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**Review Article**



# The Chocolate "Medications" With Natural Antioxidants

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## Abstract

The oxidation of ILLEXAO SC 70 confectionery fat (Sweden) in the presence of cocoa and natural antioxidants of wild rose, stigma of crocus flowers, and saffron was studied. It has been established that the presence of a powder of whole rosehip, as well as its parts, with a slight difference, serve as an antioxidant of oils. The proposed use of whole rosehip powder will enable waste-free chocolate production. The use of powders from the components of the rosehip allows you to expand the range of antioxidants for use in fat-intensive confectionery.

It has been established that the proposed use of saffron will create the possibility of obtaining high-quality chocolate, the use of crocus flower stigma powders will expand the range of antioxidants for use in high-fat confectionery products, as well as replace expensive saffron.

A new convenient method for extracting the organic part of saffron or stigma of crocus flowers is proposed. The effect of various powders (30 wt %) of the components of rosehip and (3 wt %) saffron on the dynamics of confectionery fat oxidation at 80°C was studied. Peroxide number was determined as a quantitative indicator of fat oxidation. The estimated composition of the stigma of crocus flowers and Iranian saffron was determined using GC-MS, to find antioxidant components. The presence of adipates and crocin was specified.

**Keywords:** Chocolate; Cacao; ILLEXAO SC 70 confectionery fat (Sweden); Natural antioxidant; Rosehip; The stigmas; The crocus flower; Crocus speciósus; Iranian saffron; The placebo effect; Iodometric method; HPLCh; GC-MS.

## Introduction

It is known that chocolate is a bridge between pharmaceuticals and confectionery and cocoa powder was used to make medicines long before the first chocolate bar appeared. At the beginning of the 19th century, the French pharmacist Jean-Antoine Brutus Meunier came up with the idea of adding chocolate to medicinal powders and covering bitter pills with it. Thus, the drugs were given a pleasant taste. Moreover, he managed to establish a successful pharmaceutical factory, which produced all kinds of "chocolate" medicines.

The basis of the action of chocolate medicines is the placebo effect. It is believed that placebo-based substances can be effective as real medicines, which gave impetus to the idea of breathing

Placebo chocolate medicines. In our opinion, chocolate tablets have more psychological impact, relieving people from anxiety and sadness. This a business idea is based on the actions of designer Stephanie Beneteau, who founded a company producing delicious medicines from chocolate that are available in the form of powder, lozenges and capsules.

In all cases, what chocolate did not serve as its fundamental factors are the composition and shelf life [1]. The presence of oils in chocolate, which are easily oxidized, thereby spoiling, leads to deterioration in the above factors. One of the ways to solve these problems is the introduction of antioxidants into the mass of chocolate (for example, biologically active additives - dietary supplements), often of synthetic origin, which adversely affect human health. Therefore, the use of plants and natural antioxidants is currently of great interest [2–4].

The main ingredient of chocolate is cocoa products (cocoa butter, cocoa mass, cocoa powder) [1]. However, the production of chocolate is greatly complicated by the fact that there is not enough oil contained in cocoa beans to make chocolate products. The high price of cocoa beans also matters. Therefore, in the production of chocolate, cocoa butter (20% of the chocolate mass) is replaced with confectionery fat of equal physical and chemical properties [1].

It should also be considered the fact that if cocoa butter is highly resistant to oxidation, then confectionery fat is subject to rapid deterioration due to oxidation, which leads to a reduction in the shelf life of the product [1]. It is more expedient to solve this problem by introducing powdered additives containing natural antioxidants into the composition of fat, for example, powders from rosehip or saffron components. It is known that the introduction of 3...6% rosehip powder into confectionery products can increase the biological value, reduce the calorie content, and improve the physicochemical and organoleptic properties of the product [2].

An important factor is the processing of natural antioxidants to maximize the preservation of biologically active substances in them. For example, fresh rosehip is a seasonal product; a powder form of additives was chosen for its use, since it has a high nutritional value, biochemical stability during storage, a smaller volume during transportation, and is most convenient for use in production [5].

The antioxidant properties of the proposed raw material as wild rose are mainly due to the significant content of ascorbic acid (vitamin C) and tocopherols (vitamin E). In terms of the content of these two antioxidant vitamins, rosehip surpasses many types of raw materials introduced into confectionery products [2-6].

This article also presents the results of a study on the possible use of the stigmas of the crocus flower - Crocus speciósus [7,8] and saffron from Iran as natural antioxidants. Saffron has been used since ancient times as a medicine. It is known that the use of saffron has a beneficial effect on the human nervous system and serves as a medical preparation [9-11]. In all likelihood, the antioxidant activity of the investigated stigmas of crocus - Crocus speciósus, can also be used for the noted purposes in similar products.

The antioxidant properties of saffron are mainly due to the significant content of crocin, as well as adipic acid and its esters, which contributes to its high antioxidant activity [9]. On the other hand, it is known that the stigmas of the crocus flower, moreover saffron, contain a yellow dye and serve as a dye for food [9,10]. So, the use of these substances will be doubly beneficial for the food industry. The question about the cost-effectiveness of using saffron will be resolved in the use of the substance, when milligrams of this spice are many times more effective in antioxidant activity compared to other antioxidants used grams.

This report presents the results of studies on the use of wild rosehip, its parts, as well as the stigmas of crocus flowers - Crocus speciósus and Iranian saffron to produce chocolate products with supposed antioxidant activity. It was believed that the additively of the antioxidant activities of both cocoa and the addition of the above natural antioxidants would increase the shelf life of chocolate products. And the resulting products will serve as chocolate medicines.

## Materials and methods of research

### The initial natural antioxidants

Wild rosehip (Kotayk region, RA) was studied as a raw material of plant origin antioxidant. Characteristics of freshly picked fruits: oval, average dimensions 25±3 x 13±2 mm, average weight of peeled fruits – 4.13 g/piece, pulp with peel – 67.7%, seeds – 26.3%, hairs - 6%.

The stigmas of crocus flowers - Crocus speciósus, growing in the Goris region of the Syunik region of the Republic of Armenia (altitude 1450-1500m above sea level) in natural flora were studied as a raw material of an antioxidant of plant origin. Flowers were collected in October 2022. They had a lilac-violet color with longitudinal veins. The anthers of the stamens were yellowish orange, the stigmas were separate, orange. Their size was several times the length of the stamens. The saffron stigmas of Saharkhiz Saffron Shops (Iran) were purchased from a regular spice shop.

### Drying of wild rosehip was carried out by a known method:

Rosehips were blanched with steam for 30 seconds, then the prepared fruits were placed in an even layer on mesh trays, which were loaded into a dryer with active ventilation and dried for 7 hours at a temperature of 70°C. This drying mode sets the minimum loss of vitamin C (15-20%) and the required residual moisture (no more than 12%), which ensures the microbiological stability of the product [6].

### Procedure for extracting the organic part of the stigmas of the Crocus flower and Iranian saffron.

Separated stigmas of crocus were dried at room temperature in a ventilated place, where the sun's rays did not fall, to a constant weight and stored in a dark place.

Extraction of crocus stigmas was carried out by maceration with hexane. Each batch of crocus flower and saffron samples was extracted as described:

1 g of stigmas of both crocus and saffron was ground in a ceramic mortar to a powder state (particle size 1 mm). Hexane was added to the resulting powder in a ratio of 1: 6 (6 ml of hexane per 1 g of

powder), kept at room temperature for 6 hours. The orange-colored organic extract was placed in a centrifuge tube and centrifuged at 5000 turn/min for 3 min. Then, 6 ml of a mixture of hexane was added to the residue of the extract and treated for another 10 minutes. The newly formed organic extract was centrifuged for 3 min at 5000 turn/min. After decantation, the organic extracts were combined and concentrated to 10 ml. The resulting organic extract was stored at 4°C in a refrigerator in the absence of light until analysis by GC-MS. For GC-MS analysis, 1 ml of the extract was used.

Whole rose hips are used to obtain powders, thereby avoiding the separation of residues - skins and seeds. After drying, the fruits are cooled and subjected to crushing. Thus, there is a rational use of wild rosehip and utilization of the entire mass of raw materials. It is possible to obtain powders both from whole fruits and from their individual parts - pulp with skin and seeds.

As a result of drying, 474.5 g of dried fruits are obtained from the studied 1 kg of fresh rosehip, and 245 g of dried pulp, 196 g of dried seeds are obtained from fruits previously cut in half. The dried rosehip components were ground in a knife mill to a particle size of 50 μm, then the content of vitamins C and E was determined in the obtained powders.

The content of vitamin E in the pulp of wild rosehip – 4.3 mg%, in the seeds – 23.4 mg% according to the results of HPLC: The results of titration (vitamin C is most contained in the pulp of rosehip, and less in seeds) and HPLC (vitamin E is most contained in rosehip) correspond to the literature data [2,5]. Vitamin C was determined by visual titration with a solution of sodium 2,6-dichlorophenolindophenolate according to GOST 24556-89, and vitamin E was determined by high performance liquid chromatography (HPLC).

The studies were carried out with a high-performance liquid chromatograph – HPLCh (Water 486-detector system, Water 600S - controller, Water 626 - Pump) on a 250x4 mm column filled with micro spherical silica gel sorbents with C18 groups on the surface, the flow rate of the mobile phase was 1 ml/min. UV-254 detector.

## Analysis by gas chromatography-mass spectrometry (GC-MS)

GC-MS analyzes were performed on a PerkinElmer Clarus 680 gas chromatograph with a PerkinElmer SQ 8 T mass spectrometric detector equipped with an Rxi-5MS (5% diphenyl, 95% dimethylpolysiloxane) capillary column, 30 m long, 0.25 mm inside diameter, and stationary liquid phase 0.25 μm. GC-MS analyzes were performed as follows. The oven was first heated to 40°C and kept at this temperature for 2 minutes. The temperature was then raised at a rate of 5°C/min to 250°C, then at a rate of 15°C/min to 280°C with a final hold of 1 minute. Helium (99.999%) was used as a carrier gas at a flow rate of 1 ml/min. The injector temperature was 250oC. The components were identified based on a comparison of the characteristics of the mass spectra with the data of the electronic library (NIST Mass Spectral Library, 2011).

## The oxidation of ILLEXAO SC 70

The oxidation of ILLEXAO SC 70 confectionery fat (Sweden) under the influence of rosehip powders (30 wt.%) both from individual parts of rosehip and, for comparison, cocoa powder for 8 hours at a temperature of 80°C was studied. The oxidation of ILLEXAO SC 70 confectionery fat (Sweden) was studied under the influence of the stigma of crocus (Crocus speciósus) flowers crushed in it, as well as Iranian saffron for 8 hours at a temperature of 80°C. For comparison, the oxidation of fat with cocoa powder was carried out under the same conditions.

## The usual materials

The saffron stigmas of the Iranian manufacturer Saharkhiz Saffron Shops were purchased from a regular spice shop. They were darker in color with a reddish tint. ILLEXAO SC 70 confectionery fat (Sweden) was purchased from the Yerevan Chocolate Factory. Methanol (high purity), ethyl acetate (high purity), hexane was purchased from the "Chemical reagents" store in Yerevan. Hexane used after distillation at 65-66°C. Methanol and ethyl acetate were purchased and used off the shelf.

## The discussion of the results

At the beginning of the experiment, the peroxide number of the fat sample, expressed as a percentage of iodine, was determined by the iodometric method with a two-hour interval. The results are shown in figures 1 and 2.

Fat oxidation is slowed down by the addition of powders containing antioxidants. Fat oxidation occurs at different rates depending on the powders from the rosehip components. Antioxidants react with free radicals in chain reactions of fat oxidation and interrupt the process with the formation of inactive products. In this case, free fatty acid radicals are switched off from the chain reaction, and the oxidative process is suspended.

Confectionery fat with rosehip seed powder oxidizes least of all, then cocoa powder, powder from the whole fruit, and powder from the pulp come in ascending order. This dependence is determined by the content of tocopherols and ascorbic acid. Increasing the concentration of seeds (tocopherols) proportionally increases the stability of confectionery fat. The peroxide number of confectionery fat with rosehip seed powder increases to 0.06% $I_2$ within 8 hours, and without the addition of an antioxidant - up to 0.3% $I_2$.

It follows from the figure 1 that at the initial moment, when semi-finished products are introduced into the studied fat, a sharp decrease in the peroxide number is observed, which is explained by the interaction of tocopherol with peroxide radicals; then it increases to a certain limit and again decreases. Apparently, there is a breakdown of peroxide radicals into secondary oxidation products. For confectionery fat (curve 1), after 6 hours, a sharp jump in peroxide number is observed. This can be explained by the activation of oxygen and the readiness of the system (double bonds of unsaturated fatty acids) to react to it. In fat with additions, active oxygen attaches tocopherol.

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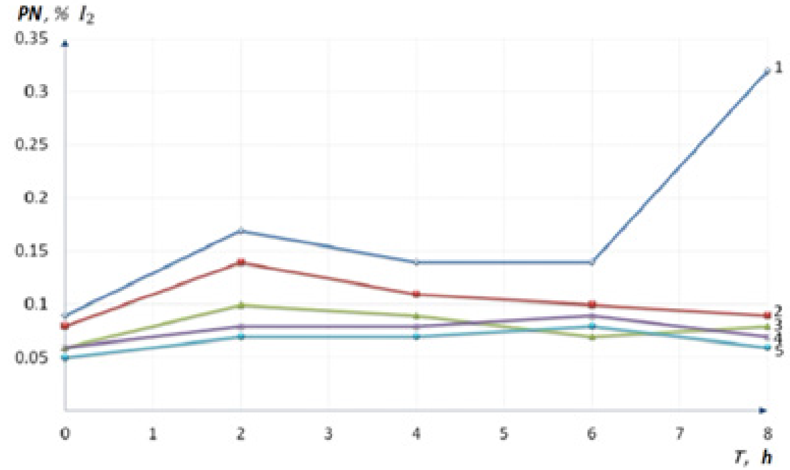


**Figure 1.** Influence of various powders (30 wt.%) on the dynamics of confectionery fat oxidation at 80oC: 1 - without powder, 2 - rosehip pulp powder, 3 - whole rosehip powder, 4 - cocoa powder, 5 - rosehip seed powder.

Ascorbic acid, being a synergist, enhances the action of tocopherol and acts only when it is present. It is possible that this acid reduces oxidized tocopherol, thereby ensuring its reparticipation in the reaction. Similarly, derivatives of crocus, as well as the studied saffron, were studied. Fat oxidation is slowed down by the addition of crocus flower stigma powders and Iranian saffron. Fat oxidation occurs at different rates depending on the type of antioxidant.

Confectionery fat with Iranian saffron powder oxidizes the least, then cocoa powder, powder of dried flower stigmas, crocus stigmas - Crocus speciósus, and the least active powder is undried stigmas - Crocus speciósus. This dependence is determined by the content of crocin and adipates. The peroxide number of confectionery fat with Persian saffron increases to 0.05% I2 in 8 hours, and without the addition of an antioxidant - up to 0.3% I2.

It follows from the figure 2 that at the initial moment, when semi-finished products are introduced into the studied fat, a sharp decrease in the peroxide number is observed, which is explained by the interaction of antioxidants in the crocus flower and saffron with peroxide radicals; then it increases to a certain limit and again decreases. Apparently, there is a breakdown of peroxide radicals into secondary oxidation products. For confectionery fat (curve 1), after 6 hours, a sharp jump in peroxide number is observed. This can be explained by the activation of oxygen and the readiness of the system (double bonds of unsaturated fatty acids) to react to it. In fat with additions, crocin attaches active oxygen.

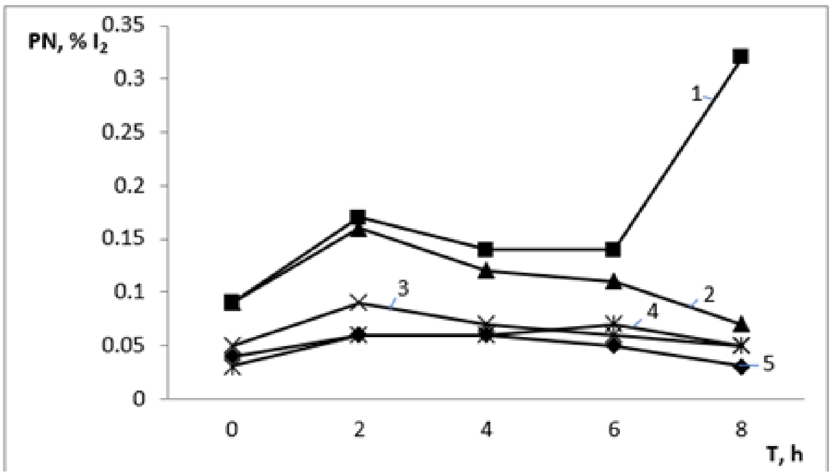


**Figure 2.** Influence of powders of crocus flower stigmas and saffron (3 wt.%) on the dynamics of confectionery fat oxidation at 80 oC: 1 - without powder, 2 - powder of crocus flower stigmas, 3 - powder of dried crocus stigmas, 4 - cocoa powder, 5 - powder from Persian saffron.

## Conclusions

It is proposed the new convenient method for procedure for extracting the organic part of saffron or stigmas of crocus flowers. It is shown that the presence of the powder of the whole rosehip fruit, as well as its parts, with a slight difference, serves as an antioxidant of oils. It has been established that the proposed use of whole rosehip powder will create an opportunity for waste-free chocolate production. The use of powders from rosehip components can help expand the range of antioxidants for use in fat-intensive confectionery. It is established that the proposed use of saffron will create an opportunity for obtaining high quality chocolate. It has been established that the use of crocus flower stigma powders can help expand the range of antioxidants for use in fat-intensive confectionery products, as well as replace expensive saffron.

## Acknowledgment

None.

## Conflict of interest

None.

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