



Effects of Heating and Storage on Nutritional value of Sunflower Oil

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ABSTRACT

It is known that prolonged heating of oils and exposure to air increases the rancidity of oils. The objective of the present study was to analyse the composition of fresh and smoked sunflower oil and assess the impact of heating and storage on the nutritive value of the oils with respect to free fatty acid content, degree of primary oxidation, total polyphenol content and flavonoid content.

Methods: Three brands of sunflower oil were purchased from the market, heated to their smoke point and assayed (both fresh and smoked) at 7 day intervals for 4 weeks. The following parameters were estimated: acid value, peroxides (by peroxide value method), polyphenols (Foilin-Ciocalteu method), and flavonoids (aluminum chloride method).

Results and Conclusion: Prolonged heating increased the free fatty acid content in the oil which would increase its susceptibility to rancidity on exposure to air. Smoking of oil also significantly decreased the total polyphenol and flavanol content in the oils, thereby decreasing their antioxidant nutritive values. Storage in airtight containers did not affect the nutritive content of the oils. The increased acid value and peroxide value in smoked oils is associated with a decreased shelf life.

Key words: Flavanols, Polyphenol, Smoking, Storage, Sunflower oil.

INTRODUCTION

Vegetable oils are triglycerides extracted from plants: Sunflower oil is obtained from the compression of sunflower (*Helianthus annuus*) seeds. It is mostly a triglyceride with mixed monounsaturated/polyunsaturated fatty acids (oleic and linoleic group of oils).

Though variations exist in different varieties of sunflower oils, these variations are minor and the values reported are a mean of most published values.

The British Pharmacopoeia lists the following profile (1)

- Palmitic acid (saturated) : 5%
- Stearic acid (saturated): 6%
- Oleic acid (monounsaturated omega-9): 30%
- Linoleic acid (polyunsaturated omega-6): 59%

Sunflower oil is high in the essential vitamin E and low in saturated fat.

The nutritive value of oils, and the comparative advantages and disadvantages of various types of oils are due to the differences in their fatty acid composition. The human body is unable to synthesize some essential polyunsaturated fatty acids (such as linoleic and linolenic acids) and thus require these to be present in their diet; Unsaturated fatty acids (especially PUFAs) have also been shown to decrease the risk of heart attacks and strokes, whereas saturated fats and *trans* fats have been shown to raise LDL cholesterol and triglycerides in blood plasma, while simultaneously lowering HDL cholesterol causing increased risk of cardiovascular disorders (2). Polyphenols (a class of organic compounds characterized by the presence of large multiples of phenol structure units) in certain oils, such as olive oil, provide certain health benefits because of their antioxidant, antimicrobial and anti-inflammatory activities (3). Flavonoids- a class of plant secondary metabolites- have become the focus of intense research because of their biological and pharmacological activities in *in-vitro* studies; they have been shown to have anti-inflammatory, anti-oxidant and anti-microbial activities (4,5). Heating for prolonged periods as well as exposure to air/oxidation are known to decrease the nutritive value of oils. Thermal decomposition of flavanols and polyphenols has been reported after heating of Extra Virgin Olive oil at 220° C for 100 min and on storage at 25° C for 2 weeks (6,7). Most of the literature available is done on varieties of Olive oil and Corn oil. Limited work is available for Sunflower oil. Also in most studies the effect of heating or the effect of storage has been recorded. Here we have done the effect of both heating and storage together. This is primarily to see if heating decreases the shelf life of oils.

METHODS

Experimental Design

Three popular brands of sunflower oil were purchased from the market. The oils were heated till visible smoke could be seen for assessment of smoke point. Heating was done for 30 minutes after reaching the smoke point. Assays for each of the tests listed below were done at weekly intervals for each of the oils varieties (in triplicate); each test was done with a 7 day gap, and all the sample readings were taken on the same day. The oils were stored in plastic containers in a cool dry place in the interim (as recommended on by the manufacturer).

Acid Value Determination

Acid Value of the oils was determined by a standard titrimetric method. 5 grams of an oil sample was taken in a titration flask. To this, 25 mL of solvent (ethanol + ethyl ether) was added and shaken well so that the oil dissolved in it. 2 drops of 1 % phenolphthalein solution were added to the titration mixture and mixed well. This was now titrated against the 0.1N KOH till a persistent faint pink color was observed.

The volume of KOH used was noted. The titration was repeated until three concordant readings of volume of KOH were recorded. Similarly, three concordant readings were recorded for each oil sample.

$$\text{Acid value} = \frac{\text{titer value} \times \text{normality of KOH} \times 56.1}{\text{Weight of sample (g)}}$$

Peroxide value determination

Peroxide value is defined as the amount of peroxide oxygen per 1Kg of fat or oil. S.I. Unit of this parameter is millimoles/Kilogram. The value is determined by Titrimetric analysis. The amount of Iodine formed by the reaction of peroxide with iodide ion is a measure of peroxide oxygen.



The base hence released is taken up by Acetic Acid. The liberated I_2 is titrated against 0.1 N Sodium Thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$).



Total Polyphenol Content

The concentration of polyphenols was done by Folin-Denis method. Triplicates of standards of Gallic acid were prepared in distilled water. The oil samples, in triplicates, were prepared by mixing with n-hexane and methanol: water (80:20) followed by centrifugation. The lower layer was separated and vortexed again with methanol: water, and the lower layer was collected and stored overnight. Folin-Denis reagent was added to standards and samples followed by incubation and addition of Sodium carbonate and another round of incubation. Absorbance was measured at both 700 and 750 nm and the polyphenol content was determined by extrapolation of the plotted graph (8).

Total Flavonoids Content

Triplicates of standards of Quercetin in DMSO were prepared. The oil samples, in triplicates, were prepared by extraction in n-hexane followed by extraction in methanol: water(1:1). The final extract was incubated overnight at 25° C and then used for flavonoid estimation by Aluminum chloride method (9).

RESULTS AND DISCUSSION

All tests were performed in triplicate for each brand and the results presented are a mean \pm S.E of n=9. Variation between brands was similar to variation within brands.

The Smoke point of fresh and smoked oil as shown below was not significantly different.

- a. Fresh: 221.44 ± 1.09 °C
- b. Smoked: 227.21 ± 3.869 °C
- c.

The following observations could be made of the result shown below:

1. There was an increase in the acid value of smoked oil, which showed a statistical significance of $p \leq 0.05$ after 3 weeks of storage. (Table-I and Figure-I)
2. There was a general trend of increasing peroxide values, and thus of amount of oxidation in the oil, with time (Table-I and Figure-II). There was no difference in peroxide values in fresh versus smoked oils, except after 4 weeks of storage which showed a decrease in peroxide value in smoked oils but the decrease was not significant.
3. There was a significant ($p \leq 0.05$) decrease in concentration of polyphenol content in smoked oil after 4 weeks of storage.(Table-I and Figure-III)
4. There was a decrease in flavonol concentration in the oils after smoking, however the decrease was not significant. (Table-I and Figure-IV)

Table-I: Summary of the results for acid value, peroxide value , polyphenol and flavanol contents of fresh and smoked oil. (n=9)

| Test | Units | WEEK 1 | WEEK 2 | WEEK 3 | WEEK 4 |
|--------------------------|---------------------------|-----------------|-----------------|-----------------|-----------------|
| Acid Value | FRESH (mEq/g) | 0.748 ± 0.0934 | 0.6545 ± 0.0934 | 0.748 ± 0.0934 | 0.561 ± 0 |
| | SMOKED (mEq/g) | 0.935 ± 0.0934 | 0.8415 ± 0.1618 | 1.0283 ± 0.1337 | 0.6545 ± 0.0934 |
| Peroxide Value | FRESH (mEq/Kg) | 7.333 ± 2.402 | 8.0 ± 1.998 | 10.666 ± 2.905 | 13.333 ± 3.527 |
| | SMOKED (mEq/Kg) | 6.666 ± 1.333 | 6.666 ± 1.333 | 10.666 ± 2.403 | 7.333 ± 3.3336 |
| Total Polyphenol Content | FRESH (µg/mL of extract) | 13.833 ± 3.3832 | 10.332 ± 1.9528 | 11.444 ± 2.8822 | 14.777 ± 2.4058 |
| | SMOKED (µg/mL of extract) | 11.333 ± 1.5892 | 7.777 ± 1.6026 | 9.775 ± 2.310 | 8.666 ± 1.332 |
| Flavonoid content | FRESH (µg/mL of extract) | 0.1098 ± 0.018 | 0.032 ± 0.0063 | 0.134 ± 0.012 | 0.097 ± 0.008 |
| | SMOKED (µg/mL of extract) | 0.092 ± 0.015 | 0.0285 ± 0.003 | 0.085 ± 0.006 | 0.080 ± 0.007 |

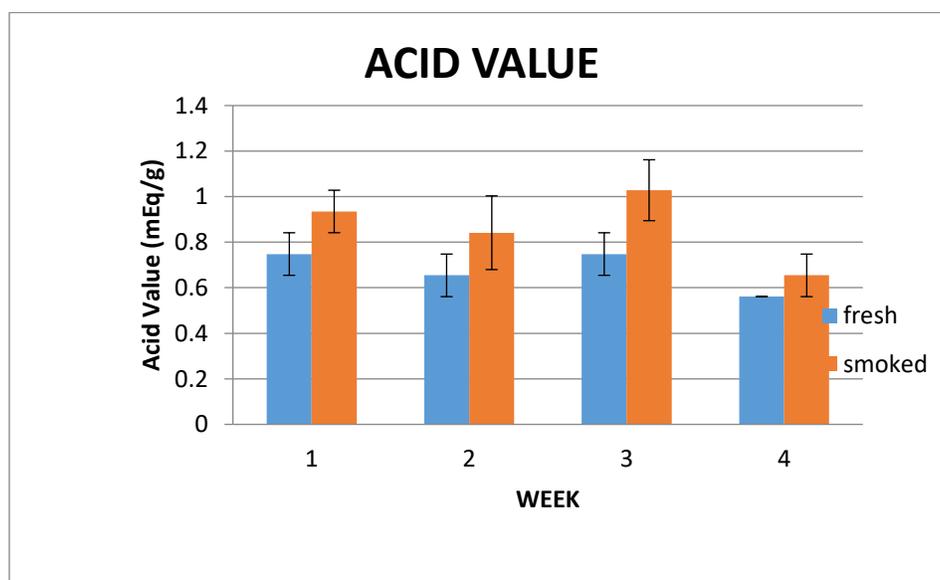


Figure-I: The graph shows Acid Values in mEq/g of commercially available Sunflower Oil samples (n=9) represented as mean ± S.E.

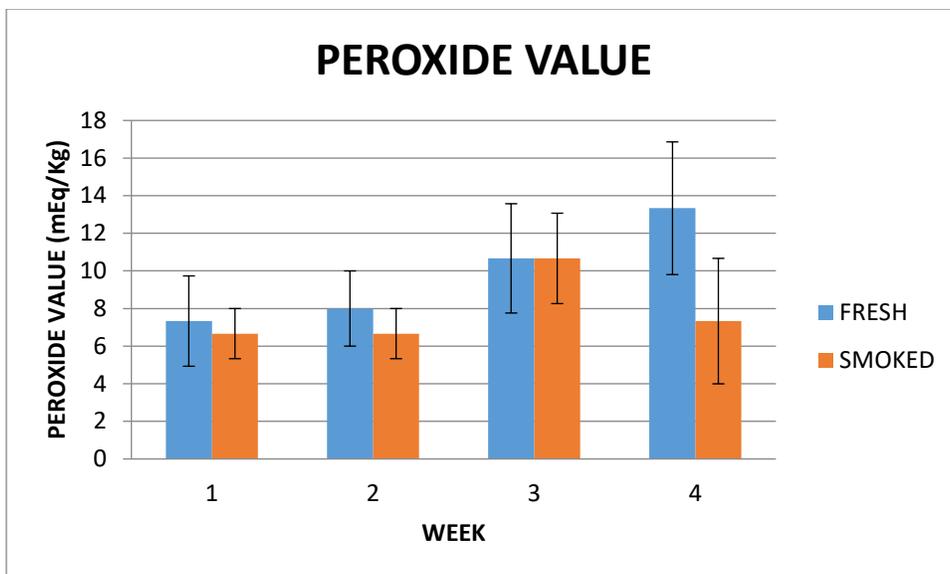


Figure-II: The graph shows Peroxide Values in mEq/Kg of commercially available Sunflower Oil samples (n=9) represented as mean \pm S.E.

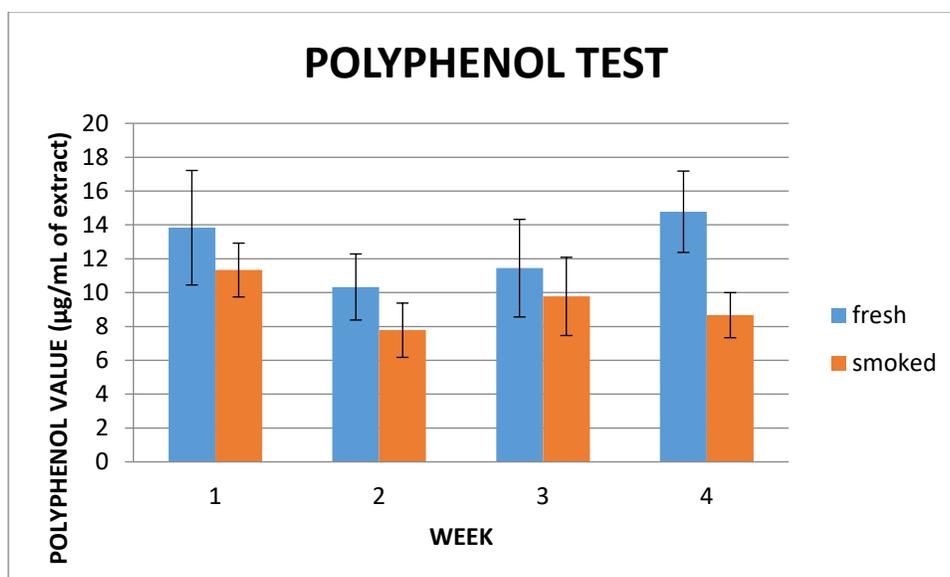


Figure-III: The graph shows Polyphenol Values in Gallic Acid Equivalence of commercially available Sunflower Oil samples (n=6) represented as mean \pm S.E.

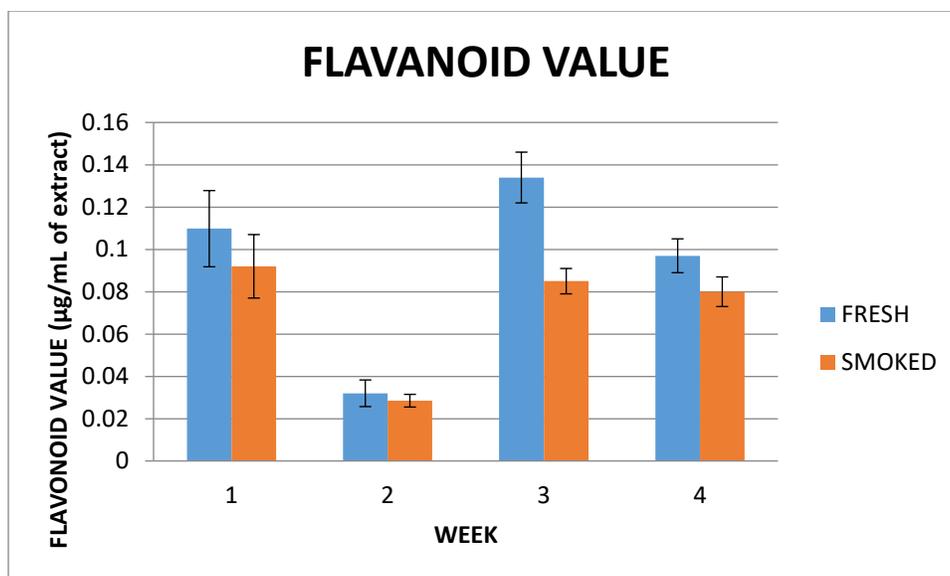


Figure-IV: The graph shows Flavanoid Values in of commercially available Sunflower Oil samples (n=6) represented as mean \pm S.E.

An increment in the acid value of any oil is indicative of an increment in the amount of FFA (Free fatty acid) which indicates hydrolysis of triglycerides. Such a reaction occurs by the action of lipase enzyme and it is an indicator of inadequate processing and/or storage conditions (i.e., high temperature and relatively high humidity). In the present study, the increase in acid value seen in smoked oils shows that smoked oils have a lower shelf life as compared to non-smoked oils. The fall in acid value after 4 weeks of storage can probably be accounted for by the conversion of the free fatty acids, particularly PUFA, to oxidation and accumulation of their breakdown products like ketones, alcohols, and aldehydes. The peroxide value is a parameter specifying the content of oxygen present as peroxide, especially hydroperoxides. Measurement of the concentration of peroxides and hydroperoxides formed is indicative of the initial stages of lipid oxidation. It is a shelf life indicator test for the initial stage of auto-oxidation process. Detection of peroxide gives the initial evidence of rancidity in unsaturated fats and oils and it gives a measure of the extent to which an oil sample has undergone primary oxidation. The present study confirms reports that storage of oils increases their susceptibility to oxidation. Oils such as sunflower oil, with a high degree of unsaturation, are most susceptible to auto-oxidation. Increased acid value and peroxide value in smoked oils is associated with a decreased shelf life (10). The present study shows that heating oils and their subsequent storage will increase their susceptibility to auto-oxidation and accumulation of rancid byproducts.

Smoking of oil also significantly decreased the total polyphenol and flavanol content in the oils, thereby decreasing their antioxidant nutritive values. Several studies have revealed that phenols, mainly the type of flavonoids, from some plant oils are safe and bioactive, and have antioxidant properties and exert anticarcinogenic, antimutagenic, antitumor, antibacterial, antiviral, and anti-inflammatory effects. The overall decrease in total polyphenol and flavanoid content also indicates a decrease in the nutritional values of oils after smoking and storage (3,5).

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