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Antioxidant activity of rosemary (*Rosmarinus officinalis* L.) extracts on natural olive and sesame oils

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RESUMEN

Actividad antioxidante de extractos de romero *(Rosmarinus officinalis L.)* en aceites de sésamo y de oliva.

Se determinaron las actividades antioxidantes de extractos de cloroformo y de metanol de romero (*Rosmarinus officinalis* L.) en aceites de sésamo y de oliva almacenados a 55 °C mediante medidas de los índices de peróxidos a intervalos regulares. Se utilizaron concentraciones al 1% y 2% de extractos y ácido cítrico. Los extractos (excepto para los días 12, 16 y 20 de almacenamiento de aceite de oliva) mostraron una alta actividad antioxidante comparados con la muestra control en ambos aceites. Los efectos antioxidantes de ambos extractos y los niveles de ácido cítrico en el aceite de oliva tuvieron diferencias significativas después de 4 días de almacenamiento ($p < 0.01$). La concentración más efectiva en aceite de sésamo durante el almacenamiento fue del 2% en extracto de cloroformo. Además, especialmente concentraciones del 2% de ambos extractos de disolventes de romero mostraron una actividad antioxidante significativa en comparación con el ácido cítrico en aceite de sésamo.

PALABRAS-CLAVE: Aceite de oliva - Aceite de sésamo - Efecto antioxidante - Estabilidad - Romero.

SUMMARY

Antioxidant activity of rosemary (*Rosmarinus officinalis* L.) extracts on natural olive and sesame oils.

The antioxidant activities of chloroform and methanol extracts of rosemary (*Rosmarinus officinalis* L.) were tested in natural olive and sesame oils stored at 55 °C, by measuring peroxide values after regular intervals. The concentrations of extracts and citric acid had been used as 1% and 2%. The extracts (except for 12,16 and 20 days in storage of olive oil) exhibited high antioxidant activity compared with control sample in olive and sesame oil. Antioxidant effects of both extracts and citric acid levels in olive oil showed statistically different after from 4 days of storage ($p < 0.01$). The most effective concentration on sesame oil during storage had 2% chloroform extract. Furthermore, especially 2% concentrations of both solvent extracts of rosemary shown significantly antioxidative activity in compared with citric acid on sesame oil.

KEY-WORDS: Antioxidant effect - Olive oil - Rosemary - Sesame oil - Stability.

1. INTRODUCTION

Synthetic antioxidants are widely used to retard undesirable changes as a result of oxidation in many foods. Excessively oxidized fats and oils are not suitable for nutritive purposes. Because, the oxidation products of oils have toxic effects. Many synthetic substances such as butylated hydroxyanisol (BHA), propyl gallate and citric acid are commonly used in lipids to prevent oxidation. Recently, these synthetic substances have been shown to cause such as enlarge the liver size and increase microsomal enzyme activity. Therefore, there is need for other compounds to effect as antioxidants and to render food products safer for mankind (Farag *et al.,*1989, Farag *et al.,*1990, Brookman, 1991).

Plant originated antioxidants have been used in oils or lipid containing foods in order to prevent oxidative deterioration (Gur and Gulden, 1997). The antioxidant activity displayed by spices or other antioxidants depends on several factors such as the concentration, the temperature, the hydrophobic, hydrophylic or amphiphatic character, the presence of synergists and the chemical nature of the food or medium to which they are added (Logouri and Boskou, 1995). Chang *et al.* (1977) obtained similar results while investigating the antioxidative effect of rosemary and sage due to the peroxide value. Essential oils such as rosemary and sage oils lack any antioxidant activity although the herbs are known antioxidants and find many applications in food preparations (Chipault *et al.*, 1952; Chipault *et al.*, 1956; Bishou *et al.*, 1977; Hermann *et al.*, 1981; Barbut *et al.*, 1985; Pizzocaro *et al.*, 1985; Inatani *et al.*, 1984; Houlihan *et al.*, 1984; Özcan and Akgül, 1995). Naturally occurring compounds in rosemary extracts (Wu *et al.*, 1982; Ho *et al.*, 1983) have been reported to exhibit antioxidant properties greater than BHA and equal BHT.

The extracts rosemary (Chang *et al.*, 1977; Economou *et al.*, 1991; Banlas *et al.*, 1992), were examined in order to determine their antioxidative activity against autoxidation in different substrates, mostly in lard. Their antioxidative activity depends on the solvent used, but the structure activity relationship of them have not been completely investigated (Chang *et al.*, 1977; Economou *et al.*, 1991; Banlas *et al.*, 1992).

Antioxidant effects of 35 methanol extracts and 20 essential oils from Turkish spices were tested in sunflower oil stored at 70 °C (Özcan and Akgül, 1995).

Thus, the objective of this study was to evaluate to efficacy of adding a natural rosemary oleoresin to sesame and olive oils and to compare it with a commercial citric acid used as an antioxidant.

2. MATERIALS AND METHODS

Plant Material and Preparation of Extracts: Rosemary was purchased from market. Ground material was extracted with pure methanol and chloroform for 3 hr in a stirred vessel, at a liquid-to-solid ratio 4:1 and a temperature of 60 °C. The mixture was filtered and concentrated in rotary evaporator and solvent was completely removed. Extracts were kept in sealed bottles under refrigerated using.

Olive and Sesame Oils: Naturel olive and sesame oils without adding any antioxidant were kindly supplied by Kristal and Salur company in Yzmir and Konya, respectively. Their peroxide numbers were 15 and 18.1 meq/kg, the same respectively. The sesame oil was selected for their high degree unsaturation levels and for being the most widely used as edible and tehina (sesame paste) oil in Turkey.

Citric Acid: Citric acid (E.Merck, Darmstadt) was preferred because of using commonly as prevent to the deterioration at oil company.

Antioxidant Activity Measurement: The rate of oxidation was followed by periodic determination of peroxide values of the oil stored at 55 °C by using chloroform and methanol as extraction solvents which are at different polarities. A calculated quantity of the extract and citric acid was added at the 1 and 2% concetrations into olive and sesame oil, and the mixture was stirred. A control sample was prepared under the same conditions without adding any antioxidant. All samples of 20 g each were storaged in 10 x 100 mm open beakers at 55 °C in the dark. For the peroxide number, a known weight of olive and sesame oils (2 g) was dissolved in a mixture of CH_3COOH: $CHCl_3$ (3:2, v/v), and saturated solution of KI (1ml) was then added. The liberated iodine was titrated with sodium thiosulfate solution (0.01N) in the presence of starch as an indicator (A.O.C.S., 1989). The codes of the samples are shown in Table I. It should be mentioned that in experiments, with the plant extracts at various concentrations, raw olive and sesame oils were used.

Statistical Analyses: Findings of the research were analysed for statistical significance by analyses of variance, and differences among groups were established according to Düzgünes *et al.* (1987). Experiments and analysis were replicated and duplicated.

Table I
The codes of the extract and citric acid added samples

Olive oil samples	Control				A_0
	Containing 1% (w/w) chloroform extract of rosemary				A_1
	"	2	"	"	A_2
	"	1	Methanol	"	A_3
	"	2	"	"	A_4
	"	1	citric acid		A_5
	"	2	"		A_6
Sesame oil samples	Control				B_0
	Containing 1% (w/w) chloroform extract of rosemary				B_1
	"	2	"	"	B_2
	"	1	Methanol	"	B_3
	"	2	"	"	B_4
	"	1	citric acid		B_5
	"	2	"		B_6

3. RESULTS AND DISCUSSION

Table II represents the antioxidant effect of the chloroform and methanol extracts of rosemary, and citric acid in olive and sesame oils as determined by the peroxide value.

After 4 days, the extract concentrations showed antioxidant effect in varying degrees on olive and sesame oil compaered with the control test ($p < 0.01$). Peroxide values of all the samples partly increased during storage. After 12 days, peroxide values of sesame oil at all the concentrations had higher than those of olive oil. At both extract concentrations of chloroform and methanol peroxide values were high according to control on 16 and 20 days. But, antioxidant effects of both solvent extract concentrations (1%) in olive oil are higher than that of the same citric acid concentration as from 4,8 and 12 days. But, the same concentrations (1%) of extracts in sesame oil showed antioxidant effect according to citric acid (1%) concentration.

The 2% concentration of chloroform and methanol in sesame oil had more effect than those of only 2% concentration of chloroform and methanol extracts and both concentrations of citric acid ($p < 0.01$). The most effective concentration on sesame oil during storage had 2% chloroform (Fig.1). Furthermore, especially 2% levels of both solvent extracts of rosemary exhibited remarkable antioxidative activity in comparison with citric acid on sesame oil ($p < 0.01$).

Overall strongest activity of rosemary was not surprising, because of various findings reported on its stabilizing effect (Chang *et al.*, 1977; Bracco *et al.*, 1981), and related active components such as carnosol, rosmanol, rosmariquinone, carnosic and ursolic acids etc. (Wu *et al.*, 1982; Inatani *et al.*, 1983; Houlihan *et al.*, 1985; Chen *et al.*, 1992).

Table II

Antioxidant effect of rosemary extract added to olive and sesame oils* stored in the dark at 55 °C (meq/kg)

Days	Oils	Control	Chloroform Extract (%)		Methanol Extract (%)		Citric Acid (%)	
			1	2	1	2	1	2
4	Olive	25.00 ± 0.62K**	23.70 ± 0.63J	19.30 ± 0.64H	24.30 ± 0.29H	24.50 ± 0.32I	19.50 ± 1.10J	19.40 ± 0.92I
	Sesame	51.70 ± 0.32F	49.70 ± 0.87F	23.00 ± 1.15G	21.20 ± 0.18I	26.80 ± 0.39H	49.00 ± 0.29E	37.60 ± 0.67E
8	Olive	28.20 ± 0.52J	30.20 ± 0.76I	20.70 ± 1.41H	25.60 ± 0.55G	30.50 ± 1.77G	25.05 ± 0.73I	29.80 ± 0.65H
	Sesame	72.10 ± 0.65E	56.70 ± 0.59E	24.30 ± 0.59G	24.90 ± 1.45GH	38.30 ± 0.97E	56.00 ± 0.18D	53.90 ± 0.91D
12	Olive	31.70 ± 0.70I	34.10 ± 0.54H	32.40 ± 0.42F	33.50 ± 0.66F	31.30 ± 0.84G	27.10 ± 0.42H	31.00 ± 1.13GH
	Sesame	98.00 ± 0.39D	65.80 ± 0.29D	34.50 ± 1.20E	44.20 ± 0.39D	45.60 ± 0.59D	57.80 ± 0.55CD	77.80 ± 0.10C
16	Olive	32.80 ± 0.68HI	34.50 ± 0.63H	34.30 ± 0.39E	33.90 ± 0.57F	31.40 ± 0.80G	36.20 ± 1.50G	32.50 ± 1.14G
	Sesame	104.90 ± 0.65C	68.80 ± 0.76C	48.50 ± 0.84C	49.00 ± 0.38C	49.50 ± 0.65C	58.70 ± 0.79C	79.20 ± 0.70BC
20	Olive	33.50 ± 0.74H	35.60 ± 0.78H	35.00 ± 0.32E	34.30 ± 0.41F	34.90 ± 1.34F	37.00 ± 0.94G	35.60 ± 1.16F
	Sesame	106.60 ± 0.39B	76.80 ± 0.85B	51.90 ± 1.28B	52.90 ± 0.47B	54.80 ± 0.41B	61.10 ± 1.05B	79.70 ± 0.46B
24	Olive	48.90 ± 0.79G	39.50 ± 1.87G	38.80 ± 0.65D	37.90 ± 0.33E	38.00 ± 1.28E	40.80 ± 0.74F	36.22 ± 0.47EF
	Sesame	151.20 ± 0.99A	82.12 ± 1.42A	55.62 ± 0.39A	65.80 ± 0.82A	66.40 ± 0.42A	159.70 ± 2.26A	161.50 ± 0.71A

* Initial peroxide value of the olive and sesame oil were 15.0 and 18.1 meq/kg, respectively.
** Differences among means indicated with majuscules are significant in $p < 0.01$.

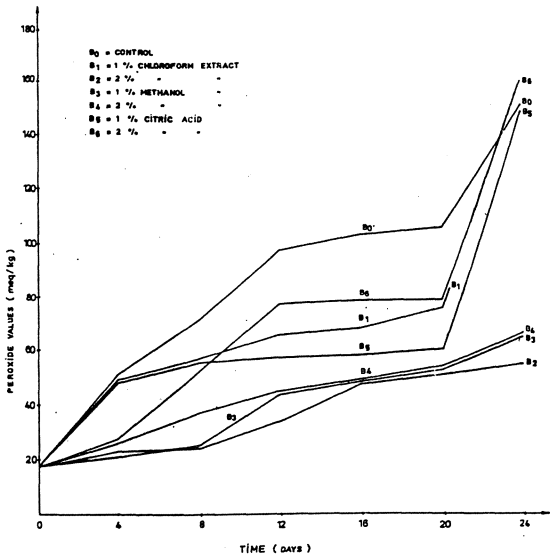

Figure 1
Changes in peroxide values in sesame oil that rosemary extract and citric acid

4. CONCLUSIONS

The results indicated that rosemary extract obtained by different polarities solvents an antioxidant activity on olive and sesame oils at 55 °C. Antioxidant effects of both extracts and citric acid levels in olive oil had found significantly different after from 4 days of storage. However, antioxidant effects of both extract concentrations of solvents were silightly weaker than that of control on 16 and 20 days of storage. Peroxide values of sesame oil, especially 12 days, had higher than those of olive oil as from 12 days of storage. The reason for this is probably that initial peroxide value of sesame oil was higher than that of other oil. However, it was seen that the antioxidant activity of the extract depends on the polarity of the solvents used for extraction.

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