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ORIGINAL ARTICLE

Capsaicin and tocopherol in red pepper seed oil enhances the thermal oxidative stability during frying

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Abstract Thermal oxidative stability of red pepper (*Capsicum annuum*) seed oil added with different levels of capsaicin or tocopherol as antioxidant during heating up to 48 h at 140±5°C was studied. Lipid oxidation of soy and pepper oil with different levels of capsaicin (0.12, 0.24%) and tocopherol (0.3, 0.6%) were evaluated during storage at 140°C for 0, 12, 24 and 48 h by monitoring peroxide value (PV), thiobarbituric acid reactive substances (TBARS) and chemiluminiscence (CL). Capsaicin content of crude pepper oil (0.16 mg/ml) was much higher than that of commercial brands (0.004–0.02 mg/ml). Oleate content was significantly ($p<0.05$) higher in soy oil (53.7%) than pepper oil (9.5%), however, linoleate and linolenate contents were significantly ($p<0.05$) higher in pepper oil (70.6, 5.8%) than in soy oil (25.9, 5.8%). TBARS, PV, and CL of pepper oil were significantly ($p<0.05$) lower than soy oil after frying. TBARS and CL values of pepper oil with different levels of capsaicin or tocopherol showed significantly ($p<0.05$) lower values than untreated pepper oil during frying and storage. TBARS and CL values of 0.6% tocopherol treated pepper oil showed significantly ($p<0.05$) lower values than those of soy oil. The study suggests that capsaicin and tocopherol may play a key role to prevent the thermal oxidation of pepper oil during frying.

Keywords Red pepper oil · Capsaicin · Tocopherol, Thermal oxidative stability · Rancidity · Chemiluminiscence

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Introduction

Rancidity in edible oils is one of the primary factors associated with oil quality and health problems (Kang et al. 1995). Increased consumption of edible oils worldwide is limited by a number of factors including trans-fatty acids content and rancidity. However, edible oils are very susceptible to lipid oxidation and off-flavour development during deep frying depending upon their fatty acid composition, storage period and processing temperature (Miyazawa et al. 1994, Choi 1996). To overcome these problems, there is a need for development of newer preservatives to provide edible oils a better thermal oxidative stability during deep frying. Spices are known for their antioxidative properties. Potential antioxidants including vitamin C, β-carotene, tocopherol, capsaicin and some spice extracts (Cort 1974, Aoyama 1996, Lee et al. 2008) have been investigated. Due to an increasing demand for new ethnic foods, red pepper (*Capsicum annuum* L.) seed oil is gaining popularity as one of the edible oils in Korea and neighbouring countries. Red pepper seed oil is very rich in linoleic acid (Choi and Ko 1990). Antioxidative mechanism of alpha tocopherol (Husain et al. 1987) and capsaicin (Kogure et al. 2002) have been reported. Our preliminary experiments showed that capsaicin retarded lipid oxidation of soybean oil during deep frying at 200°C (Lee and Lee 2001); however, it is not effective at 100°C (Lee et al. 2008). Thus, this study was planned to evaluate the effects of capsaicin and tocopherol levels on the thermal oxidative stability of pepper oil during deep frying at 140°C.

Materials and methods

Crude pepper (*Capsicum annuum*) oil was made from red pepper seed by simple oil extraction in a local oil mill. Three other commercial brands (Nonghyup, Ottogi and Saimdang) of pepper oils were purchased from local market (Chungju, Korea) for comparison. Standard capsaicin, alpha-tocopherol and 2-thiobarbituric acid (TBA) were purchased from Sigma (USA). All other chemicals used were of analytical grade.

Experimental plan: Following treatments were formulated. Pepper oil without any additive as control (Pep), Pepper oil with 0.12% capsaicin (Pep 1), Pepper oil with 0.24% capsaicin (Pep 2), Pepper oil with 0.3% tocopherol (Pep 3), and pepper oil with 0.6% tocopherol (Pep 4). Soy oil was taken for comparison. Additives were mixed well with pepper oil, then fried at 140±5^{0}C and hold at this temperature for 48 h. Samples were taken for evaluation at 12 h intervals up to 48 h for analysis.

Determination of capsaicin content: Capsaicin and dihydrocapsaicin content in the crude and commercial pepper oils were determined by the HPLC method (Lee 1977). Capsaicin was extracted with 25 ml solvent (citric acid : methanol, 1:9, v/v) from pepper oil by taking 1 g sample. The mixture was put into a 50 ml Erlenmeyer flask and boiled for 30 min. The distilled methanol layer was concentrated in a rotary vacuum evaporator (Korea Bio-Tech Co. Ltd. Seoul).

Determination of fatty acids: The oils were extracted by the method of Bligh and Dyer (1959) and then methylated with 14% boron trifluoride-methanol at 100°C for 60 min (AOCS 1998). The fatty acid methyl esters were separated by gas chromatography (Carlson and Werkman 1996) using 30 m × 0.25 mm I. d. factor, four capillary column (Varian CP 3380, USA) and detected by flame ionization detector (Shimazu Co., Tokyo, Japan). The chromatograms were recorded and the percent composition of individual peak was calculated with a Chromatopac C-R6A (Shimazu Co., Tokyo, Japan). The fatty acid esters were identified by comparing their retention times with standards.

Determination of PV: The samples of 10 ml were evenly distributed in 25 ml air-tight vials (Wheaton, Millville, NJ, USA) and placed at 140±5°C in an incubator (Vision Scientific, Seoul, Korea). Samples were taken every 12 h, and PV was determined to monitor the extent of lipid peroxidation (AOCS 1998).

Determination of thiobarbituric acid reactive substances (TBARS): The extent of lipid oxidation in oil samples was determined with TBARS by the method of Tarladgis et al. (1960). The TBA was expressed as mg of malonaldehyde per kg sample.

Measurement of chemiluminiscence (CL) counts: A photon counter (CLA1 100) of a CL analyzer (Tohoku Electronic Industrial Co., Ltd, Sendai, Japan) was used for the determination of thermal rancidity of fried oils (Miyazawa et al. 1991). The sample of 3 g was taken on a stainless-steel plate (50 mm in diameter, 10 mm in height) and monitored at 100^{0}C for 10 min. The emission intensity was expressed in terms of total counts for 10 min.

Statistical analysis: The experiment was repeated 3 times and all the analyses were done in triplicate. Data obtained were analyzed with analysis of variance using SPSS statistical program, and the level of significance among samples was tested at $p<0.05$ with Duncan's multiple range test.

Results and discussion

Capsaicin contents: Capsaicin and dihydrocapsaicin contents of crude pepper oil was 0.16 mg/ml and 0.07 mg/ml, respectively (Table 1). Capsaicin and dihydrocapsaicin of refined commercial pepper oil from Nonggyup, Ottogi and Saimdang were 0.004-0.02 and 0.003-0.01 mg/ml, respectively. Capsaicin and dihydrocapsaicin contents of crude pepper oil was significantly ($p<0.05$) higher than those of commercial pepper oils which is in agreement with earlier reports (Lee 1977, Kim and Lee 1980). These results suggested that decrease of capsaicin and dihyrocapsaicin of commercial pepper oils might be due to the refining process. The higher levels of capsaicin in crude pepper oil is expected to have better oxidative stability as indicated in earlier reports on soybean oil (Lee 1977, Lee and Lee 2001).

Fatty acid composition: The main fatty acids were palmitic (C 16:0), oleic (C 18:1), linoleic (C 18:2), linolenic (C 18:3) and arachidonic (C 20:4) (Table 2). The palmitate,

Table 1 Capsaicin and dehydrocapsaicin contents (mg/ml) of crude and commercial red pepper seed oils

	Capsaicin	Dihydrocapsaicin
Crude pepper oil	0.16 ± 0.008^a	0.07 ± 0.004^a
Nonghyup	0.02 ± 0.001^b	0.01 ± 0.001^b
Ottogi	0.01 ± 0.003^b	0.003 ± 0.001^c
Saimdang	0.004 ± 0.001^c	0.003 ± 0.001^c

^{a,b,c}means with different superscripts in a column differ significantly ($p < 0.05$), ($n = 3$)

Table 2 Main fatty acids composition % of soybean and red pepper seed oil

Fatty acids	No. of carbon	Soybean	Red pepper*
Palmitate,	C 16:0	11.3±0.73^a	13.7±0.29^b
Oleate,	C 18:1	53.7±7.51^a	9.47±1.66^b
Linoleate,	C 18:2	25.9±3.39^a	70.63±0.29^b
Linolenate,	C 18:3	3.40±2.57^a	5.80±0.21^b
Arachidonate,	C 20:0	0.30±0.07^a	0.40±0.01^a
UFA		88.7^a	86.3^a
SFA		11.3^a	13.7^a

^{a,b}means with different superscripts in a row differ significantly ($p < 0.05$), ($n = 3$)

*Lee et al. (2008), UFA: Unsaturated fatty acids, SFA: Saturated fatty acids

linoleate and linolenate contents of pepper oil were significantly ($p<0.05$) higher than those of soybean oil, however, oleate content was significantly ($p<0.05$) higher in soy oil than pepper oil. In case of soy oil oleic acid (53.7%) is the major contributor and 88.7% is unsaturated fatty acid (UFA), whereas, in case pepper oil linoleic acid (70.6%) is the major contributor and 86.3 % is UFA. The contrasting differences between the 2 oils were that oleate content was very high in soy oil and linoleate content was very high in pepper oil. The results showed that the level of UFA was little higher in soy oil but the high level of linoleic acid indicated a huge contrast in pepper oil which confirms the earlier reports (Kim and Lee 1980, Choi and Ko 1990).

Changes of peroxide values (PV): The peroxide formation in soy oil increased sharply from 0 to 48 h (4.6 to 15.3 meq/kg) of storage but it has not increased to that extent in pepper oil (4.2 to 8.7 meq/kg) (Table 3). Significant ($p<0.05$) increase in the PV was evident between soy and pepper oil at 24 and 48 h storage. This difference might be due to the antioxidative activity of capsaicin and tocopherol which are present more in pepper oil than in soy oil and similar observations were also reported by Speek et al. (1985) and Packer (1991).

Changes in TBARS value: TBARS values in pepper oils were significantly ($p<0.05$) lower than that in soy oil during storage which indicated the antioxidative activity of capsaicin naturally present in pepper oil (Table 4). When capsaicin at 0.12 and 0.24% was added to control pepper oil, the rate of increase in TBARS value reduced significantly ($p<0.05$) and it further supports the antioxidative ability of capsaicin as also reported by Lee and Lee (2001). Similarly, pepper oil with both levels of tocopherol tried showed significant ($p<0.05$) decrease of malonaldehyde formation compared to control. It was also observed that capsaicin at 0.24% and tochopherol at 0.3% are more effective. The TBARS value measures the amount of malonaldehyde in carbonyl compounds and secondary oxidation products. Our results suggested that formation of peroxides and malonaldehyde were inhibited by the addition of capsaicin and tochopherol to the pepper oil during deep frying at 140±5 for 48 h. Similar observations were also reported by Lee and Lee (2001) and Aoyama et al. (1986) on capsaicin and tocopherol, respectively. It was further observed that tocopherol is more effective than capsaicin to retard lipid oxidation of pepper oil as indicated in the change of TBARS value during storage at 48 h after frying which is in agreement with the observation of Aoyama et al. (1986).

Changes in CL: The CL counts of pepper oil were significantly ($p<0.05$) lower than those of soybean oil during storage indicating that additives in pepper oil retarded the

Table 3 Peroxide values (meq/kg) of soy and red pepper seed oil during storage at 140 ± 5°C Storage period, h

Groups	0	12	24	48
Soy oil	4.6 ± 0.03^{a}	5.1 ± 0.02^{a}	12.6 ± 0.02^{a}	15.3 ± 0.02^{a}
Pepper oil	4.2 ± 0.02^{a}	5.2 ± 0.01^{a}	6.2 ± 0.02^{b}	8.7 ± 0.02^{b}

^{ab}Means ± SE with different superscripts in a column are significantly ($p < 0.05$)

Table 4 TBARS values and chemiluminescence counts of soy and red pepper seed oil with different levels of capsaicin and tocopherol during storage at 140 ± 5°C

Heating time (hour) Groups	0	12	24	48
Soy	41.8 ± 0.21^{a}	85.3 ± 0.56^{a}	109.1 ± 0.69^{a}	484.7 ± 1.93^{a}
Pep	29.2 ± 0.23^{d}	75.0 ± 1.08^{b}	88.6 ± 1.01^{b}	145.3 ± 1.28^{b}
Pep 1	33.9 ± 2.17^{b}	60.2 ± 1.55^{c}	67.5 ± 2.30^{c}	143.1 ± 2.60^{b}
Pep 2	25.7 ± 0.40^{e}	59.8 ± 2.57^{c}	65.4 ± 2.70^{c}	137.4 ± 4.07^{b}
Pep3	28.5 ± 2.21^{d}	52.7 ± 0.95^{d}	58.9 ± 0.59^{d}	100.9 ± 1.73^{c}
Pep4	31.5 ± 2.41^{c}	55.2 ± 0.36^{d}	66.6 ± 1.31^{c}	102.8 ± 2.72^{c}
	0	12	24	48
Soy	24180 ± 6159^{a}	53407 ± 3712^{a}	121110 ± 13794^{a}	437660 ± 18977^{a}
Pep	33223 ± 3225^{a}	43435 ± 6495^{b}	117206 ± 3154^{a}	277191 ± 4882^{b}
Pep 1	36035 ± 5677^{a}	27030 ± 4390^{c}	107739 ± 4989^{a}	314132 ± 19431^{a}
Pep 2	39630 ± 4140^{a}	28403 ± 2640^{c}	93343 ± 6967^{b}	255042 ± 18688^{c}
Pep 3	38679 ± 6022^{a}	29442 ± 2771^{c}	42072 ± 2524^{c}	241109 ± 11820^{d}
Pep 4	38360 ± 4419^{a}	30995 ± 3023^{c}	35959 ± 3812^{c}	249236 ± 24263^{c}

$(n=3)^{a-d}$ Means with different superscripts in a column are significantly different ($p<0.05$)

Soy : Soybean oil, Pep : pepper oil, Pep1 : pepper oil with 0.12% capsaicin

Pep2 : pepper oil with 0.24% capsaicin

Pep3: pepper oil with 0.3% tocopherol Pep4: pepper oil with 0.6% tocopherol

extent of lipid oxidation (Table 4). The addition of capsaicin to pepper oil, at both levels, reduced the extent of lipid oxidation significantly ($p<0.05$) after storage for 48 h. Similarly, addition of tocopherol to pepper oil, at both levels, also significantly ($p<0.05$) reduced the extent of lipid oxidation compared to control or soy oil. It was further observed that capsaicin at 0.24% and tocopherol at 0.3% were more effective at 48 h of storage. Several researchers have reported the antioxidant activities of capsaicin (Lee and Lee 2001, Kogure et al. 2002, Lee et al. 2008) and tocopherol (Cort 1974, Husain et al. 1987) in edible oils.

Conclusion

Pepper oil exhibited antioxidant activity during frying when used alone or in combination with capsaicin or alpha-tocopherol. It suggested that red pepper seed oil can be used to avoid thermal oxidation in place of soybean oil during deep frying and thermal acidation can be further prevented by adding capsaicin or tocopherol as antioxidant.

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References

AOCS (1998) Official methods and recommended practices. 5th edn, American Oil Chemists' Society, Champaign, IL

Aoyama M, Maruyama T, Kanematsu H, Matsumoto (1986) Comparison of effects between the mixture of tocopherols and other antioxidants and synergists in the fryer test. Oil Chem 35: 449–453

Bligh EG, Dyer WJ (1959) A rapid method of total lipid extraction and purification. Canadian J Biochem Physiol 37:911–917

Carlson SE, Werkman SH (1996) A randomized trial of visual attention of preterm infants fed docosahexaenoic acid until two months. Lipids 31:85–90

Choi OS (1996) Emulsification stability of oleoresin red pepper and changes in antioxidant activity during thermal cooking. J Korean Soc Food Nutr 25:104–109

Choi YJ, Ko YS (1990) Studies on the lipid composition of red pepper seed oil. Int J Human Ecol 28:31–36

Cort WM (1974) Antioxidant activity of tocopherols, ascorbyl palmitate, ascorbic acid and their mode of action. J Am Oil Chem Soc 51:321–325

Husain SR, Cillard J, Cillard P (1987) Hydroxyl radical scavenging activity of flavonoids. PhytoChem 26:2489–2491

Kang MH, Song ES, Chung HK, Shim KB, Kang CW, Ryu YH, Lee JB (1995) Comparison of oxidation stability in sesame, corn and safflower oils. Korean J Int Agric 12:115–120

Kim JC, Lee JS (1980) The study on the refine and analysis of red pepper seed oil. Korean J Food Sci Technol 12:126–132

Kogure K, Goto S, Nishimura M, Yasumoto M, Abe K, Ohiwa C, Sassa H, Kusumi T, Terrada H (2002) Mechanism of potent antiperoxidative effect of capsaicin. Biochim Biophys Acta 47: 1700–1704

Lee KR (1977) Capsaicinoids content in the red pepper species. J Food Sci 6:21–25

Lee CH, Lee IH (2001) The effect of capsaicin on the thermal and oxidative stability of soybean oil. Animal Resources Res (Konkuk University) 22:9–17

Lee CH, Han KH, Kim AY, Lee SK, Hong GE, Pyun CW, Choi KD, Yang CY (2008) Effect of hot pepper seed oil, capsaicin and alpha-tocopherol on thermal oxidative stability in lard and soy bean oil. Korean J Food Sci Anim Resourc 28: 660–666

Miyazawa T, Fujimoto K, Kinoshita M, Usuki, R (1994) Rapid estimation of peroxide content of soybean oil by measuring thermoluminescence. J Am Oil Chem Soc 71: 343–345

Miyazawa T, Kikuchi M, Fuzimoto K, Endo Y, Cho SY, Kaneda T (1991) Shelf-life dating of fish meats in terms of oxidative rancidity measured by chemiluminescene. J Am Oil Chem Soc 68:39–43

Packer L (1991) Protective role of vitamin E in biological systems. Am J Clin Nutr 53:1050–1055

Speek AJ, Schrijver J, Schreuers WHP (1985) Vitamin E composition of some seed oils as determined by HPLC with fluorometric detection. J Food Sci 50:121–124

Tarladgis BG, Watts BM, Jounathane (1960) A distillation method for the quantitative determination of malonaldehyde in rancid food. J Am Oil Chem Soc 37:44–48