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Oxidative stability of olive, corn and soybean oil under different conditions

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Abstract

To follow the relative rates of oxidative deterioration in edible oils, refined olive, corn and soybean oils were analyzed periodically for their peroxide value (PV), *p*-anisidine value (*p*-AV) and iodine value (IV), following exposure to air or air-light for 30 days. Changes in the above values of the oils were also examined and after their use for deep-frying of French fries at 180 °C for varying periods of time, namely 30, 60 and 90 min. PV and *p* -AV values increased in the order: deep-frying > air-light exposure > air exposure while the values with respect to the oils increased in the order: soybean > corn > olive. Decrease in IV followed the same pattern, i.e. deep-frying > air-light > air and soybean > corn > olive. Deep-frying of French fries in corn oil was also carried out in the presence of caffeic, ferulic, vanillic acid and crude tea extract as antioxidants. All antioxidants effectively reduced the oxidation rate in the oil, as detected by decrease in PVs and *p* -AVs and relatively low reduction rate in IVs for all the frying times. The order of antioxidative activity was caffeic acid > vanillic acid > ferulic acid > tea extract.

Keywords: Oxidative deterioration; %Free fatty acid; Peroxide value, Iodine value; *p*- Anisidine value; antioxidant; Deep frying

1. Introduction

Though vegetable oils, the ideal cooking media of the day, are beneficial and popular due to their cholesterol-lowering effect, some important issues regarding their judicious use are largely ignored by consumers and the medical community. In contrast to animal fats, which are predominantly saturated and hence do not react readily with other chemicals, especially oxygen, unsaturated vegetable oils are more reactive (Matalgyto & Al-Khalifa, 1998). Exposure to air (Isabei & Mariano, 2001; Kristina & Hans, 1998; Zhao-jie, Chang-hu, Hong, En-Chen, & Hong-Jun, 2000), heat (Isabel, Satue-Gracia, German, & Frankel, 2000; Matalgyto & Al-Khalifa, 1998; O'Neill, Galvin, Morrissey, & Buckley, 1998; Witting, Detlef, & Roland, 1999; Yuki & Sadaaki, 2001), light (Xiaoying & Ahn, 1998), trace metals (Haneda & Yoshino, 1998; Kristina & Hans, 1998; Xiaoying & Ahn, 1998) and moisture enhances their chemical reactivity. The oxidation is also influenced by antioxidants and the fatty acid composition of the oils (Christian, Sabine, & Kochhar, 2000).

Off-flavourings, nutritional losses and other deteriorative changes in oil arise by reaction with atmospheric oxygen, i.e., oxidative rancidity, or by hydrolytic reactions catalyzed by lipases from food or from microorganisms. The effects of hydrolytic reactions can be minimized by cold storage, good transportation, careful packaging and sterilization. However, oxidative rancidity or autoxidation cannot be stopped by lowering the temperature of storage since it is a chemical reaction with low activation energy.

Research into the problems of oxidative deterioration has been pursued for many years but it has been boosted by the recognition that such oxidations can cause damage to cell membranes and DNA (Peter & Hakan, 1998), and may be involved in the aging process (Yulan

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et al., 1998), hypertension (Carla et al., 1998) and cancer growth (Navarro et al., 1999).

Autoxidation can be inhibited or retarded by vacuum packaging, packing under an inert gas to exclude oxygen (modified atmosphere) and refrigeration/freezing. The use of antioxidants is the most preferable way of suppressing the oxidation (Bozidar, Djilas, & Canadanoric-Brunet, 1998; Dolores, Anna-Maija, Anu, & Afaf, 1998; Rudnik, Szczucinska, Gwardiak, Szule, & Winiarska, 2001; Witting, Upston, & Stocker, 1998; Xiaoying & Ahn, 1998) because the above methods are not always applicable and it is seldom realized how little oxygen is needed to initiate and maintain the oxidative process, or how difficult and expensive it can be to remove the last traces of air from a food product.

The study was designed to determine the exact onset of oil starts deterioration under the conditions in which it is normally stored. Though it is well known that air, light, heat and moisture are the main contributing factors towards this autoxidation this study attempts to find the contributions of each factor, as well as combined effects, so that a clear conclusion can be drawn about how long an oil sample could be prevented from noticeable oxidation. Another aim is to observe decline in the rate of oxidation following addition of plant extracts, such as tea (*Camellia sinensis*) and different purified phenolic acids (ferulic, caffeic, vanillic and gallic) as antioxidants.

2. Materials and methods

2.1. Samples

Refined olive, corn and soybean oils were purchased from the local market in 2.5 l packs. The oil samples were stored in accordance with the experimental conditions.

2.2. Analysis of the oil exposed to air

250 ml, each, of olive, corn and soybean oils were taken in clean, dry, amber coloured glass bottles (500 ml) in triplicate. The oil samples in these bottles, with a surface area of 44 cm^2 exposed to air, were kept opened in a $12 \times 14 \times 12$ ft^3 dark chamber (RH 60–70%, 30 °C) in which circulation of air was maintained by means of electric and exhaust fans. The sample bottles were shaken well and the oil samples, drawn from each bottle with the help of disposable syringes, were analyzed for PV (IUPAC Standard Methods 2.501, 1987), *p*-AV (IUPAC Standard Methods 2.504, 1987) and IV (IUPAC Standard Methods 2.505, 1987), after 1, 5, 10, 15, 20, 25 and 30 days. Each of the analyses was done three times for each bottle in triplicates. The results were compared with the values obtained for the oil samples analyzed immediately after opening the cans (controls).

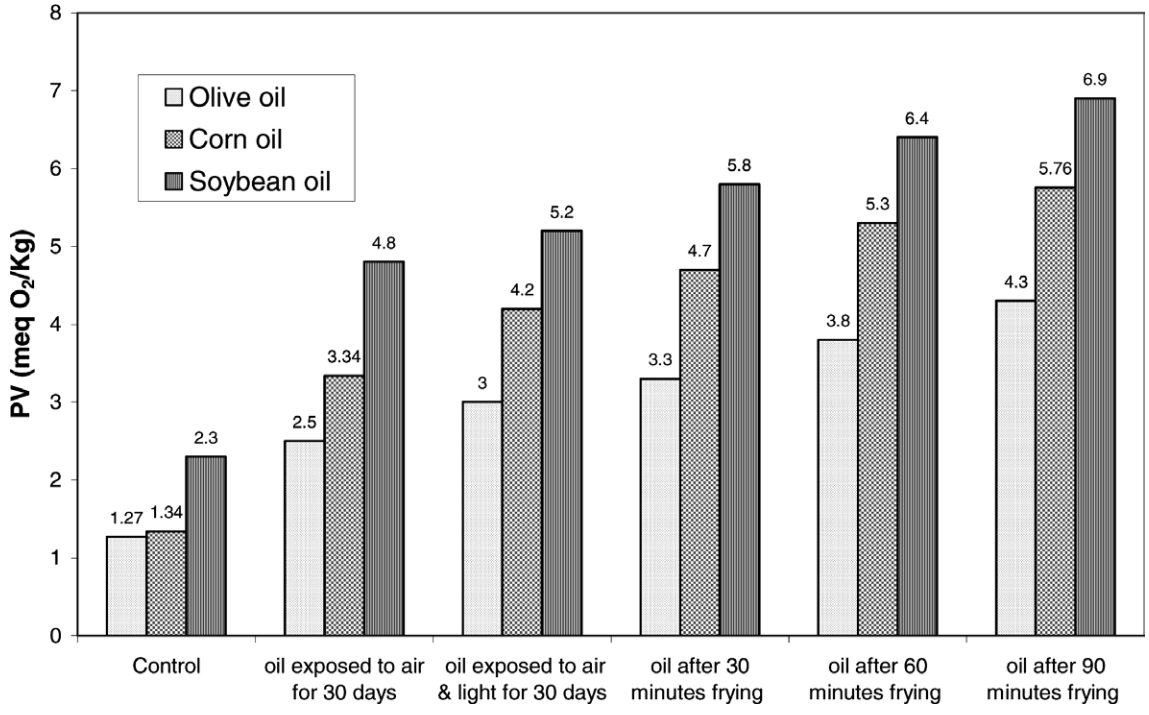


Fig. 1. Effect of air, light and deep-frying on PV of olive, corn and soybean oil.

2.3. Analysis of the oil exposed to air-light

250 ml, each, of the three oil samples taken in clean and dry bottles (500 ml) in triplicates were kept opened in a chamber ($12 \times 14 \times 12$ ft^3, RH 60–70%, 30 °C) which was aerated and exposed to daylight. Each of the three oil samples (taken from each of the triplicates) was then analyzed for PV, *p*-AV and IV after 1, 5, 10, 15, 20,

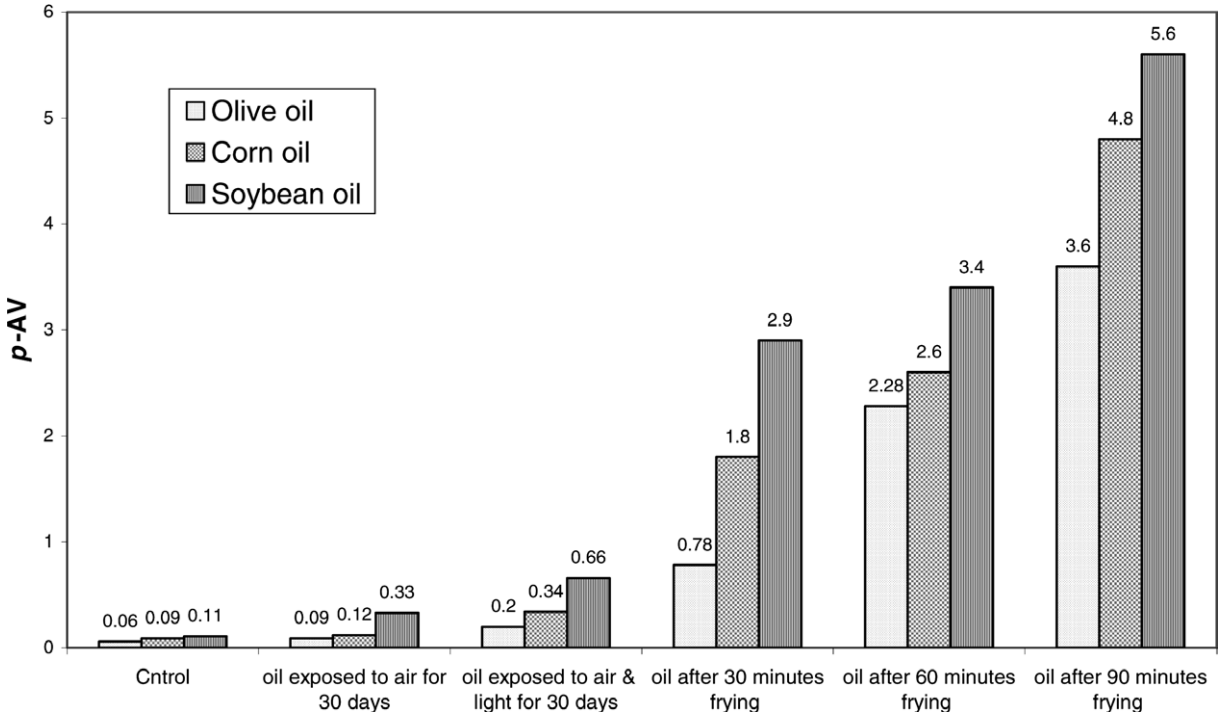


Fig. 2. Effect of air, light and deep-frying on *p*-AV of olive, corn and soybean oil.

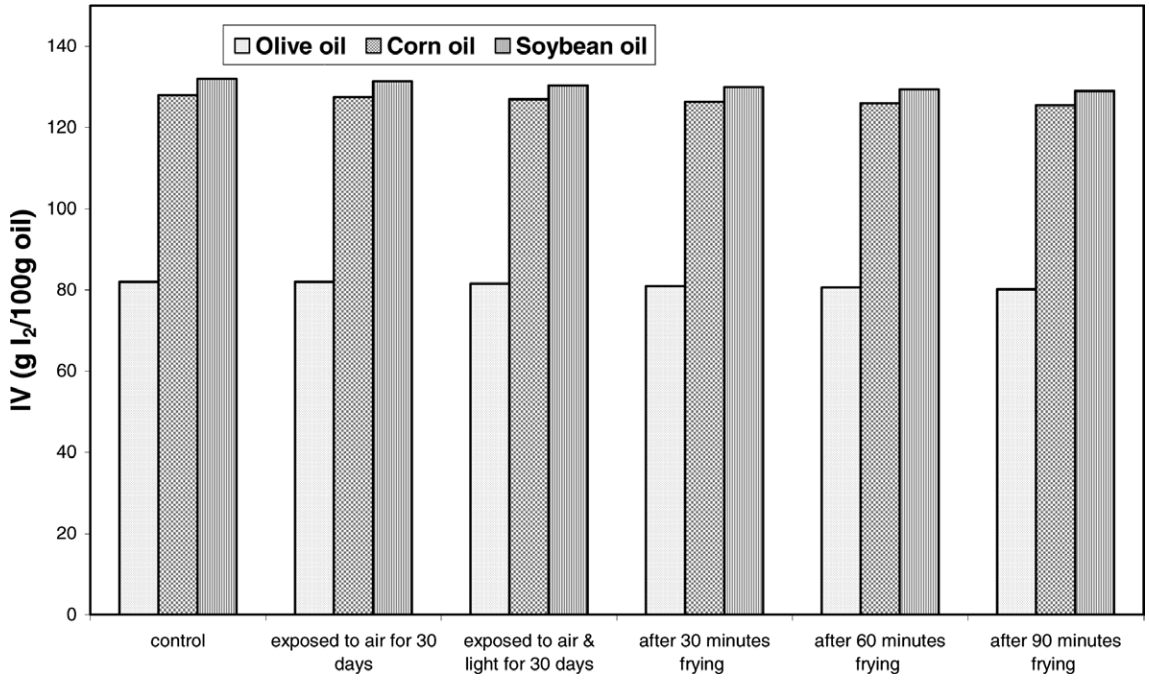


Fig. 3. Effect of air, light and deep-frying on IV of olive, corn and soybean oil.

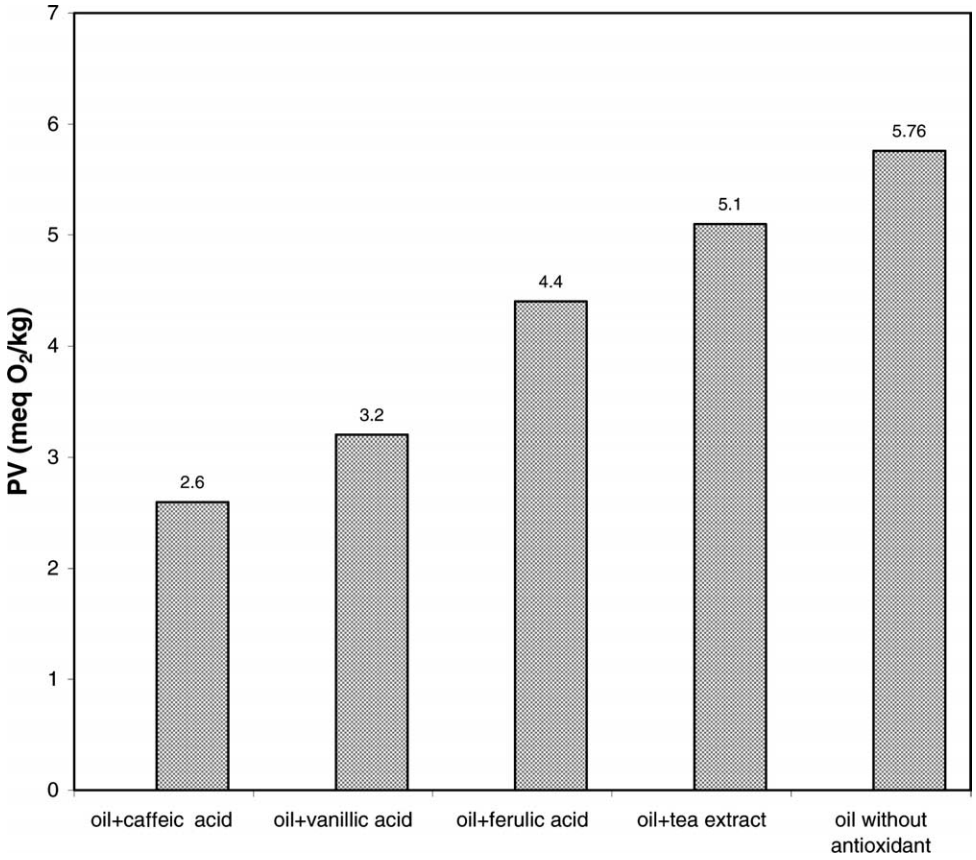


Fig. 4. Effect of adding antioxidant on PV of the corn oil used for deep-frying of French fries at 180 °C for 90 min.

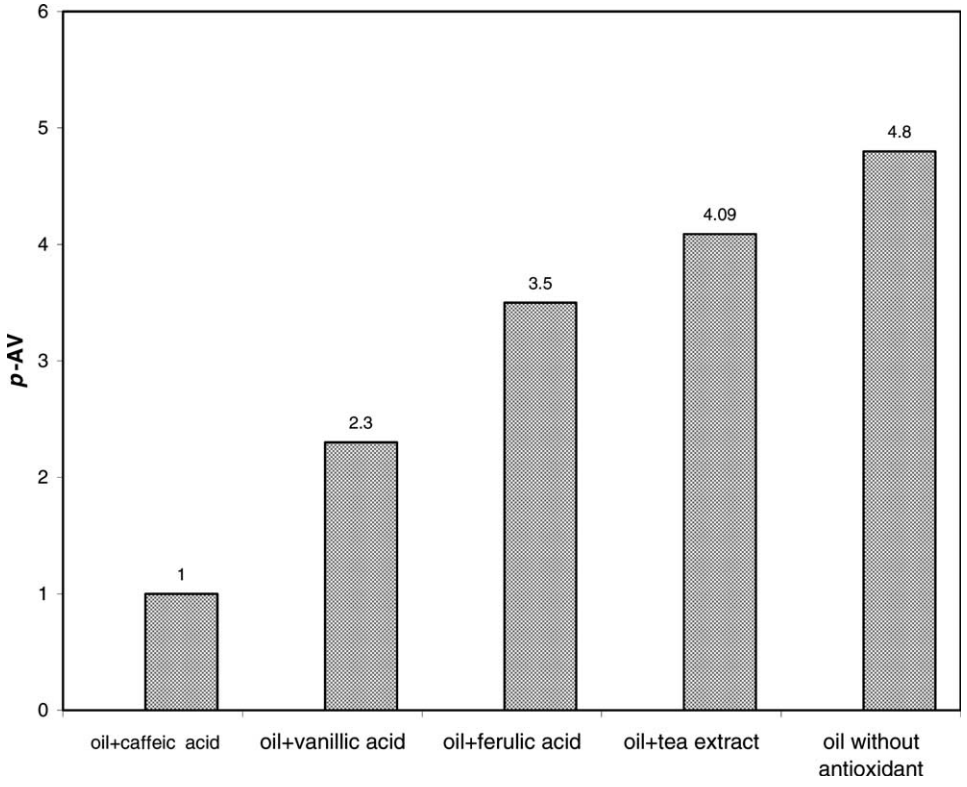


Fig. 5. Effect of adding antioxidant on *p*-AV of the corn oil used for deep-frying of French fries at 180 °C for 90 min.

25 and 30 days. Each of the observations was taken three times for all triplicates.

2.4. Analysis of the oil used for deep-frying

2.5 l, each, of the three oil samples were placed in a deep-fryer. 250 g of peeled potatoes were cut into cubical bars ($10 \times 10 \times$ 90 mm) and then fried at 180 °C for 30, 60 and 90 min. After frying, oil samples were cooled to room temperature and then analyzed in triplicate for change in PV, *p*-AV and IV.

2.5. Analysis of corn oil used for deep-frying in presence of added antioxidants

0.5 g of each antioxidant, namely caffeic acid (3,4-dihydrocinnamic acid, RDH, [331-39-5]), ferulic acid (4-hydroxy-3-methoxycinnamic acid, RDH, [1135-24-6]) or vanillic acid (4-hydroxy-3-methoxybenzoic acid, RDH, [121-34-6]) was dissolved in 25 ml of absolute ethanol. The ethanolic solution was then mixed with 2.5 l of the corn oil to be used for deep-frying. 0.5 g of ground, black tea leaves (mesh size 60) was extracted in 100 ml of ethanol. The extract was concentrated to 25 ml and then mixed with another 2.5 l of the three oil samples to be used for frying. Deep-frying for 90 min and further analysis was carried out as described in Section 2.4.

3. Results and discussion

The refined vegetable oils selected for the study were olive, corn and soybean. The selection of corn and soybean oils was made owing to their common use as cooking media and also high relative reaction rates of their unsaturated fatty acids with oxygen (List & Erickson, 1985).

The reason for including olive oil in the study was its relatively low reactivity with O_2 so that a comparison could be made between the reaction rates of oils of varying inherent stability (Christian et al., 2000).

To follow the oxidation rate in each oil sample, the samples were analyzed periodically for PV, *p*-AV and IV, since a single reaction criterion is not enough to account for the oxidative changes at various stages under different conditions.

PV and *p*-AV values increased in the order: deep-frying > air-light exposure > air exposure (Isabei & Mariano, 2001; Matalgyto & Al-Khalifa, 1998) (Figs. 1 and 2). Since autoxidation, which starts with the

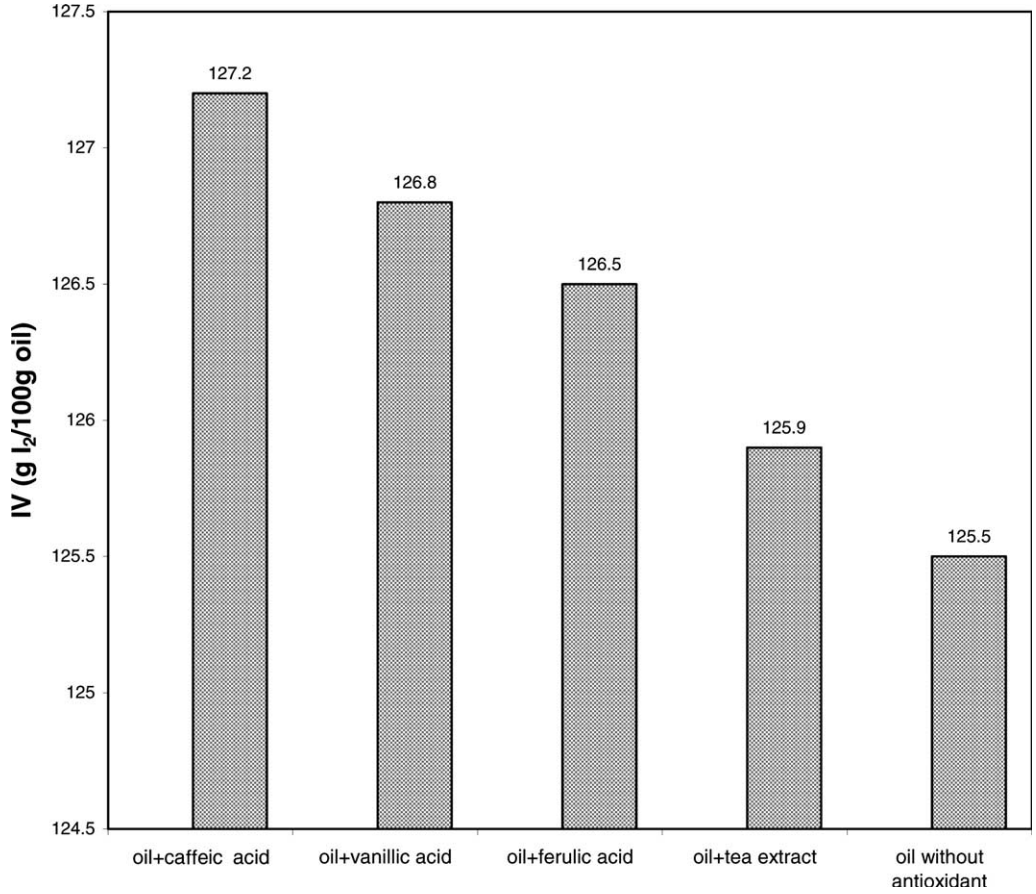


Fig. 6. Effect of adding antioxidant on IV of the corn oil used for deep-frying of French fries at 180 °C for 90 min.

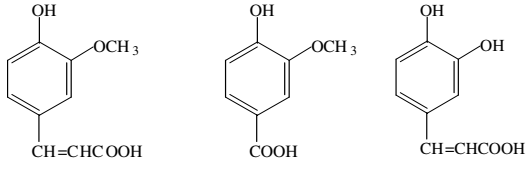
abstraction of hydrogen adjacent to a double bond in a fatty acid (RH), is catalyzed by light and heat to form a free radical (R·) PV and *p*-AV values in the oils exposed to air only were significantly lower than those in oils exposed to air-light and the oil used for deep-frying (Isabei & Mariano, 2001; Matalgyto & Al-Khalifa, 1998). Olive oil gave the lowest values while soybean gave the highest. The values of corn oil were intermediate between the two. The lower values given by olive oil compared to soybean and corn oil are as expected from the fatty acid composition of the oils and, hence, their inherent stability.

IVs of all the oil samples exposed to air and air-light did not change significantly whereas deep-frying substantially reduced the IVs (Fig. 3). Oxidation, which consists of a complex series of chemical reactions, is characterized by a decrease in the total unsaturated content of the oil due to abstraction of hydrogen adjacent to a double bond and the formation of free radicals. Hence the deep-frying, which could accelerate the oxidation in the oil at a faster rate, would also cause maximum reduction of the IVs.

The effects of adding antioxidants (caffeic, vanillic and ferulic acids) and the crude tea extract on PV, IV and *p*-AV of the corn oil were analyzed after deep-frying for 30, 60 and 90 min at 180 °C. All antioxidants effectively reduced the oxidation rate in the oil, as detected by decrease in PVs and *p*-AVs and relatively low reduction in IVs (Figs. 4–6). The order of antioxidative activity was: caffeic acid > vanillic acid > ferulic acid > tea extract (Xiaoying & Ahn, 1998; Bozidar et al., 1998). This difference in activity may be accounted on the basis of their chemical structures (see Fig. 7).

Vanillic and ferulic acids are hindered phenols, since the -OCH_3 group *ortho* or *meta* to the hydroxyl group suppresses antioxidant activity. This steric hindrance is likely responsible for the relative ineffectiveness of vanillic and ferulic acids. In addition, the caffeic acid, having two -OH groups at adjacent positions, acts as a chelator for most of the metal ions that act as pro-oxidants and that may catalyze the reaction even if present in trace amounts.

The least affect of the tea extract as an antioxidant may be attributed to impurity or crudeness of the antioxidants in the extracts.



Ferulic acid Vanillic acid Caeffic acid

Fig. 7. Phenolic structures.

4. Conclusion of the study

Continuous exposure of oil to air and light enhances oxidative changes in the oil and these changes become very fast in frying oil. The level of primary oxidation products (indicated by PV) may be enhanced on exposure of oil just to air and/or light and the levels of secondary oxidation products (indicated by *p*-AV) become significant upon heating/frying. It is obvious from the values obtained in the case of the control, samples exposed to air or air-light that, though the oxidative changes in these samples are not too fast, initiation of the reaction is possible even at very low concentration of O_2 and diffused light in a very short period of time.

The addition of an antioxidant to oils is most useful at the initiation stage as the PV and *p*-AV, after 90 min frying of the corn oil in the presence of caffeic acid, are very close to the values obtained for the control.

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