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Pinoresinol and its Dimethyl Ether from *Araucaria angustifolia* *

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Pinoresinol and its dimethyl ether have been isolated from the coniferous wood *Araucaria angustifolia*, order *Araucariales*.

The resin obtained by ethanol extraction of "ligno-tubers" (outgrowths from the roots, the sap wood of which had decayed) from *Araucaria angustifolia*, was investigated some years ago at this Institute. In connection with this work a colourless, crystalline substance, m. p. 106—107°, was isolated by chromatography on aluminium oxide but was not further investigated.

We have now reinvestigated the extract and found that the same substance is easily obtained from the neutral fraction. It melted at 107—109° and had a specific rotation of +65° in chloroform. These values agree with those of the lignan derivative pinoresinol dimethylether [1], m. p. 107—108°, $[\alpha]_D$ +65°, and the melting point was undepressed on admixture with that substance. From the phenolic fraction pinoresinol was isolated in a low yield and characterised as its diacetate. Pinoresinol dimethylether has not been found in Nature before but its optical antipode, eudesmine, has been isolated from several *Eucalyptus* species [2]. The phenol, pinoresinol, has been isolated from several pine and spruce species (*Pinus* and *Picea*, order *Pinales*) and the pinoresinol type of lignans is widespread in Nature. (*Cf.* Ref.[3]). It is of interest that these lignans have now been found in another order of *Coniferae*, *Araucariales*.

EXPERIMENTAL

The resin (55 g) was triturated with ether (3 × 100 ml). The ether was distilled off, the residue (9.2 g) dissolved in ethanol (15 ml) and a solution of potassium hydroxide (10 g) in water (4 ml) was added. Yellow crystals slowly deposited and after 24 hours the salt (0.7 g) was collected and recrystallised from ethanol. The potassium salt was acetylated by heating with acetic anhydride (5 ml) for 2 hours on the steam bath, the solution

* Also XXI. contribution on the Constitution of resin phenols and their biogenetic relations. Part XX, this journal 10 (1956) 134.

was poured into ice water and the precipitate collected and crystallised twice from ethanol. Yield, 80 mg. M. p. 162—163°, undepressed on admixture with authentic pinoresinol diacetate.

The alkaline mother liquors were concentrated under reduced pressure, water was added and the solution extracted with ether. The ether solution was washed with water, dried over anhydrous sodium sulphate and concentrated. The residue (0.8 g) partly crystallised on standing and was purified by crystallisations from methanol. Yield, 240 mg. M. p. 107—109° (corr.). $[\alpha]_D^{20}$ + 65° (*c* 2.0 in chloroform). A mixture of the substance and authentic pinoresinol dimethyl ether showed no depression of m. p.

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