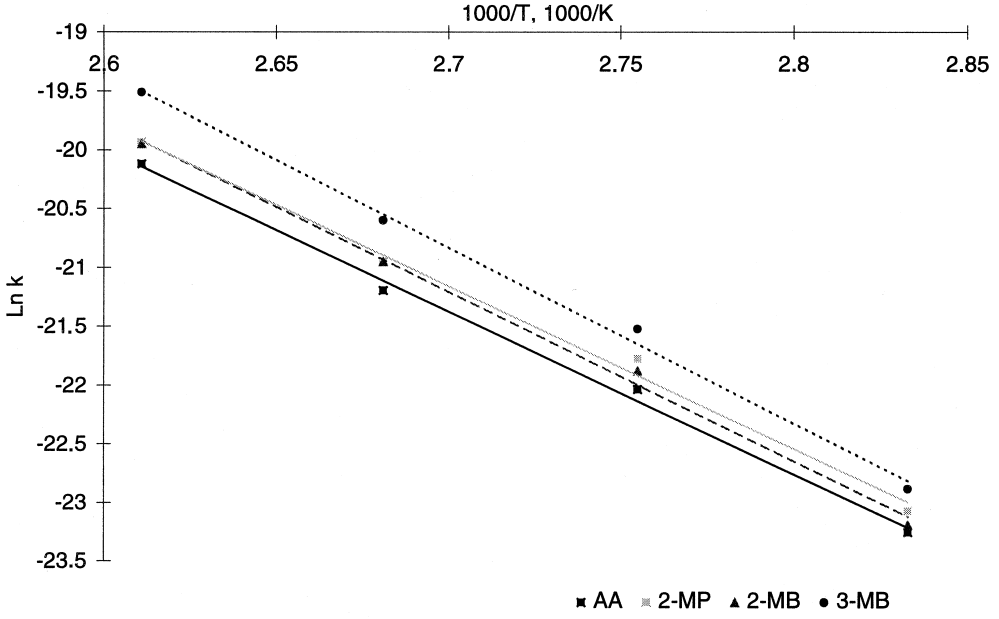

Fig. 7. Arrhenius plots for the formation of Strecker aldehydes in a low moisture model system (a_w-value 0.52) containing glucose, alanine, valine, isoleucine and leucine at a molar ratio of 20:1:1:1:1.

formation followed a zero order reaction within a certain reaction period. Also, Chan and Reineccius (1994), who determined the activation energies for Strecker aldehyde formation in aqueous glucose/amino acid model systems, found that Strecker aldehyde formation followed a zero order kinetic at different temperatures. Lerici, Barbanti, Manzano and Cherubin (1990) determined the activation energy of the Strecker degradation reaction in an aqueous glucose/amino acid model system by measuring the production of carbon dioxide, which also followed a zero order reaction kinetic.

The zero order reaction rate constants for Strecker aldehyde formation in the model G/AVIL were determined at different temperatures and the activation energies calculated by using the Arrhenius equation. Fig. 6 shows the isotherms of the formation of the Strecker aldehydes in the model system G/AVIL, dependent on heating time. Fig. 7 shows the resultant Arrhenius plots. The r^2 values of the linear regression of the isotherms in Fig. 6 ranged from 0.991 to 0.999. The activation energies obtained were 115 (AA), 115 (2-MP), 120 (2-MB), and 124 kJ/mol (3-MB), respectively. The standard deviation of the activation energies was estimated to be at a 5% level. A connection between the degree of substitution of the β-carbon atom of the amino acids and the activation energies determined cannot be derived. The activation energy of 3-MB formation, determined by Chan and Reineccius (1994) in an aqueous model system, was 80.4 kJ/mol, which is lower than our value determined in a low moisture model system. This observation confirms the general accepted fact that Maillard reaction activation energies increase with decreasing moisture content as, for example, has been pointed out by Hendel, Vernon and Harrington (1955).

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