Agric. Chem. Biotechnol. 41(8), 578-582 (1998)

Article

Characterization of Grape Seed Oil

Han-Chul Kang*, Won-Jong Park[1], Si-Dong Kim and Jong-Cheon Park

Grape Experiment Center, Rural Development Administration, Okcheon 373-880, Korea
[1]Department of Food Science and Technology, Kong-Ju University, Yesan 340-800, Korea

Received October 7, 1998

Grape seed oil was characterized to assess the usefulness in the food industry. Among the various oils, the initial antioxidant activity was the highest for grape seed oil. Heating the oil at 180°C for 20 min retained 86% of the initial activity. Grape seed and sesame oils showed a low peroxide value, about 2, implying a less oxidative reaction. The oxidation of grape seed oil was increased to a less extent by heat-treatment than other oils. Light exposure for 1 month resulted in a slight decrease in the antioxidant activity of grape seed oil, maintaining 96% of the initial activity. Other oils were all light-susceptible and the activities decreased significantly. The peroxide values of all the oils increased by light exposure, but the extent of oxidation was still the least for grape seed oil. The addition of grape seed oil to perilla oil was very effective, in that the peroxide value was 5-times decreased by 1 : 5 composition of grape seed oil versus perilla oil. These results indicate that grape seed oil can be used as a good cooking oil or an additive for other oils.

Key words : *grape seed oil, antioxidation, peroxide value.*

The vegetable oils are produced for cooking from many sources such as sesame, perilla, soybean, corn, and other plants. These oils are widely used and show the characteristics proper to the sources.

An oxidation of plant oils occurs spontaneously at low or room temperatures. Besides this type of oxidation, high temperature including frying induces an oxidation and the mechanism is different from the former spontaneous oxidation. The plant oils in foods show some chemical reactions such as polymerization and hydrolysis as well as oxidation during storage or heating process.[1-7] The peroxidyl products occurred through an oxidation reaction are hydrolysed to aldehydes, ketones, alkene, and *n*-alkane or reacted with various radicals, resulting in new products.[8,9] These products influence significantly on the quality of foods and oils, causing a detriment to human health.[10,11] Thus the development of antioxidant has been an important issue in the food biotechnology. Furthermore, the oils used for frying are often recycled for economical purpose. Thus, heating temperature and time are very important factors on the oxidation of oils.

Even though perilla oil has some advantages in the physiological functions, this oil comprises an unsaturated linolenic acid as a major fatty acid, resulting in easy oxidation. The lignan-type substances such as sesamol, sesamin, and sesamolin were known to function as an antioxidant.[1] and the other natural antioxidants from cereals and legumes were reviewed.[12] Commercial butylated hydroxyanisole and butylated hydroxytoluene show an excellent antioxidative function at room temperature but these substances are hydrolyzed or volatile under high temperature, resulting in less efficiency of antioxidation.[13,14] In an attempt to use the frying oils further, some methods were employed to eliminate various substances such as the free fatty acids, pigments, and polymers using some adsorbents.[15-18]

It is interesting to compare the extent of oxidation in plant oils such as grape seed, perilla, soybean and sesame oils under different conditions including heating. Despite some potential advantages, the grape seed oil was scarcely investigated. We focussed the studies of grape seed oil on the antioxidation, and these characteristics were compared with those of the other plant oils.

Materials and methods

Plant materials. Grape vine of 5 years old vitis (Campbell early) was cultivated in a green house under 14 h of day light and 10 h of darkness at temperatures ranging from 20 to 30°C. After 3 months from fruit-bearing, the ripe grapes were harvested. Grape seeds were collected and stored at -20°C after washing until use. The other plant sources such as sesame, perilla, soybean, and corn were

*Corresponding author
Phone: 82-475-733-6851; Fax: 82-475-733-8938
E-mail: oksipo@chollian.net

Abbreviations: DPPH, 1,1-diphenyl-2-picryl hydrazyl.

collected from Kangwon-do.

Preparation of crude oils. The grape seeds were dried in the shade at room temperature. The seeds were fully homogenized using sample mill (Cyclotec). The homogenate was mixed with chloroform methanol solution (2 : 1, v/v) and stirred vigorously for 30 min. After eliminating the pellet with filter paper (Whatman No. 541), the resulting filtrate was further clarified by centrifugation at 10,000 g for 20 min. The remaining organic solvents were removed using evaporator at 50°C. The other oils from corn, sesame, soybean and perilla were prepared by the same method. Unless mentioned otherwise, all the oils prepared were stored at -20°C until further use.

Analytical methods. Peroxide value was measured according to A.O.C.S. method.[19] For the measurement of antioxidant activity, the oil samples (30 μl) were introduced into the reaction mixture consisting of 100 μM 1,1-diphenyl-2-picrylhydrazyl (DPPH), 50% ethanol, and Tris/HCl (pH 7.2, 20 mM). The reaction was carried out at 37°C for 30 min and a decrease in the absorbance at 516 nm were measured. The decrease of absorbance from the control test was calculated to a reduction of DPPH (%) for the activity assessment. All the experiments relating to the antioxidant activity and peroxide value were performed in duplicate and mean values were used.

Other methods. Thermo-stability of antioxidant activity was analyzed using the oils that were heated from 60 to 120°C for 20 min. The changes in peroxide value was measured by heat-treatment at 150°C for 1~4 h. For the test of light effect on the oxidation, the plant oils were stored under dark or light condition for 1 month at room temperature. These oils were used for the analysis of antioxidative activity and peroxide value. The additive effect of grape seed oil was performed with the perilla oil as a model of plant oil. The grape seed oil (2 ml) was added to 5 ml of the perilla oil. This oil mixture was tested for the analysis of antioxidant activity and peroxide value. The effect of grape seed oil was compared with that of butylated hydroxytoluene.

Results and discussion

Antioxidant activities of the different plant oils were tested using DPPH (Table 1). Among the 5 oils tested, the extent of decrease in absorbance was the highest for the grape seed oil, resulting in 1.89 of the $\triangle Abs_{516nm}$ which was equivalent to 89% of DPPH reduction. This activity was about 11-times higher than that of the corn oil under the experimental condition. The sesame oil also showed a relatively high antioxidant activity with 56% of DPPH reduction. By the analysis of the scavenging capacity against the free radical, the grape seed oil was considered to possess an excellent antioxidant activity.

The initial oxidation of various oils was evaluated by determining the peroxide values (Table 1). The oils from grape seed and sesame showed the same value and the lowest, only 2 meq/kg·oil. This value was 7 times lower than that of perilla oil. This result suggested that grape seed and sesame oils were initially less oxidized than the other oils. The easy oxidation of perilla oil may have resulted from a high proportion of linolenic acid.

Table 1. DPPH scavenging activity and Peroxide values of different plant oils.

Seed oils	DPPH reduction (%)	Peroxide value (meq/kg·oil)
Grape	89	2
Sesame	56	2
Perilla	34	14
Soybean	18	6
Corn	8	4

The initial activity of antioxidant was tested for the different plant oils (30 μl) using DPPH. The activity is presented as the reduction (%) of DPPH from the control value. The control test was carried out with the minus oil sample. The initial oxidation was measured using the plant oils (1 ml) from different sources. The oxidation was assessed by the test of peroxide value.[19]

The heat stability of antioxidant activity was assessed for the grape seed oil and compared with those of the other oils (Fig. 1). All the oils more or less lost their antioxidant activities with the increase in temperature. But the grape seed oil retained strong antioxidant activity by heat-treatment at 180°C, resulting in the 86% of the initial activity. This degree of retention was slightly lower than that of perilla oil, 89%. The activity of sesame oil decreased more rapidly with temperature, showing 69% of activity retention versus the initial activity. The rate of decrease in activities were similar between grape, sesame and soybean. The heat-stability of antioxidants was considered to have a similar capacity, but the total remaining

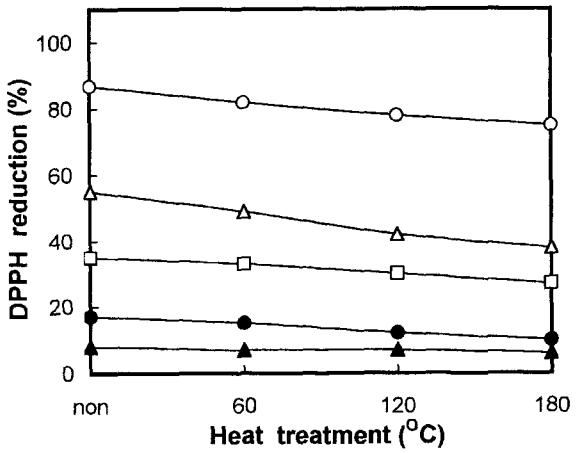

Fig. 1. Effect of heat treatment on the DPPH scavenging activity of different plant oils. The plant oils were heated as indicated for 20 min and the antioxidant activity measured using DPPH. The activity was expressed as the reduction (%) of DPPH from the control test. Symbols ○—○, △—△, □—□, ●—● and ▲—▲ correspond to the oils from grape, sesame, perilla, soybean, and corn, respectively.

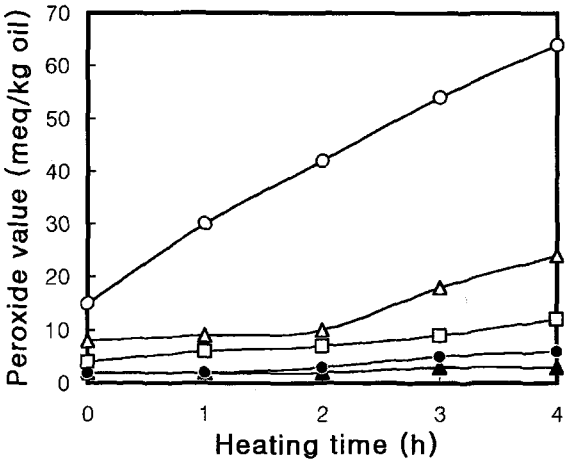

Fig. 2. Effect of heat treatment on the peroxide value of different plant oils. The plant oils were heated for the indicated times up to 4 h at 150°C and then the peroxide values were measured. Symbols ○—○, △—△, □—□, ●—● and ▲—▲ represent the values of the oils from perilla, soybean, corn, sesame, and grape seed, respectively.

activity of antioxidation was still the highest for the grape seed oil after the heat-treatment.

The changes in peroxide values of the oils were measured by prolonging the heating time at 150°C (Fig. 2). The peroxide values of all the oils were increased by the heat-treatment, and the peroxide production prevailed over the hydrolysis of peroxide under the experimental condition. The extent of increase showed a considerable variations among the oils. The extents of oxidation were increased by the order of perilla > soybean > corn > sesame > grape seed. The heat treatment for 4 h resulted in a slight increase of peroxide value of grape seed oil, showing only 3 meq/kg·oil, 21-times lower than that of perilla oil. Though higher than the grape seed oil's value, the sesame oil also showed a relatively low peroxide value. The increase in peroxide values did not exactly correlate with the antioxidative activity profile of the plant oils. This discrepancy might be explained from the various factors including fatty acids, involved in the oxidative- stability.[20,21]

Generally, oxidation of oils or free fatty acids can be facilitated by light-exposure. In this connection, the potential protective capacity of antioxidants from light was tested for the different plant oils. The crude oils were stored under dark or light condition for 1 month at room temperature, and the antioxidant activities were measured (Table 2). All the plant oils retained most of their antioxidant activities under dark storage condition compared with the initial activities of plant oils, except some were lost in the sesame and soybean oils. The antioxidant activity of grape seed oil was similar regardless of the light condition, resulting in 3% decrease of activity by the light-exposure. This result suggests that the antioxidative substances in the grape seed oil were well preserved from the light. The sesame oil also showed a significant

Table 2. DPPH scavenging activity and the peroxide values of plant oils stored under light or dark condition.

Seed oils	DPPH reduction (%)		Peroxide Value (meq/kg·oil)	
	dark	light	dark	light
Grape	87	84	3	6
Sesame	38	26	3	10
Perilla	30	0	18	32
Soybean	11	0	8	12
Corn	7	2	7	30

Various oils were stored under dark or light condition. Change of antioxidant activity and peroxide values measured. The antioxdant activity measured with 30 μl of each sample are expressed as the reduction (%) of DPPH from the control tests that were considered as 0% reduction. The oxidation was assessed by the test of peroxide value. The control samples were merely consisted of organic solvents that were used for crude oil extraction.

increase in antioxidant activity after storage in the light. The other plant oils from perilla, soybean, and corn lost considerably their antioxidant activities under the light exposure.

The peroxide values were tested for the plant oils stored for 1 month under dark or light condition at room temperature (Table 2). The value of all the oils increased by the exposure to the light. Among the oils tested, the perilla and corn oils were significantly oxidized, resulting in 32 and 30 of peroxide value. The grape seed oil showed a slight increase in oxidation, showing 6 of the peroxide value. Under the dark storage condition, the grape seed and sesame oils were considerably stable from oxidation since 3 of peroxide value was similar to the initial values of oils. These results indicate that the grape seed and sesame oils show a significant stability in oxidation from the exposure to light.

The additive effect of grape seed oil on the peroxide value was measured using the perilla oil as a model of plant oil (Fig. 3-A). This effect was compared with that of butylated hydroxytoluene (Fig. 3-B). Without any additives, the peroxide value of perilla oil increased by the heat-treatment at 150°C (Fig. 2). But the peroxide value of perilla oil rapidly decreased by the addition of grape seed oil, resulting in 5-times decrease by 1.0 ml of grape seed oil (i.e., 1/5 of grape seed oil/perilla oil). On the other hand, the perilla oil was mixed with butylated hydroxytoluene (0~1.0 mg/ml), and the protection from oxidation was tested. The peroxide value of the mixed oil decreased to 58% of the initial value by the addition of 1.0 mg of butylated hydroxytoluene. The extent of decrease by 1.0 mg of butylated hydroxytoluene was approximately equivalent to the addition of 0.3 ml of grape seed oil. The decrease of peroxide value due to a low quantity of grape seed oil suggests that the grape seed oil can be mixed with the perilla oil for the purpose of antioxidation.

The grape seed oil was characterized as a preliminary assessment for the utility of cooking oil or an additive.

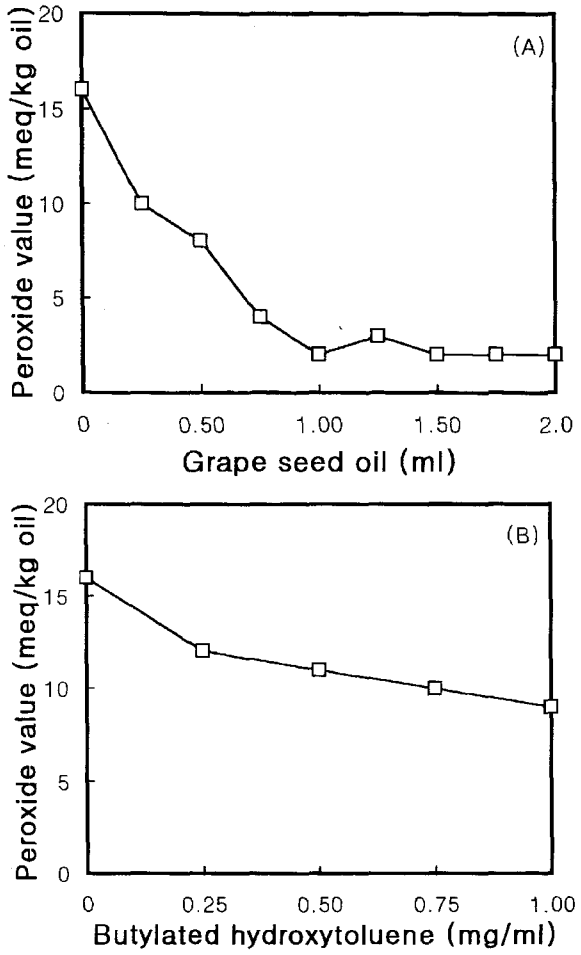

Fig. 3. Change of peroxide value of perilla oil in the presence of grape seed oil (A) or butylated hydroxytoluene (B). Grape seed oil or butylated hydroxytoluene was added to 5 ml of the perilla oil as indicated. The mixed oil was heated for 1h at 150°C and then peroxide values were measured.

The oil initially showed a strong antioxidant activity and a low peroxide value. The antioxidant activity was still highly retained by the heat-treatment at 180°C for 20 min. The peroxide value slowly increased up to 4h at 150°C, being distinguishably different from the other plant oils. The grape seed oil retained a strong antioxidant activity against the light exposure, whereas the other oils lost considerably their activities. The peroxide value only slightly increased by the storage with a transparent glass for 1 month, showing less oxidation against the light than the other oils. Sesame oil comprises various anti-oxidative substances such as sesamol, sesamin, sesamolinol, and sesamolin and, therefore, this oil has been known to be a good oil.[23-26] However, in this work the grape seed oil shows a better antioxidant activity than the sesame oil. The perilla oil is one of the good flavoring sources and shows various physiological functions. But the linolenic acid, an unsaturated fatty acid, is the major fatty acid in this oil, resulting in an easy oxidation. The oxidation of perilla oil decreased considerably by the addition of small proportion of grape seed oil. In conclusion, the grape seed oil can supplement the disadvantage of other plant oils by increasing the antioxidative activity. Thus, the grape seed oil is considered as a good cooking oil or an additive for the other plant oils.

References

1. Fukuda, Y., Nagata, M., Osawa, T. and Namiki, M. (1986) Chemical aspects of the antioxidative activity of roasted sesame seed oil and the effect of using the oil for frying. *Agric. Biol. Chem.*, **50**, 857-862.
2. Manley, C. H., Vallon, P. P. and Erickson, R. E. (1974) Some aroma components of roasted sesame seed (*Sesamum indicum* L.). *J. Food Sci.* **39**, 73-76.
3. Sleeter, R. T. (1981) Effects of processing on quality of soybean oil. *J. Am. Oil Chem. Soc.* **58**, 239-244
4. Nawar, W. W. (1985) Chemistry of thermal oxidation of lipids. In *Flavor chemistry of fats and oils*, Min, D. B. and Smouse, T. H. (eds.) pp. 39-47, American Oil Chemist's Society, Champaign, IL.
5. Nawar, W. W. (1985) Lipids. In *Food chemistry,* Fennema, O. R. (2nd ed.) pp. 139-148, New York.
6. Richardson, T. and Finley, J. W. (1985) Chemical changes in food during processing, pp. 410, AVI Pbulishing Company, Inc., Westport, Connecticut.
7. Yoon, S. H., Kim, S. K, Kim, K. H, Kwon, T. W. and Teah, Y. K. (1987) Evaluation of physicochemical changes in cooking oil during heating. *J. Am. Oil Chem. Soc.* **64**, 870-873.
8. Rojo, J. A. and Perkins, E. G. (1987) Cyclic fatty acid monomer formation in frying fats. determination and structural study. *J. Am. oil Chem. Soc.* **64**, 414-421.
9. Chang, S. S., Peterson, R. J. and Ho, C. T. (1978) Chemical reactions involved in the deep-fat frying of foods. *J. Am. Oil Chem. Soc.* **55**, 718-723.
10. Artman, N. R. (1969) The chemical and biological properties of heated and oxidized fats. *Adv. Lipid Res.* **7**, 245-330.
11. Kitts, D. (1996) Toxicity and safety of fats and oils. In *Bailey's industrial oil and fat products,* Hui, Y. H. (5th ed.) vol. **1**, pp. 249-251, John Wiley and Sons Inc., New York, NY.
12. White, P. J. and Xing, Y. (1997) Antioxidants from cereals and legumes. In *Natural antioxidants,* Shahidi, F. (ed.) pp. 30, AOCS Press, Champaign, IL.
13. Jung, M. Y. and Rhee, K. C. (1994) Quality improvement and extension of useful life of frying cottonseed oil by adsorbent or chemical treatment. *Foods and Biotech.* **3**, 65-70.
14. Peled, M., Gutfinger, T. and Letan, A. (1975) Effects of water and BHT on stability of cottonseed oil during frying. *J. Sci. Foods Agric.* **26**, 1655-1659.
15. McNeil, J., Kakuda, Y. and Basil, K. (1986) Improving the quality of used frying oils by treatment with activated carbon and silica. *J. Am. Oil Chem. Soc.* **63**, 1564-1569.
16. Manicini-Filho, J., Smith, L. M., Creveling, R. K. and

Alshaikh, H. F. (1986) Effects of selected chemical treatments on quality of fats used for deep frying. *J. Am. Oil Chem. Soc.* **63**, 1452-1457.
17. Yates, R. A. and Caldwell, J. D. (1992) Adsorptive capacity of active filter aids for used cooking oil. *J. Am. Oil Chem. Soc.*, **69**, 894-897.
18. Yates, R. A. and Caldwell, J. D. (1993) Regeneration of oils used for deep frying: A comparison of active filter aids. *J. Am. Oil Chem. Soc.* **70**, 507-511.
19. A. O. C. S. (1990) Official methods and recommended practices of the American Oil Chemist's Society (4th ed.) pp. 8-53, American Oil Chemist's Society, Champaign, IL.
20. Gebhardt, B. (1996) Oils and fats in snack foods. In *Bailey's industrial oil and fat products*, Hui, Y. H. (5th ed.) vol. **3**, pp. 412-416, John Wiley and Sons Inc., New York, NY.
21. Warner, K. and Mount, T. L. (1993) Frying stability of soybean and canola oils with modified fatty acid compositions. *J. Am. Oil Chem. Soc.* **70**, 983-988.
22. Lyon, C. K. (1972) Sesame: Current knowledge of composition and use. *J. Am. Oil Chem. Soc.* **49**, 245-249.
23. Fukuda, Y., Osawa, T., Namiki, M. and Ozaki, T (1985) Studies on antioxidative substances in sesame seed. *Agric. Biol. Chem.* **49**, 301-306.
24. Fukuda, Y., Osawa, T. and Namiki, M. (1986) Contribution of lignan analogues to antioxidative activity of refined unroasted sesame oil. *J. Am. Oil Chem. Soc.* **63**, 1027-1032.
25. Kikugawa, K., Arai, M. and Kurechi, T (1983) Participation of sesamol in stability of sesame oil. *J. Am. Oil Chem. Soc.* **60**, 1528-1532.
26. Osawa, T., Nakata, M., Namiki, M. and Fukuda, Y. (1985) Sesamolinol, a novel antioxidant isolated from sesame seeds. *Agric. Biol. Chem.* **49**, 3351-3356.