

Constituents of Pine Heartwood

X. The Heartwood of *Pinus contorta* var. *latifolia* S. Wats

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P*inus contorta* Dougl., a *Diploxylon* pine which grows in Western North America, occurs in two varieties, 'shore pine' and 'lodgepole pine'¹. 'Shore pine' is the coast form, and 'lodgepole pine' grows in the mountains. The latter has sometimes been considered to be a separate species (*P. Murrayana* Balf.). The wood used in this investigation came from a cultivated tree (lodgepole pine), grown in the neighbourhood of Nyköbing, Denmark.

The extraction was carried out according to the general scheme given in Part IX. The ether extract (3.8 % of the heartwood) was crystalline. A phenolic fraction, amounting to only 0.1 % of the whole extract, could be prepared from it, using the method given in the preceding paper.

The acetone extract was divided into fractions in the usual manner. The sodium carbonate fraction contained a mixture of pinocembrin (5,7-dihydroxiflavanone) and pinobanksin. The last-mentioned substance was first isolated by Erdtman from *P. Banksiana*², and shown to contain one hydroxyl group more than pinocembrin. He assumed it to be 3,5,7-trihydroxiflavanone, and this structure seems to be correct. Studies on the structure of pinobanksin are in progress and will be published in forthcoming papers. The pinobanksin from *P. contorta* melted at 174—176°* and had $[\alpha]_D^{20} + 16^\circ$ (in methanol). (The value $[\alpha]_D^{20} + 1.5^\circ$ reported by Erdtman² is due to a misprint. Should be $+ 15^\circ$.) The pinocembrin had m. p. 194—195°, $[\alpha]_D^{20} - 56^\circ$ (in methanol). Both substances were obtained in very small quantities.

The 0.3 % sodium hydroxide extract yielded pinosylvin and an additional quantity of pinocembrin. From the 4 % sodium hydroxide extract a very small quantity of pinosylvin monomethyl ether could be isolated.

* All melting points uncorrected.

The water-soluble part of the acetone extract was not investigated. Later, when arabinose had been isolated from several other pines, a second extraction of the heartwood of an American lodgepole pine was carried out. The water-soluble part of its acetone extract yielded *l*-arabinose.

The following products were isolated from 2.5 kg of air-dry heartwood:

Ether extract	95 g (3.8 %)
'Membrane substances'	2.1 g (0.08 %)
Pinocembrin	0.47 g (0.02 %)
Pinobanksin	0.08 g (0.003 %)
Pinosylvin	0.30 g (0.01 %)
Pinosylvin monomethyl ether	0.10 g (0.004 %)
Neutral fraction of acetone extract	2.0 g (0.08 %)

1.7 kg of heartwood yielded 1.0 g of *l*-arabinose (0.06 %).

The yields of crystalline compounds were extremely low. It is especially remarkable that the quantity of pinosylvin monomethyl ether was inferior to that of the pinosylvin.

EXPERIMENTAL

2.5 kg of heartwood were extracted with ether and acetone in the manner described for *P. montana*³. The ether extract was concentrated to a pale yellow syrup, which soon crystallised. Yield, 95 g or 3.8 % of the heartwood. 10.1 g of this extract were treated with 150 ml of light petroleum. A brown sticky precipitate remained undissolved. The solution was decanted, and the residue boiled with 200 ml of water. The aqueous extract was filtered, cooled and extracted with ether. The ether was dried with sodium sulphate and evaporated to dryness. The residue (0.024 g) was a yellow resin. Its alcoholic solution gave a dark violet colour with ferric chloride.

From the acetone extract, «membrane substances» (2.1 g) were precipitated with ether (600 ml). The filtrate was extracted with saturated sodium bicarbonate (3 × 200 ml, extract = B), saturated sodium carbonate (3 × 200 ml, extract = C), 0.3 % sodium hydroxide (3 × 150 ml, extract = H₁) and 4 % sodium hydroxide (2 × 100 ml, extract = H₂). The remaining «neutral fraction» was concentrated. A viscous brown oil (2 g) was obtained.

B was discarded.

C was acidified and extracted with ether. The ether solution was dried over sodium sulphate and the ether evaporated. The residue, a yellowish-brown solid, was difficult to purify by simple recrystallisations. Extraction with boiling water yielded an aqueous solution, from which a crystalline precipitate was obtained on cooling. The crystals (1.7 g) melted between 165 and 180°. After several recrystallisations from toluene and from 50 % acetic acid, 0.47 g of pinocembrin could be isolated. M. p. 194–195°, mixed m. p. with pinocembrin from *P. montana* 193–194°. $[\alpha]_D^{20} - 56^\circ \pm 1^\circ$ (methanol, *c* = 2.7).

From the mother liquors a small quantity of crude pinobanksin, m. p. 170–173°, could be isolated after a very tedious process of separation.

After removing the crystalline precipitate from the aqueous extract of C, the filtrate was extracted with ether, the yellow ether solution dried over sodium sulphate and filtered through aluminium oxide (most of the colour removed) and evaporated. A brown syrup remained, which was dissolved in hot toluene. On cooling, crystals were obtained which were recrystallised from 50 % acetic acid and, finally, twice from toluene. Thus a small quantity of pinobanksin (83 mg) was obtained, m. p. 174–176°. The m. p. was not depressed on admixture with pure pinobanksin from *P. Banksiana*. $[\alpha]_D^{20} + 16^\circ \pm 1^\circ$ (methanol, $c = 2.5$).

H_1 was acidified, extracted with ether, and the ether extract concentrated. A brown oil was obtained, which partly crystallised. After treatment with benzene (1–2 ml), a light brown crystalline powder was obtained (3.4 g), melting between 110 and 145°. It was dissolved in 1.5 l of ether and shaken with 175 ml of 0.6 % sodium hydroxide.

From the alkali phase a small quantity of partly racemised pinocembrin was isolated by vacuum sublimation and several recrystallisations from dilute acetic acid. M. p. 194–196°. One of the mother liquors contained a small amount of crude pinosylvin (m. p. 151–153°). An additional quantity of pinosylvin was isolated from the ether phase after concentrating, vacuum distillation of the residue, filtration through aluminium oxide (coloured impurities removed), and three recrystallisations from benzene. Yield, 0.30 g. M. p. 156–158°, no m. p. depression when mixed with an authentic specimen of pinosylvin.

H_2 was also acidified and extracted with ether. The ether solution was filtered through aluminium oxide, and the filtrate evaporated. A brown oil was obtained, which was distilled *in vacuo*. On cooling, the distillate immediately crystallised. After three recrystallisations from 50 % acetic acid, the substance melted at 120–121° and gave no m. p. depression when mixed with pinosylvin monomethyl ether. Yield, 0.10 g. The first mother liquor was precipitated with water and the precipitate dried and recrystallised from benzene. A small amount of pinosylvin, m. p. 154–155°, was obtained.

Isolation of *l*-arabinose from American lodgepole pine

Fine-ground heartwood (1.7 kg) was extracted with ether for 24 hours and then with acetone for 60 hours. The acetone extract was evaporated, yielding a brown resinous product and about 150 ml of an aqueous solution. The solution was decanted and the resinous product treated with ether to precipitate »membrane substances». The latter were separated, dried and stirred with 100 ml of cold water. The suspension was filtered and the filtrate combined with the main water solution. The water was removed by vacuum distillation, and the remaining syrup dissolved in hot ethanol. The alcoholic solution was filtered and concentrated to a small volume. On cooling, colourless crystals were precipitated. After three recrystallisations from ethanol, a fraction (0.3 g) melting at 156–157° was obtained. $[\alpha]_D^{20} + 104.5^\circ \pm 0.5^\circ$ (equilibrium rotation in water, $c = 2.8$). Reported for *l*-arabinose + 105.5°. *p*-Bromophenylhydrazine yielded a colourless crystalline precipitate in cold acetic acid solution. A strong red pentose colour reaction was obtained with phloroglucinol and hydrochloric acid. Less pure arabinose was isolated from the mother liquors (m. p. 151–154°). Total yield of *l*-arabinose, 1.0 g.

SUMMARY

l-Arabinose, pinobanksin (probably 3,5,7-trihydroxiflavanone), pinocebrin, pinosylvin and its monomethyl ether have been isolated from the heartwood of *Pinus contorta* var. *latifolia* S. Wats.

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