39 *Egypt. J. Chem.* **53**, No. 4, pp. 581 - 596 (2010)

Effect of Serine on Chemical Composition and Antioxidant Activity of Beef fat/ Cysteine Model Systems

A.H. El-Ghorab, K.F. El-Massry, S.A. Shedid*, M.S. Shaheen, F. Osman and A.F. El-Hadaad*
*Flavour and Aromatic Department, National Research Center, and *Chemistry Department, Al-Azhar University, Cairo, Egypt.*

THE PRESENT work aimed to examine the chemical composition and antioxidant activity of the constituents generated during the reaction between beef fat with cysteine and serine model system. Sixty three and seventy three volatile compounds were isolated and identified with the predominance of esters and sulfur-containing compounds. Sensory evaluation was also performed for the model systems according to (ISO) and the results revealed that the presence of volatiles having roasted meat–like aroma might be due to presence of certain classes such as pyrazine and thiazoles derivatives as the main compounds. The radical scavenging activity of the model systems was quantified spectrophotometrically, using DPPH radical and β-carotene bleaching assays.

Keywords: Maillard reaction, Serine, Fat, Meat like aroma, Antioxidant activity and DPPH.

The non-enzymatic browning (NEB), also known as Maillard reaction, is one of the most prevalent and studied chemical reactions that occurs in foods during heating or storage. Several factors influence the generation of flavours during 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, however the reaction temperature and time mainly influence the kinetics of the reaction, whilst leaving the nature of the volatiles broadly unchanged [(1)], and chemical nature of the reactants (type of amine and carbonyl groups involved); pH; relative humidity; temperature and time of heating [(2)].

The aromas in most thermally processed foods, such as bread, cereal products, roasted peanuts, and roasted coffee, are largely due to the Maillard reaction. Among these Maillard-type flavors, the heterocyclic compounds with desirable aromas and low odor thresholds make the most significant contribution. These heterocyclic compounds include furans, thiazoles, thiophenes, oxazoles, pyrroles, pyridines, and pyrazines. The nitrogen sources of these heterocyclic

compounds come from amino acids. Thus, the nature of the nitrogen source has a profound effect on both the kinds and amounts of flavors formed [3].

Serine is a ubiquitous amino acid in nature, and is classified as a nonessential amino acid. There have been few studies on serine-containing model systems as compared to other amino acids. In an early work on pyrolysis of serine, pyrazines, pyrroles, 2,5-diketo-3,6- dimethylpiperazine, and appreciative amounts of paraldehyde were identified. Adams *et al*. studied the model reactions involving serine and fructose, glucose, diacetyl, or cyclotene [3] have in an aqueous solution.

Their results showed that the generation of pyrazines, pyridines, and carbonyl compounds increases with rising temperature, while the generation of furans, furanones, and pyranones decreases. The effects of different amino acids on the Maillard reaction have been widely studied. In 2007, Adams *et al.* [3], investigated the degradation rates of amino acids with dicarbonyl compounds and found that the basic and hydroxy amino acids reacted strongly, while the acidic and nonpolar amino acids had the least reactivity.

Sulfur-containing amino acids, such as cysteine and cysteine are indispensable components for generating meat-like aromas through a reaction with reducing sugars [4]. In a previous study, we have learned that cysteine was a good sulfur and nitrogen source for the formation of meat-like aroma compounds and glutathione was better able to supply the sulfur source to form the polysulfur-containing aroma compounds [5]. When cysteine and glutathione both reacted with glucose, respectively, more sugar-amino acid interaction products were produced in cysteine than in glutathione [6].

Fat typically does not participate directly in the browning reaction, yet may be quite important in influencing flavour formation *via* browning. Fat is required to give the "species" notes to meat-like reaction flavours (except for beef. which may become "beefy" without beef tallow in the reaction). While fat will make a flavour contribution due to primary degradation products (*e.g.*, unsaturated aldehydes formed from chicken fat during heating), fat will also make a flavour contribution by participating in the browning reaction. Fat makes its contribution to browning flavours by yielding long chain aldehydes for participation in browning [7]. There is no source of long chain aldehydes in foods except for the fatty acids. As the fat degrades due to heat treatment, the various long chain carbonyls formed will readily participate in browning, producing uniquely flavored saturated and unsaturated compounds.

In this study, we evaluated the effect of serine on the formation of aroma compounds produced by heating a model system containing cysteine and additionally fats as by-products from slaughtering process commercial source to obtain natural flavour, with antioxidant prosperities.

Materials and Methods

Chemicals

L-Cysteine (L-Cys) , L- Serine (L-Ser), β-carotene, linoleic acid, 1,1-diphenyl-2-picrylhydrazyl ($DPPH^0$), tert-butyl hydroquinone (TBHQ), polyoxyethylene sorbitan monopalmitate (Tween-80), chloroform (99%) and sodium sulphate anhydrous (Na_2SO_4) were purchased from Merck (Darmstadt, Germany). Dichloromethane (DCM) (99.8%), pressurized sealed bottles: with thermal taps were purchased from Aldrich and Sigma Company (Germany).

Preparation of reaction mixtures of meat -like aroma model system

Two reaction mixtures were made up in presence or absence of distillated water; each mixture containing cysteine (I mmol), L-Serine (0.05 mmol), and beef fat or beef triglycerides (10 g). The mixtures were as follows:

A: Beef fat + L-Cys+ L-Ser

B: Beef triglycerides + L-Cys + L-Ser

Each reaction mixture was heated at 140^0C degree for 30 min in a 1000 ml sealed bottlel, fitted with an airtight and was then allowed to cool and subjected to the further study.

Extraction of volatile compounds of Maillard reaction model systems

The reaction mixtures obtained from pressurized bottle after reaction complete were subjected to a simultaneous steam distillation (1 L of water) and solvent (dichloromethane, 200 ml) extraction. The dichloromethane extract was dried over anhydrous sodium sulfate. After the solvent was removed by rotary evaporator, the obtained concentrates were analyzed using gas chromatography and gas chromatography-mass spectroscopy [8].

Analysis of volatile compounds

The obtained volatiles samples were thermally desorbed, using a modified injector port, directly on the front of a (DB5) (60 m x 0.32 mm i.d) fused silica capillary column, in the oven of a Hewlet-packed HP 5890 gas chromatography, and temperature increase from 45 ^{0}C -240 ^{0} C by the rate 2^0C/ min.

Kovat's indices were determined by co-injection of the sample with a solution containing homologous series of n-hydrocarbons (C_6-C_{26}) under the same conditions as described above. The separated components were identified by matching with NIST mass -spectral library data, and by comparison of Kovat's indices with those of authentic components and with published data [9].

Gas chromatography and Gas chromatography-mass spectrometry

The obtained volatile samples were thermally desorbed, using a modified injector port, directly on the front of a (DB5) (*60 m x 0.32 mm i.d*) fused silica capillary column, in the oven of a Perkin-Elmer XL gas chromatography and temperature increase from 40 ^{0}C -240 ^{0} C by the rate 2^0C / min. Kovat's indices were determined by co-injection of the sample

with a solution containing homologous series of n-hydrocarbons (C_6-C_{26}) under the same conditions as described above. The separated components were identified by matching with NIST mass-spectral library data, and by comparison of Kovat's indices with those of authentic components and with published data. GC/MS analysis of the two model systems namely beef $_{fat}$ / cysteine/ serine and beef $_{tg}$/ cysteine/ serine were performed on an HP model 6890 GC interfaced to an HP 5791A mass selective detector (GC/ MS) was used for mass spectral identification of the GC components at (MS) ionization voltage of 70 eV. A 30 m x 0.25 mm i.d. (DF = 0.25 lm) DB5 bonded-phase fused-silica capillary column was used for (GC). The linear velocity of the helium carrier gas was 30 cm/s. The injector and the detector temperatures were 250 ºC. The oven temperature was programmed from 40 to 240 ºC at 2 ºC / min [9].

Antioxidant activity of Maillard reaction products (MRPs)

β- Carotene bleaching method

Antioxidant activity of the aqueous solution was determined by a β-carotene/ linoleic acid system, as described by Matthus [10].

DPPH free radical scavenging method

DPPH free radical scavenging assay carried out according to Yara *et al.* [11].

Sensory evaluation

The sensory analysis was carried out under the conditions specified by the international standards (international standardization organization, ISO); guidelines after ISO 6658-1985;unstructured graphical scales(ISO 4121-1988) were presented as straight lines 100 mm long, provided with descriptions on either end (odour acceptability; 0mm = very little agreeable, 100 = very strong agreeable); odour intensity:0 = very weak, 100mm = very strong). The sensory profile was based on free choice profiling , and the following descriptors were retained (out of 32 collected descriptors):1 = roasted, bread crust , roasted peanuts; 2 = burnt, caramel, bitter; 3 = like-boiled meat; 4 = like-roasted meat; 5 = spicy , sulphury, onion, garlic; 6 = sharp, punget, burning; 7 = earthy, musty, moldy, sweat, 8 = malty, sweet; 9 = solvents, synthetic, chemicals; 10 = others-specify which); in the profile evaluation: 0 mm = absent, 100mm = very strong . Odour profiles were tested by sniffing from ground wide-neck glass bottles [12].

Statistical analysis

All analyses were performed in triplicate. The data were recorded as means ± standard deviations and analyzed by SPSS. One-way analysis of variance (ANOVA) and Turkey multiple comparisons were carried out to test for any significant differences between the means; the mean value of antioxidant activities and sensory analyses of model systems.

Results and Discussion

Table 1 shows the identified volatile compounds with relative area percentages and kovat indices of the beef fat/ cysteine/ serine and beef triglycerides/ cysteine/ serine model systems. Sixty five and seventy five volatile compounds were isolated in the two model systems, respectively including carbonyls, esters, mercaptoalcohols, mercaptoketones, sulphur-containing thiols, thiophenes, disulphides and others .

TABLE 1. Volatile compounds of beef fat/ cysteine and beef fat/ cysteine/ serine model systems .

No.	K.I[a]	Identified compound [b]	A	B	Methods of identification
1	604	2- Butanone	nd	0.1	KI
2	610	Eethyl acetate	nd	0.03	KI&MS
3	624	Methylbutenol	0.91	0.05	KI
4	644	2-Methylbutanal	nd	0.03	KI&MS
5	696	Pentanal	0.91	0.08	KI
6	726	2,3-Pentanedione	0.1	0.05	KI&MS
7	731	3-Penten-2-one	0.02	0.01	KI
8	747	Pyrazine	0.1	5.39	KI&MS
9	760	Pyrrol	nd	2.54	KI
10	783	Dimethyldisulphide	1.05	4.31	KI&MS
11	798	3-Mercapto-2-butanone	0.1	1.63	KI
12	805	1-Pentanol	3.51	1.08	KI&MS
13	814	2-Methylthiophene	0.1	nd	KI
14	826	2-Furfural	nd	1.24	KI&MS
15	833	2-Methylthiazole	0.1	0.1	KI
16	841	Methylpyrazine	0.18	nd	KI
17	853	2.4-Dimethylfuran	0.08	nd	KI
18	858	2-Furylmethanol	0.1	2.4	KI&MS
19	870	2-Methyl-3-furanthiol	0.12	1.25	KI
20	872	3- Ethylthiophene	0.06	0.12	KI&MS
21	876	2,5-Dimethylthiophene	0.02	0.08	KI&MS
22	883	1-Heptanol	0.15	nd	KI
23	886	2-Heptanone	nd	0.94	KI&MS
24	897	3- Mercapto-2-pentanol	0.04	0.2	KI&MS
25	906	3-(methylthio)Propanol	0.5	1.31	KI
26	911	2-Furylmethanethiol	0.1	0.02	KI
27	926	2-Acetylpyrrole	0.04	0.04	KI&MS
28	928	2,5-Dimethylpyrazine	0.1	nd	KI
29	935	Methyldihydrofuranthiol	0.09	0.64	KI
30	940	Mercaptomethylpentanone	0.03	0.06	KI&MS

TABLE. 1. Cont.

No.	K.I[a]	Identified compound[b]	A	B	Methods of identification
31	949	2-Pentanol	nd	1.76	KI
32	955	4,5-Dihydro-3-(*2H*)thiophenone	0.03	0.45	KI&MS
33	961	3-Mercaptothiophene	2.28	nd	KI
34	966	2-Methyl-4,5-dihydro-3-furanthiol	0.08	0.03	KI&MS
35	981	2-Thiophenethiol	nd	0.05	KI
36	987	3-Hydroxy-(*2H*)pyran-2-one	0.1	0.59	KI&MS
37	991	2-Octanone	0.2	nd	KI
38	1000	2,4,5-Trimethylthiazole	0.06	0.01	KI&MS
39	1007	2-Furylmethylsulphide	0.27	1.61	KI
40	1020	2-Acetylthiazole	nd	1.75	KI&MS
41	1030	1,3-Dithiane	0.81	nd	KI
42	1044	4-Hydroxy-5-methyl-3--(*2H*)-thiophene	1.63	0.54	KI&MS
43	1063	2-Ethyl-3,6-dimethylpyrazine	1.17	nd	KI
44	1071	3-Methyl-1,2-dithiolan-4-one	nd	0.73	KI
45	1075	3,6-Nonadienal	nd	0.8	KI&MS
46	1131	Methylcyclohexanoate	1.4	0.28	KI&MS
47	1153	Nonanol	2.21	0.09	KI
48	1163	2- Acetyl-3-methylthiophene	nd	0.22	KI&MS
49	1166	2-Methyl-3-(methyldithio)furan	0.34	0.18	KI
50	1172	2,3-Diethyl-5-methyl pyrazine	nd	0.15	KI&MS
51	1189	2,5-Dimethyl-3-isobutylpyrazine	4.5	1.52	KI
52	1199	(E)or(Z)-3,5-Dimethyl-1,2-dithiolan-4-one	0.24	0.27	KI
53	1204	3-Methyl-2-formylthiophene	0.54	2.57	KI
54	1258	2-Decenal	0.4	0.37	KI&MS
55	1264	Dimethylpyridine	0.51	1.14	KI
56	1290	Dihydrothienothiophene	0.3	1.56	KI&MS
57	1304	Tridecane	1.02	5.62	KI
58	1317	Methylthienothiophene	nd	0.17	KI
59	1325	1,2,4,5-Tetrathiane	nd	0.25	KI&MS
60	1334	Methyldecanoate	7.6	1.91	KI
61	1382	(E,Z)-3,6-Nonadien-1-ol	0.51	0.22	KI&MS
62	1399	Methylene bis-(methyl sulphide)	2.52	2.01	KI
63	1422	Methyldihydrothienothiophene	0.96	1.46	KI
64	1430	2-Ethylthienothiophene	nd	1.48	KI
65	1473	Ethyl-(E)or(Z)-2,4-decadienoate	nd	1.32	KI&MS
66	1499	3,4,6-Trimethyl-1,2,3-trithiane	nd	1.46	KI

TABLE. 1. Cont.

No.	K.I[a]	Identified compound[b]	A	B	Methods of identification
67	1508	2-Methyl-3-furyl-1-methyl-2-oxopropyldisulphide	1.3	1.83	KI&MS
68	1526	Tridecanal	nd	1.39	KI
69	1531	3-Mercaptohexanol	1.92	2.87	KI
70	1541	*Bis*-(2-methyl-3-furyl)disulphide	0.23	0.44	KI&MS
71	1569	2-Methyl-3-furyl-1-ethyl-2-oxopropyldisulphide	1.12	0.15	KI
72	1580	2-Methyl-3-furyl-1-methyl-3-oxobutyldisulphide	1.21	nd	KI&MS
73	1589	2-Methyl-3-furyl-1-methyl-3-oxopropyldisulphide	1.55	0.25	KI
74	1596	2-Methyl-3-furyl-1-methyl-2-oxopropyldisulphide	1.1	22	KI&MS
75	1636	2-Methyl-3-furyl-2-furylmethyldisulphide	15.87	1.66	KI
76	1698	2-Methyl-3-furyl-3-thienyldisulphide	7.65	0.31	KI
77	1740	2-Methyl-3-furyl-2-methyl-3-thienyldisulphide	1	1.09	KI&MS
78	1760	Methylfuraneol	2.27	0.55	KI
79	1788	2-Furyl-methyl-2-thienyldisulphide	2	3.64	KI&MS
80	1858	Hexadecanol	1.47	1.03	KI
81	1905	Ethylhexadecanoate	10.61	3.63	KI
82	1933	2-Methyl-3-thienyl-3-thienyldisulphide	4.59	0.28	KI
83	1942	Trimethylphenylbutenone	7.92	0.57	KI

a: kovat indices, b: identified compounds, A: beef fat/ cysteine/ serine, B: beef triglycerides/ cysteine/ serine,.

Carbonyl compounds

Aldehydes

The aldehydes were identified in (A and B) model systems as pentanal (A=0.12%, B=0.91%), while 2-methylbutanal and 2-pentanal were identified in a model system only with (0.1% and 0.2%), respectively and 2-decenal was released in B model system only. From the above results it is concluded that aldehydes may be formed due to the oxidation of unsaturated fatty acids in the systems [13]. They found that aldehydes such as 2- methylbutanal and 2-pentanal formed from the oxidation of fat.

Ketones

3-Penten-2-one (0.1% and 0.02%) and 2,3-pentadione (0.09% and 0.1%) were generated in (A and B) model systems, respectively while 2-methylcyclopentanone, 2-heptanone (0.23% and 0.17%) were generated in (A) model system, however 2-octanone was identified in B model system only with (0.2%). Trimethylphenylbutenone (7.92%) has the highest concentration among other

ketones in (A) model system. The presence of ketones in the fat/ cysteine/ L-serine system can be explained by (MR and SD) of cysteine, which can lead to form short chain ketones as 2-butanone, methylcyclopentanone [14]. However, the formation of other ketones such as 2-heptanone and trimethylphenylbutenone can not be explained by these mechanisms; they may have been formed by the condensation reaction other carbonyl compounds [15].

Dicarbonyl like 2,3-pentanedione is important intermediate in the formation of mercaptoketones; it can produce important meat-like volatiles and was identified in the volatiles of cooked meat. It was also reported to contribute to increase meatiness in some flavour isolates [16]. 2-Mercapto-ketones as 2-mercapto-2-butanone (A=0.1%, B=1.63%) and mercapto-methylpentanone (A=0.03%, B=0.06%) were produced in (A and B) system. The mercaptoketones were probably formed *via* the reaction of the corresponding alkanedione (breakdown of lipids) with hydrogen sulphide. 3-Mercapto-2-butanone and mercaptomethylpentanone have been identified in meat aroma model system [6].

Alcohols

Alcohols are derived mainly from the oxidative decomposition of fats. Different alcohols are detected in the (A and B) model system such as methylbutenol (A = 0.91%, B = 0.05%), 1-heptanol (A = 0.15%), 1-pentanol (A = 3.51%, B =1.08%), 2-pentanol (B = 1.76%), nonanol (A = 2.21%, B = 0.09%), (E,Z)-3,6-nonadien-1-ol (A = 0.51%, B = 0.22%) and hexadecanol (A = 1.47%, B = 1.03). The flavour note of straight-chain primary alcohol has been reported as greenish, woody and fatty–floral. Mercaptoalcohols which formed in the two model systems are 2- mercapto-2-pentanol (A = 0.04%, B = 0.2%) and 3-mercaptohexanol (A = 1.92%, B = 2.87). The mercaptoalcohols were formed from the reaction of the corresponding alkanols with hydrogen sulphide [17].

Esters

Esters are also thought to have a little impact on meat aroma. They are associated with fruity note [8]. Where the identified esters include methylcyclohexanoate (A = 1.4%, B = 0.28%), methyldecanoate (A = 7.6%, B = 1.91%) and ethylhexadecanoate (A = 10.61%, B = 3.63%).

Hydrocarbons

Tridecane (A = 1.02%, B = 5.62%) was detected in the (A and B) system. Hydrocarbons have also been reported to be found in cooked beef [18].

Sulphur-containing compounds

The sulphur-containing furans/ thiophenes and other related disulphides were among the most numerous classes of flavour compounds found in the reaction mixture of two model system, although many of them were present at low concentrations. Where sulphur-containing compounds differentiated into thiols, thiophenes, disulphides, however, 2-thiophenethiol was also detected in the reaction mixture of the (B) system with (0.05%).

The thiols identified included eight thiols 2-methyl-3-furanthiol (A=0.12%, B=1.25 %), 3-(methylthio) propanol (A=0.5%, B=1.31%), 2-furylmethanethiol (A=0.1%, B=0.02 %), methyldihydrofuranthiol (A=0.09%, B=0.64 %), 2-methyl-4, 5-dihydro-3-furanthiol (A=0.08%, B=0.03 %) and 2-methyl-3-(methyldithio) furan (A=0.34%, B=0.18 %).The compounds 2-methyl-3-furanthiol and 2-methyl-4,5-dihydro-3-furanthiol were probably found through the reaction of hydrogen sulphide (SD product of cysteine) with 4-hydroxy-5-methyl-3-(*2H*)-furanone while 2-furylmethanethiol was probably formed by the reaction of hydrogen sulphide with 2-furfural and nucleotides breakdown product [19].

Farmer *et al* . [20] found that 2-methyl-3-furanthiol and 2-thiophenethiol in the reaction mixture of cysteine/ ribose were generated via the thermal degradation of cysteine. They have been found in the volatiles from different systems and some have been reported as volatile compounds in cooked meat where 2-methyl-3-furanthiol is considered to play an important role in the flavour of meat and both in chicken and bovine broth [21] .

Generally it was reported that, some heterocyclic sulphur compounds were possessing meat-like aroma [15]. Thiophene derivatives were detected in beef fat or triglycerides, L-cysteine and L-serine systems with (A=466%, B=8.64%), respectively. Sulphur-containing heterocyclic compounds could be generated either from thermal degradation of cysteine.

3-Mercaptothiophene is the only thiophene with meaty aroma [22], but other thiophenes have sulphurous note or green/sweet odour [23]. The main routs for their formation involve the reaction of furfural and furanones with hydrogen sulphide or the condensation of mercaptoacetaldehyde with α-β-unsaturated aldehydes [24].

Several di-tri and tetra-sulphur containing five or six membered heterocyclic rings were identified in the two system such as (E) or (Z)-3,5-dimethyl-1,2-dithiolan-4-one (A = 0.24%, B = 0.27%), while, 1,3-dithiane was detected in A system only with (0.81%) as well as 3-methyl-1,2-dithiolan-4-one, 1,2,4,5-tetrathiane, 3,4,6-trimethyl-1,2,3-trithiane were identified in B model system with (0.73 %,0.25 % and 1.46 %), respectively. Dithiolanes are probably formed from the reaction between breakdown of lipids and cysteine, thermal degradation of cysteine or can be generated from the reaction of aldehydes/ hydrogen sulphide [25].

Whitfield *et al.* [26] reported that 1, 3-dithiane has been identified in boiled beef while, 3-methyl-1, 2, 4-trithiane has been identified in commercial beef extract and cysteine/ ribose model system. The compound 2, 4, 6- trimethyl-1, 3, 5-trithiane was reported in cooked beef and also in cooked chicken flavour .

3-Methyl-1,2-dithiolan-4-one was found in model system containing cysteine/ ribose and phospholipids and in different meat samples [22, 26].

Three bicyclic compounds were generated in the two system, *i.e.* methyldihydrothienothiophene (A = 0.96%, B = 1.46 %) while methylthienothiophene and (B =)2-ethylthienothiophene were detected in B model system with (0.17 % and 1.48%), respectively. It has been reported that a number of alkylthienothiophenes were reported in the volatile components of cysteine/ribose model system [17].

In (A and B) model system sulphides and disulphides were detected with (41.46%, 39.58%), respectively as shown in Table 1. These results confirm previous observations that the formation of furyl and thienly sulphide and disulphides [15].

Thiazoles, including a series of alkylthiazoles and acetylthiazole were generated in the two systems such as 2-methylthiazole (A and B = 0.1%) and 2,4,5-trimethylthiazole (A = 0.06%, B = 0.01 %), while, 2-acetylthiazole (B = 1.75%) has been reported in the model system containing cysteine/ ribose. However, 2-methylthiazole and 2,4,5-trimethylthiazole have been found among the volatiles of roasted, fried and cooked beef [27].

Vernin and Parkany [25] reported that the thiazoles formed during heat degradation of thiamine or thermal degradation of cysteine. The breakdown of lipids appears to be the main source of furan, furfurals and furanones. 2-Furfural (B = 1.24 %), 2, 4-dimethylfuran (A = 0.08%), methylfuraneol (A = 2.27%, B = 0.55%), 2-furfural and 2,4-dimethylfuran have been reported in cysteine/ ribose model system [17].

Nitrogen-containing compounds

Pyrazine (A = 0.1%, B = 5.39%), 2,5-dimethyl-3-isobutylpyrazine (A = 4.5%, B = 1.52%) were generated in the two models while methylpyrazine, 2,5-methylethylpyrazine and 2-ethyl-3,6-dimethylpyrazine were identified in (A) model system with (0.18%, 0.1% and 1.17%), respectively and 2,3-diethyl-5-methylpyrazine was detected in (B) with (0.15%).

Pyrazine derivatives were formed *via* the reaction mixture of pyrrolysis of L-serine and lipids degradation products [28]. Where the widely accepted mechanisms for the formation of pyrazines: The (SD) and the ammonia/ acylation reaction. The Strecker degradation is involved with α-amino acids and the α-dicarbonyl which are derived from lipids degradation products to form alkylpyrazines.

The pyrazines which formed in the systems were reported to be found in cooked beef aroma [4, 18]. The odour of pyrazines has been traditionally regarded as nutty, roasted and burnt odour. While, the other nitrogen compounds which were identified in the system were 3-hydroxy-2-(*2H*) pyran-2-one (A = 0.1%, B = 0.59%), dimethylpyridine (A = 0.51%, B = 1.14%), pyrrole (B = 2.54%) and 2-acetylpyrrol (A = B = 0.04%), which can be generated from the Strecker degradation which involves via the interaction of nitrogen-containing molecules, *e.g.* α-amino acid with lipid degradation products [29].

Pronounced differences were observed in the odour profiles. As expected, intensities of roasted, burnt, caramel and sweet notes were higher in (A) model system than (B) which may be attributed to presence of thiazole, pyrazines and thiol compounds in (A) model system, respectively (Table 1).

Roasted meaty aroma contains more thiazoles, pyrazines in comparison to boiled meat. Higher intensity of roasted meat note is responsible, due to the presence of pyrazines and thiazole derivatives, which were reported as responsible for the roasted aroma in meat [12].

Other descriptors gave insignificant results, as the ratings were too low; therefore, they are not included in Fig.1 & 2.

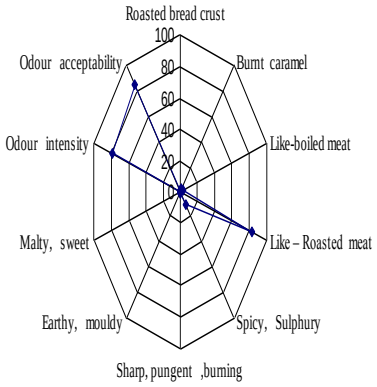

Fig.1. Sensory profile of model system .

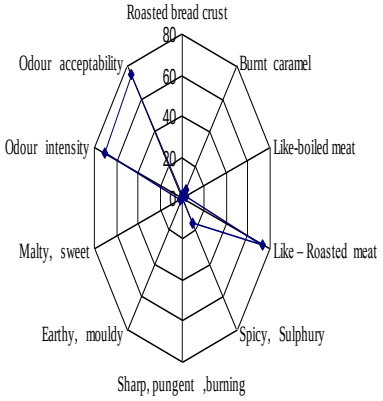

Fig.2. Sensory profile of B system .

Antioxidant activity of (A and B) model systems

It is well known that natural antioxidative food compounds are important for food technology, because they prolong the shelf life of processed food stuffs. More recently they also gained more interest because it was suggested that, their intact is beneficial for health and they are protective, *e.g.* against coronary heart diseases. The radical scavenging activity of the two model systems were measured by DPPH and β-carotene methods. As shown in Fig. 3 & 4 the model system of beef $_{fat}$ / cysteine/ serine has higher antioxidant activity (78.0% at 400 µg/ml) than beef tg/ cysteine/ serine model system (65% at 400 µg/ml) in comparison with TBHQ (98.73% at 400 µg/ml).

The Maillard reaction products of beef fat model system was found to be higherly efficient than beef triglyceride model system which may be due to the presence of phospholipids in (A) model system that, participate in Maillard reaction to generate several heterocyclic volatiles with antioxidant activity as

sulphides, thiazoles, pyrazines and thiols derivatives. As expected, (A) model system has higher antioxidative efficiency than (B) model in β-carotene-linoleate method, (A) model system inhibited the bleaching by (73.5% at 400 µg/ ml) compared TBHQ with (98.86% at 400 µg)

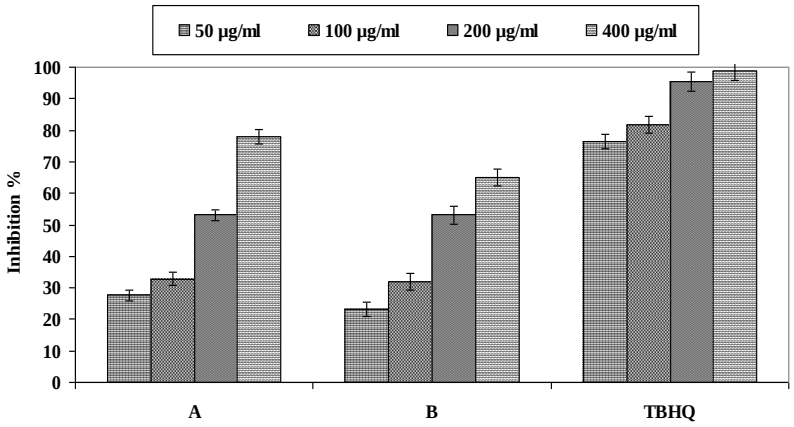

Fig. 3. Antioxidant activity of A and B model systems by DPPH method .

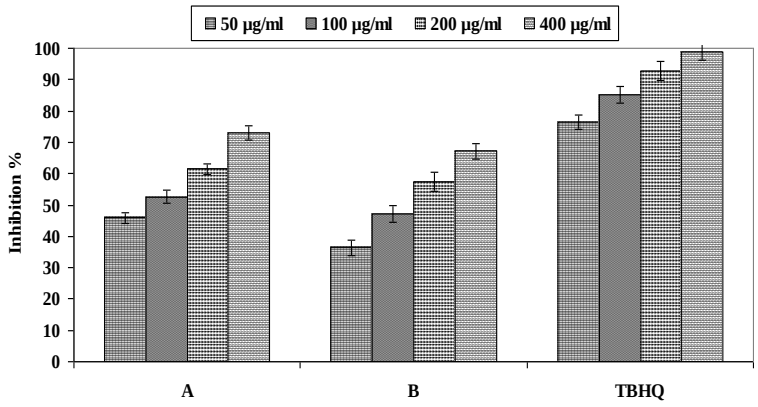

Fig. 4. Antioxidant activity of A and B model systems by beta- carotene method .

Conclusion

Effect of amino acids (cysteine and serine) was studied for the same model systems which depend on serine as β-hydroxy amino acid and leucine which are reported to be important in the generation of meaty aroma. Significant differences in concentrations of volatiles were observed between buffalo fat and triglyceride model systems with serine and cysteine.Triglyceride/ cysteine/ serine

model system showed higher concentrations of aldehydes (53.6%) and sulfides (21.6%), while alcohols (12.2%), thiazoles (7.42%) and pyrazines (7.0%) were more dominant in fat/ cysteine/ serine model system. This is due to the participation of lipid-derived volatiles in the later model system than triglycerides. Incorporation of leucine in model systems, buffalo fat and triglyceride with cysteine, leads to characteristic meat aroma with more browning for fat model system easily noted by the furans formed (4.5%) in comparison to the triglyceride model system, only (0.9%). Sulfur-derivatives were predominant with lower browning reaction, thiols and sulfides identified as (13.5% and 9.2%), respectively in triglyceride system, while they were only (1.22 and 5.5%) in fat one.

It is well-known that, sugar accelerates caramelization and forms newly volatile classes and derivatives. Two model systems were designed including ribose in order to study its effect for buffalo fat/ cysteine and buffalo triglyceride / cystine model systems. Aliphatic hydrocarbons are more predominant in the first model system in comparison to the second, with the formation of more aldehydes (28.0%) and ketones (41.6%), while thiols and aliphatic-s-compounds are higher in triglyceride system; (36.7 and 6.3%), respectively.

The radical scavenging activity of the designed model systems was compared to that of TBHQ at 400µg/ml and showed that, buffalo fat/ cysteine/ serine model system recorded the highest activity among the other model systems; (76.7%). Such activity maybe due to presence of volatile classes, *e.g.* furans (4.5%), thiols (7.3%), thiophenes (7.6%) and thiazoles (7.4%). It is documented that, certain compounds have an antioxidant activity and have been identified in such model system, *e.g.* 2-furylmethanethiol, 2-acetyl thiazoles and furaneol. Pronounced differences were observed in the odour profile along with intensity and acceptability. Buffalo fat/ cysteine/ serine model system has the highest pyrazines content (7.0%), which is agreeable to the highest roasted note recorded for this system. The aroma of like-boiled meat was intensive in buffalo fat/ cysteine model system in presence of water, due to the preponderance of aliphatic sulfur compounds.

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(*Received* 23/ 8 / 2010;
accepted 13/10 /2010)

تأثير السرين على التركيب الكيميائي و كفاءة نشاط تضاد الاكسدة للمركبات الطيارة المسئولة عن رائحة اللحم في تفاعل ميلارد

احمد حسن رجب الغراب ، خالد فاروق المصري ، سعيد احمد شديد*، محمد سعد الدين محمد احمد شاهين ، فؤاد محمد عثمان و عاطف فتوح الحداد*
قسم مكسبات الطعم و الرائحة - المركز القومي للبحوث و*قسم الكيمياء العضوية - جامعة الازهر- القاهرة- مصر.

تهدف الدراسة الى توضيح تأثير الحمض الأميني السرين على التركيب الكيماوى ونشاطية التضاد للأكسدة للمركبات الطيارة المسئولة عن رائحة اللحم أثناء تفاعل ميلارد بين الحمض الأميني السيستئين مع مخلفات دهن الابقار كمصدر اقتصادي لمكسبات الطعم و الرائحة و ايضا كمضادت اكسدة طبيعية فعالة.

تم استخدام التحليل الغازي الكروماتوجرافي- طيف الكتلة وتم التعرف على ٨٣ مركب وتقسيم هذه المركبات إلى مجاميع كيميائية.أظهرت الاختبارات الحسية فاعلية النواتج ذات رائحة اللحم المحضرة لوجود المركبات الطيارة المسئولة عن نكهة اللحم مثل السلفيد و الثيولات و الثيوفينات. وتم عمل دراسة نشاط تضاد الاكسدة للنواتج و اظهرت النتائج نشاطية النواتج كمضادات اكسدة طبيعية مقارنة بمضاد اكسدة صناعي مثل TBHQ.

يمكن استخدام مركزات النكهة الناتجة من هذة تفاعلات ميلارد من الناحية التطبيقية كمكسبات للطعم و الرائحة طبيعية لها نشاط مضاد للاكسدة و خواص حسية مرغوبة .