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Milk thistle and Moldavian dragonhead oils

New sources of polyunsaturated fatty acids

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ABSTRACT: Milk thistle and moldavian dragonhead are sources of fatty oils with high content of polyunsaturated fatty acids, especially linoleic acid and α-linolenic acid. These fatty acids, together with other biologically active substances have positive effects on regeneration processes in the skin, help improve the natural functions and provide an effective protection against negative external effects. As a consequence of the naturally high polarity of both oils, the oils can be used in cosmetic products in high concentrations, without negative effects on their useful properties, such as absorption, spreading or feeling of stickiness. Milk thistle and Moldavian dragonhead oils are especially ideal for the creation of formulas designated for ageing, sensitive or irritated skin.

Milk thistle (*Silybum marianum (L.)* Gaert.) is the yearling plant from family *Asteraceae* which occurs in moderate belt of northern hemisphere from Middle East trough Balkan Peninsula up to Western Europe. This plant has been used for its healing effects since time immemorial. It was described for the first time in the 4th century B.C. by Theophrast under the name "Pternix" and later, in the 1st century A.D. also by Dioscoride in the manuscript *Materia medica* as well as by Plinius in the manuscript *Historia naturalis*, while both of the authors call this plant species already by the same name as "Sillybum". During the centuries, milk thistle used to be described in all significant herbal books of healing plants as a plant the fruits of which promote healing of some diseases of the liver and spleen.

Currently milk thistle is grown artificially in field production and it is classified as the medicinal herb described in pharmacopoeias of various countries for its healing characteristics, especially as regards liver and digestive tract diseases (1). This biological activity is attributed to substances from the category of flavonolignanes, contained especially in the fruit of milk thistle (achenocarp). However, we now know that the fruit also contains other biologically valuable substances, which are no longer commonly used in the pharmaceutical industry. This especially means the fatty oil, with content fluctuating around 20-25 percent (2). The oil can be extracted from the fruit using various methods, from standard pressing, through the extraction of sorted fruit with the application of nonpolar solvents to the extraction based on carbon dioxide under supercritical conditions. Depending on the extraction method, individual products differ from each other with the ratio of content substances.

Cold pressing is the most usual method guaranteeing the preservation of all biologically active substances without the risk of degradation. With this method of oil isolation, the virgin milk thistle oil contains triacylglycerols in particular, in which higher fatty acids are bound, especially the linoleic acid which belongs to group of ω-6 fatty acids. In addition to this double unsaturated fatty acid, the concentration of which in a blend of the present fatty acids fluctuates around 60 percent, other unsaturated acids include the oleic acid (approximately 20 percent) and traces of α-linolenic acid. The two most important unsaturated fatty acids of the milk thistle oil, i.e. linoleic acid (L) and oleic acid (O), are bound in triacylglycerols at approximately the following ratios: LLL: 20 percent; OLL: 20 percent; OOL: 7 percent; OOO: 2 percent. In addition to fatty acids, virgin oil also contains a significant quantity of phytosterols, ranging between 1 and 2 percent. This is especially β-sitosterol and Δ^7-stigmasterol; Δ^5-avenasterol, stigmasterol and campesterol are present in small quantities only. In addition to this, the oil contains a significant quantity of natural vitamin E and its derivatives, and also a small quantity of flavonolignans, the content of which is limited by their solubility in the oil (3-5). The comparison of the content of lipophilic vitamins and carotenoids for milk thistle and Moldavian dragonhead virgin oils obtained from the crop 2008 is introduced in

moldavian dragonhead (*Dracocephalum moldavica L.*) is the yearling plant from family *Lamiaceae* which occurs in moderate belt of northern hemisphere from Black Sea area through Balkan Peninsula up to central Europe.

Moldavian dragonhead is known especially for its high content of essential oils in the blooming top (6). It has been collected and grown especially for this essential oil, with the odour and composition similar to that of the essential oil found in garden balm. It has lately been discovered that the fruit of moldavian dragonhead has high content of fatty oils (approximately 20 percent), especially triple unsaturated α-linolenic acid from the group of ω-3 fatty acids, representing over 60 percent of all present fatty acids. This unique content, also with respect to the presence of other unsaturated fatty acids, i.e. linoleic acid (approximately 18 percent) and oleic acid (approximately 10 percent), makes this oil an important source of essential fatty acids for the human organism. These three most important unsaturated fatty acids of the moldavian dragonhead oil, i.e. α-linolenic acid (Ln), linoleic acid (L) and oleic acid (O), are bound in triacylglycerols at approximately the following ratios: LnLnLn: 25 percent; LLnLn: 20 percent; LLLn: 5 percent; OLnLn: 6 percent. In addition to fatty acids, the cold pressed moldavian dragonhead oil includes an important share of phytosterols, especially β-sitosterol; campestrol and Δ^5-avenasterol are only present in smaller quantities (7-9). The content of vitamin E in moldavian dragonhead virgin oil is substantial and comparable with that in milk thistle oil with one big difference: in milk thistle oil α-tocopherol is the dominant substance among all forms of vitamin E whereas in moldavian dragonhead oil predominates γ-tocopherol (Table 1).

Substance	Milk thistle oil ($mg.kg^{-1}$)	Moldavian dragonhead oil ($mg.kg^{-1}$)
Retinol	0.6	0.4
α-tocopherol	511	48
γ-tocopherol	87	828
δ-tocopherol	2	11
β-carotene	0.2	1.6
Lutein (xantophyl)	0.5	6.3
Lycopene	<0.1	<0.1

Table 1. The content of lipophilic vitamins and carotenoids in milk thistle and moldavian dragonhead oils.

Fatty acid	Milk thistle oil (% Weight)	Moldavian dragonhead oil (% Weight)
Oleic	15-25	6-14
Linoleic	53-65	14-23
α-linolenic	<2	55-66
Sum of other unsaturated	<1	<2

Table 2. The unsaturated fatty acids compositions of milk thistle and moldavian dragonhead oils.

The typical general profiles of unsaturated fatty acids compositions of both milk thistle and moldavian dragonhead oils are summarized in Table 2. The ratio between fatty acids may vary in dependence on the concrete cultivar of the plant, climate conditions during plant growing, kind of crop collection, post-harvesting treatment and technology used for the oil isolation.

BIOLOGICAL ACTIVITY OF POLYUNSATURATED FATTY ACIDS

Unsaturated fatty acids from the fruit of milk thistle and moldavian dragonhead rank among essential fatty acids, i.e. acids which the human organism cannot synthesize but needs to obtain from external sources. These acids serve as basis for many cellular structures and tissues in the human body. One of the most important structural functions is the participation in the building of cell membranes. On the other hand, these substances are the basic structural elements in the biosynthesis of other biologically active substances, such as prostaglandins, leukotrienes, tromboxanes etc., controlling the fine balance of immunological, inflammatory and other responses of the organism (10).

During topical application, these fatty acids, in the form of oils, for example, where they are bound predominantly in the form of triacylgylcerols, are easily absorbed via the skin barrier and can thus directly participate in the biochemical processes in the skin. Here they play an important role in the regeneration of damaged cells, accelerating the new formation of cells in the damaged tissue. Because these unsaturated fatty acids are strong antioxidants, they prevent the damaging of living structures by the effects of external and internal oxidative stress, thus significantly contributing to the improvement of skin qualities and slowing down ageing. This effect is also supported by the fact that as a consequence of the presence of double bonds in the molecules of these fatty acids, their natural sun protection factor becomes evident. Moreover, linoleic acid and α-linolenic acid have strong antimicrobial activity, which can play an important role in the products for sensitive or damaged skin threatened by microbial infections.

USE OF OILS IN COSMETIC PRODUCTS

Thanks to the presence of mono- and 1,2-diacylglycerols and 1,3-diacylglycerols in quantifies from 1.5 to 3 percent in the milk thistle virgin oil, the polarity of the oil increases and therefore the oil is one of the high-polar vegetable oils, such as for example avocado oil. The low phase tension on the boundary of separation of aqueous and oil phase, with the value of 16 $mN.m^{-1}$ allows for the oil to be easily spread and absorbing. The physical and chemical properties are close to those of natural sebum, and are dramatically different from the behaviour of non-polar or mineral oils. With its rheologic behaviour, milk thistle oil can be compared with the fatty acid esters with alcohols of a medium-long chain, e.g. decyl oleate.

Similarly, in the moldavian dragonhead oil, the presence of mono- and diacylglycerols, and the low solidification point play an important role in the spreading characteristics. Both oils, i.e. milk thistle and moldavian dragonhead, thus do not leave the skin with the persistent greasy feeling or stickiness when applied. They can therefore be used for cosmetic products, even in higher concentrations, without a negative effect on the useful properties of the final product, for example of massage oils, emulsions and jellies. On the other hand, they can be used for highly sophisticated products for the treatment of damaged and ageing skin, where highly positive effects are achieved in the regeneration processes, in the presence of auxiliary substances accelerating transdermal penetration. This fact is also supported by the above-mentioned active substances of virgin oils, especially vitamin E and its derivatives, as well as phytosterols which contribute to an increased skin elasticity and water retention, thus helping optimize the hydration (11).

The milk thistle and moldavian dragonhead oils are suitable for the formulation of products for sensitive skin, skin suffering from chronic inflammatory disorders, psoriasis, constitutional dermatitis, acne, as well as for sensitive skin of people suffering from diabetes. Special attention was paid to the testing of milk thistle oil in products for new-born babies and toddlers, where no negative effects were identified of their application on baby skin in the form of baths, oils, ointments and creams.

POSSIBILITIES OF SEMISYNTHETIC DERIVATIVES

An important possibility regarding the transformation of vegetable oils is the re-esterification using alcohols with a medium-long chain. The milk thistle oil can easily be subject of re-esterification, for example with decyl alcohol, whereby this reaction produces a mixture of 80-85 percent fatty acid esters, originally present in the source milk thistle oil with decyl alcohol, approximately 5 percent of partially treated mono- and diacylglycerols and residual quantities of 5-7 percent source unreacted triacylglycerols (12). A significant fact is the preservation of the complete composition of fatty acids in the final product - liquid wax - comparison with the source oil. It is the form of liquid wax which easily absorbs in the epidermis, as a consequence of the lower molecular weight. The chemical structural similarity of liquid waxes with the products of skin sebaceus glands is high and we therefore see good compatibility with the natural constituents of the skin such as corneocytarine intercellular cement. From the cosmetic perspective, these liquid waxes prove to have excellent emollient properties, leaving the skin silky and soft, without the feeling of grease. A very important fact is the increase in the chemical stability of the present unsaturated fatty acids with respect to oxidation, in comparison with the source oil.

Another type of semisynthetic derivatives includes conjugated fatty acids. These substances are produced naturally, in small quantities, by the effects of the physiological micro flora in the digestive tract of ruminants, from the source polyunsaturated fatty acids. Subsequently, they are resorbed from the animals' gastrointestinal tract and deposited in the meat and milk fat, from where they enter the human food chain. The importance of these substances is especially in the ability to strengthen the immunity systems of organisms, protect against cancer diseases and regulate fat metabolisms (13, 14). These properties may also have a positive effect if administered topically. Polyunsaturated fatty acids from milk thistle and moldavian dragonhead oil can be converted using a chemical reaction to these conjugated fatty acids, or their esters with lower alcohols (15). These products are low-viscosity liquids which are easily manipulated and which especially have a significantly higher stability towards oxidation in comparison with free acids, while retaining their biological properties.

CONCLUSION

Fatty oils produced from the seeds of milk thistle and Moldavian dragonhead are an important source of polyunsaturated fatty acids. While the milk thistle oil contains especially the linoleic acid in the spectre of fatty acids (60 percent), the moldavian dragonhead oil contains the α-linolenic acid (60 percent). With the use of individual oils or their combinations, at ratio set between ω-3 and ω-6 fatty acids, it is possible to formulate a series of cosmetic products focusing on specific areas of use.

Both oils are appreciated for their high polarity leading to pleasant feelings and high absorption of the effective substances through the skin. Oils may be transformed into semisynthetic derivatives, especially through re-esterification with alcohols with medium-long chain or the rearrangement of double bonds in the molecules of fatty acids to conjugated forms. These derivatives provide further opportunities for the use of milk thistle and moldavian dragonhead oil, even in highly sophisticated cosmetic products.

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