

CHEMICAL CONSTITUENTS OF FIVE NORTHEASTERN BARKS¹

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ABSTRACT

A study was undertaken to characterize the major chemical constituents of five barks common to northeastern United States. The species examined were white pine (*Pinus strobus*), red pine (*P. resinosa*), shagbark hickory (*Carya ovata*), red oak (*Quercus rubra*), and red maple (*Acer rubrum*). Chemical analysis results showed that both within species and among species variation in ash, ethanol-benzene extractives, and suberin content occurred among the species examined. Significantly higher alcohol-benzene extractive and suberin contents were measured in shagbark hickory bark compared to the other barks examined in this study.

Both within species and among species differences in holocellulose content were measured. In general, a higher holocellulose yield was obtained from hardwood bark compared to softwood bark, with the exception of red maple bark. With but one exception, no within species differences in Klason lignin content and aromatic content were detected. However, statistical differences were measured among the species examined. In general, the softwood species contained a higher aromatic content and Klason lignin content than did the hardwood barks examined in this study.

Keywords: Barks, chemical constituents, white pine (*Pinus strobus*), red pine (*Pinus resinosa*), shagbark hickory (*Carya ovata*), red oak (*Quercus rubra*), red maple (*Acer rubrum*).

INTRODUCTION

The chemical characterization of bark has received little attention by investigators and, compared to wood, less information is available on the chemical constituents in bark (Jensen et al. 1955). To date, most of the published information deals with bark extractives obtained from western and southern pine species (Browning and Sell 1957; Erman and Lyness 1965; Hergert 1960; Hergert and Kurth 1952). These studies were conducted to evaluate the potential use of bark as a source of silvichemicals. Most other bark studies were designed to isolate and characterize individual chemical components found in bark (Hemingway 1976; Hergert 1960; Howard 1974; McGinnes and Parikh 1975; Pearl 1975a, b). Considering that information dealing with the overall chemistry of barks is scant, a study was undertaken to characterize the major chemical constituents obtainable from barks from five northeastern tree species.

EXPERIMENTAL

Bark collection and preparation

Bark from five northeastern tree species were selected for study; two softwoods and three hardwoods (Table 1).

The barks selected for study were obtained from trees located in The Pennsyl-

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TABLE 1. *Barks selected for study.*

Common name	Genus and species
Red pine	<i>Pinus resinosa</i>
White pine	<i>Pinus strobus</i>
Shagbark hickory	<i>Carya ovata</i> (Mill.) K. Koch
Red oak	<i>Quercus rubra</i> L.
Red maple	<i>Acer rubrum</i>

vania State University Experimental Station forestlands near University Park. Bark samples were collected from three randomly selected trees of each species. Sample trees ranged from 30 to 70 years in age, and a total of 15 bark samples were collected during the fall of 1981. In selecting trees for this study, considerable care was taken in choosing trees without visible indication of mechanical injuries or diseases. Outer bark (rhytidome) was obtained by scraping with a drawknife around and down the tree bole from a height of 6 ft to the base of the tree. Extreme care was taken to exclude tree cambium from the bark samples. The stripped bark was collected on a plastic tarp and transferred to paper bags; it was air-dried in the bags for about 2 weeks prior to milling. The air-dried bark samples were Wiley-milled to pass through a 40-mesh screen and stored in sealed mason jars for chemical testing.

Chemical analysis

Each tree bark sample was chemically analyzed in triplicate for ethanol-benzene extractives content, ash, holocellulose, aromatic content, Klason lignin, and suberin content. This resulted in a total of nine replications for each chemical test and for each species of bark examined. The scheme used for the determination of chemical constituent in bark is shown in Fig. 1.

Ash and ethanol-benzene (1:2 by volume) extractive content was determined using methods as described by Moore and Johnson (1967). Ethanol-benzene extractive yields were determined, and the bark residue was dried and used to determine holocellulose, aromatic content, Klason lignin, and suberin content of the extractive-free barks.

Since suberin interferes with the Klason lignin determination, ethanol-benzene extracted bark was treated with 40 ml of 1% KOH in anhydrous EtOH (ethanol) for about 1 h at 70 C to remove the waxlike material. The mixture was filtered on VWR 9-cm filter paper and washed with distilled water; the residue was oven-dried to a constant weight and weighed. The weight difference between ethanol-benzene extractive-free bark and the final bark residue weight was reported as the suberin content in bark.

Holocellulose content was determined by Wilson's procedure (1961) with modifications as described by Labosky (1979). To determine the residual lignin content remaining in the acid-chlorite holocellulose, 0.5 g of acid chlorite holocellulose extract was treated using a standard Klason lignin procedure.

The aromatic content in bark was determined using methods described by Brauns and Brauns (1960) with slight modifications. Oven-dried ethanol-benzene extracted bark was treated with 1% KOH in anhydrous EtOH at 73 C for 1 h in a water bath. The residue obtained was filtered, washed with distilled water, and

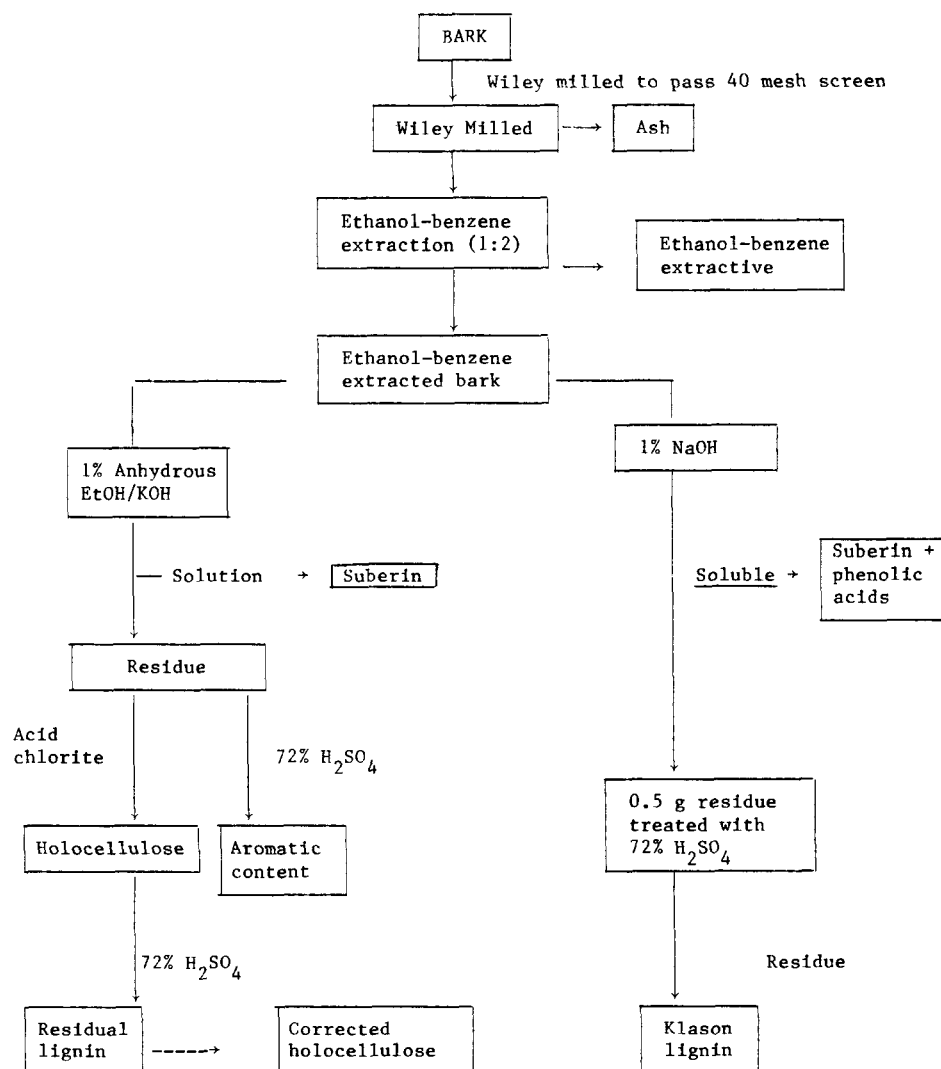


FIG. 1. Scheme used for the determination of chemical constituents in bark.

subsequently treated with 72% H_2SO_4 . The oven-dried product obtained after filtering was reported to consist of a mixture of phenolic acids and bark lignin (Brauns and Brauns 1960) and was therefore reported as aromatic content in this study.

Klason lignin content was determined on ethanol-benzene extracted bark. The extractive-free bark was treated with 1% NaOH for a period of 1 h at 70 C, and the residue was filtered, washed and air-dried. One-half gram of (O.D.) residue was treated with 72% H_2SO_4 for Klason lignin determinations.

The data collected were analyzed using the least squares analysis of variance. Differences in means within and among species were determined using Duncan's multiple range test (Steel and Torrie 1960).

TABLE 2. Average within species chemical constituent yields¹ of individual barks from five tree species.

Chemical constituents	Red pine			White pine			Shagbark hickory			Red oak			Red maple		
	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
Ethanol/benzene	%														
extractives	6.2a ²	6.7a	4.9b	65.2	5.2a	5.3a	10.4a	11.6a	10.9a	6.5a	6.8a	5.9a	4.5b	6.9a	4.6b
Holocellulose	44.2a	42.7a	44.7a	39.0b	41.6a	40.3ab	45.6ab	47.7a	42.5b	45.7b	49.2a	46.4ab	43.3a	41.6a	41.7a
Suberin	6.7a	2.8b	7.1a	2.4a	5.0a	3.0a	7.8a	8.1a	6.0a	5.1a	3.2a	5.0a	5.5a	2.6ab	1.1b
Klason lignin	44.4a	41.4a	40.7a	48.2a	51.2a	50.5a	38.2a	38.3a	37.4a	36.4a	37.7a	40.1a	36.6a	38.4a	37.2a
Aromatic content	51.8a	49.1a	43.0a	53.3a	57.5a	51.0a	41.1a	43.9a	41.5a	45.4a	38.7b	44.2a	49.3a	54.4a	53.5a
Ash	2.2a	1.2b	2.2a	0.8a	0.8a	1.3a	9.2	7.8b	6.3c	5.4a	9.5a	9.7a	9.9a	5.8b	6.9b
Residual lignin in holocellulose	0.6	0.7	0.2	3.1	0.7	0.6	2.0	1.0	1.0	4.1	2.3	4.1	4.7	4.9	5.9
Corrected holocellulose	43.6a	42.0a	44.5a	35.9b	40.9a	39.7a	43.6ab	46.7a	41.5b	41.6b	46.9a	42.3b	38.6a	36.7a	35.8a
Total ³	104.3	95.1	96.8	92.4	104.2	95.0	101.7	106.5	95.3	97.8	95.4	101.2	103.3	97.5	97.3

¹ Yields based on the dry weight of ethanol-benzene extracted bark.² Means within a row within a species followed by the same letter among composites for a species are not significantly different at the 0.05 level.³ A satisfactory chemical analysis should account for 100%. Variations from 100% caused by constituents losses and contaminations.

TABLE 3. Average chemical constituent yields of bark from five tree species.¹

Chemical constituents	Species				
	Red pine	White pine	Shagbark hickory	Red oak	Red maple
	%				
Ethanol/benzene extractives	5.8b	5.7b	11.0a	6.4b	5.3b
Holocellulose	43.9ab ²	40.3c	45.3a	47.1a	42.2ab
Suberin	5.5ab	3.5c	7.3a	4.6bc	3.1c
Aromatic content ³	48.0b	53.9a	42.1c	41.8c	52.4ab
Klason lignin ⁴	42.2b	50.0a	38.0ac	38.1c	37.4c
Ash	1.9b	1.0b	7.8a	8.2a	7.5a
Residual lignin in holocellulose	0.5	1.4	1.3	3.5	5.2
Corrected holocellulose	43.4	38.9	44.0	43.6	37.0
Total ⁵	98.9	97.3	101.2	98.2	100.0

¹ Yields based on the oven dry weight of ethanol-benzene extracted bark.

² Grand means within a row followed by the same letter are not significantly different at 0.05 level.

³ Ethanol-benzene extracted bark treated with 1% KOH/EtOH followed by treatment with 72% H₂SO₄.

⁴ Ethanol-benzene extracted bark treated with 1% NaOH followed by treatment with 72% H₂SO₄.

⁵ A satisfactory chemical analysis should account for 100% of the constituents. Sum total of average constituent yields, aromatic content, ash, holocellulose, suberin, and residual lignin are taken into account. Realizing that contamination loss of constituent will occur, the results obtained exhibit a close approximation of the bark constituents for the five selected bark species.

RESULTS AND DISCUSSION

Extractives

Significant differences ($P \leq 0.05$) in ethanol-benzene extractive content were measured within and among bark species examined (Table 2). Within species differences in ethanol-benzene bark extractive yields were observed for red pine and red maple; however, no within species differences were observed for white pine, shagbark hickory, and red oak barks. Among species comparisons in extractives content showed that shagbark hickory contained significantly higher ethanol-benzene extractive yields than did the other barks examined in this study. Species average alcohol-benzene extractive yields ranged from about 5.0 to 11.0% for all barks examined.

Alcohol-benzene extractive yield results observed in this study are comparable with yields reported in the literature. Steller (1982) reported ethanol-benzene extractive yields of 13.9% for shagbark hickory bark and 5.2% for white pine bark. An ethanol benzene extractive yield of 13.1% was reported for red maple bark and this value is considerably higher than that observed in this study (Murphey et al. 1970). Murphey et al. (1970) and Hergert and Kurth (1952) reported differences in extractives content in their studies with that reported in the literature and they attributed these differences to the age and geographic location of the sample trees.

Suberin.— Yields of dissolved saponified materials observed in this study varied widely both within and among species (Table 2). Within species variations were again measured for red pine and red maple; however, no within species differences were measured in white pine, shagbark hickory, and red oak. Suberin yields ranged from a low of 3.1% to a high of 7.3% (Table 3). Shagbark hickory bark was found to contain a significantly higher suberin content compared to the other barks examined.

Ash.—Ash content values ranged from a high of 8.2% for red oak to a low of 1.0% for white pine bark (Table 3). Statistical differences in ash contents were observed within the red pine, shagbark hickory, and red maple barks and between softwood and hardwood barks (Table 3).

Holocellulose.—Significant differences ($P \leq 0.05$) in holocellulose content were measured within and among species examined (Tables 2 and 3). The highest average holocellulose yield (corrected value) was measured for shagbark hickory (44.0), whereas red maple (37.0) exhibited the lowest among the five bark species examined (Table 3). With the exception of red maple, in general, holocellulose yields were lower for the softwood species compared to the hardwood species examined. Within species variations in bark holocellulose were observed for white pine, shagbark hickory, and red oak (Table 2).

One of the difficulties experienced in the isolation of bark holocellulose was that suberin appeared to remain in the bark even after treatment with 1% anhydrous EtOH/KOH. Although six acid-chlorite delignification treatments were used to obtain a relatively pure holocellulose, both red oak and red maple holocellulose still exhibited some traces of brown residues, which could be an indication of incomplete delignification reaction. Residual lignin analysis performed on the holocellulose samples tended to support this observation (Table 2). Nevertheless, holocellulose results obtained in this study support earlier observations of bark holocellulose contents ranging between 35 to 45% (Jensen et al. 1955; Labosky 1979, McGinnes and Parikh 1975).

Klason lignin and aromatic content

No within species differences in Klason lignin content were measured; however, among species differences were observed (Tables 2 and 3). Both white pine bark (50.0%) and red pine bark (42.2%) exhibited a higher Klason lignin content than did the three hardwood barks, shagbark hickory (38.0%), red oak (38.1%), and red maple (37.4%) (Table 3). With the exception of red maple bark, similar trends were observed in aromatic content yields. Results obtained from this study indicate that the aromatic content appeared to be highest in white pine bark (53.9%) while red oak contained the lowest amount (41.8%) as shown in Table 3.

Bark lignin is basically similar to wood lignin (Hemingway 1976). However, the presence of phenolic acids (tannins and polyflavonoids) and suberin complicates the isolation of bark lignin such that it contaminates the preparations and results in a higher lignin content (Jensen et al. 1955). Earlier studies (Jensen et al. 1955; Labosky 1979) reported a range of 40 to 55% for conifer bark lignin and 40 to 50% for hardwood lignin. Average Klason lignin determinations in this study ranged from 42 to 50% for coniferous bark and 37 to 38% for deciduous bark.

Total chemical constituent yields were obtained by summing all fractions (Table 3). These fractions include corrected holocellulose (holocellulose minus holocellulose residual lignin), suberin, aromatic content, and ash. A satisfactory chemical analysis should account for 100% of the constituents. In spite of possible contaminations and loss of constituents, these results gave a close approximation of the total bark constituents for the five bark species examined.

CONCLUSIONS

On the basis of observations made in this study, the following conclusions can be drawn:

1. Ash content for hardwood and softwood barks ranged from about 1 to 10% with a higher ash content measured for hardwood barks compared to softwood barks.
2. Significant differences in ethanol-benzene extractives content and suberin content were measured within and among species examined. Shagbark hickory bark contained significantly higher ethanol-benzene and suberin yields than did the other barks.
3. Bark holocellulose content for softwoods ranged from about 36 to 44%, whereas hardwood holocellulose content ranged from about 36 to 47% (Table 2).
4. Hardwood bark Klason lignin content ranged from about 36 to 38%, whereas softwood bark Klason lignin ranged from about 42 to 50%.
5. In general, a higher aromatic content was measured for softwood barks (48 to 54%) compared to hardwood barks (41 to 52%) (Table 2).

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