TALL OIL PRECURSORS IN SWEETGUM[1]

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(Received February 1983)

ABSTRACT

Sweetgum is the major hardwood species being used by the kraft pulp industry of the southeastern United States. An accurate description of the diethyl ether extract is necessary to determine the quantity and quality of tall oil obtainable from this wood. The tall oil precursors content of fresh sweetgum sapwood was shown to be less than 0.2% on the oven-dried wood basis, about one-tenth the amount in southern pines. The proportion of neutrals was nearly six times larger than that found in pines; the major components were sitosterol and stigmastanol. The major components of the acids fraction were linoleic, linolenic, palmitic, oleic, and stearic acids; this is typical of hardwoods.

Keywords: Sweetgum, *Liquidambar styraciflua* L., wood extract, tall oil, fatty acids.

The inventory of hardwoods in the southeastern United States has been increasing over the past 25 years (Boyce and Knight 1980; Stone and Spelter 1980). Many of these trees have low value for the lumber and veneering markets and, therefore, are being used as a source of fiber for the pulp industry. The inclusion of hardwood species in the feed to kraft pulp mills will have a proportionate effect on the yield and quality of tall oil, an important chemical by-product of these mills. Sweetgum (*Liquidambar styraciflua* L.) is the major hardwood species used for pulping.

Walkup et al. (1956) reported that total diethyl ether extractives were higher (0.49%) in swamp-grown sweetgum than in highland-grown trees (0.22%). Characterization of the extractives from the air-dried wood was limited to chemical class identification. A more recent study of sweetgum (Choong and Fogg 1976) reported that the ether extractives from oven-dried wood were 0.72% of the sapwood and 1.05% of the heartwood. The composition of the extractives was not determined. The objective of this work was to define the amount and composition of tall oil precursors in fresh sweetgum wood.

EXPERIMENTAL

Tree samples were collected from four different sites. The specific tree and site descriptions were as follows: One tree 37-yr-old (by ring count) and 17-cm diameter-at-breast-height (dbh) cut in January 1981 from a sandy, well-drained site near Alexandria, Louisiana; three trees (37-yr-old and 16-cm dbh, 35-yr-old and 18-cm dbh, and 43-yr-old and 15-cm dbh) cut from Olustee swamp south of

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[2] The Laboratory is maintained in cooperation with the University of Wisconsin. This work was supported in part by the Pulp Chemicals Association. The use of trade, firm, or corporation names in this publication is for the information and convenience of the reader. Such use does not constitute an official endorsement or approval by the U.S. Department of Agriculture of any product or service to the exclusion of others that may be suitable.

TABLE 1. *Composition of the diethyl ether extractives of sweetgum sapwood (mg/g of oven-dried extractives free wood).*

	Average[a]	Range
Total extractives	3.5	2.4–4.6
Neutrals	1.9	1.7–2.2
Fatty acids	1.0	0.9–1.2
Nonsaponifiables	0.7	0.6–0.8
Free acids	0.2	0.1–0.4
Strong acids	trace	
Total tall oil precursors[b]	1.9	1.6–2.4

[a] Average of 8 trees.
[b] Tall oil precursors = total fatty acids + nonsaponifiables.

Olustee, Florida, in June 1981; three trees (16-yr-old and 15-cm dbh, 22-yr-old and 14.5-cm dbh, and 28-yr-old and 18-cm dbh) collected in June 1981 from a Georgeville silty clay loam site in southern Newberry Co., South Carolina; and one tree 44-yr-old and 23-cm dbh tree collected in September 1981, from a dry site near Biloxi, Mississippi. The boles were transported as rapidly as practical to the laboratory (arriving in less than 48 h from time of cutting), frozen on arrival, and kept frozen until the time of analysis.

The boles were debarked, and areas of knot formation and pith were discarded. The still frozen sapwood (there was no heartwood in any of the tree samples) was ground in a Wiley Mill to pass through a 20-mesh screen. The milled wood was extracted with diethyl ether for 22 h in a soxhlet apparatus. The ether extract was fractionated into neutrals, fatty acids, and nonsaponifiables as previously described by Zinkel (1975).

The nonsaponifiable fraction was treated with hexamethyldisilazane and analyzed by gas-liquid chromatography (GLC) at 250 C (u_{He} = 30 cm/second) on a 10-meter, wall-coated, open-tubular glass capillary column coated with SP-2100 (Supelco Inc., Bellefonte, PA). The fatty acid fractions were methylated with diazomethane and analyzed at 170 C using a 10-ft × ⅛-in. column containing 10% EGSS-X polyester (Supelco, Inc.) coated on 80/100-mesh Chromosorb W-AW. Methyl heptadecanoate was added as an internal standard. Mass spectra were obtained with a Finnigan Model 4510 gas chromatograph-mass spectrometer (GC-MS).

RESULTS AND DISCUSSION

A summary of the extractives data for sweetgum is given in Table 1. The total extractives contain a considerable (average = 40%) and variable amount of material that is not eluted from DEAE-Sephadex by acetic acid. These components of the extract are probably complex phenolics, but they were not characterized because they would not contribute to the tall oil product. No correlation of the amount of total extractives with the site water table was observed as suggested by Walkup et al. (1956). Indeed, both the tree with the lowest total extractives and the one with the highest came from the same Olustee, Florida, site.

The amount of tall oil precursors (nonsaponifiables + total fatty acids) is a more important number than the total extractives. The 1.9 mg of tall oil precursors per g of oven-dried extractives-free (ODEF) wood found in sweetgum is only about

TABLE 2. *Composition of acids fractions of a typical sweetgum sapwood extractives (normalized % of fraction).*

Fatty acid[a]	Free acids	Esterified acids	Total acids[b]	Total acids of birch[c]
12:0	0.1	tr	tr	0.1
14:0	1.5	0.4	0.6	0.3
15:0	0.5	0.1	0.2	0.2
15:1	0.2	0.9	0.8	0.2
16:0	19.2	6.6	8.8	9.2
16:1	1.9	tr	0.3	0.2
17:0	2.1	0.5	0.8	0.3
18:0	29.4	0.6	2.1	2.9
18:1	14.0	2.5	4.5	8.4
$18:2^{9,12}$	36.8	75.6	69.3	68.4
$18:3^{9,12,15}$	9.3	10.7	10.5	3.9
20:0	2.2	0.1	0.5	1.4
22:0	2.3	0.2	0.7	1.5
23:0	0.9	tr	0.2	0.2
24:0	tr	0.4	0.3	0.2
25:0	tr	tr	tr	tr

[a] Trace amounts of 15:2, 17:2, 20:2, 20:3, 20:4 and 21:0 were observed in both free and esterified fractions. 19:0 was not seen but was probably obscured by the large amount of 18:2.
[b] Calculated from free and esterified data.
[c] See Ekman and Pensar (1973).

10% of the amount found in southern pine species (Zinkel and Foster 1980). At this low concentration, the recovery of a tall oil product from sweetgum weak black liquor by skimming may be impractical, and excessive evaporation may be necessary for recovery from the strong liquor. Recovery by the blending of sweetgum black liquor with softwood black liquor may also be contraindicated, as dilution may reduce the effectiveness of skimming the softwood liquor and there will be a detrimental effect on the final product by increasing the neutrals content (Drew and Propst 1981). The nonsaponifiables are 37% of the sweetgum tall oil precursors, compared to about 8% for pine wood (Zinkel and Foster 1980).

Gas liquid chromatography and GLC-MS analysis showed that the major components of the nonsaponifiables fraction were sitosterol (53%) and stigmastanol (18%). There were several minor components, all less than 2%, that could not be identified by comparison with a series of known compounds.

The methylated acids fractions (free and esterified) were analyzed by GLC and GLC-MS; the composition of the fractions from a typical tree is given in Table 2. The variation of relative concentration of the major components of all comparable fractions was less than about 7%. The figures in the column labeled Total Acids are calculated from the free and esterified acid data. The only current study of the composition of extractives from hardwood is that by Ekman and Pensar (1973). A summary of their data for birch (*Betula verrucosa*) is included in Table 2 for the reader's convenience.

Linoleic acid ($18:2^{9,12}$) is the major component of both the free and esterified acids fractions; it is present at the same relative level, based on the total acids, as was found in birch. Oleic acid (18:1) is the next most abundant C-18 acid in the unsaturated free acids fraction, but it is a notably minor component of the esterified fraction. The total oleic acid content is about one-half the amount found

in birch. Conversely, linolenic acid ($18:3^{9,12,15}$) is nearly three times higher in sweetgum than in birch.

The most abundant saturated fatty acids are palmitic (16:0) and stearic (18:0). As generally observed in naturally occurring mixtures, the even-carbon-numbered saturated fatty acids (i.e., 14:0, 16:0, 18:0, etc.) predominate, but the odd-numbered acids are present. As usual, the saturates are a much higher proportion of the free acids fraction than of the esterified acids. Small amounts of branched chain (iso- and antiiso-) saturated fatty acids were reported in birch wood extract (Ekman and Pensar 1973). These acids were not found in sweetgum wood extract.

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