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Oxidative Stability of Conventional and High-Oleic Vegetable Oils with Added Antioxidants

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Abstract The oxidative stability of conventional and high-oleic varieties of commercial vegetable oils, with and without added antioxidants, was evaluated using the oil stability index (OSI). Oil varieties studied were soybean (SOY), partially-hydrogenated soybean (PHSOY), corn (CORN), sunflower (SUN), canola (CAN), high-oleic canola (HOCAN), very high-oleic canola (VHOCAN), oleic safflower (SAF) and high-oleic sunflower (HOSUN). One or more commercial antioxidants were added to the four most stable oils at supplier-recommended levels: rosemary extract (RM; 1,000 ppm), ascorbyl palmitate (AP; 1,000 ppm), tert-butylhydroquinone (TBHO; 200 ppm), and mixed tocopherols (TOC; 200 ppm). OSI in hours (h) at 110 °C of the conventional oils were 5.2, 7.6, 8.4, 9.8, 10.9 and 14.3 h for SUN, SOY, CAN, CORN, PHSOY and SAF, respectively. OSI of high-oleic variants were 12.9, 16.5 and 18.5 h for HOCAN, HOSUN and VHOCAN, respectively. Maximum OSI values for the four most stable oils when treated with antioxidants, were 40.9, 48.5, 48.8 and 55.7 h for HOCAN, VHOCAN, SAF and HOSUN, respectively. Addition of TBHQ, alone and in combination with other antioxidants, resulted in the greatest increase in oxidative stability of SAF and other high-oleic oils evaluated. AP had a positive synergistic effect when used with TBHQ, while RM decreased TBHQ effectiveness.

Keywords High oleic vegetable oil · Oxidative stability · Antioxidant · Long-term storage

Introduction

The relatively short shelf-life of most commercially available vegetable oils limits their usefulness in various applications. A high-stability vegetable oil could be used to reduce inventory turn-over and extend the life of frying oils and fried foods. Highly stable oil could also have application in rations for emergency preparedness, extended space travel, international food-aid and military uses.

Oxidative rancidity is the primary mechanism affecting stability during storage of properly processed and packaged vegetable oils [1]. Factors affecting the oxidative stability of vegetable oil include the fatty acid (FA) composition of the oil, antioxidants, oxygen, light and storage temperature.

The FA composition of vegetable oil is affected by botanical source, genetic variations and commercial hydrogenation. Traditional plant breeding and genetic manipulations of conventional oilseed crops have resulted in high-oleic oil varieties [2]. Use of genetic manipulation, such as recombinant DNA techniques, results in commodities referred to as genetically modified (GM) products.

Various antioxidants are used to increase the oxidative stability of vegetable oils. In addition to naturally occurring antioxidants such as tocopherols, and rosemary extract, other antioxidants include ascorbyl palmitate (AP), butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), propyl gallate (PG), *tert*-butylhydroquinone (TBHQ), and citric acid. With the exception of citric acid, which is used for metal chelation, all of these antioxidants function by quenching free radicals [1, 3].

Many studies have been published relating to stabilization of oil with antioxidants. Chu and Hsu [4] tested various antioxidants, including AP, rosemary extract and tocopherols, in peanut oil using the OSI. They found that, while all three antioxidants increased the OSI value,

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rosemary extract had the greatest effect, followed by AP and tocopherols. Martinez-Tome et al. [5] tested the antioxidant properties of spice extracts against traditional antioxidants using the OSI in refined olive oil. Rosemary extract was again found to be the most effective, followed by PG, BHA, and BHT. Silva et al. [6] showed that PG was a more effective antioxidant than tocopherols in sunflower (SUN) oil. Rodriguez et al. [7] reported that, OSI stability of hake liver oil was best when treated with TBHQ followed by PG > BHA > BHT > AP > TOC.

Synergistic effects have also been shown with mixtures of two or more antioxidants. Allam and Mohamed [8] tested combinations of antioxidants using the Rancimat and observed both positive and negative synergistic effects in SUN oil. A combination of TBHQ, AP, and monoacylglycerol citrate proved to be the most effective antioxidant combination in their study.

While considerable research has been conducted on various combinations of oils and antioxidants, a comparison of the most common traditional oils and their higholeic variants in commercial production has not been reported. Nor has an extensive study of antioxidant effects on these high-stability oils been undertaken.

The purpose of this study was to evaluate the oxidative stability of conventional and high-oleic varieties of commercially produced vegetable oils, with and without antioxidants, using the oil stability index (OSI).

Materials and Methods

All oils used were commercially processed and sourced directly from the manufacturer. Soybean (SOY) and canola (CAN) oils were obtained from Bunge (St. Louis, MO); oleic safflower oil (SAF) was obtained from California Oilseeds Co. (Richmond, CA); partially-hydrogenated soybean (PHSOY), corn (CORN), SUN, high-oleic sunflower (HOSUN), high-oleic canola (HOCAN), and very high-oleic canola (VHOCAN) oils were obtained from Cargill (Minneapolis, MN).

Tocopherol analytical standards were obtained from Calbiochem (La Jolla, CA). Guardian 08 rosemary extract (RM); Grindox Toco-70, mixed natural tocopherols (TOC), with a typical composition of 9, 1.5, 19, and 40.5% (w/w) of α -, β -, δ -, and γ -tocopherols, respectively; TBHQ (Grindox 443) and AP (Grindox 520) were obtained from Danisco (New Century, KS). Anhydrous granular citric acid was obtained from EMD Chemicals, Inc. (Gibbstown, NJ).

Upon receipt, oils were stored in their original container in

the dark at 4 °C until evaluated for FA composition, initial

Methods

quality and stability. FA composition was determined using AOCS Method Ce 2-66 [9] to prepare FA methyl esters, followed by gas chromatographic detection using AOCS Method Ce 1-62 [9]. The column was a Phenome CGO-5052 (Cyanopropylphenyl) 30 m \times 0.25 mm with a 0.25 µm film thickness. The carrier gas was helium.

For tocopherol analysis, samples were prepared according to AOCS Method Ce 8-89 [9]. Tocopherols were measured by HPLC according to the method of Peterson and Qureshi [10] using an Agilent 1100 instrument fitted with a Waters normal phase Prisil column having dimensions of 3.9×300 mm. Hexane with 0.2% (v/v) isopropanol was used as the mobile phase, and analysis was carried out in duplicate for each sample. Quantification of the α , β , γ and δ isomers was done using external standards.

Citric acid was measured in four replicates according to the method of Law and Berger [11]. A measure of 50 g oil was extracted three times using 25 ml of 60 °C distilled water. The combined aqueous extracts were filtered, evaporated and brought to volume in a 5-mL volumetric flask using distilled water. A 1 mL aliquot of the aqueous extract was transferred to a 10-ml volumetric flask, along with 1.3 mL pyridine and 5.7 mL acetic anhydride. The contents of the flask were mixed and allowed to stand in a 35 °C water bath for 30 min before bringing to volume with distilled water. Absorbance at 366 nm was measured using a spectrophotometer (Milton Roy Spectronic 20D). A reagent blank was prepared and analyzed at the same time using 1 mL distilled water in place of aqueous concentrate. Citric acid concentration was determined using a standard curve.

Peroxide value (PV) was measured in triplicate according to AOCS Method Cd 8b-90 [9]. The test procedure was modified from the official method in that the starch indicator solution was added to the sample immediately before initiating titration. This change is consistent with industry practice (Personal communication, JD Weber, Ventura Foods, Albert Lea, MN).

OSI of original oils and oils with added antioxidants was measured in duplicate using an Oxidative Stability Instrument according to AOCS Method Cd 12b-92 [9] at 110 °C using an airflow rate of 2.5 ± 0.2 mL/sec. Cleaning of OSI glassware and tubing was carried out according to manufacturer guidelines [12].

Antioxidant/Oil Preparations

The four oils having the highest OSI values were selected for use in the antioxidant portion of the study. All oils evaluated in this study were commercially prepared oils with citric acid added by the supplier during processing. In order to minimize effects from differing levels of citric acid during the antioxidant study, oils selected for this phase of the experiment were standardized at 11.8 ppm, which was the highest level detected in the oils used for this portion of the study. In order to dissolve the citric acid, the oils were heated to 50 °C for 30 min. For consistency, all oils were heated regardless of citric acid addition. The supplier recommended levels of antioxidants used were 1,000 ppm for RM, 1,000 ppm for AP, 200 ppm for TBHQ and 200 ppm for TOC. TBHQ was added and dissolved with stirring under nitrogen for 24 h. RM, TOC and AP were dissolved with stirring for 5–10 min. Antioxidants were added to the selected oils separately and in all possible combinations. OSI values were measured in duplicate for each oil-antioxidant combination, with treatments measured in a randomized order.

Statistical Analyses

The number of OSI replications required was determined using a statistical power-analysis which considered within and between treatment variability and the minimum difference between treatments deemed to be of practical significance. For the power-analysis, a minimum OSI difference of 5 h between oil-antioxidant treatments was considered significant in a practical sense by potential commercial users of these oils. Based on a preliminary evaluation of five different oil samples evaluated in duplicate it was determined that a single replication (n = 2) of the OSI analysis would allow sufficient differentiation between samples.

Original oil data, as well as OSI values for all oil and antioxidant combinations were analyzed using a mixed model analysis of variance (PROC MIXED) of Statistical Analysis System Version 9.1[®] software (SAS Institute Inc., Cary, NC). Significant differences were determined using the Tukey-Kramer method for all pair-wise comparisons with a significance level of $\alpha = 0.05$.

Results and Discussion

Fatty Acid Composition

The oils evaluated covered a wide range of monounsaturated fatty acid (MUFA) to polyunsaturated fatty acid (PUFA) ratios (Table 1). Conventional SUN had the lowest ratio (0.4:1); whereas HOSUN had the highest (6.4:1). On this basis, the oils can be grouped into low-ratio MUFA:PUFA oils (SUN, SOY, CORN and PHSOY), medium-ratio MUFA:PUFA oils (CAN, HO-CAN) and high-ratio MUFA:PUFA oils (VHOCAN, SAF and HOSUN).

All high-oleic oils were similar with respect to 18:1, 18:2, and 18:3 contents. These oils had higher amounts of 18:1 (59.1–76.2%), and lower amounts of 18:2 (10.6–23.9%) and 18:3 (1.6–3.9%) compared to the conventional varieties, which had lower amounts of 18:1 (25.1–54.4%), and higher 18:2 (21.5–58.0%) and 18:3 (1.6–10.1%) levels.

The extent of variation possible through traditional plant breeding of oilseeds is evident when comparing the FA composition of SUN and HOSUN. The former oil had one of the lowest 18:3 levels (1.6%) but the highest level of 18:2 (58%), while the latter had the lowest 18:2 level (10.6%) and the highest 18:1 content (76.2%). The FA composition of the oils used in this study are consistent with data reported by other researchers evaluating oil from similar genetic variants [13–16].

 Table 1
 Fatty acid composition (wt%), and monounsaturated (MUFA) and polyunsaturated (PUFA) fatty acid ratios in conventional and higholeic vegetable oils from commercial sources

	Oil									
	SOY	PHSOY	CORN	SUN	CAN	HOCAN	VHOCAN	SAF	HOSUN	
C14:0	0.1	<0.1	0.0	<0.1	0.0	0.0	<0.1	0.2	0.0	
C16:0	10.9	11.9	12.0	6.2	5.1	4.7	4.2	5.2	3.8	
C16:1	0.1	0.1	0.1	0.0	0.3	0.3	0.3	0.1	0.1	
C18:0	4.2	4.0	2.3	4.8	2.3	2.6	2.7	2.5	3.6	
C18:1	26.5	35.8	28.5	25.1	54.4	59.1	71.3	72.8	76.2	
C18:2	46.1	39.1	52.0	58.0	21.5	23.9	12.3	12.1	10.6	
C18:3	8.2	4.0	1.9	1.6	10.1	3.5	3.9	1.6	1.6	
C20:0	2.1	2.9	1.9	2.4	2.9	2.8	2.3	2.7	1.9	
C20:1	1.4	1.9	1.3	1.4	3.1	3.0	2.7	2.5	1.8	
C22:0	0.2	0.3	0.0	0.5	0.2	0.3	0.2	0.3	0.6	
MUFA/PUFA ratio	0.5:1	0.9:1	0.6:1	0.4:1	1.8:1	2.3:1	4.6:1	5.5:1	6.4:1	

SOY soybean oil, CAN canola oil, SAF oleic safflower oil, PHSOY partially hydrogenated soybean oil, CORN corn oil, SUN sunflower oil, HOSUN high oleic sunflower oil, HOCAN high oleic canola oil, and VHOCAN very high oleic canola oil

Initial Oil Quality and Stability

The initial PV for all oils ranged from 0.0 to 0.6 (Table 2). Although within expected levels for commercial oils with varying production dates and storage times, the PV were different enough to potentially have had some effect on OSI values.

As shown in Table 2, initial OSI testing of the oils at the time they were received showed a significant range of oxidative stabilities, from a low of 5.2 h for conventional SUN to 18.5 h for VHOCAN. Stability of the conventional oils, with the exception of SAF, ranged from 5.2 to 10.9 h, with PHSOY exhibiting the greatest stability. SAF, which is naturally high in oleic acid (often referred to as Oleic Safflower), had the greatest stability of the conventional oils, with an OSI value of 14.3 h.

Possibly due to differences in botanical source, as well as processing, initial tocopherol levels and tocopherol profile also varied across the different oil variants (Table 2). SOY, PHSOY and CORN had high levels of the very effective γ - and δ -tocopherols, whereas SUN, HOSUN and SAF had significant amounts of α -tocopherol and only small amounts of γ - and δ -tocopherols. The canola oil variants were all similar in having higher levels of γ -tocopherol, very little δ -tocopherol, and moderate amounts of α - and β -tocopherol.

The FA composition of the oils can partially explain differences in OSI stability. Comparing the four oils highest in oleic acid (HOCAN, VHOCAN, SAF and HOSUN), HOCAN had the lowest amount of 18:1 (59.1%), the highest amount of 18:2 (23.9%) and a high 18:3 content (3.5%); its OSI was the lowest (12.9 h). However, the FA composition does not explain why VHOCAN (18.5 h) stability was higher than SAF (14.3 h). VHOCAN and SAF had similar amounts of 18:1 and 18:2, but VHOCAN had

higher amounts of 18:3 (3.9% compared to 1.6% in SAF). Nor does FA composition explain why HOSUN (16.5 h) was less stable than VHOCAN (18.5 h). Tocopherol levels and the profile of tocopherol isomers in the oils could help explain these discrepancies. Normand et al. [14] noted that in oils of similar FA composition, those oils having higher amounts of tocopherols have greater stability. The oils with the lowest tocopherol levels were HOSUN (819 ppm) and SAF (941 ppm), with the α -tocopherol isomer comprising greater than 90% of the total in these two oils. VHOCAN (1,438 ppm) and HOCAN (1,184 ppm) had significantly higher total tocopherols, with appreciable levels of γ - and δ -tocopherols. The higher antioxidant efficacy of γ - and δ -tocopherols, as compared to α - and β -isomers, could have a marked effect on stability of oils having appreciable levels of the more active isomers; even though total tocopherol levels may be somewhat lower [3]. This would help explain the differences in stability between SUN and SAF, which have mostly α -isomer, and CAN, which has more γ -isomer; as well as helping to account for the greater initial stability of VHOCAN over SAF and HOSUN, which have comparable or lower PUFA levels.

Influence of Antioxidants on Oil Stability

Based on an interest in identifying oils for use in long-term storage, the four oils having the longest initial OSI values, HOSUN, HOCAN, VHOCAN and SAF, were selected for further evaluation of the effect of free radical quenching antioxidants on stability. Table 3 shows the effect of antioxidant addition on OSI values for these oils.

Considering the effect of individual antioxidants, addition of TBHQ resulted in a dramatic increase in the stability of all four oils. For the two canola oils, TBHQ alone provided as much protection against oxidation as any

п	Vegetable oil									
	SOY	PHSOY	CORN	SUN	CAN	HOCAN	VHOCAN	SAF	HOSUN	SE
2–3	0.43 ^{AB}	0.00^{B}	0.58 ^A	0.59 ^A	0.22 ^{AB}	0.60 ^A	0.14 ^{AB}	0.64 ^A	0.53 ^A	0.10
2	7.6 ^F	10.9 ^D	9.8^{DE}	5.2^{G}	8.4^{EF}	12.9 ^C	18.5 ^A	14.3 ^C	16.5 ^B	0.28
4	ND	ND	ND	ND	ND	8.66 ^B	11.77 ^A	8.28^{B}	6.96 ^C	0.22
3	204 ^H	174 ^I	351 ^E	1092 ^A	329 ^F	239 ^G	479 ^D	923 ^B	769 ^C	1.4
3	$44^{\rm F}$	35^{G}	67 ^D	$57^{\rm E}$	224 ^A	193 ^C	210 ^B	$0^{\rm H}$	0^{H}	0.60
3	1495 ^A	1172 ^B	1507 ^A	19 ^E	506 ^D	736 ^C	731 ^C	17^{E}	45^{E}	5.8
3	470 ^A	372 ^B	60 ^C	2^{EF}	14 ^D	16 ^D	18 ^D	1^{F}	$5^{\rm E}$	0.82
	2213 ^A	1753 ^C	1985 ^B	1170 ^E	1073 ^F	1184 ^E	1438 ^D	941 ^G	819 ^H	8.0
	n 2-3 2 4 3 3 3 3	$\begin{array}{c ccc} n & & Vegetabl \\ \hline SOY \\ \hline 2-3 & 0.43^{AB} \\ 2 & 7.6^{F} \\ 4 & ND \\ \hline 3 & 204^{H} \\ 3 & 44^{F} \\ 3 & 1495^{A} \\ 3 & 470^{A} \\ & 2213^{A} \\ \end{array}$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	n Vegetable oil SOY PHSOY CORN 2-3 0.43^{AB} 0.00^B 0.58^A 2 7.6^F 10.9^D 9.8^{DE} 4 ND ND ND 3 204^H 174^I 351^E 3 44^F 35^G 67^D 3 1495^A 1172^B 1507^A 3 470^A 372^B 60^C 2213^A 1753^C 1985^B	n Vegetable oil SOY PHSOY CORN SUN 2-3 0.43^{AB} 0.00^B 0.58^A 0.59^A 2 7.6^F 10.9^D 9.8^{DE} 5.2^G 4 ND ND ND ND 3 204^H 174^I 351^E 1092^A 3 44^F 35^G 67^D 57^E 3 1495^A 1172^B 1507^A 19^E 3 470^A 372^B 60^C 2^{EF} 2213^A 1753^C 1985^B 1170^E	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$				

Table 2 Original oil analyses for SOY, PHSOY, CORN, SUN, HOSUN, CAN, HOCAN, VHOCAN, and SAF (See Table 1 for abbreviations)

Like superscripts within rows indicate no significant difference (p > 0.05)

n number of replicate determinations, SE standard error of the mean, ND Not determined

Table 3 Effect of addition of rosemary extract (RM; 1,000 ppm), ascorbyl palmitate (AP; 1,000 ppm), tert-butylhydroquinone (TBHO; 200 ppm) and mixed tocopherols (TOC; 200 ppm) on oxidative

stability of HOCAN, VHOCAN, HOSUN, and SAF vegetable oils (See Table 1 for abbreviations)

Antioxidant addition	OSI 110 °C (h) ^a								
	HOCAN	VHOCAN	SAF	HOSUN					
Control-no antioxidants	11.9 ± 0.18 $^{\rm Da}$	$16.9 \pm 0^{\mathrm{Fa}}$	$12.2\pm0.11^{\rm Fa}$	$13.8\pm0.57^{\rm Ea}$					
TOC	$12.1 \pm 0^{\text{Db}}$	$17.4\pm0.07^{\mathrm{Fab}}$	$17.3 \pm 2.12^{\mathrm{EFab}}$	19.6 \pm 0.04 $^{\rm Da}$					
RM	$15.7 \pm 0.14^{\text{CDb}}$	$21.2 \pm 0.25^{\text{DEFa}}$	$16.7\pm0.18^{\rm EFab}$	19.3 ± 0.32^{Dab}					
AP	$17.3\pm0.18^{\rm CDb}$	$24.4\pm0.35^{\rm CDEa}$	$15.8\pm0.42^{\rm EFb}$	$19.7\pm0.64^{\rm Dab}$					
TBHQ	$36.0\pm0.85^{\rm ABb}$	46.9 ± 1.87^{ABa}	$41.0\pm0.32^{\rm BCb}$	49.6 ± 0.92^{Ba}					
TOC-RM	$16.0\pm0.67^{\rm CDb}$	$21.0\pm0.64^{\rm EFab}$	$20.5\pm0.11^{\rm DEab}$	$24.7\pm0.04^{\rm CDa}$					
TOC-AP	$18.0\pm0.18^{\rm Cc}$	$23.6 \pm 0.81^{\text{CDEab}}$	$20.2 \pm 1.31^{\text{DEbc}}$	26.0 ± 0.04^{Ca}					
RM-AP	$20.0\pm1.63^{\rm Cc}$	$27.2\pm1.38^{\rm Ca}$	$20.7\pm0.85^{\rm DEbc}$	25.5 ± 0.35^{Cab}					
TBHQ-RM	$35.2\pm0.67^{\rm Bc}$	$43.4\pm2.51^{\rm ABb}$	$39.1 \pm 2.02^{\text{Cbc}}$	50.3 ± 0.11^{ABa}					
TBHQ-AP	$37.9 \pm 1.06^{\rm ABc}$	$47.9\pm0.85^{\rm ABab}$	$44.5\pm0.21^{\rm ABCb}$	51.8 ± 0.04^{ABa}					
TBHQ-TOC	37.4 ± 0^{ABc}	$46.3\pm1.03^{\rm ABb}$	$45.0\pm0.07^{\rm ABb}$	54.3 ± 0.49^{ABa}					
TOC-RM-AP	$19.7\pm0.95^{\rm Cc}$	$26.5\pm0.42^{\rm CDab}$	$24.2 \pm 2.19^{\text{Dbc}}$	$29.9\pm2.23^{\rm Ca}$					
TBHQ-TOC-RM	$35.3\pm0.14^{\rm Bc}$	42.7 ± 0.07^{Bb}	$43.6\pm2.23^{\rm ABCb}$	53.9 ± 0.11^{ABa}					
TBHQ-RM-AP	$39.1\pm0.71^{\rm ABc}$	$45.0\pm1.84^{\rm ABb}$	47.3 ± 2.4^{ABab}	50.8 ± 1.13^{ABa}					
TBHQ-TOC-AP	$40.9\pm0.04^{\rm Ac}$	$47.8\pm1.41^{\rm ABb}$	$48.8\pm0.78^{\rm Ab}$	55.7 ± 4.24^{Aa}					
TBHQ-TOC-RM-AP	$37.6\pm0.85^{\rm ABc}$	$48.5\pm2.4^{\rm Aab}$	46.1 ± 2.97^{ABb}	$53.2\pm2.23^{\rm ABa}$					

^a Values are expressed as mean \pm SD (n = 2). Standard error of the mean (balanced design) = 0.90. Like capital superscripts within columns and lower-case superscripts within rows indicate no significant difference (p > 0.05)

other combination of antioxidants. AP was an effective antioxidant in both HOSUN and VHOCAN. RM and TOC were effective in significantly increasing the stability of HOSUN. It is possible that at higher concentrations these natural antioxidants might have a greater effect on stability. Interestingly, HOSUN had the least amount of total tocopherols of any of the oils studied (Table 2). The amount of natural tocopherols present in an oil will significantly affect the stabilizing effect from antioxidant addition. However, Warner [17] demonstrated that the natural tocopherol profile of SUN oil was less effective than that of SOY oil in inhibiting autoxidation. This may help explain why addition of natural tocopherols having a more favorable antioxidant profile, had such a marked effect in HOSUN.

Analysis of variance across all treatments showed only two significant interactions between antioxidants. A positive interaction (p < 0.05) was found between TBHQ and AP; whereas a negative interaction (p < 0.0001) was observed between TBHQ and RM, indicating that RM actually decreased the effectiveness of TBHO. The positive contribution of AP was also specifically evident in HO-SUN, where the addition of AP to either TOC or RM resulted in greater stability than either single antioxidant. VHOCAN was more stable with the combination of AP/ TOC/RM than with TOC/RM; while SAF, was more stable in the presence of AP/TBHQ/RM than TBHQ/RM. This may be attributed to the ability of AP to regenerate the reactive phenolic ring in the antioxidant system [3].

The negative interaction between TBHQ and RM mirrors the negative synergism reported between RM and α -tocopherol in other studies [18, 19], wherein the effect was attributed to carnosol, a specific diterpene found in RM [19]. It is possible that carnosol has a similar negative effect on TBHQ, though why it was not apparent in TOC in this study is unclear.

The lack of significant interaction between TBHQ and TOC also was observed by Che Man et al. [20] during deep-fat frying. One concern often raised with the use of tocopherols as antioxidants relates to the prooxidant effect at elevated α -tocopherol levels [21, 22]. It has more recently been proposed that the tocopherols themselves are not prooxidants, but may act synergistically with prooxidants already in the system [23].

The maximum OSI for any antioxidant combination for SAF and HOSUN was TBHQ/TOC/AP, resulting in OSI values of 48.8 and 55.7 h, respectively. These OSI values were significantly different from OSI values of SAF and HOSUN without antioxidants, showing an increase of 400%. For VHOCAN and HOCAN, addition of TBHQ alone resulted in an increase in stability from the original oil of 250 and 300%, respectively. Clearly, the addition of TBHQ, alone and in combination with other antioxidants, was most effective in increasing the stability of the oils studied.

The oil-antioxidant combination having the maximum OSI (55.7 h), HOSUN containing TBHO/TOC/AP, demonstrated a seven-fold increase in stability over the most commonly utilized domestic commercial oil, which is standard soybean oil (SOY) (OSI 7.6 h). The question remains as to whether these results, obtained in an accelerated test at an elevated temperature, would translate into similar increases in oxidative stability at ambient temperatures. High correlations of OSI at 110 °C with sensory evaluation of oxidative stability in oils held at room temperature were found by Coppin and Pike [24] ($r^2 = 0.92$), and Broadbent and Pike [25] ($r^2 = 0.89$). Gordon and Mursi [26] reported a high correlation between Rancimat at 100 °C and PV of oils stored at 20 °C ($r^2 = 0.966$). These studies support the practice of using high temperature accelerated studies, such as OSI, to predict results that would be seen at ambient temperatures over longer periods of time. However, further studies at ambient temperatures would be required to determine the actual shelf life of higholeic oils containing antioxidants.

Some consumers and manufacturers are adverse to the use of GM oils or synthetic food additives. If a non-GM oil is required for a long-term storage application, the oils of choice would be HOSUN and SAF, both of which are products of traditional plant breeding techniques. HOCAN and VHOCAN are GM variants. If only natural antioxidants can be used, then the choice is limited to TOC, RM, and possibly AP, based on the antioxidant levels used in this study. Though not as effective as TBHQ, these antioxidants still have a significant impact on oxidative stability of conventional and high-oleic vegetable oils.

References

- Nawar WW (1996) Lipids. In: Fennema OR (ed) Food chemistry. Marcel Dekker, New York, pp 225–320
- Hu XY, Sullivan-Gilbert M, Gupta M, Thompson SA (2006) Mapping of the loci controlling oleic and linolenic acid contents and development of *fad2* and *fad3* allele-specific markers in canola (*Brassica napus* L.). Theor Appl Genet 113:497–507
- 3. Frankel EN (2005) Lipid oxidation, 2nd edn. PJ Barnes, Bridgewater, England, pp 165–183, 209–253
- Chu YH, Hsu HF (1999) Effects of antioxidants on peanut oil stability. Food Chem 66(1):29–34
- Martinez-Tome M, Jimenez AM, Ruggieri S, Frega N, Strabbioli R, Murcia MA (2001) Antioxidant properties of Mediterranean spices compared with common food additives. J Food Prot 64(9):1412–1419
- Silva FAM, Borges F, Ferreira MA (2001) Effects of phenolic propyl esters on the oxidative stability of refined sunflower oil. J Agric Food Chem 49(8):3936–3941

- Rodriguez A, Barreraarellano D, Grompone MA (1993) Oxidative stability of hake liver oil. Grasas Aceites 44(4–5):270–273
- Allam SSM, Mohamed HMA (2002) Thermal stability of some commercial natural and synthetic antioxidants and their mixtures. J Food Lipids 9(4):277–293
- 9. (1997) Official methods and recommended practices of the American Oil Chemists' Society, 5th edn. American Oil Chemists' Society, Champaign
- Peterson DM, Qureshi AA (1993) Genotype and environment effects on tocols of barley and oats. Cereal Chem 70(2):157–162
- Law KS, Berger KG (1984) Citric acid in the processing of oils and fats. PORIM Bull 11:1–32
- Pike OA (2001) Assessment of oxidative stability for lipids. In: Wrolstad RE, Acree TE, An H, Decker EA, Penner MH, Reid DS, Schwartz SJ, Shoemaker CF, Sporns P (eds) Current protocols in food analytical chemistry, vol 1. Wiley, New York, pp D2.3.1–5
- Matthaus B (2006) Utilization of high-oleic rapeseed oil for deepfat frying of French fries compared to other commonly used edible oils. Eur J Lipids Sci Technol 108:200–211
- Normand L, Eskin NAM, Przybylski R (2006) Comparison of the frying stability of regular and high-oleic acid sunflower oils. J Am Oil Chem Soc 83:331–334
- Martin-Polvillo M, Marquez-Ruiz G, Dobarganes MC (2004) Oxidative stability of sunflower oils differing in unsaturation degree during long-term storage at room temperature. J Am Oil Chem Soc 81:577–583
- Fujisaki M, Mohri S, Endo Y, Fujimoto K (2000) The effect of oxygen concentration on oxidative deterioration in heated higholeic safflower oil. J Am Oil Chem Soc 77:231–234
- Warner K (2005) Effects on the flavor and oxidative stability of stripped soybean and sunflower oils with added pure tocopherols. J Agric Food Chem 53:9906–9910
- Hras AR, Hadolin M, Knez Z, Bauman D (2000) Comparison of antioxidative and synergistic effects of rosemary extract with α-tocopherol, ascorbyl palmitate and citric acid in sunflower oil. Food Chem 71:229–233
- 19. Hopia AI, Huang SW, Schwarz K, German JB, Frankel EN (1996) Effect of different lipid systems on antioxidant activity of rosemary constituents carnosol and carnosic acid with and without α -tocopherol. J Agric Food Chem 44:2030–2036
- 20. Che Man YB, Jialong L, Liu JL (1999) The effects of TBHQ and α -tocopherol on quality characteristics of refined-bleached and deodorized palm olein during deep-fat frying. J Food Lipids 6(2):117–129
- 21. Huang SW, Frankel EN, German JB (1994) Antioxidant activity of α and γ -tocopherols in bulk oils and in oil-in-water emulsions. J Agric Food Chem 42:2108–2114
- Cillard J, Cillard P, Cormier M, Girre L (1980) α-Tocopherol prooxidant effect in aqueous media: increased autoxidation rate of linoleic acid. J Am Oil Chem Soc 57:252–255
- Eitenmiller R, Lee J (2004) Vitamin E, Food Chemistry. Composition and Analysis. Marcel Dekker, New York, p 104
- Coppin EA, Pike OA (2001) Oil stability index correlated with sensory determination of oxidative stability in light-catalyzed soybean oil. J Am Oil Chem Soc 78:13–18
- Broadbent CJ, Pike OA (2003) Oil stability index correlated with sensory determination of oxidative stability in canola oil. J Am Oil Chem Soc 80:59–63
- Gordon MG, Mursi E (1994) A comparison of oil stability based on the Metrohm rancimat with storage at 20 °C. J Am Oil Chem Soc 71:649–651