Methods to detect color imitation of red wines

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Abstract. The most traditional object of falsification, taking into account the volume of consumption and cost, is wine. A significant proportion of adulteration of red wines accounts for the imitation of their color by introducing color compounding ingredients to white base wine: synthetic coloring agents, natural food coloring agents, or products with a secondary coloring effect. The purpose of this research was to study physicochemical parameters of original red wines and fakes obtained using coloring agents of different origin. It was shown that monomeric anthocyanins were absent in model systems with the addition of synthetic coloring agents, and the extinction maximum did not correspond to the wavelength of 520 nm, typical for original wines. It was found that, regardless of the nature of color compounding ingredient, the content of phenolic substances in model samples did not exceed 900 mg/l. The mass concentration of monomeric anthocyanins in model samples with the addition of natural coloring agent did not exceed 2% of the total amount of phenolic substances. Therefore, the quantitative content of monomeric anthocyanins, phenolic substances, spectral characteristics can be recommended as criteria in a plan of actions to identify the authenticity of juice and wine products.

1 Introduction

Falsification (from Latin falsifico - falsify) of wine products means any changes in the type or composition and properties of wine due to the modification of raw material composition, as well as production use of techniques, methods or substances that are prohibited or unauthorized by regulatory documentation [1-2].

The most traditional object of falsification, taking into account the volume of consumption and cost, is wine. A significant proportion of adulteration of red wines accounts for the imitation of their color by introducing color compounding ingredients to white base wine: synthetic coloring agents (indigo carmine, carmoisine, etc.), natural food coloring agents (anthocyanins), or products with a secondary coloring effect (extracts of red berries: blueberry, currant, etc.) [1-3]. The presence of fake products on the market not only creates a negative attitude towards wine producers, but also poses risks to human health. Synthetic coloring agents (SCA), which are carcinogenic, mutagenic and allergenic, are of particular danger [4, 5].

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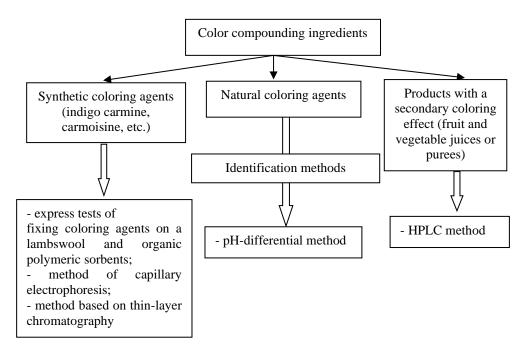


Fig. 1. Methods to identify color compounding ingredients in wine products

Detection of defective products requires extensive analytical experience, availability of reliable comparative data, as well as knowledge of current market conditions. In wine industry, the use of any coloring agent is prohibited, regardless the method of coloring. Today, many different methods are used to identify color falsification of wine products: the presence of synthetic coloring agent is determined by the method of staining defatted white wool, sedimentation on polyamide powder, solid-phase extraction (SPE), preparative thin-layer chromatography [1-2, 6-11]. At the same time, all methods are quite laborious due to the necessity to extract and concentrate the synthetic coloring agent from a very complex matrix. Methods of liquid chromatography, capillary electrophoresis, UV and IR spectroscopy, as well as HPLC are also effective for detecting SCA.

The pigmentation of natural coloring agents is due to the presence of anthocyanins - a group of water-soluble plant pigments, causing red, blue and purple color of fruits, flowers, leaves or other plant components [12, 13].

Quantitative content of monomeric anthocyanins in berries varies significantly depending on the botanical type of raw material and can be up to 3000 mg/l. In young red wines, the mass concentration of monomeric anthocyanins is about 500 mg/l, and in some cases this value can reach 2000 mg/l [14].

The purpose of this research was to study physicochemical parameters of original red wines and fakes obtained using coloring agents of different origin.

2 Materials and methods

The objects of research were red wines, blueberry, blackberry, currant, cherry, black elderberry and beet root extracts, a mixture of synthetic coloring agents (carmoisine E122, tartrazine E102, indigo carmine E132), a complex food additive - natural coloring agent "ECOTAN Anthocyanin" (E163). Model samples were prepared by adding color

compounding ingredients to dry white wine to imitate the color of red wines. The selection series consisted of 76 samples of authentic wines, 50 model systems.

The scheme of preparing extracts included the following steps: crushing berries, pressing the pulp and separating the juice, extracting the pomace with 96% ethyl alcohol for 7 days. The ratio of raw material-extracting agent was 1:1.

To determine the content of anthocyanin pigments we used a modified method of pHdifferential spectrophotometry, based on the variability in optical density of solution depending on pH [13]. The content of total phenolic substances was determined using the Folin-Ciocalteu's reagent. Changes in the color range of wine blends were evaluated visually and spectrophotometrically [6].

The experimental data obtained were processed using methods of mathematical statistics based on the Excel MS Office application software program.

3 Results and Discussion

The first stage of research involved a comparative evaluation of optical characteristics of red wines and model systems. The data analysis showed that the maximum extinction of berry extracts falls at a wavelength of 520 nm, which is also characteristic of red wines [15]. It should be noted that for synthetic coloring agents, the maximum value of optical index varies depending on the color of preparation - red (carmoisine E122, Allura red) - 500-510 nm, orange (tartrazine E102, Sunset) - 480 nm, blue (indigo carmine E132) - 610 nm (Fig. 2). The peak of absorbance of a mixture of synthetic coloring agents that imitate the color of red wines also deviates from the characteristics of natural wines and falls at a wavelength of 490 nm. This fact can be used later as an express criterion for evaluating the presence of synthetic coloring agents in beverages and wines.

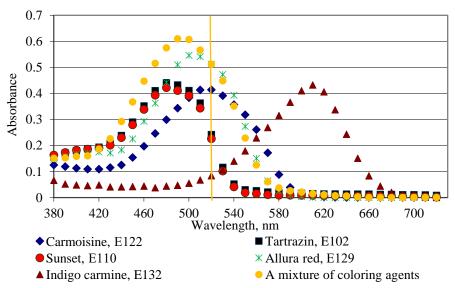


Fig. 2. Optical parameters of solutions of synthetic coloring agents

The analysis of physicochemical parameters of original wines shows that the total content of phenolic substances in them varies in a wide range of values from 1,238 to 3,598 mg/l. The mass concentration of monomeric anthocyanins in wines amounts 109-364 mg/l. Thus, the proportion of anthocyanins is 6.1-32.7%. As a result of the study of wine color

characteristics, a strong mathematical correlation between the values of absorbance A420 (r= 0.89), A520 (r= 0.90), A620 (r= 0.79) and quantitative content of monomeric anthocyanins was established.

In model systems with introduction of products with a secondary coloring effect (berry extracts), the total content of phenolic substances was less than 900 mg/l, which was below the values typical for wines (Fig. 3).

When beet root juice was added, the mass concentration of monomeric anthocyanins showed negative expression. It can be explained by the fact that beet root coloring substances are not represented by anthocyanins, but by a group of plant pigments of alkaloid class - betacyanins, namely betanin, which determines the red color of beet root [13].

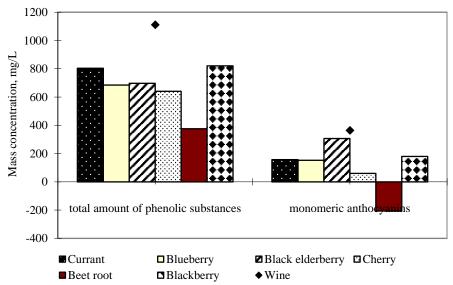


Fig. 3. The content of anthocyanins in model systems with berry extracts

Similar data were obtained in the study of model systems using synthetic coloring agents. Introduction of these components to white wine gave samples with a color that, according to visual assessment, was close to the color of natural red wine. The mass concentration of phenolic substances in terms of quantitative content corresponded to white wines. The analysis of aqueous solutions of synthetic coloring agents using the pH-differential method showed the absence of monomeric anthocyanins in its composition, which was confirmed by theoretical ideas about the structural features of most coloring agents of artificial origin, according to which they do not undergo reversible transformation with a change in pH.

When introducing the food additive E163 "Anthocyanin", declared as a natural grape coloring agent, the mass concentration of monomeric anthocyanins in model samples, regardless of the color intensity, did not exceed 20 mg/l, which was 2% of the total amount of phenolic substances. At the same time, the content of coloring substances in the model systems exceeded the level of monomeric anthocyanins by 10 times. The mass concentration of phenolic substances was below the level established for original wines.

The studies of spectral characteristics of wines and model samples showed that at a wavelength of 620 nm the optical density was 1.5-3 times lower than the values obtained for original wines (Fig. 4), indicating a low content of free anthocyanins in the quinone form of model samples.

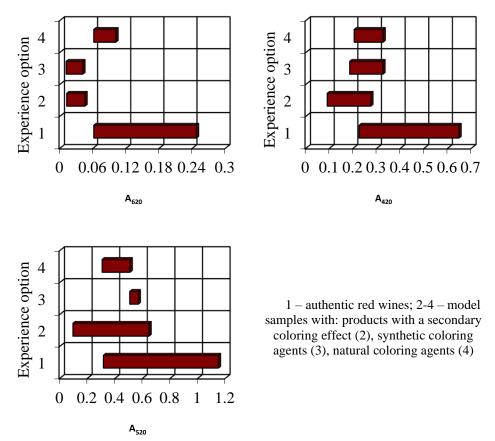


Fig. 4. Influence of color compounding ingredients on the value of chromatic characteristics

4 Conclusion

Thus, a spectrum of variation in color characteristics of berry extracts in the range of absorbance A380-A720 was obtained. It was shown that monomeric anthocyanins were absent in model systems with the addition of synthetic coloring agents, and the extinction maximum did not correspond to the wavelength of 520 nm, typical for original wines. It was found that, regardless of the nature of color compounding ingredient, the content of phenolic substances in model samples did not exceed 900 mg/l. Therefore, the quantitative content of monomeric anthocyanins, phenolic substances, spectral characteristics can be recommended as criteria in a plan of actions to identify the authenticity of juice and wine products.

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