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Development of Natural Antioxidants Stable at Frying Temperatures

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고온에서 안정한 천연 항산화제 개발

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요 약

유지류는 산화에 의해 품질이 저하되며 이를 방지하기 위해 항산화제를 첨가하는 방법이 널리 이용되어 왔다. 그러나 현재까지 많이 이용되어온 tocopherol과 BHA는 상온에서는 높은 항산화 효과가 있지만 튀김 식품과 같이 180℃ 이상의 고온처리가 필요한 경우에는 열안정성이 매우 낮아 이들 항산화제들은 대부분 분해되거나 산화방지능력을 상실한다. 식물체에서 안정한 자유 라디칼을 형성할 수 있는 구조를 갖는 스테롤, 즉 곁사슬에 에틸리덴기를 갖는 citrostadienol, Δ^5-avenasterol과 fucosterol이 고온에서 안정한 항산화 효과가 있다고 보고되었으며 그 중에서 Δ^5-avenasterol이 고온에서 가장 높은 항산화 효과가 있다고 한다. 따라서 식품의 기호성과 저장성을 높이기 위하여 고온에서 안정성을 갖는 천연 항산화제의 개발이 필요하므로 문헌 고찰을 하여 정리하였다.

주요어 : 천연 항산화제, 스테롤, 에틸리덴기

INTRODUCTION

Fats and oils are easily deteriorated by oxidation. Lipid oxidation not only produces off-flavor by the formation of undesirable flavor compounds of low molecular weight, but also decreases the nutritional quality of lipid foods due to the destruction of essential dietary factors. This results in decrease of consumer acceptability, economic losses in the food industry and potential health risks[1~5].

The addition of antioxidants to fats, oils and foods containing fats and oils is desirable for several reasons. Antioxidants can increase the shelf life of foods by 15~200%, allowing food to be transported and stored for long periods, and may spare essential fatty acids, carotene, vitamin A and biotin from destruction by autoxidation[6~9].

In the food industry, synthetic antioxidants are often used because they are effective and less expensive than natural antioxidants. There is a concern about the possible toxicity of synthetic antioxidants, so the popularity of natural antioxidants has increased[10].

Common antioxidants, including butylated hydroxyanisole(BHA) or tocopherols(Fig. 1), are effective in protecting oxidation at ambient temperatures, but these antioxidants are heat-sensitive and volatile, so they quickly lose antioxidant activity at frying temperature[11~15]. Of the various additives which have been used to minimize oxidation deterioration during heating, the methyl polysiloxanes and certain sterols have been reported to reduce frying oil deterioration[16~18]. All the sterols effective at preventing oxidation at frying temperatures have an ethylidene group in

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their side chain[16]. Many plant extracts have been reported to have antioxidant properties and some of them contain particularly strong antioxidant activities[19~23]. Even though strong antioxidant activities of some plant extracts have been reported, only oleoresin extract of rosemary is practically used as natural antioxidants[23].

The objectives of this review were threefold. The first was to summarize the available literature concerning tocopherols as common natural antioxidants. The second was to review on novel natural antioxidants which are effective at frying temperature. The third objective was to point up the need for further applied research and practical information about the development of natural antioxidants.

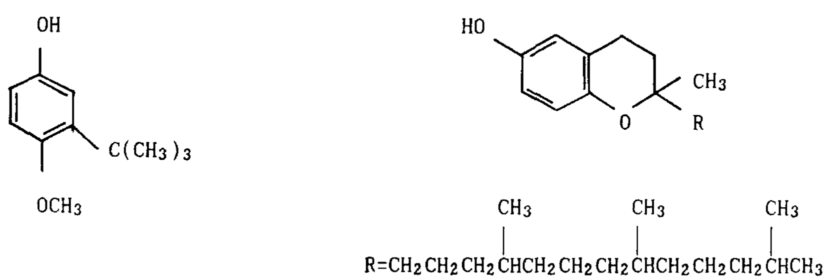
TOCOPHEROLS AS NATURAL ANTIOXIDANTS

The most important natural antioxidants in fats and oils are tocopherols. Tocopherols exhibit vitamin E activity which is important nutritionally, as well as their antioxidative effects in food systems. There are eight natural compounds of tocopherols, namely α-, β-, γ-, δ-tocopherols and four tocotrienols which have three double-bonds in the side chain[24~27]. The tocopherols and tocotrienols are light yellow, viscous oils, soluble in alcohol and fat solvents, but insoluble in water[28]. Their ability to take up oxygen gives them important antioxidant properties[29,30].

Tocopherols occurs mainly in a variety of plant materials, especially oil seed crops(vegetable oils), some grains, nuts, and green leafy vegetables[31~35]. The amount in plant foods is affected by species, variety, stage of maturity, season, time and manner of harvesting, processing procedures, and storage time[28]. Tocopherols are not destroyed to any great extent by normal cooking temperatures, but there are appreciable losses of tocopherol activity in oils heated long periods of time at high temperature, such as in deep fat frying, because rancidity develops[28]. It is reported that the deep fat frying of foods causes tocopherol losses of 32 to 75%[28].

Many studies have been made on the antioxidant effectiveness of tocopherols in foods[26,27,36~40], on the changes in the content of tocopherols[11~14,35,41~44], and on the singlet oxygen quenching of tocopherols[29,30,45~48].

Gordon and Kourimska[11] studied the changes in tocopherol content of oil used for deep-fat frying of potatoes and reported α-tocopherol was



BHA

5, 7, 8-Trimethyl	α-Tocopherol
5,8-Dimethyl	β-Tocopherol
7,8-Dimethyl	γ-Tocopherol
8-Methyl	δ-Tocopherol

Tocopherols

Fig. 1. Structure of BHA and tocopherols.

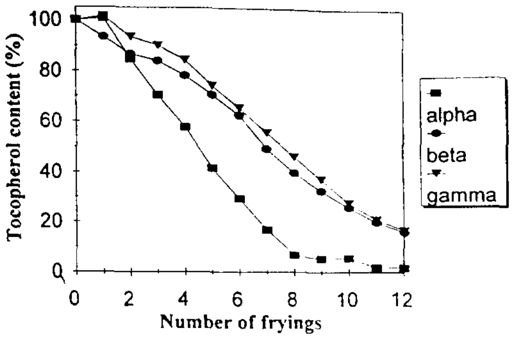


Fig. 2. Relative change in tocopherol content during frying of potato chips in rapeseed oil[11].

lost much faster than β-, γ- or δ-tocopherol, with a reduction of 50% α-tocopherol after 4~5 frying operations compared with values of about 7 and 7~8 frying operations for β- and γ-tocopherol, respectively(Fig. 2).

Fourie and Basson[41] investigated possible changes in the tocopherol content of almond, pecan, and macadamia kernels during 16-months' storage at 30℃ and 55% relative humidity. The large amount of total tocopherols, mainly α-tocopherol, in almonds accounted for their good storage ability.

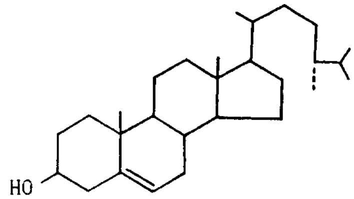
The thermal degradation products of tocopherols(TDP) formed in the oil as a result of the heat treatment are of interest with respect to nutrition and safety of foods[49]. Most of studies were quantitative determination of α-tocopherol and degradation of α-tocopherol during storage, but did not include thermal degradation products during heating. It is reported that natural α-tocopherol in seaweed meal degraded during storage[35]. The rate of α-tocopherol degradation in the seaweed meal was found to be accelerated by increasing the storage temperature or the moisture content. The degradation of α-tocopherol was expressed as zero order because of the near-linear plots obtained when concentration data were graphed as a function of time. Livingston et al.[42] reported that α-tocopherol degraded during the storage of dry alfalfa. These authors reported the rate of α-tocopherol loss increased as moisture content of the alfalfa increased.

The tocopherols function as antioxidants by quenching singlet oxygen molecules in addition to being free radical chain terminators. Tocopherols react in the mode of inhibition of free radicals produced by singlet oxygen oxidation of free fatty acids and in the mode of direct quenching of singlet oxygen. These compounds not only quench singlet oxygen(physical quenching) but also react with singlet oxygen(chemical quenching). The proportion of physical quenching vs. chemical quenching is dependent on structure and solvent system. Physical quenching is the major mechanism in the tocopherols. Tocopherols deactivate about 120 singlet oxygen molecules before they are destroyed[30].

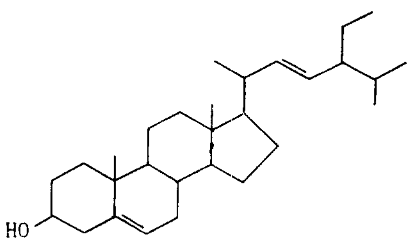
Grams and Eskins[29] studied correlation between singlet oxygen reactivity and vitamin E activity in photooxidation of tocopherols in methanol using methylene blue as a photosensitizer, and reported that α-tocopherol was most reactive with singlet oxygen, followed by β-, γ- and δ-tocopherol.

STEROLS FROM VEGETABLE OILS

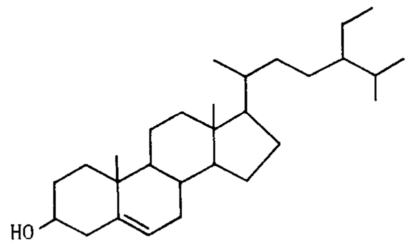
Sterol fractions from a number of major vegetable oils have already been analyzed by several authors using GLC. Fedeli et al.[50] analyzed the sterol fractions from 18 vegetable oils : linseed, peanut, olive, rice bran, palm kernel, corn, sesame, oiticica, palm, coconut, rapeseed, grapeseed, sunflower, poppy seed, castor, tea seed, cocoa butter and soybean. Campesterol, stigmasterol and β-sitosterol(Fig. 3) were identified in every oil studied. Itoh et al.[51] analyzed the compositions of the sterol fractions from 19 vegetable oils with TLC, GLC and GC-MS, reported that sterols other than the three major sterols, campesterol, stigmasterol and β-sitosterol, were identified in a few oils, and demonstrated the widespread occurrence of stigmastanol, Δ^5- and Δ^7-avenasterols(Fig. 4). Sims et al. and Fioriti et al.[16, 20] analyzed the unsaponifiable fraction from



Campesterol

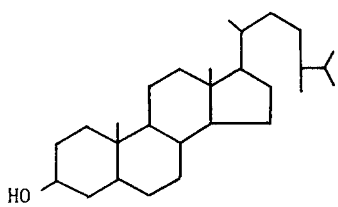


Stigmasterol

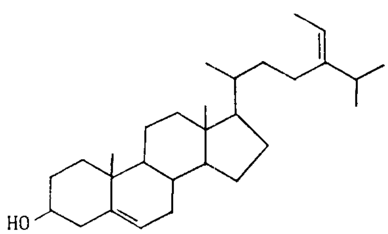


β-Sitosterol

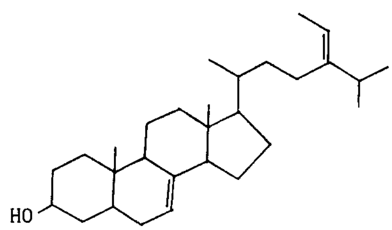
Fig. 3. Structure of campesterol, stigmasterol and β-sitosterol.



Stigmastanol

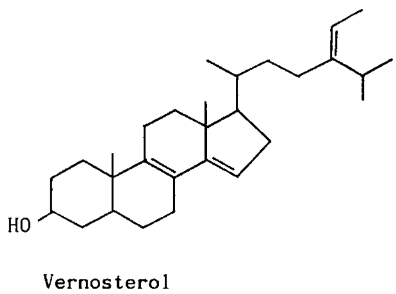


Δ^5-Avenasterol



Δ^7-Avenasterol

Fig. 4. Structure of stigmastanol, Δ^5-avenasterol and Δ^7-avenasterol.



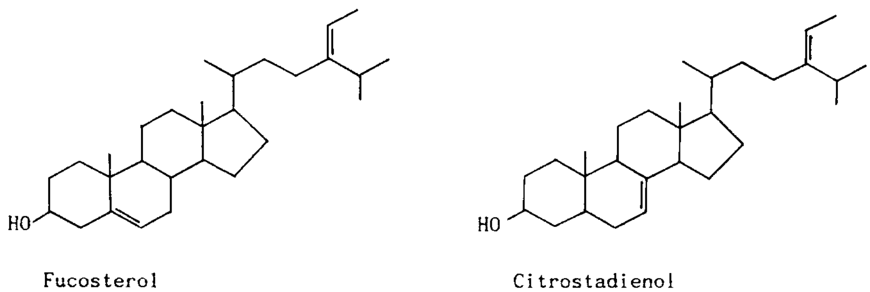


Fig. 5. Structure of vernosterol, fucosterol and citrostadienol.

olive, corn, wheat germ and *Vernonia anthelmintica* seed oil. The unsaponifiable fraction contained relatively large quantities of sterols and was effective in retarding oxidation. Sims et al.[16] reported that the order of effectiveness as antioxidants in safflower oil at 180℃ was vernosterol, Δ^7-avenasterol and fucosterol(Fig. 5). Citrostadienol, 4-α methyl-$\Delta^{7,24(28)}$-stigmastadiene-3β-ol (Fig. 5), was also effective as an antioxidant. These observations can be explained by the hypothesis that sterols with a structure that allows them to react rapidly with lipid free radicals to form relatively stable free radicals are effective as antioxidants. Relatively stable free radicals interrupt the triglyceride autoxidation chain reaction. The antioxidant effect is greatest when free radical formation from the sterol is relatively rapid due to the presence of unhindered hydrogen atoms on an allylic carbon atom, and when the free radical thus formed can isomerise to a tertiary free radical(Fig. 6), which is known to be relatively stable[18].

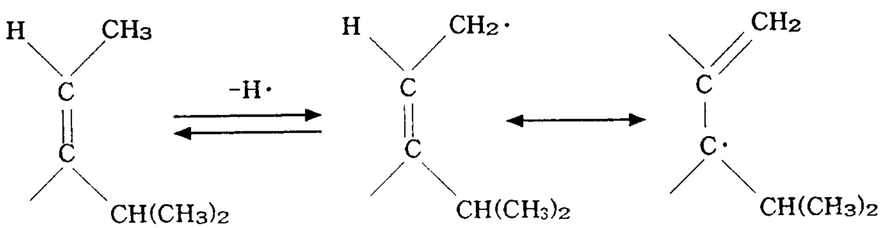


Fig. 6. The tertiary free radical.

Table 1. Protective indices(PI) of additives during the heating of technical trioleylglycerol at 180℃[18]

Additive	Concentration	PI after heating for:		
	(%)	24h	48h	72h
α-Tocopherol	0.02	0.97	1.01	1.01
BHA	0.02	0.96	1.04	1.00
Cholesterol	0.1	0.96	1.12	1.12
Stigmasterol	0.1	0.95	1.11	1.09
Fucosterol	0.1	1.52	1.71	1.66
Δ^5-Avenasterol	0.1	1.78	1.69	1.59
Δ^5-Avenasterol	0.05	1.16	1.19	1.09
Δ^5-Avenasterol	0.01	1.10	1.09	1.07

Boskou and Morton[17] reported that olive oil sterol mixtures containing Δ^7-avenasterol and Δ^5-avenasterol alone reduced the extent of oxidation, while β-sitosterol was initially ineffective and became slightly prooxidant after prolonged heating. Gordon and Magos[18] reported that α-tocopherol, BHA, cholesterol and stigmasterol were ineffective, whereas Δ^5-avenasterol and fucosterol were effective as antioxidants at 180℃ in a triglyceride mixture similar in composition to olive oil. The antioxidant effect of Δ^5-avenasterol increased with concentration in the range 0.01% to 0.1% (Table 1). Lipid free radicals react rapidly with sterols that have unhindered allylic carbon atoms such as the ethylidene group. Isomerization then produces a stable allylic tertiary free radical and interrupts the oxidation chain. The results confirm the findings of Sims et al.[16] who demonstrated the activity of sterols with an ethylidene side chain.

Some sterols present in oats have been shown to retard thermal changes at frying temperature[52~56]. White and Armstrong[52] reported that a specific sterol found in oats, Δ^5-avenasterol was effective in retarding soybean oil deterioration at 180℃. The antipolymerization activity of the sterol at frying temperature is thought to reside in its side chain, which contains an ethylidene group. Duve and White[53] studied a simple, inexpensive extraction procedure to remove antioxidants and sterols from oats. They reported the greatest antioxidant activities were obtained with methanolic antioxidant extracts derived from Noble and Ogle oats and hulls. All oils with added oat and hull extracts reduced polymerization of soybean oil during 14 days at frying temperature. An improved procedure for producing the methanolic extract from oat resulted in effective antioxidant activity in soybean and cottonseed oils stored at 30℃ in the light and dark and at 60℃ in the dark[54]. Tian and White[56] tested for the antipolymerization activity of oat extract in soybean and cottonseed oils under frying conditions. The soybean and cottonseed oils containing 0.005 or 0.007% oat extract were effective in reducing polymerization at frying temperature.

NATURAL ANTIOXIDANTS IN DEVELOPMENT

Fats and oils are slowly oxidized even at ambient temperature, and their oxidation becomes rapid at high temperatures. This results in a darkened color, increased viscosity, increased foaming, and chemical changes affecting the sensory characteristics, nutritional quality and safety of foods[1~5]. The addition of antioxidants to fats and oils or to foods that contain fats and oils is one of the most effective ways to prevent oxidation of the lipids. An antioxidant's primary function is generally agreed to be its chain-breaking activity (i.e. peroxyl radical trapping), and there is no doubt, from a mechanism point of view, that both natural and synthetic antioxidants exhibit the same fundamental chemical activity. The reasons for preferring natural antioxidants over synthetic antioxidants are not based purely on their antioxidant activity[7], but based on the possible toxicity of synthetic antioxidants[8,10].

Solvent extraction is the major method used to isolate natural antioxidants from plant parts. Most commonly used solvents for extracting natural antioxidants are methanol, ethanol, ethyl acetate, petroleum ether and diethyl ether. Generally, solvents with higher polarity yield greater antioxidative activity[54]. Chang et al.[23], in a patent for extraction of antioxidants from rosemary and sage, found methanol and ethanol to be the most successful solvents. Duve and White[53] compared the activity of eight solvent extractions of oats and concluded that the greatest antioxidant activity was derived from the methanol extracts of undefatted oat. Kim et al.[21] studied the effects of the type of extraction solvent on the antioxidant activities of selected herbs. They reported that the antioxidant activities of most herb extracts were greatly dependent on the kinds of solvents used for the extraction. However, some plant extracts showed strong antioxidant activities regardless of kinds of extracting solvents. The reason for the different antioxidant activity with different extracting solvents might be due to the differences in solubility of antioxidant components of herbs in solvents. In most cases, the antioxidant activity of herbal extracts showed strong antioxidant when the extracts were prepared with methanol as an extracting solvents[53].

Since medicinal herbal plants are used for the development of natural antioxidants, the developed natural antioxidants are expected to contain positive physiological function to human[57~65]. Zhang et al.[61] isolated and identified the effective antioxidants from the herbal plant Tanshen (***Salvia miltorrhiza*** Bung). They reported antioxidative components of Tanshen may have the potential of being used as natural antioxidants in foods. Six species[*Taraxacum platycarpum*(Korean name:min-dle-re), *Plantogoasiatica*(jil-kyung-ii), ***Rhus*** *javanica* L.(buk-na-mu), *Lycopus lucidus*(tac-ran-yup), *Astragalus membranaceus*(hwang-gi), *Taraxacum platycarpum* H.(po-gong-young)] among herbal plants seemed to have strong antioxidative activity and high extracting yields. The *Rhus javanica* L. ethanol extract retarded greatly the induction period of the oxidation in palm oil and lard[63]. The antioxidant activities of *Epimedium koreanum* N.(eum-yang-kwak) methanol extract on the oxidation of fat and oils were studied by measuring peroxide values. The methanol extract showed high antioxidant activity on the oxidation of lard and corn oil, and antioxidant effectiveness increased as the concentrations of the extract in lard increased[65]. Thus, the herbal plant extracts need to be studied effectiveness at retarding oxidation at the high temperatures.

The natural antioxidant with physiological activity will provide not only effective way of food preservation but also disease preventive effects[4,5]. If the positive physiological properties and non-toxicity of the natural antioxidants are proven, it will replace, to a great extent, the synthetic antioxidants in lipid containing foods, fats and oils, because the need for novel natural antioxidants is obvious, and industry continues to look for useful natural antioxidants which are effective at retarding oxidation at the high temperatures. Furthermore, antioxidants should, in the future, not only be used wherever necessary, but should also be regarded as an ingredient(such as vitamins or some of the trace elements) which represents added value in a food product[7].

ABSTRACT

The addition of antioxidants to fats and oils is one of the most effective ways to prevent oxidation of lipids. The popularity of natural antioxidants has increased because of the possible toxicity of synthetic antioxidants. Common natural antioxidants, tocopherols, retard oxidation at ambient temperatures, but they are ineffective at retarding oxidation at frying temperatures. The need for the development of novel natural antioxidants which are effective at frying temperatures is obvious. Sterols present in vegetable oils and certain herbal plant extracts have been reported to have antioxidant properties. Some sterols have been shown to retard thermal changes at frying

temperatures. All the sterol effective at preventing oxidation at frying temperatures have an ethylidene group in their side chain. These effects can be explained by the hypothesis that sterols with a structure that allows them to react with lipid free radicals to form relatively stable free radicals are effective as antioxidants.

(Key words : natural antioxidants, sterols, ethylidene group, herbal plant extracts)

REFERENCES

1. Perkins, E.G. : Nutritional and chemical changes occuring in heated fats. *Food Technology*, **13**, 508 (1960).
2. Kinsella, J.E. : Food lipids and fatty acids. *Food Technology*, **42**, 124 (1988).
3. Pokorny, J. : Flavor chemistry of deep fat frying in oil. In *Flavor Chemistry of Lipids Foods*, Min, D.B. and Smouse, T.H.(eds.), The American Oil Chemists' Society, Campaign, IL, p.113 (1989).
4. Kaunitz, H., Johnson, R.E. and Pegus, L. : A long-term nutritional study with fresh and mildly oxidized vegetable and animal fats. *J. Am. Oil Chem. Soc.*, **42**, 770 (1965).
5. Luc, G. and Fruchart, J. : Oxidation of lipoproteins and atherosclerosis. *Am. J. Clin. Nutr.*, **53**, 206 (1991).
6. Quast, D.G. and Karel, K. : Effects of environmental factors on the oxidation of potato chips. *J. Food Sci.*, **37**, 584 (1972).
7. Loliger, J. : Natural antioxidants for the stabilization of foods. In *Flavor Chemistry of Lipids Foods*, Min, D.B. and Smouse, T.H.(eds.), The American Oil Chemists' Society, Campaign, IL, p.302 (1989).
8. Finley, J.W. and Given Jr., P. : Technological necessity of antioxidants in the food industry. *Food Chem. Toxic.*, **24**, 999 (1986).
9. Almeida-Dominguez, N.G., Higuera-Ciapara, I., Goycoolea, F.M. and Valencia, M.E. : Package, temperature and TBHQ effects on oxidative deterioration of corn-based snacks. *J. Food Sci.*, **57**, 112 (1992).
10. Branen, A.L. : Toxicology and biochemistry of BHA and BHT. *J. Am. Oil Chem. Soc.*, **52**, 59 (1975).
11. Gordon, M.H. and Kourimska, L. : Effect of antioxidants on losses of tocopherols during deep-fat frying. *Food Chem.*, **52**, 175 (1995).
12. Kajimoto, G., Kanomi, Y., Kozono, S., Tamura, K. and Taguchi, N. : Influence of blend ratio of vegetable oils on their thermal oxidation and decomposition of tocopherol. *Nippon Eiyo Shokuryo Gakkaishi*, **44**, 499 (1991).
13. Kajimoto, G., Kanomi, Y., Kawakami, H. and Hamatani, M. : Effects of antioxidants on the thermal oxidation of oils and decomposition of tocopherol in vegetable oils. *Nippon Eiyo Shokuryo Gakkaishi*, **45**, 291 (1992).
14. Kajimoto, G., Kanomi, Y., Tanaka, E., Yoshida, H. and Shibahara, A. : Effects of air screening with aluminum foil on the deterioration of oil and decomposition of tocopherol in oil by heating. *Nippon Eiyo Shokuryo Gakkaishi*, **45**, 285 (1992).
15. Kopelman, I.J., Mizrahi, S. and Schab, R. : Equilibrium vapor pressure of butylated hydroxyanisole and butylated hydroxytolune in high temperature oil solution. *J. Am. Oil Chem. Soc.*, 11, 103 (1975).
16. Sims, R.J., Fioriti, J.A. and Kanuk, M.J. : Sterols additives as polymerization inhibitors for frying oils. *J. Am. Oil Chem. Soc.*, **49**, 298 (1972).
17. Boskou, D. and Morton, I.D. : Effect of plant sterols on the rate of deterioration of heated oils. *J. Sci. Food Agric.*, **27**, 928 (1976).
18. Grdon, M.H. and Magos, P. : The effect of sterols on the oxidation of edible oils. *Food Chem.*, **10**, 141 (1983).
19. Farag, R.S., Badei, A.Z.M.A. and El Baroty, G.S. A. : Influence of thyme and clove essential oils on cottonseed oil oxidation. *J. Am. Oil Chem. Soc.*, **66**, 800 (1989).
20. Fioriti, J.A., Kanuk, M.J. and Sims, R.J. : The unsaponifiables of *Vernonia anthelmintica* seed oil. *J. Am. Oil Chem. Soc.*, **48**, 240 (1971).
21. Kim, S.Y., Kim, J.H., Kim, S.K., Oh, M.J. and Jung, M.Y. : Antioxidant activities of selected oriental herb extracts. *J. Am. Oil Chem. Soc.*, 71, 633 (1994).
22. Takagi, T. and Iida, T. : Antioxidant for fats and oils from canary seed. *J. Am. Oil Chem. Soc.*, **57**, 326 (1980).
23. Chang, S.S., Matijasevic, B.O., Hsieh, O.A.L. and Huang, C. : Natural antioxidants from rosemary and sage. *J. Food Sci.*, **42**, 1102 (1977).
24. Hahm, T.S., King, D.L. and Min, D.B. : Food antioxidants. *Foods and Biotechnology*, 2, 1 (1993).
25. Lehmann, J.W., Putnam, D.H. and Qureshi, A.A. : Vitamin E isomers in grain Amaranths(*Amaranthus* spp.). *Lipids*, **29**, 177 (1994).
26. Lea, C.H. and Ward, R.J. : Relative antioxidant activities of the seven tocopherols. *J. Sci. Food Agric.*, **10**, 537 (1959).
27. Fennema, O.R. : Food Chemistry. 2nd Edition, Marcel Dekker, Inc., New York, p.203 (1985).
28. Ensminger, A.H., Ensminger, M.E., Konlande, J.E. and Robson, J.K. : Foods and Nutrition Encyclopedia. 2nd Edition, Vol. 2, CRC press, Inc. p.2266 (1994).
29. Grams, G.W. and Eskins, K. : Dye-sensitized photooxidation of tocopherols, correlation between singlet oxygen reactivity and vitamin E activity. *Biochemistry*, 11, 606 (1972).
30. Min, D.B., Lee, E.C. and Lee, S.H. : Singlet oxidation of vegetable oils. In *Flavor Chemistry of Lipids Foods*, Min, D.B. and Smouse, T.H.(eds.), The American Oil Chemists' Society, Campaign, IL, p.57 (1989).

31. Chase, G.W., Akoh, C.C. and Eitenmiller, R.R. : Analysis of tocopherols in vegetable oils by high-performance liquid chromatography. *J. Am. Oil Chem. Soc.*, **71**, 877 (1994).
32. Carpenter, A.P. : Determination of tocopherols in vegetable oils. *J. Am. Oil Chem. Soc.*, **56**, 668 (1979).
33. Lozano, Y.F., Mayer, C.D., Bannon, C. and Gaydou, E.M. : Unsaponifiable matter, total sterol and tocopherol contents of avocado oil varieties. *J. Am. Oil Chem. Soc.*, **70**, 561 (1993).
34. Eggitt, P.W.R. and Norris, F.W. : The chemical estimation of vitamin-E activity in cereal products. *J. Sci. Food Agric.*, **7**, 493 (1956).
35. Jensen, A. : Tocopherol content of seaweed and seaweed meal. *J. Sci. Food Agric.*, **20**, 622 (1969).
36. Dugan Jr, L.R. and Kraybill, H.R. : Tocopherols as carry-through antioxidants. *J. Am. Oil Chem. Soc.*, **33**, 527 (1956).
37. Parkhurst, R.M., Skinner, W.A. and Sturm, P.A. : The effect of various concentrations of tocopherols and tocopherol mixtures on the oxidative stability of a sample of lard. *J. Am. Oil Chem. Soc.*, **45**, 641 (1968).
38. Jung, M.Y. and Min, D.B. : Effects of α-, γ-, and δ-tocopherols on oxidative stability of soybean oil. *J. Food Sci.*, **55**, 1464 (1990).
39. Huang, S.W., Frankel, E.N. and German, J.B. : Antioxidant activity of α-tocopherols in bulk oils and in oil-in water emulsions. *J. Agric. Food Chem.*, **42**, 2108 (1994).
40. Jung, M.Y., Choe, E. and Min, D.B. : α-, γ- and δ-Tocopherol effects on chlorophyll photosensitized oxidation of soybean oil. *J. Food Sci.*, **56**, 807 (1991).
41. Fourie, P.C. and Basson, D.S. : Changes in the tocopherol content of almond, pecan and macadamia kernels during storage. *J. Am. Oil Chem. Soc.*, **66**, 1113 (1989).
42. Livingston, A.L., Nelson, J.W. and Kohler, G.O. : Stability of α-tocopherol during alfalfa dehydration and storage. *J. Agric. Food Chem.*, **16**, 492 (1968).
43. Bruhn, J.C. and Oliver, J.C. : Effect of storage on tocopherol and carotene concentrations in alfalfa hay. *J. Dairy Sci.*, **61**, 980 (1978).
44. Widicus, W.A. and Kirk, J.R. : Storage stability of α-tocopherol in a dehydrated model food system containing methyl linoleate. *J. Food Sci.*, **46**, 813 (1981).
45. Yamauchi, R., Matsui, T., Satake, Y., Kato, K. and Ueno, Y. : Reaction products of α-tocopherol with a free radical initiator, 2,2'-Azobis(2,4 dimethylvaleronitrile). *Lipids*, **24**, 204 (1989).
46. Clough, R.L., Yee, B.G. and Foote, C.S. : Chemistry of singlet oxygen. 30. the unstable primary product of tocopherol photooxidation. *J. Am. Chem. Soc.*, **101**, 683 (1979).
47. Grams, G.W., Eskins, K. and Inglett, G.E. : Dye-sensitized photooxidation of α-tocopherol. *J. Am. Chem. Soc.*, **94**, 866 (1972).
48. Clements, A.H., Van Den Zngh, R.H., Frost, D.H., Hoogenhout, K. and Nooi, J.R. : Participation of singlet oxygen in photosensitized oxidation of 1, 4-dienoic systems and photooxidation of soybean oil. *J. Am. Oil Chem. Soc.*, **50**, 325 (1973).
49. Onyewu, P.N., Ho, C.T. and Daun, H. : Characterization of β-carotene thermal degradation products in a model food system. *J. Am. Oil Chem. Soc.*, **63**, 1437 (1986).
50. Fedeli, E., Lanzani, A., Capella, P. and Jacini, G. : Triterpene alcohols and sterols of vegetable oils. *J. Am. Oil Chem. Soc.*, **43**, 254 (1966).
51. Itoh, T., Tamura, T. and Matsumoto, T. : Sterol composition of 19 vegetable oils. *J. Am. Oil Chem. Soc.*, **150**, 122 (1973).
52. White, P.J. and Armstrong, L.S. : Effect of selected oat sterols on the deterioration of heated soybean oil. *J. Am. Oil Chem. Soc.*, **63**, 525 (1986).
53. Duve, K.J. and White, P.J. : Extraction and identification of antioxidants in oats. *J. Am. Oil Chem. Soc.*, **68**, 365 (1991).
54. Tian, L.L. and White, P.J. : Antioxidant activity of oat extract in soybean and cottonseed oils. *J. Am. Oil Chem. Soc.*, **71**, 1079 (1994).
55. Daniels, D.G.H. and Martin, H.F. : Antioxidants in oats. *J. Sci. Food Agric.*, **18**, 589 (1967).
56. Tian, L.L. and White, P.J. : Antipolymerization activity of oat extract in soybean and cottonseed oils under frying conditions. *J. Am. Oil Chem. Soc.*, **71**, 1087 (1994).
57. Hirosue, T., Kawai, H. and Hosogai, Y. : On the antioxidative activities of crude drugs. *Nippon Shokuhin Kogyo Gakkaishi*, **25**, 691 (1978).
58. Hirosue, T., Kawai, H. and Hosogai, Y. : Antioxidative substances in *Glycyrrkixae radix*. *Nippon Shokuhin Kogyo Gakkaishi*, **29**, 418 (1982).
59. Toda, S., Tanizawa, H., Arichi, S. and Takino, Y. : Inhibitory effects of methanol extracts of crude drugs on the air oxidation of linoleic acid. *Yakugaku zassi*, **104**, 394 (1984).
60. Lee, Y.B., Kim, Y.S. and Ashmore, C.R. : Antioxidant property in ginger rhizome and its application to meat products. *J. Food Sci.*, **51**, 20 (1986).
61. Zhang, K.Q., Bao, Y., Wu, P., Rosen, R.T. and Ho, C.T. : Antioxidative components of Tanshen(*Salvia miltiorrhiza* Bung). *J. Agric. Food Chem.*, **38**, 1194 (1990).
62. Taga, M.S., Miller, E.E. and Pratt, D.E. : Chia seeds as a source of natural lipid antioxidants. *J. Am. Oil Chem. Soc.*, **61**, 928 (1984).
63. Choi, U., Shin, D.H., Chang, Y.S. and Shin, J.I. : Screening of natural antioxidant from plant and their antioxidative effect. *Korean J. Food Sci. Technol.*, **24**, 142 (1992).
64. Shin, D.H., Lee, Y.J., Chang, Y.S. and Kang, W.S. : Stability of some fried foods prepared with oils containing *Rhus javanica* Linne ethanol extract with several synergists. *Korean J. Food Sci. Technol.*, **24**, 547 (1992).
65. Kim, S.Y., Jim, J.H. and Kim, S.K. : Isolation and characterization of antioxidant components in *Epim-*

edium koreanum NAKAI extract. *Korean J. Food Sci. Technol.*, **24**, 535 (1992).

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