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FATTY AND WAXY COMPONENTS OF SOUTHERN PINE BARK— AMOUNTS PRESENT AS FREE EXTRACTIVES

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SOUTHERN FOREST EXPERIMENT STATION

Whole bark from six mature trees of each of the four major southern pines was extracted with petroleum ether and with toluene. Trees were 20 to 58 years old and 8.0 to 11.8 inches in d.b.h. Percentages of petroleum ether-solubles were: slash pine, 1.94; loblolly, 2.29; longleaf, 2.64; and shortleaf 3.05. Percentages obtained by toluene extraction were: loblolly, 3.04; slash, 3.18; longleaf, 3.38; shortleaf, 3.77. Extractives were light to medium yellow, resinous in odor, and slightly tacky. Several procedures for removing these components from aqueous and ethanolic alkali extracts were tried, including organic solvent extraction of basic and acidified extracts, and acidification and filtration followed by solvent extraction. None of the methods increased the yield of lipids, and products were generally softer and stickier than those obtained by direct extraction.

ADDITIONAL KEYWORDS: Bark utilization, chemical composition, extractives, fatty acids, neutrals, *Pinus echinata*, *P. elliotii* var. *elliottii*, *P. palustris*, *P. taeda*.

Although much work has been done on oleoresin and tall oil constituents in wood, and a considerable amount of organic-solvent solubles from barks of other species, information specific to southern pine bark is meager. Knowledge of such components is essential not only to possible commercial applications of these substances, but also because their presence will affect various possible uses of whole or fractionated bark in pulping systems, board products, pyrolysis, extracts, or other products. Because some of these compounds may also be obtained by alkaline processes, inclusion of barked chips in pulping will probably modify the composition of tall oil if bark differs considerably from wood in this respect.

Most investigations on organic-solvent extracts have dealt with the bark of Douglas-fir and western pines. For bark of other pines, various researchers list extractable lipid contents ranging generally from 3 to 8 percent. Several authors have reported alcohol-benzene extractive contents of southern pine bark, but because ethyl alcohol is polar these extracts also contain substances other than those of interest in the present study. Data from southern pine bark extractions with solvents that

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are nonpolar or of low polarity are very limited. Hall and Grisvold (1935) and Hall (1936) reported that 5.5 percent of the phloem from slash pine saplings was extractable in petroleum ether, and they identified some of the components. Martin and Brown (1952) obtained 4.6 percent ether solubles and 7.2 percent alcohol-benzene solubles from shortleaf pine bark. Rowe (1965) found that the benzene extract of loblolly pine was 4.6 percent of **ovendry** bark, and he examined the sterols.

The present study determined the amounts of fatty and waxy material available as free extractives when southern pine bark is extracted with nonpolar solvents. Petroleum ether and toluene were the solvents chosen. Because of health hazards associated with continued exposure, benzene was not used; toluene gives similar results and is less toxic.

METHODS

Six trees each of loblolly (*Pinus taeda* L.) , longleaf (*P. palustris* Mill.), shortleaf (*P. echinata* Mill.), and slash pine (*P. elliottii* Engelm. var. *elliottii*) were selected from sites scattered through central Louisiana. The trees ranged from 20 to 58 years old and 8.0 to 11.8 inches d.b.h. Diseased, injured, or severely suppressed trees were avoided. In mid-October, trees were felled and hand-peeled up to a 4-inch top (o.b.) . Inner bark was included. The material was segregated according to position on the stem (lower, middle, or upper third), sealed immediately in vapor-proof bags, and placed in a freezer.

To subdivide the bark into a smaller sample representative of each tree, bags were weighed and a proportionate weight was taken from each bag to yield approximately 25 pounds per tree. While still frozen, samples were run through a garden **mulcher**, then returned to the freezer. Before final grinding to pass a 1-mm screen, the bark was freeze-dried for 2 to 3 days to avoid the oxidation and polymerization that oven- or air-drying would produce.

Soxhlet apparatus was used for extraction with toluene and with **30-60°** petroleum ether. The total number of extracts was 144: (4 species) (6 trees/species) (3 replications/tree)

(2 solvents). Solvent flasks containing the waxy material were vacuum-evaporated (**under 50°C**), flushed with nitrogen, and weighed. Yields are expressed as a percent of bark dry weight. In an attempt to determine the amount of extractives removed, the bark was weighed before and after extraction. This approach proved unsatisfactory, presumably because of difficulty in completely removing solvents from the bark residue.

RESULTS

Extractives from' both solvents were light to medium yellow; the petroleum ether-solubles were paler in color than toluene-solubles and contained a whitish waxy component that solidified earlier than the other compounds as the material cooled. A resinous odor and somewhat tacky texture were observed for all species, probably resulting from the presence of resin acids.

Tree averages for free extractives obtained by the two solvents are given in table 1. Individual trees within a species showed considerable variation. Because of its slightly greater polarity, toluene removed additional material not soluble in petroleum ether (33 percent more from loblolly; 28 percent more from longleaf; 24 percent more from shortleaf; and 64 percent more from slash pine). By two-way analysis of variance, the differences between solvents and between species were significant at the 0.05 level.

When toluene treatments were appraised by Duncan's multiple range test at the 0.05 level, extractive yield from shortleaf bark was greater than that from loblolly and slash pines, but not greater than that from longleaf. In the following summary, means underscored by the same line do not differ significantly:

Loblolly	Slash	Longleaf	Shortleaf
3.04	3.18	<u>3.38</u>	<u>3.77</u>

For petroleum-ether extracts, differences were:

Slash	Loblolly	Longleaf	Shortleaf
1.94	<u>2.29</u>	<u>2.64</u>	<u>3.05</u>

Table 1.-*Free extractives* (in *percent* of *ovendry* weight of *bark*) obtained by solvent extraction of *whole bark from southern pines 8 to 12 inches in d.b.h.*

Tree	Slash		Loblolly		Longleaf		Shortleaf	
	Petroleum ether	Toluene	Petroleum ether	Toluene	Petroleum ether	Toluene	Petroleum ether	Toluene
1	1.92	3.21	3.06	3.68	2.63	3.81	3.04	3.10
2	2.00	3.33	1.95	2.96	2.04	2.64	3.43	3.49
3	1.79	3.06	2.35	3.27	2.46	3.54	3.24	4.27
4	1.77	2.79	1.92	3.15	3.49	3.65	3.20	4.61
5	2.12	3.29	1.67	2.44	3.21	4.00	2.84	3.58
6	2.06	3.41	2.80	2.77	2.04	2.65	2.56	3.38
Avg.	1.94	3.18	2.29	3.04	2.64	3.38	3.05	3.77

REMOVAL OF LIPIDS BY REACTION

In hopes of increasing the yield of fatty components, and because it was felt that some problems of caustic extracts for phenolic products might be caused by soap formation, several procedures for removing these components were tried.

Aqueous caustic extracts prepared by cooking bark with 16 percent **NaOH** (based on **ovendry** bark) at **90°C** were used, both in original basic form (**pH** greater than 10) and after acidification (to **pH** 4 or lower to precipitate acids and wax salts). Three recovery methods were tried:

Treatment of basic extract with organic solvents-hexanol, toluene, cyclohexane, chloroform.

Acidification, then extraction with chloroform and cyclohexane.

Acidification and filtration, followed by solvent extraction of both precipitate and filtrate.

Ethanolysis extracts were prepared by **re**-fluxing bark with 17 percent **NaOH** in absolute ethanol; a similar cook was made with **KOH** as the alkali. The liquor was drained into water (one-fifth of ethanol volume) and chilled. Lipid recovery methods were:

Filtered while basic, precipitate and filtrate acidified, then solvent extraction of filtrate.

Acidification, evaporation of ethanol, extraction with solvent.

Ethanol evaporated, acidification, solvent extraction.

Acidification, filtration, solvent extraction of filtrate.

Emulsions formed during extractions generally required centrifuging to separate the phases. None of the methods increased yields of lipids or gave more fatty or waxy material than could be obtained by direct extraction of untreated bark. Further, the products usually appeared inferior to those obtained by direct extraction. They were soft and sticky and included mixtures of free fatty acids, fatty acid salts, free fatty alcohols, various esters and waxes, and some phenolic compounds.

CONCLUSIONS

The materials studied constitute useful classes of compounds. At present, however, extraction of southern pine bark for the sole purpose of recovering the fatty and waxy products probably is economically unattractive because of the costs of solvents and material preparation and the low yields. On the other hand, extraction might well become feasible if other fractions of the bark were simultaneously processed for other products, if a particular component were found to have a high-value use (such as sterols for pharmaceuticals) or if difficulties with primary products would be alleviated by removal of lipids.

LITERATURE CITED

- Hall, J. A.
1936. The chemistry of some parts of slash pines. Naval Stores Rev. 46 (20) : **6, 8.**
- Hall, J. A., and O. Grisvold.
1935. Chemistry of slash pine (*Pinus caribaea* Mor.). I. Fatty constituents of the phloem. J. Biol. Chem. 109: **585-595.**
- Martin, J. S., and K. J. Brown.
1952. Effect of bark on yield and quality of sulphate pulp from southern pine. **TAPPI** 35: 7-10.
- Rowe, J. W.
1965. The sterols of pine bark. **Phytochemistry** 4: 1-10.