Study of the Physicochemical Properties of *Silybum marianum* Seed Oil

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Summary: Proximate composition of *Silybum marianum* seeds showed that the seeds have oil content (26.05 %), moisture content (4.48 %), ash content (1.93 %), crude fibre (5.48 %), carbohydrates content (87.2 %), total protein (23 %), acid value (1.2 %), and saponification value (190.74). In physicochemical properties the iodine value is (108.8 g/ 100 g), peroxide value (16.17 meq/ kg), free fatty acid value (17.92 %), anisidine value (1.8979), color / optical density (0.3413). Fatty acid composition of the oil reveals that linoleic acid (64.4 %) and oleic acid (26.38 %) are the predominant unsaturated fatty acids. The saturated fatty acids found in *Silybum marianum* seed oil are palmitic acid (7.22 %) and stearic acid (2.0 %).

Introduction

Fats/ oils belong to a class of compounds known as lipids, which can either be simple or complex triacylglycerol. Fats/ 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/ oils supply essential fatty acids such as linoleic, linolenic, and arachidonic acids, which are not made 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 [7]. It is stressed that positive health benefits would be achieved by deriving 30-40 % of calories from dietary fats that has 1:1 ratio of polyunsaturated to saturated fatty acids [8].

Lack of information on the composition and utilization of many and varied oil seeds indigenous to the tropics are more of problems [9]. There exist already abundant data in literature on the proximate composition, mineral content and other characteristics of the more conventional oils seed but this is lacking on the non-conventional oils seed types [10-12]. This has created considerable interest in developing new sources of oils and fats and in evaluating their nutritional properties to establish their suitability for edible purposes. It is essential to bridge the demand and supply by some non-conventional and nontraditional plants such as *Silybum marianum* but very limited primary scientific data is available in this regard.

Silybum marianum (Milk thistle) is an annual or biennial medicinal herb that has been widely used in European traditional medicine [13], particularly in the treatment of various liver diseases [14], and belongs to the family composite. It is one of the thirteen noxious weeds and native to Asia Minor, Southern Europe, found in N.W.F.P. and the Punjab areas of Pakistan [15]. It is abundantly available as weed in Pakistan that matures in June, mostly grow wild on unutilized lands along roadside and is suitable for the control of environmental pollutants [16]. The study was carried out to investigate the proximate composition and physicochemical properties of *Silybum marianum* seed oils.

Results and Discussion

The fatty acid composition of the total seed oil reveals that linoleic acid (64.4 %) and oleic acid (26.38 %) are the predominant unsaturated fatty acids as presented in Table 1. It is well known that dietary fats rich in linoleic acid prevents disorders such as coronary heart disease, atheroselerosis and high blood pressure and also linoleic acid derivatives serve as structural components of the plasma membrane and as precursors of some metabolic regulatory compounds [17]. The other fatty acids found in

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Table-1: Fatty Acid Composition of the Oil Extracted from *Silybum marianum* Seeds.

Fatty acid Type	Amount (%)
16:0	7.22
18:0	2.00
18:1	26.38
18:2	64.40

Silybum marianum seed oil are palmatic acid (7.22 %) and stearic acid (2.0 %). The fatty acid analysis of *Silybum marianum* has earlier been reported [18], but our results show more oleic and linoleic acid content and it may be due to the variation in geographic location of plant.

The result of the proximate composition of *Silybum marianum* seeds is presented in Table 2. The oil content for the seeds is in the range 26.67 - 27.16 with mean value 26.05 % and standard deviation ± 1.52. Total protein with fats is in range 23.4-24.2 with mean value 23.8 %, standard deviation ± 0.4. The oil and protein content is in the same order with the oil content reported for some conventional oil seeds such as olive oil, sunflower [19]. The seeds have a low quantity of moisture content, which ranges from 4.24-4.72 having mean 4.48 and standard deviation ± 0.24. The ash and crude fibre content for *Silybum marianum* is in the range 1.5364-2.3243 having mean 1.9308, standard deviation ± 0.5571, and with the range 4.73-6.24 having mean 5.485 with standard deviation ± 1.068 respectively. The color/ optical density *Silybum marianum* is 0.3413, the oil is consistently liquid at room temperature. The carbohydrates content of the seed is in the range 86.3-88.1 with mean value of 87.65 and standard deviation ± 0.6363.

Table-2: Proximate Properties of *Silybum marianum* Seeds.

Parameters	Quantity		
	Range (%)	*Means	(±) Standard deviation
Oil Content	26.67-27.16	26.05	1.5218
Moisture	4.24- 4.72	4.48	0.240
Ash	1.54 – 2.32	01.93	0.5571
Crude Protein	23.4 -24.2	23.80	0.400
Crude Fibre	4.73 – 6.24	05.48	1.068
Carbohydrates	86.3 -88.1	87.65	0.6363

*Mean of triplicate analysis

The physicochemical characteristics are listed in Table 3. Acid value and Iodine value for *Silybum marianum oil* are 1.2 and 114.8 respectively. The acid value of the Silybum marianum oil is lower than sunflower oil [20]. The high iodine value of oil suggests that *Silybum marianum* oil is rich in polyunsaturated fatty acids. The uses of such oils lower the cholesterol level and facilitate its esterification and utilization in the body [21]. The high concentration of polyunsaturated fatty acids in *silybum marianum* oil makes it useful for therapeutic purposes in coronary heart diseases [22].

Table-3: Physiochemical Characteristics of *Silybum marianum* Seed Oil.

Characteristics	Quantity		
	Range (%)	*Mean	(±) Standard Deviation
Saponification value	195 -197	196	1.0
Ester value	193.9 - 195	194.8	0.9
Acid value	1.1 -1.3	1.2	0.1
Iodine value	113.4 – 116.2	114.8	1.4
Peroxide value	14.97 – 17.37	16.17	1.2
Free fatty acid (As % oleic)	16.62 – 19.22	17.92	1.0
Color/Optical Density	0.3413	--	--
Anisidine value	1.8979	--	--

*Mean of triplicate value

The saponification value is in the range 195-197 having mean value 196 with standard deviation ± 1. The high saponification value of oils suggests that it contains higher molecular weight fatty acids and also it is useful for soap production. Ester value for *Silybum marianum* is in the range 193.99-195.7 with mean 194.8 having standard deviation ±0.9. This value is close to that of sunflower oil [23]. The high Ester value is an indication that higher level of ester is present in the oil [24].

The first product formed by oxidation of oil is peroxide or hydro peroxide, and the common method of measurement is the peroxide value. The peroxide value for silybum marianum is 16.17 meq/ kg and this value is very high indicating that greater oxidation takes place in *Silybum marianum* oil. Lipid hydro peroxides formed as a result of oxidation are very unstable and break down to an alkoxy free radical [25], is measured by

anisidine value, which is 1.8979 for *Silybum marianum* oil.

Triglycerides on hydrolytic rancidity result in the formation of free fatty acid in oils. Polyunsaturated fatty acids are more susceptible to oxidation than monounsaturated fatty acids [26]. Greater the number of double bonds in the fatty acid, the more prone it is for oxidation. Foods, particularly those of vegetable origin contain linoleic and linolenic acids. The free fatty acid value is usually calculated in term of % oleic acid. Free fatty acid value for *silybum marianum* is 17.92 but this value is very high and alkali refining can reduce it.

Experimental

Sample Collection

The fully ripened, sound and healthy seeds of *Silybum marianum* were collected from Peshawar valley. The seeds were dried in sunlight, cleaned before use, grinded with electric grinder and all the samples were stored under dry and dark conditions.

Extraction

The oils were Soxhlet extracted using n-hexane (b.p. 40-60^{0}C). The solvent was initially removed with the help of rotary evaporator at 40^{0}C and then in air oven at 40-50^{0}C. Oil samples were placed at ambient temperature (25- 35 ^{0}C).

Proximate Properties

Crude protein (N % x 6.25) was determined by micro Kjedhal method. Analysis for ash, crude fibre was according to the methods of American Oil Chemist Society [27]. Saponification value and acid value were calculated as those recommended by the Association of Official Analytical Chemists [28]. Carbohydrate content was determined by difference [100.00- % (protein + crude fat + ash + crude fibre)] [29].

Physiochemical characteristics

The quality constants of oils i.e. peroxide value, free fatty acid value as % oleic acid and iodine value were determined by American Oil Chemist Society methods [30] and the color of oil was determined as absorbance (index of color development at 420 nm) using 50 % *v/v* solution in iso-octane, with the help of Shimadzu spectrophotometer model 160. Anisidine value was measured spectrophotometerically at 350 nm, based on the reactions of aldehydic compounds and para-anisidine, in presence of acetic acid. The volatiles were determined by the method [31]. The data was subjected to statistical analysis using standard deviation for significant differences among the values.

The gas chromatographic analysis of methyl esters of the oils was performed using Perkin-Elmer gas chromatograph model 3920 at the Nuclear Institute for Agriculture and Biology, Faisalabad. The esterification of the oil was performed according to method [32].

Conclusions

The seeds have high content of unsaturated fatty acids and therefore could serve as substitute for highly unsaturated fatty oils. The seeds could be utilized as a source of edible oil and protein for human consumption and as a good source of dietary fibre. However, refining the oil and long term feeding studies may be necessary before recommending this oil for edible purposes.

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