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Research review paper

Valorisation of softwood bark through extraction of utilizable chemicals. A review

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A R T I C L E I N F O

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A B S T R A C T

Softwood bark is an important source for producing chemicals and materials as well as bioenergy. Extraction is regarded as a key technology for obtaining chemicals in general, and valorizing bark as a source of such chemicals in particular. In this paper, properties of 237 compounds identified in various studies dealing with extraction of softwood bark were described. Finally, some challenges and perspectives on the production of chemicals from bark are discussed.

1. Bark – an introduction

1.1. Bark in nature

Mother Nature is a primary source of nearly all materials used either in their original form or as products of processing. It is a pity that a huge share of natural sources is subject of very ineffective ways of treatment and utilization. A genially foresighted idea was formulated by D. I. Mendeleev (Rao and Rao, 2016) who on investigating the composition of petroleum recognized the importance of petroleum as a feedstock for petrochemicals and enunciated a remark that *burning petroleum as a fuel would be akin to firing up a kitchen stove with bank notes*. Along with petroleum and other natural materials, bark can serve as another example of wasting a valuable natural source and its components. Most of hundreds million tons of bark are yearly incinerated, landfilled or used for thermal energy production without valorizing its content. There are two distinct classes of wood such as softwood and hardwood. The softwoods are derived from the coniferous species. The number of genera in the Coniferrae is not very large, approximately 40 with some 600 species. Recently several papers have been devoted to various aspects of sound and reasonable utilization of biomass in general and bark and substances isolable from it in particular (Co et al., 2012). The mentioned and other papers cover particular aspects of bark valorization (extraction techniques, kind of bark, etc.), there are still “white areas” to be assessed and evaluated. It is an ambition of the present review to contribute to complete the mosaics targeting the valorization of biomass by adding new pieces of information.

The present paper focuses on three aspects of softwood bark valorization:

1). Extraction techniques applied for obtaining applicable substances and compounds from softwood bark;
2). Yield and characterization of such substances and compounds by analytical methods;
3). Utilization of extractives in pharmacology, cosmetics, medicine and other fields of application.

The mass of dry biomass on the Earth is estimated to $(1.85–2.4) \times 10^{12}$ tons. Every year $(150–180) \times 10^{9}$ tons of biomass is produced (Blažej and Košík, 1993; Khim, 1975; Rosillo-Calle et al.,

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2007) through photosynthesis. Global primary production can be estimated from satellite observations. Satellites scan the normalized difference vegetation index over terrestrial habitats and sea-surface chlorophyll levels over oceans. This results in 56.4 billion tons Carbon/year (53.8%), for terrestrial primary production, and 48.5 billion tons Carbon/year for oceanic primary production (Field et al., 1998). Approximately 75% of all biomass is composed of saccharides, 20% is made of biopolymer named lignin, and the remainder consists of extractives (5%) (Rosillo-Calle et al., 2007). The total extractives availability in the biosphere exceeds 75 billion tons and annually increases by around 5 billion tons. A simple and clean fractionation of the main components of bark represents a very important step in the "clean", renewable carbon economy. Fractionation of feedstock is an essential operation for almost all processes at acquiring of other products. If one can easily separate the different components, we gain a significant source of raw material (Ignat et al., 2013; Košíková et al., 2006; Spiridon et al., 1995) further usable as a starting material for new composites, but also value-added chemicals as well as pharmaceutical goods and fine chemicals.

1.2. Compositions of softwood bark

Wood extractives have different functions and influence several properties of wood, such as its density, hardness and compression strength. Some of them (terpenes and glycosides) support also wood resistance to biotic influences (Dietengerg, 1999). The bark is a rich source of natural polyphenols acting as important substances in the field of nutrition, health and medicine. Flavonoids and other vegetable phenolic compounds such as phenolic acids, stilbenes, and tannines are important for normal plant development and their protection against damage and infection (Kähkönen et al., 1999; Jerez et al., 2007). Procyanidins as a subclass of proantocyanidins consisting of catechin and epicatechin-based oligomers and polymers represent a second (following lignins) most wide-spread groups of polyphenols. Stemming from their pharmacological effects, mainly concerning atherosclerosis, they are objects of intensive research (Escribano-Bailón et al., 1992). The share of bark in the total tree matter is variable and depends mainly on the tree kind and its age (Blažej and Košík, 1985). The bark contains components similar to those present in wood, e.g., cellulose, hemicelluloses, pectin, lignin and various extractives differing, however, in mutual ratio. The contents of extractives (both lipophilic and hydrophilic) and mineral substances is usually much higher (Fengel and Wegener, 1984; Hemingway, 1981; Sakai, 2001). Moreover, bark contains also substances absent in wood, such as condensed amines and suberin (Krogell et al., 2012). Bark extractives can be grouped into lipophilic and hydrophilic components. The lipophilic substances are extractable by non-polar solvents (such as diethyl ether, dichloromethane) and consist predominantly of fats, waxes, terpenoids and higher aliphatic alcohols. Hydrophilic components are extractable by water or polar solvents (acetone, ethanol) and consist of a large number of aromatic compounds (Sjöström, 1993). In practical analysis, extractives are separated based on their solubility in various solvents (Laurová et al., 2007). To determine the total contents of extractives, extraction by methanol or ethanol followed by water extraction are usually used. The kind of isolated substances depends significantly on the polarity of solvents used for extraction (Walker, 2006). Highly volatile extractives can be separated by steam distillation. These compounds predominantly include monoterpenes and other volatile terpenes, terpenoids and various low-molecular mass compounds (Guangyu and Pirjo, 2011). A group of steam-distilled compounds consists of volatile aliphatic and cyclic acids, etheric oils, volatile hydrocarbons, alcohols and aldehydes (Perelygin, 1965). Residual wood is the source of compounds soluble in ether, such as fats, saturated and unsaturated fatty acids, resins, resin acids, waxes, sterins and non-volatile hydrocarbons (Melcer et al., 1977). Following the mentioned extraction by ether, tannins, flobafens and natural dyes are extracted by ethanol (Perelygin, 1965). Finally, the last class of accessory compounds, including saccharides, cycloses (e.g. inositol, pinitol) and polysaccharides (starch, wood gum, mucilages, pectine compounds) is extracted by hot water (Melcer et al., 1977), (Perelygin, 1965). The content of extractives obtained from the bark of individual tree species differs significantly and the composition of accessory substances depends also on whether inner or outer part of bark undergoes extraction. Ånäs et al. (1983) compared the composition of extractives originating from spruce and pine bark (see Table 1) and came to a conclusion that pine bark had a higher content of extractives from both inner and outer part of the bark. Spruce bark does not contain such amount of extractives, however, due to a lower content of fatty acids, it is more popular from the viewpoint of applicability and industrial processing.

Table 1
Content of main extractive components soluble in petroleum ether (mg/g dry bark) (Ånäs et al., 1983).

Compounds	Spruce bark		Pine bark	
	Inner	Outer	Inner	Outer
Fatty acids	7.57	6.36	37.83	9.04
triglycerides	4.86	2.60	33.40	1.71
Mono- and diglycerides	0.84	1.74	2.26	5.46
Sterol esters	1.44	0.60	1.54	0.19
Free	0.43	1.42	0.63	1.68
Resin acids	6.26	1.94	7.16	2.39
Sterols and triterpene alcohols	2.94	2.98	4.50	2.98
Free	0.72	1.91	2.56	2.73
Esterified	2.22	1.07	1.94	0.25
Terpene alcohols	1.24	0.30		
Diterpene aldehydes	0.33	0.10	0.21	0.11
Fatty alcohols	0.13	1.24	1.33	1.25
Ferulic acid-	0.08	0.94	1.26	1.01
Wax–	0.03	0.07	0.03	0.09
Free	0.02	0.23	0.04	0.15
Glyceryl residues	0.32	0.31	1.76	0.68
Total weight extractives	21.40	19.54	59.06	36.11

When discussing the issue of valorization of the bark and compounds contained in it, it should be pointed out that many of the discussed compounds can be prepared also by more economical modes both synthetically at laboratory or industrial scales, or through isolation from other than bark natural sources. However, even taking this "handicap" into account, the significance of compounds and substances extracted from bark should not be undervalued.

2. Extraction and extractive compounds

Recent research has revealed that forestry wastes such as dry bark, branches, and roots potentially possess important properties, which relate to the content of the individual substances in the waste. The extraction and purification or fractionation processes of these active or bioactive substances are essential as they can be used in the preparation of fine chemicals, dietary supplements, nutraceuticals, functional food ingredients and food additives, pharmaceutical and cosmetic products. An extraction method and solvent should be chosen considering the sample matrix properties, chemical properties of the analytes, matrix–analyte interactions, efficiency and speed, environmental friendliness and cost (Co et al., 2012). Further, it has been known that extract composition can be affected by a number of factors such as species, variety, fertilization, pesticide use, harvest time, and drying. The most appropriate way is to isolate substances with added value, which are represented in this work. Extractives differ in chemical structure, but also the physico-chemical and colloid - chemical properties.

2.1. Extraction techniques and their achievements

An amount and nature of the isolated compounds greatly depend on the