

Short Communications

Constituents of Pine Heartwood XVIII*. A Note on Cryptostrobin, an Isomer of Strobopinin from the Heartwood of *Pinus strobus* L.

JOSÉ C. ALVAREZ-NÓVOA, HOLGER ERDTMAN and GÖSTA LINDSTEDT

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

The heartwood of *Pinus strobus* (Weymouth Pine) has been investigated previously¹. Among several other crystalline substances of the flavone or flavanone type, strobopinin, a substance with the composition $C_{16}H_{14}O_4$ and a m. p. of 225–227° (uncorr.), was isolated from this heartwood. The structure has not been determined, but it is believed to be a C-methyl-dihydroxyflavanone. Strobopinin is optically active, $[\alpha]_D^{20.5} - 61^\circ$ (in methanol)¹.

In the course of continued studies on the extraneous constituents of *P. strobus*, strobopinin was isolated from the acetone extract. From the mother liquors of strobopinin, a new compound was isolated in a pure state, after several recrystallisations. It formed colourless needles from dilute acetic acid, m. p. 202–203° (uncorr.), $[\alpha]_D^{20} - 33^\circ$ (methanol, $c = 1.1$). The analyses agree with the formula $C_{16}H_{14}O_4$. Thus, the new compound is an isomer of strobopinin. The presence of one C-methyl group and the absence of methoxyl groups

was indicated by the usual methods of analysis.

The name cryptostrobin is proposed for the hitherto overlooked compound. As yet it is not certain whether cryptostrobin really occurs in the heartwood. It may have been formed by a rearrangement of strobopinin under the influence of alkali during the isolation. However, its optical activity makes this assumption less probable. Work on the determination of the structures of both substances is now in progress.

Experimental. The heartwood of *P. strobus* (3 kg) was extracted, as usual, with ether and then with acetone. The extracts were separated into fractions by the method described in Part IX². The 0.2 % sodium hydroxide fraction of the acetone extract was acidified and shaken with ether. The ether solution was dried and the solvent evaporated. The remaining resinous product was dissolved in methanol, leaving an insoluble residue, consisting of crude chrysin. The methanol solution, on concentration, yielded a semicrystalline product which was triturated with benzene. The insoluble material yielded pure strobopinin after some recrystallisations from dilute acetic acid. The benzene solution was shaken with saturated sodium carbonate solution. Between the benzene and the aqueous phase a brown oily layer was formed, which was separated and acidified with dilute sulphuric acid. The emulsion obtained was shaken with ether, and the ether dried and concentrated. The residue was treated with methanol, leaving an insoluble semicrystalline product which

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*Epi-pinoresinol**

BENGT LINDBERG

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

In the naturally occurring glucosides phillyrin and forsythin, the aglycon is a lignan, related to pinoresinol. The empirical composition of phillygenol and forsythigenol is that of a pinoresinol monomethyl ether. It has recently been shown by Gripenberg that phillygenol monomethyl ether is identical to *epi*-pinoresinol dimethyl ether¹, the latter compound being the asymmetrical isomeride of pinoresinol dimethyl ether². Forsythigenol is probably identical to phillygenol³. Synthetic experiments, instituted at these laboratories, were directed towards the synthesis of the above mentioned glucosides. The glucosides of the easily available pinoresinol, however, could not be

obtained in a crystalline state, and further experiments were therefore abandoned. During these investigations, *epi*-pinoresinol was prepared. Since this substance has some interest as a potential natural product, a short description of its preparation and properties would appear to be warranted.

Epi-pinoresinol diacetate. Pinoresinol (10 g) was dissolved in a mixture of acetic acid (100 ml) and sulphuric acid (1 ml). After 40 hours the solution was poured into water (1 l), and the precipitated phenol mixture collected and acetylated with acetic anhydride (30 ml) and pyridine (20 ml). The crystalline acetates obtained were fractionated by recrystallization from ethanol. After repeated recrystallizations, a fraction of pure *epi*-pinoresinol (0.5 g), m. p. 151.5–152.5° and $[\alpha]_D^{20} + 90^\circ$ (chloroform $c = 2$), was obtained. Further recrystallizations did not change these values. The other fractions, which consisted mainly of unreacted pinoresinol diacetate, were retreated with sulphuric acid in acetic acid solution, after

* Also XIV contribution on the Constitution of resin phenols and their biogenetic relations. Part XIII, this journal 3 (1949) 982.

was recrystallised three times from toluene and finally from 60 % acetic acid. After several recrystallisations, the m. p. remained constant, 202–203° uncorr. From the mother liquors, less pure crystals could be isolated. Total yield, 2.4 g. Colour reactions: Hot nitric acid, reddish-brown; cold sulphuric acid, yellow; ferric chloride, brownish-violet; diazotised benzidine, orange-yellow.

$C_{16}H_{14}O_4$ (270.3)
 Calc. C 71.09 H 5.22 C—CH₃ 5.56
 Found » 71.13 » 5.22 » 4.62
 OCH₃ nil

The yield of acetic acid, as determined by the Kuhn-Roth method³, corresponds

to 83 % of the calculated value, which is in agreement with results obtained with similar compounds⁴. Thus, strobopinin yielded 4.69 % C—CH₃ (84 %) and methyl phloroglucinol 8.47 % (80 %).

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