Effects of Fluorescent Light Oxidation on the Physico-Chemical Properties of *Silybum marianum* and *Helianthus annuus* oils

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Summary: The effects of fluorescent light on the quality parameters of crude *Silybum marianum* oil (SMO) and crude *Helianthus annuus* (sunflower) oil (HAO) were studied. The quality constants monitored were free fatty acid (FFA), iodine value (IV), peroxide value (POV), anisidine value (AV) color (OD) and β–carotene. Results revealed an increase in FFA, POV, and AV after storage under continuous fluorescent light irradiation. However, OD and IV decreased in both oils under the test conditions. More decrease in color was observed in *Silybum marianum* oil than *Helianthus annuus* oil, while a reverse trend was found in iodine value. The decrease in β–carotene concentration in both oils remained almost same. The crude *Silybum marianum* oil is found to be very sensitive to oxidation when exposed to fluorescent light than the crude *Helianthus annus* oil.

Introduction

Fats and oils are indispensable food factors [1]. They are extensively used for nutritional and industrial purposes [2]. They are used for delivering fat-soluble vitamins as carriers and contributing flavors to food [3]. Fats and oils supply essential fatty acids such as linoleic, linolenic, and arachidonic acids, which are not made by the body but are required by the body [4]. They are also used for producing drug dispersants in therapeutics [5,6]. Fats are the major source of energy, which supply about 9 calories per gram, compared with protein and carbohydrate that supply about 4 calories per gram. In calorie deficient situation, fats together with carbohydrate spare protein and improve growth rate [7]. In general, it is stressed that positive health benefits would be achieved by deriving 30-40 % of calories from dietary fats that have a 1: 1 ratio of polyunsaturated to saturated fatty acids [8]. Lack of information on the composition and utilization of the many and varied oil seeds indigenous to the topic are more of problem than is the real shortage of oils [9]. There exists already abundant data in literature on the proximate composition, mineral content and other characteristics of the more conventional oil seeds but this is lacking on the unconventional oil seed types. This study was conducted in response to these needs and in continuation of our effort to bring into focus the unconventional seed oils [10-12].

An acute shortage of edible oils in Pakistan has created considerable interest in developing new sources of oils and fats and in evaluating their nutritional and toxicological properties to establish their suitability for edible purposes. It is essential to bridge the demand and supply by some unconventional plants such as *Silybum marianium*. This plant could be a quite new source of edible oils and protein, but very limited primary scientific data is available in this regard.

Silybum marianum is an annual or biennial medicinal herb and has been widely used in European traditional medicine belonging to the family Compositae [13]. It is one of the thirteen noxious weeds and native to Asia Minor, North Africa, Southern Europe and Southern Russia. It is abundantly available as weed in Pakistan, from January to September, (peak period from May to August) it matures in June. It mostly grows on unutilized lands and can grow upto six feet tall and grows as problematic weed in wheat crops. Requirements are negligible.

In view of the present scenario of edible oils in the country, it is essential to bridge the gap of demand and supply by some endogenous, unconventional, plants. The study was under-taken to explore the possibilities of using this unwanted weed as a

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source of edible oil and protein in comparison with *Helianthus annuus* oil in quality and stability, which is quite related to this test plant in composition. The quality and stability of crude *Silybum marianum* and crude *Helianthus annuus* oils were tested under stress condition of fluorescent light oxidation.

Results and Discussion

The oil samples were kept for 12 weeks in fluorescent light and investigated for the changes in the physicochemical constants of *Silybum marianum* and *Helianthus annuus* oil as a function of peroxide value, free fatty acid, iodine value, anisidine value, color/ optical density and β-carotene. The measurement of these parameters were repeated after two weeks storage

One of the most widely used tests for oxidative rancidity is peroxide value; it is a measure of the concentration of peroxides or hydro peroxides formed in the initial stage of lipid oxidation. The peroxide value under fluorescent light condition increased from 16.17 meq/ kg to 185.0 meq/ kg with time having mean value of 102.1 meq/ kg for *Silybum marianum* oil and from 18.60 meq/ kg to 175.4 meq/ kg with a mean value 95.2 meq/ kg for *Helianthus annuus* oil and the increasing trend regarding the effect of fluorescent light (photo oxidation) on the peroxide value is presented in Fig. 1. The effect of fluorescent light on oils is associated with the series of reactions such as oxidation, decarboxylation, polymerization, isomerization and hydrogenation *etc.* which results in the formation of various off flavor compounds such as carbonyl, peroxides, acid and other saturated compounds.

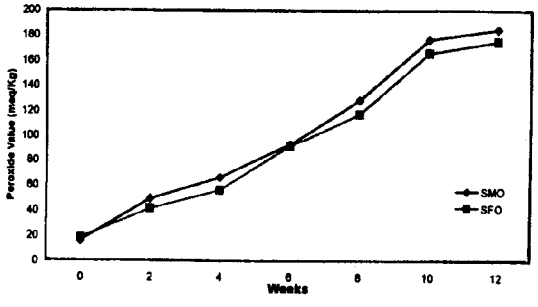

Fig. 1: Effect of fluorescent light on peroxide value of *Silybum marianum and Helianthus annuus* oil.

The effect of auto and photo oxidation on the oxidative stability of avocado oil compared with olive oil has shown that the avocado oil is more stable than olive oil [14]. Other studies have shown that the peroxide value of edible oils changes in fluorescent light with time and temperature [15].

Free fatty acids are produced by the hydrolysis of fats in the presence of water and enzymes lipase during storage. The fatty acid in *Silybum marianum* and *Helianthus annuus* oil is usually calculated in terms of (% oleic acid). In fluorescent light oxidation condition for 12 weeks storage the free fatty acid value increased from 17.92 to 20.54 % with mean value 19.06 for *Silybum marianum* oil and the range of variation for *Helianthus annuus* oil is 8.21 to 11.43 % having mean value 9.44. The increasing trend in free fatty acid value for both the oils is shown in Fig. 2.

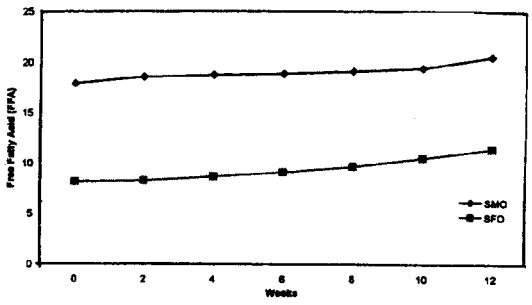

Fig. 2: Effect of fluorescent light on free fatty acid values of *Silybum marianum* and *Helianthus annuus* oil.

It has been investigated that free fatty acid value increases with light, heat and radiations [16, 17]. Earlier findings [18] have shown an increase in free fatty acid value in the oil samples exposed to the fluorescent light at room temperature. It has been reported by scientists who worked on edible rice bran oil and concluded that free fatty acid value depends upon the time factor [19].

Lipid hydroperoxide is very unstable and breaks down to an alkoxy free radical, which decomposes mainly by cleavage on either side of the carbon atom bearing the oxygen atom [14]. The anisidine value for *Silybum marianum* oil increased from 1.8979 to 11.633 in 12 weeks in fluorescent light oxidation with mean 6.278 while for *Helianthus*

annuus oil it increased from 0.8756 to 9.463 having mean value 4.985. It is clear from Fig. 3 that more increase in anisidine value has occurred in *Silybum marianum* oil during fluorescent light oxidation. Influence of fluorescent light oxidation on saturation was estimated by analyzing the oil for their iodine value.

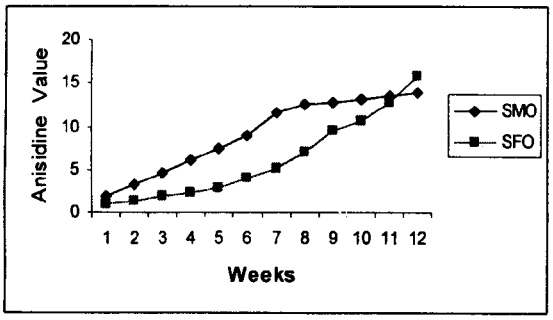

Fig. 3: Effect of fluorescent light on anisidine values of *Silybum marianum* and *Helianthus annuus* oil.

Silybum marianum oil has low iodine value 108.5 g/ 100g as compared to *Helianthus annuus* 116.07 g/ 100 g. The iodine value decrease during fluorescent light oxidation from 108.5 g/ 100 g to 86.6 g/ 100g with mean value 96.16 for *Silybum marianum* oil and for *Helianthus annuus* oil it decreases from 116.07 g/ 100 g to 92.15 g/ 100 g with mean value 103.3 g/ 100 g. It is clear from Fig. 4 that more decrease has occurred in case of *Helianthus annuus* oil in fluorescent light oxidation with passage of time. Other investigators have shown a decreasing trend in the iodine value of irradiated food samples [20,21].

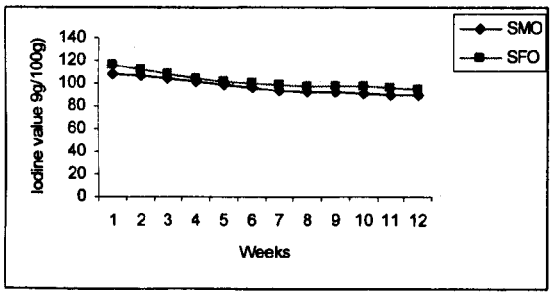

Fig. 4: Effect of fluorescent light on iodine values of *Silybum marianum* and *Helianthus annus* oil.

Natural fats and oils mostly contain β-carotene, which is the precursor of vitamin A. It acts as a strong natural antioxidant. A high level of β-carotene offers greater stability to the oil against rancidity. *Silybum marianum* oil has greater β-carotene content as compared to *Helianthus annuus* oil. In fluorescent light oxidation the value of β-carotene for *Silybum marianum* oil decreased from 18.76 ppm to 6.03 ppm with mean value 10.85 ppm and for *Helianthus annuus* oil it decreased from 13.49 ppm to 0.959 ppm with mean value 6.58 ppm as shown in Fig. 5. Earlier investigator [15] concluded that in the presence of light the rate of oxidation increased considerably with a corresponding decrease in the β-carotene. β-carotene has the ability to quench single oxygen, which is the primary source of hydro peroxides produced during auto and photo oxidation [22-24].

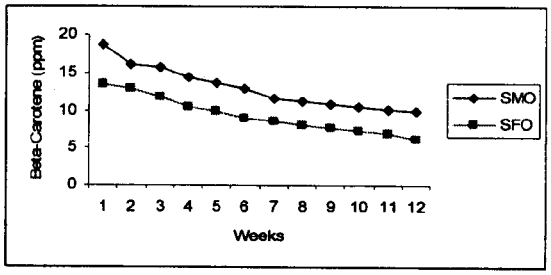

Fig. 5: Effect of fluorescent light on β-Carotene of *Silybum marianum* and *Helianthus annus* oil.

Color of oil is one of the important quality parameters. The effect of fluorescent light oxidation regarding color was determined in terms of optical density. After the completion of experimental period a decreasing trend in the range of 0.3413 to 0.2043 and from 0.2787 to 0.1880 was noted for *Silybum marianum* oil and *Helianthus annuus* oil respectively as shown in Fig. 6.

Experimental

Sample Collection

The fully ripened, sound and healthy seeds of *Silybum marianum* were collected from Peshawar valley, while *Helianthus annuus* seeds were obtained from Agriculture Research Institute, Tarnab, Peshawar.

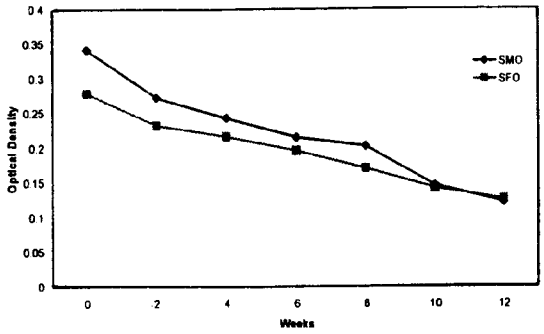

Fig. 6: Effect of fluorescent light on colour of *Silybum marianum* and *Helianthus annus* oil.

Sample Preparation

The seeds were dried in sunlight and stored under dry and dark conditions and ground with electric grinder. Extraction of oil of the seed was carried out in a soxhlet apparatus using purified *n*-hexane as solvent. The oil obtained, after distilling off the hexane, was stored in a labeled flask.

The quality constants, *i.e.* peroxide value, free fatty acid and iodine value of oils were determined by American Oil Chemist Society methods [25].

For determination of color the samples were diluted 1: 1 (v/ v) with *n*-hexane then filtered through 0.45 μm Millipore membrane filters. Samples were placed in a vacuum to remove hexane and the absorbance value was measured at 420 nm with the help of Shimadzu UV-160 Spectrophoto-meter by the method described by earlier workers [26].

The anisidine value and β-carotene were determined according to Palm oil research institute Malaysia (PORIM) test methods [27].

Acknowledgement

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