PHYSICOCHEMICAL CHANGES OF OLIVE OIL AND SELECTED VEGETABLE OILS DURING FRYING

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ABSTRACT

The performance of olive oil during intermittent frying of potato slices and cod fillets was compared to those of selected vegetable oils (corn, olive-residue and 50/50 mixture of olive and corn oils) using conditions resembling those used in home food preparations. The main scope of this study was to decide what is the best substitute for olive oil in home frying applications. Free fatty acid content, peroxide value, polar compounds, color and viscosity were increased, whereas iodine value, polyunsaturated fatty acids content and tocopherol concentration decreased. The organoleptic quality of potato slices and cod fillets fried in all oils was determined. Significant differences in the physicochemical changes were observed. The analytical and sensory data showed that the lowest deterioration occurred in olive oil and the highest in corn oil. The 50/50 (w/w) olive/corn oil mixture proved to be a good substitute for olive oil in domestic frying applications.

INTRODUCTION

Olive oil is an important commodity in the daily diet of most people in the Mediterranean region. It is extracted from the fruit of olive tree, *Olea europea*.

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Its advantage among vegetable oils is that it can be consumed in crude form, which is known as virgin olive oil. The term “olive-residue oil” applies to the oil obtained from the residue (remaining cake) after mechanical extraction of the oil from olives. The cake is coarsely ground, partially dried and extracted with a solvent, in a continuous or batch process, refined, bleached and deodorized in the refinery. Corn (maize) oil is the oil extracted from the cereal grain, *Zea mays* L. Additionally, a 50/50 (w/w) mixture of olive/corn oils was included because it is a common practice to mix such oils at home.

The previously mentioned oils were used in this study because of their major commercial role as frying oils in domestic applications in the Mediterranean countries. Deep-fried foods, especially fried potatoes and cod, are becoming more and more popular in Greece. The surplus of olive oil in countries of the Mediterranean region has made it the most common oil used for frying in home food preparations, and consumers are accustomed to its characteristic flavor. However, olive oil is a valuable natural product that provides an excellent and unique flavor and nutritional benefits. Thus, it is important to preserve these unique characteristics. Needless to say, olive oil is more expensive than vegetable oils.

This study aimed to investigate the changes in oil quality characteristics and fatty acid composition of selected oils under frying conditions using a combination of analytical methods. The main scope was to find the best substitute for olive oil in home frying preparations.

MATERIALS AND METHODS

Virgin olive, corn and olive-residue oils were obtained from a local market. The olive/corn oil mixture was prepared by mixing the oils at 50/50 (w/w).

Frying Experiment

The method used for the frying experiment of potatoes and cod was adapted from that developed by Tsaknis and Lalas (2002). Potatoes and skinless cod fillets were deep-fried independently, each in 2 L of oil. The potatoes were peeled and washed 1 h before use, and were sliced into 0.5-cm-thick and 2.5-cm-wide discs using a mechanical slicer. The skinless cod fillets were cut into square pieces ($3 \times 3 \times 1.5$ cm) and coated with wheat flour. When the oil temperature reached 175C, a 100-g batch of cod fillets was fried in separate oil samples. Five discontinuous fryings were carried out in five consecutive days at 2 h and 30 min per day. The frying time was 8 and 6 min for the cod fillets and potato slices, respectively. At the end of the fryings each day, a 50-g sample of oil was removed from each fryer and stored at 0C. The fryers were then capped with their lid and the fryings were continued the following day. Fresh oil was never added to the frying pans.

Determination of the Physical and Chemical Characteristics

Color was measured according to the AOCS (1978) cc13c-50 method. The viscosity was measured using a Brookfield viscometer (Brookfield Engineering Labs, Inc., Middleboro, MA) at 25C. Acidity (IUPAC 1987), iodine value (Pearsons 1981) and polar compounds (IUPAC 1987) were also determined.

Fatty acid composition was determined by gas–liquid chromatography (GLC) according to the method of Tsaknis *et al.* (1999). Analysis was performed on a Varian 3600 gas chromatograph (Varian, Palo Alto, CA) equipped with a Supelcowax 10 (Sigma-Aldrich Co., Bellefonte, PA)-fused silica capillary column 30 m × 0.32 mm internal diameter with a 0.25-µm film thickness.

The method used for the determination of tocopherols was adapted from Tsaknis *et al.* (1999). The samples were injected into a Waters 600E high-performance liquid chromatography (HPLC) pump (Millipore Corporation, Waters Chromatography Division, Milford, MA) fitted with a Waters µ-orasil, 125 Å, 10-µm, 3.9 × 300-mm column (Millipore Corporation). A Waters 486 tunable absorbance detector was used (Millipore Corporation).

For the determination of the oxidative state, the peroxide value (PV) was determined according to the method reported by Lea (1952). Meanwhile, sensory evaluation was carried out by a number of panelists who tasted the potatoes and cod for the overall characterization of the organoleptic properties (appearance, color, flavor and texture) after each batch was fried. A taste panel score sheet with a numerical scale of rating was developed using descriptive terms against each numerical score for each quality parameter.

RESULTS AND DISCUSSION

Iodine Value

The results showed that there were no significant changes ($P < 0.05$) between fresh and used oils 5 days after frying the potatoes. The decrease of iodine value 5 days after frying the cod was significant only in the corn oil. The decrease of iodine value correlated well with the decrease of unsaturated fatty acids ($r = 0.952$). Moreover, this analysis confirmed that less oxidation of unsaturated fatty acids took place in olive oil and the highest occurred in corn oil. Iodine value decreases are indicative of increased rate of oxidation during frying and could be attributed to oxidation and polymerization reactions involving the double bonds, whether through chain reactions adjacent to the double bond to form volatile degradation products or through direct interaction across the bond to form 1,2-diol (Alim and Morton 1974).

PV

The olive and mixed oils where the potatoes were fried showed a significant increase ($P < 0.05$) in their PV after 10 h of frying, while in the olive-residue and corn oils, a significant change ($P < 0.05$) occurred after only 8 h of frying. All the oils, except the olive-residue oil, showed an increase in PV during the heating period. The olive-residue oil showed a decrease in PV after 6 h of frying. Further frying resulted in a new increase in PV. In the oils where the cod were fried, there was a significant increase ($P < 0.05$) in PV in the corn oil after 6 h of frying, while in the other oils, the change was significant after 8 h of frying. Peroxides are unstable under frying conditions, and break down secondary oxidation products. An increase in the initial stage of frying is expected to be followed by a decrease with further heating, because the hydroperoxides tend to decompose at 180C to form secondary oxidation products (Perkins 1967). The overall increase in PVs connected with the cooling period of the oil. The length of time required to cool the oils at room temperature (25C) when frying was finished was more than 4 h. During the cooling period, the oils were exposed to air at high temperature and hydroperoxides were formed again (Augustin and Berry 1983).

Color

The results showed that in both foods, the increase in color was significant ($P < 0.05$) in the olive and mixed oils after 8 h of frying, while in corn oil, the increase was significant after only 6 h. The increase in color content was attributed to the alpha, beta-unsaturated carbonyl compounds, which are intermediates to give nonvolatile decomposition products containing carbonyl group and have the ability to absorb energy of the magnitude of visible light (Gutierrez *et al.* 1988).

Viscosity

The results showed that in both foods, the increases in viscosity were significant in olive oil after 8 h of frying, while all the other oils showed a significant increase ($P < 0.05$) after only 6 h of frying. As the oxidation accelerated by heat proceeded, the values of viscosity progressively increased (Tyagi and Vasishtha 1996). These results clearly indicated the higher deteriorative effect of oxidation and polymerization of corn and olive-residue oils

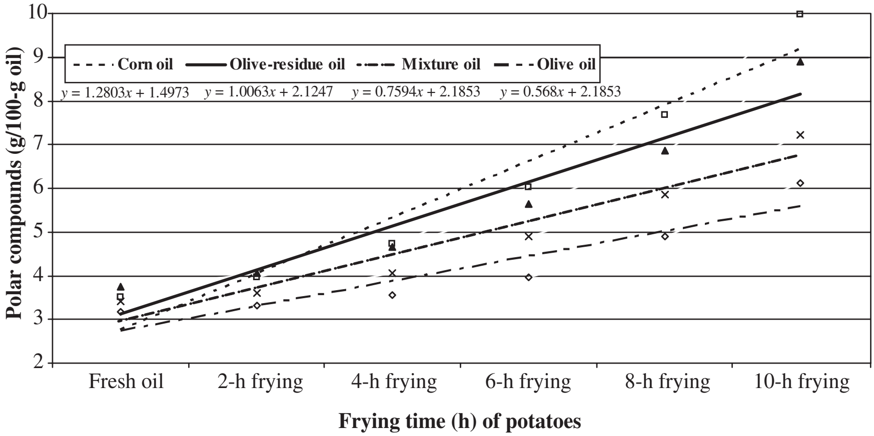

FIG. 1. LINEAR ADJUSTMENTS ($y = Ax + B$) OF POLAR COMPOUNDS VERSUS FRYING TIME (h) OF POTATOES
◇, olive oil; □, corn oil; ▲, olive-residue oil; ×, mixture oil.

compared to olive and mixed oils. The increase in viscosity of frying oils was a result of polymerization that resulted in formation of higher molecular weight compounds (carbon-to-carbon and/or carbon-to-oxygen-to-carbon bridges) between fatty acids (Al-Harbi and Al-Kabtani 1993).

Polar Compounds

The results showed that in both foods, the increases of polar compounds were significant in olive oil after 8 h of frying, while all the other oils showed a significant increase after only 6 h of frying. Fritch (1981) reported that the analysis of percentage polar compounds is considered to be one of the more reliable indicators of the state of the oil deterioration. This statement is supported by those of other researchers (Gutierrez *et al.* 1988). Billek *et al.* (1978) stated that any heated cooking oil with 27% or more polar compounds should be discarded. These results showed that using this criterion, the used frying oils had not reached the end of their useful heating life after 10 h of intermittent frying. The determination of the total hours of frying before the polar compounds reach the 27% critical level mark was carried out using the linear equation, which is more adequate because there was no replenishment with fresh oil, and the polar compounds kept increasing until the end of the fryings (Tsaknis and Lalas 2002). The linear equations (Figs. 1 and 2) showed that the critical level of 27% of polar compounds would be reached after: (1) 43 or 36.9 h (potatoes and cod, respectively) of frying in olive oil; (2) 32.7 or 29.1 h

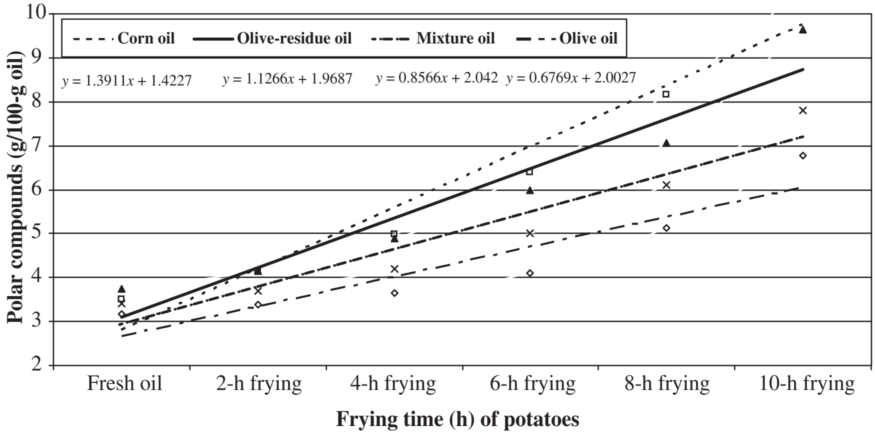

FIG. 2. LINEAR ADJUSTMENTS ($y = Ax + B$) OF POLAR COMPOUNDS VERSUS FRYING TIME (h) OF COD
◇, olive oil; □, corn oil; ▲, olive-residue oil; ×, mixture oil.

(potatoes and cod, respectively) of frying in mixed oil; (3) 24.7 or 22.2 h (potatoes and cod, respectively) of frying in olive-residue oil; and (4) 19.9 or 18.4 h (potatoes and cod, respectively) of frying in corn oil. Figures 1 and 2 represent estimation of the frying life (before having to discard) of the four oils used for frying by using a linear equation.

Free Fatty Acid (FFA) Content (Acidity)

A slight but not significant increase was observed after 10 h of frying in all the oils at the 95% level of significance for both products (Student's *t*-test). Olive oil showed the lowest increase, while corn oil showed the highest. The increase in FFA could be attributed to oxidation and hydrolysis, which produces FFAs (Peeled *et al.* 1975; Abdel-Aal and Karara 1986). Moreover, FFA content is a dynamic value because at the same time that the acids are being produced, they have sufficient vapor pressure at frying temperatures to evaporate from the surface (Peeled *et al.* 1975).

FAME Analysis by GLC

Experiments showed that after 10 h of frying, the saturated fatty acid content of all four oils increased as the polyunsaturated fatty acid (PUFA) content decreased. However, this decrease was not significant in the used oils, with the only exception of corn oil, which showed a significant decrease ($P < 0.05$) in linoleic acid, when it was fried with cod. The loss of linoleic acid was noted to be the lowest in olive oil. Varela (1980) showed that PUFAs found in olive oil, such as linoleic acid, are more readily oxidized and polymerized than the less PUFAs. Subsequently, such monounsaturated oils as olive oil are less altered during frying than other polyunsaturated ones such as corn or safflower oils. The present results also confirm this observation.

HPLC of Tocopherols

The relative decomposition rates of tocopherols after 10 h of frying with potato oils were $\delta > \gamma > \alpha$. The decrease of α-tocopherol in the four oils was 36.9, 39.1, 41.2 and 47.5% for the mixed, corn, olive and olive-residue oils, respectively. The changes of γ- and δ-tocopherols were γ- (–55.6%), δ- (–100%) and γ- (–57.9%), δ- (–78.5%) for the mixed and corn oils, respectively. The decrease of tocopherols in the oils where the cod were fried seemed to follow the same trend. Furthermore, the results demonstrated that α-tocopherol is more stable during frying of oils than γ- and δ-tocopherols. The oxidative stability of olive oil is related to some extent with the higher amount of α-tocopherol that it contains, compared with the other three oils. The results are in agreement with those of Sonntag (1991), who reported that the decomposition rates of tocopherols, after 10 h of frying, were $\gamma > \delta$. Lea (1960) showed that the order of antioxidant activity changed with the oil used for the experiment. In contrast Miyagawa *et al.* (1991), using a mixture of soybean and rapeseed oils, found in his experiments that the decomposition rates of tocopherols were $\gamma > \delta > \alpha$ after 32 batches of frying.

Sensory Evaluation

The results of food acceptance tests carried out by a trained team of tasters by means of triangular identification tests complemented by evaluation tests showed that of all the oils tested for frying instability, olive oil was the most stable; e.g., on frying potatoes, olive oil can be used 20 times without quality deterioration, but for mixed, olive-residue and corn oils, frying in the same way could only be done 15, 12 and 10 times, respectively; while on frying of cod, olive oil can be used 15 times without quality deterioration, but for mixed, olive-residue and corn oils, frying in the same way could only be done 12, 10 and 7 times, respectively.

Correlation Between Analytical Methods During Frying

Correlation coefficients (r^2) between each pair of analytical values were calculated to study the degree of association between two characteristics taken under consideration. The highest correlation was obtained between FFAs and polar compounds ($r^2 = 0.963$), and between polar compounds and viscosity ($r^2 = 0.953$).

All the analytical methods used in this study are indicators of the state of oil deterioration. However, no parameter alone can judge heating life adequately in all situations. The changes in characteristics and composition of used oils showed that olive oil was more stable during frying, while corn oil proved to be the least stable. Between the two foods used, cod caused a more rapid deterioration in the oil quality because of the leaching of fish oil from the cod, which is rich in PUFAs that are rapidly oxidized. The mixed oil (50/50 w/w, of olive/corn oils) proved to have the second stable oil during frying. Therefore, the olive/corn oil mixture appears to be a good substitute for olive oil in domestic frying applications.

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