# The Neutral Diterpenes from Pine Wood Resin

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The composition of the resin acids from the wood of Scots pine (*Pinus silvestris*) has been investigated previously [1]. A systematic investigation of the higher neutral terpenes is now in progress in this laboratory, and in this communication a brief summary of some of our results concerning the diterpenes is given.

Certain by-products from the sulphate pulp industry such as "tall oil" and "sulphate turpentine", extracts from sound pine wood and from the wood of pines, which have been attacked by a fungus, *Peridermium pini*, are also being studied. The pine responds to the attack of this fungus by an excessive production of resin; the content of which may rise to 20–40 %.

Variations in the composition of the terpene fractions from these different sources may be due to chemical changes during the strongly alkaline cook, or to the method used for the production of tall oil and sulphate turpentine, as well as, from the fact that the wood, used in the sulphate process contains various amounts of spruce wood besides the main raw material, which is pine wood. A study of the qualitative differences, if any, between the higher terpenes produced by sound and *Peridermium* infested wood was also of interest.

We intend to describe the results of this investigation in detail in a future communication, which will also cover the sesquiterpene fractions.

The diterpene aldehydes, alcohols and hydrocarbons were isolated from the ether extract of the wood in the following way. The part of the extract which was soluble in light petroleum was treated with Girard P reagent [2]. The recovered aldehyde fraction was distilled *in vacuo* (the fraction b.p. 165–185° at 1 mm was collected).

The residual part of the extract was hydrolyzed with methanolic sodium hydroxide; an acidic and a neutral fraction were collected. The latter was distilled *in vacuo* to remove the mono- and sesquiterpenes and to separate the diterpene hydrocarbons (b.p. 155–165° at 1 mm) and alcohols (b.p. 185–200° at 1 mm).

The three main diterpene fractions were further purified by chromatography on alumina (neutral, activity I). Hydrocarbons were eluted with light petroleum, aldehydes with benzene and alcohols with ether. The individual components of these fractions were then separated by chromatography on silver nitrate impregnated silica gel [3]. The columns were eluted with light petroleum containing 0–2 % ether for the hydrocarbons, 0–5 % for the aldehydes and 0–20 % for the alcohols.

From extracts from *Peridermium* infested wood, the constituents listed below were isolated in a pure state and characterized by physical constants and derivatives.

1. Dehydroabietinal (0.02 %, dry wood basis), m.p. 53–55°, $[\alpha]_D^{22}$ + 52°. (Also prepared by Rosenmund reduction of dehydroabietic acid [4].)
2. Abietinal (0.02 %), m.p. 45–48° (not previously obtained crystalline), $[\alpha]_D^{22}$ −77°, ($\lambda_{max}^{EtOH}$ 241 mμ (ε 14 000), $\nu^{KBr}$ 2730 (infl.), 1 720 cm$^{-1}$; abietic acid has $\lambda_{max}$ 241 mμ (ε 20 400) [5]).
3. Pimarinal (0.54 %), m.p. 50–52°, $[\alpha]_D^{22}$ + 99° (optical rotation not previously reported). 2,4-Dinitrophenylhydrazone m.p. 194–195°. (Lit. m.p. 50–52° and 195–196°, respectively [6].)
4. Isopimarinal (0.12 %), m.p. 35–37° (not previously obtained crystalline), $[\alpha]_D^{22}$ −15.0°. 2,4-Dinitrophenylhydrazone m.p. 182–183°. (Lit. m.p. 180–182° [6].) It was oxidised by chromic acid to isopimaric acid m.p. 162–164° [7].
5. Abietinol (0.001 %), m.p. 85.5–87°, $[\alpha]_D^{22}$ −130°. (Also prepared by lithium aluminium hydride reduction of abietic acid [8].)
6. Pimarinol (0.05 %), m.p. 87.5–89.5°, (previously obtained as an oil [9]), $[\alpha]_D^{22}$ + 94°. (Also prepared by sodium borohydride reduction of pimarinal).
7. Isopimarinol (0.001 %), m.p. 84–86°, $[\alpha]_D^{22}$ −24.6° [19]. (Also prepared by sodium borohydride reduction of isopimarinal).
8. Pimaradiene (0.008 %), m.p. 24.5–27°, $[\alpha]_D^{22}$ + 101° [11]). (Also prepared by Wolff-Kishner reduction of pimarinal).
9. Isopimaradiene (0.002 %), oil, $[\alpha]_D^{22}$ −31.3° [12]. (Also prepared by Wolff-Kishner reduction of isopimarinal).

The IR spectra, UV spectra (Nos. 1, 5) and mixed melting points of the isolated and authentic compounds (Nos. 1, 5, 6, 7, 8)

*Table 1.* (+ = isolated and characterised, × = presence indicated by chromatographic methods, − = sought for, but not found).

| | Extract from wood: Sound | *Peridermium* infested | Sulphate turpentine | Tall oil |
|---|---|---|---|---|
| Dehydroabietinal | × | + | | − |
| Abietinal | × | + | | − |
| Pimarinal | × | + | × | − |
| Isopimarinal | × | + | | − |
| Dehydroabietinol | × | × | | |
| Abietinol | × | + | | |
| Pimarinol | × | + | | |
| Isopimarinol | × | + | | |
| Dehydroabietadiene | − | − | − | |
| Abietadiene | − | − | − | |
| Pimaradiene | × | + | + | − |
| Isopimaradiene | × | + | × | − |

were identical as were the retention times (gas-liquid chromatography [3]) and the $R_F$ values (thin layer chromatography on silver nitrate impregnated silica gel [3]). The compounds not previously isolated from any natural source (all except No. 3) gave correct analyses.

The occurrence of diterpenes in the different pine products investigated is shown in Table 1. As seen from this table, no hydrocarbons corresponding to the "rearranged" diterpene acids (abietic and dehydroabietic acids) were found. If confirmed this observation may have biosynthetic significance.

It is certainly of interest to note that no qualitative difference was observed between the composition of the resin from sound and from *Peridermium* infested wood.

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