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The effect of pH on the formation of aroma compounds produced by heating a model system containing L-ascorbic acid with L-threonine/L-serine

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ABSTRACT

The identification of aroma compounds, formed from the reactions of L-ascorbic acid with L-threonine/L-serine at five different pH values (5.00, 6.00, 7.00, 8.00, or 9.55) and 143 ± 2 °C for 2 h, was performed using a SPME–GC–MS technique, and further use of LRI. The results showed 35 aroma compounds. The reaction between L-ascorbic acid and L-threonine/L-serine led mainly to the formation of pyrazines. Many of these were alkylpyrazines, such as 2-methylpyrazine, 2,5-dimethylpyrazine, 2-ethylpyrazine, 2-ethyl-6-methylpyrazine, 2-ethyl-5-methylpyrazine, 3-ethyl-2,5-dimethylpyrazine, 2,3-diethyl-5-methylpyrazine, and 3,5-diethyl-2-methylpyrazine; other compounds identified were furans and aldehydes. More volatiles were generated in L-ascorbic acid with L-threonine systems than in L-ascorbic acid with L-serine systems. The studies showed that furans, such as furfural, 2-furanmethanol, benzofuran, 2,5-furandicarboxaldehyde and 2-furfurylfuran were formed mainly at acidic pH. In contrast, higher pH values could promote the production of pyrazines.

1. Introduction

The Maillard reaction is considered as the most important reaction in food chemistry. It results in the formation of odour, aroma and pigments which are characteristic of baked, roasted and broiled foods. After reducing carbohydrates, L-ascorbic acid (ASA) appears to be the most widely studied carbonyl component in the processes of non-enzymatic browning. This is due, on the one hand, to its significant presence in food products and, on the other, to the interesting chemical transformations which it undergoes over the course of these processes. A series of researches on the behaviour of ASA in the presence of amino acids via the Maillard reaction is reported in the literature (Davidek, Velisek, Zelinkova, & Kubelka, 1977; Davies & Wedzicha, 1994; Fan et al., 2006; Hartmann, Scheide, & Ho, 1984; Kennedy, Rivera, Warner, Lloyd, & Jumel, 1989; Loscher, Kroh, Westphal, & Vogel, 1991; Míková & Davídek, 1975; Obretenov et al., 2002; Rogacheva, Kuncheva, Panchev, & Obretenov, 1995; Rogacheva, Kuntcheva, Panchev, & Obretenov, 1999; Rogacheva, Verhé, & Obretenov, 1996; Seck & Crouzet, 1981; Yano, Hayashi, & Namiki, 1976; Yin & Brunk, 1991).

In contrast, there is a lack of research findings on the formation of aroma compounds. In the reaction of L-dehydroascorbic acid with ammonia and glycine, five alkylpyrazines were identified (Davidek et al., 1977). Five derivatives of imidazole were found in the reaction mixture of ASA and ammonia/glycine (Míková & Davídek, 1975). Rogacheva et al. (1996) reported aroma compound formation in the interaction of ASA with glycine/lysine/glutamic acid and Seck and Crouzet (1981) reported formation of volatile compounds in ASA–phenylalanine model systems during heat treatment. As far as we know, data on the formation of aroma compounds produced by heating a model system containing ASA with L-threonine (Thr)/L-serine (Ser) are not available.

Several factors influence the generation of flavours by the Maillard reaction. The pH at which the reaction is conducted greatly influences the nature of the volatiles formed and, hence, the flavour of the final product and the reaction temperature and time mainly influence the kinetics of the reaction, whilst leaving the nature of the volatiles broadly unchanged (Jousse, Jongen, Agterof, Russell, & Braat, 2002). High temperature is a favourable condition for Maillard reaction (Ellis, 1959). Solid-phase microextraction (SPME) is a suitable technique for the analysis of flavour release from Maillard reaction solutions (Obretenov et al., 2002). In this study, we evaluated the effect of pH on the formation of aroma compounds produced by heating a model system containing ASA with Thr/Ser. Experiments were performed over 2 h at 143 ± 2 °C in pH 5, 6, 7, 8, and 9.55 aqueous solutions. Aroma compounds were extracted by SPME.

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2. Materials and methods

2.1. Reagents

ASA (analytical grade) was from Sinopharm Chemical Reagent Co., Ltd. (China). Thr and Ser (99% enrichment) were from Shanghai Yuanju Biological Technology Co., Ltd. (China). Na_2HPO_4, NaH_2PO_4 and NaOH were of analytical grade.

2.2. Model reaction of amino acid with ASA

Four millimoles of ASA were dissolved in 40 ml of phosphate buffer (0.2 M), and the pH of the solution was adjusted to 5.00, 6.00, 7.00, 8.00, or 9.55 using NaOH. Four millimoles of amino acid (Thr or Ser) were added to the solution. The mixtures were then sealed in 48 ml Synthware® glass vials (Beijing Synthware Glass, Inc, China) and heated whilst stirring at 143 ± 2 °C for 2 h in an oil bath. The reactions were stopped by cooling under a stream of cold water.

2.3. Headspace-SPME–GC–MS

2.3.1. SPME sampling

The assayed fibres were divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) (50/30 μm thickness) and carboxen/polydimethylsiloxane (CAR/PDMS) (75 μm thickness) (Supelco, Bellefonte, PA, USA). Before the SPME fibre was inserted into the vial, the sample was equilibrated for 15 min at 40 °C. The extraction time was 50 min at 40 °C.

2.3.2. Gas chromatography–mass spectrometry

Analyses were performed using an Agilent 6890 N gas chromatograph coupled to a Agilent 5975i mass selective detector (Agilent Technologies, Inc., USA). Volatiles were separated using a DB-5 capillary column [30 m × 0.25 mm(i.d) × 0.25 μm]. The SPME fibre was desorbed and maintained in the injection port at the oven temperature (250 °C) and for the time (4.0 min) suggested by the manufacturer. The injection port was in split mode and split ratio was 1:30. The temperature programme was isothermal for 5 min at 40 °C, raised to 260 °C at a rate of 5 °C min^{-1} and then raised to 280 °C at a rate of 15 °C min^{-1} and held for 1 min. C5–C22 n-alkanes (Pure Chemical Analysis Co., Ltd.) were run under the same chromatographic conditions as the samples to calculate the linear retention indices (LRI) of detected compounds. The transfer line to the mass spectrometer was maintained at 280 °C. The mass spectra were obtained using a mass selective detector by electronic impact at 70 eV, a multiplier voltage of 1753 V, and collecting data at a rate of 1 scan s^{-1} over the m/z range of 30–400 u.m.a. Compounds were tentatively identified by comparing their mass spectra with those contained in the Nist05 and Wiley275 libraries and by comparison of their LRI with those reported in the literature. Area counts of volatiles

Table 1
Effect of pH on the formation of aroma compounds produced by heating a model system containing ASA with Thr/Ser (GC–TIC peak areas × 10^6).

No.	Compound	Mol. wt	LRI[a]	pH 5		pH 6		pH 7		pH 8		pH 9.55	
				Thr	Ser	Thr	Ser	Thr	Ser	Thr	Ser	Thr	Ser
1	2-Methyl-2-butenal	84	<800	ND[b]	ND	18.7	ND	36.9	ND	ND	ND	ND	ND
2	2-Methylpyrazine	94	819 ± 5.8	9.9	7.9	17.1	34.4	24.9	65.4	20.5	57.7	15.0	55.8
3	Furfural	96	826 ± 6.4	101	40.3	11.8	3.0	ND	ND	ND	ND	ND	ND
4	2-Furanmethanol	98	858 ± 3.5	ND	2.6	2.7	0.6	0.2	ND	ND	ND	ND	ND
5	2,5-Dimethylpyrazine	108	906 ± 3.5	42.3	21.4	83.9	56.2	121	146	125	183	123	172
6	2-Ethylpyrazine	108	910 ± 3.1	ND	6.4	ND	23.9	29.1	46.7	34.1	30.1	28.4	29.8
7	Benzofuran	118	988 ± 2.0	7.1	7.6	3.1	7.3	2.0	1.4	ND	ND	ND	ND
8	2-Ethyl-6-methylpyrazine	122	991 ± 1.2	2.0	1.6	8.1	4.7	41.1	23.1	52.6	31.1	55.1	35.4
9	2-Ethyl-5-methylpyrazine	122	994 ± 1.6	24.4	13.6	67.1	47.4	31.1	126	45.6	170	51.3	184
10	2-Ethyl-3-methylpyrazine	122	995 ± 1.7	ND	ND	ND	ND	132	ND	125	ND	131	ND
11	2,5-Furandicarboxaldehyde	124	1034 ± 1.2	19.1	12.9	16.1	10.8	9.1	10.8	5.9	9.4	6.1	9.8
12	3-Ethyl-2,5-dimethylpyrazine	136	1071 ± 0.8	33.7	5.2	99.5	15.7	300	46.1	370	50.7	382	54.5
13	2-Ethyl-3,5-dimethylpyrazine	136	1077 ± 1.1	4.1	ND	7.4	2.1	19.3	9.4	24.6	13.9	25.5	15.8
14	5-Ethyl-2,3-dimethylpyrazine	136	1079 ± 0.8	ND	ND	7.7	4.0	26.3	14.7	33.8	20.1	40.9	22.9
15	3-Ethyl-2-hydroxy-2-cyclopenten-1-one	126	1082 ± 0.9	32.1	17.3	45.3	30.6	22.1	24.7	10.7	15.2	9.1	13.8
16	2,5-Diethylpyrazine	136	1085 ± 0.8	2.0	1.3	8.9	4.7	27.5	16.8	30.0	16.5	29.5	17.2
17	2-Methyl-5-propylpyrazine	136	1088 ± 0.8	ND	ND	ND	ND	8.6	ND	6.8	2.3	7.0	3.1
18	2-Furfurylfuran	148	1089 ± 0.7	8.8	6.7	8.0	6.7	ND	3.4	ND	ND	ND	ND
19	2-Allyl-5-methylpyrazine	134	1090 ± 0.8	ND	ND	ND	ND	6.5	8.3	8.3	ND	8.5	16.4
20	2-Isopropyl-5-methyl-2-hexenal	154	1097 ± 0.7	3.4	ND	7.5	ND	12.1	ND	10.1	ND	14.1	ND
21	3-Butylpyridine	135	1101 ± 0.6	ND	ND	ND	ND	5.2	ND	4.3	ND	3.6	ND
22	2,3-Diethyl-5-methylpyrazine	150	1145 ± 0.8	4.4	1.2	18.2	2.7	87.3	7.5	127	7.2	131	7.5
23	3,5-Diethyl-2-methylpyrazine	150	1148 ± 0.4	8.3	2.0	35.3	5.2	181	15.1	287	14.4	302	14.9
24	3,5-Dimethyl-2-propylpyrazine	150	1152 ± 0.5	5.9	ND	6.4	ND	9.7	ND	12.0	ND	12.0	ND
25	2-Acetyl-3-ethylpyrazine	150	1158 ± 0.5	ND	ND	ND	ND	10.0	ND	17.0	ND	18.0	ND
26	1-Furfurylpyrrole	147	1172 ± 0.4	6.1	7.9	12.9	9.8	20.9	8.2	21.0	4.1	23.4	3.9
27	3-Sec-butyl-2,5-dimethylpyrazine	164	1187 ± 0	ND	ND	ND	ND	ND	ND	2.7	ND	2.8	ND
28	2,6-Diethyl-3,5-dimethylpyrazine	164	1217 ± 2.8	ND	ND	1.8	ND	6.1	ND	ND	ND	ND	ND
29	2,5-Diethyl-3,6-dimethylpyrazine	164	1219 ± 1.2	ND	ND	ND	ND	ND	ND	10.8	ND	12.2	ND
30	2,3,5-Trimethyl-6-propylpyrazine	164	1233 ± 2.7	ND	ND	1.6	ND	5.4	ND	8.0	ND	10.0	ND
31	2-Isoamyl-6-methylpyrazine	164	1249 ± 6.2	ND	ND	2.2	ND	4.5	ND	3.1	ND	6.8	ND
32	2,5-Dimethyl-3-isoamylpyrazine	178	1308 ± 0	2.3	ND	5.9	ND	7.7	ND	9.1	ND	10.7	ND
33	2,3,5-Trimethyl-6-isopentylpyrazine	192	1379 ± 0	ND	ND	1.8	ND	2.2	ND	3.2	ND	3.1	ND
34	2,4-Di-t-butylphenol	206	1502 ± 0.5	12.5	9.0	18.2	12.0	17.6	25.6	25.2	19.8	25.7	21.7
35	3,6-Dibutyl-2,5-dimethylpyrazine	220	1612 ± 0	ND	ND	8.3	ND	4.8	ND	12.2	ND	9.0	ND

[a] LRI: LRI calculated for a DB-5 capillary column and LRI in agreement with literature (Ansorena, Gimeno, Astiasarán, & Bello, 2001; Baek, Kim, Ahn, Nam, & Cadwallader, 2001; Beal & Mottram, 1994; Moon, Cliv, & Li-Chan, 2006; Parker, Hassell, Mottram, & Guy, 2000; Rostad & Pereira, 1986; Sanz, Czerny, Cid, & Schieberle, 2002; Siegmund & Murkovic, 2004; Wagner, Czerny, Bielohradsky, & Grosch, 1999).
[b] ND: not detected.

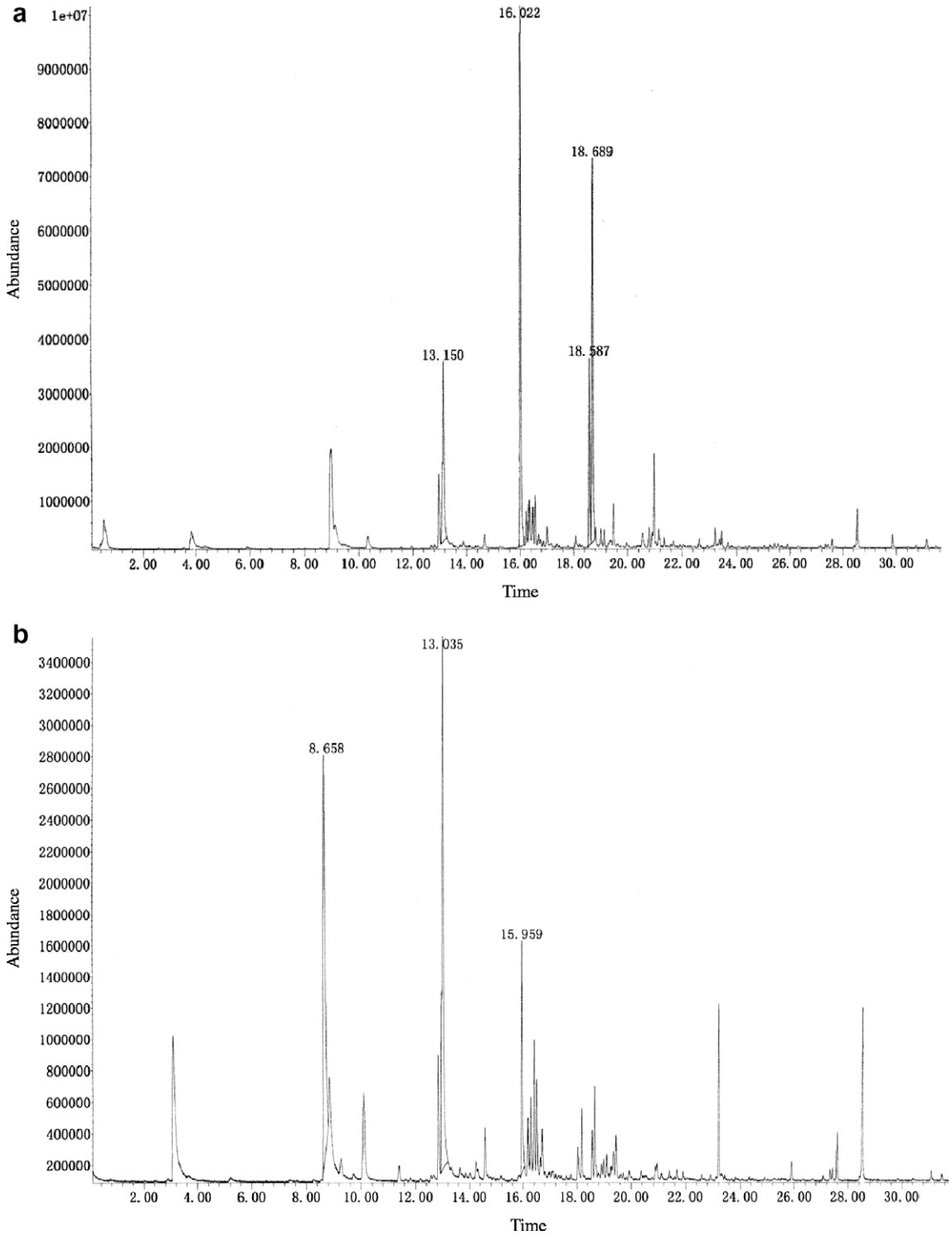

Fig. 1. Total ion chromatogram of aroma compounds produced by heating a model system containing ASA with Thr (a)/Ser (b) at pH 7 and 143 ± 2 °C for 2 h.

were provided by integrating in the initial threshold 16.5 using Agilent chemstation.

3. Results and discussion

As a result of our experiments, we discovered that DVB/CAR/PDMS-coated fibres extracted higher total amounts of volatile compounds than did CAR/PDMS. The volatile compounds extracted by DVB/CAR/PDMS included all compounds extracted by CAR/PDMS. Therefore, in this study, we report the volatile compounds extracted by DVB/CAR/PDMS. The major headspace components of the model system involving ASA with Thr/Ser at five different pHs (5.00, 6.00, 7.00, 8.00, 9.55) are listed in Table 1, according to their elution order. Total ion chromatograms of aroma compounds produced by heating a model system containing ASA with Thr/Ser at pH 7 and 143 ± 2 °C for 2 h, extracted with DVB/CAR/PDMS fibres, are shown in Fig. 1. The 35

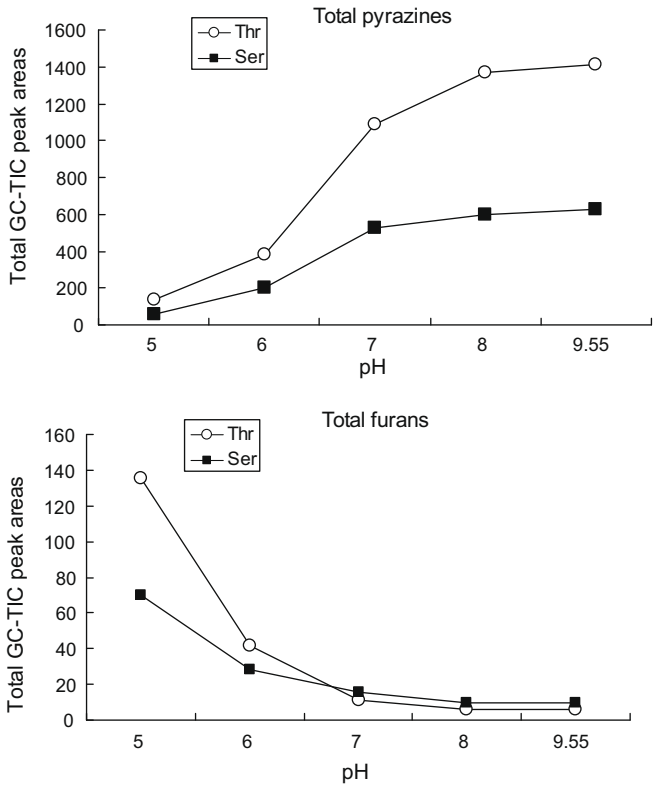

Fig. 2. Comparison of total pyrazines and total furans [furfural (3), 2-furanmethanol (4), benzofuran (7), 2,5-furandicarboxaldehyde (11), and 2-furfurylfuran (18)] generation in pH 5, 6, 7, 8, and 9.55 aqueous solutions by heating a model system containing ASA with Thr/Ser. Total GC–TIC peak areas $\times 10^6$.

compounds presented were those which gave significant peaks in GC–TIC. They can be classified as pyrazines, furans, aldehydes, and others.

More volatiles were generated in ASA with Thr systems than in ASA with Ser systems. The volatile compounds identified in the model system involving ASA with Thr included all compounds identified in Ser, and 2-methyl-2-butenal (1), 2-ethyl-3-methylpyrazine (10), 2-isopropyl-5-methyl-2-hexenal (20), 3-butylpyridine (21), 3,5-dimethyl-2-propylpyrazine (24), 2-acetyl-3-ethylpyrazine (25), 3-sec-butyl-2,5-dimethylpyrazine (27), 2,6-diethyl-3,5-dimethylpyrazine (28), 2,5-diethyl-3,6-dimethylpyrazine (29), 2,3,5-trimethyl-6-propylpyrazine (30), 2-isoamyl-6-methylpyrazine (31), 2,5-dimethyl-3-isoamylpyrazine (32), 2,3,5-trimethyl-6-isopentylpyrazine (33), and 3,6-dibutyl-2,5-dimethylpyrazine (35), not be identified in the model system involving ASA with Ser.

In Fig. 2, the formations of total pyrazines and total furans are compared; the total peak areas of total pyrazines increased significantly as the pH increased, but the total peak areas of total furans decreased as the pH increased in the model system involving ASA with Thr/Ser at five different pHs. The results indicate that low pH conditions favoured the formation of furfural (3) and, also, 2-furanmethanol (4), benzofuran (7), 2,5-furandicarboxaldehyde (11) and 2-furfurylfuran (18). As shown in Fig. 2, total furan peak areas in the reaction solution of ASA with Thr increased markedly from 41.7×10^6 at pH 6 to 136×10^6 at pH 5. Like the Thr system, the formation of total furans (furfural (3), 2-furanmethanol (4), benzofuran (7), 2,5-furandicarboxaldehyde (11), and 2-furfurylfuran (18)) also increased obviously whilst the pH of the reaction solution was lower than 6 in the Ser system. For furfural, whilst the pH of the reaction solution was lower than 6, its content in the reaction solution increased markedly. High pH values did not

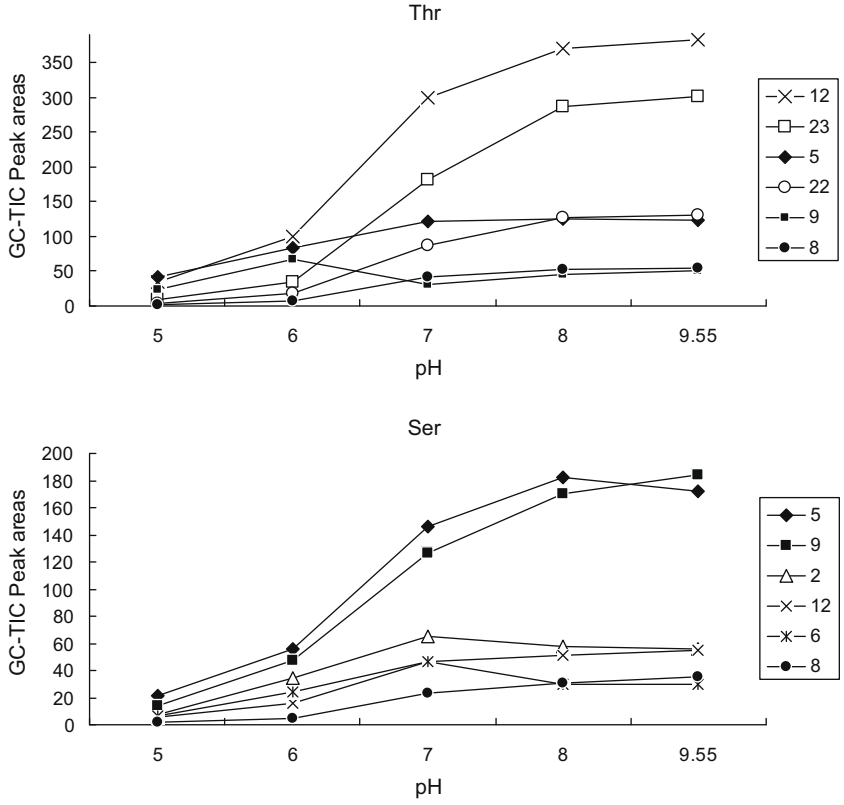

Fig. 3. Comparison of main pyrazines generation in pH 5, 6, 7, 8, and 9.55 aqueous solutions by heating a model system containing ASA with Thr/Ser. Note: Nos. 2, 5, 6, 8, 9, 12, 22, and 23 indicate 2-methylpyrazine, 2,5-dimethylpyrazine, 2-ethylpyrazine, 2-ethyl-6-methylpyrazine, 2-ethyl-5-methylpyrazine, 3-ethyl-2,5-dimethyl-pyrazine, 2,3-diethyl-5-methylpyrazine, and 3,5-diethyl-2-methylpyrazine, respectively. GC-TIC peak areas $\times 10^6$.

favour the formation of the five reaction products (namely furfural (3), 2-furanmethanol (4), benzofuran (7), 2,5-furandicarboxaldehyde (11), and 2-furfurylfuran (18)). In contrast, high pH values could promote the production of pyrazines. When the pH of reaction solution was above 6, the total pyrazines increased obviously in the model system involving ASA with Thr/Ser. In Fig. 3, the main pyrazines [2-methylpyrazine (2), 2,5-dimethylpyrazine (5), 2-ethylpyrazine (6), 2-ethyl-6-methylpyrazine (8), 2-ethyl-5-methylpyrazine (9), 3-ethyl-2,5-dimethylpyrazine (12), 2,3-diethyl-5-methylpyrazine (22), and 3,5-diethyl-2-methylpyrazine (23)] generation in pH 5, 6, 7, 8, and 9.55 aqueous solutions, by heating a model system containing ASA with Thr/Ser, are compared. Higher amounts of pyrazines were identified from the reaction of ASA with Thr/Ser from pH 8.00 to 9.55. The thermal degradation of ASA can produce many carbonyl compounds (Vernin, Chakib, Rogacheva, Obretenov, & Párkányi, 1998). The base catalysis was probably due, both, to the increased reactivity of the amino group of the amino acid toward the carbonyl and to the increased rearrangement and fragmentation of ASA (Koehler & Odell, 1970). Pyrazines may contribute to the toasted, roasted, nutty, and burnt notes.

Benzofuran (Shephard, Nichols, & Braithwaite, 1999), furfural (3) and 3-ethyl-2-hydroxy-2-cyclopenten-1-one (Vernin et al., 1998) were products from the thermal degradation of ascorbic acid. 2-Furanmethanol (4) was formed by reduction of furfural. 2-Furfurylfuran was possibly formed by reduction of 2-furoylfuran, which was a product from thermal degradation of ascorbic acid (Vernin et al., 1998).

Pyrazine is one of the most important groups amongst the identified volatiles in the studied systems. They are widely distributed in food systems, especially foods processed at high temperatures and low humidity. A review on pyrazines in food has been published (Maga, 1992). There are several precursors or pathways for pyrazine compound generation. The α-amino carbonyls, which can be formed from the reactions between dicarbonyl compounds and amino acids during Strecker degradation, are generally considered to be the precursors of pyrazines. The dicarbonyl compounds, such as ethylglyoxal, butanedione, glyoxal and pyruvaldehyde, can be produced by thermal degradation of ascorbic acid (Vernin et al., 1998). Thr and Ser can release ammonia when heated in an aqueous solution (Sohn & Ho, 1995). During Maillard reactions and thermal degradation of ASA, some active intermediates, such as 2-hydroxypropanal, hydroxyacetaldehyde, hydroxyacetone and acetoin, can be produced (Vernin et al., 1998). These intermediates react with ammonia to generate α-amino ketones and then form pyrazines. An alternative pyrazine formation pathway is recognised in pyrolysis of serine or threonine. These α-amino carbonyls may react with each other to generate pyrazines during thermal processing (Wang & Odell, 1973).

4. Conclusions

The results have shown that the reaction between L-ascorbic acid and L-threonine/L-serine leads mainly to the formation of pyrazines. Many of these are alkylpyrazines, such as 2-methylpyrazine, 2,5-dimethylpyrazine, 2-ethylpyrazine, 2-ethyl-6-methylpyrazine, 2-ethyl-5-methylpyrazine, 3-ethyl-2,5-dimethylpyrazine, 2,3-diethyl-5-methylpyrazine and 3,5-diethyl-2-methylpyrazine; other compounds identified are furans and aldehydes. More volatiles are generated in ASA with Thr systems than in ASA with Ser systems. A clear tendency is observed for some classes of compounds to be formed more at higher or lower pH; for instance, furans, such as furfural, 2-furanmethanol, benzofuran, 2,5-furandicarboxaldehyde and 2-furfurylfuran, are more readily formed at lower pH, whilst pyrazines are inhibited by acidic conditions. These findings support an earlier observation that pH has a great influence on volatile compounds formed in Maillard-type reactions.

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References

Ansorena, D., Gimeno, O., Astiasarán, I., & Bello, J. (2001). Analysis of volatile compounds by GC–MS of a dry fermented sausage: Chorizo de Pamplona. *Food Research International, 34*, 67–75.

Baek, H. H., Kim, C. J., Ahn, B. H., Nam, H. S., & Cadwallader, K. R. (2001). Aroma extract dilution analysis of a beeflike process flavor from extruded enzyme-hydrolyzed soybean protein. *Journal of Agricultural and Food Chemistry, 49*, 790–793.

Beal, A. D., & Mottram, D. S. (1994). Compounds contributing to the characteristic aroma of malted barley. *Journal of Agricultural and Food Chemistry, 42*, 2880–2884.

Davidek, J., Velisek, J., Zelinkova, Z., & Kubelka, V. (1977). Pyrazine in the reaction of L-dehydroascorbic acid with ammonia and glycine. *Journal of Food Science, 42*, 277–278.

Davies, C. G. A., & Wedzicha, B. L. (1994). Ascorbic acid browning: The incorporation of C_1 from ascorbic acid into melanoidins. *Food Chemistry, 49*, 165–167.

Ellis, G. P. (1959). The Maillard reaction. In M. L. Wolfrom (Ed.), *Advances in carbohydrate chemistry* (pp. 63–134). New York: Academic Press.

Fan, X., Reneker, L. W., Obrenovich, M. E., Strauch, C., Cheng, R., Jarvis, S. M., et al. (2006). Vitamin C mediates chemical aging of lens crystallins by the Maillard reaction in a humanized mouse model. *Proceedings of the National Academy of Sciences of the United States of America, 103*, 16912–16917.

Hartmann, G. J., Scheide, J. D., & Ho, C. T. (1984). Effect of water activity on the major volatileś produced in a model system approximating cooked meat. *Journal of Food Science, 49*, 607–613.

Jousse, F., Jongen, T., Agterof, W., Russell, S., & Braat, P. (2002). Simplified kinetic scheme of flavor formation by the Maillard reaction. *Journal of Food Science, 67*, 2534–2542.

Kennedy, J. F., Rivera, Z. S., Warner, F. P., Lloyd, L. L., & Jumel, K. (1989). Analysis of carbohydrates and amino acids in aqueous solutions of L-ascorbic acid and correlation of their role in nonenzymic browning of vitamin C. *Journal of Micronutrient Analysis, 6*, 1–17.

Koehler, P. E., & Odell, G. V. (1970). Factors affecting the formation of pyrazine compounds in sugar–amine reactions. *Journal of Agricultural and Food Chemistry, 18*, 895–898.

Loscher, J., Kroh, L., Westphal, G., & Vogel, J. (1991). L-Ascorbic acid – A carbonyl component of nonenzymic browning reactions. Part 2. Amino-carbonyl reactions of L-ascorbic acid. *Zeitschrift für Lebensmitteluntersuchung und - Forschung A, 192*(32), 3–327.

Maga, J. A. (1992). Pyrazine update. *Food Reviews International, 8*, 479–558.

Míková, K., & Davídek, J. (1975). Formation of alkylimidazoles in a system containing L-ascorbic acid and ammonia. *Nahrung, 19*, 155–161.

Moon, S. Y., Cliv, M. A., & Li-Chan, E. C. Y. (2006). Odour-active components of simulated beef Xavour analysed by solid phase microextraction and gas chromatography–mass spectrometry and olfactometry. *Food Research International, 39*, 294–308.

Obretenov, C., Demyttenaere, J., Abbaspour Tehrani, K., Adams, A., Kersiene, M., & De Kimpe, N. (2002). Flavor release in the presence of melanoidins prepared from L-(+)-ascorbic acid and amino acids. *Journal of Agricultural and Food Chemistry, 50*, 4244–4250.

Parker, J. K., Hassell, G. M. E., Mottram, D. S., & Guy, R. C. E. (2000). Sensory and instrumental analyses of volatiles generated during the extrusion cooking of oat flours. *Journal of Agricultural and Food Chemistry, 48*, 3497–3506.

Rogacheva, S., Kuncheva, M., Panchev, I., & Obretenov, C. (1995). L-Ascorbic acid in nonenzymatic reactions. Reaction with glycine. *Zeitschrift für Lebensmitteluntersuchung und -Forschung A, 200*, 52–58.

Rogacheva, S., Kuntcheva, M., Panchev, I., & Obretenov, C. (1999). Melanoidin formation in L-ascorbic acid–amino acids interaction. A comparative study. *Nahrung, 43*, 105–108.

Rogacheva, S., Verhé, R., & Obretenov, C. (1996). Aroma compounds formation in the interaction of L-ascorbic acid with α-amino acids. In A. Taylor & D. Mottram (Eds.), *Flavour science. Recent developments* (pp. 250–253). Cambridge, UK: The Royal Society of Chemistry.

Rostad, C. E., & Pereira, W. E. (1986). Kovats and lee retention indices determined by gas chromatography/mass spectrometry for organic compounds of environmental interest. *Journal of High Resolution Chromatography, 9*, 328–334.

Sanz, C., Czerny, M., Cid, C., & Schieberle, P. (2002). Comparison of potent odourants in a filtered coffee brew and in an instant coffee beverage by aroma extract dilution analysis (AEDA). *European Food Research and Technology, 214*, 299–302.

Seck, S., & Crouzet, J. (1981). Formation of volatile compounds in sugar–phenylalanine and ascorbic acid–phenylalanine model systems during heat treatment. *Journal of Food Science, 46*, 790–793.

Shephard, A. B., Nichols, S. C., & Braithwaite, A. (1999). Moisture induced solid phase degradation of L-ascorbic acid part 3, structural characterisation of the degradation products. *Talanta, 48*, 607–622.

Siegmund, B., & Murkovic, M. (2004). Changes in chemical composition of pumpkin seeds during the roasting process for production of pumpkin seed oil (Part 2: Volatile compounds). *Food Chemistry, 84*, 367–374.

Sohn, M., & Ho, C. T. (1995). Ammonia generation during thermal degradation of amino acids. *Journal of Agricultural and Food Chemistry, 43*, 3001–3003.

Vernin, G., Chakib, S., Rogacheva, S., Obretenov, T., & Párkányi, C. (1998). Thermal decomposition of ascorbic acid. *Carbohydrate Research, 305*, 1–15.

Wagner, R., Czerny, M., Bielohradsky, J., & Grosch, W. (1999). Structure–dour-activity relationships of alkylpyrazines. *Zeitschrift fur Lebensmitteluntersuchung und -Forschung A, 208*, 308–316.

Wang, P.-S., & Odell, G. V. (1973). Formation of pyrazines from thermal treatment of some amino-hydroxy compounds. *Journal of Agricultural and Food Chemistry, 21*, 868–870.

Yano, M., Hayashi, T., & Namiki, M. (1976). Formation of free radical products by the reaction of dehydroascorbic acid with amino acids. *Journal of Agricultural and Food Chemistry, 24*, 815–821.

Yin, D. Z., & Brunk, U. T. (1991). Oxidized ascorbic acid and reaction products between ascorbic and amino acids might constitute part of age pigments. *Mechanisms of Ageing and Development, 61*, 99–112.