EFFECT OF TOMATO PEEL PIGMENTS AND SOME NATURAL ANTIOXIDANTS ON OXIDATIVE STABILITY OF SUNFLOWER OIL.

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(Manuscript received 13 March 2004)

Abstract

Tomato peel pigments (more than 90% lycopene) areexcellent antioxidant which can protect the human health from therisk of dangerous diseases. Different concentrations of lycopene pigments extracted by sunflower oil were used to improve thestability of this oil. Moreover a-tocopherol as well as β-carotene were used as natural antioxidants. Also, BHT as one of the mostimportant synthetic antioxidant was used in different concentrations for comparison. The color of oil previously treated with lycopene and B-carotene gave a high degree of red units, which increased gradually by increasing the concentrations of lycopene and Bcarotene from 20 to 80 ppm, while oil treated with a- tocopherol and / or BHT showed no change. In addition, there was no change in the yellow units occurred in all examined samples. Regarding the natural antioxidants, the lycopene exhibit the best result (even with the lowest concentration, 20ppm). The used average incubation period with this treatment was 10 h at 100°C .This incubation period regarded as 10.19 month at room temperature. The highest mean of induction period was 12.00h at 100°C (it means about 12.23 month at room temperature) was scored by using 200 ppm of BHT. As for mixing of natural antioxidants, the best treatment was mixing 20 ppm of each of lycopene and β -carotene. The induction period was 10.30 h at 100°C (it means about 10.50 month at room temperature). An obvious gradual decrease in lycopene was observed in tomato peels exposed to atmospheric condition for 5 weeks, compared to treatment of bottled oil which showed slight decrease.

INTRODUCTION

Tomato represent 600 to 1200 million pound generated from processing of tomato fruits (Osman et al 1999). Lycopene is a carotenoid responsible for the red color of tomatoes. More than 90% of firm red tomato surface color is lycopene (Fraser *et al* 1994). Lycopene as an a cyclic unsaturated carotenoid, whose major source from tomatoes and tomato products, is high demand by different industries (e.g., Cosmetic, Pharmaceutical, food and feed industries) owing to its bioactivity being associated with several healthy benefits. In the last few years, cancer prevention

activity of lycopene has been demonstrated and previous work by several authors has established that the antioxidant properties of lycopene inhibit the oxidation of LDL, consequently, lower the risk for atherosclerosis (Shi and Maguer 2000). Most of carotenoids from tomatoes have been found in different tissues of human and animal bodies. Single oxygen was quenched by lycopene at a rate of almost twice that of B-carotene (Devasagayam *et al.* 1992).

In addition to their coloring property, lycopene and (3-carotene have an antioxidant activity which protect lipids from free radical autoxidation by reacting with peroxyl radicals, thereby inhibiting propagation and promoting termination of the oxidation chain reaction (Britton, 1995). Carotenoids may also inhibit photoxidation in vegetable oils by filtering light, there by reducing sensitizer excitation and subsequent transfer of average to form single oxygen (Fakourdis *et al.*, 1987).

Lindenschmidt *et al.* (1987)mentioned that, tumor promotion by BHT in rodents is achieved by repeated weekly administration for the agent after carcinogen exposure.

The aim of this investigation is to fulfill the following items

1. Extracting tomato peel pigments (lycopene) by sunflower oil

- (simple technique) and to study its effect on the stability of this oil compared to β -carotene, a-tocopherol and BHT.
- 2. Supporting sunflower oils with lycopene to protect human health form the risk of dangerous cancer and cardiac diseases.
- 3. Using environmental technology for one of the most important wastes remaining from food processing.

MATERIALS AND METHODS

Materials

- 1. Tomato peels (peto 86 variety) was used as a source of lycopene.
- 2. Refined sunflower oils (free from synthetic antioxidants) produced by Tanta oil and Soap Co. was obtained form the local market.
- 3. Butylated hydroxyl toluene (BHT), β -carotene and α -tocopherol (vitamin E) were obtained from Sigma Chemical Co. USA.

Methods

A-Technological methods

1-Ten kg of tomato peels were boiled in water, (to get rid of sugars and inhibit the oxidative enzymes) strained thorough cheese cloth, dried at 55 c, grinded then

packed in polyethylene bags and kept in refrigerator at 5°c until using. Tomato peel pigments were extracted by sunflower oils. Lycopene (the major pigment in tomato peel) was determined in the oil and its concentration was diluted to 20, 40, 60 and 80 ppm. by the same oil.

2-a-Tocopherol , $\beta\text{-}carotene$ and BHT were dissolved in the same sunflower oil at concentrations of 20, 40, 60 and 80 ppm, while BHT, have additional dilution of 200 ppm .

3-A mixture of 20 ppm of each of(β -carotene + a-tocopherol), (lycopene + a-tocopherol) and (lycopene + β -carotene) with sunflower oils were prepared.

4-Dried tomato peels ,containing 138.87mg /100g lycopene.,exposed to air under atmospheric conditions while sunflower oil containing 20mg/100ml lycopene kept in closed bottles under the same conditions. Lycopene degradation in both samples was determined at intervals of 1, 2, 3, 4 and 5 weeks.

All samples in duplicate were kept in dark bottles for analysis.

B-Analytical methods

- 1 -Lycopene content in tomato peels and oil was determined according to Ranganna (1979).
- 2-Stability of different oil samples was determined using Rancimat Metrohm 679 as described by Hasenhuttle and Wan (1992) and the induction period (I.P.) was conducted with Rancimat at 100°c and calculated at 25°c using the temperature coefficient of 2.2 for induction period (Hadorn and Zurcher , 1974) and 2.5 from expired period (Pardun and Kroll, 1972).
- 3-Color of the oil samples was determined using Lovibond model E, 51/4 cell according to the Egyptian standard specification for oils (1993).

RESULTS AND DISCUSSION

1- Effect of different concentrations of lycopene, β -carotene,

a-tocopherol and BHT on the color of sunflower oils.

Results in Table (1) show the color of sunflower oil treated with different concentrations of natural antioxidants as lycopene, β -carotene & α -tocopherol and compared to synthetic antioxidant BHT. Color results of treated oil with lycopene and β -carotene were characterized by having a high degree of red color units which increased gradually by increasing the concentration of lycopene and β -carotene

from 20 to 80 ppm oil. However, treatment with lycopene scored the highest value , while the color of the oil treated with a-tocopherol and BHT showed no change. No change in the yellow color units was also observed in all samples. These results could be related to the color of lycopene and β -carotene while a-tocopherol and BHT are colorless.

2- Effect of different concentrations of α-tocopherol, β-carotene lycopene and BHT on the stability of sunflower oil.

Different concentrations of natural antioxidants were added to sunflower oil and the induction periods were determined compared with that for the synthetic antioxidant BHT. The obtained results are shown in tables 2, 3.

Data in table (2) represent the effect of mixing different concentrations (20, 40, 60, and 80 ppm) of a-tocopherol on the stability of sunflower oil. The control sample gave the mean average of induction period 7.05h (the means in months 7.18). the average of induction period increased gradually to 7.54 h (7.69 months) and 8.60h (8.77 months) by increasing the concentration for a-tocopherol from 20 to 40 ppm. On the other hand, increasing the concentration to 60 and 80 ppm the average of induction period dropped to 8.20 h (8.36 months) and further to 7.84 h(7.99 months) respectively. This would be related to the adhering effect of the the a-tocopherol content in the oil. Hence increasing the a-tocopherol content by adding 60 and 80 ppm to the oil may act as pro-oxidant as mentioned by Ismael, (1989). They reported that the addition of more a-tocopherol will provide no further increase in stability, if added at higher concentration may even have a depressing effect on the oxidative stability of oil.

Table 1. Effect of different concentrations of natural antioxidantsand BHT on the color units of sunflower oil.

Concentration	внт		Lycopene		a-Tocopherol		β-Carotene	
(ppm)	Yellow	Red	Yellow	Red	Yellow	Red	Yellow	Red
20	35	2.	35	14	35	2	35	8
40	35	2	35	16	35	2	35	10
60	35	2	35	18	35	2	35	12
80	35	2	35	20	35	2	35	14
200	35	2	-		-	-	-	

*Control sunflower oil yellow 35 and red 2 units .

Antioxidants	Oxidation stability				
concentration	I.P. at 100°C	d at ambient tempe	t temperature at 25°C.		
(ppm)	Mean (hours)	Induction (months)	Expired (months)	Mean (months)	
Control	7.05 ±0.5	3.9	10.46	7.18 ±4.64	
a-Tocopherol(20)	7.54 ±0.36	4.18	11.19	7.69 ±4.96	
β-carotene(20)	7.41 ±0.157	4.11	10.99	7.55 ±4.86	
a-Tocopherol(40)	8.6 ±0.915	4.77	12.76	8.77 ±6.45	
β-carotene(40)	7.66 ±0.513	4.25	11.36	7.81 5	
a-Tocopherol(60)	8.2 ±0.2	4.55	12.16	8.36 ±5.38	
β-carotene(60)	8.05 ±0.176	4.46	11.94	8.2 ±5.01	
a-Tocopherol(80)	7.84 ±0.014	4.35	11.63	7.99 ±5.15	
β-carotene(80)	7.75 ±0.234	4.3	11.49	7.9 ±4.88	

Table 2. Effect of different concentrations of a-tocopherol and β -carotene on the stability sunflower oil.

I.P.: Induction period.

Data in Table (2) reveal that the stability of sunflower oil increased with increasing the concentration of β -carotene. It reached to 7.41 h (7.55 months), 7.66 h (7.81 months) and 8.05h (8.20 month) at 20, 40 and 60 ppm, respectively, while it reached to 7.75 h (7.90 months) at 80 ppm. These results agree with those obtained by Xu Sa *et al* (1999). They noticed that carotenoids remarkably protect lipids against photoxidation.

The effect of different concentrations of lycopene (20, 40, 60 and 80 ppm) extracted from tomato peels on the stability of sunflower oil was studied. Lycopene as a major component represents more than 90% of tomato peel pigments showed the best effect on the stability of sunflower oil. Results given in table (3) showed that means of induction periods were 10.00 h (10.19 months) and 10.10 h (10.29 months) at 20 and 40 ppm respectively, while they scored 9.58 (9.76 months) and

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9.57h (9.75 months) at 60 and 80 ppm, respectively. These data are in accordance with those obtained by Xu Sa *et al* (1999).

Data in table (3) indicate the effect of the synthetic antioxidant BHT on the stability of sunflower oil. The highest mean of induction period was 12.00h (12.23 months) and observed at 200 ppm of BHT. However it is limited to use BHT more than 200 ppm as recommended by Eastman Chemical Company ,1993). Other concentrations revealed that the mean of induction period was 9.25h (9.42 months) at a concentration of 20 ppm. Slight increase was observed by increasing the concentration from 40, 60 to 80 ppm. The corresponding values were 9.40 h (9.58 months), 9.48 h (9.66 months) and 10.07 h (10.20 months).

It could be concluded from the aforementioned results that on comparing the natural antioxidants, lycopene was the best antioxidants for sunflower oil even at the lowest concentration 20 ppm.

3- Effect of mixing 20 ppm of each of (β -carotene +a-tocopherol) and (lycopene + a ·tocopherol) and (lycopene + β -carotene) on the stability of sunflower oil.

It could be observed from Table (3) that on applying the aforementioned mixes; the induction periods were 8.18 h (7.94 months), 9.08h (9.25 months) and 10.30 h (10.50 months) respectively. The best treatment was noticed in case of mixing 20 ppm of each of lycopene and B-carotene to sunflower oils. It may be related to the effect of lycopene , which showed the best natural antioxidant at 20 ppm as mentioned before

4 Stability of lycopene in dried tomato peels exposed to air and in closed bottles sunflower oil at ambient temperature .

Table (4) and figure (1) reveal the degradation of lycopene in tomato peels exposed to air and that soluble in sunflower oil kept in closed bottles at ambient temperature. An obvious gradual decrease in lycopene content was observed in tomato peels. It decreased from 138.87 to 12.32 mg/l00g after 5 weeks , while a slightly decreased was scored in sunflower oil .It decreased from 20 to 18.18 mg/l00ml oil .The degradation percentages were 91.12 and 9.10 after 5 weeks, respectively. These highly variation between two treatments may be related to the effect of exposure to air in the first treatment which may decompose the lycopene in tomato peels while oil kept in closed bottle protect lycopene oxidation in the second treatment.

It could be concluded that sunflower oil samples containing lycopene or BHT gave the best results . Lycopene was the best natural antioxidant at a concentration of 20ppm . Generally, it could be recommended that, supporting the sunflower oil with lycopene would improving the stability of sunflower oil as will as protect the human health from the risk of some dangerous diseases . Also, it would reduce the Environmental pollution caused by tomato processing wastes.

Table 3. Effect of different concentrations of lycopene extracted from tomato peels B H T and mixing from antioxidants on the stability surflower oil

Antioxidants	nd mixing from antioxidants on the stability sufflower oil. Oxidation stability					
concentration	I.P. t 100°C Calculated at ambient temperature at 25°C.					
(ppm)	Mean	Induction	Expired	Mean		
(ppm)	(hours)	(months)	(months)	(months)		
Control	7.05	3.9	10.46	7.18		
Concron	±0.5			±4.64		
B.H.T.(20)	9.25	5.13	13.72	9.42		
	±0.241			±6.07		
Lycopene(20)	10.00	5.54	14.83	10.19		
	±0.2		4	±6.57		
B.H.T.(40)	9.4	5.21	13.94	9.58		
	±0.608			±6.17		
Lycopene(40)	10.1	5.6	14.98	10.29		
	±0.361			±6.63		
B.H.T.(60)	9.48	5.25	14.06	9.66		
	±0.541			±6.23		
Lycopene(60)	9.58	5.31	14.21	9.76		
	<u>±0.189</u>			±6.29		
B.H.T.(80)	10.07	5.58	14.94	10.2		
1	±0.456			±6.62		
Lycopene(80)	9.57	5.3	14.2	9.75		
	±0.208			±6.29		
B.H.T.(200)	12.00	6.65	17.8	12.23		
	±0.5	<u> </u>		±7.88		
β-carotene(20)+	8.18	4.32	11.56	7.94		
a-tocopherol(20)	<u>±0.352</u>			±5.12		
Lycopene(20)+	9.08	5.03	13.47	9.25		
a-tocopherol(20)	±0.157			±5.97		
Lycopene(20)+	10.3	5.71	15.28	10.5		
β-carotene(20)	±0.21		L	±6.77		

I.P.: Induction period.

Table 4. Stability of lycopene in dried tomato peels exposed to air and in closed bottle sunflower oil at ambient temperature .

Period time per weeks	Tomato lycopene peels mg/100gm	Degradation of lycopene %	Lycopene in sunflower o mg/100ml	Degradation of lycopene %
0	138.87	-	20.00	_
1 1	83.61	39.79	19.39	3.05
2	33.54	75.85	19.25	3.70
3	24.7	82.21	18.92	5.40
4	16.09	88.41	18.58	7.10
5	12.32	91.12	18.18	9.10



Figure 1. Stability of lycopene in dried tomato peels exposed to air and in closed bottle sunflower oil at ambient temperature

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تأثير صبغات قشور الطماطم وبعض مضادات الاكسده الطبيعية على الثبات الأكسيدي لزيت عباد الشمس

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تحــتوى صبغات قشور الطماطم على أكثر من ٩٠% ليكوبين وهو مضاد ممتاز للأكسده يحمى صحة الإنسان من مخاطر أمراض خطيرة مثل السرطان والقلب. تم إستخلاص تلك الصبغات بواسطة زيت عباد الشمس وتم عمل تركيزات مختلفة من الليكوبين في الزيت وإستخدم لتحسين الثبات له.

وتم إستخدام بعض مضادات الأكسدة الطبيعة الأخرى مثل ألفا-توكوفيرول (فيتامين هـ) وبيتا-كاروتيـن فـي هذا البحث. وكذلك تم إستخدام واحد من أهم مضادات الأكسدة الصناعية وهو BHT بتركـيز ات مختلفة للمقارنة. وقد أعطى لون الزيت المعامل بالليكوبين والبيتا كاروتين زيادة تدريجيه في وحدات اللون الأحمر مع زيادة التركيز من ٢٠ إلى ٨٠ جزء في المليون بينما لم يحدث تغير في اللون بالنسبه للزيت المعامل بالألفا توكوفيرول وكذلك لم يحدث نغير في اللون الأصفر فـي جميع العينات. بمقارنة مضادات الأكسدة الطبيعية وجد أن الليكوبين قد أعطى أفضل نتيجه حتى في التركيز المنخفض ٢٠ جزء من المليون. حيث كان متوسط فترة التحضين ١٠ ساعات على ١٠٠ م (يعسادل ١٩.١ شــهر على درجه حرارة الغرفه) وقد أعطى Tr شهر على درجة حرارة الغرفي أعلى متوسط فترة تحضين ١٢ ساعه على ١٠٠ م الغرفي أعلى متوسط فترة تحضين ١٠ ساعات على ١٠٠ م الغرفي أعلى متوسط فترة تحضين ١٠ ساعت على ٢٠٠ م الغرفه). وبالنسبة لمعاملات خلط مضادات الأكسدة الطبيعيه فقد وجد أن الموتين ١٠ ساعات على ١٠٠ سالميون أعلى متوسط فترة تحضين ١٠ ساعه على ١٠٠ م الغرفه). وبالنسبة لمعاملات خلط مضادات الأكسدة الطبيعيه فقد وجد أن الميون ١٠ ساعات على ١٠٠ سالميون أعلى متوسط فترة تحضين ١٠ ساعه على ١٠٠ م الغرفه). وبالنسبة لمعاملات خلط مضادات الأكسدة الطبيعيه فقد وجد أن أحسن معامله كانت عند خلط م م الغرفه). وبالنسبة معاملات خلط مضادات الأكسدة الطبيعيه فقد وجد أن أحسن معامله كانت عند خلط ساعة على ١٠٠ م (يعادل ١٠، شهر على درجة حرارة الغرفه) و م الغرفي النسبة معاملات خلط محادات الأكسدة الطبيعية فقد وجد أن أحسن معامله كانت عند خلط ساعة على ١٠٠ م (يعادل ١٠، شهر على درجة حرارة الغرفه) .

أمــا بالنســبة لتأثير ثبات الليكوبين الذائب في الزيت وكذلك الموجود طبيعيا في قشور الطماطم نتــيجه لتعرضـــه للظــروف الهوائــيه وجد أن الليكوبين الذائب في الزيت أعطى معدل هدم أقل من الموجود في قشور الطماطم.