CHEMICAL COMPOSITION OF CORK FROM *QUERCUS VARIABLIS*

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Abstract. Cork is a natural and renewable raw material harvested from the outer bark of oak (*Quercus* spp.) trees. Unique and valuable properties of cork include low density, low permeability, high elasticity, good heat and acoustic insulation properties, and resistance to chemical and microbial attack. Chemical composition of cork is affected by many factors including the *Quercus* species and the number of times that cork has been harvested from the tree (ie virgin vs reproduction cork). Differences in chemical composition can significantly influence cork properties. In this study, chemical composition of virgin and reproduction cork from *Quercus variablis* trees in Shaanxi Province, China, was investigated. Cork samples were sequentially extracted with dichloromethane, ethanol, and water in a Soxhlet extractor. Eluted fractions were analyzed using ion chromatography. Chemical composition of virgin *Q. variablis* cork was 34.3% suberin, 20.6% lignin, 17.4% extractives, and 15.2% polysaccharides. Composition of reproduction cork was 36.9% suberin, 19.9% lignin, 12.7% extractives, and 12.0% polysaccharides. These results show that composition of virgin and reproduction *Q. variablis* cork was similar. Virgin *Q. variablis* cork had greater extractives and polysaccharides content than reproduction cork but a little less suberin. Chemical composition of *Q. variablis* cork from China is significantly different from that of *Quercus suber* L. cork from Europe.

Keywords: Cork, *Quercus variablis*, chemical composition, properties.

INTRODUCTION

Cork is a unique natural material with many interesting and useful properties, ie light weight, elastic, chemically stable and resilient, relatively impermeable to liquids and gases, and resistant to wear and fire (Anjos et al 2008; Santos et al 2010). Cork is most commonly used for producing wine stoppers, but it also has application as thermal, electrical, and acoustical insulation; as building and decorating material; and as energy-absorbing medium in flooring, shoes, and packaging (Gameiro et al 2007).

Cork is a protective layer of dead suberized cells formed from phellogen tissue in the outer bark of oak (*Quercus* spp.) trees. The first stripping of cork bark (ie virgin cork) is performed approximately 20 yr after *Quercus* saplings are planted. After that, reproduction cork is harvested from the trees every 9-12 yr. Chemical composition of cork, which is relevant to its quality, depends on such factors as geographic origin, climate and soil conditions, genetic origin, tree dimension, tree age (ie virgin or reproduction cork), and growth conditions (Pereira 1988; Silva et al 2005).

There are four main species of cork oak in the world. *Quercus suber* L. grows widely in Europe

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and Africa. Europe accounts for about 60% of world's cork forests and more than 80% of all cork production. The other three species of cork oak, *Q. variabilis, Q. occidentalis*, and *Q. pseudosuber,* grow mainly in China, Korea, and Japan (Zheng 2005). *Q. variablis* is cultivated for cork production in China, however its yield is less than that of *Q. suber*.

There are many reports about chemical composition of European cork from *Q. suber* (Table 1) (Holloway 1972; Parameswaran et al 1981; Silva et al 2005). Cork is mainly composed of suberin, lignin, and polysaccharides plus smaller amounts of extractives, ash, and other ingredients (Pereira et al 1996; Conde et al. 1998). Cork extractives mainly consist of aliphatic, phenolic, and triterpenic components (Liu 2008). Parameswaran et al (1981) reported that compared with reproduction cork, virgin cork contains more benzene extractives but less suberin, lignin, and ash. Pereira (1984, 1988) compared chemical composition of cork from different regions of Portugal and found differences in chemical composition between virgin and reproduction cork in relation to extractives and suberin. Variability of virgin cork chemical composition with geographical location was also found in relation to some components. Elvira (1998) analyzed chemical composition of reproduction cork in Spain. Detailed chemical composition of lipophilic extractives of cork and cork byproducts has been investigated by Sousa et al (2006). Dichloromethane and supercritical carbon dioxide (CO_2) extract were used to identify the triterpene fraction of cork extractives from *Q. suber* (Castola et al 2002, 2005). Fifteen phenol compounds in cork were recently identified by Santos et al (2010).

Use of cork from *Q. variabilis* for decorating and industrial purposes has recently increased, however, to the author's knowledge, only three studies have reported chemical composition of *Q. variablis* cork (Wei 2007; Liu 2008; Zhang 2009). Wei (2007) reported lignin, cellulose, and benzene extractive content of *Q. variablis* cork and found that chemical composition of cork can significantly affect their function. Liu (2008) found that suberin consists of fatty acid and phenolic acid. Zhang (2009) discovered that virgin cork from sprout *Q. variabilis* has a higher suberin content and less lignin content than other cork from *Q. variabilis*. However, none of these studies reported the monosaccharide composition of polysaccharides in *Q. variablis* cork. More detailed information about chemical composition of *Q. variablis* cork will provide important information for the cork industry.

In China, *Q. variabilis* mainly grows in the Dabie, the Qinling, and the Taihang Mountains as well as western Hubei and eastern Sichuan provinces (Zheng 2005). In this study, we analyzed chemical composition of *Q. variablis* cork grown in the Qinling Mountains. The goal of our experiment was to learn more about chemical composition of virgin and reproduction cork from *Q. variablis* in northwest China. This information could constitute a basis for use and modification of this bark.

MATERIALS AND METHODS

Materials

Cork samples were collected from *Q. variablis* trees in Ningshan County, Shaanxi Province. The geographic location of the region is

Table 1. Summary of literature reports about chemical composition of virgin and reproduction cork from *Quercus suber* L.

	Virgin cork (% oven-dry mass)		Reproduction cork (% oven-dry mass)				
Chemical component	Caldas (1986)	Pereira (1988)	Gil (2000)	Caldas (1986)	Pereira (1988)	Parameswaran et al (1981)	Holloway (1972)
Suberin	45	45	42	48	33.5	33	37
Lignin	27	21	21.5	29	26	13	14.8
Polysaccharides	12	13	16	12	25	6	
Extractives	10	19	13	8.5	13	24	15.8
Ash	5	1.2		2.1	2.5		
Other		0.8	7			6	

Table 2. Average tree and cork characteristics at sample site.

Sample	Diameter at breast height (mm)	Tree age (yr)	Cork thickness (mm)
Virgin cork	270	60	28
Reproduction cork	310	60	30

32°41″34°22′ N, 107°99″109°01′ E. Tree and cork characteristics (diameter at breast height, tree age, and cork thickness) are shown in Table 2. Cork samples were ground in a high-speed mill (Xinsheng, China), and the 40-60 mesh fraction was used for analysis.

Dichloromethane, anhydrous alcohol, sodium methylate, sodium sulphate, methanol, chloroform, 95% sulfuric acid, and sodium hydroxide were purchased from the North Tianyi Chemical Reagent Factory (Tianjin, China). The chemicals were all analytical reagent grade. Standards for galactose, rhamnose, glucose, fructose, xylose, mannose, and arabinose were purchased from the Kejie Analysis Instrument Co. (Nanjing, China).

Chemical Analyses of Cork

The extraction process is shown in Fig 1. Cork extractives can be divided into two main types: polar compounds (eg phenols and triterpenes) and nonpolar compounds (eg monosaccharides). These compounds were isolated using successive Soxhlet extractions with solvents of increasing polarity (ie dichloromethane, ethanol, and water).

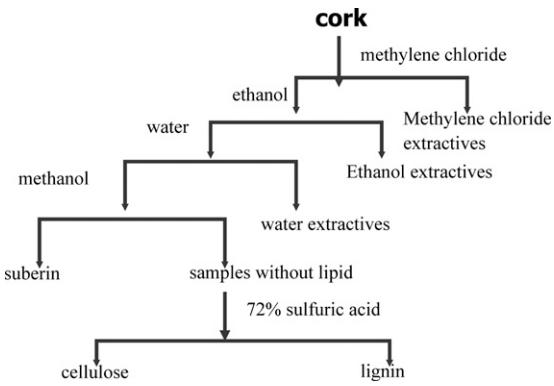

Figure 1. The extraction process.

Soxhlet extractions were performed using 3-g samples of virgin or reproduction cork. Samples were placed in a filter paper thimble inside a Soxhlet extraction column and packed with cotton. Methylene chloride (150 mL) was added to the 250-mL round-bottomed flask at the base of the Soxhlet assembly and heated in a 65°C water bath. Samples were refluxed until a clear solution was obtained in the upper part of the Soxhlet column. Extraction time was generally 7-8 h. Methylene chloride was evaporated from the flasks, and then samples were dried in a 100°C oven for 3 h. The flasks were weighed until reaching a constant weight (±0.001 g) and then washed, dried, and weighed again. Mass of the methylene chloride extractives was determined by subtraction.

Following methylene chloride extraction, samples were extracted with 150 mL ethanol. Temperature of the water bath was raised to 85°C. Samples were refluxed for 8-10 h. Mass of the ethanol extractives was determined by subtraction as described previously.

The Soxhlet devices were removed, and the filter paper thimbles were put directly into the bottom of the flasks and refluxed in 150 mL distilled water for 24 h at 100°C. Mass of the water extractives was determined by subtraction. Cork residue in the thimbles was air-dried and kept for subsequent analysis (Pereira 1988).

Suberin content was determined in extractive-free material using methanolytic depolymerization. Samples were refluxed in 150 mL methanol for 4 h, and then the residue was acidified with H_2SO_4 to pH 6 and evaporated to dryness on a rotary evaporator. Residue was suspended in water and extracted with 200 mL chloroform three times. The extractive (suberin) was dried over anhydrous Na_2SO_4, filtered, evaporated, and weighed.

Lignin content was determined on previously extracted and desuberinized cork residue after hydrolysis with 72% H_2SO_4 (Pereira 1988). Samples were dried and transferred to 250-mL Erlenmeyer flasks and refluxed in 45 mL 72% sulfuric acid for 2.5 h. Samples were filtered and dried to constant weight.

Polysaccharide Analysis

Polysaccharide analysis was conducted using high-performance liquid chromatography (HPLC). Suberin and lignin were removed from the cork samples, and then monosaccharides were separated by reverse-phase HPLC on a Carbopac PA10 column at 30°C using 52 mol·L^{-1} sodium hydroxide (NaOH) as the mobile phase and 0.7 mL·min^{-1} as the flow rate. Standard solutions (1.0 mg·mL^{-1}) were prepared by dissolving 10 mg of arabinose, galactose, glucose, xylose, mannose, rhamnose, or fructose in distilled water. Monosaccharide content was calculated as a proportion of the total polysaccharides content of the cork.

RESULTS AND DISCUSSION

Extractives, Suberin, and Lignin Contents

Extractives, suberin, and lignin contents of virgin *Q. variablis* cork were different from those of reproduction cork (Table 3). Total extractives content of virgin cork was 1.37 times that of reproduction cork. Dichloromethane extractives content was similar in virgin and reproduction cork, accounting for approximately 30% of total extractives content and 5% of total cork dry weight. Dichloromethane extractives content of virgin cork was 1.06 times that of reproduction cork. Ethanol soluble extractives accounted for about 16-32% of total extractives content of reproduction cork. Ethanol soluble extractives content of virgin cork was 0.7 times that of reproduction cork. Water extractives accounted for 29-53% of total extractives dry weight. Water extractives content of virgin cork was 2.49 times greater than that of reproduction cork, indicating a very high content of polar compounds in virgin cork. Waxes are the main nonpolar substances in cork. Waxes have waterproof properties that prevent moisture from adhering to cell walls, thus improving water resistance of cork products. The main polar compounds in cork are phenolic and triterpenic acids. These compounds increase resistance of cork to insects and diseases and prevent bacterial attack. These properties prolong the useful life of cork products and enhance their environmental characteristics (Liu 2008).

Suberin comprised 34.3% of virgin *Q. variablis* cork dry weight and 36.9% of reproduction cork dry weight (Table 3). Suberin is a macromolecule composed of long chain fatty acids, hydroxy fatty acids, and phenolic acids linked by ester groups. The unique properties of suberin make cork resistant to acids and alkali, corrosion, and aging. Suberin and wax lamella interlace to form the thick secondary cell wall of cork, enhancing the waterproof properties of cork cell walls. These properties make cork impenetrable to liquid and resistant to penetration by bacteria and chemicals.

Lignin comprised 20.6% of virgin *Q. variablis* cork dry weight and 19.9% of reproduction cork dry weight. In comparison, lignin content of most woody plants ranges between 20 and 35% (Liu and Zhao 2004). Lignin consists of polymeric aromatic molecules that form interlaced nets in the primary cell wall. Lignin hardens the cell walls, increasing stress resistance, mechanical strength, and durability of cork.

Virgin cork from *Q. variablis* contained less suberin and lignin than virgin cork from *Q. suber*. Specifically, virgin *Q. variablis* cork contained 34.3% suberin and 20.6% lignin (Table 3). In comparison, *Q. suber* cork contained 45% suberin and 21-27% lignin (Table 1). For reproduction cork, suberin and lignin contents of

Table 3. Chemical composition of virgin and reproduction cork from *Q. variablis*.

	Percent oven-dry mass					
Sample	Total extractives	Dichloromethane extractives	Ethanol extractives	Water extractives	Suberin	Lignin
Virgin cork	17.4	5.3	2.8	9.2	34.3	20.6
Reproduction cork	12.7	5.0	4.0	3.7	36.9	19.9

Table 4. Polysaccharides content and composition of *Q. variablis* cork.

Sample	Total Polysaccharides (% oven-dry mass)	Percent of total polysaccharides			
		Glucose	Xylose	Arabinose	Galactose
Virgin cork	15.2	38.35	49.80	7.69	4.14
Reproduction cork	12.0	38.58	36.92	15.08	9.41

Q. variablis were similar to those of *Q. suber*, however extractives content of *Q. suber* was greater than that of *Q. variablis*.

Polysaccharide Content and Composition

In addition to suberin and lignin, polysaccharides also exert an important influence on the chemical and physical properties of cork. Polysaccharide content and composition of virgin and reproduction cork are shown in Table 4. Glucose and xylose accounted for 65-90% of total polysaccharide content in virgin and reproduction cork. Glucose and xylose contents in virgin cork were greater than those in reproduction cork. Virgin cork had more total polysaccharides than reproduction cork (15.2 and 12.0%, respectively).

Compared with other woody materials, glucose content of cork was relatively low. Cellulose is chiefly composed of glucose, therefore it can be reasoned that cellulose content of cork is also relatively low. Cellulose is the main component of cell walls in woody plants, accounting for 40-50% of wood dry weight (Liu and Zhao 2004), but our results showed that cellulose is not the main constituent of cork cell walls. Hemicellulose and xylans in particular probably play the role of cellulose in cork.

In this study, total polysaccharide content of cork from Chinese *Q. variabilis* was 15.2%. In comparison, total polysaccharide content of European cork was 21.3% (Pereira 1988). Cork from both Chinese *Q. variablis* and European *Q. suber L.* had high glucose and xylose content but low arabinose and galactose content. Hemicellulose is primarily composed of xylan. Glucose and xylose accounted for more than 50% of total polysaccharide content of cork in this study. Mannose and rhamnose were not detected in *Q. variabilis* cork. However, *Q. suber* cork contained 1.1% mannose and 0.1% rhamnose (Pereira 1988).

CONCLUSIONS

Cork from *Q. variablis* had high extractive content, which is an important feature. Extractive content of virgin cork was 1.37 times that of reproduction cork. Dichloromethane extractive content of virgin cork was 1.06 times that of reproduction cork. In contrast, ethanol extractive content of virgin cork was 0.7 times that of reproduction cork. Water extractive content of virgin cork was 2.48 times that of reproduction cork.

Suberin is the main component of *Q. variablis* cork. Suberin content of virgin cork was 0.93 times that of reproduction cork. High suberin content is one of the main reasons for cork's unique properties.

Lignin content of virgin *Q. variablis* cork was 1.04 times that of reproduction cork. Lignin was the second largest component of cork.

Polysaccharide content of *Q. variablis* virgin cork was 15.2 vs 12.0% for reproduction cork. In virgin cork, polysaccharide composition was 38.35% glucose, 49.80% xylose, 7.69% arabinose, and 4.14% galactose. In reproduction cork, polysaccharide composition was 38.58% glucose, 36.92% xylose, 15.08% arabinose, and 9.41% galactose. Glucose and xylose were the major monosaccharides in virgin and reproduction *Q. variablis* cork.

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