

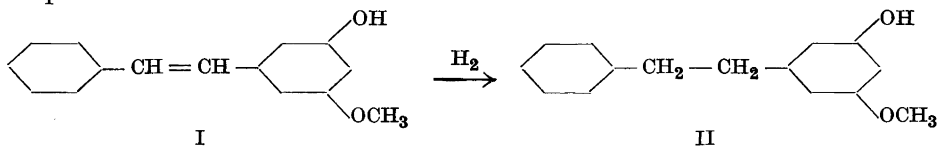
Constituents of Pine Heartwood

XXIII*. Isolation of Dihydropinosylvin Monomethyl Ether from the Heartwood of *Pinus albicaulis* Engelm.

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In Part XX of this series¹, the general methods for analysing pine heartwood extracts by paper partition chromatography were described. In the same paper it was mentioned that heartwood extracts of pines belonging to the section *Haploxyton* give rather complicated chromatograms, indicating the presence of some unknown phenolic compounds in addition to those already isolated. The most distinct one of these unknown spots has R_F about 0.80 in the standard solvent and is rather sharp. When sprayed with diazotised benzidine solution, it acquires a brownish red colour, which becomes visible immediately. The coloured spots of flavones and flavanones generally require some time (0.5–10 min.) to develop, but phenols of the pinosylvin type give visible spots at the first moment of contact with the reagent. From the R_F values given in Part XX¹, it is evident that hydrogenation of a double bond causes a small increase in R_F . Since pinosylvin monomethyl ether has $R_F = 0.71$, one might suspect the new spot to be due to a dihydro derivative of this compound.



Dihydropinosylvin monomethyl ether (II = 3-hydroxy-5-methoxy-dibenzyl), which has not been synthesised before, was easily prepared by catalytic hydrogenation of pinosylvin monomethyl ether (I). The reaction product,

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when purified by vacuum distillation, slowly crystallised on cooling, m. p. 50—52°*. It was characterised as its phenylurethan, m. p. 124—125°. When investigated on the paper chromatogram, dihydropinosylvin monomethyl ether gave a spot which was identical with that found on chromatograms of heartwood extracts.

The spot of dihydropinosylvin monomethyl ether has been found on chromatograms from most pines belonging to the section *Haploxyylon* hitherto investigated, but never in the section *Diploxyylon*. However, the spot generally is rather weak, except for three species, *P. koraiensis*, *P. cembra* and *P. albicaulis*, which, according to many botanists², constitute a separate group, *Cembrae*. These three pines give strong spots for the new compound, and they would thus be the most suitable source for its isolation. Since a large sample of heartwood from *P. albicaulis* was available, this wood was chosen as the starting material.

When the heartwood extract was divided into fractions in the usual manner, the new compound accumulated in the 4 % sodium hydroxide fraction, just as does pinosylvin monomethyl ether. The two compounds were separated by repeated distillation at low pressure, after the main part of the pinosylvin monomethyl ether had been deposited as crystals. The dihydropinosylvin monomethyl ether thus obtained proved to be identical with the synthetic sample in every respect. The yield was comparatively high, 3.2 g of the pure product being isolated from 3.7 kg of air-dry heartwood (0.09 %). Since only a part of the total quantity could be separated from pinosylvin monomethyl ether, the content of dihydropinosylvin monomethyl ether in the heartwood must be estimated to be at least 0.2 %.

EXPERIMENTAL

Hydrogenation of pinosylvin monomethyl ether

Pinosylvin monomethyl ether from *P. excelsa* (4 g) was dissolved in absolute ethanol and hydrogenated at room temperature with platonic oxide (0.2 g) as catalyst. The hydrogen uptake corresponded to 1.0 moles of hydrogen per mole of pinosylvin monomethyl ether. The reaction product, after evaporation of the solvent, consisted of a greenish brown oil, which boiled at 195—200° when distilled at 5 mm pressure. The distillate (2.7 g) was a thick, pale yellow oil, which slowly crystallised in the refrigerator. After further purification by vacuum distillation, it melted at 50—52°. A faint brownish-violet colour was obtained with ferric chloride in ethanol solution, and diazotised ben-zidine gave a strong brownish red colour.

* All melting points uncorrected.

$C_{15}H_{16}O_2$ (228.3)	Calc.	C 78.9	H 7.07	OCH_3 13.6
	Found	» 79.0	» 6.96	» 13.8

The phenylurethan was prepared by heating the phenol with phenyl isocyanate and one drop of pyridine. The product thus obtained was recrystallised from ligroin and from ethanol. Colourless needles, m. p. 124–125°.

$C_{22}H_{21}O_3N$ (347.4)	Calc.	OCH_3 8.95
	Found	» 8.93

Isolation of dihydropinosylvin monomethyl ether from
P. albicaulis

The wood sample came from a tree which had grown on Mount Hood, Oregon, U. S. A.

The air-dried heartwood (3.7 kg) was extracted in the usual way with ether and then with acetone. The ether extract, which, according to the paper chromatogram, contained considerable amounts of phenols, was concentrated and treated with light petroleum, which precipitates the phenols but dissolves resin acids. The sticky brown precipitate was added to the acetone extract, which was concentrated to a small volume, and then dissolved in ether, which precipitates "membrane substances". The ether solution was then extracted with saturated sodium carbonate, 0.2 % sodium hydroxide and 4 % sodium hydroxide. Each fraction was investigated by paper chromatography. Since the 4 % sodium hydroxide extract seemed to contain the greatest quantity of the compound desired, this extract was further investigated.

The alkaline solution was acidified and extracted with ether, and the ether solution dried and concentrated to a brown syrup. This syrup soon deposited considerable amounts of crystals of pinosylvin monomethyl ether. These crystals were separated by suction. The filtrate, on standing, deposited additional crystals, which were removed in the same way. When no more crystals could be separated, the dark brown syrup (18.5 g) was distilled at 2 mm pressure. The distillate was divided into three fractions, boiling at 179–185°, 185–191°, and 191–200°, respectively. All fractions were viscous, pale yellow oils. Total weight of distillate = 11 g. Each fraction was investigated on the paper chromatogram. Fractions 1 and 2 consisted mainly of dihydropinosylvin monomethyl ether with small amounts of pinosylvin and its monomethyl ether, but fraction 3 gave almost equally strong spots of pinosylvin monomethyl ether and its dihydro derivative.

Fractions 1 and 2 (7.2 g) were once again distilled at 2 mm pressure. The first fraction (b. p. 189–198°) contained almost pure dihydro derivative, with traces of pinosylvin, which were completely removed by washing an ether solution of the distillate with 0.3 % sodium hydroxide. On concentration of the ether solution, an almost colourless oil (3.2 g) was obtained, which soon solidified in the refrigerator, forming a colourless crystalline cake, melting between 48° and 53°. The melting range was unchanged on admixture with synthetic dihydropinosylvin monomethyl ether.

The phenylurethan, prepared as described above, melted at 124–125° alone or on admixture with the corresponding derivative of the synthetic phenol.

SUMMARY

From the heartwood of *Pinus albicaulis* Engelm., dihydropinosylvin mono-methyl ether (3-hydroxy-5-methoxy-dibenzyl) has been isolated. This compound has also been prepared by catalytic hydrogenation of pinosylvin mono-methyl ether. The new substance was detected by the aid of paper chromatography. It seems to be present in the heartwood of most pines from the section *Haploxylon*.

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