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Traditional usage of heartwoods from different arboreal species in inland and coastal regions of Bulgaria

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Abstract: Plants have been used in Bulgarian traditions for thousands of years. Apart of the knowledge about the healing potential of some popular tree species, stems and heartwood are used traditionally in Bulgaria for coloring of hard alcoholic beverages. Popular believes suggest that colored drinks in small quantities could possess certain health beneficial effects due to the plant constituents extracted during the process of coloration. Here we present an overview of the arboreal species, known to be used for manufacturing of barrels for maturation or for coloring of beverages at home in Bulgaria. Based on the existing data, we suggested that the specific phytochemical characteristics of the heartwoods of different species could contribute for the organoleptic characteristics of the colorized beverages as well as for their beneficial effects on the metabolism when consumed in moderate quantities.

Key words: heartwood aqueous-ethanolic extracts; mulberry; black locust; oak; smoketree.

Introduction

Plants represent an inexhaustible source of components for the development of new drugs, thanks to their properties to absorb simple molecules and include them in complex, biologically active products. The rapidly growing scientific knowledge in this field is explained by the revived interest of researchers in the healing power of plants based on traditional medicine and folklore data.

The Hellenic nature explorer and philosopher Theophrastus notes in his work "Enquiry into Plants" that Thrace is the richest region of medicinal plants in the then world (Petkov 1982). Due to the diverse climatic conditions and soil diversity of the region, Bulgarian plants contain a high percentage of biologically active substances. They are rich in various chemical compounds such as alkaloids, glycosides, saponins, polysaccharides, tanning agents (tannins), flavonoids, lignans, coumarins, essential oils, vitamins, trace elements, etc. The healing effects and the application of many of them have been already studied. In the world practice, about 40% of the pharmaceuticals/medical products produced by the chemical and pharmaceutical industry are prepared from plant raw materials.

The knowledge about the healing potential of some popular tree species is based on the beneficial effects of various preparations of their fruits, flowers, leaves and bark. Although the heartwoods of these plants are used to produce barrels facilitating the aging and coloring of high-alcoholic beverages, there is still insufficient scientific data on the effect of the extracted active heartwood components on human health.

Material and methods

The focus of our interest was on the arboreal species traditionally used for manufacturing barrels for colorization and maturation of alcoholic beverages and we collected information about the plant constituents extracted during the process of coloration and maturation. We used the PubMed database (https://www.ncbi.nlm.nih.gov/pubmed/) searches with keywords, as well as highly regarded publications in the field

from which other sources were identified using the "Cited by" link in Google Scholar (scholar.google.com) and Science Direct (www.sciencedirect.com). Recent developments in the field were emphasized by searching articles published in targeted journals in the last 20 years, whilst still including significant historical sources. Books devoted to Bulgarian traditional medicine were the sources of information about the healing effects of the plants.

Results

Grape brandy is the most commonly used alcoholic beverage in Bulgaria (Marinov 2005). Its production is part of the national cultural identity. Wood-colored brandy, used in small quantities, exhibits a known beneficial effect on health, according to the traditional perceptions of the population. The production of high-quality beverages necessarily involves the stage of maturation - aging in wooden barrels to improve the organoleptic characteristics of the end product. According to Alañón et al. (2011) the maturation of beverages is a key step not only in shaping the ultimate flavor characteristics but also increases their antioxidant capacity.

The role of heartwood in the alcohol aging process is as follows:

1. Extraction of various phenolic components from the wood; 2. Change in the aroma as a result of chemical reactions between these components and the active ingredients of the distillate; 3. Change in color due to the oxidation of certain phenolic compounds by atmospheric oxygen and the formation of new anthocyanin derivatives and tannins (Flamini et al. 2007, Alañón et al. 2011).

Sometimes in domestic production, except aging in barrels, wood (core/heartwood or young branches) of white or black mulberry (*Morus alba* L., *Morus nigra* L.), black locust (*Robinia pseudoacacia* L.), oak chips (*Quercus robur* L.) and relatively rarely (mainly in Northeastern Bulgaria) of the smoketree (*Cotinus coggygria* Scop.) is used to color the brandy. There was no difference in the species applied in inland and coastal regions of the country.

While in the other parts of the plants the biologically active components are more often represented as free molecules, in the wood they are interconnected by means of low energy intermolecular interactions, forming the biopolymers cellulose, hemicellulose and lignans, and compounds of another nature defining the mechanical properties of the tree. Cellulose is a compound, consisting of a unbranched chain of several thousand glucose residues joined together by β-1-4-glycosidic bonds. Hemicellulose is a heterobiopolymer, which besides glucose contains other hexoses and pentoses. Its molecule is a long chain of glucose residues joined by β-1-4-glycosidic bonds, and shorter side chains formed by other types of carbohydrates attached.

The process of heat pre-treatment of wood as a factor in changing the color and aroma of the beverage is equally as important as the specific wood species profile. Toasting significantly affects the chemical composition and thus changes the quantity and quality of the extracted substances. This process produces a large number of low molecular weight compounds resulting from the thermal decomposition of biopolymers such as cellulose, hemicellulose, lignans which can pass into the alcohol when contacting the wood (Cabrita et al. 2012). Two classes of phenolic acids, hydroxylated derivatives of benzoic (hydroxybenzoic acids) and cinnamic (hydroxycinnamic acids) are found in the wood. The benzoic acid derivatives differ in the hydroxylation or methylation of the aromatic ring. The most common derivatives are hydroxybenzoic, vanillic, syringic, protocatechinic (Sanz et al. 2012). They are usually conjugated to a carbohydrate residue, bound to cell wall components (Strack 1997). The four most widely distributed hydroxycinnamic acids are p-coumaric, caffeic, ferulic and sinapic acids.

Thermal decomposition or thermolysis of polysaccharides leads to the formation of furan derivatives. Hemicellulose is the thermally most sensitive biopolymer that is degraded upon heating and this explains the high levels of furfural (pentose derivatives) and 5-methyl furfural (from cellulose and glucose) among the furan aldehydes identified in the alcoholic extracts (Calderia et al. 2006). According to the authors, the duration of the thermal treatment is also important. Lignans are thermally the most stable polymers. Their thermal decomposition leads to the release of phenolic aldehydes (syringaldehyde and vanillin) (Kozlovic et al. 2010), followed by an increase in their corresponding acids and monomeric products: eugenol and syringol, as well as various types of coumarins, derived products of cinnamic acid (Mosedale & Puech 1998).

According to Csonka-Rákosa (2005), the differences in structure are a factor that influences the thermal stability of flavonoids (number and position of hydroxyl groups and of the glycosidic bond). Using a spectrophotometric analysis of different flavonoids found in heat-treated black locust wood (*R. pseudoacacia*), the same author notes that the color changes of quercetin and robinetine are different due to the difference in the number and position of the hydroxyl groups in their structure. The most stable

Table 1 presents the phenolic compounds identified in alcoholic extracts (wine, vinegar, 50% aqueous-ethanol solution) of four types of wood used to color brandy in Bulgaria.

Plant species	Phyto-chemical composition	References
Morus nigra L.	trimethoxyphenol, syringaldehyde, vanillin;	Flamini et al. (2007)
	2-aryl benzofuran	Ferlinahayati (2008)
Robinia pseudoacacia L.	syringaldehyde, hydroxybenzaldehyde, vanillin, anisaldehyde;	Flamini et al. (2007)
	dihydro robinetin, robinetine, furfural, 5-methylfurfural, guaiacol,, vanillin, kempferol, rutin;	Cerezo et al. (2009)
	dihydro robinetin, robinetin, robin, fustin, butin, catechin, quercetin, myricetin, myricetin-3- glucoside;	Kozlovic et al. (2010)
	2,4-dihydroxybenzaldehyde; gallic, ellagic, caffeic, p-coumaric acids	Sanz et al. (2012)
Cotinus coggygria Scop.	sulfuretin, fustin, gallic acid, methylgallate, catechins, quercetin, dihydro quercetagetin.	Antal et al. (2010)
Quercus robur L.	furfural, eugenol, vanillin, β-methyl-γ-octa-lactones, 4-ethylphenol;	Kozlovic et al. (2010)
	phenolic acids (gallic, ellagic, protocathetic, vanilic, cinnamic, p-cummaric), vanillin, ruburiins (A-E), syringaldehyde;	Alañón et al. (2011)
	vanillin, eugenol, methoxyeugenol, syringaldehyde, a-terpineol, catechin, quercetin, myricetin; gallic, ellagic, ferulic, caffeic, p-cummaric acids	Sanz et al. (2012)

are robinetine and myricetin, which have three hydroxyl groups in the B-ring. Catechin and epicatechin, from the representatives of the group of flavanols are dominant secondary metabolites found in black locust and oak wood (Sanz et al. 2012).

There are data available in the literature about identification of various phenolic compounds extracted into alcohol from different woods. The studies are mainly focused on changes in the chemical composition and on the organoleptic characteristics of wine stored in barrels produced from different tree species. Predominantly oak, acacia, cherry and chestnut are being analyzed.

Discussion

The reported beneficial effects of colored beverages when consumed in moderate quantities may be due to some biologically active components of the heartwood (polyphenols: flavonoids and tannins, phenolic acids and secondary metabolites) that pass into the distillate during the process of aging. These compounds show powerful antioxidant activity, thus explaining the so-called "French paradox" - reducing the coronary mortality rate by moderate consumption of red wine, probably due to its polyphenol composition (Hernandez et al. 2007).

The main route for the biologically active compounds of the heartwood to enter the human body and to exhibit their metabolic activity is by direct consumption of extracts from this part of the tree. Popular application of wood of various plant species in the food industry is their use in the production of containers (casks, vats, barrels) for storage, aging and coloring of various alcoholic beverages for direct human consumption (wine, rum, whiskey, brandy). Since ancient times, oak is the most popular material for making such containers because of its unique physical and chemical properties and the ability to release a large amount of aromatic volatile compounds that contribute to the final tasting qualities of the beverage (Mosedale & Puech, 1998).

The knowledge about the healing effect of tree species is mainly based on the application of their leaves, flowers, fruits and bark. There are scarce data on the use of branches and wood for curative purposes.

The oak has long been known in the world phytotherapy. The bark is the one most commonly used, rarely are the seeds and fruits. Dried bark infusion

is used as an anti-inflammatory agent and antiseptic remedy in dysentery, intermittent fever and haemorrhages (Calderia et al. 2002). Bulgarian traditional medicine recommends an oak bark infusion for diarrhoea, worms, cough, bronchitis, bladder inflammation, heartburn and stomach ache (Dimkov 1991). Compresses are applied externally to treat lymph gland inflammation, eczemas and wounds, also as a gargle for stomatitis (Ahtardjiev 1980).

By using an agar diffusion method, Andrenšek et al. (2004) detect antimicrobial activity of 80% methanolic extract from *Q. robur* bark in cases of *Staphylococcus aureus*, *Enterobacter aerogenes* and *Candida albicans*. The main compounds found in oak wood are tannins. According to Bronze et al. (1997) the *Q. robur* heartwood may contain up to 10% of ellagitannins. Active components derived from the oak heartwood have been shown to be potential anti-ulcer agents in their ability to inhibit the growth of *Helicobacter pylori* (Lin et al. 2005). This is also confirmed by the study by Martin & Wallace (2006), who prove that tannins and phenolic acids have the ability to protect the gastric mucosa against the action of toxic substances and can prevent gastrointestinal inflammation. An in vitro study found a high antioxidant activity of aqueous - ethanol extract from *Q. robur* leaves (Almeida et al. 2008).

Data on the use of black locust flower infusion as a powerful remedy against neuralgia, gingivitis and gastrointestinal disorders and of aqueous infusions with expectorant, antispasmodic and diuretic effect are available in the experience of traditional healers in Bulgaria (Ikonomov 1941). The robinia bark in small doses is used in cases of hyperchlorhydria, ulcers in the stomach and intestines, but only under medical supervision because it contains the toxalbumine robinin (Stoyanov 1973).

Ethanol infusion from young branches relieves gastrointestinal inflammation, reduces blood pressure (Stoyanov 1973) and shows positive results in treatment of exaggerated gastritis and increased gastric acid secretion (Nazina et al. 2005).

Resorcinol - a polyphenolic compound derived from the *R. pseudoacacia* heartwood is used in the pharmaceutical industry for the production of ointments for the treatment of dermatitis, acne and fungal infections (Hahn et al. 2006).

Leja et al. (2005) found high content of flavonoids and anthocyanins in pollen from *R. pseudoacacia* and they established a correlation between the polyphenol content and the inhibition of lipid peroxidation in in vitro experiments.

Amorphashibol (APH-1) is a trans-stilbene extracted from seeds of locust tree. Kim et al. (2012) establish the biological activity of APH-1 as an agonist of peroxisome proliferator-activated receptor gamma (PPARγ) and a potential source for treatment of diabetes type 2 by inducing glucose and lipid metabolism. Ethanol extracts from different plant organs exhibit antibacterial and antifungal activity (Rosu et al. 2102).

Ploetz (2000) describes Eurasian smoketree (*C. coggygria* Scop.) as one of the fifteen most popular medicinal plants in Bulgaria. In Bulgarian folk medicine, the leaves are often used plant substances, the decocts of which have anti-inflammatory and haemostatic activities. They are mainly used for mouthwashes in cases of toothache and gingivitis, as well as for fomentation in purulent wounds, boils and swellings, for vaginal lavages in leucorrhoea, fomentation in acne, hemorrhoid baths, and as after burns remedy (Lambev & Boyadjieva 2009). Smoketree leaf infusions are generally used externally – on the skin and on mucosa, as the plant is considered to be poisonous (Vodenicharov & Petrov 2001, Landjev 2010). In Bulgarian folk medicine, there are very few reports about oral administration of plant infusions - against diarrhea, stomach ulcer, asthma, kidney disease, hemorrhoids, leucorrhoea, gonorrhea (Landjev 2010). Pharmacological study of syrup from *C. coggygria* establishes its hepatoprotective and health strengthening activity (Shen et al. 1991). Sulphuretin was found to be the most abundant among all stem flavonoids, demonstrating a strong antioxidant and anti-inflammatory properties (Antal et al. 2010).

Recent *in vivo* studies have found positive effects of aqueous leaf infusions and of aqueous-ethanol infusions from wood core from *C. coggygria*, expressed in improved lipid profile and an increase in serum antioxidant capacity (Ivanova et al. 2013, Pavlov et al. 2013), as well as gastroprotective effect in a model of indomethacin-induced ulcerogenesis in rats (Pavlov 2015).

A number of phytochemical and biochemical studies establish that the biological activity of aqueous and aqueous-ethanolic extracts from *C. coggygria* could be contributed to the high polyphenols content and the antioxidant capacity (Ivanova et al. 2005, Niciforovic et al. 2010, Pavlov 2015).

The exploration of the experience of the Bulgarian folk medicine and the national traditions of application of the plants, both for treatment and in the household, is supported by the increased capacity of modern pharmaceutical, medical and clinical methods and technologies. Most of these studies relate to analysis of chemical composition, biochemical properties and metabolic activity of plant components.

Conclusions

Based on the existing data, we suggested that the specific phytochemical characteristics of the heartwoods of different species could contribute for the organoleptic characteristics of the colorized beverages as well as for their beneficial effects on the metabolism when consumed in moderate quantities.

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