

DETERMINATION OF THE CARBON ISOTOPE $^{13}\text{C}/^{12}\text{C}$ IN ETHANOL OF FRUIT WINES IN ORDER TO DEFINE IDENTIFICATION CHARACTERISTICS

L. A. Oganesyants*, A. L. Panasyuk, E. I. Kuzmina, and L. N. Kharlamova

All-Russian Research Institute of Brewing, Nonalcoholic and Wine Industry,
Rossolimo Str. 7, Moscow, 119021 Russian Federation

* e-mail: institute@vniinapitkov.ru

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Abstract: In recent times we can notice a large number of counterfeit fruit wines in the market as it is difficult to discover exogenous alcohols in them. This is due to the fact that while producing table fruit wines it is allowed to add cane or beet sugar during fermentation to provide necessary alcohol conditions. Our measurements were carried out with the help of the method “Détermination du rapport isotopique $^{13}\text{C}/^{12}\text{C}$ par spectrométrie de masse isotopique de l'éthanol du vin ou de l'éthanol obtenu par fermentation des moûts concentrés ou des moûts concentrés rectifiés” OIV-MA-AS312-06. Analyzing Russian crops of fruit and berries in 2015, with the exception of pomegranate (Azerbaijan), we have obtained the following results: black currant – minus $25.75 \pm 0.08\%$, cherry – minus $25.62 \pm 0.06\%$, chokeberry – minus $26.13 \pm 0.26\%$, pear – minus $27.04 \pm 0.06\%$, plum – minus $26.24 \pm 0.41\%$, apple – minus $27.58 \pm 0.54\%$ and pomegranate – minus $28.21 \pm 0.22\%$. These results suggest the following conclusions: using exogenous alcohols derived from plants C3 – photosynthesis type leads to a slight change in isotopic characteristics of carbon ethanol in fruit wines, while adding sugars or alcohols from plants C4 – type leads to an increase of the isotope ^{13}C , resulting in significant changes of the indicator $\delta^{13}\text{C}$. To establish significant differences of exogenous alcohols C3 – type introduced from the outside and obtained by fermentation of adding beet sugar, in some cases it is not enough to use the only one indicator $\delta^{13}\text{C}$ (‰). Therefore promising researches are connected with defining isotope ratios of other biophilic elements of fruit ethanol, namely, oxygen $^{18}\text{O}/^{16}\text{O}$ and hydrogen D/H.

Keywords: fruit wine, ethanol, isotope mass spectrometry, stable isotopes, the ratio $^{13}\text{C}/^{12}\text{C}$, isotopic characteristics

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INTRODUCTION

Currently the Russian market is characterized by a large number of counterfeit wines of both domestic and foreign production. In this regard objective quality assessment and identification of wine products throw this issue into sharp relief. During the formation of a civilized market it is important not only to know the quality requirements to wines, but also indicia of counterfeit, defective products and me-too products.

Standards of the Russian Federation have physical and chemical indicators, norms and testing methods. However, they are not always able to define wine authenticity and detect counterfeit, as indicators of the type standard “General specification” are primarily for the positioning of wine, referring it to a specific group of goods and formulating security requirements.

One of the main tasks currently facing the wine industry is to improve the quality of products with the help of modern technological methods. However, their implementation is often troubled due to unfair competition of counterfeit products producers, who sell wines at dumped prices. The greatest damage is done

by ethyl alcohol. Its use is illegal in the production of table grape and fruit wines.

Until recently a large number of counterfeit products in the market was due to the lack of instrumental techniques which could detect presence of alcohols produced not from grape. However, in recent years science has made a significant step forward and today it is possible not only to determine wine composition, but also to detect the nature of raw materials used in their production.

Most biophilic elements (elements that make up the organic matter of living systems) are poly isotope elements and contain “light” isotopic atoms that make up the bulk of the element and “heavy” isotopic atoms – the minor part of the element (carbon ^{12}C and ^{13}C , oxygen ^{16}O and ^{18}O , hydrogen ^1H and ^2H).

Biochemical differences in photoassimilation of atmospheric carbon dioxide by plants are accompanied by significant differences in the isotopic characteristics of the synthesized organic material [1–2].

A relatively wide range of variation of carbon isotopes abundances is due to the discrimination of

isotope ^{13}C to ^{12}C , which is explained by different ways of assimilation and carbon fixation by plants.

The photosynthesis is the process of carbon dioxide assimilation by green plants and the formation of organic matter with the help of sunlight energy.

There are two ways of CO_2 assimilation:

– using enzyme ribulozodifosfat carboxylase/ oxygenase, which oxidizes ribulozodifosfat to phosphoglyceric acid;

– using phosphoenolpyruvate carboxylase enzyme, which synthesizes oxaloacetic acid from phosphoenolpyruvate, CO_2 and water.

Plants which have phosphoglyceric acid as the first product of CO_2 fixation are called C_3 plants, and those with synthesized oxaloacetic acid – C_4 plants.

Plants assigned to $\text{C}_3 - \text{CO}_2$ assimilation type have specific characteristics of the carbon isotopic composition of biomass. They are determined by the significant carbon isotope fractionation compared with atmospheric CO_2 as a primary carbon source. The value $\delta^{13}\text{C}$ characterizing the carbon isotopic composition of carbohydrates of these plants ranges from minus 31‰ to minus 24‰ . Representatives of these plants are fruit trees, shrubs, and vineyards. In addition, each type of fruit is characterized by a well-defined narrower range. Maize, sugarcane and sorghum are plants with $\text{C}_4 - \text{CO}_2$ type assimilation. C_4 plants are characterized by a value $\delta^{13}\text{C}$ measured in a range from minus 15‰ to minus 9‰ [3–7].

High-precision measurement of the corresponding pairs of stable isotopes such as ^{13}C and ^{12}C showed that the substances are chemically identical, but produced differently. They have significant differences of isotope ratios. Methods of analysis of carbon stable isotopes, hydrogen, oxygen, allow us to obtain an isotopic label that characterizes raw material for products and production processes.

The analytical base of methods using isotope mass spectrometry is a measurement of natural abundances of stable isotopes of biophilic elements [8].

The standard PDB is taken as an international standard, representing the isotopic composition of carbon calcium carbonate of fossil Belemnitella Americana Late Cretaceous period from the formation PDB (South Carolina, United States). International

comparison sample PDB is characterized by uniform isotopic composition. Currently, Viennese equivalent of the PDB-VPDB is used as an international standard.

The value $\delta^{13}\text{C}_{\text{VPDB}}$ is calculated by the formula (1)

$$\delta^{13}\text{C}_{\text{VPDB}} = \frac{\left(\frac{^{13}\text{C}}{^{12}\text{C}}\right)_{\text{sample}} - \left(\frac{^{13}\text{C}}{^{12}\text{C}}\right)_{\text{VPDB}}}{\left(\frac{^{13}\text{C}}{^{12}\text{C}}\right)_{\text{VPDB}}} \cdot 1000, \quad (1)$$

where $\left(\frac{^{13}\text{C}}{^{12}\text{C}}\right)_{\text{VPDB}}$ is carbon isotope ratio of masses 13

and 12 in the comparison sample, equal to 0.0112372; $^{13}\text{C}/^{12}\text{C}$ is the ratio of carbon isotopes with masses 13 and 12 in the test sample; $\delta^{13}\text{C}$ is characteristic of the carbon isotopic composition of the sample with respect to the international sample, ‰.

The method of isotope mass spectrometry regarding $^{13}\text{C}/^{12}\text{C}$ stable carbon isotopes allows to detect with the required reliability spirits of non-grape origin in grape wine and brandy, to determine the nature of sugars in semi-dry, semi-sweet and sweet wines, to define the origin of carbon dioxide in sparkling wines [9–16].

In order to achieve this aim we have carried out a research to define a carbon isotope ratio range of ethanol in wines, produced from grapes grown in Russia. It was discovered that the wine made from grapes grown in the Krasnodar Region and Rostov Region contain alcohol, which isotopic characteristics ($\delta^{13}\text{C}_{\text{VPDB}}$ (‰)) are in the range from minus 26.2‰ to minus 28.9‰ (Table 1).

Additional research of alcohol contained in wines from Rostov region produced from grapes breed Sibirkovy and Krasnostop Zolotovskyy showed ratio $\delta^{13}\text{C}$ in the range from minus 26.8‰ to minus 29.0‰.

However, variations of the $^{13}\text{C}/^{12}\text{C}$ isotope relations typical for major wine regions of Russian Federation were specified. To this end, samples of grapes were selected from various industrial viticulture production points during the harvest season in 2013.

Grapes were processed in mini winery and the obtained juice was fermented with pure cultures of wine yeast. Then this wine material was analyzed. The test results are summarized in Table 2.

Table 1. Carbon isotopes ratio ($\delta^{13}\text{C}_{\text{VPDB}}$, ‰) of ethanol in wines, produced from grapes grown in the Krasnodar Region and Rostov Region.

Year	Krasnodar Region		Rostov Region	
	Aligote	Cabernet Sauvignon	Aligote	Cabernet Sauvignon
2008	- 26.8 ± 0.1	- 27.6 ± 0.1	no data	no data
2009	- 26.9 ± 0.1	- 27.5 ± 0.1	- 26.2 ± 0.1	- 27.8 ± 0.1
2010	- 28.7 ± 0.1	- 26.6 ± 0.1	- 26.5 ± 0.1	- 27.5 ± 0.1

Table 2. The ratio of carbon ethanol isotopes ($\delta^{13}\text{C}_{\text{VPDB}}$, ‰) in wine samples obtained from grapes in major wine regions of the Russian Federation

Region	Geographical coordinates	Firm	Grape varieties	$\delta^{13}\text{C}_{\text{VPDB}}$, ‰
Krasnodar Region	44°45'07" N 37°38'21" E	“Villa Victoria”	Chardonnay Cabernet Franc	-26.55 ± 0.1 -26.70 ± 0.1
	44°45'07" N 37°38'21" E	“Myshako”	Riesling Cabernet Sauvignon	-27.01 ± 0.1 -27.14 ± 0.1
	45°11'26" N 36°50'51" E	Fanagoria	Aligote Cabernet Sauvignon	-26.48 ± 0.1 -26.59 ± 0.1
	45°11'25" N 36°50'50" E	“South Farm Firm”	Pervenec Magarach Cabernet Sauvignon	-26.83 ± 0.1 -26.52 ± 0.1
Rostov Region	47°40'55" N 42°23'56" E	“Wines of Tsimlyansk”	Krasnostop Zolotovskiy Cabernet Sauvignon Tsimlyanskii Black	-27.11 ± 0.1 -27.24 ± 0.1 -27.05 ± 0.1
	47°40'55" N 42°23'56" E	Miller’s winery Branch “Vederniki”	Rkatsiteli Cabernet Sauvignon Krasnostop Zolotovskiy	-27.28 ± 0.1 -27.81 ± 0.1 -27.64 ± 0.1
Stavropol Region	44°44'20" N 44°28'31" E	“Levokumskoe”	Rkatsiteli Floral Cabernet Sauvignon Саперави	-27.97 ± 0.1 -26.87 ± 0.1 -27.85 ± 0.1 -27.61 ± 0.1
Republic of Dagestan	42°17'59" N 47°39'51" E	“Kirovskii”	Rkatsiteli	-26.38 ± 0.1
	47°40'55" N 42°23'56" E	“Tatlyar”	Rkatsiteli Agadai	-26.53 ± 0.1 -26.73 ± 0.1
	41°59'35" N 48°09'53" E	“Mugarti”	Aligote Chardonnay Cabernet Sauvignon	-26.68 ± 0.1 -27.14 ± 0.1 -26.81 ± 0.1

As we can see from Table 2, all the data are in the range from minus 26.38 ‰ to minus 27.97 ‰, i.e. they are within the range established by the interstate standard All-Union Standard 32710-2014 “Alcohol and raw materials for its production. Identification. The method of determining the isotope ratio of $^{13}\text{C}/^{12}\text{C}$ alcohols and sugars in juice and wine”.

However, the problem of detecting the presence of exogenous alcohol in fruit wines remains unsolved. This is due to the fact that there is not enough research on $^{13}\text{C}/^{12}\text{C}$ ratio changes in fruit alcohols, depending on the geographical location of gardens and berry plantations, soil and climatic conditions, year of crop and on the fruit type. Moreover while producing table fruit wines it is allowed to add cane or beet sugar make before and during fermentation in order to provide the necessary alcohol conditions. The obtained alcohol consists of both fruit ethanol molecules which are endogenous component of wine and molecules of cane or beet ethanol, which on the one hand, are exogenous substance, but on the other hand they are allowed and their presence is justified by technological necessity. This fact makes it complicated to discover this type of fraud.

In 1997 C. Bauer-Christoph Back et al. studied isotopic characteristics of carbon ethanol of various origins, including those obtained by fermentation of

fruit juice. [17] In their research the authors present the following results to determine $\delta^{13}\text{C}_{\text{VPDB}}$ (‰), which characterizes the ratio of carbon isotopes $^{13}\text{C}/^{12}\text{C}$ in fruit alcohols: ethanol apple – minus 25.90, pear – minus 26.16, Bartlett pear varieties – minus 26.84, cherry – minus 25.55, Mirabell – minus 25.71, plum – minus 26.11.

As we can see from the above data, $\delta^{13}\text{C}_{\text{VPDB}}$ indicator for ethanol produced from different fruit varies in a very small range – from minus 25.71‰ to minus 26.84‰.

For comparison they give data on some other alcohols and alcoholic beverages: grape spirit – minus 26.16‰, alcohol from grape husks – minus 27.09‰, grain (wheat) alcohol – minus 25.29‰, Scotch whiskey – minus 24.63‰, Bourbon whiskey (corn) – minus 13.48‰.

Using the method of isotope mass spectrometry Winterova R. et al. [18] determined isotopic characteristics of ethanol in fruit brandy (brandy) made from pears, apples, cherries, sweet cherries, plums and apricots. They were compared with the isotopic characteristics of beverages obtained from sugar beet, corn, sugarcane, grain, potato and synthetic alcohol. It was shown that isotopic characteristics (D/H) I distillates obtained from sugarcane, corn, and especially from synthetic materials are significantly

higher than the corresponding isotopic characteristics of fruit distillates. On the other hand distillates obtained from sugar beets, have lower isotope (D/H) I characteristic than fruit distillates. It was stated that distillates obtained from sugar cane and corn have value of $^{13}\text{C}/^{12}\text{C}$ from minus 13‰ to minus 11‰, which is significantly lower than in fruit distillates. According to the research the authors concluded that it was quite difficult to distinguish fruit spirits using only isotopic characteristics due to the imposition of $\delta^{13}\text{S}$ index within the same numerical range for alcohols from various fruits. On the other hand, the isotope parameters allow us to distinguish real fruit drinks from the beverage containing alcohol of non-grape origin (such as beet, cane or corn).

The aim of this work is to study the isotopic characteristics of ethanol obtained from domestic fruit and berries in order to give the possibility of using the method of isotope mass spectrometry while determining adulteration of table fruit wines.

OBJECTS AND METHODS OF STUDY

Objects of the research were fruit wines and ciders. Wine materials were obtained from seven types of fruits and berries (apple, pear, cherry, plum, pomegranate, black chokeberry (aronia), currants). Fermentation was performed at yeast race Cherry 33 without the addition of water and sugar. In order to study the possible impact of the variety of features and habitats of fruit on isotopic characteristics of biophilic elements, the research had several stages using fruits and berries of different breeds grown in different geographical regions.

All the measurements were made in accordance with standard All-Union Standard 32710-2014 "Alcohol and raw materials for its production. Identification. The method of determining the isotope ratio of $^{13}\text{C}/^{12}\text{C}$ alcohols and sugars in juice and wine", based on the methodology of the International Organization of Vine and Wine (OIV) "Détermination du rapport isotopique $^{13}\text{C}/^{12}\text{C}$ par spectrométrie de masse isotopique de l'éthanol du vin ou de l'éthanol obtenu par fermentation des moûts concentrés ou des moûts concentrés rectifiés" Résolution (Oeno 17/2001) OIV-MA-AS312-06.

The tool base for getting data on a carbon isotopic composition characteristics was a mass spectrometric complex Delta V Advantage of Thermo Fisher Scientific company (USA), providing precise analysis of the prevalence ratio of isotope $^{13}\text{C}/^{12}\text{C}$. Measurements of carbon isotopic characteristics were carried out on an international comparison sample V-PDB.

RESULTS AND DISCUSSION

Table 3 presents data on the carbon isotopic composition of domestic fruit and berry crops in 2014 and ethanol contained in obtained fermented wine materials. Investigations were carried out on five samples of each type of fruit and berries.

As it can be seen from Table 3, the carbon ethanol of fruit wine is noticeably lighter than carbon of organic components of fruits and berries. This is due to the fact that escaping carbon dioxide takes heavier carbon atoms with it [4]. As for the dependence of index values from the type of the original raw fruit, they are from minus 24.55 to minus 27.64‰ for fresh fruit and berries, and from minus 25.53 to minus 28.53‰ for ethanol of fermented wine.

Analyzing fruit and berry crops in 2015, grown in Russia, with the exception of pomegranate (Azerbaijan), the following results have been obtained: the black currant – minus $25.75 \pm 0.08\%$, cherry – minus $25.62 \pm 0.06\%$, chokeberry – minus $26.13 \pm 0.26\%$, pear – minus $27.04 \pm 0.06\%$, plum – minus $26.24 \pm 0.41\%$, apple – minus $27.58 \pm 0.54\%$ and pomegranate – minus $28.21 \pm 0.22\%$.

As we can see from these results isotopic characteristics of carbon ethanol in fruit wines obtained from different raw materials have similar values. For all fruits and berries it is possible to mark the total range of isotopic variations – from minus 25 to minus 28‰, which is consistent with literature data. However, the range may be quite narrow for wines obtained from separate raw materials.

Isotopic characteristics of ethanol in fruit wines were obtained through analysis of laboratory samples which had no exogenous sugars. In order to define possible differences industrial samples obtained from different manufacturers were analyzed. Physical and chemical parameters of analyzed wines are presented in Table 4.

Table 3. The ratio of $^{13}\text{C}/^{12}\text{C}$ isotope in fruit and ethanol in fermented fruit wine materials of the harvest in 2014

Raw material	$\delta^{13}\text{C}_{\text{VPDB}}$, ‰	
	Fresh raw material (direct combustion)	Fermented wine material (ethanol)
Strawberry	- 24.55 ± 0.08	- 25.92 ± 0.06
Raspberry	- 26.31 ± 0.32	- 27.46 ± 0.02
Blackcurrant	- 25.35 ± 0.08	- 26.24 ± 0.08
Cherry	- 25.13 ± 0.02	- 25.53 ± 0.07
Apricot	- 25.40 ± 0.55	- 25.54 ± 0.08
Apple	- 27.64 ± 0.01	- 28.53 ± 0.15
Chokeberry	- 25.69 ± 0.40	- 26.39 ± 0.12
Plum	- 25.71 ± 0.03	- 26.65 ± 0.24

Table 4. Physical and chemical parameters of fruit wines and the ratio of $^{13}\text{C}/^{12}\text{C}$ isotope in contained ethanol

Indicator name	Fruit wine "Blackcurrant"	Fruit wine "Chokeberry"	Fruit wine "Cherry"	Apple cider	Pear cider (pure)
Ethanol volume ratio, %	12.4	12.6	12.5	4.7	4.6
Total sugars, g/dm ³	1.8	2.6	1.7	1.0	1.2
Total titratable acids, g/dm ³	10.0	6.1	6.9	5.8	4.7
Total residual extract, g/dm ³	18.8	53.3	26.8	11.3	12.8
$\delta^{13}\text{C}_{\text{VPDB}}$, ‰	-22.34 ± 0.10	-19.07 ± 0.10	-25.76 ± 0.10	-21.74 ± 0.10	-25.87 ± 0.10

As we can see from Table 4, $\delta^{13}\text{C}_{\text{VPDB}}$ (‰) in samples "Black currant", "Chokeberry" and apple cider significantly differs from the values of fruit ethanol. This is due to using the allowed method (sweetening with sugar cane before fermentation) or the banned use of glucose-fructose syrup and alcohol.

It is known that sugar beet and sugarcane belong to different groups according to the type of photosynthesis. Carbohydrates of sugar beets come in a range of carbon values from minus 24.5 to minus 26.0‰. Carbohydrates of sugar cane are enriched by "heavy" isotope ^{13}C due to the peculiarities of photosynthesis and have a carbon isotopic characteristics of minus 10 to minus 12‰.

During fermentation of carbohydrates of vegetable raw metabolic carbon dioxide, as it was mentioned previously, takes "heavy" isotopes of carbon with it, therefore, ethanol formed after fermentation contains less ^{13}C isotope than carbohydrates do.

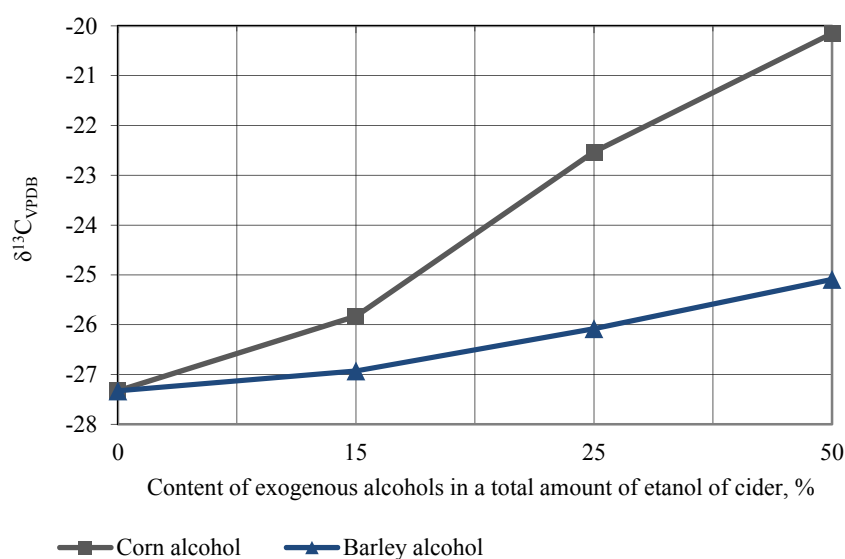
In order to determine isotope ratios of ethanol biophilic elements formed as a result of fermentation of sugars of various origins, we prepared distillates from beet and cane sugars in laboratory conditions. Ethanol from sugar beet had $\delta^{13}\text{C}_{\text{VPDB}}$ (‰) in the range from minus 26.86 to minus 27.00, and from cane sugar the range was from minus 11.86 to minus 12.30.

According to the research results carbon isotope characteristics of ethanol samples from sugar beet

practically coincide with $\delta^{13}\text{C}_{\text{VPDB}}$, typical for ethanol of fruit wines from various types of raw materials. Thus, this indicator does not always objectively and reliably detect falsification of products if exogenous sugars or alcohols derived from sugar beet are added. At the same time, the ethanol indicator $\delta^{13}\text{C}$ from sugar cane significantly differs from isotopic characteristics of beet and fruit ethanol.

We conducted research in order to determine processes of carbon isotopic characteristics change when alcohols of different exogenous origin were added in fruit wine materials. Spirits were added to fruit wine materials. Under laboratory conditions we prepared two samples of cider with added corn and barley spirits with isotopic characteristics of minus 13.8‰ and minus 24.59‰ respectively. Spirits were added to apple wine material substituting 15%, 25% and 50% of native spirits by exogenous ethanol. The test results are shown in Fig. 1.

According to the results presented below, adding 50% of alcohol from corn considerably changed isotope characteristics of carbon ethanol and went beyond determined ranges for apple ethanol. Barley alcohol alters isotopic characteristics of the product, but the ratio of carbon isotopes does not reveal the presence of exogenous alcohol, even if the amount of it is substantial.

**Fig. 1.** Dependence of $\delta^{13}\text{C}_{\text{VPDB}}$ ‰ ethanol in cider depending on the amount of added (exogenous) spirits.

The current regulatory and technical documentation for fruit wines and cider allows adding sugar-containing components of various origins in their production. Under laboratory conditions we prepared fruit wine samples by adding various concentrations of cane and beet sugar in order to define possible fractionation of carbon isotopes, hydrogen and oxygen ethanol when adding sugars of various nature.

The work was carried out on the example of cherry wine. 6 samples of cherry wine with 15%, 25% and 50% sugars of various origins were prepared. Adding sugar replaced 15%, 25% and 50% of native sugar pulp. Control was made with the help of wine material

without adding exogenous sugars. The initial mass concentration of sugars in cherry is 117 g/dm³. Fermentation of the pulp was carried out on yeast *Saccharomyces cerevisiae* strain WET 136, at the rate of 0.25 g per 1 kg of raw material. Fermentation temperature was 20 ± 2°C, the fermentation process lasted 9 days. As exogenous sugars we used beet and cane sugar with their known isotopic characteristics: beet sugar with carbon isotopic characteristics minus 26.86‰; cane sugar with carbon isotopic characteristics of minus 12.3‰. Table 5 shows the main physical and chemical parameters and isotopic characteristics of ethanol in cherry wine.

Table 5. Basic physical and chemical parameters and isotopic characteristics of ethanol in cherry wine

Sample	Indicator name		
	Ethanol volume ratio, %	Total sugars, g/dm ³	$\delta^{13}\text{C}_{\text{VPDB}}$, ‰
cherry pulp + 15% of cane sugar	6.8	1.7	-25.20 ± 0.1
cherry pulp + 25% of cane sugar	6.7	2.1	-22.20 ± 0.1
cherry pulp + 50% of cane sugar	6.4	2.1	-19.32 ± 0.1
cherry pulp + 15% of beet sugar	6.9	1.1	-26.01 ± 0.1
cherry pulp + 25% of beet sugar	6.8	1.6	-25.94 ± 0.1
cherry pulp + 50% of beet sugar	6.7	1.7	-25.87 ± 0.1
control	6.9	1.1	-26.38 ± 0.1

As we can see from the data presented in Table 5, adding exogenous sugars leads to the shift of isotopic characteristics of ethanol in produced wine. This effect of re fractionation of stable biophilic isotopes is particularly noticeable when adding sugar from sugar cane. In this case adding even 15% of sugar increases “heavy” carbon isotope more than one unit.

The obtained results lead to the following conclusions:

- Carbon isotope characteristics of ethanol in fruit wines produced from different raw materials, have similar values. For all fruits and berries it is possible to mark the total range of isotopic variations of minus 25 to minus 28‰. The range may be quite narrow for wines obtained from separate raw materials.
- Using exogenous alcohols obtained from plants C3 – photosynthesis type results in a slight change of

isotopic carbon characteristics of ethanol in fruit wines. When adding alcohols obtained from plants C4 – type the indicator $\delta^{13}\text{C}_{\text{VPDB}}$ changes noticeably; that allows us to detect their presence even in small amounts.

- In production of fruit wines and ciders when according to technology it is not allowed to add sugar to increase alcohol level, this method can detect exogenous alcohols from plants C4 type.
- To define significant differences between exogenous C3 alcohols introduced from the outside and obtained by fermentation of added beet sugar, in some cases it is not enough to use the only one indicator $\delta^{13}\text{C}_{\text{VPDB}}$ (‰). Therefore researches connected with determining isotope ratios of other biophilic elements of fruit ethanol, namely, oxygen ¹⁸O/¹⁶O and hydrogen D/H are promising.

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