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Effects of antioxidants on peanut oil stability

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Abstract

Several antioxidants including phospholipids (PL), ascorbyl palmitate (AP), rosemary (ROS), tocopherol (TOC) and catechin (CAT) were chosen to study the effects on peanut oil stability. Among these antioxidants, catechin alone and composites of catechin with other antioxidants showed significant increases in oil stability as compared to control oil. A response surface design was used to study the effects of three antioxidant composites on the peanut oil stability. Results showed the OSI (Oxidation Stability Index) values are significantly influenced by CAT ($p < 0.0001$), followed by ROS ($p < 0.05$) and PL ($p < 0.5$). TOC was the least significant ($p > 0.5$) in the increase of OSI value. By considering cost, handling and minimum usage of antioxidants, the OSI value of peanut oil would reach 15–16 h by the addition of 1500 ppm of CAT and a maximum level of either 400 ppm of ROS or PL. © 1999 Elsevier Science Ltd. All rights reserved.

1. Introduction

The oxidative stability of oils and fats may be influenced by many factors, such as light, metal ions, oxygen, temperature and enzymes (Nawar, 1985). The addition of antioxidants to the oil helps to prevent or decrease oil oxidation. Traditionally, chemically synthesized compounds such as butylated hydroxyanisole (BHA) and butylated hydroxytoluene (BHT) are used as antioxidants in oil products. However, some research papers have shown that these compounds are toxic to experimental animals (Bran, 1975; Ford et al., 1980; Whysner et al., 1994). Therefore, the use of natural antioxidants is now a trend in both research and industrial applications. Several compounds, including ascorbyl palmitate (Cort, 1974), tocopherol (Hildebrand, 1984; Huang et al., 1994), catechin (Hirose and Iwama, 1984; Namiki, 1990), rosemary extract (Angel et al., 1988; Namiki, 1990; Wada and Xin-Fang, 1994) and phospholipid (Dashiell, 1989; Gopala-Krishna and Prabhakar, 1994; Gordon and Kourimska, 1995) have been investigated and most of them were more effective than BHA and BHT in decreasing oil oxidation. The synergistic antioxidative effects of AP, TOC, ROS and PL on soybean oil stability (Chu, 1991), ROS and TOC on sardine oil stability (Wada and Xin-Fang, 1994), and PL and TOC on fish oil stability (Hara et al., 1992; Segawa et al., 1994) have been previously reported. However, no literature has reported the effects between CAT and other antioxidants on oil stability. In this paper, the effects of antioxidant composites on peanut oil stability were studied.

Peanut is an important oilseed crop in Taiwan and one third of these seeds is processed for edible oil. Peanut oil, like sesame oil, is obtained from roasted seeds and these two oils are prevalent in south eastern Asia. In Taiwan, all of the peanut oil is processed by seed roasting, followed by expeller-pressing. Peanut oil is less stable than sesame oil, the latter containing unique antioxidants, i.e. sesamin, sesamol and sesamolin, in addition to tocopherol (Sonntag, 1979). In order to increase the quality of peanut oil, several nutrient or natural antioxidants were chosen to study the effects on oil stability.

2. Materials and methods

2.1. Materials

Expeller-pressed and filtered peanut oil, without alkali refining, was obtained from a local plant. High purity of phospholipids (at least 98% acetone insolubles, composed of phosphatidylethanolamine (PE) 26.26%, phosphatidylcholine (PC) 25.43%, phosphatidylinositol (PI) 23.07%, phosphatidylserine (PS) 1.52%,

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phosphatidic acid (PA) 22.73%) were the products of Central Soya Co. (USA). Catechin and ascorbyl palmitate were purchased from Sigma Chemical Co. (St. Louis, MO) and E. Merck (Darmstadt, Germany), respectively. γ-Tocopherol was obtained from Eastern Kodak Co. (Rochester, NY). Rosemary concentrate was obtained from a local company.

2.2. Method

A statistical design was employed to optimize the conditions of antioxidant addition for the increase of peanut oil stability. TOC, AP, PL, CAT and ROS were selected as the variables to maximize the response (OSI) as shown in Tables 1 and 2.

2.3. Analyses

American Oil Chemists' Society methods were used for the determination of acid value (AV) (Method Cd 3d–63), peroxide value (PV) (Method Cd 8–53), oxidation stability index (OSI) (Method Cd 12b–92), trace metals (Method Ca 18–79) and fatty acid compositions (Method Ce 1–62) (Firestones, 1993).

2.4. Statistical analyses

All the data were analyzed by Statistical Analysis System (SAS, 1985).

3. Results and discussion

The quality of expeller-pressed and filtered peanut oil meets the Chinese National Standard and the analytical data are as follows: AV, 0.85 ± 0.02 mg KOH g^{-1}; PV, 3.28 ± 0.36 meq kg^{-1}; copper, 0.07 ± 0.01 ppm and lead, 0.08 ± 0.02 ppm. The fatty acid compositions of peanut oil with 80% unsaturated fatty acids were similar to the results from Chiou et al. (1995). The OSI value of control peanut oil without any antioxidants was only 4.77 h. In order to increase the oil stability, several nutrient or natural antioxidants including tocopherol, ascorbyl palmitate, phospholipids, catechin, and rosemary concentrate were investigated in this study. The OSI values of each oil with different antioxidant additions at three levels are shown in Table 1. For TOC, increasing the amount of TOC to 1000 ppm significantly ($p < 0.05$) increased the OSI value as compared with 500 ppm. For AP, the OSI value was insignificantly ($p > 0.05$) improved as the concentration of AP increased. Hence the amount of AP was limited to 100 ppm in our study due to lower oil solubility for AP more than 100 ppm. For PL and ROS, the OSI values were significantly ($p < 0.05$) improved as the concentrations of PL and ROS increased. However, the concentration of ROS was limited to 1000 ppm due to the generation of undesirable odor of more than 1000 ppm of ROS; PL was limited to 1500 ppm due to both the lower oil solubility and occurrence of foaming at higher concentrations (> 1500 ppm). For CAT, an extract from tea leaves showed the greatest OSI value at 1500 ppm. However, the level of CAT was limited to 1500 ppm due to the occurrence of turbidity at higher concentrations.

Several reports (Kikugawa et al., 1990; Coulter, 1988) indicated that composites of several antioxidants showed synergistic effects for increase of oil stability. Hence the effects of several composites of TOC, AP, PL, CAT and ROS on peanut oil stability were investigated in this study. To better understand the effect of the interaction of these five antioxidants and to determine where the oil stability is located, a 2^5 full-factorial experiment design was performed. The results in Table 2 showed that the OSI values of oils treated with antioxidant composites containing catechin were more than 13 h, as compared to 4.77–8.18 h for those composites without catechin. Moreover, among these antioxidants, as shown in Table 3, CAT most significantly ($p < 0.0001$) improved the OSI value of peanut oil, followed by PL, ROS and TOC, whereas AP had an insignificant ($p > 0.5$) effect on oil stability. Similar results were obtained for the effects of PL, AP and ROS on rapeseed oil stability (Gordon and Kourimska, 1995). Hence, TOC, PL, ROS, and CAT were chosen as

Table 1
Effects of several antioxidants on OSI values of peanut oils

Antioxidant	ppm	OSI (h)
TOC	1500	5.91^a
	1000	6.08^a
	500	5.52^b
AP	300	5.18^a
	200	5.06^a
	100	4.94^a
PL	3500	6.85^a
	3000	6.61^b
	2500	6.47^c
	2000	6.25^d
	1500	6.06^e
	1000	5.71^e
	500	5.39^f
CAT	3000	21.43^a
	2500	21.75^a
	2000	18.58^b
	1500	13.50^c
	1000	9.44^d
	500	7.25^e
ROS	1000	5.82^a
	500	5.39^b
	300	5.17^c
Control		4.77

[a–f] Means with different superscripts are significantly different ($p < 0.05$).

Table 2
OSI values of 2^5 factorial design of five antioxidants

Run no.	TOC (ppm)	AP (ppm)	PL (ppm)	ROS (ppm)	CAT (ppm)	OSI (h)
1	1000	100	1500	1000	1000	16.00[bcde]
2	0	100	1500	1000	1000	16.50[abc]
3	1000	0	1500	1000	1000	16.89[a]
4	0	0	1500	1000	1000	16.39[abcd]
5	1000	100	0	1000	1000	15.45[e]
6	0	100	0	1000	1000	16.80[a]
7	1000	0	0	1000	1000	16.69[ab]
8	0	0	0	1000	1000	16.00[bcde]
9	1000	100	1500	0	1000	16.50[abc]
10	0	100	1500	0	1000	16.12[abcde]
11	1000	0	1500	0	1000	16.89[a]
12	0	0	1500	0	1000	15.75[cde]
13	1000	100	0	0	1000	16.00[bcd]
14	0	100	0	0	1000	15.78[de]
15	1000	0	0	0	1000	15.89[cde]
16	0	0	0	0	1000	13.50[f]
17	1000	100	1500	1000	0	8.18[g]
18	0	100	1500	1000	0	7.52[h]
19	1000	0	1500	1000	0	8.15[g]
20	0	0	1500	1000	0	7.41[hi]
21	1000	100	0	1000	0	6.54[j]
22	0	100	0	1000	0	5.99[k]
23	1000	0	0	1000	0	7.02[ij]
24	0	0	0	1000	0	5.88[k]
25	1000	100	1500	0	0	6.96[ij]
26	0	100	1500	0	0	6.19[k]
27	1000	0	1500	0	0	7.04[hij]
28	0	0	1500	0	0	6.04[k]
29	1000	100	0	0	0	5.80[k]
30	0	100	0	0	0	4.91[l]
31	1000	0	0	0	0	5.90[k]
32	0	0	0	0	0	4.77[l]

[a–h] Means with different superscripts are significantly different ($p < 0.05$).

the main components of antioxidant composites in this subsequent study. Peanut oil stability was significantly improved ($p < 0.05$) for any composites of at least two antioxidants containing catechin as compared to those without catechin, as shown in Table 4. The results indicate that catechin has substantial effects on peanut oil stability. The OSI value of peanut oil with CAT combined with any of the following antioxidants, e.g. ROS, PL or TOC, was significantly ($p < 0.05$) improved as compared to that of oil with CAT only. Due to the defects of low oil solubility and strong flavour of PL (>1500 ppm) and ROS (>1000 ppm) at higher concentration, these antioxidants could not be used together in the composites.

Table 3
Analysis of variance on effects of several antioxidants on the response (OSI)

Antioxidant	F Value
TOC	5.53[a]
AP	0.14
PL	24.59[a]
ROS	22.29[a]
CAT	3329.66[a]

[a] Significant at 5% level.

Table 4
OSI values of several antioxidant composites

Composites	OSI value (h)
TOC-PL-ROS-CAT	16.89[a]
PL-ROS-CAT	16.39[abc]
TOC-ROS-CAT	16.69[ab]
TOC-PL-CAT	16.89[a]
TOC-PL-ROS	8.15[f]
ROS-CAT	16.00[bcd]
PL-CAT	15.75[cd]
TOC-CAT	15.89[cd]
PL-ROS	7.41[g]
TOC-ROS	7.02[g]
TOC-PL	7.04[g]
CAT	13.50[e]
ROS	5.88[h]
PL	6.04[h]
TOC	5.90[h]
CONTROL	4.77[i]

[a–i] Means with different superscripts are significantly different ($p < 0.05$).

Table 5
Coded levels and actual levels of three variables

Test run	Variable (ppm)	Coded level of variable				
		−1.682	−1	0	1	1.682
A/B	TOC	159	500	1000	1500	1841
	PL/ROS	659	1000	1500	2000	2341
	CAT	318	1000	2000	3000	3682

The composites of TOC–ROS–CAT or TOC–PL–CAT were significantly ($p<0.05$) different from CAT with either ROS, PL, or TOC in affecting the OSI value of oils. Hence the coded and actual levels of three variables in Table 5 were selected to optimize the response (OSI value) and to determine the interaction of CAT with the other two antioxidant species. The SAS RSREG (Statistical Analysis System-RSREG, 1985) procedure was used to fit a second order polynomial equation to the results (Table 6). The fitted equations are given by:

$$\begin{aligned}\text{A.OSI(h)} = {} & 18.19 - 0.36X_1 + 0.41X_2 + 5.37X_3 \\ & + 0.09X_1^2 - 0.20X_1X_2 + 0.18X_2^2 \\ & + 0.25X_1X_3 - 0.09X_2X_3 - 0.51X_3^2 \\ r = {} & 0.9950\end{aligned}$$

where X_1 is TOC; X_2 is PL; X_3 is CAT.

$$\begin{aligned}\text{B.OSI(h)} = {} & 18.84 + 0.09X_1 + 0.51X_2 + 5.05X_3 + 0.25X_1^2 \\ & - 0.22X_1X_2 + 0.37X_2^2 - 0.25X_1X_3 \\ & + 0.19X_2X_3 - 0.55X_3^2 \\ r = {} & 0.9973\end{aligned}$$

where X_1 is TOC; X_2 is ROS; X_3 is CAT.

Table 6
Coded level combinations for a three-variable central composite orthogonal and rotatable design (CCD)

Coded level of variable			Response (OSI (h))	
TOC	PL/ROS	CAT	A (PL)	B (ROS)
0	0	0	17.48	18.33
0	0	0	18.68	19.10
0	0	0	18.20	19.05
−1.682	0	0	20.23	19.53
1.682	0	0	17.83	19.73
0	−1.682	0	18.80	19.25
0	1.682	0	19.75	20.68
0	0	−1.682	7.98	9.53
0	0	1.682	26.65	25.23
−1	−1	−1	12.28	12.58
1	−1	−1	11.13	13.70
−1	1	−1	13.05	13.75
1	1	−1	12.75	14.08
−1	−1	1	21.60	23.30
1	−1	1	23.13	23.50
−1	1	1	23.68	25.30
1	1	1	22.73	24.53

The combination of three variables for each equation showed a more linear (F ratio = 425.5, $p<0.0001$) than quadratic (F ratio = 9.581, $p<0.01$) influence on the OSI value. From the coefficients of each equation, the most significant impact on the increase of OSI value was CAT ($p<0.0001$), followed by ROS ($p<0.01$), PL ($p<0.05$), and the most insignificant variable was TOC ($p>0.5$). Thus, in the study of peanut oil stability, TOC was excluded in the composites of CAT plus PL or ROS. Therefore, by neglecting the TOC factor, the interactions between CAT and PL, and between CAT and ROS, respectively, were determined, and were shown by the following equations:

$$\begin{aligned}\text{A.OSI(h)} = {} & 18.31 + 0.41X_1 + 5.37X_2 + 0.15X_1^2 \\ & - 0.09X_1X_2 - 0.54X_2^2 \\ r = {} & 0.9880\end{aligned}$$

where X_1 is PL; X_2 is CAT.

$$\begin{aligned}\text{B.OSI(h)} = {} & 19.15 + 0.51X_1 + 5.05X_2 + 0.29X_1^2 \\ & + 0.19X_1X_2 - 0.62X_2^2 \\ r = {} & 0.9950\end{aligned}$$

where X_1 is ROS; X_2 is CAT.

The contour maps shown in Fig. 1(A) and (B) were plotted by the equations as shown above. From these plots, obviously, CAT was more significant ($p<0.0001$) than either ROS ($p<0.01$) or PL ($p<0.5$) in the increase of OSI value of peanut oil. The OSI value of peanut oil was at least 15 h if the CAT amounted to 1500 ppm in combination with either PL or ROS. By comparing ROS and PL in combination with CAT, ROS was more effective ($p<0.01$) than PL ($p<0.5$) in the increase of OSI value of peanut oil. The OSI values of peanut oil would be 17.0 h for 1500 ppm of CAT plus 400 ppm of ROS, and 15.2 h for 1500 ppm of CAT plus 400 ppm of PL, respectively. These two plots showed that increasing the amount of PL or ROS more than 400 ppm would not significantly increase the OSI value of peanut oil. CAT in this study was found to play a key role in the increase of peanut oil stability.

Peanut oil is always blended with soybean oil in Taiwan. Due to the low stability of peanut oil, some antioxidants are required. TOC, ROS, PL and CAT were found individually to have antioxidative effects on peanut oil stability. Among these antioxidants, CAT was the most powerful additive for increasing peanut oil stability. TOC ($p>0.5$) showed the most insignificant effect on oil stability when combined with CAT. The antioxidant composites of CAT plus PL or ROS significantly increased peanut oil stability as compared to CAT only. However, in order to obtain the most stable

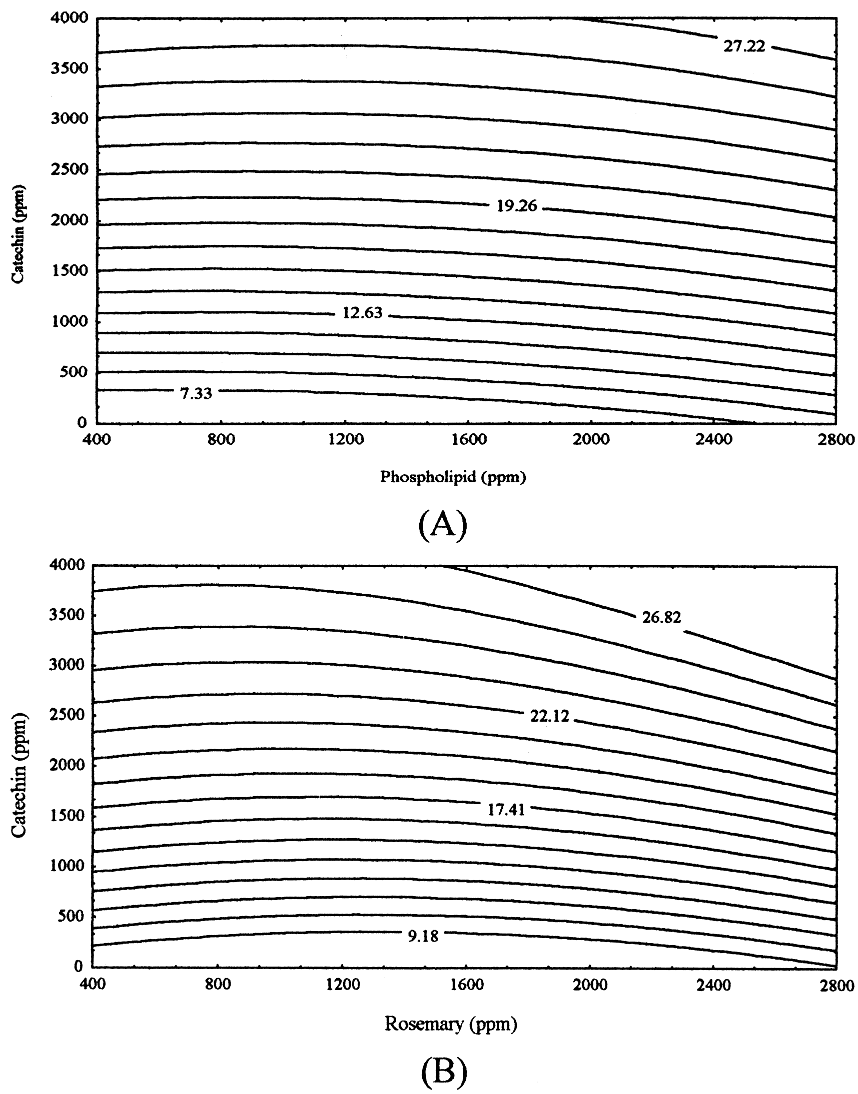

Fig. 1. (A) Response surface plot of OSI value (h) with respect to the amount (ppm) of PL and CAT. (B) Response surface plot of OSI value (h) with respect to the amount (ppm) of ROS and CAT.

peanut oil, the choice and the levels of antioxidants used in the oil should not affect the oil performance and flavour quality.

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