STANDARDIZATION, CERTIFICATION, QUALITY AND SAFETY

IDENTIFICATION OF AROMATIC ALDEHYDES IN THE EXPRESS ASSESSMENT OF QUALITY OF HERBAL DISTILLED DRINKS

E. Yu. Egorova[a,*], Yu. V. Morozhenko[a], and I. Yu. Reznichenko[b]

[a] Polzunov Altai State Technical University,
Lenina Ave. 46, Barnaul, 656038, Russian Federation

[b] Kemerovo Institute of Food Science and Technology (University),
Stroiteley blvd. 47, Kemerovo, 650056, Russian Federation

* e-mail: egorovaeyu@mail.ru

Received January 23, 2017; Accepted in revised form March 10, 2017; Published June 29, 2017

Abstract: Despite a long study of main types of the herbs used in the Russian alcoholic beverage production, the structure of the components participating in the formation of "bouquet" of the alcoholic beverages obtained on their basis has not been studied yet. A study of content of aromatic aldehydes characteristic of distilled drinks in aqueous-alcoholic extracts of shell of pine nuts, common St. John's wort herb and wild camomile flowers, and also in the distilled drink simulated on the basis of these extracts became the purpose of this work. The raw materials obtained from the plants growing in the Altai Territory and the Altai Republic of the Russian Federation have been used for this work. The extracts were obtained by infusing the air and dry raw materials of the corresponding type in the 40% water solution of ethyl alcohol within 15 days at a temperature of 20 ± 2°C, with periodic agitation of extraction mixture, separation of extract by decantation and cleaning with filtering. The identification and quantitative determination of aromatic aldehydes were performed using the system of capillary electrophoresis "Kapel'-105M". By the results of studies it has been established that the extracts differ, as for the content of aromatic aldehydes, both from the freshly obtained oak extracts and from the aged cognac distillates. A content of aldehydes has been revealed in the extracts of wild camomile flowers and St. John's wort herb at a level equal and higher than in the extract of shell of pine nuts within the total limits for the three considered extracts of, mg/dm^3: for vanillin – from 18.5 to 96.4, for syringic aldehyde – from 8.5 to 19.4, for sinapic aldehyde – from 9.6 to 17.5, for coniferylic aldehyde – from 22.0 to 47.9. There is no direct correlation between the content of aromatic aldehydes in the imitated distilled drink and the content of these aldehydes in the initial extracts. The obtained data on the content of aromatic aldehydes in the nuts and herbs extracts are one of the evidence of similarity of the processes proceeding when obtaining these extracts and the processes that are the basis of technology of cognacs. In future, the obtained data can be put in a basis of techniques of express control of readiness of extracts and authenticity of new drinks in merchandising and technological practice.

Keywords: Alcoholic beverage products, cognacs, brandy, extracts of vegetable raw materials, pine (cedar) nuts, wild camomile, common St. John's wort, aromatic aldehydes, identification criteria

DOI 10.21179/2308-4057-2017-1-144-153 *Foods and Raw Materials*, 2017, vol. 5, no. 1, pp. 144–153.

INTRODUCTION

A natural consequence of development of the world consumer market of alcoholic products is the increase in the share of the forged drinks and the related search of new ways of prevention of possibility of realization of counterfeits. As for distilled drinks (cognacs, brandy, whisky etc.), this problem has managed to become a global trend as the market of these drinks mostly depends on the state of world economy and is rather unstable [1–3].

Distilled drinks are produced by means of the "enrichment" of distillates of grape wine, fermented fruit juices or aqueous-alcoholic infusions of vegetable raw materials. Such drinks are naturally enriched with volatile aromatic components – the products of biochemical and physical and chemical transformations of polyphenolic substances of vegetable raw materials (for the majority of distillates – oak wood) which considerably distinguishes them from other drinks with a high content of ethyl alcohol.

According to foreign experts, today the share of the forged production grows quicker than the alcohol market develops [4]. This relates to the fact that for the identification of cases of falsification and identification of authenticity of kind, age and the region of origin of the most branded distilled drinks the most modern

methods are applied: thin-layer [5], highly effective liquid [6, 7] and gas-liquid chromatography [8, 9], spectrophotometry [10], fluorescent [11] and chromatic mass spectrometry [12–14] and capillary electrophoresis [15, 16]. The existence and levels of content of such components of structure of drinks as highly volatile ethers [2, 12, 17], tannins and phenolic acids [2, 8], aromatic aldehydes [2, 5, 7, 16] and some ketones, aldehydes, alcohols and low-molecular volatile acids [12, 17–19] characteristic of distilled drinks are considered as the valid and potential criteria of authenticity. As one of the express methods of identification of the forged production it is also offered to use the dependence between the light absorption of test specimen in the infrared spectrum and a concrete type of drink – cognac, armagnac, brandy and others [10].

When searching new approaches to the assessment of authenticity and quality of alcoholic beverages the main attention has been paid for many years to the so-called aged distillates (cognacs, brandy, Calvados, whisky) – the most expensive drinks in the considered segment. The composition of aromatic components of cognacs and brandy as most known and popular drinks with consumers, has been studied in most detail: the main dependences of qualitative structure of aromatic components on the grade and the region of origin of wine material, on the duration of its contact with oak wood or oak staff have been described [17, 20]. Attempts to define the list of the most important substances forming the aromatic profile – the so-called "skeleton of aroma" of drinks [12, 18] have been made. In recent years great importance has been attached also to the search of methods of confirmation of authenticity for other distilled drinks: sherry, whisky, aromatic alcohols of juniper, tequila, mescal, absinthe, vermouths and some other drinks [21–26]. Studies concerning the further improvement of methods of control and identification of drinks fermented on the basis of vegetable raw materials [27, 28] also continue.

A feature of alcohol branch in Russia is the use of distilled drinks of more various vegetable raw materials (including wild-growing raw materials) in production, mainly in the form of extracts and infusions of the flowers, herbs and roots rich with polyphenolic compounds and ethereal oils. In this regard, most often extracts of pine nuts (*Pinussibirica Du Tour*) or their shell, extracts of wild camomile flowers (*Chamomílla recutita (L.) Rauschert*), common St. John's wort herb (*Hypéricum perforatum L.*) and some other species of the plants, wild-growing and those which are specially cultivated for this purpose, are used.

The frequency of application of alcoholic beverages of pine nuts, camomile and common St. John's wort in domestic production is in many respects caused by the fact that the extracts on their basis allow to "smooth" the sharp taste and smell of ethyl alcohol in drinks and to give a characteristic color tone and gloss close to cognac to the finished goods. In turn, the composition of volatile components of these raw materials provides the unique identity of aroma of the obtained drinks.

The analysis of literary data shows that the chemical composition of pine nuts (shell and perikernel film) is slightly similar to oak wood as for the content of polyphenolic substances and lignin [29]. According to the classical technology of cognac production, it is the most important extractive substances that go through hydrolysis and ethanolysis to aromatic aldehydes in the course of ageing cognac materials and necessary for the formation of unique "bouquet" of cognac wine materials and ready-for-use drinks. Besides, as it is noted in some works, there are compounds in the structure of aromatic components of cognacs – in particular, scopoletin, that give a resinous cedar shade of "old" drink to the "bouquet" and a taste of the aged cognacs [30, 31]. The noted data explain to some extent the range of application of pine nuts in the production of Russian alcohol products and cause the theoretical possibility of their use when obtaining the drinks similar to cognac distillates [32, 33].

When studying the properties and composition structure of volatile components of aqueous-alcoholic extracts of wild camomile flowers and common St. John's wort herb the main attention is traditionally paid to the composition of terpens and the polyphenolic compounds various in structure and properties. Among terpenes and polyphenolic compounds, the flavonoids, phenolic acids and anthracene derivatives [34–37] causing the therapeutic properties of the medicinal and cosmetic preparations produced on the basis of these plants by a lot of Russian enterprises are considered to be the most important ones. However the literary data on the existence of aliphatic alcohols, aldehydes, ketones and average esters in the composition of extracts of wild camomile flowers and common St. John's wort herb allow to assume a possibility of formation of more complex compounds including those which have an aromatic molecular structure in the course of extraction, as well.

It is necessary to know the content of the most characteristic compounds the number of which in the drink can also change with its age to authenticate the falsification of a drink.

When authenticating cognac production the confirmation of duration of contact with oak wood determined by the results of analysis of volatile and nonvolatile components is considered to be the major feature.

The main processes in the formation of the volatile compounds characteristic of cognac distillates and necessary for the formation of the "bouquet" typical for cognacs and brandy, include the processes of oxidation of tannins and lignin.

Aromatic aldehydes (Fig. 1) and the products of their subsequent oxidation – aromatic acids – make up to 30% of the polyphenolic complex of cognac distillates and the cognacs aged in contact with oak wood. At the same time, the content of vanillin in cognacs can vary from 0.2 to 2.4 mg/dm^3, the content of sinapic and coniferylic aldehydes is 0.3–2.4 mg/dm^3 and 0.3–2.6 mg/dm^3 respectively. The content of syringic aldehyde – to 7.8 mg/dm^3 of drink [38] can be the most considerable.

The data on the composition of aromatic aldehydes in the aqueous-alcoholic infusions and extracts on the basis of pine nuts or their shell, wild camomile flowers,

common St. John's wort herb and many other types of the vegetable raw materials traditional for domestic alcoholic beverage products, are not available in Russian and foreign literature. In this regard a study of aromatic aldehydes in the extracts obtained from the types of vegetable raw materials which are most popular with the industry and an assessment of the possibility use of these data in merchandising and technological practice for the identification and control of quality of drinks on the basis of such extracts seem appropriate.

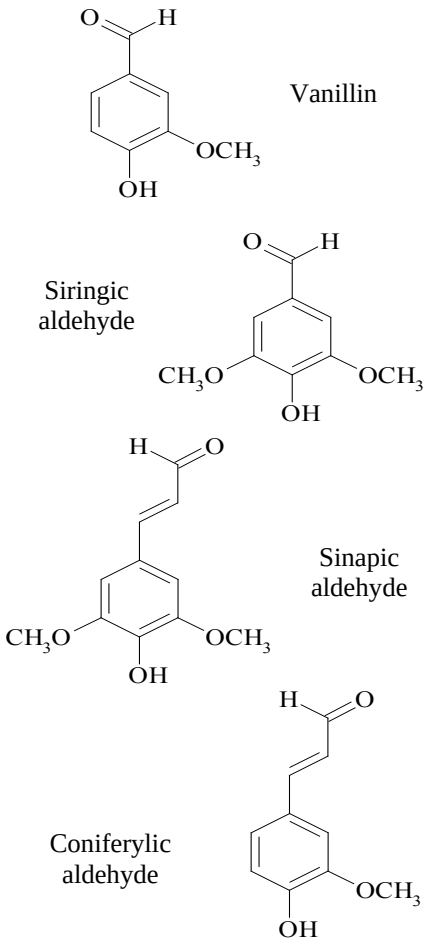

Fig. 1. Characteristic aromatic aldehydes of cognac distillates.

The purpose of work is the research of composition and content of the main aromatic aldehydes in the aqueous-alcoholic extracts of shell of pine nuts, wild camomile flowers and common St. John's wort herb for the identification of these substances in the composition of new distilled drinks.

The following tasks act as solvable in the work:
– the systematization of literary data on the content of aromatic aldehydes in cognac distillates;
– the determination of content of aromatic aldehydes in the composition of aqueous-alcoholic extracts of shell of pine nuts, wild camomile flowers and common St. John's wort herb and the comparative analysis of the obtained results with the literary data on cognac wine materials;
– the assessment of possibility of use of the data on the content of aromatic aldehydes in the studied aqueous-alcoholic extracts in merchandising and technological practice of identification and control of quality of distilled drinks of various producers.

OBJECTS AND METHODS OF STUDY

The following is used as the **study object**:
– raw materials – the pine nuts prepared in the cedar forests of the Republic of Altai (*Pinus sibirica Du Tour*) and their shell, wild camomile flowers (*Chamomílla recutita (L.) Rauschert*) and common St. John's wort herb (*Hypéricum perforatum L.*) prepared in the Biysk district of Altai Krai;
– the aqueous-alcoholic (40% vol.) extracts of shell of pine nuts, wild camomile flowers and common St. John's wort herb;
– the imitation of distilled drink – the blend made by mixing of the obtained aqueous-alcoholic extracts of shell of pine nuts, wild camomile flowers and common St. John's wort herb according to the receipt given below.

Study methods. Methods of data collection and processing, of comparative analysis and systematization of information from scientific publications and periodicals were used when studying the literary data.

The aqueous-alcoholic extracts of shell of pine nuts, wild camomile flowers and common St. John's wort herb were obtained infusing the air and dry raw materials of the corresponding type in the 40% aqueous solution of ethyl rectified alcohol within 15 days (the conditions of extraction had been chosen earlier, by the results of preliminary studies [39]) at a temperature of 20 ± 2°C, with periodic shaking of the extraction mixture and the separation of the obtained infusion (extract) by decantation with the subsequent filtering through the paper filter of the brand "White Ribbon". The ratio raw materials : extragent was chosen by the results of patent search and was 1 : 3 during the extraction of shell of pine nuts, and 1 : 10 for wild camomile flowers and common St. John's wort herb.

The experimental blend of aqueous-alcoholic extracts – an imitation of distilled drink – was prepared by mixing of individual extracts in the ratios providing a characteristic golden and cognac color with "gloss" (see Photo 1) and the aroma of drink close to the cognac one.

Photo 1. Drink with an experimental composition.

The receipt of experimental blend:
– an extract of shell of pine nuts – 91.2 dL;
– an extract of wild camomile flowers – 25.4 dL;
– an extract of common St. John's wort herb – 12.4 dL;
– a water solution of ethyl rectified alcohol, 40% vol. – 871 dL.

The total of tannins in the extracts of shell of pine nuts, wild camomile flowers and common St. John's wort herb was determined in terms of gallic acid according to the method of HPLC using the chromatograph "Waters-Alliance" (USA) with a spectrophotometric detector M 2998.

The identification and quantitative determination of aromatic aldehydes in the individual extracts of shell of pine nuts, wild camomile flowers and common St. John's wort herb were performed in 3 weeks after preparation using the technique M 04–53–2008 [40] based on the system of capillary electrophoresis "Kapel'-105M" (Russia) in the mode of direct detecting with the use of universal borax buffer (0.02 M solution).

The injection of test specimen was performed under conditions recommended by the technique [40]: under the pressure of 30 Mbar for 20 sec. Analysis conditions: the wavelength is 373 nanometers, the temperature is 20°C, the voltage is +25 kV; the analysis duration is 10 minutes.

Characteristics of the capillary: the internal diameter is 75 microns, the effective length is 50 cm, the total length is 60 cm. Calculation method: absolute calibration with the use of standard samples of vanillin, sinapic, coniferylic and syringic aldehydes (the standards of Aldrich, Fluka). The identification of peaks was performed using the method of addition of standard samples.

Under similar conditions the analysis of experimental blend of aqueous-alcoholic extracts was performed, also in 3 weeks after its preparation.

The studies were repeated 3–4 times. The processing of experimental data was performed with the use of IBM PC with the Elforan software (Lumex Group).

RESULTS AND DISCUSSION

According to the literary data, the accumulation of aromatic aldehydes in the distilled drinks like cognac, brandy and whisky is determined by the degree and rate of degradation of lignin of oak wood. It is shown that the maximum rate of decay of lignin is in the distillates with the content of ethyl alcohol of 80% vol.**,** but the maximum concentration of aromatic aldehydes has been recorded in the distillates with the content of ethanol of 65% vol. [38].

At the initial stages of ageing of cognac alcohols there are processes of hydrolysis and ethanolysis of lignin with the transition to the aqueous-alcoholic solution of extractive substances and the formation of sinapic and coniferylic aldehydes. Afterwards there is a process of "saturation of ethylenic bonds" and the formation of syringic aldehyde and vanillin the further oxidation of which produces syringic and vanillic acids [41]. The described sequence of stages is also confirmed during lignin oxidation by chemical means [42]. And if the content of highly volatile aromatic volatile compounds – aliphatic alcohols, ethyl aldehyde, volatile acids and esters – depends in many respects on the ampelography of the grapes [17] processed for alcohol, then the content of aromatic aldehydes in cognac wine materials is substantially interrelated with the type and geography of growth of oak [43, 44] as the source of the extractive substances which are transformed to aromatic components of cognacs in the course of their ageing.

In cognac wine materials all aromatic aldehydes begin to collect during their first year of ageing in contact with oak wood, with a steady tendency to the accumulation of their total content with an increase in the ageing period. It is offered to use the intensity of the chromatographic peak of the syringic aldehyde prevailing in the composition of aromatic aldehydes, that reflects its concentration and is in direct correlation with ageing duration as the "age index" of cognacs and brandy. The value of this index, as a rule, does not exceed 1 for ordinary cognacs and brandy, and it can reach 9 for branded and collection ones [6].

The nature of accumulation of individual aldehydes is considered a feature of no less importance: for vanillin, coniferylic and syringic aldehydes an exact dynamics has been established that reflects a continuous increase in their concentration to a certain age of cognac alcohol after which a reverse trend of slow decrease is observed [1]. One of the natural consequences of these processes is the change of ratio of syringic aldehyde and vanillin in the course of ageing of distillate reaching 2–4 for collection cognacs [6].

Despite long studies in this regard, the published literary data on the content and ratio of aromatic aldehydes in cognacs and cognac semi-finished products are still rather contradictory. The information on the content of vanillin in cognacs and cognac distillates and the possible dependence of content of total and individual aromatic aldehydes, as well as the products of their further oxidation, on the duration of ageing and concentration of distillate (Table 1) is especially ambiguous.

For other drinks of the group of distillates data on the regularities of accumulation of aromatic aldehydes are not provided in scientific literature. At the same time, when obtaining infusions and extracts of vegetable raw materials for blends of alcoholic beverage products in Russia lower concentrations of ethyl alcohol, within 35–50% vol., are used. The choice of extragents in such concentrations is caused by the fact that in these conditions the maximum of the polyphenols [32, 33] that give an attractive color to the extracts and have at the same time a high antioxidant activity are derived [45].

Table 1. Content of phenolic substances and aromatic aldehydes in the aqueous-alcoholic extractsof oak wood and the cognac distillates of different ageing periods (the ageing from 2.5 to 15 years)

Aldehyde	Concentration of aldehydes / Data source					
	in cognac distillates					in extracts, mg/g of raw materials [43]
	[6]	[7]	[16]	[30]*	[38]	
Total of phenolic substances, g/dm^3	not applicable			0.398–1.013	not applicable	29.3–116.8
Vanillin, mg/dm^3	(peak areas in the HPLC)	0.1–1.6	0.19–2.41	2.053–3.953	0.2–2.4	0.013–0.80
Siringic aldehyde, mg/dm^3		0.2–2.8	0.63–7.84	2.275–7.533	up to 7.8	0.008–0.20
Sinapic aldehyde, mg/dm^3		0.5–2.4	0.33–0.87	not applicable	0.3–2.4	0.14–0.88
Coniferylic aldehyde, mg/dm^3		0.9–2.6	0.26–0.79	0.587–1.668	0.3–2.6	0.007–0.66
Syringic aldehyde / vanillin ratio	2–4 : 1	2 : 1	2–4 : 1	1.5–2.5 : 1	2–4 : 1	1 : 2–3

Note. * Data are provided for waterless alcohol.

When receiving extracts from the studied raw materials it is necessary to consider the features of their morphology. The features of morphology of the considered raw materials consist in the following:
– the shell of pine nuts needs 1 year to be formed and is rich with lignin, as well as oak wood is;
– camomile flowers need no more than one month to be formed and are not rich with lignin;
– common St. John's wort herb and blooms need from two to three months to accumulate lignin before the end of blossom time.

Taking into account the features of morphology of the considered raw materials, it is possible to assume that the rate of stages of degradation of lignin and accumulation of aromatic compounds under conditions of receiving extracts from the shell of pine nuts, wild camomile flowers and common St. John's wort herb should be the same (for example, in the extracts of shell of pine nuts), or higher than that of the similar processes in cognac wine materials.

It is also possible to assume the participation of the polyphenolic compounds of extracts of nuts and herbs with a lower molecular weight which constitute more than 50% of extractive substances of these raw materials in the processes of hydrolysis, ethanolysis and oxidation [32, 36, 46]. In particular – tannins (Table 2) with the prevalence of hydrolyzed substances which are part of them [37, 47]. Therefore, it is possible to predict both the equal, and a higher content of aromatic aldehydes in the studied extracts and various alcoholic beverages made on their basis.

The electrophoregrams given in Figures 1–3 show the composition of aromatic aldehydes in the aqueous-alcoholic extracts of shell of pine nuts, wild camomile flowers and common St. John's wort herb. The analysis of electrophoregrams and the comparison of the obtained results (Table 3) to the literary data shows that the content of aromatic aldehydes in the undiluted extracts exceeds the levels of content of the corresponding aldehydes in the cognac distillates of different ages (Table 1).

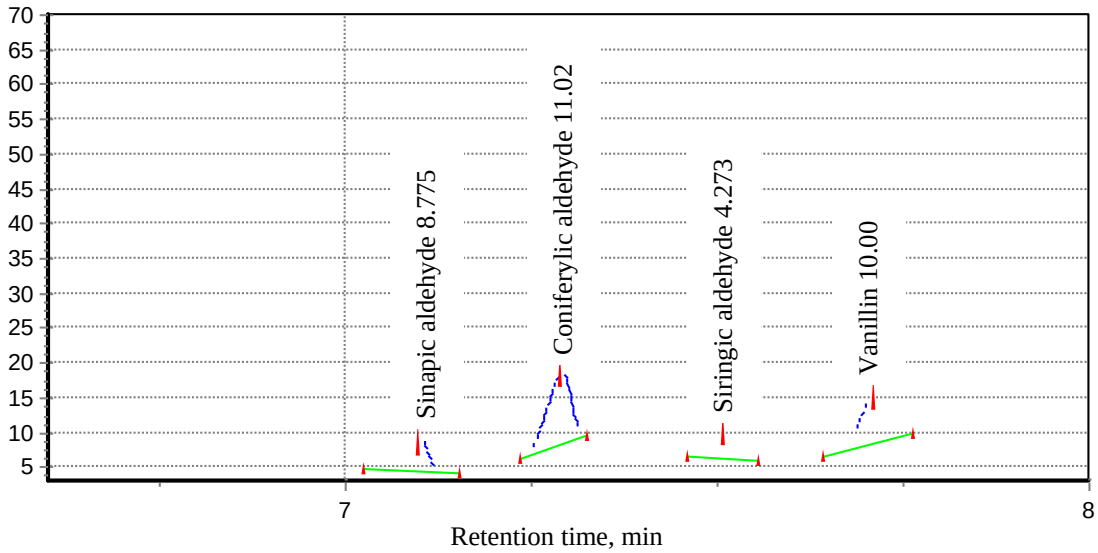

Fig. 1. Electrophoregram of aqueous-alcoholic extract of shell of pine nuts (2-time dilution).

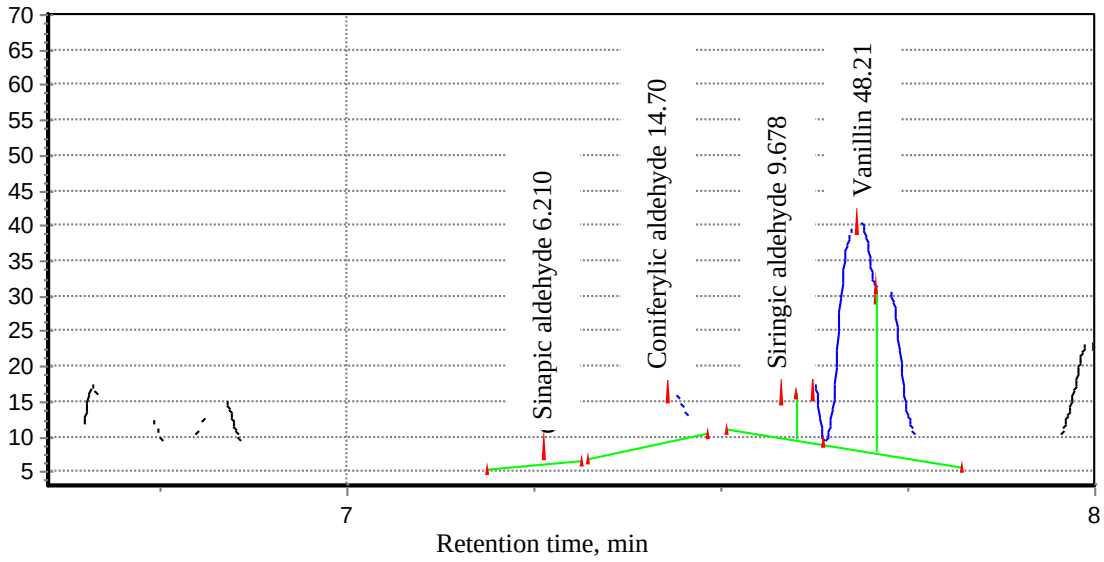

Fig. 2. Electrophoregram of aqueous-alcoholic extract of wild camomile flowers (2-time dilution).

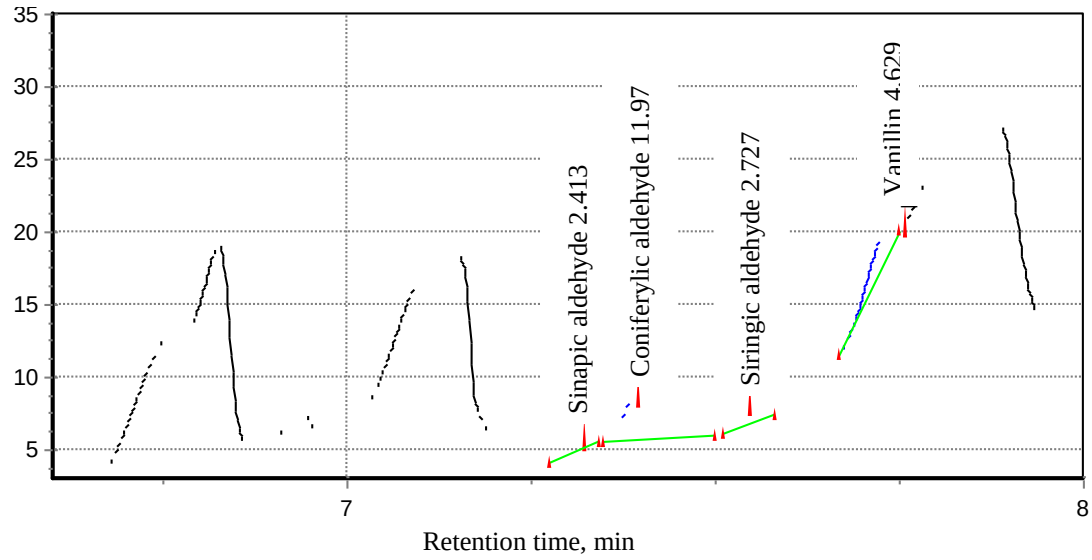

Fig. 3. Electrophoregram of aqueous-alcoholic extract of common St. John's wort herb (4-time dilution).

Table 2. Content of total of tannins in the extracts of shell of pine nuts, wild camomile flowers and common St. John's wort herb

Extract	Content of total of tannins	
	Data of the authors of the article, mg/dm^3 of the extract	Reference data [Source]
Pinus sibirica shell	0.07 ± 0.01	1.5–3.0% in the extract [29]
Hypéricum perforatum herbs	0.48 ± 0.05	10.3–12% in the raw materials [37]
Chamomílla recutita flowers	0.34 ± 0.04	not applicable

No doubt, the choice of extraction module with an increase of which a higher gradient of concentration of lignin containing material on the surface and, respectively, a higher speed of biochemical processes of hydrolysis and the subsequent oxidation of extractive polyphenolic substances is provided is of great importance in the achievement of similar levels of content of aromatic substances in extracts.

It is authentically established that, as for four analyzed aromatic aldehydes, all the three extracts differ both from the freshly obtained oak wood extracts [43], and from the aged cognac distillates. Despite the forecasts, a content of aldehydes at the level equal or even higher than in the extract of shell of pine nuts has been revealed in the extracts of wild camomile flowers and common St. John's wort herb. Vanillin is the strongly prevailing aldehyde in the composition of extract of wild camomile flowers (96.42 ± 9.64 mg/dm^3), the ratio of syringic aldehyde : vanillin in the extract shifts to 1:5. In the extract of

common St. John's wort herb, on the contrary, a predecessor of vanillin – coniferylic aldehyde (47.88 ± 4.80 mg/dm^3) prevails.

The extract of shell of pine nuts for which the established ratio of syringic aldehyde : vanillin is mostly approximated to the corresponding value for cognac distillates and is 1:2.3 can be considered the most balanced as for the ratio of the noted aromatic aldehydes.

It is also necessary to note that there is no direct correlation between the content of aromatic aldehydes in the experimental mixture of extracts – an imitation of distilled drink (Fig. 4) and the content of these aldehydes in the initial extracts (Table 3). Presumably, processes of the second oxidation stage, with the formation of products of oxidation of aromatic aldehydes, first of all – vanillin which is formed of coniferylic aldehyde continued in the simulated drink within three weeks before performing an electrophoretic study.

As an alternative hypothesis, it is also possible to consider the oxidation of aromatic aldehydes to syringic and vanillic acids continuing in the blend. In particular, the actual concentration of syringic aldehyde in the experimental blend is the basis of the similar hypothesis. At the same time, this hypothesis demands additional instrument-based confirmation – a study of composition of aromatic acids in the individual extracts and the experimental blend.

It is known that vanillin and syringic aldehyde have a more characteristic and intensive aroma than their predecessors – coniferylic and sinapic aldehydes, and give pleasant vanilla tones to drinks [38]. The threshold concentration of smell with the concentration of ethyl alcohol in the drink of 40% vol. for vanillin is 0.01 mg/dm^3, and the threshold of taste in cognac alcohols is 0.1 mg/dm^3. The increase in the concentration of vanillin to 30 mg/dm^3 provides the distortion and deterioration in the taste and aroma of drink. The threshold concentration of aroma and taste for coniferylic aldehyde is 3 and 10 mg/dm^3 respectively, for syringic aldehyde is 50 and 100 mg/dm^3. Sinapic aldehyde can be felt only with the concentration of no less than 200 mg/dm^3 [38]. Therefore, taking into account the obtained results and threshold concentrations of taste and smell of individual aromatic aldehydes, the aqueous-alcoholic extracts of the vegetable raw materials considered in the work can be used for the direct simulation of taste and "bouquet" of alcoholic beverages.

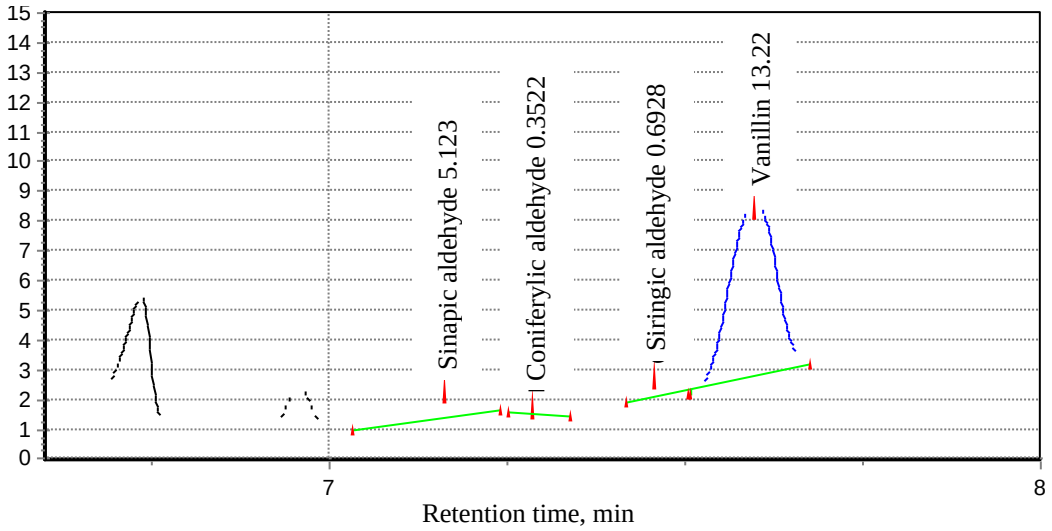

Fig. 4. Electrophoregram of experimental mixture of extracts – imitation of distilled drink.

Table 3. Content of characteristic aromatic aldehydes in the aqueous-alcoholic extracts of vegetable raw materials and the experimental blend (an imitation of distilled drink)

Aldehyde	Concentration of aldehydes, mg/dm^3				
	in aqueous-alcoholic extracts			in a blend of extracts	
	Pinus sibirica shell	*Chamomílla recutita* flowers	*Hypéricum perforatum* herbs	design*	actual
Vanillin	20.00 ± 1.95	96.42 ± 9.64	18.52 ± 1.85	4.51 ± 0.45	13.22 ± 1.30
Syringic aldehyde	8.55 ± 0.90	19.36 ± 1.94	10.91 ± 1.10	1.41 ± 0.15	0.69 ± 0.14
Sinapic aldehyde	17.55 ± 1.80	12.42 ± 1.24	9.65 ± 1.00	2.03 ± 0.20	5.12 ± 0.62
Coniferylic aldehyde	22.04 ± 2.20	29.40 ± 2.94	47.88 ± 4.80	3.35 ± 0.32	0.35 ± 0.03
Syringic aldehyde / vanillin ratio	1 : 2.3	1 : 5	1 : 1.7	1 : 3.2	1 : 19

Note. * The value is calculated on the basis of experimental data on the content of aromatic aldehydes in individual extracts taking into account their prescription dosage when obtaining a blend (see Study methods).

Taking into account that in the course of storage of distilled drinks the hydrolysis and oxidation of polyphenolic compounds and aromatic aldehydes continue, it is possible in our case to predict a further increase in the content of syringic aldehyde and vanillin in the drinks on the basis of the extracts considered in this article. The character and dynamics of these processes demand a further study.

CONCLUSIONS AND RECOMMENDATIONS

The obtained data on the content of aromatic aldehydes in the extracts are one of the evidence of similarity of the processes proceeding when receiving extracts from nuts and herbs, and the processes making a basis of technology of cognac production. The submitted data on the content of aromatic aldehydes in the considered extracts can be used for the direct simulation of "bouquet" of distilled drinks on their basis [48]. In the long term, the obtained data can be put in a basis of techniques of technological express control of readiness of aqueous-alcoholic extracts and authenticity of new drinks in investigation practice.

The existence of four characteristic aromatic aldehydes and other volatile components inherent in cognac production in the composition of the studied extracts testifies to a potential possibility of substitution of cognac distillates to cheaper raw components. In this regard there is a need of collection of information and formation of special statistical database on the structure and content of aromatic aldehydes in extracts and finished goods on the basis of vegetable raw materials which are widely used by Russian enterprises when producing drinks of the distillates group.

REFERENCES

1. Oseledtseva I.V., Guguchkina T.I., and Sobolev E.M. Practical realization of modern ways for determination authenticity of brandy production. *News institutes of higher Education. Food technology*, 2010, no. 2–3, pp. 104–107. (In Russian).
2. Delgado R., Durán E., Castro R., et al. Development of a stir bar sorptive extraction method coupled to gas chromatography-mass spectrometry for the analysis of volatile compounds in Sherry brandy. *Analytica Chimica Acta*, 2010, no. 672 (1–2), pp. 130–136. DOI: https://doi.org/10.1016/j.aca.2010.05.015.
3. *Cognac supplement. Essense of france*. Drinks International (drinksint.com). Zurich House, 2011. 34 p.
4. Von Gesche Wüpper. Die Furcht der Franzosen vor der russischen Cognac-Mafia. *Welt-zeitung*. 17.05.2009.
5. Butskiy K.N. Vozmozhnost' kachestvennoy identifikatsii aromaticheskikh al'degidov metodom tonkosloynoy khromatografii [The possibility of quality identification of aromatic aldehydes using the method of thin-layer chromatography]. *Kriminalistichniy visnik* [Criminal bulletin], 2013, no. 1 (19), pp. 196–202.
6. Kochetova M.V., Larionov O.G., and Ulyanova E.V. The investigation of qualytative composition of cognacs by HPLC. *Sorption and chromatographic processes*, 2008, vol. 8, no. 4, pp. 658–667. (In Russian).
7. Nezalzova E. High-performance liquid chromatography for determination of aromatic aldehydes in wine distillates. *Chemistry Journal of Moldova.* 2011, vol. 6, no. 1, pp. 81–85. DOI: dx.doi.org/10.19261/cjm.2011.06(1).06.
8. Oseledtseva I.V. and Guguchkina T.I. Correlations between Levels of Characteristic Extractive Ingredients in Cognacs and Related Products. *Winemaking and viticulture*, 2011, no. 6, pp. 18–22. (In Russian).
9. Ledauphin J., Le Milbeau C., Barillier D., and Hennequin D. Differences in the volatile compositions of french labeled brandies (Armagnac, Calvados, Cognac, and Mirabelle) using GC-MS and PLS-DA. *Journal of Agricultural and Food Chemistry*. 2010, vol. 58, no. 13, pp. 7782–7793. DOI: 10.1021/jf9045667.
10. Picque D., Lieben P., Corrieu G., et al. Discrimination of cognacs and other distilled drinks by mid-infrared spectropscopy. *Journal of Agricultural and Food Chemistry*, 2006, vol. 54, no. 15, pp. 5220–5226. DOI: 10.1021/jf060465u.
11. Sádecká J., Tóthová J., and Májek P. Classification of brandies and wine distillates using front face fluorescence spectroscopy. *Food Chemistry*, 2009, vol. 117, no. 3, pp. 491–498. DOI: 10.1016/j.foodchem.2009.04.053.
12. Ledauphin J., Saint-Clair J.F., Lablanquie O., et al. Identification of trace volatile compounds in freshly distilled Calvados and Cognac using preparative separations coupled with gas chromatography-mass spectrometry. *Journal of Agricultural and Food Chemistry*, 2004, vol. 52, no. 16, pp. 5124–5134. DOI: 10.1021/jf040052y.
13. Sarvarova N.N., Cherkashina Yu.A., and Evgen′ev M.I. Application of chromatographic methods to the determination of cognac quality indicators. *Journal of Analytical Chemistry*, 2011, vo. 66, no.12, pp. 1190–1195. DOI: 10.1134/S1061934811120094.
14. Zhao Y., Xu Y., Li J., et al. Profile of volatile compounds in 11 brandies by headspace solid-phase microextraction followed by gas chromatography-mass spectrometry. *Journal of Food Science*, 2009, vol. 74, no. 2, pp. 90–99. DOI: 10.1111/j.1750-3841.2008.01029.x.
15. Gun'kin I.N. *Otsenka kachestva kon'yakov elektroforeticheskim i spektroskopicheskim metodami* [Assessment of quality of cognacs using electrophoretic and spectroscopic methods]. Cand. chem. sci. thesis. Krasnodar, 2010. 23 p.
16. Panossian A., Mamikonyan G., Torosyan M., et al. Analysis of aromatic aldehydes in brandy and wine by high-performance capillary electrophoresis. *Analytical Chemistry*, 2001, vol. 73, no. 17, pp. 4379–4383. DOI: 10.1021/ac0014818.
17. Oseledzeva I.V. and Kirpicheva L.S. Assessment of the influence of long factor on variation of parameters of the factions volatile cognac wine materials and young brandy distillate. *Agricultural Bulletin of Stavropol Region*, 2015, no. 1 (17), pp. 246–252. (In Russian).

18. Ferrari G., Lablanquie O., Cantagrel R., et al. Determination of key odorant compounds in freshly distilled cognac using GC-O, GC-MS, and sensory evaluation. *Journal of Agricultural and Food Chemistry*, 2004, vol. 52 (18), pp. 5670–5676. DOI: 10.1021/jf049512d.
19. Savchuk S.A. and Kolesov G.M. Chromatographic determination of fhthalic acid esters as an indicator of adulterated cognacs and cognac spirits. *Journal of Analytical Chemistry*, 2007, vol. 62, no. 8, pp. 761–772. DOI: 10.1134/S1061934807080126.
20. Malfondet N., Gourrat K., Le Quéré J.-L., Brunerie P. Aroma characterization of freshly-distilled french brandies; their specificity and variability within a limited geographic area. *Flavour and Fragrance Journal*, 2016, no. 31 (5), pp. 361–376.
21. Rodríguez Dodero M.C., Guillén Sánchez D.A., Schwarz Rodríguez M., and García Barroso C. Phenolic compounds and furanic derivatives in the characterization and quality control of brandy de Jerez. *Journal of Agricultural and Food Chemistry*, 2010, vol. 58 (2), pp. 990–997. DOI: 10.1021/jf902965p.
22. Mignani A.G., Ciaccheri L., Gordillo B., et al. Identifying the production region of single-malt Scotch whiskies using optical spectroscopy and pattern recognition techniques. *Sensors and Actuators B: Chemical*, 2012, vol. 171–172, pp. 458–462. DOI: https://doi.org/10.1016/j.snb.2012.05.011.
23. Sádecká J., Uríčková V., Hroboňová K., and Májek P. Classification of juniper-flavoured spirit drinks by multivariate analysis of spectroscopic and chromatographic data. *Food Analytical Methods*, 2015, vol. 8, no. 1, pp. 58–69. DOI: 10.1007/s12161-014-9869-8.
24. Magana A.A., Wrobel K., Elguera J.C.T. et al. Determination of small phenolic compounds in tequila by liquid chromatography with ion trap mass spectrometry detection. *Food Analytical Methods*, 2015, vol. 8, no. 4, pp. 864–872. DOI: 10.1007/s12161-014-9967-7.
25. Avila-Reyes J.A., Almaraz-Abarca N., Delgado-Alvarado E.A., et al. Phenol profile and antioxidant capacity of mescal aged in oak wood barrels. *Food Research International*, 2010, vol. 43, no. 1, pp. 296–300. DOI: https://doi.org/10.1016/j.foodres.2009.10.002.
26. Wiśniewska P., Śliwińska M., Dymerski T., et al. Application of gas chromatography to analysis of spirit-based alcoholic beverages. *Critical Reviews in Analytical Chemistry*, 2015, vol. 45, no. 3, pp. 201–225. DOI: 10.1080/10408347.2014.904732.
27. Krasnova T.A., Gora N.V., and Golubeva N.S. Beer quality assurance by controlling wort polyphenolic content with adsorption method. *Foods and Raw materials*, 2016, vol. 4, no. 1, pp. 36–43. DOI: 10.21179/2308-4057-2016-1-36-43.
28. Campo E., Cacho J., and Ferreira V. Solid phase extraction, multidimensional gas chromatography-mass spectrometry determination of four novel aroma powerful ethyl esters: Assessment of their occurrence and importance in wine and other alcoholic beverages. *Journal of Chromatography A*, 2007, vol. 1140, no. 1–2, pp. 180–188. DOI: 10.1016/j.chroma.2006.11.036.
29. Egorova E.Yu. *Nauchnoe obosnovanie i prakticheskaya realizatsiya razrabotki pishchevoy produktsii s ispol'zovaniem produktov pererabotki kedrovykh* orekhov [Scientific substantiation and practical realization of the development of food production with the use of products of processing of cedar nuts]. Dr. eng. sci. diss. Kemerovo, 2012. 484 p.
30. Lukanin A. and Sidorenko A. Kriterii opredeleniya vozrasta kon'yachnykh spirtov [Criteria for determination of age of cognac alcohols]. *Visnyk agrarnoi' nauky* [Bulletin of agricultural science], 2016, no. 10, pp. 51–60.
31. Vivas N. *Manuel de tonnellerie a l'usage des utilisateurs de futaille*. Editions Feret, Bordeaux, 2002. 207 p.
32. Egorova E.Yu., Budaeva V.V., Lobanova A.A., and Ilyasov S.G. Shell of a pine nut in manufacture of alcoholic and non-alcoholic beverages. *Beer and Drinks*. 2005, no. 5, pp. 44–46. (In Russian).
33. Egorova E.Yu. Receiving extracts from an amniotic membrane of pine nuts. *Alcoholic Beverage Production and Winemaking*. 2012, no. 11–12, pp. 23–25. (In Russian).
34. Pavlova L.V., Platonov I.A., Arkhipov V.G., et al. Gas-chromatographic analysis of chamomile (*Chamomilla recutita R.*). *Analytics and Control*, 2013, vol. 17, no. 1, pp. 66–75. DOI: 10.15826/analitika.2013.17.1.009. (In Russian).
35. Bazarnova Yu.G. and Ivanchenko O.B. Investigation of the composition of biologically active substances in extracts of wild plants. *Nutrition problems*, 2016, vol. 85, no. 5, pp. 100–107. (In Russian).
36. Temerdashev Z.A., Milevskaya V.V., Kiseleva N.V., et al. Sorption-chromatographic determination of gallic, caffeic acids, rutin and epicatechin in herbs. *Analytics and control*, 2013, vol. 17, no. 2, pp. 211–218. DOI: 10.15826/analitika.2013.17.2.012. (In Russian).
37. Pravdivtseva O.E. and Kurkin V.A. Issledovaniya po obosnovaniyu novykh podkhodov k standartizatsii syr'ya i preparatov zveroboya prodyryavlennogo [Researches on justification of new approaches to standardization of raw materials and preparations of Hypéricum perforatum L]. *Chemistry of plant raw material*, 2008, no. 1, pp. 81–86.
38. Skurikhin I.M. *Khimiya kon'yaka i brendi* [Chemistry of cognac and brandy]. Moscow: DeLi Print Publ., 2005. 296 p.
39. Egorova E.Yu. and Morozhenko Yu.V. Methodological approaches to the development and quality assessment of new drinks of the group of Distillates. Part 1. Formulation of the new drink. *Polzunovskii Herald*, 2016, no. 3, pp. 4–8. (In Russian).
40. *M 04–53–2008. Kon'yaki, brendi i kon'yachnye spirty. Metodika vypolneniya izmereniy massovoy kontsentratsii vanilina, sinapovogo al'degida, koniferilovogo al'degida, sirenevogo al'degida metodom kapillyarnogo elektroforeza s ispol'zovanie sistem kapillyarnogo elektroforeza «Kapel'-105» i «Kapel'-105M»* [Cognacs, brandy

and cognac alcohols. Technique for mass concentration of vanillin, sinapic aldehyde, coniferylic aldehyde, syringic aldehyde using the method of capillary electrophoresis with the use of capillary electrophoresis systems «Kapel'-105» and «Kapel'-105M»]. St. Petersburg, 2008. n. p.

41. Pochitskaya I. M., Kurchenko V. P., Ursul O. N. Issledovanie fiziko-khimicheskikh protsessov pri vyderzhke kon'yachnykh spirtov [The study of physical and chemical processes when aging cognac]. *Pishchevaya promyshlennost': nauka i tekhnologii* [Food processing industry: science and technology]. 2009, no. 2 (4), pp. 82–89.
42. Koropachinskaya N.V. *Kataliticheskoe okislenie ligninov v aromaticheskie al'degidy v prisutstvii oksida medi* [Catalytic oxidation of lignins in aromatic aldehydes in the presence of copper oxide]. Cand. agr. sci. thesis. Krasnoyarsk, 2004. 18 p.
43. Aksenov P.A. *Otbor duba dlya ispol'zovaniya ego drevesiny v vinodelii* [Selection of oak for the use of its wood in winemaking]. Cand. agr. sci. thesis. Moscow, 2012. 24 p.
44. Oseledtseva I.V., Guguchkina T.I., Markosov V.A., and Prostak M.N. Osobennosti khimicheskogo sostava kon'yachnykh distillyatov, vyrabatyvaemykh v raznykh geograficheskikh zonakh [Peculiarities of the chemical composition of cognac distillates produced in different geographical zones]. *Magarach. Vinogradarstvo i vinodelie* [Grape growing and winemaking], 2013, no. 2, pp. 26–28.
45. Lantto T.A., Dorman H.J.D., et al. Chemical composition, antioxidative activity and cell viability effects of a Siberian pine (*Pinus sibirica* Du Tour) extract. *Food Chemistry*, 2009, vol. 112, no. 4, pp. 936–943. DOI: https://doi.org/10.1016/j.foodchem.2008.07.008.
46. Shefer E.P. *Sovremennye podkhody k izucheniyu khimicheskogo sostava semyan sosny kedrovoy sibirskoy i razrabotka metodov standartizatsii lekarstvennykh preparatov na ikh osnove* [Modern approaches to the study of chemical composition of *Pinus sibirica* seeds and the development of methods for standardization of preparations on their basis]. Cand. pharm. sci. thesis. Moscow, 2000. 24 p.
47. Pozharitskaya O.N., Shikov A.N., Laakso I., et al. Polifenol'nye soedineniya semyan *Pinus sibirica* (*Pinaceae*) [Polyphenolic compounds of *Pinus sibirica* (*Pinaceae*) seeds]. *Rastitel'nye resursy* [Vegetable resources]. 2007, Vol. 43, Iss. 2, pp. 39–46.
48. Egorova E.Yu., Sysoeva D.Yu., Rozhnov E.D., and Morozhenko Yu.V. Aromatic aldehydes of plant product extracts that are used in liqueurs and spirits manufacture. *Polzunovskii Herald*. 2014, no. 4 (2), pp. 126–131. (In Russian).

Please cite this article in press as: Egorova E.Yu., Morozhenko Yu.V., and Reznichenko I.Yu. Identification of aromatic aldehydes in the express assessment of quality of herbal distilled drinks. *Foods and Raw Materials*, 2017, vol. 5, no. 1, pp. 144–153. DOI: 10.21179/2308-4057-2017-1-144-153.