Acid Fraction Evolution in Wood Extractives of *Pinus pinaster* Ait.

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The changes in the acid fraction of wood extracts from *Pinus pinaster* Ait. have been studied. Qualitative and quantitative compositions have been determined in samples that were just extracted and then seven and twelve months after extraction. Samples were prepared according to Technical Association of Pulp and Paper Industry Standards, extracted with petroleum ether (b.p. 40–60°C) in a Soxhlet apparatus and saponified with ethanolic 0.4N potassium hydroxide. The acid fraction was methylated with diazomethane, and its qualitative composition was determined by combined gas chromatography/mass spectrometry. The quantitative composition was determined by gas chromatography with a DEGS packed column. An increase was observed in the percentage of palmitic, oleic, pimaric and dehydroabietic acids, and there was a decrease in the percentage of linoleic and abietic acids. No variation was observed in extract composition after seven and twelve months.

KEY WORDS: Extractives, fatty acids, *Pinus pinaster* Ait., resin acids, wood.

Fatty and resin acids from coniferous wood can be obtained either from the oleoresin by tapping living pine trees, from tall oil as by-product of softwood kraft pulping or by solvent extraction of stumps (1).

Literature about quantitative extracts from felled trees (2–4) and about thermal isomerization of resin acids (5–8) is available, but little is known about the changes in composition of the extracts over time. Knowledge of acid fraction changes after extraction is of interest to improve use.

This work studies the acid fraction of wood extracts from *Pinus pinaster* Ait. and their composition seven and twelve months after the extraction.

EXPERIMENTAL PROCEDURES

Samples of *P. pinaster* Ait., Mediterranean subspecies, from mountain "El Alijar" in Las Navas del Marqués (Avila, Spain), were prepared according to Technical Association of Pulp and Paper Industry Standards (9). The bark was removed. Samples were chipped and ground to a size of 40–60 mesh and the moisture was determined. Powdered wood was extracted with petroleum ether (b.p. 40–60°C) in a Soxhlet apparatus for 24 h.

Extracts were saponified with ethanolic 0.4N potassium hydroxide at 70°C for 4 h. After dilution with water (1:1, vol/vol), the unsaponifiables were extracted with petroleum ether (b.p. 40–60°C), and the water solution was acidified with 0.4N sulfuric acid and extracted with diethyl ether. The acid fraction was methylated with diazomethane and studied by combined gas chromatography/mass spectrometry (GC/MS).

Qualitative analyses were made with a Hewlett-Packard (Palo Alto, CA) 5995 GC/MS equipped with a 50 m × 0.20 mm capillary column of crosslinked 5% Ph Me Silicone under the following conditions: injection temperature, 250°C; carrier gas (N_2) flow rate, 1 mL/min; column temperature, 120–220°C, 20°C/min; electron energy setting, 70 eV. Acids were identified by comparing their methyl esters' mass spectra with previously published data (10,11).

Quantitative analyses were made with a Hewlett-Packard 5840A GC, equipped with a 2 m × 1/8 inch packed column of 10% DEGS (Supelco, S.A., Gland, Switzerland) and a flame-ionization detector (FID) under these conditions: injection temperature, 200°C; carrier gas (N_2) flow rate, 20 mL/min; column temperature, 180°C; FID temperature, 250°C.

Quantitative analyses were made of the fresh methylated sample and then after seven and twelve months of storage. Samples were stored at room temperature after the extraction.

RESULTS

Figures 1 and 2 show acid fraction chromatograms on a DEGS column of methylated fresh sample and of a sample stored seven months. No variation was observed between samples stored for seven months and those stored for twelve months. Quantitative compositions of the fresh extracts and of those stored for seven months are shown in Table 1.

Other minor acids found were 14:0, 10 Me-14:0, 15:0, 2 Me-15:0, 7-16:1, 17:1, 17:0, 5,9-18:2, 9,12-19:2, 10-19:1.

DISCUSSION

Neoabietic acid was not detected in the initial extracts. Increases were observed in the percentages of palmitic, oleic, pimaric and dehydroabietic acids, and decreases in the percentages of linoleic and abietic acids. Abietic acid was not detected in the extracts stored for seven months.

A decrease of abietic acid and an increase of dehydroabietic has been reported in tall oil destillation (12). Thermal isomerization of methyl abietate upon heating at 200°C to yield methyl esters of palustric, neoabietic and dehydroabietic acids has also been reported (7).

TABLE 1

Quantitative Composition over Time of the Acid Fraction of Wood Extracts from *Pinus pinaster* Ait.

Acid	Initial extract (%)	Extract seven months later (%)
Palmitic	1.9	4.2
Oleic	18.7	31.6
Linoleic	12.0	4.5
Pimaric	7.0	10.5
Sandaracopimaric	1.1	1.9
Levopimaric	2.3	3.4
Isopimaric	6.9	7.0
Abietic	24.5	—
Dehydroabietic	20.6	30.1
Neoabietic	—	1.9

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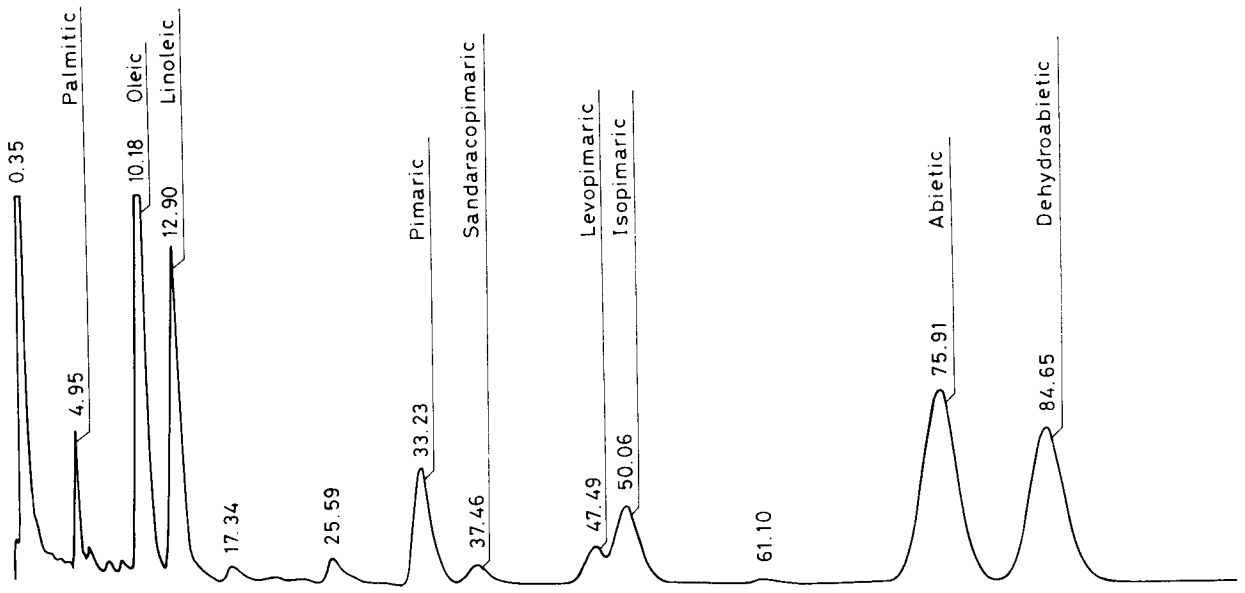

FIG. 1. Gas chromatogram of fresh methylated acid fraction. Conditions: packed column 2 m × 1/8 inch 10% DEGS; carrier gas, N_2 20 mL/min; 180°C; flame-ionization detector temperature, 250°C.

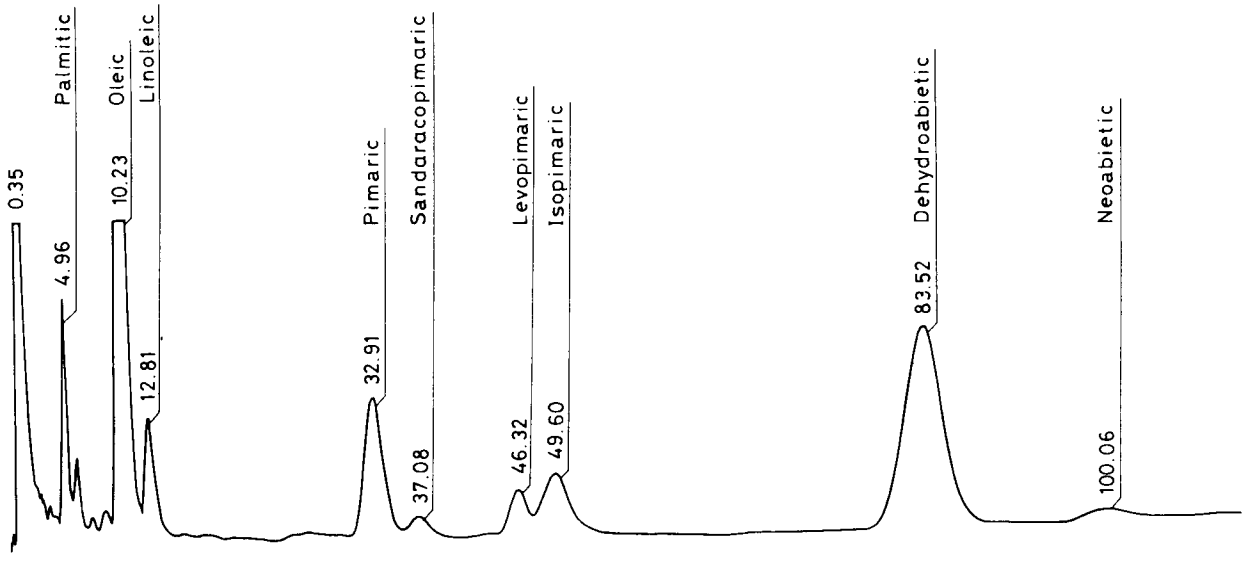

FIG. 2. Gas chromatogram of methylated acid fraction seven months after the extraction. Conditions as in Figure 1.

Levopimaric isomerization, reported in the literature (6,8,13) to form abietic, dehydroabietic and neoabietic acids, was not observed.

Isomerization of abietic acid was observed without heating the extracts. The objection that these reactions may occur in the column must be dismissed because the reactions did not appear in the analysis of the initial extracts.

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