

**MORPHOLOGICAL AND CHEMICAL CHARACTERISTICS
OF STEM AND KNOT POPLAR WOOD**

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BRATISLAVA, SLOVAK REPUBLIC**ABSTRACT**

Scanning electron microscopy showed differences in the ultrastructure of stem- and knotwoods. In contrast to stem, knotwood has more compact deformed structure. Its more dark colour is caused by relatively high lignin content as results from the chemical analysis. The lignin extractability of both wood samples was examined by acidolysis in dioxane – water. The chemical character of knots is different from normal stemwood. The characteristics of knotwood lignins, comprising elemental analysis, average molecular weight, polydispersity factor, degree of branching and cross linking density were determined. The results obtained confirm of knotwood lignin exhibits rather higher molecular weight related to stem. The observed lower accesibility of lignin component could explain a negative impact of knots on pulping process.

KEY WORDS: *Populus nigra* L., knotwood, stemwood, scanning electron microscopy, lignin

INTRODUCTION

Trees are very special plants, in particular because they live so very long. Therefore trees have through evolution developed very efficient chemical defence systems, and trees are a rich source of various natural bioactive compounds. The chemical analysis of different parts of a tree such as knots, stumps, roots or branches is becoming an important field of investigation with regard to full-tree, whole-tree and biomass utilization (Fengel and Wegener 1984). Wood knots, i.e. the part of the branches that are embedded in the stem, have been a dismissed and forgotten part of trees. It is known that knotwood contains large amounts of extractives (Willfor et al. 2002). Knots decrease the quality of thermomechanical pulp (Sahlberg 1995) and produce excessive screen rejects in kraft pulping (Allison and Graham 1988). Knots distribution by size and by location along the stem and the knot size variation along the stem were described by Lipinsh and Sarmulis (1998). Recently, it was discovered that wood knots in trees (i.e., the branch based in side stems) containing high concentrations of polyphenols, which are potent natural antioxidants and biocides (Holmbom 2008). The objective of the present study was to determine ultrastructure of knotwood from black poplar (*Populus nigra* L.) as well as chemical and molecular properties of lignin component related to that of stemwood.

EXPERIMENTAL

As starting material sawdust of black poplar (*Populus nigra* L.) from stem and knot were analyzed. Klason lignin was determined according to TAPPI, Standard T 22. The dioxane lignins were isolated from sawdust pre-extracted with benzene-alcohol by 8 h acidolysis 90°C in dioxane-water 9:1 containing 0.1 M HCl. The isolated lignins were analysed by gel permeation chromatography on a column (53 x 0.8 cm) on Sephadex LH 60 using a mixture of dioxane and water containing 0.005 M aqueous NaOH and 0.01 M LiCl (7:3) as the eluant. The column was calibrated using a series of lignin fractions of molecular weights of which have been determined by ultracentrifugation. The average molecular weights (M_w) of the samples were calculated from molecular weight distribution (Faix et al. 1981). Viscosimetric measurement of dioxane lignin were performed on a viscomatics MS FICA viscosimeter in θ solvent (dioxane-ethanol 10:24.5). Degree of branching ρ and cross-linking density ρ_c were calculated according to Pla and Robert (1984). The scanning electron microscopy JSM-U3 was used for the observation of cross sections of wood coated with gold.

RESULTS AND DISCUSSION

Scanning electron microscopy (SEM) was applied to determine of the ultrastructure of stem- and knotwood. In contrast to structure of stemwood (Fig. 1), the micrograph of the transversal section of knotwood (Fig. 2) indicates, that the knotwood has deformed compact less accessible structure. Its dark colour indicates relative high lignin content in the comparison with stemwood. This observation is in accordance with the chemical analysis of knot- and stemwood (26.4 % and 24.4 %, respectively). A comparison of the corresponding values for stemwood and knotwood indicates that latter contains more lignin.

In addition, both wood samples were investigated from the viewpoint of their extractability by acidolysis in dioxane-water (9:1). The data in Tab. 1 show that the yield of dioxane lignin from knotwood was substantially lower compared to that of stemwood. The observed lower methoxyl content of lignin in knotwood could be explain by the presence of lignan-like polymeric phenolic compounds which were recently detected in the spruce knots, while stemwood contained any detectable amounts of lignans (Willfor et al. 2002).

To determine the differences in the macromolecular properties of knots and stem, the dioxane lignins were isolated from both samples by dioxanolysis and characterized by GPC analysis. The data summarized in Tab. 1 revealed that lignin present in the knots is less accessible for extraction compared to stemwood lignin. Moreover, the molecular characteristics as average molecular weight, polydispersity factor, degree of branching ρ and cross linking density ρ_c were determined for both lignin samples (Tab. 2). The obtained values indicate that lignin isolated from knot exhibits higher molecular weight in comparison with that isolated from stemwood. This observation could explain a negative impact of knots on pulping and pulp quality. The development of economic pre-extraction of trees before pulping in order to remove polyphenols – sources for production of natural bioactive compounds present in knotwood would be useful for chemical treatment of whole-trees and biomass utilization.

Tab. 1: Characterization of dioxane lignins isolated from stem- and knot poplar woods

Sample	Yield % of wood	Elemental composition %			OCH ₃ %
		C	H	O	
Stemwood	25.10	61.37	5.58	33.05	18.20
Knotwood	17.50	60.03	5.99	33.98	14.60

Tab. 2: Selected molecular characteristics of dioxane lignins isolated from black poplar

Sample	Mw	Mn	MwC9	D	MWD (%)			η ml/g	ρ	ρ'
					<10 ³	10 ³ -10 ⁴	>10 ⁴			
Stemwood	6111	2152	199.0	2.8	10.5	83.6	5.9	44.71	0.0033	0.0227
Knotwood	10201	3066	198.8	3.3	4.6	86.4	9.0	6.59	0.3469	0.0197

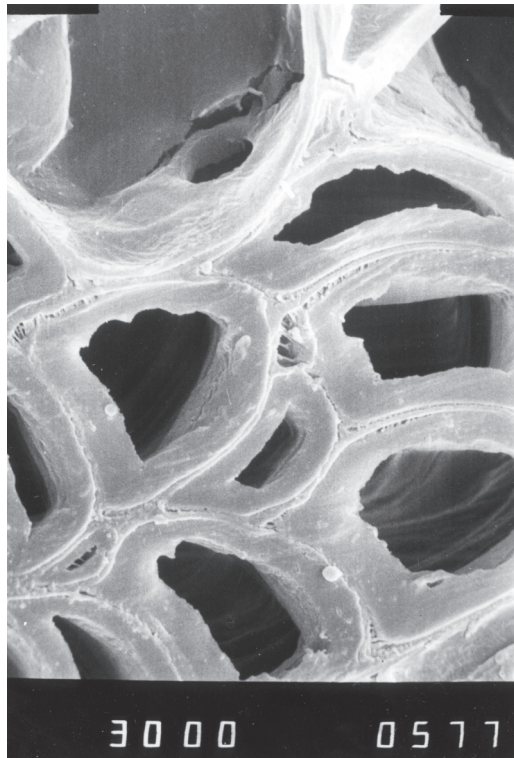


Fig. 1: Scanning electron micrograph of transversal section of stem poplar wood. Magnification 3000 x.

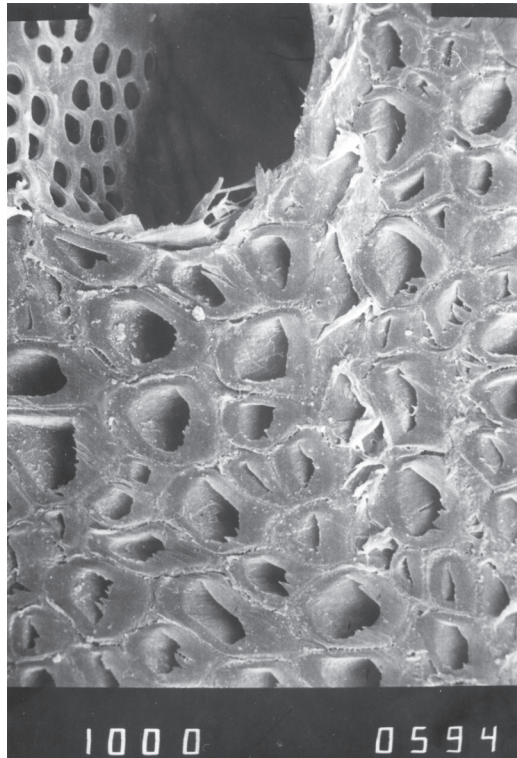


Fig. 2: Scanning electron micrograph of transversal section of knot poplar wood. Magnification 1000 x.

CONCLUSION

The determined ultrastructure of knotwood correlated with its chemical composition as well as with the yield and chemical analysis of dioxane lignins isolated from knots. The obtained results concerning to extractability of lignin from knotwood and its molecular properties are a contribution to explanation of a negative impact of knots in tree on pulping. Moreover, the chemical analysis of different parts of a tree such as knots, stumps, roots or branches is becoming important field of investigation with regard to full-tree, whole-tree and biomass utilization.

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