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Constituents of Pine Heartwood

XIX. * The Heartwood of *Pinus pinea* L., *Pinus pinaster* Aiton, *Pinus halepensis* Mill., and *Pinus nigra* Arnold var. *calabrica* (Loudon) Schneider

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The present paper deals with an investigation of the heartwood of four pines belonging to the section *Diploxylon*, all of which are endemic to Southern Europe. The extractions were carried out according to the general scheme given in Part IX [1].

The heartwood of *Pinus pinea* (Stone Pine) gave a very high yield of ether extract (37 % of the heartwood). From the acetone extract, *l*-arabinose, pinocembrin, and pinosylvin monomethyl ether could be isolated.

The sample of *Pinus pinaster* (Maritime Pine) investigated was poorer in ether extractable compounds (10 % of the heartwood). One would expect a high content of resins, since *P. pinaster* is utilised for the commercial production of resins. *l*-Arabinose, pinobanksin, and pinocembrin were isolated from the acetone extract, but neither pinosylvin nor its monomethyl ether were found. This, of course, does not necessarily mean that these two substances are totally absent in the heartwood. Small quantities may easily escape detection, especially when they are accompanied by more or less resinous products. The heartwood of *P. pinaster* is known to show little resistance to decay, which is in accordance with the absence of significant quantities of pinosylvin phenols.

The heartwood of *Pinus halepensis* (Aleppo Pine) was extremely rich in resins. (Ether extract = 42 %.) The acetone extract contained a water-soluble fraction which reduced Fehling's solution, but no crystalline products could be isolated from it. The ether-soluble part of the acetone extract con-

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tained pinosylvin and its monomethyl ether. However, no pinocembrin or pinobanksin could be isolated.

The heartwood of *Pinus nigra* var. *calabrica* (Corsican Pine = *P. laricio* Poiret) yielded 31 % of ether extract. *l*-Arabinose (in a crude state) and pinosylvin monomethyl ether were isolated from the acetone extract. The heartwood of the Austrian form of this species, *P. nigra forma austriaca* Aschers and Graebner, had been investigated previously [2]. It contained pinosylvin and its mono- and dimethyl ethers. Pinocembrin or pinobanksin have not been isolated from either of the two varieties.

The yields of the different substances (expressed in percent of air-dried heartwood) are listed in the table below.

Species	Ether extract	Membrane substances	*l*-Arabinose	Pinobanksin	Pinocembrin	Pinosylvin	Pinosylvin monomethyl ether
P. pinea	37	0.4	0.05	—	0.3	—	0.02
P. pinaster	10	0.3	0.3	0.02	0.08	—	—
P. halepensis ..	42	0.2	—	—	—	0.03	0.2
P. nigra var. *calabrica*	31	0.06	0.03	—	—	—	0.4

EXPERIMENTAL

The sample of *P. pinea* came from Valladolid, Spain, and the three other samples from Sierra de Cazorla, Jaén, Spain.

Pinus pinea

The heartwood (15 annual rings) gave a rather weak colour reaction with diazotised benzidine solution.

The wood (1.6 kg) was first cut into chips (2 × 4 × 30 mm) and digested with ether for 24 hours to remove most of the resins. The chips were then air-dried, milled, and extracted with ether and acetone, in the usual manner [1]. The milling of fresh wood proved impossible because of the high resin content. The total content of ether extract was 37 %. It was pale yellow and crystallised immediately.

The acetone extract was concentrated and treated with cold water (800 ml). The aqueous solution (= W) was decanted, and the sticky, insoluble residue was then shaken with ether (500 ml). A brown precipitate of insoluble »membrane substances» (5 g) separated from the ether solution, which was then extracted with saturated sodium bicarbonate (7 × 100 ml, extract = B), saturated sodium carbonate (5 × 100 ml,

extract = C), 0.3 % sodium hydroxide (5 × 100 ml, extract = H_1), and with 5 % sodium hydroxide (2 × 100 ml, extract = H_2).

W: The aqueous solution was concentrated to a brown syrup by vacuum distillation. This syrup was dissolved in hot ethanol, filtered, concentrated to a small volume, and cooled. Colourless crystals were formed, which melted at 155—157° *. No m. p. depression with *l*-arabinose. $[\alpha]_D^{20}$ + 105° ± 1° (equilibrium rotation in water, c = 2.4). Yield, 0.8 g.

B was acidified and extracted with ether. On concentration, the ether solution yielded a brown syrup which did not deposit any crystals.

C was acidified and extracted with ether. The ether solution was dried over anhydrous sodium sulphate and decolourised by filtration through a small amount of aluminium oxide. The filtrate was evaporated to dryness and the residue recrystallised from benzene and from 50 % acetic acid, yielding colourless crystals, m. p. 192—193°, no m. p. depression with pinocembrin. $[\alpha]_D^{20}$ − 53° ± 1° (methanol, c = 3.3).

H_1 yielded an additional amount of pinocembrin which was combined with the material isolated from *C*. Total yield of pinocembrin 5 g.

H_2 was acidified and extracted with ether, and the ether solution dried and concentrated to a yellowish-brown crystalline residue. After recrystallisation from benzene and from 50 % acetic acid, it yielded 0.3 g of pinosylvin monomethyl ether, m. p. 118—119°.

Pinus pinaster

The colour reaction with diazotised benzidine was rather weak. 2.1 kg of heartwood were extracted. The extractions were carried out in the same way as described for *P. pinea*. The ether extract soon deposited crystals. The *W* fraction yielded 6 g of *l*-arabinose, m. p. 153—155°, $[\alpha]_D^{\xi C}$ + 104° ± 1° (equilibrium rotation in water, c = 2.3).

The *C* fraction deposited a crystalline yellow precipitate, which was separated, acidified, and recrystallised twice from toluene, yielding pinobanksin (0.33 g), m. p. 176—177°, $[\alpha]_D^{20}$ + 13° ± 1° (methanol, c = 3.9). From the sodium carbonate solution and from H_1, pinocembrin (1.6 g) was isolated. M. p. 193—194°, $[\alpha]_D^{20}$ − 49° ± 1° (methanol, c = 2.9).

The H_2 fraction yielded a very small amount of a sticky brown product, from which no crystalline substances could be isolated.

Pinus halepensis

The colour reaction with diazotised benzidine was of medium strength. 2.1 kg of heartwood were extracted. Like *P. pinea*, the wood had to be cut into chips and pre-extracted with ether before milling. The ether extract crystallised very soon. The *W* fraction yielded a small quantity of a brown syrup, but no crystalline sugars could be isolated from it. The water solution reduced Fehling's solution.

B and *C* also yielded resinous products, from which no crystalline substances could be isolated.

H_1 was acidified and extracted with ether. The ether extract was dried and concentrated, and the sticky brown residue vacuum-distilled. The distillate soon deposited crystals, which were recrystallised from benzene. Large, glistening, colourless leaflets,

* All melting points uncorrected.

m. p. 153—155°, were obtained. The m. p. was not depressed on admixture of pinosylvin. Yield, 0.7 g.

H_2 contained pinosylvin monomethyl ether, which was recrystallised from benzene. Yield, 3.6 g, m. p. 120—122°.

Pinus nigra var. *calabrica*

The heartwood gave a rather strong red colour reaction with diazotised benzidine solution. 1 kg of heartwood was cut into chips, pre-extracted with ether, milled, and extracted with ether and acetone in the usual manner. The ether extract (31 %) was pale yellow and deposited large crystals of resin acids.

l-Arabinose was isolated from the *W* fraction. Yield, 0.4 g, m. p. 153—155°, $[\alpha]_D^{20}$ + 101° ± 1° (equilibrium rotation in water, $c = 1.3$).

The *B*, *C* and H_1 fractions did not yield any crystalline products.

H_2 yielded 3.5 g of pinosylvin monomethyl ether, m. p. 118—119°.

SUMMARY

The heartwood constituents of four pines of Spanish origin have been investigated. The following substances were isolated.

From *Pinus pinea* L.: *l*-arabinose, pinocembrin, and pinosylvin monomethyl ether.

From *Pinus pinaster* Aiton: *l*-arabinose, pinobanksin, and pinocembrin.

From *Pinus halepensis* Mill.: pinosylvin and pinosylvin monomethyl ether.

From *Pinus nigra* var. *calabrica* Schneider: *l*-arabinose and pinosylvin monomethyl ether.

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