RESEARCH OF SOME PHENOLIC COMPOUNDS IN OAK CHIP EXTRACTS

Zakalashvili S.G. and Bezhuashvili M.G.

Agricultural University of Georgia

Abstract. Based on the analysis of spirit extracts of industrial oak chips, some phenolic compounds they contain were studied. We analyzed the spirit extracts of oak chips of different degree of baking: light, medium and strong. In the extracts we determined the following low molecular phenolic compounds: vanillin, vanillic acid, syringic aldehyde, syringic acid, coniferylic aldehyde, sinapic acid, syringol, gallic acid, gayacol, 4-vinylphenol and 4-ethylphenol. The variation of concentration of the above-listed compounds depending on the degree of baking of oak chips: light, medium and strong. It was inferred that the spirit extracts of oak chips aresuitable for production of alcoholic beverages.

Keywords: oak chips, phenolic compounds.

Introduction

Oak bark is an important raw material in the production of alcoholic beverages. Each component of oak bark plays a particular role in formation of the quality of alcoholic products. The oak bark is rich in chemical compounds of various classes, the most important of which are phenolic compounds: lignin, tannins and flavor-forming low molecular compounds. In the oak bark, lignin is represented in three fractions, the tightest fraction of which is linked to carbohydrate components. We studied the most widespread oak species in Georgia *Quercus iberica* in order to determine the structure and localization of lignin. As a result, it was found that lignin is mostly located in the cell wall and connective tissues. Lignin located in the cell wall is represented by phenylpropan, guaiacyl, syringyl and small amounts of pyrocatechol-type structural units, while lignin represented in the connective tissues produces mainly guaiacyl and syringyl types of monomers[1]. Lignin is mainly located in the connective tissues and is more methoxylated compared to the lignin of cell walls. The use of oak bark in aging of cognac spirits is based on the feature of lignin to produce aromatic phenolic aldehydes and phenolic acids with time. During aging of cognac spiritsboth in oak barrels and on oak staves, lignin is extracted and transformed into various low molecular compounds, which significantly determine the bouquet of cognac spirits. Main processes of cognac spirit aging are the following: lignin ethanolysis, tannin emission and oxidation, and hemicelluloses hydrolysis [2,3]. As a result of lignin ethanolysis during cognac spirit aging, there are formed vanillin, syringic, coniferic, sinapic and other aldehydes, which then undergo partial conversion and are accumulated iin aged cognac spirits. According toLashkhi's research, during cognac spirit aging in oak barrels, aromatic compounds are formed in the process of slow natural oxidation of lignin. [4].

During thermal oxidation of vanillin and syringic aldehydewith air oxygen, pyrocatecholmonoethyl ether is formed from vanillin as a final product, while pyrogallol monomethyl ether is formed from syringic aldehyde. The above-mentioned products were identified in Georgian cognac spirits of different age, aged in oak barrels [5-7]. Further transformations of ligninderivativesformed during aging of Armagnac in oak utensils were studied by Puesh (1981). From aromatic aldehydes, syringic, sinapic, coniferic aldehydes and vanillin were dominant, while, from phenolic acids, such were syringic, vanillic, ferulic, cinnamic, para-coumaric and para-oxybenzoic acids. The process of cognac spirits aging is based not only on oak components, but also on subsequent conversion of spirit components, as well as on the products of interaction of these compounds. There are a lot of technological methods to accelerate the aging process of cognac spirits, which are divided into three main groups: 1. Oxidative; 2. Extractive; 3. Physical and thermal. In most cases, the combination of these three methods is used to accelerate the aging of spirits. Thermal processing methods of oak bark are very important, and a lot of scientific investigations were dedicated to them [8-12]. As a result of research of the thermal oxidation of oak bark of *Quercus iberica* widespread in Georgia, it was established that ethanolysis of lignin has the following features: 1. Thermal oxidation increases the solubility of oak bark lignin during ethanolysis. 2. The structural specific feature of ethanolysis of thermally oxidized oak lignin consists in the prevalence of phenolic

acids over phenolic aldehydes. From phenolic aldehydes, vanillin is dominant in the formation ofethanolate flavor[13].

From phenolic compounds, simple phenol derivatives known as volatile phenols are of great importance. These substances are characterized by intense specific odor, and their existence in such beverages as whisky, cognac and wine leads to formation of relevant flavor. Studies have established the ways volatile phenols are formed, particularly, these are microbiological processes resulted from fermentation and thermal degradation of lignin. It was also established that volatile phenols are formed as a result of conversion of phenol carboxylic acids. Volatile phenolsderived from phenol carboxylic acids were identified in cognac spiritsagedwith the help of oak bark. The authors of work [14] studied how volatile phenols emerged from phenol carboxylic acids existing in cognac spirits under relatively mild conditions (heating to $90^{O}C$). The following was established: emergence of guaiacol from vanilic acid, of para-vinylguaiacol, vanillin, vanilic acid, guaiacol and para-ethylphenol- from ferulic acid, of para-vinylphenol, para-ethylphenol, para-oxybenzaldehyde, para-oxybenzoic acid and phenol - from para-coumaric acid. Volatile phenols emerge as a result of heating of oak bark and lignin. The same authors established a decrease in the concentration of phenolic acids in oak barrels during cognac spirits aging and an increasein the concentration of volatile phenols.

According to the above, oak bark lignin is an important source for formation of diverse range of phenolswhich to a certain extent determine the flavor of cognac spirits and alcoholic beverages. Degradation of oak bark lignin and the processes of formation and capabilities of low molecular aromatic compounds represent a topical research trend. Thus, the objective of our experiment was to study some phenolic compounds of spirit extracts of industrial oak chips.

Objects and Methods of Research

As the object of our research, we used industrial oak chips of three degrees baking: low, medium and high. We prepared water-spirit extracts from oak chips. We carried out the qualitative analysis of phenolic acids and phenolic aldehydes in the extracts by the method of thin-layer chromatography, solvent system - chloroform:methanol (90:10). Chromatograms were revealed by diazotized sulfanilic acid. Phenolic acids, phenolic aldehydes and volatile compounds in the same extracts were quantitatively determined using high-performance liquid chromatography-HPLC [15].

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Results and Discussion

The content (mg / l)of some Phenolic Compounds in alcoholic extracts of Oak Chips

No.	Component Name	Low burn	Medium burn	High burn
1	Vanilin	1.3	1.9	0.7
2	Vanilic acid	4.7	4.03	3.85
3	Syring aldehyde	0.05	0.77	1.45
4	Syringic acid	5.3	6.38	4.63
5	Coniferyl aldehyde	2.5	5.26	0.03
6	Sinapic acid	0.2	5.66	4.23
7	Syringol	Traces	0.54	1.02
8	Gallic acid	3.7	1.57	0.88
9	Guaiacol	0.25	1.22	2.28
10	4-Vinylphenol	0.2	1.33	Traces
11	4-Ethylphenol	Traces	Traces	Traces

According to the table data, the degree of baking of oak chips has a significant impact on the concentration of phenolic aldehydes, phenolic acids and other phenolic compounds in the relevant

spirit extracts. The obtained data definitely indicates the correlation between the degree of baking and the formation of the above-mentioned compounds in oak chips. This impact is differently expressed in the change of each component. Particularly,as the degree of baking increases, the concentration of vanillin decreases due to the formation of various compounds as a result of its oxidation. The highest concentration of vanilic acid was found in oak chips of the lowest degree of baking, and its concentration decreased from 4.7 mg/l to 3.85 mg/l as the degree of baking increased. Syringic aldehyde increased with the degree of baking, while the product of its oxidation syringic acid was found in high concentration in the extract of medium baked oak chips, and its concentration decreased to 4.63 mg/l with high degree of baking. Syringol is one of the products formed in the result of oxidative conversion of the syringylic structure of oak bark lignin, which increased with the degree of baking from traces to 1.02 mg/l. As for guaiacol –the product formed during oxidation of the guaiacylic structure of lignin, its concentration significantly increased proportionally to the degree of baking. The amount of coniferylic aldehyde increased with the increase in the degree of baking from low to medium, while with high degree of baking, its amount sharply decreased. The maximum amount of sinapic acid was found in the extracts ofmediumbaked oak chips, while, with the high degree of baking, it decreased again. In all cases 4-ethylphenol was present in trace amounts. 1.33 mg/l Vinylphenol in the amount of 1.33 mg/l was found in medium baked oak chips.

Thus, the performed research showed that the degree of baking affects significantly the formation of various phenolic compounds in oak chips, which is reflected in their content in spirit extracts of chips. Aromatic aldehydes, acids and other compounds found in the extracts of oak chips indicatethe possibility of their usage in production of alcoholic beverages.

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РЕЗЮМЕ

ИССЛЕДОВАНИЕ НЕКОТОРЫХ ФЕНОЛЬНЫХ СОЕДИНЕНИЙ В ЭКСТРАКТАХ ДУБОВЫХ ЧИПСОВ

Закалишвили С.Г., Бежуашвили М.Г.

Грузинский аграрный университет

На основе анализа спиртовых экстрактов промышленных дубовых чипсов изучены некоторые входящие в них фенольные соединения. Анализировались спиртовые экстракты дубовых чипсов разной степени обжарки: легкой, средней и сильной. В экстрактах мы определили низкомолекулярные фенольные соединения: ванилин, ванильная кислота, сиреневый альдегид, сиреневая кислота, конифериловый альдегид, синаповая кислота, сирингол, галловая кислота, гваякол, 4-винилфенол, 4–этилфенол. Определено изменение концентрации перечисленных фенольных соединений в зависимости от степени обжарки дубовых чипсов. Сделан вывод о возможности использования экстрактов дубовых чипсов в производстве алкогольных напитков.

Ключевые слова: дубовые чипсы, фенольные соединения.