THE USE OF FOOD DYES: PROBLEM, SOLUTION AND SOURCE OF PERSPECTIVE

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Abstract. For consumers, the colour presents an indicator that characterizes the quality of the food. As a result of the processes of caramelization of carbohydrates and products of the Maillard reaction, brown compounds are formed with a negative impact on the external appearance of food, which has led to the massive use of synthetic dyes, stable from a technological point of view. The objectives of the European Union foresee the transition to the exclusive use of natural dyes, because synthetic dyes significantly affect the health of the population. Compounds with "azo" type chromophore groups (amaranth, tartrazine) present carcinogenic dangers, being banned in several European countries. The aim of the present study was to evaluate the problem of synthetic dyes and their substitution in food, obtaining, stabilizing and using natural dyes for the food industry. The study highlighted that safflower (Carthamus tinctorius L.) presents a promising source of yellow and red dyes, necessary for use in the food industry, but insufficient information was found regarding the technological properties of safflower petals, the methods of simultaneous extraction of yellow and red dyes and the peculiarities of the use of dyes in the finished product.

Keywords: natural dyes, synthetic dyes, safflower, chalcones, carthamine.

Rezumat. Pentru consumători culoarea prezintă un indicator care caracterizează calitatea alimenelor. În urma proceselor de caramelizare a glucidelor și produselor reacției Maillard se formeză compuși de culoare brună cu impact negativ asupra aspectului exterior al alimenelor, ceea ce a condus la utilizarea masivă a coloranților sintetici, stabili din punct de vedere tehnologic. Obiectivele Uniunii Europene prevăd trecerea la utilizarea exclusivă a coloranților naturali, deoarece coloranții sintetici afectează semnificativ starea de sănătate a populației. Compuși cu grupări cromofore de tip „azo” (amarant, tartrazina) prezintă pericole cancerigene, fiind în mai multe țări europene interzise. Scopul prezentului studiu a constat în evaluarea problemei coloranților sintetici și substituirii lor în alimentoare, a obținerii, stabilizării și utilizării coloranților naturali pentru industria alimentară. Studiul a scos în evidență, că șofrănelul (Carthamus tinctorius L.) prezintă o sursă de perspectivă de coloranți galbeni și roșu, necesari pentru utilizare în industria alimentară, însă nu au fost găsite suficiente informații referitor la proprietățile tehnologice ale petalelor de șofrănel, metodele de extrație concomitentă a coloranților galbeni și roșu și particularitățile utilizării coloranților în produsul finit.

Cuvinte cheie: coloranți naturali, coloranți sintetici, șofrănel, calcone, cartamina.
1. Introduction

In recent years, an increased interest is addressed to the field of research that ensures the stability of nutritional compounds in order to protect the sensory quality of food products. The evolution of human society led to the identification of some criteria about the quality of food according to their external appearance. Among these compounds, food dyes are a particularly important part. One of the main directions of use of dyes, according to European Parliament and Council Directive 94/36 EC of June 30, 1994 [1], consists in their introduction into food products to restore color, which has been affected following processing, storage, packaging and distribution of the finished product or for coloring a product, initially colorless.

Based on the list of colorants recommended for use of the Codex Alimentarius, each state approves the list of colorants that are permitted for use in that geographic and political space. In the Republic of Moldova, the official list of dyes allowed for use in food industry, which was published in the Sanitary Regulation on food additives, approved by Government Decision no. 229 of 20.03.2013 [2].

At the same time, a special attention of researchers is given to the assessment of the possible toxicity of synthetic food dyes. As a result of voluminous and multilateral researches, carried out recently, fundamental requirements were formulated, to which they must correspond, to be used.

The properties of a food coloring must satisfy the following restrictions [2]:
- the chemical compound, which provides color, must not be toxic, allergic and carcinogenic;
- the dye in industrial and commercial forms must not contain harmful impurities;
- the food coloring must not change the natural taste and smell of the product, it is included in the composition;
- on food product storage, the dye must be stable at certain pH values, product storage temperatures and, where applicable, ultraviolet and visible solar radiation.

The aim of the present study was to evaluate the problem of synthetic dyes and their substitution in food, obtaining, stabilizing and using natural dyes for the food industry.

2. The impact of chemical compounds modification on the appearance of food products

Thermal processing of food compositions is one of the most frequently process in the manufacture of food products. At "room" temperatures of 20–25 °C, the change in food color is little significant, gradually increasing in the temperature range from 25 to 80 °C [3] the change accelerates. The chemical reactions that cause food colors to change are different. The speed of appearance change reactions depends on the chemical composition of food, temperature, pH values, water activity and others. To protect the natural appearance of food, it is necessary to know those chemical changes that cause color degradation.

An example of color modification is the caramelization of mono- and disaccharides in food compositions. Caramelization is a complex chemical process. Prolonged heat treatment causes the decomposition of glucose, fructose with their transformation into 5-hydroxymetilfurful, (5-HMF), yellow and brown derivatives [4].

The muscle tissue protein, myoglobin, determines the red color of the meat. Myoglobin, an important sensory characteristic in forming the appearance of meat and meat products. The metal-organic nucleus of myoglobin contains Fe(II), which determines the red color of fresh meat. Myoglobin by chemisorption adds an oxygen molecule and turns into
pronounced red oxymyoglobin [5]. Over a long period of time, the two-valent iron cation present in the structure of oxymyoglobin oxidizes, in three-valent iron, Fe(III), which leads to the transformation of oxymyoglobin into metmyoglobin, a stable brown color, which changes the natural appearance of the meat. [5].

The interaction reaction of proteins, peptides and amino acids with reducing sugars or with carbonyl compounds leads to the formation of brown compounds, which are called melanoids. The Maillard reaction takes place spontaneously in the process of obtaining products of plant and animal origin. For example, the interaction of D-fructopyranose with the amino acid glycine leads to the formation of 1-fructosylamine with a gray appearance [6].

The transformation of polyphenols from a reduced state to an oxidized state leads to the formation of brown products that distort the appearance of freshness of food products. The maximum speed of the enzymatic reaction between molecular oxygen and polyphenols is observed in the first minutes when cutting or crushing fruits and vegetables. During this time, leucoanthocyanins, catechins, anthocyanins, caffeic and chlorogenic acids undergo oxidation, which easily oxidize and turn into orange and brown compounds.

In the official list of functional classification of food additives, developed by the International Codex Alimentarius Commission, food additives have been divided into classes. Within the coding system of all additives, food colorings have been placed in a special class E100 – E199.

From the point of view of chemical structures, food dyes can be divided into three groups:
- natural dyes (chlorophylls, anthocyanins, carotenoids, chalcones, naphthoquinones, betalains, etc.);
- artificial dyes, obtained by chemical modification of natural compounds: oxidation or modification of the structures of functional groups, complexation of natural compounds with metal ions;
- synthetic dyes (azo compounds – tartrazine, ponceau; synthetic derivatives of indole, etc.).

3. Functional properties of synthetic dyes and their particularities of use

Synthetic dyes obtained through chemical synthesis are much more effective from a technological point of view. They have a higher coloring power compared to natural compounds, they are quite resistant to changes in temperature and pH values. Synthetic food dyes related to a fairly wide range of compounds from different classes (Tabel 1).

<table>
<thead>
<tr>
<th>Number E</th>
<th>Name of colorants</th>
<th>Color</th>
<th>Mode of use</th>
</tr>
</thead>
<tbody>
<tr>
<td>E 102</td>
<td>Tartrazine</td>
<td>Yellow</td>
<td>ADI</td>
</tr>
<tr>
<td>E 104</td>
<td>Quinoline yellow</td>
<td>Yellow</td>
<td></td>
</tr>
<tr>
<td>E 110</td>
<td>Sunset yellow FCF</td>
<td>Yellow</td>
<td></td>
</tr>
<tr>
<td>E 122</td>
<td>Azorubine</td>
<td>Red</td>
<td></td>
</tr>
<tr>
<td>E 124</td>
<td>Ponceau 4R</td>
<td>Red</td>
<td></td>
</tr>
<tr>
<td>E 129</td>
<td>Allura Red AC</td>
<td>Red</td>
<td></td>
</tr>
<tr>
<td>E 131</td>
<td>Patent BlueV</td>
<td>Blue</td>
<td></td>
</tr>
<tr>
<td>E 142</td>
<td>Green S</td>
<td>Green</td>
<td>ADI</td>
</tr>
<tr>
<td>E 143</td>
<td>Fast Green FCF</td>
<td>Green</td>
<td></td>
</tr>
</tbody>
</table>

Note: ADI – acceptable daily intake
From the point of view of technological use, synthetic dyes are widely used in food processing. The stable color shade, the excellence of modern production technologies, the very high yields and the modest cost of obtaining by the synthetic route – all these have led to the predominant use of synthetic dyes in the manufacture of food products.

The chemical structure of synthetic dye molecules includes chromophore groups of the "azo" type (–N = N–), auxochromic carboxylic, hydroxyl, amine groups, etc.

Tartrazine, E 102, (Figure 1) is a heterocyclic azo-compound, which has yellow color, is water-soluble dye and is used in the manufacture of various food products. Tartrazine is often used in non-alcoholic beverages together with another synthetic yellow dye, sunset yellow FCF, E 110.

Azorubine, E122, is a red water-soluble dye, stable at 100°C, which is why it is used to color foods, which are subjected to different heat treatments, (Figure 2).

Some investigations show that azorubine interacts with proteins, disrupting the normal biological function of serum albumin, also having a negative effect on the collagen structure, which present a risk to the skin. Phytotoxicity research has found that high concentrations of azorubine have a significant inhibitory effect on grain growth [7].

Despite the fact that the use of certain synthetic dyes is prohibited in EU countries, however, in some countries in Eastern Europe and Asia, their use is absolutely legal [8]. The legislation of these countries provides for the diminish the risks that synthetic dyes present to human health. Thus, their used in food compositions must the following requirements:
- the respect the acceptable daily dose, DZA,
- not to exceed the concentration allowed in the food product [8].

On the other hand, a group of dyes is under strict control, for its negative effects. These dyes include: brilliant blue FCF, E 133, quinoline yellow, E 104, tartrazine, E102, azorubine, E122. It is found that these dyes cause some negative effects, especially on the nervous system [9]. Hyperactivity disorders, attention deficit disorder, various allergic reactions, food intolerances and others have also been found [10]. Allura red is potentially carcinogenic, because use of that dye has been banned in several European countries [11]. Table 2 shows a group of synthetic dyes, the incorporation of which in food products is strictly regulated by the directives of the European Commission [12].
In addition to the fact that synthetic dyes are used in food products to restore the natural attractive color, there is another problem related to adulteration of food products with the use of dyes in order to mask the defects of adulterated foods [13, 14]. The most commonly counterfeited food groups include foods such as wine, meat, fish, honey, etc. [15]. For example, to obtain a reddish color of fish, similar to the color of salmon roe, a mixture of synthetic dyes ponceau 4R, E 124 and orange yellow, E 110 is used, and to give a golden yellow color to smoked fish, use the mixture of tartrazine, E 102 with sunset yellow FCF, E 110.

Table 2

<table>
<thead>
<tr>
<th>Name of colorants</th>
<th>Number E</th>
<th>Color</th>
<th>Area of use</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tartrazine</td>
<td>E 102</td>
<td>Yellow</td>
<td>Soft drinks, jellies, candies</td>
</tr>
<tr>
<td>Quiniline yellow</td>
<td>E 104</td>
<td>Yellow</td>
<td>Beverages, pharmaceutical drugs</td>
</tr>
<tr>
<td>Sunset yellow FCF</td>
<td>E 110</td>
<td>Yellow</td>
<td>Sweets, ice cream, beverages with alcohol</td>
</tr>
<tr>
<td>Azorubine</td>
<td>E 122</td>
<td>Red</td>
<td>Yogurts, jellies, jams, preserves</td>
</tr>
<tr>
<td>Ponceau 4R</td>
<td>E 124</td>
<td>Red</td>
<td>Marzipan, sauces, sweets</td>
</tr>
<tr>
<td>Allura red AC</td>
<td>E 129</td>
<td>Red</td>
<td>Alcoholic drinks, jellies</td>
</tr>
</tbody>
</table>

As the manufacture of natural dyes can be affected by insufficient harvest followed by climate change, there are cases where the natural dyes themselves have been counterfeited, for example, natural saffron dye and paprika powder have been mixed with Sudan Red III [16], the use of which is prohibited in the European Union.

The contemporary trend of elaborated and manufacturing new food products, which can correspond in terms of organoleptic and nutritional properties with foods rich in animal proteins, leads to the selection of non-traditional vegetable raw materials, as well as the development of food compositions based on insects, or, in a more distant perspective – of special cell cultures [17]. Arising from the need to develop this direction, it is necessary to elaborating and manufacturing a new naturals dyes, which will be able to be used in the obtaining of these products.

More than that, the existence of an EU strategic plan to replace synthetic dyes with natural ones, led to the formation of the new direction of investigations, which aims to identify harmless natural dyes, for their further use in food technology.

4. The functional properties of natural dyes and their particularities of use

Natural dyes present pigments from plant or animal origin. As a rule, these dyes are obtained by extracting from plants, seeds, roots, etc. Some natural dyes present biologically active compounds, for example, carotenoids, catechins, cyanidin glycosides, which demonstrate a positive impact on the biological values of food.

Coloring food products with natural dyes is usually seen as a healthier option compared to synthetic dyes [18]. Table 3 presents the list of natural dyes [19], admitted for use in the food industry of the Republic of Moldova.

In general, a part of natural dyes from edible sources are not harmful and are considered bio-dyes [20]. Because of their edibility, bio-colorings can be used in food
products according to the principle of quantum satis, which involves the addition of colorants in unlimited amounts (reasonable from the point of view of economic necessity), to obtain a desired sensory effect.

Analyzing the literature, it is observed that red dyes from different classes (anthocyanins, betanin and chalcone - carthamine, which is the object of study of this paper), have many common characteristics, which refer to their low stability in relation of heating, rapid degradation in basic medium, the strong dependence of their shade on pH, interactions with biopolymers.

Table 3

<table>
<thead>
<tr>
<th>Number E</th>
<th>Name of colorants</th>
<th>Color</th>
<th>Mode of use</th>
</tr>
</thead>
<tbody>
<tr>
<td>E 100</td>
<td>Curcumin</td>
<td>Yellow</td>
<td>Quantum satis</td>
</tr>
<tr>
<td>E 101</td>
<td>Riboflavin</td>
<td>Yellow</td>
<td>Quantum satis</td>
</tr>
<tr>
<td>E 120</td>
<td>Carmine</td>
<td>Red</td>
<td>Quantum satis</td>
</tr>
<tr>
<td>E 132</td>
<td>Indigo/indigo carmine</td>
<td>Blue</td>
<td>Quantum satis</td>
</tr>
<tr>
<td>E 140</td>
<td>Chlorophyll, chlorophyllin</td>
<td>Green</td>
<td>Quantum satis</td>
</tr>
<tr>
<td>E 150 a, b, c, d</td>
<td>Carotenoids: carotene, annatto, lycopene, red pepper extract</td>
<td>Brown</td>
<td>Quantum satis</td>
</tr>
<tr>
<td>E 160 a, b, c, d, e</td>
<td>Lutein (b), cantaxin (g)</td>
<td>Orange</td>
<td>Quantum satis</td>
</tr>
<tr>
<td>E 161 b, g</td>
<td>Betaine</td>
<td>Red</td>
<td>Quantum satis</td>
</tr>
<tr>
<td>E 162</td>
<td>Anthocyanin</td>
<td>Red, violet, blue</td>
<td>Quantum satis</td>
</tr>
<tr>
<td>E 163</td>
<td>Anthocyanins</td>
<td>Red, violet, blue</td>
<td>Quantum satis</td>
</tr>
</tbody>
</table>

Anthocyanin pigments, E 163, are found in most fruits, vegetables and products made from them. The basis of the chemical structure of anthocyanins is the phenylbenzopyryllium (flavyllium) cation, formed by the benzopyryllium nucleus (A) and the phenolic ring (B). In the absence of the carbohydrate bonds of the flavyl core, the flavyl cation is called an anthocyanidin. Chemically, anthocyanins are glycosides of the flavylium cation, (Figure 3).

![Figure 3. Chemical structure of the flavylium cation.](image)

Given that anthocyanin dyes are unstable, their use in the food industry is almost impossible for a wide range of products. Anthocyanin extracts in acid medium have a stable red color, and in alkaline medium they acquire a blue color, therefore the use of anthocyanins
depends on the pH of the food product. Anthocyanins are widely used in the beverages, juice [21] and confectionery industries.

Carotenoids form a group of additives coded by E160a. The most obvious distinguishing feature of this group is the shape of the molecule, which presents a polyene chain, which can be extended up to 15 conjugated double bonds, (Figure 4) [22]. They possess the characteristic absorption spectrum in the visible region of the spectrum, with $\lambda_{\text{max}}$ 420...480 nm and, consequently, the yellow or orange color.

![Figure 4. Chemical structure of the β-carotene molecule, E160a.](image)

In addition to coloring properties, some representatives of carotenoids have provitamin properties, because they have the ability to break down in the human body and turn into vitamin A.

Initially, extracts of paprika, anatto, tomato and pumpkin were used as sources of carotenoids. It should be noted that these extracts do not represent carotenoids in a pure state, or a mixture with a constant chemical composition, composed of the same substances, but contain components with different properties, one of which is the very strong aroma. This fact considerably limits the use of extracts in the food industry [22].

Betanin, E162, is a natural red food coloring, approved for use in the food industry by Regulation (EU) no. 1129/2011 of the commission of november 11, 2011 and the health regulation on food additives of the Republic of Moldova [2]. Betanin extracts are stable over a wide pH range, from 3 to 7, which ensures the use of betanins to protect the red colors of acidic and neutral foods. High temperatures of more than 60°C negatively influence the stability of betanins, causing dye degradation and color loss, (Figure 5).

![Figure 5. Chemical structure of the betanin molecule, E 162.](image)

Betanin extracts have been shown to be more sensitive to high temperatures than anthocyanin or carotenoid extracts [23]. The satisfactory stability at low temperatures makes betanins suitable colorants for their incorporation into ice creams, yogurts and soft drinks,
fruit cocktails, sweets, jellies and meat products [24]. The main source of betanin is beetroot [25], but more and more sources are emerging for obtaining betanin, for example, from Opuntia stricta. The color indices of the dye obtained were compared with different dyes marketed as a concentrate (beetroot, red carrot and black grape skin) [26]. It was found that the dye obtained from Opuntia stricta possessed a more attractive red-violet color than those from the mentioned sources.

Currently, natural dyes from the class of carotenoids (from Bixa orellana L.), betanins (from Beta vulgaris L.), etc. are marketed and approved for use in the US and EU [27].

The study, in which pork sausages were manufactured with the addition of tomato skin powder [28] demonstrated that the color of sausages with 1,5% tomato powder was unstable during storage, but no changes were observed sausage color with 0,8% and 1,2% powder. It has been proven that to solve the problem of increasing the stability of lycopene it is necessary to reduce the temperature of the extraction process and to use stabilizing agents [29], in order to be able to replace the artificial dye allura red AC.

Hofmann also demonstrated that anthocyanins extracted from radishes and red potatoes can be used as an alternative to replace the synthetic allura red dye, E 129, for the production of a type of maraschino cherry preserve [30]. By comparing the color indices of anthocyanins at pH 3,5 with the synthetic dye, they demonstrated the identity of the red shade of the synthetic and natural dye. At the same time, it should be noted that the respective sources are of purely scientific interest not practical, since the extraction of dyes from them is not economically advantageous.

In the research, carried out at the FTA UTM by Ghendov-Moșanu et al., it was demonstrated that sea buckthorn fruits (Hippophae rhamnoides L.) contain significant amounts of phytonutrients, some of which are carotenoids, which act as antioxidants and manifest other functional properties, for example, help in collagen synthesis [31].

Despite the fact that the consequences of the use of synthetic dyes, previously mentioned, are serious, tartrazine and azorubin, whose advantage is a good solubility in water, are widely used for the manufacture of food in the Republic of Moldova. Considering the above, it is of particular interest to study new vegetable sources, which contain large amounts of pigments, which are economically advantageous to obtain and, at the same time, have the technological properties necessary for their use in food products.

5. Safflower, the perspective plant for obtaining food dyes

The perspective plant for obtaining biologically active substances is safflower, (Figure 6). Safflower (Carthamus tinctorius L.) is an annual herbaceous plant from the Asteraceae family. Safflower is cultivated worldwide on large areas in China, the USA, Kazakhstan, Turkey, the Russian Federation, Ukraine and Romania [32]. In recent years, significant amounts of safflower have been cultivated in Iran, where its use as a food coloring is gradually increasing.

Strong point of safflower culture is that this plant is resistant to heat and prolonged drought, tolerates strong sunlight, which makes this plant even more attractive for cultivation prospects in the context of water scarcity and global warming [34].

The growing season depends on the variety and climatic conditions, ranging from 93 to 152 days. Flower picking takes place in summer, from july to august, in dry weather to prevent rotting of the plant and speed up the drying process. The flowers are dried in the open air, immediately in the shade and in very well ventilated places.
Safflower is a special culture, because all the organs of the plant can be used industrially. Safflower leaf tea is used to prevent heart disease in traditional and modern Chinese medicine [35]. The stalks are used as animal feed and have a yield with higher forage value than oats or alfalfa [36].

The most well-known way of processing safflower is to obtain oil from its seeds. It was found that safflower seed oil is rich in fat-soluble biologically active substances: linoleic acid [37], oleic acid, tocopherol, which makes it advantageous for the manufacture of quality cosmetic products [38].

Considering the high content of chalcone dyes, the safflower plant (Carthamus tinctorius L., Asteraceae;) is of particular interest for conducting research in the field of obtaining and using natural dyes.

It should be noted that information about the saffron plant even in scientific literature is often confused with another plant, saffron (Crocus sativus L., Iridaceae, Sofran), because the names are similar in different languages, the outer appearance of the petals. ripened by Carthamus tinctorius is almost identical to the appearance of Crocus sativus stigmas [39].

Of particular interest to us were the petals of the safflower plant, which contain two pigments: yellow and red. It is known that until the 19th century, when synthetic dyes became available much cheaper than the natural ones and which are part of the aniline derivatives, saffron was cultivated to obtain red dyes and was used, mainly in Egypt, to color the cotton. and silk. By the 18th century, yellow "Egyptian dye" from safflower was used in Italy, France and Great Britain to color cheese and salami [40].

Currently, the Institute of Genetics, Physiology and Plant Protection of the Republic of Moldova is conducting research on the possibilities of cultivating the safflower plant in our countries. The positive results, obtained at this moment, can serve as a practical basis for the surface of a new species of plants in the agriculture of the Republic of Moldova [41].

Despite the fact that safflower would become a valuable plant for agriculture and the economy of our country, no internal studies have been conducted of chemical composition of different parts of the plant and their processing into commercial products.

For the Republic of Moldova, the greatest practical interest would be anthocyanin dyes, since the country's agriculture produces large quantities of red grape pomace. Considering that the chromotory of anthocyanins is very unstable to the influence of oxygen, sensitive to pH values, i.e. the color changes from red to purple [42] occur very quickly, the problem of obtaining these colors is very complicated. Moreover, obtaining the anthocyanin
dye is a problem not only from the point of view of physico-chemical properties, but also from the point of view of high energy costs, which are consumed to block the oxidative processes and remove excess moisture from the pomace through different methods.

For this reason, it is of interest to study different vegetable sources with low initial water content, which contain pigments and possess technological properties necessary for the further use of these pigments in the food industry.

In this sense, safflower, a plant resistant to insufficient humidity [43] present a plant with great prospects specific to the climatic and pedological conditions of the Republic of Moldova.

The chemical composition the petals contains flavanoid pigments, derived from chalcone. Unlike the widespread O-glycosylated derivatives, safflower chalcones belong to the rare group of C-glucosylchalcones, i.e. deoxyglucose derivatives, the best known being hydroxysaffron yellow A, anhydrosaffron yellow B and precarthamine. The yellow C-glucosylated pigments, which predominate in the structure of the petals, are soluble in water. Phytochemical and pharmacological research has shown that these water-soluble components are responsible for the therapeuatic effects, especially C-quinochalonic glycosides, which are considered the main active compounds [44]. Hydroxysafflor yellow A, the substance identified and obtained by us, is the basic biologically active component of yellow compounds in safflower petals, hydroxysafflor yellow A has been shown to limit platelet aggregation, regulate blood circulation, possess antioxidant properties and accelerate metabolism [45]. Yellow pigments constitute 25% of the petal mass. Sometimes, even in the scientific literature, you can find erroneous information about the naming of yellow dyes. Thus, one of them is called cartamidine [46]. In reality, carthamidine does not belong to the class of chalcones, being a closed-cycle dihydroflavone.

The process of biosynthesis, which takes place in the safflower flower, gradually changes the colors of the petals from yellow to red. The enzyme β-glucoseoxidase contributes to this change in the flowering stage. This enzyme is distributed in vegetative tissues and is active at pH 4,8 [47]. The color changes of the petals in the red shade are a proof of the formation of cartamine pigment (Figure 7), the fact that the molecule is composed of two chalcone residues. Cartamine occurs in petals as a result of enzymatic oxidation of precarthamine [48] and constitutes about 5% of dry petal mass. Cartamine produces the most valuable pigment in safflower petals, red in color, non-anthocyanin in nature.

![Figure 7. The red pigment molecule - carthamine.](image-url)
Different methods of obtaining yellow dyes are described [49-51]. Most of the principles of obtaining dyes are based on the primary removal of yellow dyes, after which the red dye is removed in individual form. Various bibliographic sources describe methods of extracting dyes with solutions, which have a high toxic level (trichloroacetic acids, trifluoroacetic acids - TFA), which obtaining of harmless natural dyes. Moreover, from various sources, obtaining yellow dyes is achieved with the use of alkaline solutions (NaOH, KOH), which, according to our results, leads to the degradation of red dye - carthamine. We demonstrated that it is possible to simultaneously obtain yellow and red dyes from the same aqueous extract [52]. Dyes can be obtained both in the form of a liquid concentrate and in a solid state. Due to its water-soluble properties and high stability, the yellow dye can be used in a fairly wide range of food products: juices, jellies, caramels, sauces, etc.

Fatahi et al. investigated the influence of pH, temperature and light on yellow dyes and carthamine [53]. In terms of temperature stability (10, 30, 50 and 70 °C), yellow dyes have been shown not to undergo significant degradation. In terms of pH stability, yellow dyes have been shown to be much more stable than carthamine. The effect of the degradation of yellow dyes is manifested in alkaline medium, therefore, it does not significantly influence the research, because there are no food products with such pH values. At the same time, the same team of researchers reports the degradation of carthamine at pH values, which correspond to the acidic medium. These claims have not been confirmed by the author of this article. Carthamine is a compound unstable to light and oxygen, but according to our results, it does not decompose in weakly acidic medium. At low acidic pH values, carthamine stabilization occurs.

Carthamine is a quinoidal chalcone glycoside, which in its native state in aqueous medium decomposes very easily with the formation of yellow-orange compounds. Various bibliographic sources confirm that the red dye, carthamine, has been used since ancient times to color textile fabrics. Thus, it can be concluded that in some conditions of technological treatment stabilization with carthamine can take place.

A method to stabilize carthamine was reported by Saito et al. [54], who investigated the possibility of stabilizing cartamine by adding sugars to the solution. They have, that monosaccharides and disaccharides show little promise as stabilizers, but polysaccharides exert a positive action on the pronounced red colors of carthamine. The results of carthamine stabilization on cellulose, reported by Saito, correlate with the research results, reflected in the present article. The FTIR spectra obtained by Saito show that the interaction of cellulose with cartamine leads to the appearance of several new bands at 1600 and 1500-1350 cm⁻¹, which were not identified in the spectra of carthamine and cellulose in the individual state [54]. But information about the concrete mechanism, which leads to the formation of the complex between cartamine and cellulose, was not found in the literature.

The appearance of new bands whose values are not identical to those reported by Saito has been highlighted. The reason for using other types of cellulose ("Sigma-Aldrich", "Flo-109") [55], as much as possible, is that it could benefit from other works, where classical FTIR was used in KBr in oil fluorinated, we used the ATR variant of FTIR spectroscopy. The results of author of this article [55], show that carthamine rearranges the intermolecular hydrogen bonds of cellulose on itself, thus forming the chemical bond.

The previously mentioned carthamine stabilization method leads to the fact that carthamine in aqueous systems behaves as a suspension, which does not allow its...
incorporation into transparent and homogeneous media with a high water content, for example, in soft drinks, etc.

Another study proposes the solubilization method of carthamine using its complexation with glycosylhisperidine [56]. The latter has the ability to prevent the formation of crystals in an aqueous solution. This study demonstrated that the color shade of glycosylhisperedin-linked carthamine, Hsp-G, was redder than that of cellulose with cartamine [53]. As a result, the authors of this research propose the method, which includes the addition of glycosylhisperedin to the alkaline extract of safflower petals, replacing the cellulose. At the same time, the investigations carried out during the works allow us to question the effectiveness of these methods, considering that in alkaline environments they destroy carthamine.

6. Conclusions
1. The analysis of bibliographic sources allows to state that the problem of obtaining and using natural dyes for the food industry remains current from a theoretical and applicative point of view. The structure and properties of the dyes used influence food quality assurance. Therefore, solving the problems related to the natural obtaining and use of dyes from new vegetable sources in the food industry is current for the Republic of Moldova.

2. A large number of bibliographic sources indicate that the safflower plant presents a promising source of yellow and red dyes for use in the food industry, few publications, especially local ones, include research in this field.

3. At the same time, not enough extensive information was found on the technological properties of safflower petals, for the extraction of dyes, despite the fact that they directly influence the yield of obtaining and the peculiarities of the use of dyes in the finished product. There is also a lack of information on the existence of methods for the simultaneous extraction of yellow and red dyes from safflower petals.

4. The studied bibliographic sources contain insufficient information about the need to solve the stabilization problems in food compositions of the chemical structures of carthamine, as well as about the physico-chemical and technological characteristics, which will make possible the use of carthamine in the food industry.

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References


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