

## Constituents of Pine Heartwood

XII. The Heartwood of *Pinus ponderosa* Dougl.

GÖSTA LINDSTEDT

*Organisk-kemiska Institutionen, Kungl. Tekniska Högskolan, Stockholm, Sweden*

*Pinus ponderosa*, 'Western yellow pine', is endemic to Western North America and is one of the largest and commercially most important of the American pines. It belongs to the section *Diploxylon*. The wood used in this investigation came from Oregon, U. S. A.

The heartwood was extracted with ether and acetone as described for *P. montana*<sup>1</sup>. The ether extract (2.7 % of the heartwood) did not crystallise. A phenolic fraction could be prepared from it in the usual way. Its weight (1 % of the ether extract) was small when compared to the content of pinosylvin phenols in the acetone extract.

From the water-soluble part of the acetone extract, a small amount of *l*-arabinose was isolated. The 0.2 % sodium hydroxide extract yielded a small amount of pinocembrin. The 5 % sodium hydroxide extract contained pinosylvin and a large quantity of its monomethyl ether.

A parallel run was made on an acetone extract from 4 kg of heartwood prepared by Dr. A.B. Anderson, Portland, Oregon, U.S.A. From this extract a very small quantity of pinobanksin was isolated, but no pinocembrin was found. Pinosylvin and its monomethyl ether were isolated as in the first extraction.

The following products were isolated from 5.4 kg of air-dry heartwood:

Ether extract	147 g (2.7 %)	
'Membrane substances'	4.5 g (0.08 %)	
<i>l</i> -Arabinose	0.6 g (0.01 %)	
Pinocembrin	0.1 g (0.002 %)	(Parallel run 0.002 % of pinobanksin)
Pinosylvin	0.6 g (0.01 %)	(Parallel run 0.03 %)
Pinosylvin monomethyl ether	21.8 g (0.4 %)	(Parallel run 0.4 %)
Neutral fraction of acetone extract	5.5 g (0.1 %)	

The two specimens of *P. ponderosa* investigated here were both relatively rich in pinosylvin phenols, but the yields of pinocembrin and pinobanksin were extremely low.

#### EXPERIMENTAL

The wood was provided by Dr. A. B. Anderson, Portland, Oreg., U. S. A. 5.4 kg from the periphery of the heartwood of a large tree were used for the extraction. The heartwood gave a strong red colour when stained with diazotised benzidine solution. It was extracted with ether and acetone in the usual way<sup>1</sup>. The weight of the ether extract was 147 g. 11.8 g of the ether extract were treated with 200 ml of light petroleum. The solution was decanted from the sticky brown residue, and the latter boiled with 300 ml of water. The water solution was filtered, cooled, and extracted with ether. After evaporation, the ether solution yielded 0.10 g of a yellowish-brown syrup. Its alcoholic solution gave a brown violet colour with ferric chloride.

On evaporation, the acetone extract yielded a brown resinous residue and about 100 ml of a water solution (= W), which was decanted from the resin. The resin was treated with 400 ml of ether, the undissolved 'membrane substances' (4.5 g after drying in the air) separated from the solution, and the latter was shaken with 100 ml of water which was combined with W. The 'membrane substances' were also stirred with about 100 ml of cold water which was added to W. W was then shaken with about 50 ml of ether which was combined with the ether solution of the resin.

The ether solution was then shaken with saturated sodium bicarbonate (total volume 1 l, extract = B) and with saturated sodium carbonate (total volume 1.8 l). The sodium carbonate was first shaken with ether (ether phase = C<sub>2</sub>) and then acidified and extracted with ether (C<sub>3</sub>).

After the sodium carbonate extraction, the ether solution was diluted to about 600 ml and shaken with 0.2 % sodium hydroxide. Alkali phase = H<sub>1</sub>. Finally, the ether phase was shaken with 5 % sodium hydroxide. Alkali phase = H<sub>2</sub>. The remaining ether phase was concentrated to a reddish-brown, turpentine-smelling oil (5.5 g).

*W*: The water was removed from the solution by vacuum distillation. The residue, a brown syrup, was extracted with hot ethanol. When the ethanol solution was concentrated to a small volume, colourless crystals precipitated which were recrystallised twice from ethanol. *l*-Arabinose (0.47 g) melting at 158–159° and 0.13 g of less pure material melting at 155–157° were obtained.  $[\alpha]_D^{20} + 104.0^\circ \pm 0.5^\circ$ . (Equilibrium rotation in 2.5 % aqueous solution.) The sugar gave no melting point depression with *l*-arabinose and a strong pentose colour reaction with phloroglucinol-hydrochloric acid.

C<sub>2</sub> was concentrated to a brown semi-solid oil, which showed a small tendency to crystallise. When the oil was stirred with a little ether, a crystalline precipitate was formed, from which a small quantity of pinosylvin monomethyl ether (m. p. 120–121°) could be obtained by recrystallisation from chloroform-light petroleum.

C<sub>3</sub> yielded a reddish-brown syrup, from which a few mg of a crystalline solid melting at 152–158° were obtained. A mixture with pinosylvin gave a large m. p. depression. The crystals might perhaps be a mixture of pinocembrin and pinobanksin.

H<sub>1</sub> was acidified, extracted with ether and the ether solution evaporated. A reddish-brown viscous oil, which did not crystallise, remained. It was distilled in a high vacuum, and part of the distillate crystallised. The crystals were recrystallised from benzene and

from 50 % acetic acid. 0.12 g of a crystalline substance melting at 197–198° was obtained. The mixed melting point with pinocembrin (m. p. 193–195°) was 193–197°. The high melting point indicates that the pinocembrin had become partly racemised during the distillation.

$H_2$  was acidified, extracted with ether, and the ether solution concentrated to a reddish-brown, semi-crystalline mass. Vacuum distillation yielded a reddish distillate, which partly crystallised. After two recrystallisations from 50 % acetic acid, pinosylvin monomethyl ether (21.8 g), m. p. 121–122°, was obtained.

The first mother liquor was precipitated with water, and the sticky reddish-brown precipitate dissolved in ether and filtered through aluminium oxide. Most of the colour of the solution was removed. The filtrate was concentrated to a brown oil, which was extracted by boiling water. When cooled, the extract yielded crystals, which were recrystallised from benzene. Yield, 0.55 g of crystalline leaflets, m. p. 154–155°, which showed no m. p. depression with pinosylvin.

The second mother liquor contained a small amount of crude pinosylvin monomethyl ether, m. p. 114–119° after one recrystallisation from 50 % acetic acid.

A second investigation was made on an acetone extract of 4 kg of heartwood which had been prepared by Dr. A. B. Anderson, Portland, Oreg., U. S. A. The result was similar to that stated above except that no pinocembrin could be isolated and that 0.09 g of pinobanksin was isolated from the C fractions. This pinobanksin had m. p. 176–177° and showed no m. p. depression with pure pinobanksin.  $[\alpha]_D^{20} + 13^\circ \pm 1^\circ$ . (2.4 % in methanol.) From the same extract were isolated 1.1 g of pinosylvin and 16.5 g of pinosylvin monomethyl ether.

#### SUMMARY

Pinosylvin and its monomethyl ether, *l*-arabinose and, in very small amounts, pinocembrin and pinobanksin have been isolated from the heartwood of *Pinus ponderosa* Dougl.

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#### REFERENCES

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