Comparative Evaluation of Properties of Pectin Substances in Pomace of Grape Varieties for Development of Functional Foods

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Abstract — This article presents the results of comparative studies of analytical characteristics of pectin substances in grape pomace depending on the variety. Grape pomace is a wine making secondary raw material. Industrial grape varieties processed for wine production in the southern part of Russia were chosen as the object of research. The results of studies have shown that grape pomace can be considered as a source of pectin for the development of functional nutrition products.

Keywords: grape pomace, pectin, etherification degree, free carboxyl groups, methoxyl component, acetyl groups

I. INTRODUCTION

Main motivation for the development of modern society is to prolong active life term of a human by upgrading the quality of life. The quality of the environment can be considered as one of its main aspects. Widespread pollution of the environment almost everywhere leads to a number of diseases, unfortunately, characteristic of modern human society. These are oncological, skin and allergic diseases. Thus, according to the report of the IARC (International Agency for Research on Cancer WHO) in 2018 about 18.1 million new cases of cancer were recorded in the world.

Allergic diseases have become the fastest spread in the world for the past 30 years. According to WHO epidemiological studies in different regions of the world, the prevalence of allergic diseases ranges from 15 to 35 %. At the same time, they currently take the third place in their prevalence after cardiovascular and cancer, and in some environmentally unfriendly regions they are at the first place [5].

The main factors influencing the increase in the number of diseases are carcinogens consisting of physical, chemical, biological substances that contribute to the development of malignant tumors or their occurrence. Currently, more than 500 carcinogenic substances are known in the biosphere, most of them are mutagens at the same time. However, according to the estimated toxicity scale of Corte-Dubinin for pollutants recommended by the World Health Organization (WHO), toxic metals are ranked first in terms of the degree of negative impact on the body (135 points) [1].

In addition, monitoring of the nutritional status of a modern human in industrialized countries showed that his or her diet is characterized by excessive consumption of animal fats and easily digestible carbohydrates, but deficient in the following essential substances: dietary fiber (this group includes pectin), vitamins, macro- and microelements.

This leads to nutritional deficiency, reduced regulatory capacity of the body, changes in its physiological functions, which contributes to the formation and spread of diseases such as atherosclerosis, hypertension, diabetes, alimentary obesity, etc.

In view of the above, the organization of rational nutrition is relevant in modern society. It is possible due to expansion of the range and growth of production of functional food.

In our opinion, pectin substances meet all the requirements of a functionally significant ingredient. Thus, they have high detoxification properties in relation to toxic metals [3]. In addition, according to the EU 432/2012 regulation, pectins are recommended to reduce cholesterol and glucose levels in the blood by 4 and 10 g/day, respectively [2].

Volumes of raw materials for industrial production of pectin are significant. This is, first of all, waste of juice industry – apple pomace and citrus squeezes. No less significant in terms of volume is secondary raw material of winemaking - grape pomace. The yield of pomace depends on the varietal characteristics of grapes and the method of processing and averages 12-18% [3].

It should also be noted that in the world production of fruits and berries grapes ranks third (about 65 million tons), behind citrus (about 90 million tons), bananas (about 67 million tons) in volumes. It becomes clear that grape
Pomace is a potential raw material for pectin production in industrial conditions. This circumstance determines the need for research of this type of raw materials from the position of development on its basis of functional products for the organization of rational nutrition.

For this purpose we set the following research tasks:

- to study the fractional composition of pectins;
- to assess the quality indicators of isolated pectins;
- to determine the functional orientation of the selected objects of study.

II. EXPERIMENTAL SITE AND RESEARCH METHODS

As an experimental site we selected 2 regions in the South of Russia, in particular the Krasnodar and Stavropol regions, which are main wine-growing regions.

Industrial grape varieties, the same for both Krasnodar and Stavropol territory are: Aligote, Chardonnay, Cabernet Sauvignon, Firstborn Magaracha, Saperavi North, Rkatsiteli, Moldova were selected the objects of our research.

It is known that technical grape varieties are divided into 2 main groups: red and white.

Red technical sorts of grapes:

- Cabernet Sauvignon is a French variety that has spread in all viticultural countries of the world. High technological advantages of varieties provided it with the title of king of red wines. The ripening period of the variety is medium-late when harvesting clusters for the production of table wines and late for the production of dessert wines.
  
  Clusters are medium (100 g), conical, often winged, medium density or loose. Berries are medium, round, dark blue, with a thick waxy coating. The skin is thick and rough. The flesh is very juicy. The taste is varietal, with a flavor of Solanaceae.

- It is used for the preparation of high-quality red wines of various categories.

- Saperavi North belongs to the European-Amur hybrids, breeding created in Russia. According to the morphological characteristics of the leaves and the shape of the berries it is close to the variety type Saperavi (Fig. 1).

  It belongs to the varieties of mid-late ripening period. Clusters are medium (105-200 g), conical, medium density. Berries are small or medium, oval, dark blue. The skin is strong. The flesh is juicy, the juice is slightly colored.

  It is used for making table and dessert wines.

- Moldova also belongs to the European-American hybrids (Fig. 2). Bred in Moldova, belongs to varieties of late ripening.

  Clusters are medium or large (320 g), cylindrical or conical, medium density, sometimes loose. Berries are large, oval, dark purple, with a thick waxy coating. The skin is thick, dense, strong. The flesh is fleshy, crispy. Tastes simple.

The variety has a beautiful appearance of clusters and berries, high transportability and excellent keeping quality when stored in refrigerators.

Fig. 1. Grape variety Saperavi North

Fig. 2. Grape variety Moldova

White technical grapes:

- Aligote is a French variety, common in Eurasia and the United States, belongs to the varieties of medium maturity.

  Clusters are medium (120-160 g), cylindrical, often winged, dense. Berries are medium, round, yellowish-green, with dark brown dots. The skin is thin but firm. The flesh is very juicy. Tastes simple.

  It is used for the production of juices, table wines and champagne wine materials.

- Chardonnay is also a French sort. It also grows in all viticultural countries of the world. Synonyms: Pinot Chardonnay, Pinot Blanc Chardonnay, etc. Belongs to varieties of medium maturity.

  The clusters are medium or small (75-100 g), cylindrical or conical, sometimes slightly winged, dense or loose. Berries are medium or small, rounded or slightly oval,
greenish-white, with a Golden tint on the Sunny side. The skin is thin but firm. The flesh is juicy, pleasant taste, with a subtle varietal aroma.

It is a high-quality variety for the preparation of champagne wine materials and white table wines.

Rkatsiteli is a Georgian variety, spread not only at home but also in Europe, China and the United States. belongs to varieties of late ripening (Fig. 3).

Bunches are medium and large (150-290 g), cylindrical or winged, medium density, rarely dense. Berries are medium, oval, golden-yellow, at full maturity rosy, with brown spots on the Sunny side. The skin is thin and strong. The flesh is juicy. The taste is pleasant, peculiar.

Grapes are processed into juices, table and dessert wines, champagne and cognac wine materials.

Firstborn Magaracha is a variety of Crimean selection. It belongs to varieties of late ripening (Fig. 4).

Clusters are medium, cylindrical, medium density. Berries are medium, oval, white. The skin is strong, elastic. The flesh is juicy, spreading. The taste is pleasant, harmonious.

It is used for the preparation of white table and dessert wines.

The choice of these varieties as objects of research is due to the fact that the area of their plantations in both regions is currently the largest among the grapes.

The method of quantitative determination of pectin substances in plant raw materials is based on the extraction of pectin from plant raw materials and its transfer to the dissolved state (Donchenko, 2000). The basis of the study of the extracts of hydropectin and protopectin is the calcium-pectatism method and precipitation with ethanol. In addition, the content of carboxyl groups (free and esterified), methoxyl and acetyl groups in pectin preparations, the degree of esterification by conductometric method were studied.

III. RESULTS AND DISCUSSION

To confirm the industrial importance of grape pomace as a pectin-containing raw material, we conducted studies to determine the content of pectin substances and their fractional composition in grape pomace of different varieties.

The results showed that the total content of pectin (PV) in grape pomace is high and ranges from 3.21 to 7.27 % in terms of absolutely dry weight.

The content of protopectin varies between 1.61-4.46%. In addition, protopectin (PP) quantitatively dominates hydropectin (RP). This ratio of fractions is observed in all varieties studied by us. The percentage of protopectin from the total amount of pectin substances (PP/PS) is 55.5-70.8 %. The varieties’ Firstborn Magaracha, Cabernet Sauvignon and Moldova ratio PP/PS is higher compared to other varieties and makes 68-70.8 %.

The amount of water-soluble pectin fraction (WSP) also varies within each variety.

Pomace of Saperavi North variety has the maximum content of hydropectin 2.01 %, slightly less than the content of WSP in the variety of Moldova.

The decrease in this indicator was noted in Cabernet Sauvignon (0.9%), and Firstborn Magaracha (1.1%). However, in all the studied varieties there was less hydropectin than protopectin.

The influence of grape varieties on the ratio of fractions of pectin in the pomace is shown in Fig.5.

![Fig. 3. Grape variety Rkatsiteli](image)

![Fig. 4. Grape variety Firstborn Magaracha](image)
Analyzing the results, we can note that the studied technical grape varieties accumulate unequal amounts of pectin substances and their individual fractions, which causes a difference in the technological parameters of pectin extraction.

Taking into account the data obtained, the extracts from the studied grape varieties for the intended purpose can be divided into two groups. Thus, grape pomace of Saperavi North, the Firstborn of Magaracha, Cabernet Sauvignon, Aligote, Moldova and Rkatsiteli due to the high value of the ratio of protopectin/pectin is advisable to use for the production of dry pectin. Grape pomace of Chardonnay is advisable to consider for the production of liquid pectin products due to the high content of soluble pectin.

To assess qualitative indicators of pectin contained in pomace of grapes of different varieties, we have studied their following analytical characteristics: contents polygalacturonase acid, metaxylene and acetyl components, the degree of esterification, jelly-forming and complexing ability.

It was found that the highest content of pure polygalacturonic acid was observed in pectins isolated from grape pomace of Saperavi North (69.09 %) and Moldova (56.93 %). The remaining 5 varieties (Cabernet Sauvignon, Aligote, Chardonnay, Rkatsiteli and Firstborn Magaracha) by the content of pure polygalacturonic acid are approximately at the same level, and on average its content is 42.8 % (Fig. 6).

Data on the methoxyl component of the isolated pectins are shown in figure 7.

From the experimental data it follows that the methoxyl component ranges between 3.7-6.8%. These values allow to foresee low jelly-forming ability of pectin.

However, it is known that jelly-forming is inversely affected by the presence of acetyl groups. The content of acetyl component in the molecule of selected pectin changed from 0.1 (for Saperavi North) to 0.39% (for the sorts of Moldova).

It is experimentally established [4-8] that at the content of acetyl groups up to 0.8% by weight of pectin, they do not have a significant effect on jelly-formation.

To make sure that this conclusion is correct, it is necessary to additionally take into account that complexation is influenced by the degree of esterification of pectin carboxylic groups by methanol, which determines the linear charge density of the macromolecule, and, consequently, the strength and method of binding of cations.

With a high degree of pectin esterification (E > 90 %), the free carboxyl groups, in which C6 atoms are included, are significantly removed from each other. In this case, calcium or strontium salts of pectin acid almost completely dissociate. With a decrease in the degree of esterification, i.e. with an increase in the charge of the macromolecule, the stability constant of pectinates increases. When the degree of esterification is less than 40 %, a conformation change occurs, leading to the aggregation of pectin molecules, the formation of a strong intramolecular chelate bond of stable pectin compounds with metals. In this case, there is also an
increase in electrostatic repulsion and a decrease in the flexibility of the macromolecule chain [4,6,8,9].

We found that pectin from grape pomace has a degree of esterification ranging from 52% to 65 % (Fig.9).

![Figure 9](image)

Fig. 9. The degree of esterification of pectin substances from the studied grape varieties. %: 1-Cabernet Sauvignon; 2-Saperavi North; 3-Moldova; 4-Aligote; 5-Chardonnay; 6-Rkatsiteli; 7-Firstborn Magaracha

Complexing properties of isolated pectins were determined by their ability to quantitatively bind Pb2+ lead ions. Complexing ability of pectins ranged from 110 (for Saperavi Northern, Chardonnay, and Rkatsiteli) to 75 mg Pb2+/g of pectin (for Cabernet Sauvignon and Moldova), which is consistent with the data on their degree of esterification.

IV. CONCLUSION

On the basis of the above it can be concluded that the selected as the object of study industrial pomace varieties are a promising source of pectin. The results of the studies allow us to characterize them as highly esterified pectins with a relatively high methoxyl component, a content of free carboxyl groups and a low content of acetyl groups [10], [11].

Thus, the results of the experimental studies provide a basis for the conclusion about the appropriateness of considering selected for the study of grape pomace as an industrial raw material for the development of functional food products [12].

Liquid pectin obtained from this secondary raw material, according to research, can be reasonably considered a basic component for the production of pectin-containing beverages on a juice basis.

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