ELSEVIER

PII: S0308-8146(97)00193-3

Food Chemistry, Vol. 62, No. 3, pp. 269–276, 1998

Printed in Great Britain
0308-8146/98 $19.00+0.00

The use of sesame oil unsaponifiable matter as a natural antioxidant

H. M. A. Mohamed[a]* & I. I. Awatif[b]

[a]*Department of Food Science, Faculty of Agriculture, Minia University, El-Minia, Egypt*
[b]*Oil and Fat Research Laboratory, Food Technology Research Institute, Agricultural Research Center, Giza, Egypt*

(Received 18 April 1997; revised versis reveived and accepted 1 August 1997)

Individual components of sesame oil unsaponifiable matter isolated from two different coloured seed varieties (white and brown) were identified and quantified. Unsaponifiables from the brown sesame variety were markedly different in their composition from those of the white variety. The brown variety contained higher amounts of total sterols and tocopherols but lower amounts of sesamin, sesamolin and total hydrocarbons than the white variety. The seeds were roasted at 180°C for 30 min. Roasting increased some effective antioxidant compounds. These included relatively higher percentages of sesamol, $\Delta^{24,28}$ ethylidene sterols (Δ^5 and Δ^7-avenasterols), squalene, as well as tocopherols and some active browning substances. These antioxidative components are effective via synergistic action. Additionally, unsaponifiable matter from unroasted (USM) and roasted white sesame seeds (RSM) was added individually to sunflower oil at levels of 0.02, 0.05 and 0.1% and their effectiveness was compared with a control (no additives) at 63°C. Results indicated that both USM and RSM had antioxidant activity which increased with increasing concentration. Compared to USM, the RSM was a better antioxidant in most cases. Moreover, the addition of 0.1% RSM gave a strong antioxidative efficiency and this could be used as an alternative natural antioxidant for food applications.

INTRODUCTION

The use of natural antioxidants in foods is recently receiving special attention because of the world-wide trend to avoid or minimize the use of synthetic food additives. Unsaponifiable lipid constituents of seed oils naturally contains hydrocarbons, terpene alcohols, sterols, tocopherols and other phenolic compounds which may act as oxidation inhibitors under a range of conditions (Bosku and Morton, 1976). The effectiveness of lipid unsaponifiable matters in retarding oil deterioration has been demonstrated by many investigators (Ushkalova, 1983; Abdel-Aziz, 1985; Rady and Awatif, 1991; Awatif *et al.*, 1996).

It has been known for many years that sesame oil is highly resistant to oxidative deterioration as compared to other edible oils (Budowski, 1962). Hallabo (1977) found that the addition of 0.1, 0.2 and 0.3% total unsaponifiable matter extracted from crude sesame seed oil increased the stability of both linoleic acid and cottonseed oil at 60°C and 100°C, respectively. However, the reasons for the superior antioxidative activity remained unclear. Much attention has been focused on the presence of a number of sesame lignans, mainly sesamin, sesamolin, sesamol, presented in sesame seeds in small amounts (Kikugawa *et al.*, 1983). In addition, Fukuda *et al.* (1986*a*) mentioned that the antioxidative activity of refined unroasted sesame seed oil is mainly attributed to a new lignan compound termed sesaminol, which was produced from sesamolin during the bleaching process with acid clay. More recently, Katsuzaki *et al.* (1994) isolated three novel sesaminol glucosides from sesame seeds. They found that these compounds had antioxidant properties.

The roasting process is an important step for making sesame oil since the colour, composition and quality of sesame oil are influenced by the conditions of roasting (Manley *et al.*, 1974). However, the oil extracted from roasted sesame seeds at 180–200°C was considered much more antioxidative than unroasted purified sesame oil (Fukuda *et al.*, 1986*b*). This strong antioxidant activity was attributed to the antioxidative lignan-type compound, sesamol, which is formed from sesamolin during the roasting process, and also the presence of γ-tocopherol (Yen and Shyu, 1987). Attempts have been made to demonstrate the stability of the

*To whom correspondence should be addressed.

roasted seed oil (Yen, 1990). The antioxidant factors responsible for the stability of roasted sesame oil seemed to be highly affected by the condition of the roasting process. The optimum roasting condition was established by Yoshida *et al.* (1995) to be 180°C for 30 min. Aoyama *et al.* (1994) examined the antioxidative activity of the water, methanol and ether extracts of roasted sesame seed on the stability of sardine oil. The results showed that the ether extract of roasted sesame seed was effective in minimizing rancidity.

The objectives of this study were to investigate: (a) the main antioxidant components in the unsaponifiable matter isolated from the oil of two different coloured sesame seed varieties (white and brown); (b) the effect of roasting at 180°C for 30 min on the individual components of these unsaponifiables; and (c) the ability of both roasted and unroasted sesame oil unsaponifiables to inhibit peroxidation.

MATERIALS AND METHODS

Materials

Two different coloured sesame seeds (*Sesamum indium* L.) varieties: white (Giza 32) and brown (Giza 24) were selected in this investigation. The seeds were cleaned and divided into two groups. The first group was kept unroasted, whereas the second was roasted at 180°C for 30 min.

Refined bleached and deodorized sunflower oil was donated from El-Nile for Oils and Detergents Company, El-Minia, Egypt.

All solvents were of analytical grade (Merck). The hydrocarbons, sterols, and tocopherol standards were purchased from Sigma Chemical Company (St. Louis, MO).

Oil extraction and saponification

Sesame oil was prepared from raw and roasted sesame seeds at 180°C for 30 min. The seeds were ground in a disintegrator. The ground seeds were extracted with n-hexane for 48 h, then filtered. This process was repeated three times using fresh solvent each time to extract most of the oils from the ground seeds. The miscella was collected, mixed and evaporated at 60°C under vacuum. Then the extracted oils were dried over anhydrous sodium sulphate. The unsaponifiable matter was extracted after saponification of oil at room temperature according to the method outlined by Mordret (1968).

Analytical methods

The oil contents was determined in triplicate by Soxhlet procedure in accordance with AOAC (1980). The colour values were determined by Lovibond tintometer according to the AOCS method Cc 13b-45 (1978). Total tocopherol was analysed according to the colorimetric method of Wong *et al.* (1988), in which tocopherols reduce ferric ions to ferrous, which reacts to form a coloured complex with dipyridyl. The sesamol content was determined spectrophotometrically according to the method of Budowski *et al.* (1950).

Gas liquid chromatography analysis of fatty acids

The fatty acid methyl esters were prepared using benzene: methanol: concentrated sulfuric acid (10:86:4) and methylation was carried out for 1 h at 80–90°C according to Stahl (1967). The compositions of fatty acids were achieved by gas liquid chromatography analysis using a PYE Unicam model PV 4550 capillary gas chromatograph fitted with flame ionization detector, the column (1.5 m×4 mm) packed with diatomite C (100–120 mesh) and coated with 10% polyethylene glycol adipate (PEGA). The column oven temperature was programmed at 8°C/min from 70°C to 190°C then isothermally at this temperature for 20 min and nitrogen flow rate was 30 ml/min. Detector, injection temperatures, hydrogen and air-flow rates and chart speed were 300°C, 250°C, 33 ml/min, 330 ml/min and 2 cm/min, respectively. The presented fatty acids were identified according to an authentic sample of fatty acids chromatographed under the same conditions. Methyl heptadecanoate was used as an internal standard.

Gas liquid chromatography analysis of unsaponifiable matters

The unsaponifiable constituents were analysed directly using the Unicam capillary gas chromatograph PV 4550 fitted with flame ionization detector on a coiled glass column (2.8 m×4 mm) packed with diatomite C (100–120 mesh) and coated with 1% OV-17 as stationary phase. The oven temperature was programmed at 10°C/min from 70 to 270°C, then isothermally at this temperature for 15 min and nitrogen flow rate was 30 ml/min. Detector, injection temperatures, hydrogen and air-flow rates and chart speed were 300°C, 250°C, 33 ml/min, 330 ml/min and 2 cm/min, respectively. The various fractions separated were identified according to an authentic sample of hydrocarbons and sterols chromatographed under the same conditions. Quantitative analysis were performed with squalane as the internal standard and adopting the corrected area normalization method.

Thin-layer chromatography separation of unsaponifiable matter

The unsaponifiable matter was separated on TLC plates (20×20 cm) precoated with silica gel (0.25 mm), previously activated by heating for 1 h at 130°C. Elution was performed using chloroform: benzene: methanol

(60:40:1 v/v/v) as the mobile phase. The plates were sprayed with 50% sulphuric acid and heated at 110°C for 5–10 min. The identification of the various compounds in the different oil unsaponifiable samples was achieved by comparison of their R_f values with reference standards as described by Kamal-Eldin *et al.* (1994). A densitometer was used to measure the area of the spots.

HPLC analysis of sesamin and sesamolin

Sesamin and sesamolin were analysed with a Perkin Elimer LC-290 HPLC. The oils were dissolved in hexane/chloroform (2:1 vol/vol) and 10 μl samples were used for injections. Reversed phase separations were performed with a C18 column packed with ODS. The chromatograph was operated with a mobile phase of 70% methanol in water at a flow rate 0.4 ml/min. The amount of each compound present was determined by the peak height at 300 nm with a UV detector. Peak identification was carried out by comparison of relative retention times with those reported by Kamal-Eldin *et al.* (1994).

Tests of antioxidant activity

The total unsaponifiable matter isolated from the oils of unroasted and roasted sesame seed, white variety, were added individually to sunflower oil at levels of 0.02, 0.05 and 0.1%. The oven test method suggested by Thompson (1966) was adopted for checking the stability. Oil samples (50 g) were placed in 250 ml beakers covered with watch glasses and incubated at 63 ± 1°C until rancidity took place. Oxidation was periodically assessed every 48 h by the measurement of peroxide value according to AOCS (1978) method Cd 8-53, TBA value as described by Sidewell *et al.* (1954) and conjugated dienes (absorbance at 234 nm) according to Kates (1972).

All analytical determinations were carried out in duplicate and all data are expressed as mean values.

RESULTS AND DISCUSSION

Oil content and characteristics of the different sesame oil samples

Table 1 clearly shows that there were almost no differences in the oil contents between the white and brown seed varieties (45.0 and 45.4%, respectively). Roasting resulted in higher amounts of oil extracted from the seeds because it caused a certain amount of protein denaturation which could have improved lipid extractability (Yoshida and Kajimoto, 1994). The unsaponifiable matter percentage of the brown sesame seed oil was slightly lower (1.1%) than that of the white sesame variety (1.2%). These values were slightly increased after the roasting process and reached 1.2 and 1.3%, respectively.

Table 1. Oil contents and characteristics of the different sesame oil samples*

Characteristics	White sesame seed		Brown sesame seed	
	Unroasted	Roasted	Unroasted	Roasted
Oil content (wt%)	45.0	53.2	45.4	53.7
Unsaponifiables matter (wt%)	1.2	1.3	1.1	1.2
Total Lovibond colour (Y + 10R)	25.0	62.0	26.0	58.0
Fatty acids (wt%)				
Palmitic	8.7	8.7	6.8	6.9
Stearic	4.9	5.1	3.2	3.6
Oleic	46.8	47.2	53.9	54.1
Linoleic	39.6	39.0	36.1	35.4

*Each value is an average of duplicate determinations.

The oils extracted from the white and brown sesame seed varieties were quite similar in their Lovibond colour values (Table 1). It was also noticeable that the oils of roasted seeds exhibited brownish colour indicating caramelization of the sugar, which was released during roasting. Husain *et al.* (1986) reported that colour formation in sesame oil could be attributed to both non-enzymic browning and phospholipid degradation during roasting. The browning process contributed to the formation of antioxidative compounds (Yoshida *et al.*, 1995). Table 1 also presents the fatty acid composition in the extracted oils. The fatty acids in sesame oil are mainly linoleic and oleic acid with small amounts of saturated acids. However, the brown seed variety was higher in oleic acid and lower in linoleic and palmitic acids. Roasting caused little difference in the fatty acid composition.

Thin-layer chromatographic separation of sesame oil unsaponifiables

Qualitatively, TLC plates indicated that sesame seed oil unsaponifiables contained 9 components (Fig. 1) with different intensities. The separation was comparable to that described previously by Kamal-Eldin *et al.* (1994). A minor unknown spot was observed at R_f 0.16; however, this spot could not be detected in the unsaponifiables of the roasted samples. The phytosterols were observed separately as three spots: desmethylsterols (R_f 0.32), monomethysterols (R_f 0.38) and dimethylsterols (R_f 0.43). Desmethylsterols dominated and gave a large spot compared to the two others. Moreover, unroasted white sesame oil unsaponifiables displayed larger spots for both sesamin (centred at R_f 0.50) and sesamolin (centred at R_f 0.69), than those observed for the brown sesame variety. Tocopherol also occurred in large spots corresponding to a R_f value of 0.56 in the centre. Two

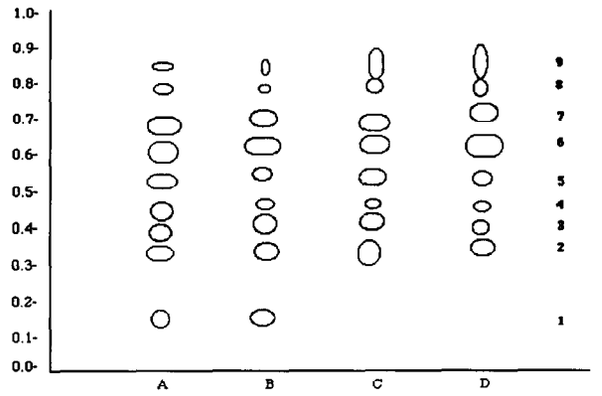

Fig. 1. Thin-layer chromatography separation of sesame unsaponifiables. A. USM, White variety, B. USM, Brown variety, C. RSM, White variety, D. RSM, Brown variety. Spots: (1) unknown, (2) desmethylsterols, (3) monomethylsterols, (4) dimethylsterols, (5) sesamin, (6) tocopherol, (7) sesamolin and (8–9) unknown.

other spots, at R_f values of 0.77 and 0.88, were not identified. However, these spots were more elongated in the unsaponifiables of roasted oils. Sesamol could not be detected in the present TLC chromatogram. Kamal-Eldin *et al.* (1991) found that sesamol occurred with the monomethyl sterol in the one dimensional TLC separation of sesame oil unsaponifiables.

Hydrocarbons and sterols in sesame oil unsaponifiables

It can be seen from Table 2 that the total hydrocarbons content varied from 41.8% (the brown variety) to 46.2% (the white variety). Furthermore, the composition of the constituent hydrocarbons was altered to some extent during the roasting stage: the lower molecular weight hydrocarbons (C_{12}–C_{19}) were decreased, whereas the higher molecular weight hydrocarbons (C_{20}–C_{32}) and squalene were increased as a per cent of the hydrocarbon fraction. Squalene has been found to have good protective action toward oxidative deterioration (Rao and Achaya, 1967).

Table 3 illustrates the GLC analytical results of sterols. Only the desmethylsterols were present in the chromatograms of the unsaponifiables constituents. The sterol composition agreed with literature data (Choi and Kim, 1985; Kamal-Eldin *et al.*, 1992). β-Sitosterol, campesterol, stigmasterol, and delta 5-avensterol were the major sterols. However, there was less total sterol content in the white sesame variety (53.8%) than in the brown variety (58.2%). Considerable differences were observed in the relative levels of these sterols after roasting. β-sitosterol and campesterol were decreased whereas stigmasterol was increased. Moreover, the $\Delta^{24,28}$ ethylidene sterols (Δ^5 and Δ^7-avenasterols) were also increased. These sterols were found to have an

Table 2. Hydrocarbons in sesame seed oil unsaponifiables*

Hydrocarbons	RRT**	White sesame seed		Brown sesame seed	
		Unroasted (%)	Roasted (%)	Unroasted (%)	Roasted (%)
C_{12}	0.10	2.2	0.2	2.0	0.1
C_{13}	0.12	2.6	0.1	2.5	0.1
C_{14}	0.14	3.3	0.4	2.3	0.2
C_{15}	0.16	2.7	0.3	0.7	0.2
C_{16}	0.18	3.1	0.7	1.6	0.3
Unknown	0.20	2.7	0.5	1.2	0.3
C_{17}	0.23	2.1	0.5	1.0	0.4
Unknown	0.25	1.1	0.2	1.5	0.4
C_{18}	0.27	2.1	0.6	2.3	0.5
C_{19}	0.32	1.9	1.9	3.1	1.2
Unknown	0.36	1.1	0.6	2.2	0.5
C_{20}	0.41	0.2	0.4	0.2	0.3
C_{21}	0.44	1.1	1.9	1.5	1.8
C_{22}	0.48	0.4	1.2	0.3	0.9
C_{23}	0.52	2.0	3.8	4.6	5.5
Unknown	0.54	0.4	1.6	0.5	1.1
Unknown	0.57	1.4	1.9	3.3	3.9
C_{24}	0.58	0.5	1.3	0.8	1.3
C_{25}	0.62	0.3	1.0	0.3	0.8
Unknown	0.63	0.3	0.7	0.3	0.5
C_{26}	0.65	0.5	1.6	0.5	1.7
C_{27}	0.68	0.4	1.4	0.3	1.5
C_{28}	0.71	4.5	7.1	3.7	5.6
Squalene	0.75	2.3	3.4	1.7	2.9
C_{30}	0.77	4.6	6.4	2.3	3.0
C_{32}	0.82	1.3	3.0	0.7	1.3
Unknown	0.83	1.1	—	0.4	0.7
Total hydrocarbons	—	46.2	42.7	41.8	37.0

*Each value is an average of duplicate GC analyses.
**Relative retention time to β-sitosterol (25.03 min) which was taken as 1.00.

Table 3. Sterol contents in sesame seed oil unsaponifiables*

Sterols	RRT**	White sesame seed		Brown sesame seed	
		Unroasted (%)	Roasted (%)	Unroasted (%)	Roasted (%)
Campesterol	0.86	12.3	9.7	10.5	8.9
Stigmasterol	0.92	4.6	6.2	3.8	5.7
β-Sitosterol	1.00	21.9	18.0	29.8	27.1
Unknown	1.02	—	5.1	1.3	5.5
Δ^5-Avenasterol	1.07	12.1	13.6	10.6	12.4
Δ^7-Stigmasterol	1.11	2.3	3.9	1.4	2.5
Δ^7-Avenasterol	1.18	0.6	0.8	0.8	0.9
Total sterols	—	53.8	57.3	58.2	63.0
β-Sitosterol/Campesterol	—	1.8	1.9	2.8	3.0

*Each value is an average of duplicate GC analyses.
**Relative retention time to β-sitosterol (25.03 min) which was taken as 1.00.

antipolymerization effect which could protect oils from oxidation during prolonged heating at high temperatures (Sims *et al.*, 1972; Gordon, 1989). The higher values of antipolymerization sterols in roasted sesame seed oil unsaponifiables are of great interest because they may add to the stability of this oil. However, the difference between the unsaponifiables from roasted and unroasted sesame oils in their hydrocarbons and sterols could not distinguish their efficiency as naturally occurring antioxidants.

Tocopherol and lignan contents

Table 4 shows that the brown sesame seeds had a higher level of tocopherol (54 mg/100 g oil) than the white seed variety (40.4 mg/100 g oil). Tocopherol levels were decreased after the roasting process to 39.0 and 33.0 mg/100 g oil, respectively, due to some degree of oxidation and polymerization. Tocopherol has been considered as a potent antioxidant in vegetable oils (Lea and Ward, 1959). Higher values of sesamin and sesamolin were found in the oil sample from the white sesame seed variety (392 and 238 mg/100 g oil, respectively). Sesamin was the major component in the unsaponifiables of sesame oil. It does not have any potential as an antioxidant or antioxidant precursor (Yoshida *et al.*, 1995).

Table 4. Tocopherol and lignan contents* in the oils extracted from sesame seeds

Component	White sesame seed		Brown sesame seed	
	unroasted	roasted	unroasted	roasted
Total tocopherol (mg/100 g oil)	40.4	33.0	54.0	39.0
Sesamin (mg/100 g oil)	391.6	352.0	302.1	265.1
Sesamolin (mg/100 g oil)	242.3	185.5	227.4	183.6
Sesamol (mg/100 g oil)	0.02	16.1	0.04	11.5

*Each value is an average of duplicate determinations.

On the otherhand, the presence of sesamolin in sesame oil could be of great value because it acts as a precursor of two phenolic antioxidants, sesamol and sesaminol (Fukuda *et al.*, 1986*b*). Roasting caused decrease in both sesamin and sesamolin contents. The degradation of sesamolin (76.5–80.7%) was greater than that of sesamin (87.7–89.9%) because sesamolin decomposed to sesamol. On the other hand, the sesamol content was detected as traces (0.2–0.4 mg/100 g oil) in the unroasted sesame oil samples, whereas an appreciable increase in sesamol was observed after roasting (11.5–16.1 mg/100 g oil) due to the conversion from sesamolin. (Fukuda *et al.* (1986*b*) reported that the addition of 0.5 g/kg sesamol was found to enhance the antioxidative action of γ-tocopherol at all concentrations. Kajimoto *et al.* (1992) found that sesamol had a great preventive effect on the thermal decomposition of tocopherol in oil.

Effect of addition of sesame oil unsaponifiables on the stability of sunflower oil

The peroxide values of sunflower oil samples treated with sesame oil unsaponifiable matter extracts are given

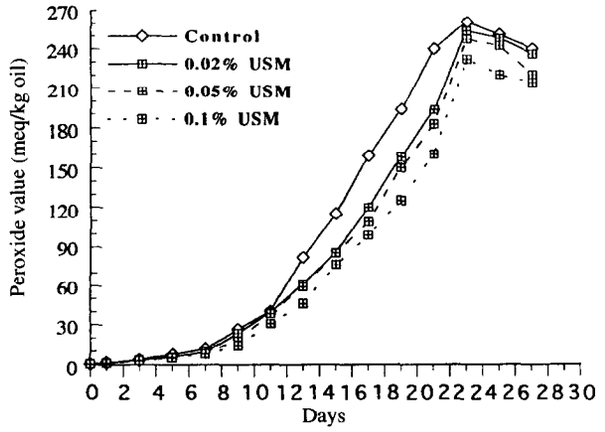

Fig. 2. Effect of unroasted sesame unsaponifiable matter (USM) on sunflower oil oxidation expressed as peroxide formation at 63°C.

in Figs 2 and 3. At a level of 0.02%, USM exhibited weak antioxidative activity. The antioxidative effect increased when the amount added increased gradually to 0.1%. On the other hand, at 0.02–0.05% level of sesame oil roasted unsaponifiable matter extracts (RSM) added to sunflower oil, the inhibition was more pronounced than the same levels of addition of USM. Additionally, stronger inhibition was achieved by adding 0.1% RSM. The antioxidant effects at different concentrations of these substances are shown in Fig. 4. Results are expressed as percentages of the control's oxidation assessed by the peroxide content of sunflower

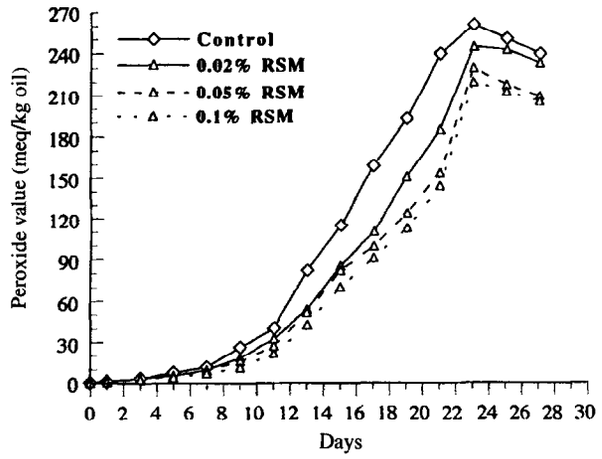

Fig. 3. Effect of roasted sesame unsaponifiable matter (RSM) on sunflower oil oxidation expressed as peroxide formation at 63°C.

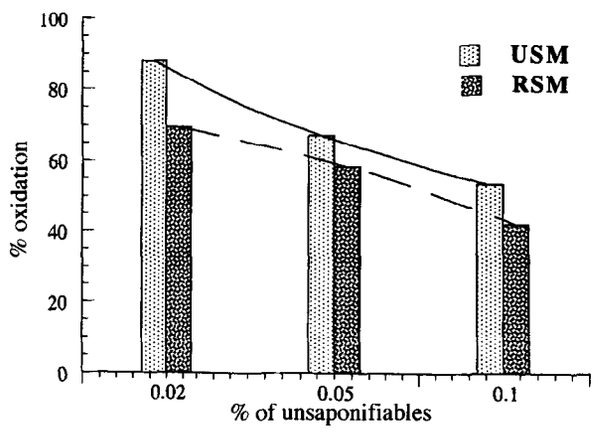

Fig. 4. Effect of different concentrations of USM and RSM on sunflower oil oxidation. Results are expressed as percentages of the control peroxide content incubated for 9 days at 63°C.

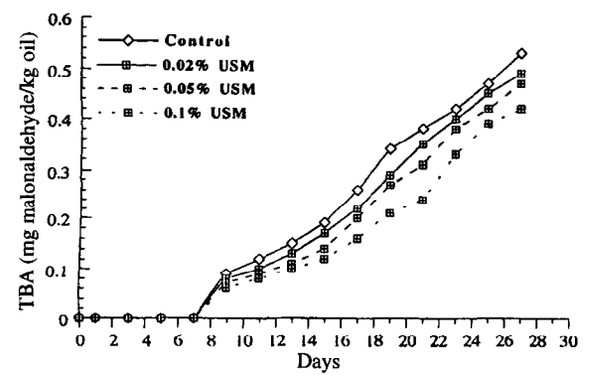

Fig. 5. Changes in the TBA values of sunflower oil treated with unroasted sesame unsaponifiable matter during storage at 63°C.

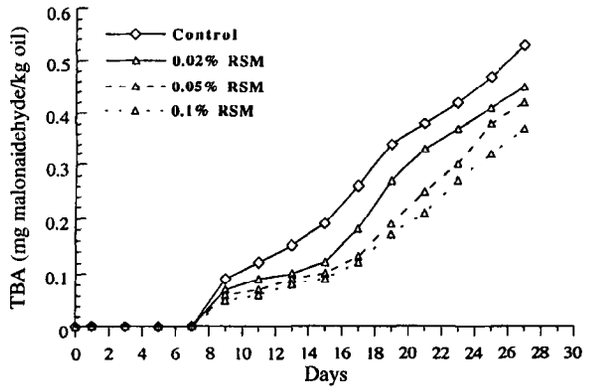

Fig. 6. Changes in the TBA values of sunflower oil treated wth roasted sesame unsaponifiable matter during storage at 63°C.

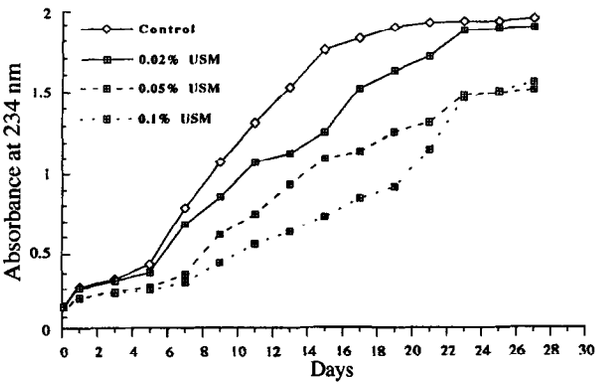

Fig. 7. Changes in the conjugated diene levels of sunflower oil treated with unroasted sesame unsaponfiable matter during storage at 63°C.

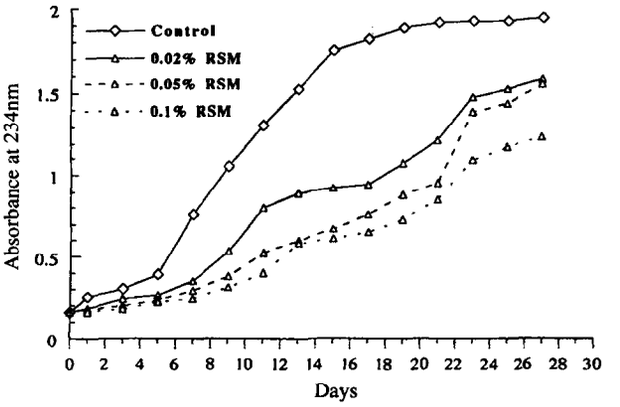

Fig. 8. Changes in the conjugated diene levels of sunflower oil treated with roasted sesame saponfiable matter during storage at 63°C.

oil incubated for 9 days at 63°C. It is apparent that the unroasted sesame oil unsaponifiables were always less effective than their roasted counterparts. The differences reflect the contents of the antioxidative components. The same effects can be seen in the TBA values (Figs 5 and 6).

The oxidation of polyunsaturated fatty acids is accompanied by an increase in UV absorbance with a maximum at about 234 nm, which is characteristic of conjugated diene systems (Figs 7 and 8). The increase in conjugated dienes is proportional to the sum of hydroperoxides and hydroperoxide decomposition products. Results are in accordance with those reported in Figs 2 and 3. Such correlations between the conjugated acid value and peroxide value have been previously observed (Noor and Augustin, 1984).

These results suggest that the unsaponifiables extracted from roasted sesame oil possess antioxidant properties and could be used as alternative natural antioxidants with wide food applications. No single compound can be considered responsible for this stability. A combination of a number of minor constituents such as tocopherols, sesamol, squalene and anti-polymerization sterols in the roasted unsaponifiables could have a synergistic role in increasing the oxidation stability.

REFERENCES

Abdel-Aziz, S. M. G. (1985) Chemical and biological evaluation of unsaponifiable matter of vegetable oils. Ph.D. Thesis, Fac. of Agric., Cairo University.

Aoyama, M., Kanematsu, H., Tsukamoto, M. and Niiya, I. (1994) Yukagaku 43: 154. (C.F. Namiki, M. 1995). The chemistry and physiological functions of sesame. *Food Review International* **11**(2), 281–329.

Awatif, I. I., Khalil, M. F. and Badawy, H. A. A. (1996) Effect of natural and synthetic antioxidants on the stability of virgin olive oil. *Annals Agric. Sci., Ain Shams Univ., Cairo* **41**(1), 269–280.

Bosku, D. and Morton, I. D. (1976) Effect of plant sterols on the rate of deterioration of heated oils. *J. Sci. Food Agric.* **27**, 928–932.

Budowski, P., Connor, R. T. and Field, E. T. (1950) Sesame oil. IV. Determination of free and bound sesamol. *J. Am. Oil Chem. Soc.* **27**, 307–310.

Budowski, P. (1962) Recent research on sesamin, sesamolin and related compounds. *J. Am. Oil Chem. Soc.* **41**, 280–285.

Choi, D. S. and Kim, H. K. (1985) Effect of extraction methods on the sterol composition of sesame oil. *J. Korean Society of Food and Nutrition* **14**(4), 365–369.

Fukuda, Y., Nagata, M., Osawa, T. and Namiki, M. (1986*a*) contribution of lignan analogues to antioxidative activity of refined unroasted sesame seed oil. *J. Am. oil Chem. Soc.* **63**, 1027–1031.

Fukuda, Y., Nagata, M., Osawa, T. and Namiki, M. (1986*b*) Chemical aspects of the antioxidative activity of roasted sesame seed oil and the effect of using the oil for frying. *Agric. Biol. Chem.* **50**, 857–862.

Gordon, M. H. (1989) Plant sterols as natural anti-polymerization agents. In *Proc. IUFOST Int. Symp: New aspects of dietary lipids. Benefits, hazards and use*, pp. 23–34. Göteborg.

Hallabo, S. A. S. (1977) Chemical studies on naturally occuring unsaponifiable matter in some vegetable oils. Ph.D. Thesis, Faculty of Agriculture, Cairo University.

Husain, S. R., Terao, J. and Matsushita, S. (1986) Effect of browning reaction products of phospholipids on auto-oxidation of methyl linoleate. *J. Am. Oil Chem. Soc.* **63**, 1457–1560.

Kajimoto, G., Kanomi, Y., Kawakami, H. and Hamatani, M. (1992) Effects of antioxidants on the thermal oxidation of oils and decomposition of tocopherol in vegetable oils. *J. Japan Soc. Nutr. Food Sc.* **45**(3), 291–295.

Kamal-Eldin, A., Yousif, G. and Appelqvist, L. Å. (1991) Thin layer chromatographic separations of seed oil unsaponifiables from four *Sesamum* species. *J. Am. Oil Chem. Soc.* **68**, 844–847.

Kamal-Eldin, A., Appelqvist, L. Å., Yousif, G. and Iskander, G. M. (1992) Seed lipids of *Sesamum indicum* and related wild species in Sudan. The sterols. *J. Sci. Food Agric.* **59**, 327–334.

Kamal-Eldin, A., Appelqvist, L. Å. and Yousif, G. (1994) Lignans analysis in seed oils from four sesame species: comparison of different chromatographic methods. *J. Am. Oil Chem. Soc.* **71**, 141–147.

Kates, M. (1972) *Techniques of lipidology*. North Holland Publishing Company, Amsterdam, London. American Elsevier Publishing Co. Inc., New York.

Katsuzaki, H., Kawakishi, S. and Osawa, T. (1994) Sesaminol glucosides in sesame seeds. *Phytochemistry* **35**(3), 773–776.

Kikugawa, K., Arai, M. and Kurechi, T. (1983) Participation of sesamol in stability of sesame oil. *J. Am. Oil Chem. Soc.* **60**, 1528–1533.

Lea, C. H. and Ward, R. J. (1959) Relative antioxidant activities of the seven tocopherols. *J. Sci. Food Agric.* **10**, 537–548.

Manley, C. H., Vallon, P. P. and Erickson, R. E. (1974) Some aroma components of roasted sesame seed (*Sesamum indicum* L.). *J. Food Sci.* **39**(1), 73–76.

Mordret, F. (1968) Comparison and study of methods of obtaining unsaponifiable matter. *J. Crops Grass* **6**, 389–397.

Noor, N. and Augustin, M. A. (1984) Effectiveness of antioxidants on the stability of banana chips. *J. Sci. Food Agric.* **35**, 805.

Association of Official Analytical Chemists (1980) *Official Methods of Analysis of the Association of Official Analytical Chemists*. Association of Official Analytical Chemists, Washington, D.C.

American Oil Chemist's Society (1978) *Official and Tentative Methods of the American Oil Chemists' Society*, 3rd edn, edited by R. O. Walker. AOCS, Champaign, IL.

Rady, A. H. and Awatif, I. I. (1991) *Improvement of oils stability*. Fourth Arab conference of Food Science and Technology, Cairo, Egypt.

Rao, M. K. and Achaya, K. T. (1967) Antioxidant activity of squalene. *J. Amer. Oil Chem. Soc.* **45**, 296.

Sidewell, G. G., Salwin, H., Benca, M. and Mitchel, J. A. (1954) The use of thiobarbituric acid as a measure of fat oxidation. *J. Am. Oil Chem. Soc.* **31**, 603–606.

Sims, R. J., Fioriti, J. A. and Kanuk, M. J. (1972) Sterol additives as polymerisation inhibitors for frying oils. *J. Am. Oil Chem. Soc.* **49**, 298–302.

Stahl, E. (1967) *Thin layer chromatography. A laboratory handbook*. Springer Verloag, Berlin, p.359.

Thompson, S. W. (1966) Survey of accelerated test for determining the stability of oils and fats. Laboratory Handbook for oil and fat analyst's. Ed. L.V.

Ushkalova, V. N. (1983) Oxidation of refined vegetable oils. *Izu. Vyssh. Uchebn. Zaved. Pishch Tekhnol.* **5**, 30–32. (C.F. C. A. 100, 33443).

Yen, G. C.and Shyu, S. L. (1987) Effect of roasting temperature on the oxidative stability of sesame oil. In *Trends in Food Science*, ed. W. S. Lien. Conference Singapore, 28 Sept–20 Oct. (C. F. FSTA 22 (6):123, 1990).

Yen, G. C. (1990) Influence of seed roasting process on the changes in composition and quality of sesame (*Sesame indicum*) oil. *J. Sci. Food Agric.* **50**(4), 563–570.

Yoshida, H. and Kajimoto, G. (1994) Microwave heating affects composition and oxidation stability of sesame (*Sesamum indicum*) oil. *J. Food Sci.*, **59**, 613–615, 625.

Yoshida, H., Shigezaki, J., Takagi, S. and Kajimoto, G. (1995) Variations in the composition of various acyl lipids, tocopherols and lignans in sesame seed oils roasted in a microwave oven. *J. Sci. Food Agric.* **68**, 407–415.

Wong, M. L., Timms, R. S. and Goh, E. M. (1988) Colorimetric determination of total tocopherols in palm oil: olein and stearin. *J. Am. Oil Chem. Soc.* **65**(2), 258–261.