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Milk thistle (*Silybum marianum)* seed oil as a new source of edible oil

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ABSTRACT

Vegetable oils play an important role in food preparation and food formulation and play a significant role in diet and health. Identification and cultivation of new oilseeds is an important step in the direction of supplying the required oil in the country. Milk thistle plant with the scientific name of *Silybum marianum* is a one-year or two-year herb that has many medical, medicinal and industrial uses since ancient times. Due to its biological characteristics, this plant requires very little fertilizer and is particularly resistant to dry conditions and weak soils, and it is compatible with the climate conditions of most regions of Iran. Milk thistle seed contains a significant percentage of oil (20-30%) with high nutritional value due to the presence of essential fatty acids such as linoleic acid (40-60%), oleic acid (20-32%) and antioxidant and bioactive compounds such as tocopherols, carotenoids and sterols. Therefore, the oil obtained from milk thistle seed can be considered as a new edible oil due to its long-term consumption in different societies and its bioactive compounds. In this review article, a brief look at milk thistle plant, oil percentage and its composition in different regions has been discussed. According to scientific reports and articles, the cultivation and development of this new and valuable oil seed with good economic value is recommended as a new source of edible oil.

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1- Introduction

Oil and fat is one of the main components of daily diet, one gram of which produces about 9 Kcal of energy in the body and creates a desirable taste in food. With the growth of public knowledge, the demand for oils that in addition to providing energy and flavor is beneficial to their health, has been increased. Recently, due to climate - changes and economic conditions, the extracted oils from special seeds have received huge attention [1]. Vegetable oils are in high demand due to consumers' interest in disease prevention and health promotion through balanced diets that include high concentrations of monounsaturated and polyunsaturated fatty acids, antioxidant and phenolic compounds [2].

Silybum marianum is biennial plant of the Asteraceae family and English name Milk thistle (MT), a green colour and prickly plant with a standing stem that can be thick, simple, or slightly branched (ramified) which leads to a green cap. The flower is pink-purple with a hairy and prickly color (Figure 1). It grows in Europe, Asia and America. In Iran, this plant is distributed in Gonbad-e Kavous areas, between Gorgan, Noodeh Kelardasht, Haraz valley, Moghan, Pushtkooh, Mollasani in Ahvaz, Shush, Hamidieh, Ramhormoz, Izeh and Kazeroon [3].

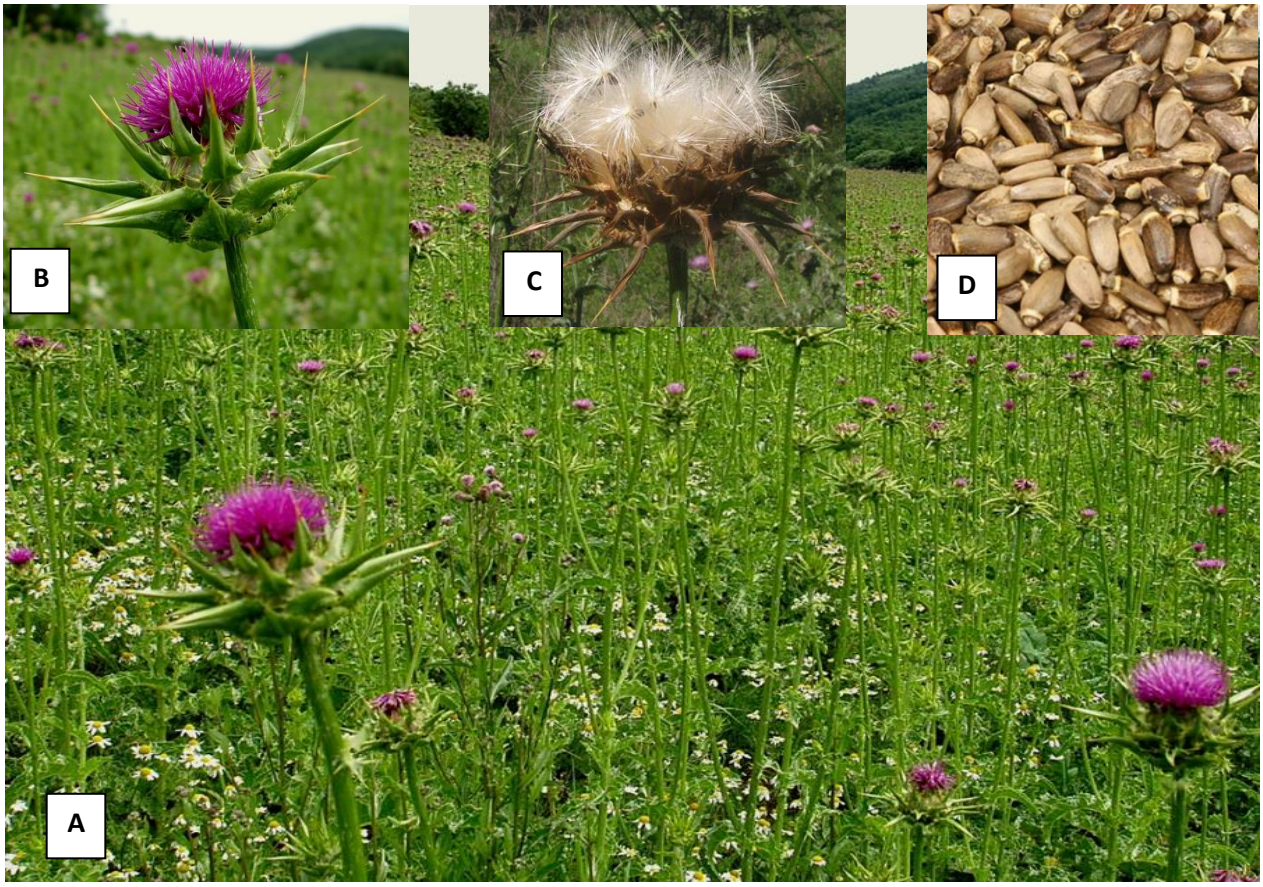

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Figure 1. Milk thistle. (A) Cultivated field, (B) Flower head with spiny bracts and variegated leaf, (C) Mature flower (D) Fruits

MT have many compounds such as Silybin A and B, Silydianin, Silicidine, Epigenin, Dihydrosilicylbine, Diaxylicristin, Dioxicilidianin. The extract of dried seeds contains 1-4% silymarin, and flavonoids such as silybin A and B, silydianin, silicristatin and diahydrosilybine (Fig. 2). Other flavonolignans in the extract of this plant include silandrin, silibinum, silyhermin [4]. MT seeds contain 20-30% oil rich in unsaturated fatty acids, which makes this product an ideal edible oil for use in food production [5]. The chemical composition of MT depends mostly on the quality of the plant. Farming technique, soil quality, climate, treatment methods are factors that influence the effective and bioactive components of the product. The products obtained from the MT plant vary in chemical composition, silymarin content and oil percentage (Table 1) [6].

Table 1. Chemical composition and silymarin content of milk thistle product [13]

Milk Thistle Product	Proximate Chemical Composition
Seed extract	Flavonolignans 1–4%, fatty Acids 5–10%, proteins 20–30%, fibre 6–10%, ash 5–10%
Seeds	Flavonolignans 1–4%, fatty acids 20–30%, proteins 20–30%, fibre 30–40%, ash 3–5%
Seed oil extract by-product	Flavonolignans and very little fatty acids, proteins, fibre, and ash
Cake	Flavonolignans .1–1%, fatty acids 10–20%, proteins 20–30%, fibre 28–40%, ash 5–10%
Expeller	Flavonolignans .1–1%, fatty acids 10–20%, proteins 15–25%, fibre 20–30%, ash 5–10%
Oil	Fatty acids 70–80%, flavonolignans (trace amounts)

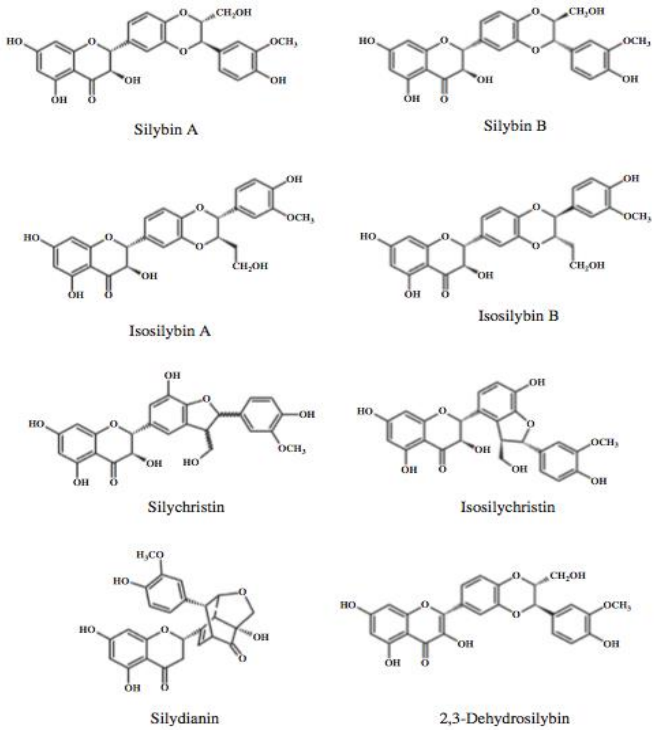

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Figure 2. Structure of the main silymarin compound [13, 16 and 17].

Silymarin has been used in various treatments in recent years due to its properties in medical, pharmaceutical and veterinary fields. (Fig 3) In addition to the hepatoprotective effect, flavonolignans also have antioxidant, anti-inflammatory, anticancer, antifibrotic, hypolipidemia, anti-tuberculosis, neurotrophic and neuroprotective effects. Silymarin is also known for its effects in reducing the side effects of chemotherapy and protecting against toxicity caused by radiation. Cardiovascular disease, one of the leading causes of death worldwide, is also associated with oxidative stress. Based on the findings of one study, the levels of free radicals in the blood of the group treated with marigoldium were lower than in the group treated with Corynebacterium Psedotuberculosis. Based on the findings, the antioxidant activity of the MT helps prevent and treat oxidative stress. Oxidative stress has been linked to a variety of problems, including diabetes, and silymarin consumption has reduced glucose levels in diabetic mice by increasing insulin levels and regenerating pancreatic cells [7].

Figure 3. Some therapeutic and medicinal uses of silymarin [3, 6]

Although silymarin has been the main

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point of interest so far, the latest research has shown that it can also find several industrial applications that have dramatically increased its economic significance. Uses in food and cosmetic applications are just a few of the new opportunities offered by the cultivation of MT. Extensive environmental suitability along with good plant yield under different climatic conditions makes it a reliable alternative to low-input and traditional agriculture that can provide good production and a suitable and cost-effective solution for semi-arid and arid agricultural and agricultural ecosystems - [8].

2- Milk Thistle Oil Market

Edible oils are one of the food items that is highly dependent on its import in our country, and also with the development of oil seeds and fruits, only about 10% of the required and consumed edible oils are produced inside the country and the rest is imported from abroad [1]. Therefore, it is necessary to pay attention to new sources of edible oils that are compatible with the climate conditions of the country which can have a high economic value as well.

The growth of the world population and the consumption of fats and oils are among several factors that have led to a sharp increase in the demand for oils and fats. The annual rate of global demand for fats and oils has nearly doubled since the late 1990s. Following this increasing demand, the total volume of vegetable oil production has nearly tripled, from 40.8 million tons in 1980 to 122.6 million tons in 2020 [9].

Increasing the caltivation of common oilseeds, and also identification and cultivation of new sources is a necessery step towards the supply of edible oils. MT has been introduced as a crop in most parts of Europe, Asia, North and South America, and Australia. In Poland, which is a major European producer of MT seeds and derivatives, the area is about 2,000 hectares. Its commercial cultivation was recently developed in North America, where MT is one of the best-selling supplements. In Italy, milk thistle, as one of the major cultivated medicinal species, ranks fourth in terms of volume used (1920,000 kg per year) and fifth for its wholesale commercial value (3494400 € per year). Due to the oil content (20-25%), this oil is marketed and sold in North America, Europe, Asia Pacific, Middle East and Africa, Latin America, - and consumed about 150,000 tons per year [10].

3- Extraction of oil from Milk Thistle seeds

The quality of seed oil is a function of several characteristics that include its bioactive compounds, physical and chemical properties and performance. These qualities are important in processing of seed oil, because they determine the flavor, nutritional and market values. To meet the market demand, edible oils are obtained using different methods. High demand for vegetable oils has led to the development of various oil extraction techniques. Pretreatment methods also

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have a significant impact on the oil extraction efficiency. Currently, several techniques are used for extraction of vegetable oils, which can be calssified as conventional methods (solvent extraction, cold and hot press) or the new extraction methods (supercritical CO_2 extraction with ultrasonication and microwaves extraction, pulsed electric field extraction and enzyme-assisted extraction). New extraction methods enable higher oil yields, reduced solvent consumption and reduced extraction time. All oil extraction methods have some advantages and disadvantages. Therefore, the cost, and recycling of extraction solvents as well as the quality of the obtained oil should be taken into account [12].

Cold press is a simple, environmentally friendly and low cost. For these reasons, cold press in the small scale and for special oil seeds are preffered compared to other methods such as solvent extraction and hot press. However, compared to hot pressing and solvent extraction, the oil efficiency of the cold press method is lower, but the higher price of extracted oils can compensate. Therefore, the oil extracted by cold press has been prefered by consumers due to its bioactive compounds content and being free of chemicals. Since the cold press process does not use heat treatment and chemical process, all the useful nutritional properties of the raw material are transferred to the extracted oil. Therefore, the oil obtained from cold press has high nutritional and sensory properties and contains useful elements with posetive health effects [9].

The use of new seed pretreatment techniques such as microwave, enzymatic digestion, pulsed electric field and sonication not only improves oil yield and qualitative characteristics, but also reduces the extraction time of oil, solvent and energy consumption (Fig 4). Studies show that pretreatment of oil seeds of MT significantly improved the oil extraction yield. High content of Phenolic compounds, carotenoids, tocopherols, phytosterols and antioxidants in the oil extracted from pretreated seeds have been reported, which have a positive effect on its health benefits such as prevention of cancer, diabetes, obesity, inflammatory and cardiovascular diseases. [12].

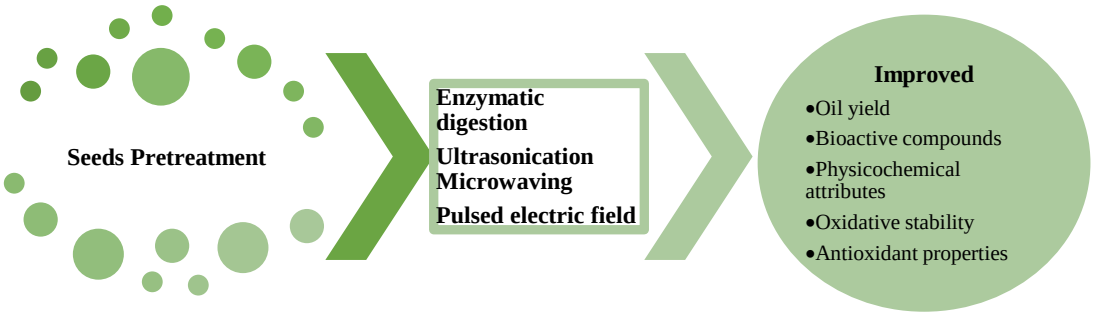

Figure 4. Summary of the effect of novel seeds pretreament trchniques on the oil quality [12]

4. Oil refining

Refining can have a severe reduction effect on the phenolic content of vegetable oils. Oils that are extracted by cold press, if the raw materials (oilseeds or fruits) are of good quality, do not need to be refined, and the extracted oils are called virgin oils. Oils that are extracted by hot press or solvents are also called crude oils that have

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high levels of impurities and must be refined before consumption. Refining has several negative effects on the nutritional value of vegetable oils. Reduction of bioactive components and health-promoting compounds such as tocopherols, carotenoids and phytosterols can reduce the nutritional value of vegetable oils. Since all the beneficial compounds and phytochemicals remain in virgin and unrefined oils and lack of toxic compounds such as trans-fatty acid isomers or phytosterol oxidation products that are formed during the refining process, so it is generally better to use virgin vegetable oils instead of refined oils [9]. Most oils from a plant sources do not have the essential fatty acid ratio suitable for consumption or lack the necessary quality characteristics in terms of oxidative and functional stability. One way to obtain a nutritionally balanced fatty acid blends is to mix different oils, including sesame and olive oils mixed with flaxseed oil. Vegetable oils such as flaxseed oil are a rich source of alfa-linolenic acid (essential omega-3 fatty acid) in the diet, which can have numerous positive effects on health [9].

Given that MT seed oil is rich in essential omega-6 fatty acids (linoleic acid) and poor in the omega-3 fatty acid (alpha linolenic acid), it can be blended with the flaxseed oil and presented to the market to be rich in bioactive compounds and also with an appropriate proportion of essential fatty acids. However, according to studies, MT oil can be used directly after extraction and if it is in a good quality, it does not need to be purified [10].

5. Oil Composition

Fatty acid composition can influence the nutritional value and also oxidative stability of oils and fats. MT seed oil has high amounts of linoleic (46-60%) and oleic (21-32%), followed by palmitic acid (5-12%) and stearic acid (3-7%) along with a small amount of other fatty acids (Table 1). The fatty acids composition of MT oil is similar to vegetable oils such as sesame, maize, sunflower oils, but has less linolenic acid than soybean and rapeseed oils. Regarding the type and amount of fatty acids, it can be said that the MT oil falls into the linoleic-oleic oil group (Table 3).

Table 2- Fatty acids composition of *Silybum marianum* seed oil

Fatty acid (%)	Reference							
	[23]	[27]	[26]	[21]	[28]	[16]	[22]	[5]
C16:0	8.02 ± 0.15	7.66 ± 0.48	8.37 ± 0.08	8.61 ± 0.007	12.74±0.2	7.75	5.50 ± 0.41	7.87 ± 0.04
C16:1	0.182 ± 0.091	0.24 ± 0.06	0.10 ± 0.00	0.10 ± 0.001	0.16±0.1	0.05	Nd*	0.07 ± 0.01
C18:0	5.15 ± 0.21	6.34 ± 0.22	5.45 ± 0.21	5.24 ± 0.001	3.24±0.3	5.07	4.75 ± 0.39	6.69 ± 0.04
C18:1 (n-9)	32.31 ± 0.32	31.76 ± 0.31	24.69 ± 0.13	22.03 ± 0.007	21.26±0.4	23.91	21.50 ± 2.11	30.59 ± 0.1
C18:2 (n-6)	48.12 ± 0.22	50.31 ± 0.78	56.46 ± 0.06	56.79 ± 0.03	59.98±0.3	55.49	60.00 ± 5.94	46.1 ± 0.2
C18:3 (n-3)	0.15 ± 0.08	0.28 ± 0.03	0.30 ± 0.00	0.76 ±0.02	0.36±0.2	0.42	Nd*	1.09 ± 0.02
C20:0	3.163 ± 0.072	2.66 ± 0.52	2.90 ± 0.04	2.88 ± 0.007	1.62±0.1	3.18	2.90 ± 0.20	4.26 ± 0.08
SFA	16.33	17.11 ± 1.01	19.53	19.53 ± 0.03	17.91	16	16.26 ± 1.58	22.06 ± 0.05
MUFA	32.49	32.3 ± 0.25	25.69	22.92 ± 0.007	21.72±0.2	23.96	22.6 ± 3.12	30.66 ± 0.18
PUFA	48.27	50.59 ± 0.76	56.76	57.55 ± 0.02	60.37±0.3	55.91	60.00 ± 5.73	47.28 ± 0.24

Table 3 – Fatty acid composition (%) of milk thistle seed oil compared with other conventional vegetable oils.

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Fatty acid	Milk thistle*	Sunflower**	Corn**	Cottonseed**	Soybean**	Sesame**	Pumpkin***	Peanut***
C16:0	5.5-12.47	5.0-7.6	8.6 - 16.5	21.4-26.4	8.0-13.5	7.9-12.0	13.1	7.5
C16:1	0.05-0.2	ND-0.3	0.0 - 0.5	ND-1.2	ND-0.2	ND-0.2	0.1	0.07
C18:0	3.24-6.69	2.7-6.5	0.0 - 3.3	2.1-3.3	2.0-5.4	4.5-6.7	5.7	2.1
C18:1 (n-9)	21.26-32.31	14.0-39.4	20.0 - 42.2	14.7-21.7	17-30	34.4-45.5	24.9	71.1
C18:2 (n-6)	46.1-60.0	48.3-74.0	34.0 - 65.6	46.7-58.2	48.0-59.0	36.9-47.9	54.2	18.2
C18:3 (n-3)	0.15-1.09	ND-0.3	0.0 - 2.0	ND-0.4	4.5-11.0	0.2-1.0	0.1	Nd
C20:0	1.62-4.26	0.1-0.5	0.3 -1.0	0.2-0.5	0.1-0.6	0.3-0.7	0.4	1.01

ND : Not Detected
*. [5, 16, 21,22, 23, 26,27,28]
**[32]
***[15]

Triacylglycerols (TAGs) are the main components (95-98%) of vegetable oils and fats. TAG composition is an indicator of the quality and purity of vegetable oils and is increasingly used in the food industry to verify authenticity. Therefore, analysis of TAG pattern in vegetable oils is of great importance to understand its physical and chemical properties. In various studies, the TAG composition of milk thistle oil has been determined using HPLC. It contains Palmitic, Stearic, Oleic, Linoleic and Linolenic fatty acids, which are determined as P, S, O, L and Ln, respectively, according to which the dominant TAG species are OLL (20.44%), PLL (17.31%), POL (14.30%) and LLL (22.30%). The amount of LLL has been reported to be up to 46% in some reports [28]. However, some studies have had conflicting results, with OLL (20-21%) being the major TAG, followed by LLL (~% 18), POL (~%15) and PLL (~%11). The differences in the results of the studies can be attributed to growing conditions, different genotypes, and the analytical methods used [5]. In general, it can be concluded that MT oil has a TAG composition similar and comparable to the cottonseed and sunflower oils.

Phenols are a large group of secondary plant metabolites that are present in most plant sources. These compounds have an aromatic ring and one or more hydroxyl groups in their structure. Their impact on human health depends on their metabolism and bioavailability. Primarily, phenols act as a antioxidant and can inhibit lipid oxidation. Therefore, phenols protects oils which are rich in PUFA against oxidation. Enriching the diet with products containing high levels of phenolic compounds helps prevent neurological disorders or cardiovascular disease [18]. The collected results from different research papers show that phenol concentration ranges from 1160 to 8120 mg/kg of MT oil [13].

Tocopherols have antioxidant properties, anti-proliferation and anti-apoptotic properties. The tocopherol family consists of four isomers (α, β, γ and δ). α-tocopherol, the main derivative of vitamin E, has the highest biological activity [19]. The amount of tocopherols in the MT oil varies from 530 to 38.91 mg/100 g oil, which is the most important isomer of tocopherol and the other isomers are present in a lower amount in this oil (Table 4).

Table 4 - Tocopherol content (mg/100g oil) of *Silybum marianum* seed oil

Compound	Reference						
	[27]	[33]	[22]	[23]	[5]	[14]	[26]

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α-tocopherol	307.84 ± 14.13	Nd*	286.22 ± 25.49	530.2 ± 2.4	527.89±1.53	465.78±0.95	38.91 ± 0.67
β-tocopherol	Nd*	48.87±0.83	3.58±0.37	23.2±2.0	43.24±0.36	51.74±0.69	2.84±0.08
γ-tocopherol	Nd*	53.60±1.74	14.24±1.25	31.3±1.6	30.86±0.56	35.71±0.56	4.34±0.20
δ-tocopherol	Nd*	14.91±1.13	14.24±1.22	2.13±0.32	12.13±0.10	80.75±0.50	Nd*

*ND : Not Detected

6- Chemical Characteristic of Milk Thistle

Fats and oils are used excessively in the food industry, but are easily oxidized during processing and storage. Oxidation leads to changes in taste, smell and color, and produces toxic metabolites and reduces the shelf life of food products [29]. From the perspective of food quality and safety, determination of peroxide value is one of the most important methods of measuring quality control for edible oils, because it is considered as an indicator of the oxidation status. This value measures the concentration of hydroperoxiodines (primary oxidation compounds) that are not stable and can be easily decomposed into secondary oxidation products (such as ketones and aldehydes). The peroxide value for refined oil ranges from 1 to 7 ($meqO_2$/kg oil) (Table 5). For virgin milk thistle oil, its peroxide value has to be less than 15 ($meqO_2$/kg oil) as mentioned in the international standard of CODEX for virgin and cold press evegatble [1].

The acid value expresses the amount of free fatty acids and is generally one of the key parameters reflecting the oil quality. - Hydrolysis of triasilglycerols can be due to the lipase activity, extraction of oil from poor quality seeds or unsuitable storage conditions. The acid value for milk thistle oil is approximately 2 to 8 (mg KOH/g oil) (Table 5). Considering the Codex standard for cold press and virgin vegetable oils, acid value should be less than 4 (mg KOH/g oil) [1].

Table 5- Chemical properties of *Silybum marianum* seed oil

Chemical properties	References					
	[27]	[14]	[20]	[1]	[22]	[16]
Acid value (mg KOH/g oil)	2.16 ± 0.07	4.24±0.21	5.04 ± 0.27	Nd*	7.59 ± 0.61	Nd*
Peroxide value (meq O2/kg oil)	1.17 ± 0.05	5.11±0.20	7.05 ± 0.05	1.59 ±0.01	3 ± 0.27	1.16
Iodine value (g/100 g oil)	120.46 ± 3.64	107.31±1.35	27.9 ± 0.11	109.57 ± 0.4	118.32 ± 10.84	118.03

7- Conclusion

Studies have shown that in many countries including the United States, Canada, China, Egypt, Jordan, Tunisia and Europe, the use of milk thistle oil as an edible oil is allowed. According to the literature review, environmental conditions are effective in the changing of the fatty acids composition in the oil extracted from seeds collected from different regions. In fact, the results show that fatty acids and also the percentage of Silymarin and seed oil content can differ depending on the environmental conditions and seed pretreatments, therefore, this infoemation can be used in future studies to identify the ecological and agronomic needs of this plant and to provide suitable conditions, - applying better pretreatment methods and combining milk thistle oil with other suitable vegetable oils to expande its uses and applications. Also, development and cultivation of genotypes compatible with the climatic conditions of each region and extraction of oil from MT seeds can be considered as an appropriate option to introduce a new source of edible oil to the market.

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روغن دانه خار مریم (*Silybum marianum*) به عنوان منبع روغنی جدید خوراکی

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چکیده

روغن‌های گیاهی نقش مهمی در تهیه غذا و همچنین فرمولاسیون مواد غذایی داشته و سهم بسزایی در رژیم غذایی و سلامت ایفا می‌کنند. شناسایی و کشت دانه‌های روغنی جدید، گامی مهم در جهت تامین روغن مورد نیاز در کشور است. گیاه خار مریم یا ماریتیغال با نام علمی *Silybum marianum* یک گیاه علفی یک ساله و یا دو ساله می‌باشد که از زمان‌های قدیم کاربردهای پزشکی، دارویی و صنعتی فراوانی دارد. این گیاه به دلیل ویژگی‌های بیولوژیکی، نیاز به کود بسیار کم و بخصوص مقاوم به شرایط خشکی و خاک‌های ضعیف است و با شرایط آب و هوایی اغلب مناطق ایران سازگاری دارد. دانه ماریتغال شامل درصد قابل توجهی روغن (۲۰-۳۰٪) با ارزش تغذیه‌ای بالا به دلیل وجود اسیدهای چرب ضروری مانند اسیدهای لینولئیک (۴۰-۶۰٪)، اولئیک (۲۰-۳۲٪) و ترکیبات آنتی‌اکسیدانی و زیست فعال همچون توکوفرول‌ها، کاروتنوئیدها و استرول‌ها است. لذا روغن حاصل از دانه ماریتغال با توجه به مصرف طولانی مدت آن در جوامع مختلف و ترکیبات زیست فعال آن می‌تواند به عنوان روغن خوراکی جدیدی موردنظر قرار بگیرد. در این مقاله مروری، نگاهی اجمالی به گیاه ماریتیغال، درصد روغن و ترکیبات آن در مناطق مختلف پرداخته شده است. با توجه به گزارش‌های علمی و مقالات، کشت و توسعه این دانه‌ی روغنی جدید و ارزشمند با ارزش اقتصادی خوب بعنوان منبع روغنی جدید توصیه می‌شود.

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