ULTRAVIOLET AND VISIBLE SPECTROSCOPY FOR THE ANALYSIS OF CRUDE EXTRACT OF COTINUS COGGYGRIA *(COTINUS COGGYGRIA SCOP; ANACARDIACEAE)*

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Abstract

Cotinus coggygria extract has been used as a dye for silk, wool and leather in Eurasia, including Azerbaijan, since ancient times. In order to be an artisanal staining of these products it is used raw – crude extract of fisetin obtained from the wood of smoke trees. To obtain a uniform color in certain product batches a dyeing bath with a certain density of fisetin is prepared. Our experiments show that in the spectrum of the crude extract fisetin in 95% ethanol, there are two characteristic UV/VIS bands. The band of the first group located, with a maximum of about 314 *nm*, arising from the ***B*** ring, the second – with a maximum around 412 *nm* arising from the ***A*** ring. This gives us reason to say that in order to establish the amount of fisetin in the dye solution, one of the earliest methods of ultraviolet and visible spectroscopy can be successfully used.

Key words: optical density, dependence of wavelength, short-wave band, dye for silk, certain density fisetin.

INTRODUCTION

Natural vegetable dyes are natural components of foods: vegetables, fruits and berries. They are used to maintain and improve the appearance and color of food, as well as to improve the nutritional value. Vegetable dyes in its composition molecules contain a variety of pigments (colored compounds: chlorophylls, carotenoids, betatsianiny, anthocyanins, etc.), which possess a wide spectrum of biological activity, exhibiting antioxidant, antibacterial, antifungal, immunomodulatory, and many others properties. One of these flavonoids - fisetin (2-(3,4-Dihydroxyphenyl)-3,7-dihydroxy-4H-chromen-4-one). Young fustic (*Cotinus coggygria* Scop; *Anacardiaceae*) has been used as a dyestuff since antiquity. It is found in various fruits and vegetables, such as strawberries, apples, persimmons, grapes, onions, cucumber etc.

Fisetin is usually used as markers for the identification of the yellow dye and for the first time some component of flavonoids were found into the historical extracts. Furthermore, preliminary experiments suggested that although the amounts of the dye components decrease with light ageing, the relative ratio of fisetin, after a first step of ageing, seems to be almost unaffected by such degradation processes raised by light. The effect of the latter on the morphology of the dyed silk fibers is briefly investigated by scanning electron microscopy [1].

We note that since medieval times Sheki silk was so famous in West and East countries, the Venice and Kenya merchants came here for getting and buying silk. The clothes were popular for its quality, artistic and aesthetic beauty, at the same time for dyeing fabrics with the natural colors. The painting is Azerbaijan people's old created and maintained public art.

The main source for fisetin is Cotinus coggygria and in our region for the extraction of fisetin, in the main are used wood of the Cotinus coggygria. Starting from the middle Ages to the present day, fisetin is used for dyeing silken women's scarves – kelegai. For Cotinus coggygria also used names: sumac koggi griya, parikova tree, zhelesnik, sumac, tanner, yellow wood, zhitnik dyeing, the Hungarian yellow tree, fizetovo tree, zheltunitsa, the Venetian sumac [2].

Fisetin is dyestuff for painting wool, silk, skin in yellow and orange colors. Austrian chemist Josef Herzig first described its chemical formula in 1891 and already modern chemistry knows 3D structure of molecule of the fisetin (Fig. 1).

It is known that fizetin is a valuable medicinal substance and many of scientific and theoretical works are carried out in this direction. At the same time, a long time ago fisetin used as a dye for to coloring silk, wool, leather, wood, etc. But the scientific work devoted to the application of the dye of fisetin in the light industry, is very rare. To dye of products basing on protein to the yellow color may be used a lot of other natural dyes of vegetable origin.

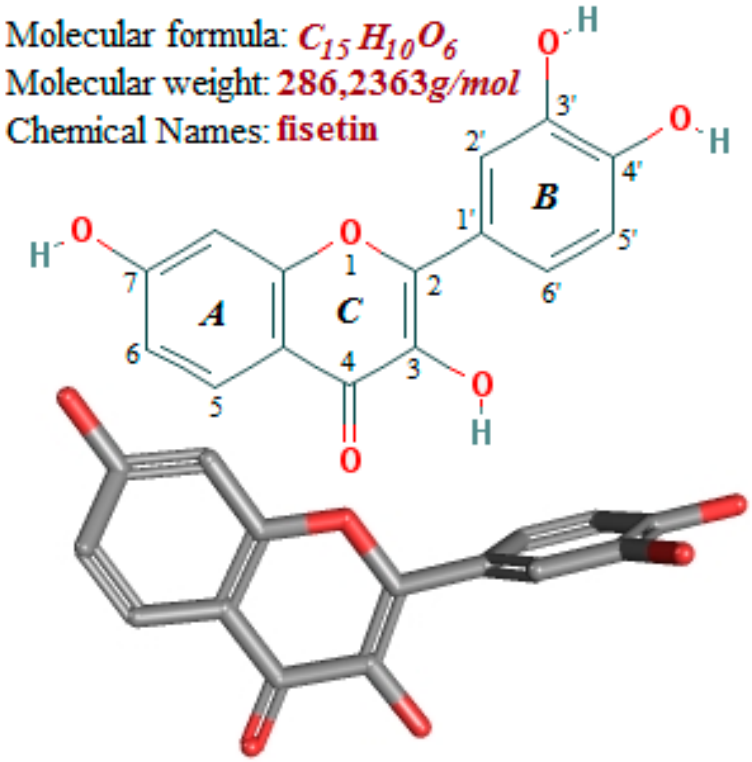

Fig. 1. *Structure of fisetin*

Among these dyes fisetin occupies a special place with its resistance to external influences. Consequently, the conducting research on the use of fisetin in light industry has a special relevance.

The objective set is to study the possibility of using UV spectroscopy to identify fisetina in the dye solution.

MATERIALS AND METHODS

The biological activity of fisetin has been studied in many laboratory assays; like other polyphenols, it has many activities. All flavonoids are optically active, able to fluoresce in UV light, have characteristic UV characterized by the presence of two peaks absorbing and IR spectra. For the quantitative determination of flavonoids in medicinal herbs used electrical-photos-colorimetric (FEC) and spectrophotometric (SPM) techniques. FEC is based on measuring the optical density of colored solutions obtained by the reaction of flavonoids with metal salts and azo coupling with diazonium salts - the general formula $R-N^+ \equiv N \cdot X^-$, wherein R, as a rule, aryl or hetaryl, and X^- - anion (Cl^-, NO^{3-}, OH^- et al.). For example, chloride benzodiazoniya $C_6H_5N^+ \equiv N \cdot Cl^-$ (Fig. 2).

For quantification identify the pigment of dye we used Electronic Absorption Spectroscopy with which detects the absorption in the region of the UV and visible light of spectrum.

According VFS42-786-78, fisetin solution was prepared as follows: 0.025 *g* (accurately weighed) fisetin dried to constant weight at 370-380 *K*, was dissolved in 95% ethyl alcohol (ethanol) in a volumetric flask with 50 *ml*. Volume of the solution was adjusted with 95% ethanol to the mark. Was taken from this flask 2ml of solution, was transferred into a volumetric flask of 50 *ml*, volume of the solution was adjusted with the 95% ethanol to the mark.

The absorbance was measured at once, for the preparation of dye solution. Measurement was carried out in a quartz cuvette with a layer thickness of 10 *mm*, taking as comparing 95% ethanol. To construct absorption spectrum of solution of fisetin, in 95% alcohol, was used a modified spectrophotometer SF-4, having a spectral range from 200 to 2000 *nm*. The measurement was carried out on individual points.

For drawing of the electronic spectrum in the spectrophotometer SF-4, was applied system of lighting OI-18 with SVD-120A lamp and an incandescent lamp for the range of spectrum $\lambda \geq 415\ nm$.

RESULTS AND DISCUSSION

A beam of monochromatic light with intensity - J_0, having passed through a layer of absorbing material thickness - l, goes out to the weakened intensity - J, is defined by expression

$$J = J_0 e^{-kl}, \quad (1)$$

where k - the absorption coefficient characterizing the properties of matter, which depends on the wavelength λ of the absorbed light. This relationship is called the law of light absorption (the law of Bouguer-Lambert-Ber). This formula is applied in the study of the nature of the absorption of substances that are dissolved in the light-non-absorbing solvent. The absorption coefficient in the law can be written in the form where $k = \varepsilon \cdot c$ - the concentration of dissolved substances and ε - coefficient that is independent of c, and characterizing the interaction of a molecule absorbing material with light having a wavelength λ (the law of A. Ber).

The optical density D is the dimensionless quantity characterizing the degree of absorption of light through the material layer and is equal to the decimal logarithm of the ratio of the intensity J_0 - of incident light, to the intensity J - of light after passing through the bed of substance:

$$D = lg(J_0/J) \quad (2)$$

where D - optical density, J_0 and J - the intensity of the incident and transmitted light through the solution, respectively.

In an improved instrument SF-4 is defined optical density D of the solution of the fisetin. UV spectrum of the fisetin - dependence of the optical density of wavelength, is built on the points and shown in the Fig. 3. As can be seen from figure, the long-wavelength part of the spectrum has a maximum at $\lambda_{max} = 412\ nm$. According to the authors of [3-4] can say that this maximum is associated with chromophore consisting of ring ***B***, conjugated with the carbonyl group. And more short-wave band - with a maximum at $\lambda_{max} = 314\ nm$, with the ring ***A*** in the macromolecule of the fisetin.

When a photon is absorbed, vinyl -*OH* group at C3, affects electron mobility. The fringe shift in the long-wavelength part of the spectrum to longer wavelengths and the absorption in the blue range of the spectrum makes it possible to fisetin acquired a yellow color. A similar effect was observed in other flavonoids, for example, in kaempferol, quercetin and myricetin. İn the ethanol they have a $\lambda_{max\,x}$, at 368, 374 and 478 *nm*, respectively.

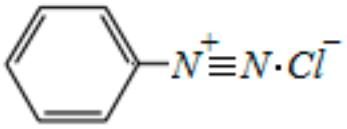

Fig. 2. *Cation phenyldiazonium*

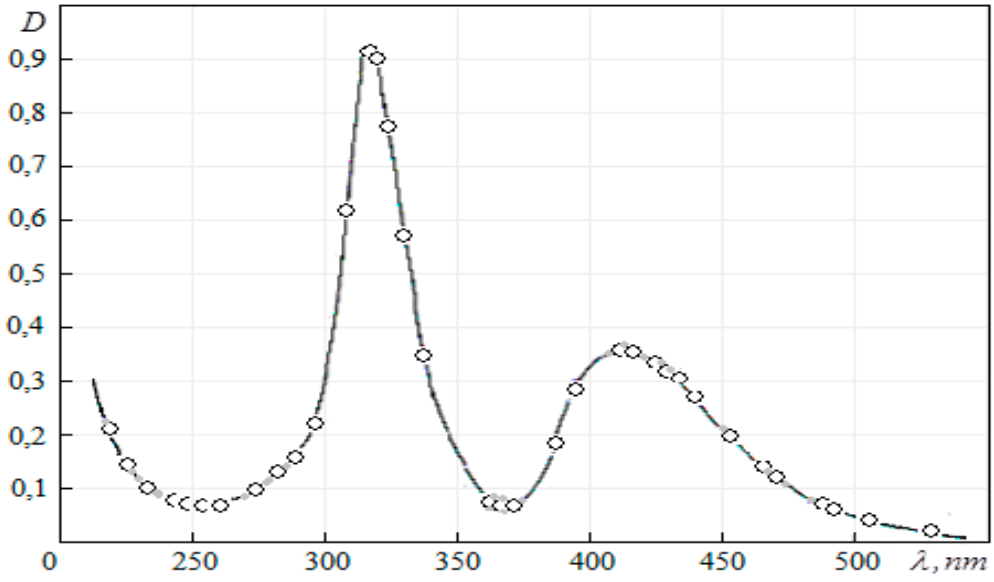

Fig. 3. *The absorption spectrum of light fizetina in the 95% solution ethanol*

In fisetin, like all classes of flavonoids, *OH*-substituents are making unbound electrons than increase the degree of delocalization, stabilize an excited state and thereby facilitate the excitation of electrons. Electronic heterocyclic oxygen atom is involved in the formation of π-bonds in the heteroaromatic ring ***B***, so that the whole molecule becomes chromophore. Methylation, glycosylation or acylation of the -*OH*-group of ***B*** ring tends to reduce or even leads to the disappearance of the bathochromic effect.

We think that the absence of hydroxyl groups in the atom C5 of molecule of fisetin leads to a shift of the absorption bands in the ultraviolet region of the spectrum towards longer wavelengths. According to Paul Francis Gordon and Peter Gregory [5], in conjugated system conjunction with one another ED (electron donor) and EA (electron acceptor)-deputy at the ends bond are the simplest situation. However, the entry into the system of conjugated double bonds between the ends of ED- and EA additional substituents ED causes the formation additional bonds between aromatic nuclei in the conjugated system. This greatly affects the absorption of light (fourth position of the theory of light emission).

According to the idea [6], when happening that OH groups (ED-substituent) be entered to the molecule of fisetin on the C5, at a short distance from carbonyl group C4 (EA-substituent) appears a new pair of unshared and moving electrons. These electrons interact with EA substituent (C4 - carbonyl groups) in the shorter conjugate chain than that at which it interacts with the first pair of electrons ED-substituent (C7 - hydroxyl group). The resulting competition reduces the constant - independent of the action of light displacement of the electrons in the area between the end (C7) and the new (C5) ED-substituents. By its action this is equivalent to shortening of the chain of conjugation and thus leads to a shift of the absorption band in shorter wavelengths, which is observed in other flavonoids wherein ring ***A*** has an -OH group at the C5 and C7.

CONCLUSIONS

1. Thus, we assume that for the determine the amount of fisetin in dye solution can be advantageously used one of the earliest methods of UV and visible spectroscopy.

2. This problem can be solved by using a spectrophotometer, or by the photo colorimeter.

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