# Composition of Tall Oil Pitch

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## ABSTRACT

Compositions of six grades of tall oil pitch (TOP), four of Finnish and two of U.S. origin were investigated. The pitch samples contained 34.6-51.6% free acids, 23.2-37.8% esterified acids, and 25.3-34.4% unsaponifiable neutral compounds. Each of the above fractions was analyzed by high resolution gas chromatography-mass spectrometry. Approximately 60% of the weight fraction in TOP consisted of high molecular components of which about half were acidic compounds. The low molecular free acids were mainly dehydroabietic, abietic, and other resin acids. The esterified acids consisted chiefly of oleic and linoleic acids. Unsaponifiable fractions were composed of diterpene alcohols, fatty alcohols, sterols, and dehydrated sterols. The alcohol components were almost completely esterified.

## INTRODUCTION

Tall oil pitch (TOP) is obtained as a nonvolatile residue in the fractional distillation process of crude tall oil. The yield of TOP in the refining process amounts to 15-40%, depending primarily on the quality of the crude tall oil. The total world production of tall oil pitch is over 200,000 tons/year. The utilization of this by-product is still an unsolved problem, even if a part of it may be used in such products as asphalt emulsions and printing inks. The recovery of sitosterols from TOP has been suggested (1). Recently it has been discovered that TOP may be used as a starting material for polyurethane lacquers (2)..

There exists scant literature data on the composition of TOP. For the characterization of the wide range of pitch grades, standard determinations such as acid-, saponification-, and iodine numbers as well as the content of unsaponifiables, fatty acids, and rosin acids have been used (3). Recently the composition of the unsaponifiable fraction of Bulgarian TOP has been reported (4).

The object of this work was to extend the knowledge on the composition of different TOP grades. New efficient chromatographic methods were used for the analytical evaluation of the fractionated samples.

## EXPERIMENTAL PROCEDURES

Samples were of ordinary grades of tall oil pitch received from three distillation plants in Finland and one in the U.S. Four Finnish and two U.S. grades were investigated.

Determinations of acid and saponification numbers were carried out according to SCAN-standards (5). Resin acid contents were analyzed by the Linder-Persson method (6). The petroleum ether insoluble fraction was determined by a mill method.

The fractionation of the samples for subsequent gas chromatographic (GC) analyses was performed as follows: 1 g TOP was dissolved in ethyl ether, and the following internal standards were added into the solution: 20-25 mg squalene, 10-12 mg heptadecanoic acid, and 6-8 mg methyl heptadecanoate. The free acids were isolated by extraction

TABLE I

Properties of Tall Oil Pitch Grades

| | Finnish | | | | American | |
|---|---|---|---|---|---|---|
| Origin | A | B | C | D | E | F |
| Yield, % of crude tall oil$^a$ | 25 | 25 | 25 | 30 | 20 | 20 |
| Acid number, mg KOH/g | 34 | 49 | 38 | 39 | 30 | 27 |
| Saponification number, mg KOH/g | 94 | 115 | 111 | 105 | 106 | 101 |
| Softening point, °C$^a$ | 46 | 30 | 25-30 | 36 | — | — |
| Resin acids, %$^b$ | 12.6 | 16.9 | 15.5 | 10.8 | 8.8 | 10.6 |
| Insoluble in petroleum ether, % | 2.4 | 7.4 | 10.0 | 9.5 | 8.5 | 0.4 |

$^a$Typical values reported by the distillation plants.
$^b$Linder-Persson method.

TABLE II

Component Group Composition of Tall Oil Pitch (wt % of pitch)

| Constituents | A | B | C | D | E | F |
|---|---|---|---|---|---|---|
| Free acids, total | 39.3 | 51.6 | 48.6 | 44.6 | 46.7 | 34.6 |
| Fatty acids | 1.4 | 1.8 | 1.3 | 0.8 | 1.3 | 2.4 |
| Resin acids | 10.6 | 12.5 | 9.7 | 6.1 | 3.3 | 6.5 |
| Other acids | 27.3 | 37.3 | 37.6 | 37.7 | 42.1 | 25.7 |
| Esterified acids, total | 30.6 | 23.2 | 23.3 | 26.8 | 27.9 | 37.8 |
| Fatty acids | 8.2 | 12.9 | 13.3 | 15.2 | 13.8 | 12.4 |
| Resin acids | 1.7 | 0.9 | 1.2 | 0.9 | 1.6 | 1.9 |
| Other acids | 20.7 | 9.4 | 8.8 | 10.7 | 12.5 | 23.5 |
| Unsaponifiables, total | 30.1 | 25.3 | 28.2 | 28.6 | 25.4 | 27.6 |
| Low molecular | 14.6 | 14.6 | 14.1 | 17.7 | 15.8 | 15.1 |
| High molecular | 15.5 | 10.6 | 14.1 | 10.9 | 9.6 | 12.5 |
| Equivalent weight for free acids | 648 | 591 | 716 | 642 | 873 | 719 |

TABLE III

Main Fatty Acid, Resin Acid, and Low Molecular Unsaponifiable Constituents of Tall Oil Pitch (wt % of Pitch)

| Constituents[a] | A | B | C | D | E | F |
|---|---|---|---|---|---|---|
| Free acids | | | | | | |
| Oleic | + | 0.5 | + | | 0.6 | 0.9 |
| Pimaric | + | 0.5 | + | | | |
| Isopimaric | + | 0.7 | 0.6 | + | + | + |
| Palustric | + | 0.6 | + | | | + |
| Dehydroabietic | 4.1 | 3.5 | 3.2 | 1.9 | 1.2 | 2.3 |
| Abietic | 2.6 | 4.4 | 2.9 | 1.9 | 0.7 | 1.7 |
| Esterified acids | | | | | | |
| Palmitic | + | + | + | + | 0.8 | 0.8 |
| Oleic | 2.2 | 4.8 | 4.6 | 3.6 | 5.6 | 5.0 |
| Linoleic | 0.6 | 1.8 | 2.2 | 2.4 | 2.3 | 1.7 |
| Conj. Linoleic *(trans-trans)* | + | 0.8 | 0.7 | 0.8 | 0.6 | 0.6 |
| Dehydroabietic | 0.6 | + | + | | 0.5 | 0.6 |
| Unsaponifiables | | | | | | |
| Unident. diterpene alcohol | 0.6 | 0.5 | | | | |
| Pimarol | + | + | 0.7 | 0.7 | 0.5 | 0.6 |
| Isopimarol | | | + | | 1.0 | 0.9 |
| Docosanol | 0.5 | 0.8 | 0.8 | 0.6 | — | + |
| Tetracosanol | 0.5 | 0.7 | 0.7 | 0.6 | 1.1 | 0.9 |
| Dehydrated β-sitosterol | 2.3 | 1.0 | + | 0.5 | 2.8 | 2.1 |
| Dehydrated sitostanol | 1.0 | | | | + | + |
| Campesterol | + | 0.6 | 0.7 | 0.7 | + | + |
| β-sitosterol | 1.3 | 4.6 | 5.6 | 6.4 | 3.7 | 3.6 |
| Sitostanol | 0.5 | 1.3 | 1.3 | 1.8 | 0.9 | 0.8 |
| Betulinol | + | 0.6 | 0.8 | 0.9 | | |

[a] All constituents amounting to more than 0.5 wt % on the pitch samples listed.

[b] + = amounts of 0.2-0.5 wt % of pitch.

with 2% aqueous KOH. The remaining neutrals were saponified in 40 ml of 94% ethanol and 10 ml toluene solution by adding 20 ml of 0.5 N KOH in ethanol and keeping 3.5 hr at 70 C. After neutralization by a cation exchanger (Dowex 50), the acids (esterified acid fractions) and the unsaponifiables were separated via extraction with aqueous KOH as above.

The purity of the isolated fractions was controlled by thin layer chromatography on precoated silica gel plates (Merck) using 70 vol % petroleum ether, 29% ethyl ether, and 1% acetic acid as eluent.

Gas chromatographic analyses were performed with a Varian 2100 instrument essentially as reported earlier (7,8). The glass capillary columns used for the runs of both the acidic and unsaponifiable fractions were 25 m long, 0.30 mm ID, and coated with SE-30. Identification of the peaks were made primarily by on-line gas chromatography-mass spectrometry with a LKB 9000 instrument.

## RESULTS AND DISCUSSION

General characteristics of the investigated samples are given in Table I. The Finnish TOP grades A-D were obtained by distillation of crude tall oil derived mainly from Scots pine but also containing 10-30% components originated from birch. The U.S. grades E-F were from Southern pine tall oil. The pitch samples A and B were two different grades from the same distillation plant. The values in Table I are within the range reported earlier. The U.S. grades show slightly lower acid numbers and resin acid contents as those of the Finnish grades.

Table II gives the composition of the weight fractions in TOP grades. As can be seen from Table II, 34.6-51.6% of the components contained acidic groups which could be extracted with alkaline water solution. The amount of 10-30% of these free acids were detected in the gas chromatograms. From the gas chromatographic peaks, fatty acids having 18-26 carbon atoms and resin acids previously found in tall oil could be identified (7). The resin acid contents obtained by GC were 2.0-5.8% lower than those resulted by the Linder-Persson method. This may be explained by the presence of modified resin acids which are not eluted in the GC analysis.

The large group "Other Acids" comprises primarily high molecular acids, which were not eluted by GC. The presence of high molecular free acids is also evident from the high equivalent weights obtained for the acids (Table II). In an earlier investigation, dimeric acids originating from both fatty and resin acids were found in a similar type of TOP as sample B (B. Holmbom and S. Pekkala, unpublished work). By employing combined GC-MS with a 0.3 m long column packed with 1% OV-1, it was found that 3% of the TOP consisted of unmodified dimeric fatty and resin acids. In the present study we observed that a part of the high molecular free acids contains ester linkages. Saponification of the free acid fraction of the sample A gave 11% unsaponifiable alcohols, which were obviously combined with acids containing two or more acidic groups. Additional true fatty acids were separated after saponification. It can be postulated that these acids amounting to 1.1% in TOP were previously combined with the hydroxy acids. The main components in the free acid fractions of all TOP grades were dehydroabietic and abietic acids (Table III).

The esterified acids liberated from the neutral components by saponification were composed primarily of fatty acids. The large group "Other Acids" consists of high molecular modified acids. Only 0.9-1.9% of TOP grades were esterified resin acids. It should be pointed out that resin acid esters are difficult to saponify even under vigorous reaction conditions. Therefore, a part of the resin acid esters might have been left unhydrolyzed. The composition of the esterified fatty acids differed appreciably from that of the combined fatty acids present in the respective crude tall oils (7). The TOP grades showed lower content of linoleic acid and higher amount of oleic acid than that of the tall oil correspondingly.

Even in the unsaponifiable part of TOP, there exist high molecular constituents. The major part of the unsaponifiable components consist of similar species of alcohols as found in crude tall oils (9). In addition, some not identified artifact diterpene alcohols were observed. The main component was β-sitosterol accompanied by sitostanol and campesterol as found in crude tall oil. During the distillation process, extensive dehydration of the sterols may occur which is indicated by the high amount of dehydrated sterols present in some TOP grades. The content of β-sitosterol varies considerably from grade to grade, indicating that all TOP grades are not acceptable starting materials for the recovery of phytosterols. The presence of free alcohols was checked by analyzing some neutral fractions prior to saponification. No free diterpene and fatty alcohols were found. About 5% of the sterols existed in free form.

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