

Tall oil precursors of Douglas fir

ABSTRACT

The sapwood and heartwood extractives of Douglas fir [*Pseudotsuga menziesii* (Mirb.) Franco] and the tall oil in the kraft black liquor were characterized. On pulping, isomerization and conversion of conjugated resin acids to dehydroabietic acid was observed. Recovery of both fatty and resin acids from pulping was lower than predicted from the extractive composition. Unusually high sterol esters and a new triterpene alcohol are reported. The lightwood-inducing effect of paraquat is limited.

KEYWORDS

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Paraquat
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Fatty acids

Daniel O. Foster, Duane F. Zinkel, and Anthony H. Conner

Forest Products Laboratory, Forest Service, U.S. Department of Agriculture, P.O. Box 5130, Madison, Wis. 53705

Douglas fir [*Pseudotsuga menziesii* (Mirb.) Franco] is the major conifer species used by many kraft mills in the western United States and Canada. Thus, it is an important determinant of the quality of tall oil from those mills. There have been several studies of the extractives and pocket oleoresin from Douglas fir (1, 2) and two studies of tall oil recovery on the mill scale (3, 4). However, this is the first to compare the tall oil precursors in fresh wood, essentially the diethyl ether extractives, and the changes in composition resulting from pulping.

Results and discussion

Analyses of the diethyl ether extractives from sapwood and heartwood and of the respective tall oils are summarized in Table I. The extractives yield of the heartwood, on a mg/g oven-dried, extractives-free (o.d.e.f.) wood basis, was nearly three times that of the sapwood. However, the amount of tall oil precursors (i.e., fatty acids, resin acids, and norisaponifiable neutrals) found in the heartwood was only 80% that of sapwood. Most of the nonprecursor materials were not eluted from DEAE-Sephadex by acetic acid and are assumed to be predominantly complex phenolics.

Neutrals

Replicate data from saponification of the sapwood neutrals fraction by the American Oil Chemists Society (AOCS) method used in the analytical procedure (5) were inconsistent, suggesting incomplete hydrolysis of an unusual ester. The infrared spectrum of neutrals from saponification showed absorbance at 1180 and 1248 cm^{-1} (C—O stretch) and at 1742 cm^{-1} (C=O stretch) to support this conclusion. Complete saponification was accomplished

by refluxing in ethanolic KOH for 4 hr.

Chromatographic elution of the sapwood neutrals from silica gel with petroleum ether/benzene gave two major fractions. The fraction that eluted first (35% of the neutrals) was predominantly sterol esters that were difficult to saponify by the AOCS method. After saponification by the ethanol/KOH method, the sterols from this fraction consisted of 25% each of sitosterol and stigmasterol, 15% each of campesterol and an unidentified triterpene alcohol, 5% each of cycloartenol and 24-methylenecycloartenol, and 10% other unidentified compounds. The structure of the triterpene alcohol appears, by NMR, to be similar to that of cycloartenol. (The complete structural elucidation will be reported elsewhere.) The major components of the second peak from silica gel chromatography (58% of the total neutrals) were readily saponifiable triglycerides.

Approximately 60% of the neutral fraction from the heartwood extractives was not extractable from water by organic solvent after saponification. Babkin *et al.* (6) recently reported that simple phenolics are eluted from DEAE-Sephadex in the neutral fraction; that is a probable characterization of the major components of this nonextractable fraction. However, these compounds were not characterized in this work because they will not affect tall oil yield or composition.

It has been reported (1) that 3.6% of the Douglas fir pocket oleoresin from a commercial source was resin acid methyl esters. Inspection of the neutrals fraction of both sapwood and heartwood by NMR shows absorbance at 63.71, which is typical of the methyl hydrogens of resin acid methyl esters. Calculations based on the NMR integration suggest that these compounds occur in the wood at about the level reported in the

I. Extractives of Douglas fir wood and black liquor

| Extractive type | Extractives, mg/g of o.d. wood | | | |
|----------------------------------|--------------------------------|--------------|-------------------|--------------|
| | Sapwood | | Heartwood | |
| | Wood ^a | Black liquor | Wood ^a | Black liquor |
| Neutrals | 5.5 | 0.7 | 7.0 | 1.1 |
| Non-saponifiables | 1.7 | 0.7 | 1.6 | 1.1 |
| Saponifiables (fatty acid) | 3.5 | ... | 1.6 | ... |
| Not recovered ^b | 0.3 | ... | 3.8 | ... |
| Free acids | 2.1 | 2.6 | 2.8 | 2.2 |
| fatty acids | 0.1 | 1.4 | 0.1 | 0.7 |
| Resin acids | 2.0 | 1.2 | 2.7 | 1.4 |
| Strong acids | 0.1 | tr | 0.1 | 0.1 |
| Tall oil precursors ^c | 7.3 | 3.3 | 6.0 | 3.3 |

^aTotal diethyl ether extractives from sapwood was 7.7 mg/g, and from heartwood 21.2 mg/g (11.3 mg/g was not eluted from DEAE-Sephadex by acetic acid). ^bNot recovered from saponification. ^cTall oil precursors = non-saponified neutrals and saponified neutrals and free acids.

oleoresin. Gas chromatographic comparison of neutrals from the pocket oleoresin from our tree sample and another pocket oleoresin (Weyerhaeuser Co., Springfield, Ore.) with authentic standards confirms the occurrence of resin acid methyl esters at the reported level; the relative composition of these derivatives is not much different than that of the free acid pool.

Fatty acids

Fatty acid recovery from the pulping liquor is considerably less than expected from the amount found by extraction. This loss has been reported in southern pine (7) and is being studied. It is not related to the incomplete hydrolysis of sterol or triterpene esters discussed earlier because the same proportional loss was seen in both sapwood and heartwood (these esters were found only in the sapwood). Table II summarizes the composition of the fatty acid fractions isolated from the sapwood and heart-

wood and the corresponding black liquors.

The composition of the tall oil soaps will be predominantly determined by the composition of the esterified fatty acids since more than 95% of the fatty acids occur in the combined state. The major components of this fraction of the extractives were linoleic (18:2, 9c, 12c), oleic (18:1), isomeric linolenic (18.3, 5c, 9c, 12c), eicosatrienoic (20:3, 5c, 11c, 14c), eicosenoic (21:1, 11c), 14-methylpalmitic (17:0 antiiso), and palmitic (16:0) acids. The characterization of the combined acids is in general agreement with that of Rogers *et al.* (8). The proportion of linoleic and linolenic acids is noticeably decreased on pulping. Corresponding increases are seen in the compounds eluting from EGSS-X at 1.72, 2.01, and 2.16 relative to stearate. It is probable that these are isomers of linoleic and linolenic acid, but they were not identified.

Oleic and linoleic were found to be the major free fatty acids. Hancock and

Swan (9) reported the major constituents to be linoleic, stearic, and palmitic acids. However, their work involved extractives from veneer, and thus it was reasonable to expect differences in extractives caused by the veneer process and drying.

Rogers *et al.* (10) found (+)-todomatuic acid (and *cis*-dihydrotodomatuic acid at a 2:1 ratio) in some Douglas fir. In surveying the variability of juvenile hormones in Douglas fir extractives, they observed the "hormones were most commonly found in trees of the coastal and coastal intermediate subvariants" (11). It has been shown previously (12) that these compounds are recovered from DEAE-Sephadex in the weak acid fraction. Todomatuic acid was not found in the extractives (weak acid fraction) from the trees we studied.

Redemann (13) reported that 4-*p*-tolylvaleric acid is extracted from Douglas fir by any nonpolar solvent to yield greater than 0.3% on a whole wood basis. Only a trace amount of this compound was present in the wood samples we studied. While the level of 4-*p*-tolylvaleric acid is too low for precise quantitation, it appears the greater concentration is in the heartwood. The compound was at the same low level in the pocket oleoresin from our tree sample; however, in the pocket oleoresin from Oregon (described earlier) it was nearly 4.5% of the free acid fraction. This latter difference is perhaps another manifestation of the coastal-interior subvariance in Douglas fir since the original report of high concentration of 4-*p*-tolylvaleric acid is from a western laboratory and probably based on coastal trees.

II. Fatty acids of Douglas fir wood and black liquor (weight %)

| Fatty acid ^a methyl ester | <i>r</i> _{18:0} ^b | Sapwood | | | Heartwood | | |
|---|---------------------------------------|---------|------------|--------------|-----------|------------|--------------|
| | | Free | Esterified | Black liquor | Free | Esterified | Black liquor |
| 14:0 | 0.33 | 0.1 | tr | tr | tr | tr | tr |
| U | 0.40 | 1.1 | 0.1 | 0.1 | tr | 0.2 | 0.2 |
| 15:0 antiiso | 0.47 | 0.4 | 0.7 | 0.6 | tr | 0.4 | 0.9 |
| 15:0 | 0.50 | 0.7 | 0.2 | tr | 0.1 | 0.1 | ... |
| U | 0.55 | 0.1 | tr | 0.5 | tr | 0.1 | 0.5 |
| U | 0.58 | tr | 0.8 | 0.6 | 0.1 | 0.3 | 5.8 |
| 16:0 | 0.62 | 20.4 | 6.1 | 4.3 | 8.3 | 2.8 | 3.8 |
| 17:0 antiiso | 0.74 | ... | 7.4 | 6.4 | ... | ... | ... |
| 17:0 ^c | 0.79 | ... | ... | ... | ... | ... | ... |
| U | 0.89 | ... | 0.2 | ... | ... | ... | ... |
| 18:0 | 1.00 | 2.5 | 0.8 | 1.2 | 4.4 | 0.6 | 1.2 |
| 18:1 | 1.14 | 30.9 | 21.6 | 25.8 | 22.7 | 16.4 | 21.0 |
| 19:0 antiiso | 1.24 | 4.1 | 2.4 | 4.1 | 2.8 | 4.8 | 5.6 |
| 18:2 | 1.36 | 5.0 | 29.5 | 10.2 | 15.9 | 38.9 | 17.3 |
| 18:3 (5,9,12) | 1.51 | 6.7 | 10.4 | 1.7 | 2.6 | 10.8 | 3.7 |
| 20:1 (11) | 1.72 | 9.2 | 7.7 | 10.9 | 4.5 | 7.1 | 10.4 |
| U | 1.90 | 1.0 | 1.4 | ... | 9.2 | 1.4 | 9.7 |
| U | 2.01 | ... | ... | 19.2 | ... | 0.2 | ... |
| U | 2.16 | ... | ... | 8.9 | ... | ... | 0.4 |
| U | 2.24 | 0.6 | 0.6 | ... | ... | 0.6 | ... |
| 30:3 (5,11,14) | 2.49 | 11.6 | 9.2 | 4.8 | 14.7 | 10.2 | 6.5 |
| U | 2.83 | 5.6 | 0.7 | 0.7 | 14.6 | 4.6 | 13.1 |

^aU = unidentified ^b10% EGSS-X on 80/100 Chromasorb W-AW. ^c17:0 was shown to be only trace amount, was used as an internal standard for GLC.

III. Resin acids of Douglas fir wood and black liquor

| | Sap wood | | Heartwood | |
|--|------------------|--------------|------------------|--------------|
| | Wood extractives | Black liquor | Wood extractives | Black liquor |
| Sandaracopimarate | 3.2 | 8.7 | 3.6 | 4.3 |
| Palustrate | 23.5 | 13.3 | 22.8 | 1.3 |
| Levopimarate | 6.2 | 0.7 | 2.3 | <0.1 |
| Isopimarate | 27.8 | 28.2 | 27.0 | 27.9 |
| Abietate | 16.1 | 30.4 | 18.9 | 49.2 |
| Dehydroabietate | 7.8 | 10.7 | 10.1 | 17.1 |
| Neoabietate | 13.8 | 7.2 | 12.2 | <0.1 |
| Unknown (4.2 <i>r</i> _{pimarata}) ^a | 1.5 | 0.7 | 3.7 | 0.2 |

^a10% EGSS-X on 80/100 Chromasorb W-AW.

Resin acids

The composition of the resin acid fraction of Douglas fir extractives (Table III) was similar to that found in the major southern pines (7). However, pimaric acid was absent; this result is contrary to the report by Hancock and Swan (9), who identified pimaric acid in resin acids isolated from Douglas fir veneer.

On pulping of both sapwood and heartwood there were significant resin acid losses (Table I). Also, isomerization of the abietadienoic acids and a small reduction of total conjugated acids (abietic, neoabietic, levopimaric, and palustric) with a concurrent formation of dehydroabietic acid was observed. These same changes during pulping have been reported in southern pine pulping (7), and are the subject of an ongoing study.

Effect of paraquat treatment

Treatment of southern pines with paraquat results in extensive formation of oleoresin-soaked wood (lightwood). Com-

mercialization of this technology offers the possibility of at least doubling current output of rosin and turpentine. Other conifers from the northern and western United States could also make an important contribution as sources of light wood naval stores (14), particularly predominant pulping species such as Douglas fir.

Sandberg *et al.* (15) found no increase in extractives in Douglas fir treated with paraquat, but the period following the August treatment was only 7 months during the least physiologically active part of the year. In our work, Douglas fir trees growing in the Arapaho-Roosevelt National Forest of Colorado were treated with 1/4, 1, and 5% paraquat solutions and harvested after 20 months. As observed with other conifers treated with paraquat, a zone of dead phloem and associated desiccated wood extended upward from the treatment site. The height to which these effects extended increased with increased paraquat concentration; trees treated with 5% paraquat had dead zones extending to about 7 m above the treatment. Oleoresin soaking of the wood was not apparent on visual inspection. However, some increase in total extractives was found, with the oleoresin (rosin and turpentine) portion increasing about three-fold (from 0.3 to about 1.08 on an o.d. basis) in the affected zone of the lower 7 m of the stem. The composition of the oleoresin materials after the paraquat treatment was essentially the same as that found in the wood from the nontreated trees.

The relatively large proportion of heartwood, the short growing season, and the low level of oleoresin synthesizing capacity limit the total amount of added oleoresin that can be produced in response to paraquat treatment. Thus, Douglas fir will not be a likely candidate species for the production of naval stores from lightwood.

Summary

The tall oil precursor content of Douglas fir is lower (by about 15%) than in southern pines (7). There is also a higher proportion of neutral components (20 - 30% in Douglas fir as compared to 5 - 8% in southern pine). Therefore, the quality for current applications is much lower. High fatty and resin acid losses were observed on pulping; this result has been reported previously.

The neutral fractions (from DEAE-Sephadex) of the sapwood extractives were about 35% sterol esters and 58% triglycerides. A previously unreported (in Douglas fir) triterpene alcohol has been found and is being characterized.

The fatty acid pool of the fresh wood is high in linoleic and oleic acids with significant amounts of linolenic, eicosa-

trienoic, eicosenoic, and palmitic acids. On pulping there was noticeable isomerization of linoleic acid.

Isomerization and reduction of the total amount of conjugated resin acids with formation of dehydroabietic acid was observed on pulping. Treatment of Douglas fir trees with paraquat resulted in some increase in resin acids, but this procedure does not show commercial potential.

Experimental

Two 45-cm bolts from the stem of a Douglas fir from Arapaho-Roosevelt National Forest of Colorado measuring 15 cm in diameter and 83 years old (by ring count) were received in our laboratory within 3 days of harvest. The wood samples were frozen on receipt and kept frozen throughout the chipping and milling steps of preparation. The bolts were cut into disks with a band saw and segregated into sapwood and heartwood. A narrow transition zone between the sapwood and heartwood was discarded, as was any area of knot formation. The composite sapwood and heartwood samples were ground in a Wiley mill to pass a 20-mesh screen.

Samples of the milled woods were extracted for 48 hr with diethyl ether in a Soxhlet apparatus. The extractives were analyzed by the scheme previously described by Zinkel (5). The AOCs method employed for saponification of the neutrals was replaced by refluxing with 1 g KOH in 30 ml ethanol for 4 hr. On completion of the saponification, water was added and the ethanol removed under a stream of nitrogen while heating on a steam bath. The resulting water solution was acidified with 6M H₂SO₄ and extracted with diethyl ether.

The tall oil was obtained from micro-scale kraft pulping of the milled wood (to about kappa no. 30) and extraction of the black liquor by the Saltzman-Kuiken procedure (16).

Gas-liquid chromatography (GLC) of the resin and fatty acid methyl esters was done with 10% EGSS-X on Chromasorb W-AW. Supplemental separations of levopimarate/palustrate were accomplished with 10% Silar 10-C on Chromasorb W-AW (17).

The 4-*p*-tolylvaleric acid, which elutes quantitatively in the free acid fraction from DEAE-Sephadex, was identified by comparison with an authentic standard on two GLC columns: (*r*_{18:0}, 200°) 0.40 for 10% EGSS-X on 80/100 mesh Chromasorb W-AW support, and 0.06 for a 10-m × 0.25-mm I.D. glass capillary column coated with SP-2100 (J. & W. Scientific, Inc., Orangevale, Calif.).

The retention characteristics (*r*_{pimarate}, 200°) for authentic todomatuic acid methyl ester (= juvabione) were 1.13 for 10% EGSS-X on 80/100 mesh Chrom-

asorb W-AW support and 0.46 for 9% SE-30 on 1% EGIP-Anakrom ABS (18).

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