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Constituents of Pine Heartwood

XIII. The Heartwood of *Pinus Jeffreyi* Balf

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Pinus Jeffreyi (Jeffrey pine) is a *Diploxylon* pine growing in the western part of North America. It is very closely related to *P. ponderosa*, and some botanists consider it to be a variety of this species [1]. The wood used for the present investigation came from California, U. S. A.

The heartwood was extracted with ether and acetone in the way described for *P. montana* [2]. The ether extract (1.7 % of heartwood) did not crystallise. A phenolic fraction, amounting to only 0.2 % of the ether extract, could be prepared from it.

A fair amount of *l*-arabinose was isolated from the water-soluble part of the acetone extract. The 0.2 % sodium hydroxide fraction contained pinocembrin, and the 4 % sodium hydroxide fraction yielded pinosylvin monomethyl ether, but no pinosylvin.

The following products were obtained from 6.4 kg of air-dry heartwood:

Ether extract	111 g	(1.7 %)
'Membrane substances'	2.9 g	(0.05 %)
l-Arabinose	7.0 g	(0.1 %)
Pinocembrin	2.1 g	(0.03 %)
Pinosylvin monomethyl ether	3.3 g	(0.05 %)
Neutral fraction of acetone extract	3.2 g	(0.05 %)

The specimen of *P. Jeffreyi* investigated here resembled *P. ponderosa* in that it yielded a rather small amount of ether extract [4]. There were, however, differences in the chemical composition of their heartwoods. Pinobanksin was isolated in a very small amount from *P. ponderosa* but has not been found at all in *P. Jeffreyi*. *P. ponderosa* contained about ten times as much pinosylvin phenols as this specimen of *P. Jeffreyi*, but the latter had more pinocembrin

in its heartwood. *P. Jeffreyi* differs from most other pines in that its turpentine contains no pinene but instead saturated aliphatic hydrocarbons, such as *n*-heptane [3]. Its heartwood constituents, however, seem to be the same as in the other *Diploxylon* pines.

EXPERIMENTAL

The wood used for the investigation was supplied by Dr. N. T. Mirov, California Forest and Range Experiment Station, Placerville, California, U. S. A. Its colour reaction with diazotised benzidine solution was not very strong.

Air-dried, fine-ground heartwood (6.4 kg) was extracted with ether for 24 hours, and then with acetone for 48 hours in the usual way [2]. Weight of ether extract was 111 g. It consisted of a dark viscous oil, which had not crystallised after two months. 8.70 g of the ether extract were treated with 150 ml of light petroleum. The solution was decanted, and the brown sticky residue boiled with 200 ml of water. The water was filtered, cooled, and extracted with ether. The ether was dried over sodium sulphate and evaporated, leaving 0.15 g of a brown resinous substance. Its alcoholic solution gave a dark violet colour reaction with ferric chloride.

The acetone extract was concentrated to a dark brown resinous substance and a small volume of a water solution, which was separated from the resin. Aqueous solution = W.

The resinous substance was treated with ether to precipitate the 'membrane substances'. The filtrate was shaken with a little water which was combined with W. The latter solution was then shaken with ether which was added to the first ether solution.

The ether solution was then extracted with saturated sodium bicarbonate (3 × 200 ml, extract = B), saturated sodium carbonate (5 × 140 ml, extract = C), 0.2 % sodium hydroxide (4 × 250 ml, extract = H_1), and 4 % sodium hydroxide (200 + 100 ml, extract = H_2). Each extract was acidified with dilute sulphuric acid and extracted with ether. The ether solutions were dried with sodium sulphate and the ether evaporated.

The 'membrane substances' were stirred with 100 ml of cold water, the suspension filtered and the filtrate combined with W. The remaining 'membrane substances', a light brown powder, weighed 2.0 g after drying in the air.

W was concentrated *in vacuo* to a brown syrup, which was dissolved in hot ethanol, the solution filtered and concentrated to a small volume. After cooling, a colourless crystalline precipitate was obtained. After this precipitate had been recrystallised twice from ethanol, 7.0 g of *l*-arabinose was obtained. M. p. 156—158°. $[\alpha]_D^{20}$ + 104.0° ± 0.5° (equilibrium rotation in water, c = 2.6). It gave no melting point depression with pure *l*-arabinose.

B yielded a brown oil (1 g) which did not crystallise.

C was concentrated to a brown oil (less than 1 g). Extraction with boiling water yielded a brown solid melting at 95—120°. No pure products could be isolated from this fraction.

From H_1 was obtained a brown sticky solid which partly crystallised. It was stirred with a little ether and the undissolved crystalline powder collected. The filtrate was evaporated and the ether treatment repeated, when a second crop of crystals remained undissolved. The crystals were combined (m. p. 188—194°), dissolved in ether and the

yellow ether solution filtered through aluminium oxide. Most of the colour of the solution was removed. The filtrate was evaporated and the residue recrystallised twice from 50 % acetic acid. Yield of pinocembrin, 1.2 g, m. p. 194—195°, no depression when mixed with pinocembrin from *P. Banksiana*. $[\alpha]_D^{20}$ — 55° ± 1° (methanol, c = 3.0).

The ether filtrate was concentrated, the residue distilled *in vacuo* and the distillate (partly crystalline) recrystallised from 50 % acetic acid. 1.0 g of pinocembrin, m. p. 194—195° was obtained. No crystalline products could be isolated from the mother liquor.

H_2: When the ether solution was evaporated, a brown semi-crystalline solid remained. Two recrystallisations from 50 % acetic acid yielded a light brown substance, m. p. 115—118° (4.0 g). It was distilled *in vacuo* and recrystallised again. Pinosylvin monomethyl ether (3.3 g), m. p. 120—121°, was obtained.

The neutral fraction of the acetone extract was a brown oil (3.2 g), which deposited a small quantity of crystals. It was not investigated any further.

SUMMARY

The heartwood of *Pinus Jeffreyi* Balf. has been investigated. *l*-Arabinose, pinocembrin and pinosylvin monomethyl ether were isolated.

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