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Effects of natural and synthetic antioxidants on the oxidative stability of borage and evening primrose triacylglycerols

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Abstract

The effects of natural and synthetic antioxidants on the oxidative stability of borage and evening primrose triacylglycerols (TAG), under Schaal oven conditions at 60 °C were evaluated. Conjugated dienes (CD) and 2-thiobrabituric acid-reactive substances were used as indicators for evaluation of primary and secondary lipid oxidation products, respectively. Results suggest that tocopherols are more effective antioxidants at 500 ppm than at 200 ppm. The most effective natural antioxidant was Tenox GT-2 (the formulation in oil was composed of 7.88 ppm of α-, 39.7 ppm of γ- and 21.8 ppm of δ-tocopherol) followed by δ- and α-tocopherols, while, among synthetic antioxidants, tert-butylhyroquinone (TBHQ) was more effective than butylated hydroxytoluene (BHA) and butylated hydroxyanisole (BHT) and served as the strongest antioxidant in borage and evening primrose oil TAG.

1. Introduction

Edible vegetable oils consist mainly (95%) of triacylglycerols (TAG). Non-triacyglycerols (also known as minor components or unsaponifiable matter) make up the remaining 5%. The minor components of vegetable oils are primarily composed of phospholipids, tocopherols, tocotrienols, flavonoids, other phenolic compounds, pigments (carotenoids, chlorophylls), sterols, and free fatty acids, as well as mono- and diacylglycerols (Hamilton, 1994; Shahidi & Shukla, 1996). Several classes of these components might be present in each oil and contribute to its oxidative stability (Shahidi & Shukla, 1996).

TAG of edible oils are usually used to evaluate the anti- and/or prooxidant activities of their minor components as well as to study the effectiveness of synthetic and natural antioxidants. TAG of edible oils have been used in order to investigate the effects of mono- and diacylglycerols (Mistry & Min, 1988), as well as tocopherols, on autoxidation (Jung & Min, 1990). The effect of the type of fatty acids present on the stability of tocopherols during microwave heating has also been reported (Yoshida, Tatsumi, & Kajimoto, 1992). Corn oil TAG and its oil-in-water emulsions have been used to compare the antioxidant and prooxidant properties of green tea (Frankel, Huang, Prior, & Aeschbach, 1997). Recently, sunflower oil TAG and its emulsions in water were used to study the antioxidant properties of myricetin and quercetin (Roedig & Gordon, 1998). Results from these studies led to the elimination/minimization of the prooxidants via implementation of proper processing steps. Alternatively, optimum concentrations and combinations of antioxidants may be used to improve the oxidative stability of edible oils.

Several chemical, instrumental and sensory techniques are commonly used to monitor oxidation of foods and to predict their shelf life stability. These techniques can also be used to evaluate the effectiveness of antioxidants in different lipid systems (King, Hahm, & Min, 1995). While sensory methods are most accurate in predicting the stability of lipids, they are cumbersome and do not lend themselves for routine analysis (Wanasundara, Shahidi, & Jablonski, 1995). Of the instrumental and chemical methods in use, loss of reactants such as oxygen or substrate fatty acids, measuring of primary (hydroperoxides or conjugated dienes) and/or secondary oxidation products [alcohols, aldehydes, hydrocarbons or ketones (Lampi, Piironen, Hopia, &

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Koivistonen, 1997)] are commonplace. Peroxide value (PV) and conjugated dienes (CD) are frequently used to measure primary oxidation products, while thiobarbituric acid-reactive substances (TBARS) and headspace volatiles are employed as indicators for monitoring secondary products of oxidation (Shahidi & Wanasundara, 1998).

A number of accelerated oxidation tests have been used to examine the oxidative stability of edible oils and thus to predict their shelf life. In the Schaal oven test, used in this study, the lipid samples are placed in a forced-air oven and the temperature is maintained between 60 and 70 °C (Frankel, 1993; Malcomson, Vaisey-Jenser, Przybylski, & Eskin, 1994). It has been observed that 1 day of storage, under Schaal oven conditions at 65 °C, is equivalent to 1 month's storage at room temperature (25 °C; Abou-Gharbia, Shehata, Youssef, & Shahidi, 1996). Furthermore, flavour scores of edible oils stored at 60 °C for 4 days, corresponded with those kept at ambient temperatures for 4 months (Warner, Frankel, & Mounts, 1989).

Borage and evening primrose oils and their TAG are used in various nutritional and clinical studies (Andreassi, Forleo, Dilorio, Masci, Abate, & Amerio, 1997; Muncuso et al, 1997; Tashiro et al., 1998; Zadak & Cervinkova, 1997). These oils are highly susceptible to oxidation due to their high levels of polyunsaturated fatty acids (PUFA; Khan & Shahidi, 2000). Moreover, oxidation of nutritional and pharmaceutical oil-in-water emulsions affects their safety and efficiency (Nijveldt et al., 1998). Therefore, this study was designed to evaluate the effects of natural and synthetic antioxidants on the oxidative stability of borage and evening primrose TAG, stored under Schaal oven conditions at 60 °C, in order to improve their safety and extend their shelf life and oxidative stability.

2. Materials and methods

2.1. Materials

Cold-pressed borage oil was obtained from Bioriginal Food & Science Corporation (Saskatoon, SK). Evening primrose oil was procured from Scotia Pharmaceuticals (Kentvill, NS). Tocopherols (α, γ, and δ), 2-thiobarbituric acid (TBA), 1,1,3,3-tetramethoxypropane (TMP), synthetic antioxidants, namely butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT) and tert-butylhydroquinone (TBHQ), were obtained from Sigma Chemical Co. (St. Louis, MO). Activated charcoal was acquired from BDH Inc. (Tornoto, ON). Celite 545 was obtained from Fisher Scientific (Fair Lawn, NJ). Silicic acid powder (mesh 100) was purchased from Mallinckrodt Canada, Inc. (Point-Claire, PQ). All other chemicals were ACS-grade or better.

2.2. Preparation of triacyglycerols

Triacylglycerols of borage and evening primrose were prepared using a column chromatographic method (Khan & Shahidi, 2000). A chromatographic column (3.4 i.d.×40 cm) was connected to a water-pump vacuum and packed sequentially with four adsorbents. The bottom layer consisted of 40 g of activated silicic acid; the next layers were 20 g of 1:2 (w/w) mixture of Celite 545-activated charcoal and 80 g of 1:2 (w/w) mixture of Celite 545-powdered sugar (sucrose); and the top layer was 40 g of activated silicic acid. All adsorbents were suspended in n-hexane. Oil (100 g) was diluted with an equal volume of n-hexane and passed through the chromatographic column. The solvent in the eluent (TAG) was evaporated under vacuum at 30 °C.

2.3. Preparation of samples for accelerated oxidation tests

Borage and evening primrose TAG samples (5 g) were used to study their oxidative stability in the dark. The samples were kept at 60°C in a forced-air Precision Oven Model 2 (Precision Scientific Co., Chicago, IL). They were removed from the oven after 24, 72, 120 and 168 h for oxidative stability determinations.

2.4. Oxidative stability tests

The oxidative stability of TAG was evaluated by determining CD [IUPAC (1987) method 2.505] and TBARS (AOCS method Cd 1990). TBARS were calculated by multiplying the absorbance readings at 532 nm by a factor of 0.145, determined from a standard line prepared using 1,1,3,3-tetramethoxypropane as a precursor of malonaldehyde.

2.5. Chemical and instrumental analyses

Fatty acid composition of the oils was analyzed according to the method described by Wanasundara and Shahidi (1997). Tocopherols in the stripped and non-stripped oils were determined using a Shimadzu high-performance liquid chromatograph (HPLC) equipped with two LC-6A pumps, SPD-6AV, Lichrosorb Si 60 analytical column (Merck, 3.2x200mm, 5μ) and UV–VIS detector (Shahidi, Amarowicz, Abou-Gharbia, & Shehata, 1997).

2.6. Statistical analysis

All experiments and/or the measurements were replicated three times. Mean±standard deviation was reported for each case. Analyses of variance and Tukey's studentized test were performed at a level of $P<0.05$ to evaluate the significance of differences among mean values.

Table 1
Chemical characteristics and fatty acid compositions of borage and evening primrose oil triacylglycerols[a]

Characteristics		Borage		Evening primrose	
		Original	Stripped	Original	Stripped
Oxidative status	CD	1.60±0.1 b	0 a	3.12±0.40 d	2.05±0.05 c
	TBARS (μmol/g)	0.56±0.1 c	0.2±0.01 a	1.65±0.20 d	0.68±0.10 b
Tocopherols (mg/kg)	α	0 a	0 a	0 a	0 a
	δ	52 c	0 a	16 b	0 a
	γ	659 d	0 a	335 c	84 b
	Total	711 a	0 a	341 c	84 b
Fatty acid composition (%)	16:0	11.3±0.09 b	11.0±0.77 b	6.77±0.33 a	6.54±0.29 a
	18:0	4.00±0.21 b	4.28±0.13 b	1.84±0.11 a	1.80±0.01a
	18:1	16.9±0.42 b	16.5±0.13 b	8.67±0.28 a	8.31±0.71 a
	18:2	36.3±1.33 a	37.0±0.11 a	73.6±1.81 b	75.8±0.27 b
	18:3 ω-6	22.1±0.92 c	22.3±1.26 c	9.16±0.58 b	7.60±0.75 a
	20:1	4.58±0.03 a	4.68±0.02 a	–	–
	22:1	2.85±0.05 a	2.59±0.01 a	–	–
	24:1	1.85±0.07 a	1.67±0.01 a	–	–
	PUFA	58.4±0.29a	59.2±0.81a	82.7±0.39 b	83.4±0.81 b

[a] CD, conjugated dienes; TBARS, thiobarbituric acid-reactive substances; PUFA, polyunsaturated fatty acids. Values are means of three determinations±standard deviations. Values with different letters in each row are different ($P<0.05$) from one another.

3. Results and discussion

3.1. Chemical characteristics of borage and evening primrose oils and their triacylglycerols

Minor components present in borage and evening primrose oils were generally removed, effectively, following a multi-layer column chromatographic procedure. Small amounts of TBARS and γ-tocopherol were, however, retained in the evening primrose oil TAG following the stripping process (Table 1). The fatty acid composition indicated that evening primrose TAG contained higher amounts ($P<0.05$) of PUFA than borage TAG. The main PUFA, linoleic acid, was present at higher than 70% and 36% in evening primrose and borage oil TAG, respectively. Borage TAG contained up to 22% of γ-linolenic acid (GLA; 18:3 ω 6) while GLA was present at 9% in evening primrose oil TAG.

3.2. Effects of natural and synthetic anioxidant

Table 2 summarizes the effects of natural and synthetic antioxidants on the formation of CD in TAG of borage oil. Alpha-, and δ-tocopherols, as well as Tenox GT-2, were more effective ($P<0.05$) at 500 ppm than at 200 ppm in preventing the formation of CD. The most effective antioxidant in stabilizing borage oil TAG was Tenox GT-2, which is a commercial product consisting of 7.88 ppm of α-, 39.7 ppm of γ- and 21.8 ppm of δ-tocopherol, followed by δ- and α-tocopherols. Moreover, antioxidant activity of α-tocopherol at 200 ppm declined after 120 h at 60 °C coinciding with an increase in CD. Similarly, a gradual decrease in the antioxidant activity of Tenox GT-2, after the same period, was observed. Meanwhile, TBHQ was a more effective ($P<0.05$) antioxidant than BHA and BHT.

The use of TBARS to evaluate the oxidative stability and effectiveness of different antioxidants in vegetable oils has been frequently reported in the literature (Ganthavorn & Hughes, 1997; Duh, Yen, Du, & Yen, 1997). Based on TBARS values the efficacy of (Table 2) α- and δ-tocopherols as well as Tenox GT-2 in borage oil TAG at 500 ppm exceeded those at 200 ppm and TBHQ was more effective than BHA and BHT. These trends in antioxidant effectiveness, as reflected in TBARS values, are similar to those obtained for primary oxidation products, as reflected in CD values.

The effects of tocopherols, BHA, BHT and TBHQ on CD and TBARS values in stripped evening primrose oil TAG, stored under Schaal oven conditions, are presented in Table 3. The effectiveness of antioxidants decreased in the following order after 168 h at 60 °C: TBHQ (200 ppm) > BHT (200 ppm) > BHA (200 ppm) = Tenox GT-2 (500 ppm) > δ-tocopherol (500 ppm) ≅ α-tocopherol (500 ppm) > Tenox GT-2 (200 ppm) > δ-tocopherol (200 ppm) > α-tocopherol (200 ppm). This trend is similar to that obtained in borage oil TAG. Thus, it is concluded that: (1) tocopherols are more effective antioxidants at 500 ppm than at 200 ppm in both borage and evening primrose TAG. Furthermore, the effectiveness of α-tocopherol at 200 ppm declined during the latter stages of storage, (2) the most effective natural antioxidant in the systems examined was Tenox GT-2, followed by δ- and α- tocopherols, while the most effective synthetic antioxidant was TBHQ, followed by BHA and BHT, and (3) the strongest

Table 2
The effects of tocopherols (TOC) and synthetic antioxidants on conjugated dienes (CD) and thiobarbituric acid-reactive substances (TBARS, μmol of malonaldehyde equivalents per g oil) in borage oil triacylglycerols stored under Schaal oven conditions at 60 °C during 168 h storage[a]

Antioxidant	Conc. (ppm)	CD after 12–168 h				TBARS (μmol malonaldehyde equivalents/ g oil) after 12–168 h			
		12	72	120	168	12	72	120	168
Control	0	4.9±0.01 e	6.64±0.4 f	13.0±2.53 f	22.2±0.08 g	3.49±0.11 h	5.18±0.02 f	5.39±0.04 f	6.40±0.47 g
α-TOC	200	4.2±0.04 cd	5.89±0.07 e	9.89±0.04 d	21.9±0.06 g	2.74±0.05 b	3.67±0.02 e	3.73±0.06 c	5.60±0.05 f
	500	4.18±0.04 c	5.63±0.04 d	10.3±0.02 e	15.2±0.34 e	3.11±0.02 f	3.19±0.06 d	3.45±0.10 b	4.31±0.07 d
δ-TOC	200	3.99±0.09 c	6.19±0.05 e	9.55±0.02 c	15.7±0.71 e	3.22±0.02 g	3.76±0.02 e	3.94±0.05 e	4.55±0.02 e
	500	4.16±0.10 c	5.59±0.14 d	10.4±0.38 e	14.7±0.13 d	3.06±0.04 f	3.26±0.15 d	3.79±0.02 de	4.22±0.01 d
Tenox GT-2	200	4.08±0.11 c	5.65±0.10 d	9.03±0.19 b	17.1±0.34 f	3.04±0.03 f	2.45±0.66 b	3.79±0.10 de	4.80±0.20 e
	500	4.13±0.06 c	4.86±0.13 c	10.0±1.52 e	9.86±0.37 c	1.88±0.01 a	2.95±0.06 c	3.36±0.06 b	3.42±0.02 b
BHA	200	2.83±0.01 b	2.94±0.12 b	2.23±0.09 a	4.57±0.20 b	2.96±0.06 e	3.16±0.04 d	±0.06 d	3.88±0.04 c
BHT	200	4.23±0.02 cd	5.80±0.14 de	11.1±0.53 e	15.3±0.40 e	2.86±0.02 be	2.52±0.06 b	3.39±0.06 b	3.81±0.12 c
TBHQ	200	2.45±0.12 a	2.66±0.07 a	2.31±0.05 a	1.71±0.08 a	1.92±0.09 a	1.23±0.02 a	2.50±0.14 a	2.59±0.09 a

[a] BHA, butylated hydroxyanisole; BHT, butylated hydroxytoluene; TBHQ, tert-butylhydroquinone. Tenox GT-2 is a commercial natural antioxidant and consists of 7.88 ppm of α-, 39.67 ppm of γ- and 21.77 ppm of δ-tocopherol. The concentrations of antioxidants used in μmol/kg are 465 for 200 ppm α-TOC; 1160 for 500 ppm TOC; 495 for 200 ppm δ-TOC; 1240 for 500 ppm δ-TOC; 1110 for 200 ppm BHA; 2775 for 500 ppm BHA; 905 for 200 ppm BHT; 2262 for 500 ppm BHT; 1205 for 200 ppm TBHQ; and 3012 for 500 ppm TBHQ. Values are means of three determinations ±SD. Values within each column with different letters are different ($P<0.05$) from one another.

Table 3
The effects of tocopherols (TOC) and synthetic antioxidants on conjugated dienes (CD) and thiobarbituric acid-reactive substances (TBARS, μmol of malonaldehyde equivalents per g oil) in evening primrose oil triacylglycerols stored under Schaal oven conditions at 60 °C during 168 h storage[a]

Antioxidant	Conc. (ppm)	CD after 12–168 h				TBARS (μmol malonaldehyde equivalents/ g oil) after 12–168 h			
		12	72	120	168	12	72	120	168
Control	0	6.79±0.02 a	17.0±0.39 f	19.7±0.39 g	35.6±0.72 h	1.66±0.02 e	2.40±0.01 f	2.45±0.14 g	4.21±0.06 f
α-TOC	200	5.97±0.07 c	10.5±0.05 e	15.5±0.18 f	31.3±0.67 g	1.62±0.01 e	1.83±0.05 d	2.12±0.01 e	3.21±0.03 e
	500	6.22±0.01 c	9.6±0.04 d	13.1±0.10 d	25.4±0.12 e	1.47±0.02 d	1.97±0.02 e	2.10±1.88 e	2.43±1.04 cd
δ-TOC	200	6.09±0.04 c	10.0±0.02 e	13.8±0.16 e	28.3±0.28 f	1.58±0.01 e	1.93±0.05 e	2.21±0.02 f	3.08±0.04 e
	500	6.24±0.04 c	9.23±0.02 d	12.3±0.12 c	24.1±0.17 d	1.46±0.04 d	1.86±0.03 d	2.05±0.04 e	2.32±0.03 d
Tenox GT-2	200	5.70±0.13 b	9.51±0.07 d	13.6±0.06 d	27.7±0.50 f	1.51±0.01 e	1.71±0.02 c	2.2±0.60 e	2.50±0.04 d
	500	6.79±0.03 d	8.51±0.08 c	11.1±0.13 b	20.4±0.52 c	1.14±0.01 c	1.61±0.02 b	1.77±0.05 d	2.05±0.02 c
BHA	200	5.78±0.09 b	6.37±0.09 b	13.3±0.49 d	21.1±0.69 c	1.21±0.02 b	1.68±0.04 b	1.52±0.06 c	2.04±0.04 c
BHT	200	5.53±0.03 b	8.79±0.22 c	10.8±0.44 a	17.7±0.19 b	1.23±0.01 b	1.04±0.06 a	1.22±0.03 b	1.42±0.03 b
TBHQ	200	4.41±0.11 a	5.36±0.24 a	12.3±0.48 c	15.6±0.62 a	0.95±0.04 a	1.04±0.04 a	1.10±0.03 a	1.00±0.03 a

[a] BHA, butylated hydroxyanisole; BHT, butylated hydroxytoluene; TBHQ, tert-butylhydroquinone. Tenox GT-2 is a commercial natural antioxidant consist of 7.88 ppm of α-, 39.67 ppm of γ- and 21.77 ppm of δ-tocopherol. For concentrations in μmol/kg see footnotes to Table 2. Values are means of three determinations ±SD. Values within each column with different letters are different ($P<0.05$) from one another.

antioxidant activity was exhibited by TBHQ among all other treatments, in both borage and evening primrose oils TAG.

The first observation suggests that the antioxidant activities of tocopherols are concentration-dependent. On a mole basis, the concentrations used (200 or 500 ppm) are very similar for tocopherols examined; thus the efficacies shown for tocopherols may only arise from existing structural differences in the compounds concerned. This theory may be supported by variations in optimum levels of different tocopherols required to stabilize vegetable oils. Optimum concentrations of α-, γ-, and δ-tocopherols, to improve the oxidative stability of soybean oil TAG, were reported to be 100, 250 and 500 ppm, respectively (Jung & Min, 1990). However, the optimum concentration of tocopherols, required for

stabilizing the oxidative stability of rapeseed, soybean and palm oils TAG during microwave heating, was 100, 150–200 and 500 ppm of α-, (β-, γ-) and δ-tocopherols, respectively (Yoshida, Kajimoto, & Emura, 1993). Moreover, maximum antioxidant activities of α- and γ-tocopherol mixtures and natural mixtures of α-, γ- and δ-tocopherols from soybean in corn oil TAG were 250 and 500 ppm, respectively (Huang, Frankel, & German, 1995).

Tocopherols are considered to be primary or chain-breaking antioxidants in free radical chain reactions, which can convert lipid radicals to more stable products, thus extending the shelf life of edible oils (Gordon, 1990). In autoxidation of vegetable oils containing unsaturated fatty acids, free alkyl radicals are formed in the slow initiation step. These radicals react rapidly with atmospheric oxygen to produce peroxy radicals, which in turn may afford hydroperoxides and new alkyl radicals which will propagate the oxidation reaction and cause a dramatic increase in the formation of primary and secondary oxidation products (Porter, Caldwell, & Kills, 1995). Tocopherols, through their chromanol moiety, can donate a phenolic hydrogen to a lipid peroxy radical to form a resonance-stabilized chromanoxyl radical, which in turn reacts with other radicals to form stable adducts and therefore terminates the free radical chain reactions (Kamal-Eldin & Appelqvist, 1996). Meanwhile, tocopherols may be oxidized and consumed during these processes, thus their antioxidant activities may decline gradually or rapidly, depending on their initial levels and temperature of the lipid system (Gordon & Kourimska, 1995). This may explain, in part, the sudden increase in CD of borage oil TAG treated with 200 ppm of α-tocopherol.

The chemical structures of tocopherols suggest that α-tocopherol is more potent as a hydrogen donor than β-, γ- and δ-tocopherols because of the absence of one or two ortho-methyl groups. The presence of these electron releasing groups in the ortho and or para positions increases hydrogen-donating ability of substituted phenols (Kamal-Eldin & Appelqvist, 1996). Although it has been reported that, under physiological conditions at around 37 °C, the antioxidant activity is in the order $\alpha > \beta > \gamma > \delta$, which supports the previous suggestion, the reverse trend $\delta > \gamma > \beta > \alpha$ has been observed at higher temperatures between 50 and 100 °C (Madhavi, Singhal, & Kulkarani, 1995). Moreover, during microwave heating of stripped vegetable oil with an equimolar mixture of tocopherols added, the stability of tocopherols decreased in the order $\delta > \beta > \gamma > \alpha$ (Yoshida, Tatsumi, & Kajimoto, 1991). Similarly, Burkow, Vikersveen, and Sasrem (1995) examined the effectiveness of different antioxidants in cod liver oil at 80 °C by the rancimat method and found that the antioxidant activity decreased in the order of δ-tocopherol > Tenox GT-2 > α-tocopherol. This might explain the higher antioxidant activity of δ-tocopherol, in borage and evening primrose TAG, than to α-tocopherol. Meanwhile, the lower stability of α-tocopherol at higher temperatures may be attributed to its higher reactivity. Therefore, when investigating the antioxidant effects of tocopherols under accelerated storage conditions, α-tocopherol is consumed first, followed by β- and γ-tocopherols. Finally, δ-tocopherol is more stable and thus consumed more slowly (Yoshida et al., 1993). The differences in the antioxidant activities of tocopherols in different lipid systems are not yet fully understood, nor can they be explained solely by structural differences. Therefore, it has been proposed that the antioxidant activity of tocopherols is dependent on concentration, temperature, light, type of substrate and solvent, as well as the presence of synergists and other chemical species that may act as pro-oxidants (Kamal-Eldin & Appleqvist, 1996).

The most effective synthetic antioxidant in both stripped oils was TBHQ. Similar observations have been reported by other invistigators. TBHQ was the most effective antioxidant in soybean, hydrogenated soybean and peanut oils compared with Tenox GT-2 and α-tocopherol (Akoh, 1994). Meanwhile, Gordon and Kourimska (1995) have examined the effects of different antioxidants on the oxidative stability of rapeseed oil during heating and the order of antioxidant activity was TBHQ > lecithin > ascorbyl palmitate > rosemary extract > BHT, BHA and δ-tocopherol. Similarly, TBHQ at 100 ppm was more effective than BHA and BHT at 200 ppm in capelin oil at 60 °C (Kaitaranta, 1992). More recently, Sharma, Semwal, Narashima, and Arya (1997) found that TBHQ was the most effective antioxidant in fried potato chips, banana chips and fried bengalgram dhal, followed by BHT and then BHA.

Synthetic phenolic antioxidants interrupt the free radical chain reaction in a similar manner to tocopherols by donating their phenolic hydrogen to fatty acid radicals, thus terminating the reaction. Phenol itself does not act as an antioxidant, but substitution of bulky alkyl groups into 2-, 4- and 6- positions increases the electron density on the hydroxyl group by an inductive effect and thus increases hydrogen donation ability (King et al., 1995). The antioxidant activity of BHA is due to the strong electron donating potency of its methoxy substitutent. The phenoxy radical formed during this process is stabilized by delocalization of the unpaired electron around the aromatic ring. The stability of phenoxy radicals reduces the rate of propagation and further reactions and thus increases the oxidative stability of lipids (Gordon, 1990). The presence of bulky branched groups, as in BHT, increases the stability of phenoxy radicals. However, it may also decrease the ability of these radicals to react with the fatty acid peroxy radicals (King et al., 1995). This might explain, in part, the higher antioxidant activity of BHT in evening

primrose TAG, but not in borage oil TAG. The introduction of a second hydroxyl group into position 2 or 4 enhances the oxidative stability (Gordon, 1990). Therefore, it has been proposed that the two para hydroxyl groups are responsible for the superior antioxidant activity of TBHQ in various edible oils (Madhavi et al., 1995). In comparing synthetic and natural antioxidants in this study, in addition to existing structural differences, the concentrations of synthetic antioxidants used, on a mole basis, are two to two and a half times higher than those of tocopherols used. Thus, concentration effects may also play an important role in the observed trends. Nonetheless, current industrial practices and regulations recommend the usage level of antioxidants on a per weight basis.

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