Oxidative Stability of *Silybum marianum* and Sunflower Oils

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Summary: *Silybum marianum* is a wild oilseed plant. With the aim of describing the oxidative stability of the oil obtained from the seeds of the plants grown in Pakistan and of comparing it to sunflower oil from the same climatic region we determined its oxidative stability under different storage conditions. Determination of oxidative stability of both the oils revealed that the formations of primary oxidation products were more affected by auto, photo oxidation and very less by dark oxidation. The peroxide value of fresh silybum marianium and sunflower oil were 5.03 meq/ kg and 3.78 meq/ kg, while after 1 month in daylight at room temperature peroxide value reached 14.41 meq/ kg and 11.42meq/ kg for silybum marianum and sunflower oil respectively. In photo oxidation (fluorescent light) the peroxide value after 1 month reached 11.24 meq/ kg, for silybum marianum and 9.01meq/ kg for sunflower oil. After 4 months storage in darkness peroxide was 7.08 meq/ kg for silybum marianum and 5.65 meq/ kg for sunflower oil. Anisidine value for silybum marianum was 1.34 and for sunflower oil was 0.74, but after 4 months storage in auto oxidation the anisidine value for silybum marianum was 5.25 and for sunflower oil was 4.03. In fluorescent light anisidine value for silybum marianum were 4.37 and for sunflower oil were 3.24, while in darkness anisidine value reached to 2.93 for silybum marianum and 2.17 for sunflower oil.

Introduction

Fats and oils are the basic and essential raw materials for food as well as other related industries. Population growth, economic progress and urbanize-tion lead to an increase in the consumption of oils and fats as well as greater dietary diversity in both the developing and developed nations. The average annual consumption of edible oils in Pakistan has increased more than six folds from 0.3 million tones in 1975 to 1.8 million tones in the year 2000. Total availability of edible oils from all sources amounted to be 1.76 million tones during July-March 2002-2003 [1]. Lack of information on the composition and utilization of many and varied indigenous oil seeds are real problems to achieve this goal [2]. There exist already abundant data in literature on the proximate composition, mineral contents and other characteris-tics of the more conventional oil seeds but this is lacking on the non-conventional oil seed types. In response to these needs and in continuation of our effort to bring into focus the non-conventional seed oils [3-5]. Exploration of non-conventional and non-traditional plants such as *silybum marianum* is essential to bridge the gap between demand and supply by some non-conventional oil. This plant could be quite a new source of edible oils and proteins, but very limited primary scientific data is available and more work is required in this regard.

Silybum marianum (milk thistle) is an annual or biennial medicinal herb that has been widely used in European traditional medicine [6]. It belongs to the family Astraceae (herbarium no. Ikhtiar Khan-61, Islamia College Herbarium, University of Peshawar). Milk thistle being found on barren land and not properly cared for, it is abundantly available as weed in Pakistan from January to September and matures in June. It can grow as a problematic weed up to six feet tall in wheat crop.

Results and Discussion

The effect of light on the oil is associated with a series of reactions such as oxidation, decarboxyla-tion, polymerization, isomerization and hydrogena-tion etc. These reactions often result in the formation of various off flavour compounds such as carbonyls, peroxides, acids and other saturated compounds. In this study the effect of storage conditions on the formation of primary oxidation products, expressed as peroxide value versus time of storage is taken. At the beginning of the experiment peroxide value of 5.03 meq/ kg for silybum marianum and 3.78 meq/ kg for sunflower oil was determined. Although the peroxide value is applicable for monitoring peroxide formation in the early stages of oxidation, it is nevertheless highly

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empirical and its accuracy questionable [7], still peroxide value determination is widely reported.

The peroxide value in auto oxidation at ambient temperature increased from 5.03 meq/ kg to 24.92 meq/ kg in the four months storage with mean value of 16.83 meq/ kg for *silybum marianum* and from 3.78 to 20.04 meq/ kg with mean value 13.32 meq/ kg for sunflower oil. Fig. 1 illustrates that in both the oils exposed to daylight for 1 month at ambient temperature, peroxide value rose sharply to 14.41 meq/ kg and 11.42 meq/ kg for silybum marianium and sunflower oil respectively. Higher rate of increase in peroxide value of the samples during the first month, but not later, can be at least partially attributed to higher temperature and longer days in June and July, when the experiment was performed. The peroxide value under the influence of fluorescent light (photo oxidation) increased from 5.03 meq/ kg to 18.64 meq/ kg during the same period of time having mean value of 12.92 meq/ kg for silybum marianum and from 3.78 meq/ kg to 15.71 meq/ kg with a mean value 10.61 meq/ kg for sunflower oil. The trend regarding the effect of fluorescent light on the peroxide value is presented in Fig. 2. In case of dark oxidation condition peroxide value of silybum marianum increased from 5.03 meq/ kg to 8.62 meq/ kg with time having mean value 7.08 meq/ kg and for sunflower oil it increased from 3.78 meq/ kg to 7.12 meq/ kg with time having mean value 5.65 meq/kg as shown in the Fig. 3.

For one-month storage period in daylight, a peroxide value of 14.41 meq/ kg for *silybum marianum*, and 11.42 meq/ kg for sunflower oil were measured. For the same period in fluorescent light, the values were 11.24 meq/ kg for silybum marianum and 9.01 meq/ kg for sunflower oil at ambient temperature. These values, attained in one month in oils is the upper limit for unrefined oils [8]. In darkness peroxide value of 8.62 meq/ kg was attained in 4 months storage at ambient temperature and this value are smaller than those of the daylight and fluorescent light storage in one month. These results are similar to those obtained earlier with other oils [9-10]. In investigation by Eidhin [11] performed on camelina oil, samilar trend has been observed.

Lipid hydro peroxide is very unstable and breaks down to an alkoxy free radical, which

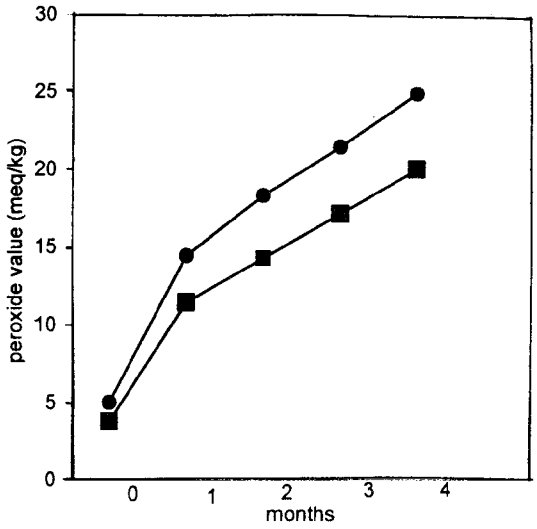

Fig.1. Effect of 4 months storage at ambient temperature on the peroxide value of (--●--) *silybum marianum* and (---■---) sunflower oil in auto oxidation condition

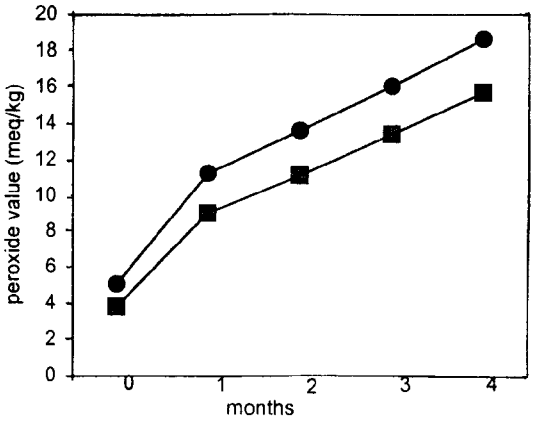

Fig. 2. Effect of 4 months storage at ambient temperature on the peroxide value of (--●--) *silybum marianum* and (---■---) sunflower oil in fluorescent light oxidation condition

decom-poses mainly by cleavage on either side of the carbon atom bearing the oxygen atom [12]. Aldehydes are included among the secondary reaction products, which give rise to flavours. *Silybum marianum* has higher anisidine value 1.34 as compared to sunflower oil 0.74. The anisidine value for *silybum marianum* increased from 1.34 to 7.81 with mean value 5.25 while for sunflower oil it increased from 0.74 to 5.87 having mean value 4.03

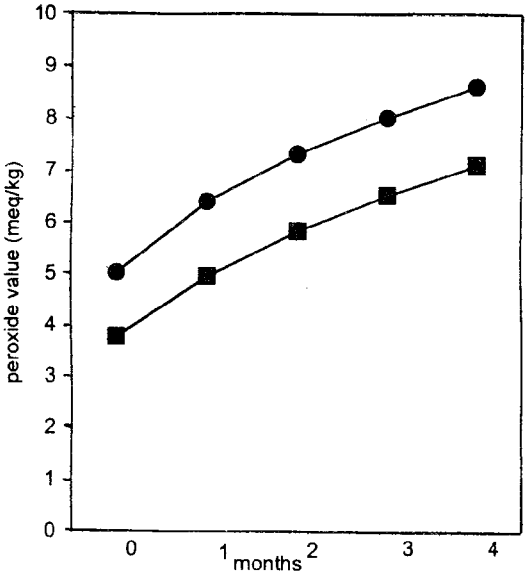

Fig. 3. Effect of 4 months storage at ambient temperature on the peroxide value of (--●--) *silybum marianum* and (---■---) sunflower oil in dark oxidation condition

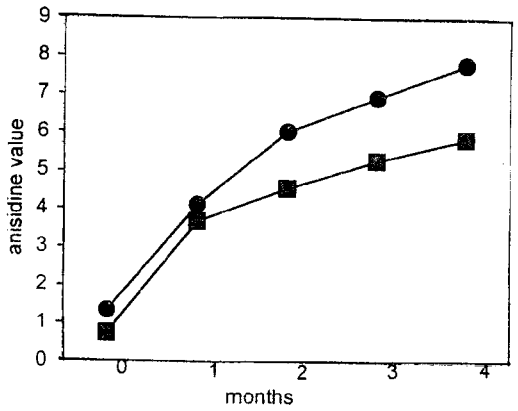

Fig. 4. Effect of 4 months storage at ambient temperature on the anisidine value of (--●--) *silybum marianum* and (---■---) sunflower oil in auto oxidation condition

in auto oxidation condition. In fluorescent light oxidation the anisidine value for *silybum marianum* increased from 1.34 to 6.35 with mean value of 4.37 while for sunflower oil it increased from 0.74 to 4.83 having mean value of 3.24. In darkness anisidine value for *silybum marianum* increased from 1.34 to 4.15 with mean value of 2.93 while for sunflower oil it increased from 0.74 to 3.28 having mean value of 2.17. Fig. 4 - 6 show a sharp increase in anisidine value for both the oils in the first month of storage and a regular increase in anisidine value in auto, fluorescent and darkness later on. Higher rate of increase in anisidine value in the first month is again attributed to longer days and higher temperature in June and July. In investigation performed on crude sunflower oil [13], anisidine value in the earlier stages of storage in open flasks in darkness remained constant, but after three months rose from 0.96 to 10.

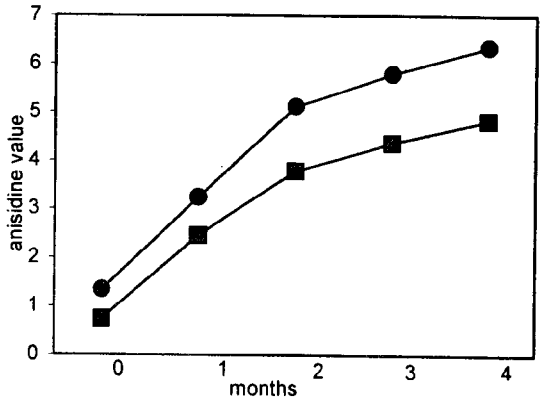

Fig. 5. Effect of 4 months storage at ambient temperature on the anisidine value of (--●--) *silybum marianum* and (---■---) sunflower oil in fluorescent light oxidation condition

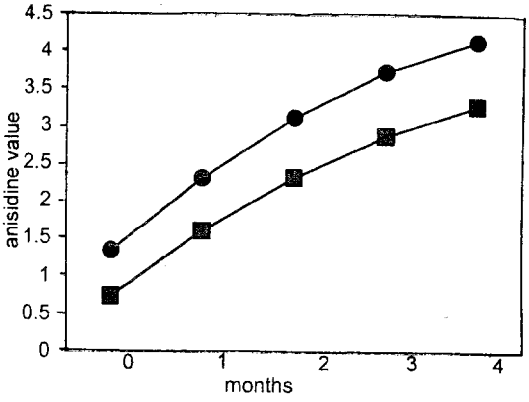

Fig. 6. Effect of 4 months storage at ambient temperature on the anisidine value of (--●--) *silybum marianum* and (---■---) sunflower oil in dark oxidation condition

Experimental

Silybum marianum seeds were collected from wildly grown plants in the periphery of Peshawar in the N.W.F. Province of Pakistan. From fully ripened, sound and healthy seeds the oil was extracted mechanically by cold pressing and filtered by filter paper. Oil samples were transferred to transparent glass bottles of (500 mL, of 15 cm diameter). The bottles were closed and subjected to different oxida-tion conditions: (i) at room temperature with expo-sure to day light, (ii) at room temperature in fluore-scent light, and (iii) at room temperature in darkness. The oil samples exposed to day light were placed approximately 1.5 m from the window and were not exposed to direct sunlight, The samples exposed to photo oxidation were placed in fluorescent light intensity of 43 lux, which was measured by means of General Electric type-214 light meter. All the samples were analysed for peroxide value by stan-dard procedure of American oil chemist society [14]. For peroxide value, 1 g of oil sample was mixed with 25 mL of solvent mixture (glacial acetic acid and chloroform, 3:2), shaken well and reacted with saturated potassium iodide for 1min.The reaction was stopped by adding 25 mL of distilled water and titrated with standard $Na_2S_2O_3$ (0.01 N) using starch as indicator.

Anisidine value was determined with the method described by palm oil research institute of Malaysia [15]. The method determines the amount of Aldehydes (principally 2 alkenal) in oils and fats. Known amount of oil (1g) was dissolved in n-hexane and made up to 25 mL. Absorbance (Ab) of the sample solution was taken at 350 nm wavelength using the solvent (hexane) as blank. In the next step exactly 5 mL of the sample solution and 5 mL of hexane were mixed and 1 mL of *para*-anisidine reagent (0.25 % in acetic acid) was added and shaken well. After 10 minutes the absorbance (Ab) of sample of the mixture was recorded.

Conclusions

The effect of storage conditions on oxidative stability of silybum marianum and sunflower oil revealed that both oils are sensitive to light. Storage in dark at ambient temperature conditions decreased the primary and secondary hydro peroxide formation substantially. The rate of oxidation of oil expressed as peroxide value, anisidine value versus time of storage is similar to that found with other vegetable oils. With proper storage conditions, oxidation can be retarded in both the oils.

Acknowledgement

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