

Formation of Volatile Compounds during Heating of Spice Paprika (*Capsicum annuum*) Powder

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Spice paprika (red pepper; *Capsicum annuum*) is the most cultivated spice worldwide and is used mainly for its color and pungency. However, current research is also focusing on the flavor as an important parameter. This paper deals with the kinetics of the formation of those volatiles that indicate a decrease in spice paprika quality due to Maillard reaction, hydrolytic reactions, and oxidative degradation reactions of lipids such as fatty acids and carotenoids. Spice paprika volatiles were quantitatively analyzed by means of headspace gas chromatography (HS-GC) and solid-phase microextraction (SPME) followed by gas chromatography–mass spectrometry (GC-MS). The kinetics of their formation were investigated, and the respective activation energies determined. Strecker aldehyde, acetone, and methanol formation followed a pseudo-zero-order reaction kinetic, and formation of dimethyl sulfide (DMS) was characterized by a first-order kinetic. The activation energies determined were between 86.3 and 101.8 for the Strecker aldehydes acetaldehyde (AA), 2-methylpropanal (2-MP), 3-methylbutanal (3-MB), and 2-methylbutanal (2-MB), 130.7 for acetone, 114.2 for methanol, and 109.7 kJ/mol for DMS. The amounts of Strecker aldehydes formed were correlated to the concentrations of the corresponding free amino acids present in the samples. The formation of hexanal and 6-methyl-5-hepten-2-one in *Capsicum annuum* during processing was confirmed, and the formation of β -ionone was probably described for the first time. During heating, the concentration of hexanal increased rapidly. The formation of 6-methyl-5-hepten-2-one confirms that *Capsicum annuum* fruits contain lycopene.

Keywords: *Capsicum annuum*, volatile compounds, kinetic, headspace gas chromatography (HS-GC), solid-phase microextraction (SPME)

INTRODUCTION

Spice paprika (red pepper; *Capsicum annuum*) is the most cultivated spice worldwide (Govindarajan, 1986a) and is used mainly for its color and pungency. However, current research is also focusing on the flavor as an important parameter. Buttery et al. (1969) identified about 60 volatile compounds in green bell peppers (*C. annuum* var. *grossum*, Sendt), among which they identified an alkyl-methoxy-pyrazine. This and other alkyl-methoxy-pyrazines are the character impact compounds of the genus *Capsicum* (Murray and Whitfield, 1975). Also more than 125 compounds have been identified and reviewed by Van Straten and Maarse (1991). Volatiles have been identified in fresh, cooked, and stir-fried bell peppers, and the effects of ripening and tissue disruption on the composition of volatiles have been determined (Whitfield and Last, 1991). Van Ruth et al. (1994, 1995) were probably the first to determine the volatiles of commercially dried bell peppers. They identified Strecker aldehydes such as acetaldehyde (AA), 2-methylpropanal (2-MP), 2-methylbutanal (2-MB), and 3-methylbutanal (3-MB) in processed bell peppers. The formation of these aldehydes indicates that the Maillard reaction occurred during drying of these peppers. Moreover, these authors identified dimethyl sulfide (DMS) and 6-methyl-5-hepten-2-one in dried bell peppers. DMS

is produced via the hydrolysis of *S*-methylmethionine (SMM), an amino acid that is typically found in many plants (Kovatscheva and Popova, 1977). 6-Methyl-5-hepten-2-one is well-known as a degradation product of lycopene (Cole and Kapur, 1957). The objective of this investigation was to determine the kinetics of the formation of those volatiles that indicate a decrease in spice paprika quality due to Maillard reaction, hydrolytic reactions, and oxidative degradation reactions of lipids such as unsaturated fatty acids and carotenoids. The compounds determined were Strecker aldehydes (indicating Maillard reaction), methanol and DMS (indicating hydrolysis of pectins respectively SMM), acetone (as a degradation product of sugars and carotenoids), hexanal (oxidation product of unsaturated fatty acids), and 6-methyl-5-hepten-2-one and β -ionone (carotenoid degradation products). All of these compounds, except acetone and methanol, have low odor thresholds (Guadagni et al., 1963; Eichner, 1973; Buttery et al., 1990) and are therefore expected to contribute to off-flavors. The low boiling volatiles were determined by means of static headspace gas chromatography (HS-GC), and hexanal, 6-methyl-5-hepten-2-one, and β -ionone by means of solid-phase microextraction (SPME), a relatively novel, solventless method of volatile extraction from gaseous, solid or liquid phases (Pawliszyn, 1997).

A further investigation was carried out in order to compare the heat induced production of Strecker aldehydes in paprika powders of different origin.

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MATERIALS AND METHODS

Samples and Chemicals. Standards of analyzed compounds (acetaldehyde, 2-methylpropanal, 2-methylbutanal, 3-methylbutanal, acetone, methanol, dimethyl sulfide, hexanal, 6-methyl-5-hepten-2-one, β -ionone), as well as diethylene glycol dimethyl ether (diglyme), magnesium nitrate hexahydrate, and sodium chloride were purchased from Fluka, Buchs, Switzerland, with a purity of >98%. Spice paprika powders were obtained from the Fuchs Company, Dissen, Germany. In aqueous suspension (5 g of powder/25 mL of water), the pH value of the paprika powders was close to pH 5. Headspace vials (22 mL volume) were purchased from Perkin-Elmer, Ueberlingen, Germany.

For HS-GC, a standard solution using diglyme as the solvent was prepared containing 1000 mg/L of each substance. The diglyme used proved to be free of methanol (HS-GC). For SPME analysis, a stock solution of 1000 mg/L of the respective standard substances was prepared using methanol as a solvent. A standard solution for SPME analysis was prepared by diluting the stock solution 1:1000 with methanol. A saturated sodium chloride solution was prepared by dissolving a surplus of sodium chloride that had been heated overnight at 550 °C before dissolution in bi-distilled water.

Quantitative Headspace-GC. Sample Preparation. Aliquots of 500 mg of paprika powder (air-dry; 10% water content) were adjusted to an A_w -value of 0.52 (mean water content 6.8%) by storing them for 4 days in a headspace vial (22 mL volume) placed in a desiccator over a saturated magnesium nitrate hexahydrate solution at ambient temperature (20 °C). After the A_w -value adjustment, the samples were analyzed quantitatively applying the standard addition method: 10, 20, and 30 μ L of the aldehyde stock solution were added to the paprika samples placed in the headspace vials. The vials were sealed immediately after filling and the samples mixed with a reaction tube mixer (vibro fix). Samples and standard addition samples were analyzed by means of headspace-GC as described below. For proving their identity, the pertinent low boiling volatiles of paprika powder were analyzed by headspace SPME-GC-MS as described by Cremer (1999).

Analytical Conditions. The prepared samples were quantitatively analyzed for the kinetics of the formation of low boiling volatiles. The heating (thermostating) temperatures and times of the samples varied from 70 to 110 °C and 3 to 120 min, respectively, prior to the automatic headspace sample injection.

A Perkin-Elmer Headspace-GC 8410 equipped with the autosampler system HS-101, a FID, and a 60 m \times 0.32 mm \times 1.0 μ m fused silica Stabilwax (Restek, Bad Homburg, Germany) capillary column was used for analysis of the headspace volatiles. The oven temperature was held at 40 °C for 5 min and then raised to 70 °C at 2 °C/min, where it was held for 5 min. The injector and detector temperatures were 130 and 230 °C, respectively. Helium was used as the carrier gas at a linear flow rate of 30 cm/s. Peak areas were integrated with a Merck-Hitachi D 2000 integrator. The autosampler parameters were as follows: needle temperature, 120 °C; sample temperature, 70–110 °C; thermostating time, variable; transferline temperature, 130 °C; pressurization time, 0.8 min; injection time, 0.06 min; injection per vial, 1; withdrawal time, 0.2 min.

SPME Analysis. Sample Preparation. A total of 500 mg of the paprika powders (air-dry; 10% water content) placed in a headspace vial (22 mL volume) was adjusted to an A_w -value of 0.52 (mean water content 6.8%) by the procedure described above. After A_w -value adjustment, the samples either remained unheated or were heated 60 min at 90 °C in a water bath after having been sealed with a septum. A total of 12 mL of a saturated sodium chloride solution was added to each of the unheated and heated samples after cooling and storing them for at least 60 min at –18 °C. The opening of the heated vials at refrigerated temperatures in order to add the sodium chloride solution did not result in a significant loss of volatile compounds as would be recognized in unreproducible recoveries of the volatile compounds during GC analysis. Moreover, it has to be pointed out that all the volatile compounds that

were of interest had boiling points above 120 °C. The sodium chloride solution which showed salting-out or salting-in effects against the volatile compounds (Cremer, 1999) was mainly used to avoid a rapid increase of suspension viscosity. Samples were stirred with a magnetic stirrer. For quantitative determination, the standard addition method was used by adding 10 and 20 μ L of the SPME standard solution to the samples analyzed. The samples were covered tightly, but not hand-crimper sealed, with a septum and a steel lid immediately after filling. The center of the steel lid was perforated to allow SPME sampling. The omission of hand-crimper sealing made it possible to rinse the SPME fiber after the adsorption process prior to withdrawing it into the needle (see below). This was necessary since the fiber had to be cleaned up from any attached paprika powder particles.

SPME Device. A Supelco SPME fiber holder (manual) and a 100 μ m poly(dimethylsiloxane) (PDMS)-coated fiber were used for the SPME method. Before use, the fiber was pre-conditioned in the GC injection port at 250 °C for 1 h. Sampling parameters were a subject of investigation, and the analysis conditions given herein have been established as the optimal parameters. Insertion of a special inlet liner was not required.

Sampling. The samples prepared for SPME analysis were stirred vigorously using a magnetic stirrer. The suspensions were maintained at ambient temperature. The SPME needle was pierced through the septum, and the plunger was depressed to expose the fiber into the suspension. Every 5 min, the exposed fiber was agitated in order to keep the fiber free of powder particles that could stick to the fiber. After 60 min, the adsorption process was stopped. The fiber was rinsed with water, withdrawn into the needle and then immediately transferred to the injection port of the GC. After the needle of the SPME device had penetrated the septum of the GC inlet, the fiber was exposed so that the analytes were thermally desorbed into the hot injection port and transferred onto the column for gas chromatographic analysis. Artifact formation through degradation of adsorbed sugars during the desorption process as described by Verhoeven et al. (1997) for the polyacrylate fiber was not observed.

Analytical Conditions. Capillary gas chromatography–mass spectrometry (GC-MS) analysis was performed using a Dani 86.10 gas chromatograph directly coupled to a Finnigan Mat Ion-Trap Detector 800 (Axel Semrau, Sprockhoevel, Germany). A Stabilwax column (Restek, Bad Homburg, Germany; 60m \times 0.32 mm \times 0.25 μ m) was used with Helium as the carrier gas at a linear flow rate of 40 cm/s. GC oven temperature was programmed as follows: 40 °C held for 3 min, increased to 220 °C at 5 °C/min, and held at 220 °C for 10 min. For thermal desorption, the SPME fiber remained in the injector for 20 min. Splitless injection mode was used, and the split valve was opened after 2 min. Mass spectra were generated in the electron impact (EI) as well as in the chemical ionization (CI) mode using methanol as the reactant gas. Identification of the volatiles was based on comparison of GC retention indices and mass spectra with those of authentic compounds. Quantitative determinations were carried out according to the standard addition method (see above) and using the most intense ions of the volatile compounds in the CI mode. The ions used were m/z 83 for hexanal, 109 for 6-methyl-5-hepten-2-one, and 193 for β -ionone.

Analysis of Amino Acids with an Amino Acid Analyzer. Free amino acids in spice paprika powders were determined according to the method described by Schröder and Eichner (1996). An Automated Amino Acid Analyzer LC 5001 (Biotronic, Maintal, Germany) was used.

Statistical Analysis. Quantitative data of volatile compounds as well as the determined activation energies were subjected to an error propagation calculation using Mathcad (version 8).

RESULTS AND DISCUSSION

Determination of Activation Energies. In Figures 1–3, the formation of volatile compounds in com-

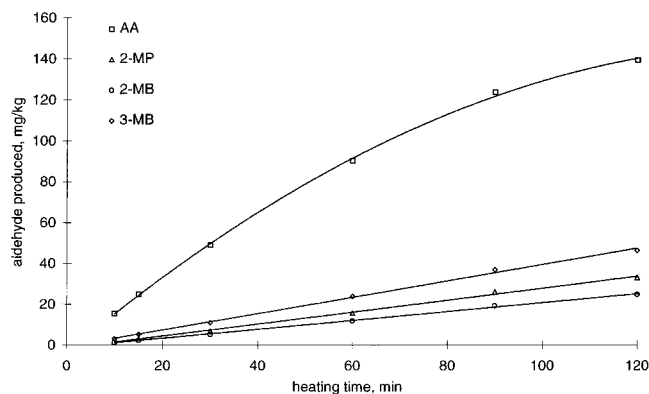


Figure 1. Formation of the Strecker aldehydes acetaldehyde (AA), 2-methylpropanal (2-MP), 2-methylbutanal (2-MB), and 3-methylbutanal (3-MB) as a function of heating time at 90 °C in commercially available spice paprika powder (A_w -value 0.52).

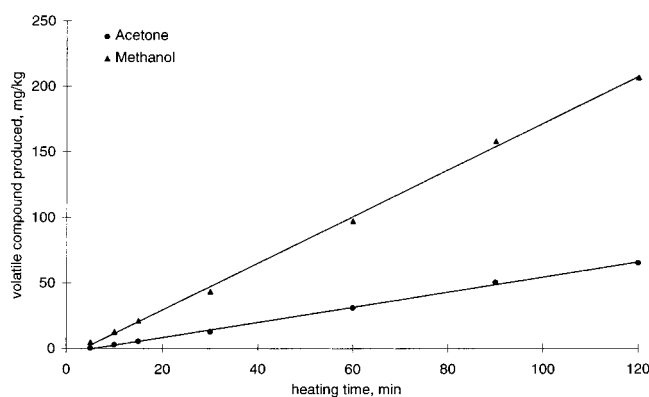


Figure 2. Formation of acetone and methanol as a function of heating time at 90 °C in commercially available spice paprika powder (A_w -value 0.52).

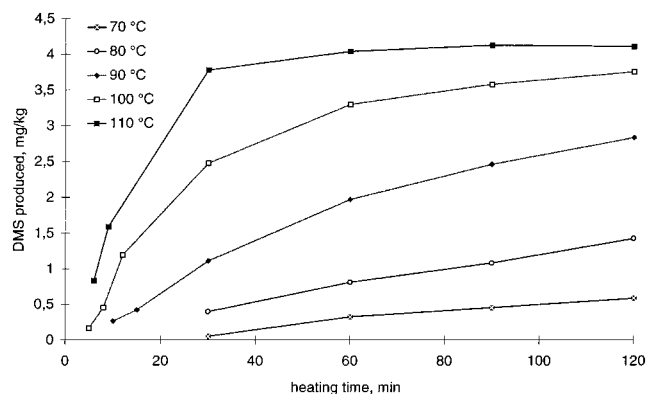


Figure 3. Formation of dimethyl sulfide (DMS) in commercially available spice paprika powder (A_w -value 0.52) as a function of heating temperature and time.

mercially dried spice paprika powders was determined by means of headspace-GC and is shown as a function of heating time and temperature. Figures 1 and 2 present the 90 °C isotherms as an example since the isotherms of the other temperatures applied (70, 80, 100, and 110 °C) showed the same characteristics.

As can be seen in Figure 1, the formation of all Strecker aldehydes except AA followed a straight line. The formation of AA can be described by a parabolic curve. However, in the range of 10–60 min, the data also fit the straight line very well ($r^2 = 0.997$). Therefore, the reaction kinetics of all aldehydes were assumed to be zero order in that time interval. Since numerous

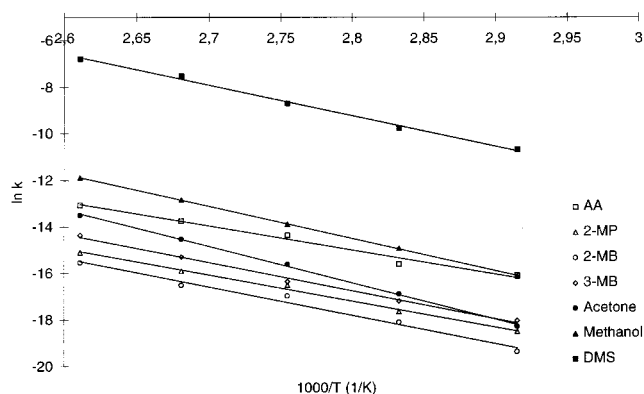


Figure 4. Arrhenius plots for the formation of volatile compounds in commercially available spice paprika powder.

reaction steps contribute to the formation of Strecker aldehydes, the observed reaction order is a pseudo-order (Westphal et al., 1996). Chan and Reineccius (1994) found that the r^2 of the curves of the formation of Strecker aldehydes in aqueous model systems were consistently the best following a zero order. Lerici et al. (1990) related the formation of carbon dioxide in aqueous glucose/glycine model systems to the Strecker degradation of the pertinent amino acid. They too found a zero-order reaction rate. The results of this study confirm the results described in the literature mentioned above. The zero-order reaction rates of the Strecker aldehyde formation were determined by calculating the slope of the function "amount of aldehyde formed versus time". These rate constants were calculated for different temperatures, and the activation energies were calculated using the Arrhenius equation (Figure 4).

The activation energies of the formation of acetone and methanol were determined similarly (Figures 2 and 4). Their formation followed a straight line too, suggesting a pseudo-zero-order reaction kinetic as well.

The formation of DMS shown in Figure 3 followed a first-order kinetic since it is produced by hydrolysis of its precursor SMM (Williams, 1973). The maximum amount of DMS produced (90 min, 110 °C) corresponds to the amount of SMM originally present in the powder after complete hydrolysis. In this way, DMS can be used for the quantitative determination of SMM (Williams, 1973; Hysert et al., 1979). Determining the first-order reaction rate constants of DMS production by plotting $\ln[C_{(\text{SMM})}^0 - C_{(\text{DMS})}]$ versus time revealed that the data fit the assumed first-order reaction kinetic (Figure 5). Thus, the activation energy of DMS formation was calculated via the Arrhenius plot (Figure 4) using the first-order rate constants from Figure 5.

As can be seen in Figure 4, all Arrhenius plots followed a straight line, revealing that each particular reaction mechanism of the formation of volatile compounds is kinetically uniform in the chosen temperature interval (Westphal et al., 1996).

Table 1 lists all activation energies obtained. The standard errors of the activation energies ranged from 6.2 to 9.2%. The activation energies given in brackets were determined by different authors. Since substrate composition, pH values, and reaction conditions were different, these activation energies cannot be directly compared with the data obtained for this study. It is important to note that in this investigation the spice paprika was heated in a dry state (water content 6.8%),

Table 1. Activation Energies for the Formation of Volatile Compounds in Spice Paprika Powder (kJ/mol)

acetaldehyde	2-methylpropanal	2-methylbutanal	3-methylbutanal	acetone	methanol	dimethyl sulfide
86.3	93.8	101.8	101.3 (80.4) ^a	130.7	114.2 (148) ^b	109.7 (115–132) ^c

^a Aqueous model system (Chan and Reineccius, 1994). ^b Citrus pectin solution, pH 5.5 (Boettger et al., 1996). ^c Different vegetables (Kovatscheva, 1978; Williams, 1973).

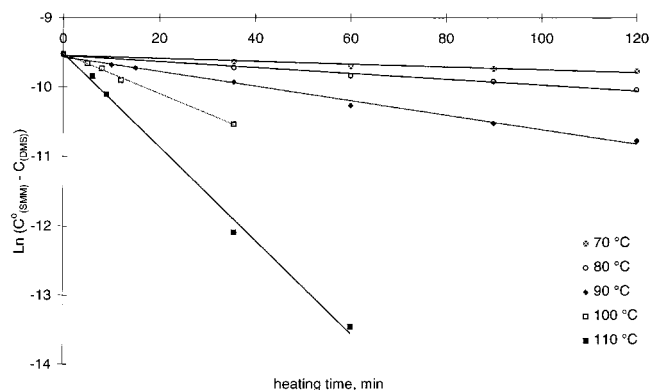


Figure 5. Determining the first order reaction rates of the formation of dimethyl sulfide (DMS) from *S*-methylmethionine (SMM) in commercially available spice paprika powder.

whereas all literature data was obtained at high water contents. The pH value of the paprika powder investigated was 5 (5 g of powder suspended in 25 mL of water). Activation energies in general may depend on the pH value which is the case here for the hydrolytic formation of methanol and DMS (Boettger et al., 1996; Williams, 1973). Boettger et al. (1996) found that the activation energies of methanol formation in citrus pectin solution decreased from 148 kJ/mol at pH 5.5 to 65 kJ/mol at pH 9. As the authors suggested, this decrease is due to a change in reaction mechanism of pectin methylester hydrolysis, which proceeds from acid catalyzed to base catalyzed. The methanol formation observed in the paprika powders of this study was due to thermally induced, nonenzymatic pectin methylester hydrolysis as was anticipated. The high value of the activation energy determined (Table 1) as well as additional investigations regarding the pH and the A_w -value dependence of the methanol formation in paprika (Cremer, 1999) unambiguously prove that under the given conditions (dry heating at 70–110 °C) methanol is solely produced by nonenzymatic hydrolysis even though the pectin methyl esterase is not completely inactivated during the drying and grinding of the paprika fruits (Cremer, 1999).

The pH dependence of the activation energy of the DMS formation is explained by a change in the hydrolysis mechanism of the precursor compound SMM (Williams, 1973). At low pH values (pH 2–5), DMS is simply formed by nucleophilic substitution of the dimethyl sulfonium group by water. At higher pH values (pH > 7), the DMS is produced by an intramolecular nucleophilic substitution caused by the SMM carboxyl group (Figure 6). This is proved by the fact that at low pH values the DMS formation is accompanied by the production of the amino acid homoserine (HS), while at higher pH values the homoserine lactone is detectable (Sawamura et al., 1978).

The activation energies for the formation of Strecker aldehydes are not influenced by the pH (Chan and Reineccius, 1994).

As can be seen in Table 1, the activation energy of the formation of AA was below those obtained for the

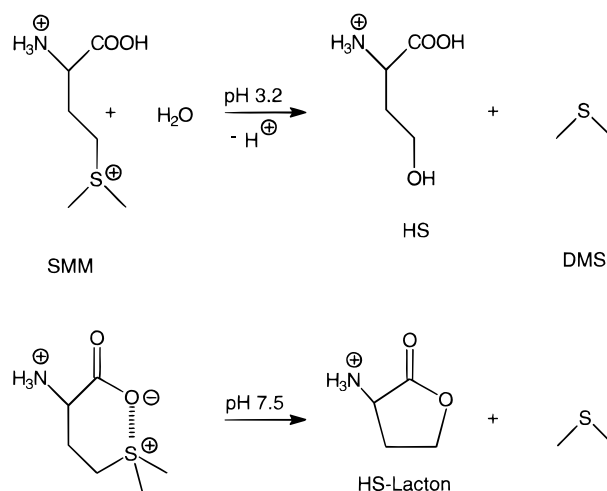


Figure 6. Proposed formation of dimethyl sulfide (DMS) and homoserine (HS) from *S*-methylmethionine (SMM) at different pH values (Sawamura et al., 1978).

other aldehydes. It could be assumed that this may be due to the fact that the β -carbon atom of alanine carries no further substitutes as valine, leucine, and isoleucine do, resulting in a lower activation energy. However, this assumption could not be confirmed in a further determination of the activation energies of Strecker aldehyde formation in a low moisture model system containing glucose, Ala, Val, Ile, and Leu at a molar ratio of 20:1:1:1:1 (Cremer, 1999). Thus, it is assumed that it is more likely that the activation energy of AA formation observed is the sum of the activation energies of different reaction pathways for AA formation such as Strecker degradation, lipid oxidation (Yasuhara and Shibamoto, 1991; Josephson and Glinka, 1989), and/or carotenoid degradation (Baltes, 1983).

Determination of Strecker Aldehydes in Different Spice Paprika Powders. This investigation was carried out in order to compare the heat-induced production of Strecker aldehydes in paprika powders of different origin. The powders analyzed were of Brazilian, Hungarian, and one unknown origin, as well as one Hungarian powder that had been produced from the Cultivar Kalocsa 622.

The characteristics of Strecker aldehyde formation as a function of heating time observed for the different samples were almost identical to the example that had already been shown in Figure 1. The amounts of Strecker aldehydes produced after heating the powders 60 min at 90 °C ranged from 79 to 119 (1.8–2.7) for AA, 14–19 (0.19–0.26) for 2-MP, 10–17 (0.12–0.20) for 2-MB and from 22 to 44 mg/kg (0.26–0.51 mmol/kg) for 3-MB for the different spice paprika samples investigated. The standard errors of these data which were determined by the standard addition method ranged from 1.4 to 4.3%. As can be seen from Figure 7, the respective normalized molar ratios of the amounts of Strecker aldehydes produced only differed slightly from sample to sample, suggesting that paprika powders can be characterized by a generalized pattern of Strecker

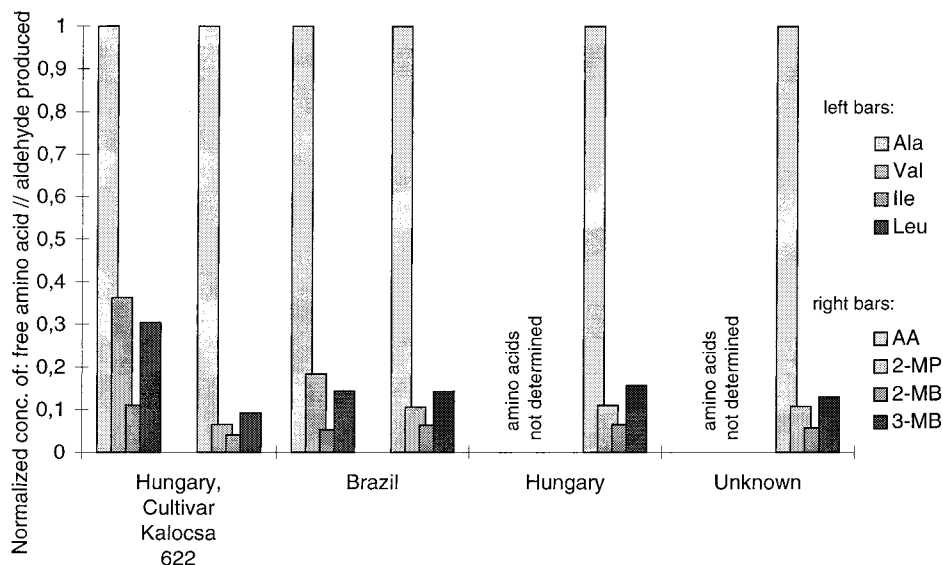


Figure 7. Normalized concentration levels of free amino acid contents in different spice paprika powders and normalized amounts of related Strecker aldehydes produced after heating the powders (A_w -value 0.52) 60 min at 90 °C.

aldehydes produced while heating the powders. The amounts of Strecker aldehydes produced can be arranged in the decreasing order $AA \gg 3\text{-MB} > 2\text{-MP} > 2\text{-MB}$ while the order of the amounts of the pertinent free amino acids present was $Ala \gg Val > Leu > Ile$ for two of the powders (Figure 7). The concentrations of the free amino acids ranged from 0.4 to 13.8 mmol/kg. Even though the concentration of Val exceeded the concentration of Leu, more 3-MB than 2-MP was formed. Thus, it can be concluded that the order of the Strecker aldehyde formation reflects the order of the amounts of the corresponding free amino acids present in paprika powders solely in a first approximation. Even though the results clearly demonstrate that the formation of Strecker aldehydes is correlated with the concentration of the corresponding free amino acids, they also suggest that other factors exist which influence the extent of the Strecker aldehyde formation. Such a factor could be, for example, the different reactivity of amino acids toward the Strecker reaction as has been reported by Cremer (1999).

Considering the concentration level of AA in Figures 1 and 7, it is important to note that the large amount of AA, which exceeds the amounts of the other aldehydes, cannot only be explained by the high concentration of free Ala present in the paprika powders. As Figure 1 clearly demonstrates, the amount of AA present in the paprika powder exceeded the levels of the other aldehydes from the beginning of heating. This has already been described in the literature for the volatiles of other fruits such as tomato (Nelson and Hoff, 1969; Kazeniak and Hall, 1970). According to the review given by Kazeniak and Hall (1970), it is likely that AA is produced by biochemical reactions in the fruit since it is an intermediate product in the respiration of higher plants (Fishbein, 1979; Podd and Van Staden, 1998). This is also supported by Mateo et al. (1997). The latter authors state that low molecular weight volatiles (2,3-butandiol, acetoin, and acetaldehyde) in processed *Capsicum* are probably produced biologically during processing of the fruits. It is also important to be aware of the fact that paprika fruits are usually dried as whole fruits (Govindarajan, 1985; Mateo et al., 1997), which is supposed to result only in a slight reduction of the

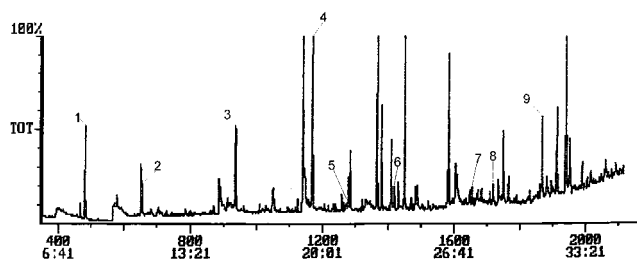


Figure 8. Gas chromatogram (GC-ITD) of the volatiles of a spice paprika powder (A_w -value 0.52) heated 60 min at 90 °C. Sampling: SPME liquid sampling, 100 μ m PDMS fiber. Peaks: (1) hexanal; (2) limonene; (3) 6-methyl-5-hepten-2-one; (4) tetramethylpyrazine (tentatively); (5) 2-methoxy-3-isobutylpyrazine; (6) phenylacetaldehyde; (7) methylsalicylate; (8) α -ionone (tentatively) (9) β -ionone.

concentration of the volatile compounds present in the paprika fruit. Other authors found either significant or only slight quantitative changes in the volatile compounds composition of plant foods (herbs) during drying as has been reported by Venskutonis (1997). Thus, it is justified to assume that part of the amount of AA found in paprika powder may have already been present in the samples prior to heating, while the other part was produced during the heating process (see Figure 1).

Determination of Hexanal, 6-Methyl-5-hepten-2-one, and β -Ionone. These compounds could easily contribute to off-flavors since they have very low odor thresholds [4.5, 50, and 0.007 μ g/L according to Buttery et al. (1990)]. According to investigations by Wilkins (1992), hexanal may contribute to an off-flavor of spice paprika. In Figure 8, a SPME-GC-MS chromatogram of a heated spice paprika powder is shown. The peaks of volatiles this paper addresses and those that are typically found in paprika were indicated by numbers. The relevant compounds were quantitatively determined by means of the standard addition method which has to be utilized to get the absolute concentrations of the volatiles by SPME (Pawliszyn, 1997). Each value was determined five times. The relative standard errors of the quantitative results ranged from 15.8 (hexanal) to 28.9% (β -ionone). The relative standard deviations (SD) determined for the GC-MS peak areas (most

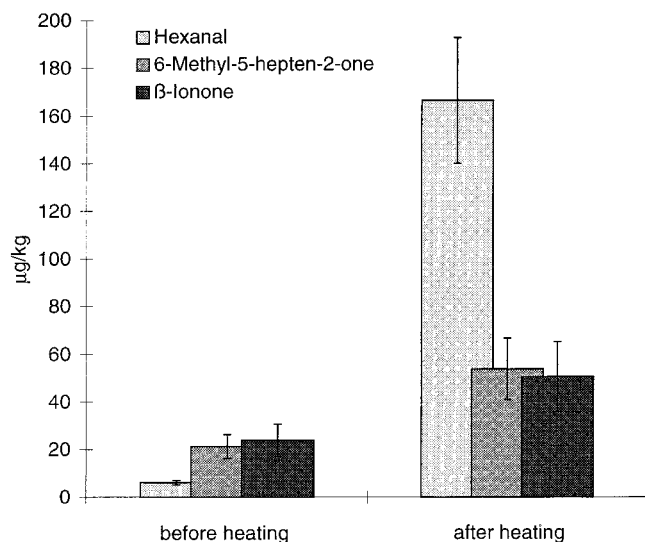


Figure 9. Content of volatile compounds in spice paprika powder before and after heating it 60 min at 90 °C.

intense ion m/z of each individual compound integrated) of eight different compounds (hexanal, m/z 83; limonene, m/z 81; 6-methyl-5-hepten-2-one, m/z 109; benzaldehyde, m/z 107; phenylacetaldehyde, m/z 121; methylsalicylate, m/z 153; β -ionone, m/z 193; and 1-nonen-4-one, m/z 123; concentration levels \approx 0.002 mg/L) after SPME liquid sampling gave a mean value of $14 \pm 7\%$. This is comparable with the results obtained by Yang and Peppard (1994). These authors report the SD of the concentrations of 25 aroma compounds determined in a test mixture (1 mg/L) by SPME. Their SD values ranged from 1.4 to 17.8% (mean value 6.8%). It is interesting to note that the concentrations chosen by these authors were approximately 500 times higher than those chosen for this study.

The analyzed volatile compounds were identified by comparing their mass spectra (recorded in the EI- and CI-mode) with those of the authentic compounds. The formation of 6-methyl-5-hepten-2-one which was first recorded by Luning et al. (1994) was confirmed, whereas the formation of β -ionone was probably described for the first time. The formation of both compounds was predictable since *Capsicum* contains β -carotene (β -ionone precursor) as well as lycopene (6-methyl-5-hepten-2-one precursor). Until recently, the carotenoids which are typically known to produce 6-methyl-5-hepten-2-one (lycopene, γ -, δ -, and ζ -carotene) had never been found in any variety nor any ripening stage of *Capsicum* (Curl, 1962; Govindarajan, 1986b; Deli et al., 1996). Probably Mueller (1997) was the first to report the occurrence of lycopene in red ripe *Capsicum annuum*. Since 6-methyl-5-hepten-2-one is regarded as a marker compound for the degradation of lycopene the results of this study as well as those of Luning et al. (1994) confirm that *Capsicum annuum* fruits contain lycopene.

In Figure 9, the amounts of hexanal, 6-methyl-5-hepten-2-one, and β -ionone present in a spice paprika sample are shown as a function of heating time. As can be seen, heating increased the concentration of these compounds. It is striking that the amount of hexanal, which is known as an oxidation product of enzymatic as well as autoxidative linoleic acid oxidation, increased strongly with heating. Thus, it could be used as a marker compound for heat treatment of paprika. Ac-

cording to Luning et al. (1995), Biacs et al. (1992), Daood and Biacs (1986), and Chen and Gutmanis (1968), it is likely that autoxidative as well as lipoxygenase (LOX, probably of type-2) catalyzed oxidation processes contribute to lipid degradation in *Capsicum*. LOX activity is located in the *Capsicum* seeds (Daood and Biacs, 1986) which are typically present at a 5% level in paprika powders (Govindarajan, 1986b). LOX activity was observed to decrease markedly from the green ripe to the red ripe stage at which the fruits are harvested (Luning et al., 1995). As a whole, it is likely that the amount of hexanal found in the unheated paprika powder originated from an auto- and enzyme-catalyzed oxidation of linoleic acid while the increased production observed during the heating experiment of this study (Figure 9) was due to autoxidative linoleic acid degradation.

ABBREVIATIONS USED

SD, standard deviation; HS-GC, headspace gas chromatography; SPME, solid-phase microextraction; GC-MS, gas chromatography mass spectrometry; EI, electron impact ionization; CI, chemical ionization; DMS, dimethyl sulfide; AA, acetaldehyde; 2-MP, 2-methylpropanal; 2-MB, 2-methylbutanal; 3-MB, 3-methylbutanal; SMM, *S*-methylmethionine; HS, homoserine.

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