Pakistan Journal of Nutrition 10 (9): 864-870, 2011
ISSN 1680-5194

Effect of Aromatic Plant Essential Oils on Oxidative Stability of Sunflower Oil During Heating and Storage

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Abstract: Oxidative degradation of lipids is a major factor limiting the shelf life of foods. The free radical reaction of lipid peroxidation is generally responsible for the deterioration of lipid-containing foods. Use of antioxidants during the manufacturing process can minimize the extent of lipid peroxidation. Spices and some herbs have received increased attention as sources of many effective antioxidants. The effect of essential oils extracted from fennel, rosemary and ginger on the oxidative stability of sunflower oil during storage at ambient temperature with light exposure was studied. The effect of heating time on the stability of oil was studied as well. The obtained results showed that the studied essential oil inhibited the formation of primary and secondary oxidation products during heating and storage of sunflower oil. It could be concluded that, essential oils of selected aromatic plants are promising as natural antioxidants.

Key words: Aromatic plants, lipid oxidation, fennel, rosemary, ginger, sunflower oil

INTRODUCTION

The oxidative deterioration of lipid and proteins is a major concern for food technologists due to the loss of quality associated with those processes. Lipid oxidation decreases nutritional and sensory properties of foods since it involves the loss of essential fatty acids and vitamins and the generation of toxic compounds, causing additionally, flavor, texture and color deterioration (Morrissey *et al*., 1998).

Oxidation is one of the major causes of chemical spoilage, resulting in rancidity and/or deterioration of the nutritional quality and safety of foods (Aruoma *et al*., 1992; Kahkonen *et al*., 1999). There is at present increasing interest both in the industry and in scientific research for spices and aromatic herbs because of their strong antioxidant and antimicrobial properties, which exceed many currently used natural and synthetic antioxidants.

These properties are due to many substances, including some vitamins, flavonoids, terpenoids, carotenoids, phytoestrogens, minerals, etc. and render spices and some herbs or their antioxidant components as preservative agents in food (Calucci *et al*., 2003).

Polyphenolic compounds are commonly bound in both edible and inedible plants and they have been reported to have multiple biological effects, including antioxidant activity (Kahkonen *et al*., 1999). Herbs are used in many domains, including medicine, nutrition, flavouring and beverages (Djeridane *et al*.,2006).

Crude extracts of herbs and spices and other plant materials rich in phenolics are of increasing interest in the food industry because they retard oxidative degradation of lipids and thereby improve the quality and nutritional value of food.

The aim of this study was to evaluate the effect of essential oils extracted from fennel, rosemary and ginger on the oxidative stability of sunflower oil during storage at ambient temperature with light exposure for 8 weeks, The effect of heating time on the stability of sunflower oil was studied as well.

MATERIALS AND METHODS

Sunflower oil: Fresh refined, bleached and deodorized sunflower oil without adding of any synthetic antioxidant was obtained from Qarya (UCVO) Food and vegetable Oil Inductries Plc, Aljeza, Jordan.

The initial characteristics of sunflower oil used in this study was checked by determining acid, peroxide, iodine and TBA values, conjugated diene and triene as described below.

Aromatic plant oils: The essential oils of three selected arromtic plants (fennel, rosemary and ginger) were obtained by distillation method.

Antioxidants: Food grade antioxidant of Butylated Hydroxyl Toluene (BHT) was obtained from sigma chemical Co., St. louis, Mo, USA.

The food additive regulation in USA had a limitation of 200 ppm of synthetic antioxidant, while others of natural antioxidant had 400 ppm as recommended usage level (Eastman chemical, 1993).

Storage of oils: Sunflower oil was divided into three portions. The first portion was kept in transparent glass bottles and exposed to diffused light. The second portion was preserved in similar glass bottles after adding synthetic antioxidant (BHT, 200 ppm). Where as, the third

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portion with individual essential oils (400 ppm) were placed in similar glass bottles and exposed to diffused light at ambient temperature for 8 weeks.

Oxidative stability of oils was evaluated by determining, acid, peroxide, iodine and TBA values, conjugated diene and triene were studied as well. The analysis was carried out every week of storage.

Thermal treatment of oils: All sunflower oil samples were heated at 180°C±5°C for 18 h at intervals of 3 h heating for 6 consecutive days.

The heated oils were sampled every day after heating in brown bottles and kept at 5°C for analytical experiments.

Analytical methods: Acid, iodine and peroxide values were estimated according to AOCS (1998).

TBA Value was estimated spectrophotometery at 532 nm according to Guzman-Chozas *et al.* (1997).

Conjugated diene and conjugated triene were determined as mentioned by Vieira and Regitano-Darce (1999).

Determination of the susceptibility to oxidation with Rancimat method: Three grams of oil was accurately weighed into each of the six reaction vessels and the following procedure was carried out according to the method described by Hasen Huettl and Wan (1992).

The Metrohm Rancimat 679 (Metrohm Ltd., Herisau, Switzerland) was switched on until the temperature of the oil batch reached 120°C. Then 60 cm^3 of distilled water was placed into each of the six conductivity cells and the air flow was set at 20 L/hr. The temperature was checked to ensure that it had a constant value. The air supply was connected to the tubes containing the oil samples and the chart recorded was started. The determination continued automatically until the conductivity reached the maximal value and the induction period was recorded.

RESULTS AND DISCUSSION

The initial characteristics of sunflower oil: The initial characteristics of sunflower oil used in this study are given in Table 1.

Tabulated dated revealed that the sunflower oil was of good quality, as indicated by its initial low Characteristics. The chemical characteristics of sunflower oil established its capability of application in either nutrition or industry.

Effect of aromatic plant essential oils on oxidative stability of sunflower oil during storage: It is well established that deterioration of edible oils could be avoided when the oil is rich with considerable amounts of natural phenolic compounds known as antioxidants.

The technological processes which are carried out on these oils to become edible, might have a direct effect on the amount of these natural antioxidants present in oil. The study was designed to determine the possible decline in the rate of oxidation following addition of aromatic plant essential oils as natural antioxidants.

The effects of storage periods at ambient temperatures on the oxidative stability of sunflower oil treated with natural antioxidants are given in Fig. 1-6.

Considerable changes were observed in the acid value of sunflower oil during storage at ambient temperatures. As shown in Fig. 1, the acid value increased after 8 weeks of storage for control oil and (oil + antioxidant); respectively. The increase was considerably higher in oil without antioxidant as compared to oil sample in which natural antioxidants (aromatic plant oils) were incorporated.

Table 1: Characteristics of sunflower oil

Characteristics	
Acid value (%oleic acid)	0.275
Iodine value	122.850
Peroxide value (meq/kg)	0.750
Thiobarbituric acid (TBA) (mg/kg)	0.073
Conjugated diene	1.300
Conjugated triene	0.590
Rancimat value (hours)	4.600

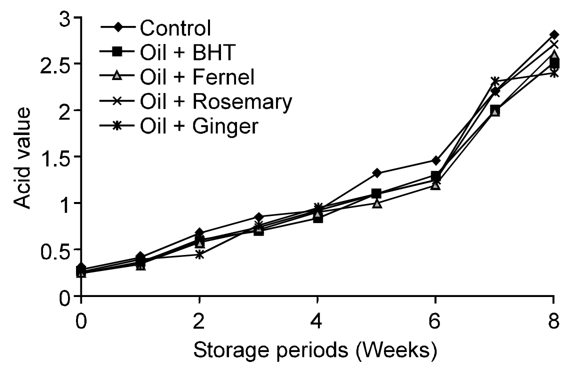

Fig. 1: Effect of storage period on acid values of sunflower oil treated with different antioxidants

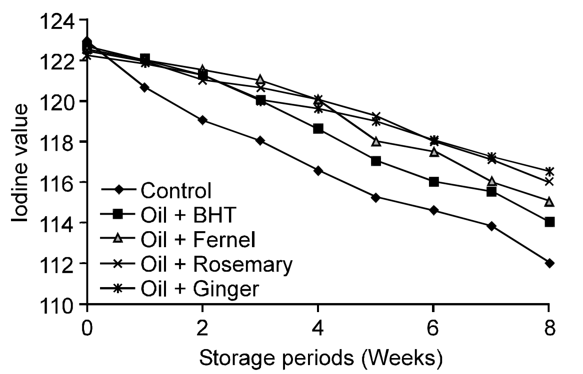

Fig. 2: Effect of storage period on iodine values of sunflower oil treated with different antioxidants

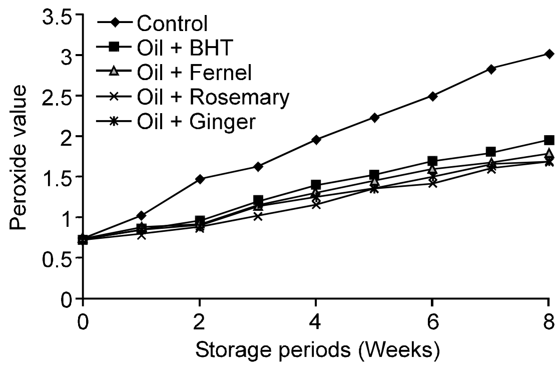

Fig. 3: Effect of storage period on peroxide values of sunflower oil treated with different antioxidants

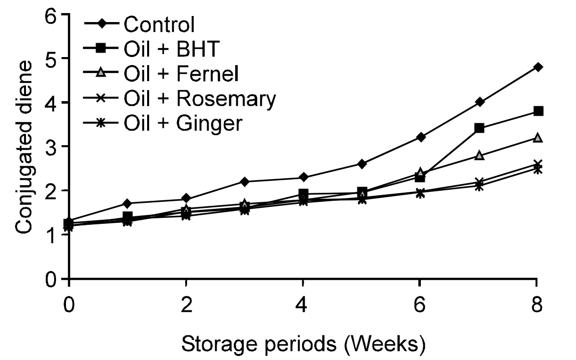

Fig. 5: Effect of storage period on Conjugated diene of sunflower oil treated with different antioxidants

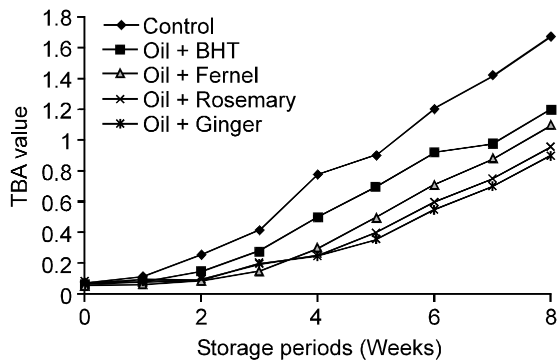

Fig. 4: Effect of storage period on TBA values of sunflower oil treated with different antioxidants

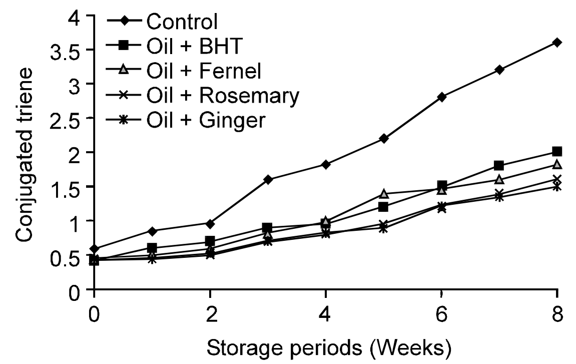

Fig. 6: Effect of storage period on Conjugated triene of sunflower oil treated with different antioxidants

The increment in the acid value indicated that light acted as an accelerator of acid formation in the oil. These results are in accordance with those outlined by Adegoke *et al.* (1998) and Byrd (2001).

Figure 2 showed that, the iodine value decreased gradually during storage. The rate of decrement in oils without antioxidants was higher than that in oils after the addition of natural antioxidants.

Autoxidation of sunflower oils affected their fatty acids composition, as polyunsaturated fatty acids were oxidized faster than saturated and mono unsaturated fatty acids (Semwal *et al.*, 1996). Oxidation caused a decrease in the relative percentage of the unsaturated fatty acids and an increase in the relative percentages of the saturated fatty acids. The addition of antioxidants to sunflower oil effectively reduced the oxidation rate in the oil, as detected by relatively low reduction in iodine values (Fig. 2).

Changes occurring in the peroxide value of sunflower oil during storage are given in Fig. 3. The peroxide value in the stored samples tended to increase to a maximal value after seven weeks of storage at ambient temperatures, then began to decline in control sample. In general, the natural antioxidant used in this study showed down the rate of peroxide formation, since peroxide value of samples which contained natural antioxidants were lower than that of control sample during storage.

The decrement which occurred in the peroxide value after seven weeks of storage could be due to the rate of hydrolysis of peroxidic compounds was higher than the rate of peroxide formation. These results are in agreement with those reported by Raghav *et al.* (1999).

The changes in TBA values of sunflower oil during storage at ambient temperatures are shown in Fig. 4. Increases in TBA values were higher in control sample compared to sunflower oil blended with natural antioxidant (crude lignan). The increase in TBA values was correlated linearly with the storage period and could be used as objective parameter for quality deterioration during storage.

Figure 5 and 6 show the changes in conjugated diene and triene contents in sunflower oil during storage at ambient temperatures.

Conjugated diene and triene contents of studied oils increased gradually as the storage time increased. Oxidative stability of sunflower oils, based on the changes of conjugated diene and triene contents, were in an agreement with those estimated by peroxide value development.

The data revealed that sunflower oil containing natural antioxidants had a much greater oxidative stability than oils from sunflower without adding natural antioxidants. These results were in accordance with previously reported results (Chul Lee *et al.*, 2004).

Depending on all the obtained results we could conclude that the antioxidants are suitable in their function for increasing oxidative stability at ambient temperature only, while they could act as prooxidants or they could breakdown into other substances, which could act as prooxidants.

On the other side, the higher efficiency of the natural antioxidants could be due to the stability of these natural antioxidants during storage.

Addition of natural antioxidants could increase shelf-life of oils. In addition, natural antioxidants are safe and impart health benefits to the consumer.

Effect of aromatic plant essential oils on oxidative stability of sunflower oil during heating: The refined vegetable oil selected for this study was sunflower oil. The selection of this oil was made owing to its common use as frying oil and also high relative reaction rates of its unsaturated fatty acids with oxygen (List and Erickson, 1985).

To follow the oxidation rate in oil samples during heating up to 18 h, the samples were analyzed periodically for acid value, iodine value, peroxide value, TBA value, conjugated diene and conjugated triene values, since a single reaction criterion is not enough to account for the oxidative changes at various stages of heating. The data illustrated in Fig. 7 show the effect of heating time on the acid values of sunflower oil treated with different antioxidants. Acid value reflected the degree of oil hydrolysis and the amount of free fatty acids involved in the heated oil samples. The tabulated data revealed that heating of sunflower oil caused an increase in the acid value. Such increment could be attributed to formation of acidic compounds and free fatty acids. The increment in the acid value in control samples was occurred during heating up to 9 h and then decreased (Fig. 7). This decrement in the acid value might be due to further cracking of the formed fatty acids, which could form low molecular weight fatty acids, which are highly volatile and/or the formation of the corresponding in alkenes via the decarboxylation reaction.

From such data, it could be observed that the oil samples treated with Butylated Hydroxytoluene (BHT) and essential oils had the least amount of free fatty acids, after heating up to 9 h, which was due to a very low degree of hydrolysis in oils as affected by addition of antioxidants. The difference in activity of the used antioxidants might be accounted on the basis of their chemical structures. These results are in accord with those of Aziz and Mohamed (1999), Chung and Choe (2001) and Al-Sharjabi (2005).

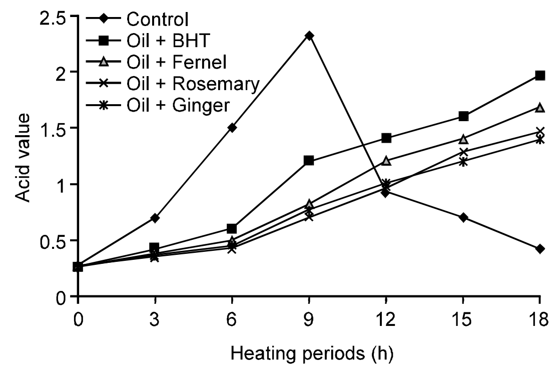

Fig. 7: Effect of heating time on acid values of sunflower oil treated with different antioxidants

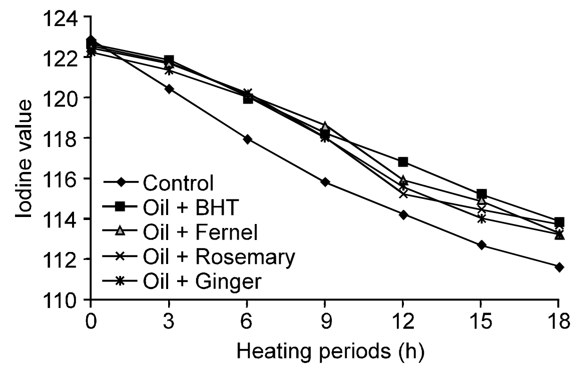

Fig. 8: Effect of heating time on iodine values of sunflower oil treated with different antioxidants

During heat treatment, a progressive decrease in unsaturation was observed in all studied samples by measurement of iodine value (Fig. 8). This decrease could be attributed to the destruction of double bonds by oxidation, scission and polymerization (Cuesta *et al.*, 1991).

The data showed that heating of oil substantially reduced the iodine values. Oxidation, which consisted of a complex series of chemical reactions, was characterized by a decrease in the total unsaturated content of the oil due to abstraction of hydrogen adjacent to double bond and the formation of free radicals. Hence heating that accelerated the oxidation of the oil caused maximal reduction of the iodine values (Gertz *et al.*, 2000; Paz and Molero, 2001).

The effect of adding antioxidants (BHT and essential oils) on iodine value of the sunflower oil were analyzed after heating up to 18 h. Both antioxidants effectively reduced the oxidation rate in the oil, as detected by increases in iodine values as compared with control samples (Fig. 8) (sunflower oil without antioxidants). Such results are in good agreement with those reported by Naz *et al.* (2004) and Naz *et al.* (2005).

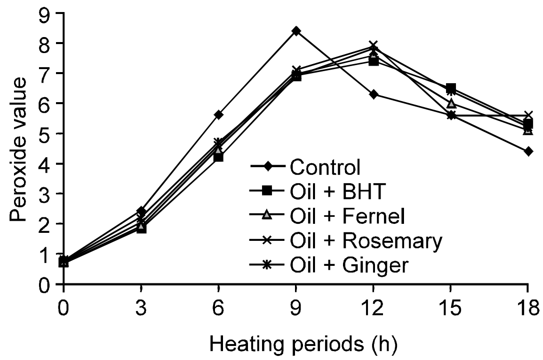

Fig. 9: Effect of heating time on peroxide values of sunflower oil treated with different antioxidants

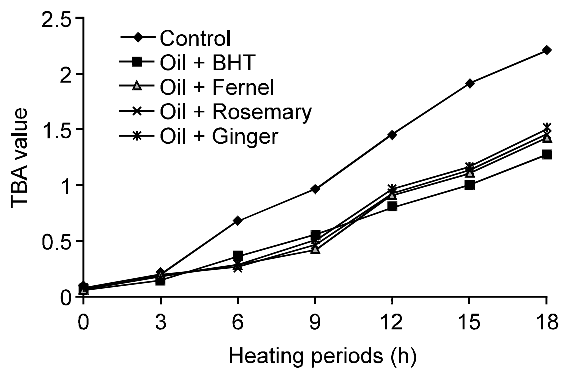

Fig. 10: Effect of heating time on TBA values of sunflower oil treated with different antioxidants

Peroxide formation in sunflower oils during heating up to 18 h is shown in Fig. 9. As heating time increased, peroxide values increased up to 9 h and then decreased. This was due to the rate difference between peroxide formation and its decomposition. At the beginning of heating, peroxide formation was faster than its decomposition. However, the reverse was the case as the heating proceeded.

The effects of adding antioxidants (BHT and essential oils) on peroxide value of the sunflower oil were tested after heating up to 18 h. Both antioxidants effectively reduced the oxidation rate in the oil, as detected by decrease in peroxide values compared to sunflower oil without antioxidant (Fig. 9). Tabulated data showed that continuous exposure of oil to air and light enhanced oxidative changes in the oil and these changes became very fast in heating oil.

The peroxide values were also less in the sunflower oil blended with antioxidants, which was an indication that antioxidants decreased the oxidation of sunflower oil, even if peroxide value determination was not a very good measure of oil oxidation during heating (Stevenson *et al*., 1984).

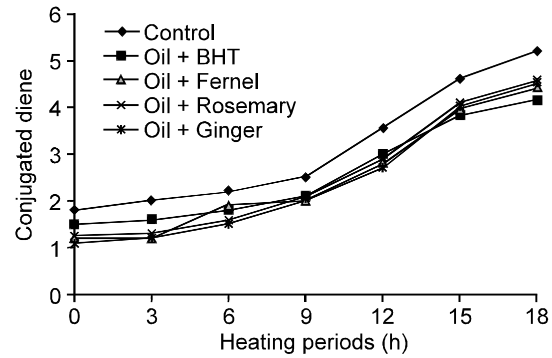

Fig. 11: Effect of heating time on Conjugated diene of sunflower oil treated with different antioxidants

Figure 10 revealed that TBA value increased gradually in sunflower oil samples during heating up to 18 h. This increment in TBA values indicating the formation of carbonyl compounds. Formation of these substances was due to heating in the presence of air. The extent to which these compounds formed might depend on the nature of oil and the heating procedures adopted. These results are in accord with those of Rehman (1986) and Lee *et al*. (1994).

The addition of antioxidants to sunflower oil was very effective since the TBA values after 18 hours of heating were significantly less than the values of the oil without antioxidants.

In general, it could be observed that exposure of studied oils to thermal treatments induced pronounced changes in chemical characteristics of these oils. This might be due to the effect of heat on unsaturated fatty acids, which in turn affected the properties of oils.

Fatty acids with conjugated unsaturation absorbed strongly in the region of 230-375 nm (diene unsaturation absorb at 232-234 nm and triene unsaturation absorb at 268-270 nm). Oil containing polyunsaturated fatty acids are oxidized to conjugated diene and triene systems that could be measured by ultraviolet absorption at 232 nm and 268 nm; respectively (Gray, 1978).

The oxidation of polyunsaturated fatty acids was accompanied by an increase in the Ultraviolet (UV) absorbance with a maximum at about 234 nm, which was characteristic of conjugated diene systems (Fig. 11). Conjugated diene formation in oil samples increased with heating time. The initial value of conjugated diene of sunflower oil was 0.62 increased to 4.80 after 18 h of heating. Blending of sunflower oil with antioxidants, resulted in a significant decrease in conjugated diene values compared with control sample. The increase in conjugated dienes was proportional to the sun of hydroperoxides and hydroperoxide decomposition products.

These results are in accord with those reported in Fig. 9. Such correlations between the conjugated diene values

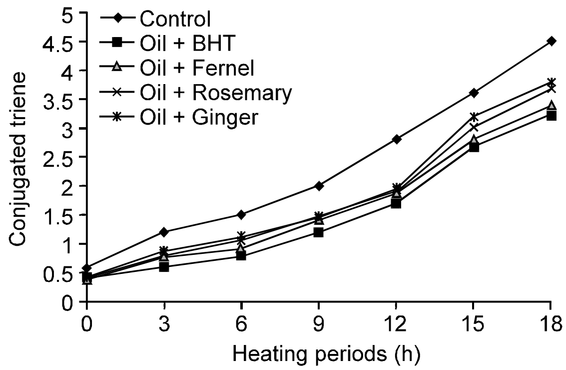

Fig. 12: Effect of heating time on Conjugated triene of sunflower oil treated with different antioxidants

and peroxide values had been previously observed (Noor and Augustin, 1984).

The same trend of results was noticed for conjugated triene at 268-270 nm (Fig. 12).

From literature, most researchers measured both conjugated diene and triene in different crude or refined edible oils, but they focused only on measurement of alterations during heating, frying or storing of different edible oils on conjugated diene at 232-234 nm, that could be due to the alterations on this UV region was very clear and not overlapping with other cromophore groups of UV spectrum.

On the contrary the other UV regions such 268-270 nm of conjugated triene might be overlapping with other components such as dienals and dienones which could be produced as secondary breakdown products in oxidation process. Specially conjugated triene formed only on fatty acids containing three or more double bonds and as mentioned previously the percentage of such fatty acids was very low in studied samples. So we could say that the cromophore groups in this UV region were not well known, also there was much overlapping between more than one cromophore groups.

The abovementioned results suggested that the unsaponifiables extracted from essential oils possessed antioxidant properties and could be used as alternative natural antioxidants with wide food applications, No single compound could be considered responsible for this stability.

A combination of a number of minor constituents in aromatic plant oils could have a synergistic role in increasing the oxidation stability. It could be concluded that, essential oils of selected aromatic plants are promising as natural antioxidants.

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