Effects of roasting on composition of chili seed and storage stability of chili seed oil

Run-Yang Zhang¹ · Hua-Min Liu¹ · Yu-Xiang Ma¹ · Xue-De Wang¹

Received: 10 December 2018 / Revised: 29 January 2019 / Accepted: 4 February 2019 / Published online: 23 February 2019
© The Korean Society of Food Science and Technology 2019

Abstract This work focused on how roasting changed the chemical components of chili (*Capsicum annuum* L.) seeds and how it affected the stability of chili seed oils during storage. The oils from chili seeds before and after roasting treatments were stored at 63 °C for 30 days and then analyzed. Results showed that roasting changed the main sugars compositions and amino acid compositions (total content decreased from 15.9 to 7.4%), which confirmed that it could form brown pigments and volatile flavor compounds in pepper seeds after roasting. Compared with oil from unroasted seeds, oils from roasted seeds had greater oxidative stability and maintained greater antioxidant capacity during storage. These effects were possibly due to the synergistic of the neo-formed products by Maillard reaction, vitamin E, and other bioactive components. This investigation showed that roasting treatment could be considered as an appropriate method for extending the storage stability of chili seed oils.

Keywords *Capsicum annuum* L. · Chili seed oil · Storage stability · Volatile flavor compounds · Sugar analysis

Introduction

Pepper (*Capsicum annuum* L.) is one of the most widely cultivated horticultural crops in the world. There are sweet and pungent varieties, in a rainbow of colors, consumed as vegetables and/or as condiments; some are also used as medicines (Gu et al., 2017). The pungent fruits are typically called chilis; they are sold whole, fresh and dried, and also processed into sauces, pastes, flakes and powders (Cao et al., 2016; Wang et al., 2017).

The seeds, accounting for 45–50% of total pepper weight, are obtained as byproducts, and are usually discarded during the preparation of chili powder (Wang et al. 2014). In fact, chili seeds contain 16–25% oil, mainly linoleic acid, palmitic acid and oleic acid (Lee et al., 1975). These oils represent a significant resource—a new source of edible oils. Finding a use for these oils, from byproduct previously discarded, would make the chili processing industry more efficient and productive.

Roasting is a versatile process, used for numerous foods to obtain characteristic aromas, generally practiced at 150–400 °C, where in food is pretreated by convection heat through radiating heat or forced air (Singh et al., 2016). Roasting foods for a short time at high temperatures initiates complex chemical reactions, such as caramelization, lipid oxidation, Strecker degradation, and Maillard reaction (Rufián-Henares et al., 2009), that change the odors, flavors and colors of the foods, imparting characteristic appearances and tastes. In edible oil processing, roasting is important as a pretreatment for various oleaginous seeds destined for oil extraction of oil or to be consumed as

Electronic supplementary material The online version of this article (<https://doi.org/10.1007/s10068-019-00578-9>) contains supplementary material, which is available to authorized users.

✉ Hua-Min Liu
liuhuamin5108@163.com

Run-Yang Zhang
zry8343@163.com

Yu-Xiang Ma
myx366@163.com

Xue-De Wang
wangxuede1962@126.com

¹ College of Food Science and Technology, Henan University of Technology, Zhengzhou 450000, China

snacks (Chirinos et al., 2016). The pretreatment can cause desirable changes in the nutritional and physicochemical characteristics of the seeds and extracted oils (Veldsink et al., 1999). One of the major desired outcomes of the pretreatment process is the increase in antioxidant capacity, mainly because of the formation of Maillard reaction products (MRPs). During roasting, the important precursors to the formation of desirable MRPs are the sugars and free amino acids in oleaginous seeds. For example, the free amino acids react with reducing sugars of fructose and glucose in soybeans to produce pyrazines, pyridines, pyrroles, oxazoles, thiophenes, thiazoles, and furans via the Maillard reaction during the roasting (Hwang et al., 1995). Beside the formation of MRPs, roasting changes the antioxidant activity of extracted oils through decreasing or increasing the passage of naturally antioxidant compounds to the oils (Durmaz and Gökmen, 2011).

Many researchers have reported the effects of various roasting conditions on the oxidative stability and chemical composition of various oil seeds and the extracted oils from their seeds (Corrales et al., 2017; Yusuf et al., 2008; Zhang et al., 2016). Jung et al. (1999) investigated that the effects of roasting on pyrazine contents and oxidative stability of pepper seed oil. The resulted showed that the pyrazine content in the oils and their oxidative stabilities increased markedly with the increase of roasting time. Recently, our research group optimized the process of subcritical butane extraction from pepper seed after roasting pretreatment, and then investigated the properties and the characteristics and volatile flavor compounds of the extracted fragrant oils (Gu et al., 2017). However, as far as we know, there have been no investigations on the changes of composition of pepper seed during the various roasting processes and the storage stability of extracted oils.

Therefore, the present work was carried out to determine the effects of various roasting conditions on the chemical composition of chili pepper seeds. Additionally, the characteristics and chemical compositions in the oils from unpretreated and pretreated pepper seeds were also monitored during the storage period to give the shelf life of the fragrant pepper seed oils.

Materials and methods

Materials

The raw materials (Chili pepper seeds) were purchased from a local market at Kuerle, Xinjiang, China. The seeds were cleaned to remove impurities and any damaged, cracked or broken seeds. Moisture content was 9.2% (based on the weight of sample) as determined by the hot air oven drying method. The dried samples were stored in sealed

packs at 4 °C until analysis. All the used chemicals and solvents used were analytical grade.

Roasting procedure and oil samples preparation

A glass laboratory roaster (volume 500 mL) was used. The roaster was loaded with 100 g dried pepper seeds (prepared as described above) and then heated up to the setting temperature in an oil bath by a magnetic heating stirrer (IKA, Germany) for the desired holding time. Agitation was set at 100 rpm/min and maintained during roasting. When the roasting processes were completed, the samples were removed and cooled by air. Four oil samples were prepared. Three of them were obtained by pressing chili seeds after roasting at different temperature (120 °C, 160 °C, 200 °C, respectively), and the last one was pressing by un-roasting seeds. More remarkable, every oil sample of the four was prepared by the identical preparation process at several times, and then took 500 g oil samples for storage stability analysis, respectively. The unpretreated and pretreatment pepper seeds by roasting were ground by a high-speed rotary cutter and then passed through a sieve (40 mesh) to obtain seed flour. This seed flour was used for the analysis and determination of sugars and amino acid compositions, volatile flavor compounds and color analysis.

Sugar analysis

The sugar compositions of pepper seeds before and after roasting was determined by a HPAEC (high performance anion exchange chromatography) system (Dionex, ICS-3000, Sunnyvale, CA, USA) coupled with pulsed amperometric detection. Briefly, the samples (50 mg) were hydrolyzed by 2 mol/L of TFA (Trifluoroacetic acid solution) at 110 °C for 6 h in a sealed tube. After hydrolysis, the excess acid was removed by washing with methanol (3 mL) for four times. The dried hydrolyse were dissolved with ultra-pure water and diluted to 100 mL. The hydrolysate diluted tenfold and then determined by a Dionex, ICS-3000 detection system equipped with an AS50 autosampler and a Carbopac PA-20 column (4 × 250 mm, Dionex). D-GalA, D-GluA, D-Fuc, D-Xyl, D-Rib, D-Man, D-Glu, D-Fru, L-Rha, D-Gal, L-Ara were used as monosaccharide standards.

Amino acid analysis

The free amines in pepper seeds before and after roasting pretreatment were determined by an automatic amino acid analyzer (S-433D, Sykam CO., Fürstenfeldbruck, Germany). Briefly, 1-10 mg of sample was mixed with 0.3 mL of hydrolysis acid (6 M HCl, 0.2% v/v phenol, 1 nmole

norvaline as internal standard). Then, the mixtures were hydrolyzed at 110 °C for 16 h after flame-sealing the tube under vacuum. After hydrolysis, the mixtures were cooled by air. Then the cooled and filtered hydrolyse were dried in vacuum desiccators at 45 °C and re-dissolved in citrate buffer (pH 2.2). Quantification and identification of these amino acids were determined by comparing retention times of the peaks with those standards.

GC/MS analysis of volatile flavor compounds

Solid phase micro-extraction of the headspace (HS-SPME) was used to determine volatile flavor compositions of roasted pepper seeds. The volatiles from the samples were extracted as described previously (Gu et al., 2017). Identities of the volatile compounds were matched with the National Institute of Standards and Technology (NIST) mass spectral database (NIST11.L). After extraction by dichloromethane, the volatiles in dichloromethane were determined by GC/MS (gas chromatography/mass spectrometry) using an Agilent 7890A GC equipped with a DB-WAXetr capillary column (60 m length × 0.25 mm i.d., 0.25 µm film thickness; J & W Scientific, Folsom, CA, USA) and an Agilent 5975 MS-selective detector.

Color analysis

The color of the pepper seeds before and after roasting was determined using a Color Difference Meter (INESA, Shanghai, China) according to CIE Lab system at room temperature. The color was expressed at L^* , a^* , and b^* values. Where, L^* value indicates the lightness from 0 (blank) to 100 (white), the a^* value is the measure from + 100 (red) to − 100 (green), and the b^* value is the degree of yellowness (+ 100) to blueness (− 100). To evaluate the color changes associated with different roasting conditions, the total difference (ΔE) of pretreated samples compared with unpretreated sample color was calculated using the following equation:

$$\Delta E = \sqrt{(L^* - L_o^*)^2 + (a^* - a_o^*)^2 + (b^* - b_o^*)^2}$$

where L_o^* , a_o^* , and b_o^* are the values for the unpretreated pepper seed.

Storage stability

To evaluate the storage stabilities of the oils extracted from pepper seeds before and after roasting, the pepper seed oils were firstly extraction by a screw press (China) and then the oils were collected from the edges of the punch. Each oil sample (100 g) was transferred to a 200 ml beaker and stored in a forced-draft air oven at 60 °C for 31 days.

Peroxide value (PV, AOCS Method No: Cd 8-53) was determined every 5 days during the 31 days of storage.

The oxidation stability of various oil samples during storage was determined using Metrohm 734 Rancimat equipment (Herisau, Switzerland) according to ISO 6886: 2006. For the measurement of oxidative stability index, 3 g of the oil sample was placed in the Rancimat apparatus at 130 °C under an air flow of 20 L/h. The time corresponding to the inflection point in the oxidation curve is the induction period (IP), and the IP was automatically recorded by apparatus software. Tocopherols were analyzed using high-performance liquid chromatograph (HPLC) system (e2695, Waters, CA, USA) equipped NH₂ column (250 mm length × 4.6 mm i.d., 5 µm, Waters, CA, USA) and the fluorescence detector (2475, Waters, CA, USA).

Statistical analysis

Experimental data were evaluated statistically by variance analysis (ANOVA). Significant differences among the means of three replicates were determined by Duncan's multiple range tests by using SPSS software. Statistical significance level used was $P < 0.05$.

Results and discussion

Effect of roasting on sugar composition of pepper seed

Maillard reaction as one type of non-enzymatic browning reactions due to the formation of brown pigments. During the initial step, the amino groups (usually amino acids) and reducing sugar were reacted in certain conditions of water activity and temperature to form a Schiff base (Spotti et al., 2013). During the roasting process, the large-chain compositions in pepper seeds such as carbohydrates and proteins were degraded into simpler and smaller molecules, some of which such as reducing sugars and amino acids were further formed other compounds through the Maillard reaction. To help understand the mechanisms of Maillard reaction during pepper seeds roasting process, the compound changes in pepper seeds at various conditions were investigated. The changes in the content of sugars in pepper seeds with various roasting conditions are shown in Table 1. As shown, the main monosaccharide sugars in raw pepper seed were mannose (mainly from hemicelluloses) and xylose (mainly from xylan) which accounted for 44.9% and 37.1% of the raw material followed by glucose (from cellulose), which accounted for 17.6%. The contents of cellulose (glucose) and xylan (xylose) in the pepper seeds initially increased with the increase of roasting temperature and then decreased with a further increase in temperature.

Table 1 Contents of sugar compositions in pepper seeds before and after roasting at various conditions

Sugar compounds	Raw material	Temperatures (°C)			Times (min)			
		120	160	200	10	20	30	40
Glc (%)	17.6	18.1	21.7	17.7	21.7	23.3	18.9	18.1
Xyl (%)	37.1	45.3	31.0	27.2	31.0	32.2	46.5	22.5
Man (%)	44.9	36.6	47.3	54.2	47.3	41.1	34.6	61.6

Glc, glucose; Xyl, xylose; Man, mannose

However, the content of mannose (hemicelluloses) decreased at first and then increased continuously in the range of temperatures tested from 120 to 200 °C. The continuously increase of the mannose yield from 120 to 200 °C was caused by the degradation of xylan and cellulose.

Table 1 also shows the effect of roasting time on the monosaccharide compositions from 10 to 40 min at 160 °C. Clearly, the content of xylose in pepper seeds increased from 31.0% at 10 min to 46.5% at 30 min., with the increasing roasting time, and then decreased to 22.5% at 40 min. In contrast, mannose decreased from 47.3 to 34.6% with a roasting time of 10–30 min, and then increased to 61.6% as the roasting time prolonged to 40 min. In a simple pepper seed degradation mechanism, hemicelluloses (mannose) could be the first to decompose at low temperature and short roasting time. Comparing these results with the sugar analysis of the raw pepper seed, the content of xylose in the pepper seeds at 200 °C and 40 min experiments were relatively lower. The cellulose contents in pepper seeds after roasting at all conditions tested were higher as compared with raw pepper seed, which indicated that most of the cellulose in the sample was not degraded during roasting process (Yu et al., 2017; 2019).

Effect of roasting on amino acid composition contents in pepper seed

The first step of the Maillard reaction is Schiff base formation. Schiff bases are formed through the condensation of nucleophilic amino groups in proteins with carbonyl groups in reducing sugars. This condensation can be tracked by tracking the disappearance of the reacted amino acids. Therefore, the analysis of free amino groups is commonly used to estimate the progress of the Maillard reaction.

To study the degree of reaction progress, free amino groups remaining in the pepper seeds before and after roasting at various temperatures were determined (Table 2). As shown, glutamic acid and asparaginic acid were the predominant amino acids in the raw pepper seed, comprising 20.8% and 14.5% of the total amino acids,

respectively. A small amount of arginine, leucine, and phenylalanine were also found in the raw pepper seed, comprised 6.3–8.2% of the total amino acids. Other amino acids such as threonine, cysteine, methionine, and tyrosine are generally found in limited amounts in the raw pepper seed; here we found that the mean observed value of these amino acids for the pepper seed ranged from 0.2 to 0.4%. Overall, roasting has an important influence on the amounts of free amino groups present. The total amino acids in the pepper seed decreased from 15.9 to 14.7% and 12.9% after roasting at 120 °C and 160 °C, respectively.

However, an obvious fluctuation was observed in the reduction of the total free amino groups after roasting at 200 °C. The reduction of the amino acids in pepper seed after roasting should be attributed to their consumption by Strecker degradation and the Maillard reaction, as free amino acids are known to undergo degradation to produce various reaction products and condensation reactions with reducing sugars. During roasting treatment process, the roasted flavor compositions were produced by Maillard reactions between the reducing sugars and free amino acids.

Additionally, lipid oxidation products were formed and absorbed by the pepper seeds during the roasting, which could provide more carbonyl substrate to react with the free amino acids, thus utilizing more of the free amino acids (Hidalgo and Zamora, 2004; Feng et al., 2017c). However, it is difficult to ascertain the influence of one component on another because of the complexity of the reactants in the pepper seed system. During the roasting, many amino acids competed to react with the reducing sugars degraded from the pepper seeds such as xylose, mannose, and glucose (see Table 1). Furthermore, the amino acids present in the pepper seeds have potentially inhibitory or synergistic influences on each other's reactivity (Boge et al., 2009).

Volatile flavor compounds in pepper seeds after roasting

The volatile flavor compounds in pepper seeds roasted at various temperatures (120 °C, 160 °C, and 200 °C) were identified by GC/MS. The major compositions and total ion chromatogram of volatile flavor in these roasted samples

Table 2 Amino acid compositions of the pepper seeds before and after roasting at various temperatures

Amino acid (% dry weight basis)	Pepper seeds before and after roasting			
	Raw material	120 °C	160 °C	200 °C
Asparaginic acid	2.3	2.0	1.8	1.0
Threonine	0.4	0.4	0.4	0.2
Serine	0.7	0.6	0.5	0.3
Glutamic acid	3.3	3.1	2.7	1.6
Glycine	0.8	0.7	0.6	0.4
Alanine	0.7	0.6	0.5	0.3
Cysteine	0.3	0.3	0.3	0.1
Valine	0.6	0.6	0.5	0.3
Methionine	0.2	0.2	0.2	0.1
Isoleucyl	0.7	0.6	0.5	0.3
Leucine	1.2	1.1	1.0	0.6
Tyrosine	0.4	0.4	0.4	0.2
Phenlalanine	1.0	0.9	0.7	0.4
Histidine	0.5	0.4	0.4	0.2
Lysine	0.8	0.7	0.6	0.2
Arginine	1.3	1.3	1.2	0.6
Proline	0.7	0.7	0.6	0.4
Total amino acid	15.9	14.7	12.9	7.4

are shown in Table 3 and Supplementary Fig. S1, respectively. During roasting, many complex reactions took place, such as caramelisation, starch degradation, the Maillard reaction, lipid thermal degradation and oxidation, all of which led to the production of various volatile flavor compositions (Frauendorfer and Schieberle 2008; Schenker et al., 2002). In the present investigation, a total of 55 volatile compounds were identified for the three roasted pepper seeds, which were 11 alkanes, 9 esters, 8 pyrazines, 6 acids, 5 alkenes, 4 alcohols, 3 aldehydes, 3 pyridines, 1 furan, 1 ketone, and 1 pyran (Table 3). It was noted that only two pyrazines derivatives, namely tetramethyl-pyrazine and 2,3,5-trimethylpyrazine were found in the pepper seed after roasting at 120 °C. A general increasing trend was found in the amount and type of pyrazine compounds as the temperature of roasting increased. Six and eight pyrazines were observed in the pepper seeds after roasting at 160 °C and 200 °C, respectively. Generally, heterocyclic compounds such as pyrazines were mostly formed at roasting temperatures above 150 °C in contrast to products from lipid degradation. Pyrazine compounds have several precursors or formation pathways (Lasekan, 2012). The α -amino carbonyls are generally considered to be the pyrazines precursors; these are formed via the reactions between amino acids and dicarbonyl compounds during Strecker degradation (Vermeir et al., 2007). Additionally, these intermediates will react with ammonia to product α -aminoketones and then form pyrazine compounds (Yu and Zhang, 2010). The unroasted pepper seed emitted a slight

odour with pepper flavor notes, whereas the roasted samples had an attractive caramel-like and nutty odour. The most striking change of flavor in the pepper seeds after roasting was attributed to the formation of pyrazines. Pyrazine compounds are closely related to cooked, roasted and nutty odour properties and have low odour thresholds (Siegmond and Murkovic, 2004). In the present investigation, the substituted pyrazines of 2,5-dimethyl-pyrazine (1), 2,3-dimethyl-pyrazine (2), 2-ethyl-6-methyl-pyrazine (5), 2-ethyl-5-methyl-pyrazine (6), 2,3,5-trimethylpyrazine (7), 3-ethyl-2,5-dimethyl-pyrazine (14), tetramethyl-pyrazine (15), and 2-ethyl-3,5,6-trimethylpyrazine (19) were identified as the key compounds most likely responsible for the roasted and nutty flavor properties of roasted chili seeds.

Besides pyrazines, lipid oxidation compounds such as benzaldehyde (4), benzyl alcohol (8), benzeneacetaldehyde (10), phenylethyl alcohol (16), α -ethylidene-benzeneacetaldehyde (25), 4-methyl-5-thiazoleethanol (26), and 2,4,7,9-tetramethyl-5-decyne-4,7-diol (32) also contributed to the odour of roasted pepper seeds. Interestingly, higher roasting temperatures generated higher concentrations of these alcohols and aldehydes than did lower roasting temperature. Octanoic acid (20), dodecane (23), dodecanoic acid (34), 2,6,10,14-tetramethyl-hexadecane (36), hexadecane (37), 2-methyl-hexadecane (38), 2,6,10,14-tetramethyl-pentadecane (40), methyl tetradecanoate (41), tetradecanoic acid (43), octadecane (45), heptadecane (46), 2,6,10,14-tetramethyl-hexadecane (47), hexadecanoic acid

Table 3 The volatile flavor compounds identified in roasted pepper seeds at various temperatures (120 °C, 160 °C, and 200 °C)

Nos.	Time (min)	Compounds	Content of compounds in various samples (%)			Flavour description
			120 °C	160 °C	200 °C	
1	4.663	2,5-Dimethyl-pyrazine	ND	0.13	5.96	Chocolate, roasted nuts, earthy, flavour of potato chips
2	5.025	2,3-Dimethyl-pyrazine	ND	0.56	0.85	Nutty cocoa-like odour, green note
3	6.764	5-Ethyl-2-furancarboxaldehyde	ND	ND	0.09	
4	6.797	Benzaldehyde	0.11	0.45	0.36	Almond bitterness, roasted-sweet odour
5	7.829	2-Ethyl-6-methyl-pyrazine	ND	ND	0.73	Roasted-sweet odour
6	7.893	2-Ethyl-5-methyl-pyrazine	ND	ND	1.35	Grass and nuts flavor
7	7.937	2,3,5-Trimethylpyrazine	0.16	1.04	4.97	Nutty, meaty, roasted hazelnut aroma
8	8.963	Benzyl alcohol	0.38	1.61	ND	Sweet flowers and fruity flavor
9	9.033	1-Methyl-2-pyrrolidinone	ND	ND	1.58	
10	9.093	Benzeneacetaldehyde	ND	1.41	1.19	Rich fragrance of flowers
11	9.341	1,3,7-Octatriene, 3,7-dimethyl-	1.20	5.60	4.00	Flowery odour, grass fragrance
12	9.665	2-Acetyl pyrrole	0.53	1.20	1.03	Aroma of liquorice, walnut, bread
13	9.887	2-Pyrrolidinone	ND	0.70	2.47	
14	10.011	3-Ethyl-2,5-dimethyl-pyrazine	ND	ND	4.91	Reported found in roasted peanuts, coffee, grilled beef
15	10.254	Tetramethyl-pyrazine	11.84	44.64	31.02	Reported present in cocoa products, coffee, peanuts
16	10.854	Phenylethyl alcohol	0.56	3.23	3.01	Rose fragrance, bread flavor
17	11.194	Bis(1-methylethylidene)-cyclobutene	ND	0.44	ND	
18	11.475	2,3-Dihydro-3,5-dihydroxy-6-methyl-4 h-pyran-4-one	0.33	6.70	4.47	Caramelly flavour
19	11.880	2-Ethyl-3,5,6-trimethylpyrazine	0.14	0.73	1.53	Reported present in cocoa products, coffee, peanuts
20	12.118	Octanoic acid	0.43	1.35	1.15	Oil rancidity flavor
21	12.463	1-Acetyl-1,2,3,4-tetrahydro-pyridine	ND	ND	0.64	
22	12.582	Methyl salicylate	0.13	0.46	ND	Fruit and nut flavor
23	12.636	Dodecane	0.28	0.59	0.70	
24	13.965	Nonanoic acid	1.03	2.16	1.98	Aroma of wax, milk and cheese
25	14.057	α -Ethylidene-benzeneacetaldehyde	ND	ND	0.52	
26	14.122	4-Methyl-5-thiazoleethanol	ND	ND	1.02	Meat, bean and nuts flavor
27	14.792	2-Methoxy-4-vinylphenol	ND	0.44	1.86	Smoky flavor
28	15.116	2-Hydroxy-3-methyl-2-Cyclopenten-1-one	ND	ND	1.00	
29	15.586	2-Methyl-tridecane	1.34	0.52	0.50	
30	15.845	Ylangene	ND	0.24	0.27	Flowers fragrance
31	15.915	Vanillin	0.39	ND	ND	
32	16.488	2,4,7,9-Tetramethyl-5-decyne-4,7-diol	0.89	3.16	4.32	Light, bright and juicy odour
33	17.709	Alpha. -ylangene	1.26	2.38	2.10	Woody fragrance
34	18.687	Dodecanoic acid	0.60	0.20	0.40	Aroma of bay oil
35	19.227	Diethyl phthalate	0.93	ND	ND	
36	19.945	2,6,10,14-Tetramethyl-hexadecane	0.71	ND	ND	
37	20.075	Hexadecane	0.46	0.08	0.10	
38	20.151	2-Methyl-hexadecane	0.45	ND	ND	
39	20.588	2-Propenoic acid pentadecyl ester	1.06	ND	ND	
40	20.761	2,6,10,14-Tetramethyl-pentadecane	1.44	ND	ND	
41	21.031	Methyl tetradecanoate	0.93	ND	ND	
42	21.285	Methoxyacetic acid, 2-tetradecyl ester	0.65	ND	ND	Banana and pear aroma
43	21.496	Tetradecanoic acid	1.03	ND	0.08	Light aroma of wax, milk

Table 3 continued

Nos.	Time (min)	Compounds	Content of compounds in various samples (%)			Flavour description
			120 °C	160 °C	200 °C	
44	21.647	3-Methyl-heptadecane	0.56	ND	ND	
45	22.030	Octadecane	0.90	ND	ND	
46	22.101	Heptadecane	0.31	ND	ND	
47	22.160	2,6,10,14-Tetramethyl-hexadecane	1.41	ND	ND	
48	22.997	Phthalic acid, isobutyl octyl ester	1.44	2.34	1.90	Fruit, nuts flavor
49	23.581	1,2-Benzenedicarboxylic acid, bis(2-methylpropyl) ester	0.47	0.59	0.45	
50	23.646	Hexadecanoic acid methyl ester	1.01	ND	ND	Grease, grass flavor
51	23.808	Palmitoleic acid	0.59	ND	ND	
52	24.067	Hexadecanoic acid	1.91	ND	ND	
53	24.164	Dibutyl phthalate	0.75	0.71	0.59	Faintly stink odour
54	26.671	4,4'-(1-Methylethylidene)-bis-phenol	1.01	0.95	1.00	
55	29.437	Hexanedioic acid, bis(2-ethylhexyl) ester	48.37	0.34	ND	

Compounds were identified by comparison with reference substances from National Institute of Standards and Technology (NIST) mass spectral database (NIST11.L)

ND not detected

methyl ester (50), palmitoleic acid (51), and hexadecanoic acid (52) were identified as the major volatile compositions in the pepper seed after roasting at 120 °C. As in chili seed, they might be derived from the degradation of lipid caused by roasting pretreatment. As roasting temperature increased, other competing reaction pathways have resulted in the evolution and, to some extent, the loss of thermally-generated volatiles such as these long chain alkanes, fatty acids and their derivatives formed at 120 °C. Many other volatile compounds were found in the roasted samples at various temperatures, some relatively powerful, such that, even though low in amount. However, low amount did not always represent minor influence on the roasted sample odor. Therefore, some of the volatile compounds with low amount might be responsible for the odor quality of the roasted pepper seeds (Feng et al., 2017a; 2017b).

Color properties of pepper seeds before and after roasting

When roasting seeds, color is an indicator for the degree of caramelization and browning reactions. Temperature and time were the important parameter that caused the changes of sample color. The L^* , a^* and b^* color parameters of the pepper seeds before and after roasting at various temperature and time are shown in Table 4. Clearly, roasted pepper seeds looked different. The “L” value indicated the

Table 4 Color values (L^* , a^* and b^*) and total color difference (ΔE) of the pepper seeds before and after roasting at various conditions

Sample	L^*	a^*	b^*	ΔE
Raw material	65.9	13.0	48.0	0
100 °C	69.3	8.3	41.7	8.6
120 °C	69.7	8.6	42.4	8.1
140 °C	70.4	8.9	42.2	8.4
160 °C	69.4	8.0	40.9	9.4
180 °C	60.3	11.0	42.7	8.0
200 °C	59.9	13.1	45.7	6.4
10 min	69.4	8.0	40.9	9.4
20 min	63.1	14.1	48.2	3.0
30 min	59.2	12.7	45.7	7.1
40 min	56.8	11.7	43.9	10.1

lightness ranging from 0 (black) to 100 (white). The “L” value for the samples roasted at temperature from 100 to 160 °C exhibited an increase as compared with the unroasted samples, whereas at 180 °C and 200 °C, the value decreased from 65.9 (raw material) to 60.3 and 59.9, respectively. On the other hand, “a” value, indicating redness, of pepper seeds roasted at 100–180 °C decreased initially, followed by a slight increase when roasting

temperature was further increased to 200 °C. For the “b” parameter, indicating yellowness, values ranged from 40.9 to 45.7 for all temperature, tested experiments being lower as compared with unroasted sample (48.0). The roasting time and temperature had the same influence on L^* , a^* and b^* color parameters of the pepper seeds. As shown, L^* value decreased continuously from 69.4 (10 min) to 56.8 (40 min) while a^* and b^* values increased with increased roasting time firstly and then decreased during the time range from 30 to 40 min at 160 °C. However, according to the value of ΔE , roasting time had a higher influence on color changes of pepper seeds than temperature. The decrease of L^* value represented a darkening, and the increase of a^* value represents a reddening. The changes of L^* , a^* and b^* color parameters of pepper seeds after roasting at various conditions are likely due to the formation of brown pigments. During roasting, brown pigments with high molecular and low molecular weights were formed in the advance stage of the browning reactions (Sharma and Gujral, 2014; Wani et al., 2016). Additionally, oxidation of phospholipids compounds in pepper seed oil might increase the formation of brown pigments, contributing to the samples’ darker color (Bolek and Ozdemir, 2017; Ng et al., 2014). However, roasting temperature and time exhibited nonlinear influences on L^* , a^* and b^* color parameters of pepper seeds during roasting process. The explanation for the observations could be that pepper pigment (mainly capsanthin and capsorubin) present in the raw seeds was degraded during roasting process (Liu et al., 2017; Xin et al., 2015).

Storage stability of oils extracted from pepper seeds before and after roasting

Changes in peroxide value

PV is a measure of the amount of hydroperoxides and peroxides formed during the first stage of lipid oxidation. Thus, PV is widely used to test the primary oxidation stage of oils and fats. In the present investigation, the oxidation degree on the oils extracted from red pepper seeds before and after roasting were determined by measuring PV during storage at 63 °C for 30 days Fig. 1A. Clearly, the PV of all the oils showed identical increasing trends during storage for 30 days. Oil from un-roasting seeds had higher PVs than oil from roasted seeds during all storage periods, especially after 30 days’ storage. Roasting treatment intensity (i.e., higher temperature for longer period) slowed down the PV increase rate of the oils during storage, which could be explained by the fact that roasting treatment of pepper seeds led to the formation of antioxidative products by Maillard reaction (Yu and Zhang, 2010). After 30 days of storage, the PV of the oils extracted from pepper seeds

were 98.8, 73.8, and 117.4 mmol/kg at 120 °C, 160 °C, and 200 °C, respectively. Among these oils, those extracted from seeds at 160 °C gave the lowest PV at storage period of 30 days. As the roasting temperature increased to 200 °C, the peroxide formation in the oil during storage was increased as compared with that of roasting at 120 °C and 160 °C. The explanation for the higher peroxide amount during storage in oil from pepper seeds roasting at 200 °C, compared with those roasted at 120 °C and 160 °C, seems to be due to be greater formation of secondary products of lipid oxidation (Harhar et al., 2011).

Acid value

AV was used to evaluate free fatty acid content in fats and oils and was regarded to be one of the major factors to exhibit the edible oil refining degree and quality as well as the quality variation during storage (Osawa et al., 2007). Free fatty acids were major formed by hydrolysis of triglycerides and the process could be get promoted by reaction of oil with moisture (Iqbal and Bhanger, 2007). The changes in AV of the oils from raw and roasted pepper seeds during storage are presented in Fig. 1B. Clearly, the AV of all samples gradually increased during all the storage period at 63 °C. After 30 days storage at 63 °C, the AV of the oils extracted from raw pepper seeds and those roasted at 120 °C, 160 °C, and 200 °C were 4.40, 4.41, 4.39, and 4.17 mg KOH/g, respectively. Thus, treatment with roasting at 200 °C could obviously inhibit an increase of AV in pepper seed oil during 30 days storage at 63 °C.

p-Anisidine values

p-Anisidine value, or pAV, plays an important role in evaluating edible food oils as it correlates well with the development of off flavors. It is also commonly applied to evaluate secondary lipid oxidation (Tompkins and Perkins 1999). The changes in the pAV of oils from pepper seeds before and after roasting during storage at 63 °C are shown in Fig. 1C. As shown, all pepper seed oil samples exhibited an increase of pAV during the storage period at 63 °C. Roasting treatment inhibited the increase of pAV in pepper seed oil during the storage period. As shown, during the storage period at 63 °C, the pAV ranged from 3.0 to 90.7 in the pepper seed oil extracted from unroasted raw material. After roasting treatment, the pAV of the oil samples from roasted pepper seeds at 120 °C, 160 °C, and 200 °C ranged from 1.5, 2.0, and 2.1 to 20.7, 14.5, and 25.1 during the storage period, respectively. As shown, the pAV increased only 7.3- to 13.6-fold increase for the roasted oil samples, whereas there was a 30.6-fold increase for the unroasted oil sample after 30 days. The results demonstrate that roasting of pepper seeds before oil extraction significantly

Fig. 1 The changes in peroxide value (A), acid value (B), p-Anisidine value (C), and oxidative stability index (D) of pepper seed oils before and after roasting pretreatment during storage period

decreased the rates of the formation of secondary oxidation products during storage. The higher resistance to oxidation of oils extracted from roasted pepper seeds could be attributed to the formation of Maillard reaction products with antioxidant activity and the phenolic compositions with higher antioxidant properties, generated during roasting (Amarowicz, 2009; Spielmeier et al., 2009; Wakamatsu et al., 2005; Zhang et al., 2011).

Oxidative stability index

Oxidative stability index (OSI) was usually used to appraise oils susceptibility to oxidative deterioration. To study the influence of roasting on the oxidative stabilities of pepper seeds oils during storage, the OSI at 120 °C of the various investigated oil samples during various storage periods were measured (Fig. 1D). Clearly, the OSI of oil from unroasted pepper seed in their initial state was 1.1 h, whereas the roasting treatment of seeds prior to oil extraction at various temperatures contributed to higher oxidative stability of the oils, and the OSIs increased to 4.7, 5.1, and 5.6 h for the oils from roasted pepper seeds at 120 °C, 160 °C, and 200 °C, respectively. These figures represent an almost four–fivefold increase than that of the value of the oil from unroasted seeds. After 15 days of

storage, the OSIs of the oils extracted from unroasted and roasted pepper seeds at 120 °C, 160 °C, and 200 °C were 0.3 h, 1.7 h, 2.5 h, and 1.9 h, respectively. Thus, roasting slowed down the OSI decrease rates of the oils during storage, although the relatively low OSI values for the oils from roasted seeds can be found at the 30 days' storage period.

Vitamin E content

Vitamin E has antioxidant properties beneficial to human health. Therefore, the changes in vitamin E content of foods during storage are of importance. The influences of roasting treatment on vitamin E in pepper seed oils during storage at 63 °C are presented in Fig. 2. In the present investigation, four tocopherol compositions (α -, β -, γ -, and δ -tocopherols) were detected and quantified. As shown from Fig. 2, before the storage experiments were initiated, γ -tocopherols were the major compositions (from 47.8 to 78.3 mg/100 g), followed by α -tocopherols (from 7.4 to 8.7 mg/100 g), δ -tocopherols (from 0.1 to 0.8 mg/100 g, no shown in Fig. 2) and no β -tocopherols were identified in all pepper seed oils neither before nor and after roasting. It can be observed that the amounts of the total tocopherols in pepper seed oil increased 30.3% after roasting at 120 °C,

Fig. 2 The changes of tocopherols amount in the pepper seed oils before and after roasting pretreatment during the storage period (**A** α-tocopherols; **B** γ-tocopherols; and **C** total tocopherols)

followed by a decreased as the roasting temperature increased to 160 °C and 200 °C, as compared with the unroasted pepper seed oil. Many authors have reported that vitamin E content is affected by the roasting temperature and time (Amaral et al., 2006; Seybold et al., 2004; Vujasinovic et al., 2012). The compositions for which amount increased were attributed to membrane proteins or linked to other compositions, and that roasting pretreatment

could cause the breakdown of these bonds to obtain a higher extraction yield of the vitamin E compositions (Amaral et al., 2006; Seybold et al., 2004; Vujasinovic et al., 2012). However, decrease in tocopherol amount was also reported for sesame seeds roasted at 160–250 °C for various times (Yoshida and Takagi, 1997).

The total vitamin E amount in unroasted pepper seed oil obviously decreased dramatically from 66.8 to 8.7 mg/100 g after 15 days of storage; this represents a rate of 5.8%/day. In contrast, total vitamin E content of pepper seed oils after roasting at 120 °C, 160 °C, and 200 °C from 87.1, 62.7, and 56.4 to 30.1, 42.6, and 39.2 mg/100 g, respectively; this represents a rate of 4.4, 2.1, and 2.1%/day during the same storage period, respectively. The result showed that the stability of vitamin E increased after roasting prior to oil extraction. Additionally, the retention of vitamin E in roasted pepper seed oils at 160 °C and 200 °C were higher as compared with that of oil roasted at 120 °C. The high retention of vitamin can be explained in terms of the Maillard reaction; that is, Maillard reaction products could have contributed to a higher retention of vitamin E in roasted pepper seed oils.

In conclusion, the present results clearly showed that roasting caused the loss or change in the amount of sugars and amino acids in pepper seeds. This may indicate that brown pigments and volatile flavor compounds were formed by reaction between amino acids and reducing sugars degraded from the pepper seeds during roasting. The increase in peroxide value and *p*-anisidine value were lower in the oils from roasted pepper seeds as compared with oil from raw seeds during storage at 63 °C. Roasting also increased the oxidative stability index of the oils during storage. The degradation rate of total vitamin E during storage was lower in roasted pepper seed oil compared with unroasted. In conclusion, roasting increased the antioxidant capacity and oxidative stability of the pepper seed oils during storage as compared with unroasted oil. These increases are possibly due to the synergetic effect of the Maillard reaction products, increased vitamin E, and other bioactive components.

Acknowledgements The authors gratefully acknowledge the financial support provided by the Plan for Scientific Technological Breakthrough of Henan Province (172102110010) and Modern Agro-industry Technology Research System (CARS14-1-29).

References

- Amaral JS, Casal S, Seabra RM, Oliveira BPP. Effects of roasting on hazelnut lipids. *J. Agric. Food Chem.* 54: 1315–1321 (2006)
- Amarowicz R. Antioxidant activity of Maillard reaction products. *Eur. J. Lipid Sci. Technol.* 111: 109–111 (2009)

- Boge EL, Boylston TD, Wilson LA. Effect of cultivar and roasting method on composition of roasted soybeans. *J. Sci. Food Agric.* 89: 821–826 (2009)
- Bolek S, Ozdemir M. Optimization of roasting conditions of *Pistacia terebinthus* in a fluidized bed roaster. *LWT Food Sci. Technol.* 80: 67–75 (2017)
- Cao ZZ, Zhou LY, Bi JF, Yi JY, Chen QQ, Wu XY, Zheng JK, Li SR. Effect of different drying technologies on drying characteristics and quality of red pepper (*Capsicum frutescens* L.): a comparative study. *J. Sci. Food Agric.* 96: 3596–3603 (2016)
- Chirinos R, Zorrilla D, Aguilar-Galvez A, Pedreschi R, Campos D. Impact of roasting on fatty acids, tocopherols, phytosterols, and phenolic compounds present in *Plukenetia huayllabambana* seed. *J. Chem.* 2016: 1–10 (2016)
- Corrales CV, Lebrun M, Vaillant F, Madec MN, Lortal S, Pérez AM, Flidel G. Key odor and physicochemical characteristics of raw and roasted jicaro seeds (*Crescentia alata* K.H.B.). *Food Res. Int.* 96: 113–120 (2017)
- Durmaz G, Gökmen V. Changes in oxidative stability, antioxidant capacity and phytochemical composition of *Pistacia terebinthus* oil with roasting. *Food Chem.* 128: 410–414 (2011)
- Feng X, Ng VK, Mikš-Krajnc M, Yang H. Effects of fish gelatin and tea polyphenol coating on the spoilage and degradation of myofibril in fish fillet during cold storage. *Food Bioprocess Technol.* 10: 89–102 (2017a)
- Feng X, Zhu Y, Liu Q, Lai S, Yang H. Effects of bromelain tenderisation on myofibrillar proteins, texture and flavour of fish balls prepared from golden pomfret. *Food Bioprocess Technol.* 10: 1918–1930 (2017b).
- Feng X, Fu C, Yang H. Gelatin addition improves the nutrient retention, texture and mass transfer of fish balls without altering their nanostructure during boiling. *LWT Food Sci. Technol.* 77: 142–151 (2017c)
- Fraundorfer F, Schieberle P. Changes in key aroma compounds of Criollo cocoa beans during roasting. *J. Agric. Food Chem.* 56: 10244–10251 (2008)
- Gu LB, Pang HL, Lu KK, Liu HM, Wang XD, Qin GY. Process optimization and characterization of fragrant oil from red pepper (*Capsicum annuum* L.) seed extracted by subcritical butane extraction. *J. Sci. Food Agric.* 97: 1894–1903 (2017)
- Harhar H, Gharby S, Kartah B, Monfalouti HE, Guillaume D, Charrouf Z. Influence of argan kernel roasting-time on virgin argan oil composition and oxidative stability. *Plant Foods Hum. Nutr.* 66: 163–168 (2011)
- Hidalgo FJ, Zamora R. Strecker-type degradation produced by the lipid oxidation products 4,5-epoxy-2-alkenals. *J. Agric. Food Chem.* 52: 7126–7131 (2004)
- Hwang HI, Hartman TG, Ho CT. Relative reactivities of amino acids in pyrazine formation. *J. Agric. Food Chem.* 43: 179–184 (1995)
- Iqbal S, Bhangar MI. Stabilization of sunflower oil by garlic extract during accelerated storage. *Food Chem.* 100: 246–254 (2007)
- Jung MY, Bock JY, Baik SO, Lee JH, Lee TK. Effects of roasting on pyrazine contents and oxidative stability of red pepper seed oil prior to its extraction. *J. Agric. Food Chem.* 47: 1700–1704 (1999)
- Lasekan O. Headspace solid-phase microextraction gas chromatography-mass spectrometry (HS-SPME-GC-MS) determination of volatile compounds in roasted plantains (*French sombre* and *Dwarf Kalapua*). *LWT Food Sci. Technol.* 46: 536–541 (2012)
- Lee KJ, Han JS, Lee SW, Park CR. Investigation of lipids in hot pepper (I. Neutral lipids of hot pepper seeds). *Korean J. Food Sci. Technol.* 7: 91–95 (1975)
- Liu Q, Tan CSC, Yang H, Wang S. Treatment with low-concentration acidic electrolysed water combined with mild heat to sanitise fresh organic broccoli (*Brassica oleracea*). *LWT Food Sci. Technol.* 79: 594–600 (2017)
- Ng S, Lasekan O, Muhammad K, Sulaiman R, Hussain N. Effect of roasting conditions on color development and Fourier transform infrared spectroscopy (FTIR-ATR) analysis of Malaysian-grown tropical almond nuts (*Terminalia catappa* L.). *Chem. Cent. J.* 8: 1–11 (2014)
- Osawa CC, Gonçalves LAG, Ragazzi S. Correlation between free fatty acids of vegetable oils evaluated by rapid tests and by the official method. *J. Food Compos. Anal.* 20: 523–528 (2007)
- Rufián-Henares JA, Delgado-Andrade C, Morales FJ. Assessing the Maillard reaction development during the toasting process of common flours employed by the cereal products industry. *Food Chem.* 114: 93–99 (2009)
- Schenker S, Heinemann C, Huber M, Pompizzi R, Perren R, Escher F. Impact of roasting conditions on the formation of aroma compounds in coffee beans. *J. Food Sci.* 67: 60–66 (2002)
- Seybold C, Fröhlich K, Bitsch R, Otto K, Bohm. V. Changes in contents of carotenoids and vitamin E during tomato processing. *J. Agric. Food Chem.* 52: 7005–7010 (2004)
- Sharma P, Gujral HS. Antioxidant potential of wheat flour chapattis as affected by incorporating barley flour. *LWT Food Sci. Technol.* 56: 118–123 (2014)
- Siegmund B, Murkovic M. Changes in chemical composition of pumpkin seeds during the roasting process for production of pumpkin seed oil (part 2: volatile compounds). *Food Chem.* 84: 359–365 (2004)
- Singh L, Varshney JG, Agarwal T. Polycyclic aromatic hydrocarbons' formation and occurrence in processed food. *Food Chem.* 199: 768–781 (2016)
- Spielmeyer A, Wagner A, Jahreis G. Influence of thermal treatment of rapeseed on the canolol content. *Food Chem.* 112: 944–948 (2009)
- Spotti MJ, Perduca MJ, Piagentini A, Santiago LG, Rubiolo AC, Carrara CR. Does dextran molecular weight affect the mechanical properties of whey protein/dextran conjugate gels? *Food Hydrocolloids.* 32: 204–210 (2013)
- Tompkins C, Perkins EG. The evaluation of frying oils with the *p*-Anisidine value. *J. Am. Oil Chem. Soc.* 76: 945–947 (1999)
- Veldsink JW, Muuse BG, Meijer MMT, Cuperus FP, van de Sande RLKM, Van Putte KPAM. Heat pretreatment of oilseeds: effect on oil quality. *Fett Lipid.* 101: 244–248 (1999)
- Vermeir S, Nicolai BM, Jans K, Maes G, Lammertyn J. High-throughput microplate enzymatic assays for fast sugar and acid quantification in apple and tomato. *J. Agric. Food Chem.* 55: 3240–3248 (2007)
- Vujasinovic V, Djilas S, Dimic E, Basic Z, Radocaj O. The effect of roasting on the chemical composition and oxidative stability of pumpkin oil. *Eur. J. Lipid Sci. Technol.* 114: 568–574 (2012)
- Wakamatsu D, Morimura S, Sawa T, Kida K, Nakai C, Maeda H. Isolation, identification, and structure of a potent alkyl-peroxyl radical scavenger in crude canola oil, canolol. *Biosci. Biotechnol. Biochem.* 69: 1568–1574 (2005)
- Wang J, Fang XM, Mujumdar AS, Qian JY, Zhang Q, Yang XH, Liu YH, Gao ZJ, Xiao HW. Effect of high-humidity hot air impingement blanching (HHAIB) on drying and quality of red pepper (*Capsicum annuum* L.). *Food Chem.* 220: 145–152 (2017)
- Wang J, Wang Y, Zheng L, Ni S, Fan Z, Yao R, Chen K. Kinetic study on extraction of red pepper seed oil with supercritical CO₂. *Chin. J. Chem. Eng.* 22: 44–50 (2014)
- Wani IA, Gani A, Tariq A, Sharma P, Masoodi FA, Wani HM. Effect of roasting on physicochemical, functional and antioxidant properties of arrowhead (*Sagittaria sagittifolia* L.) flour. *Food Chem.* 197: 345–352 (2016)
- Xin Y, Zhang M, Yang H, Adhikari B. Kinetics of argy wormwood (*Artemisia argyi*) leaf peroxidase and chlorophyll content

- changes due to thermal and thermosonication treatment. *J. Food Sci. Tech.* 52: 249–257 (2015)
- Yoshida H, Takagi S. Effects of seed roasting temperature and time on the quality characteristics of sesame (*Sesamum indicum*) oil. *J. Sci. Food Agric.* 75: 19–26 (1997)
- Yu AN, Zhang AD. 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. *Food Chem.* 119: 214–219 (2010)
- Yusuf AA, Ayedun H, Sanni LO. Chemical composition and functional properties of raw and roasted Nigerian benniseed (*Sesamum indicum*) and bambara groundnut (*Vigna subterrananea*). *Food Chem.* 111: 277–282 (2008)
- Yu X, Ang HC, Yang H, Zheng C, Zhang Y. Low temperature cleanup combined with magnetic nanoparticle extraction to determine pyrethroids residue in vegetables oils. *Food Control.* 74: 112–120 (2017)
- Yu X, Li Z, Zhao M, Lau SCS, Tan HR, Teh WJ, Yang H, Zheng C, Zhang Y. Quantification of aflatoxin B₁ in vegetable oils using low temperature clean-up followed by immuno-magnetic solid phase extraction. *Food Chem.* 275: 390–396 (2019)
- Zhang SB, Lu QY, Yang H, Li Y, Wang S. Aqueous enzymatic extraction of oil and protein hydrolysates from roasted peanut seeds. *J. Am. Oil Chem. Soc.* 88: 727–732 (2011)
- Zhang W, Wang R, Yuan Y, Yang T, Liu S. Changes in volatiles of palm kernel oil before and after kernel roasting. *LWT Food Sci. Technol.* 73: 432–441 (2016)

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.