

*Epi-pinoresinol**

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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

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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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Some Derivatives of 4-Dimethylamino-3,5-dinitrobenzoic Acid

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For separation of colourless substances it may sometimes be convenient to use chromatographic adsorption of coloured derivatives of these substances. Thus some alcohols have been separated as azobenzene carboxylates, aldehydes in form of their dinitrophenylhydrazones etc.

We have tried the azide and chloride of 4-dimethylamino-3,5-dinitrobenzoic acid (chrysanisic acid) as reagents for alcohols and amines, with which they give intensely coloured and well crystallized derivatives. These were, however, not especially suited for chromatographic separation, so the investigation has been discontinued and the purpose of this paper is only to describe some new compounds prepared in the course of the work.

4-Dimethylamino-3,5-dinitrobenzoic acid. Ten grams of 4-chlorobenzoic acid were dissolved in 200 g of conc. sulphuric acid and at a temperature of 80°, 33 g of potassium nitrate were added gradually. The temperature rose to 120–140° and was kept there for one and a half hour. The cooled solution was poured upon ice and the crystals of 4-chloro-3,5-dinitrobenzoic acid filtered by suction. After one crystallization from alcohol the melting point was 152°. Yield 98 %. The melting point of the pure compound is 158°, but it was found, that the over-all yield of 4-dimethylamino-3,5-dinitrobenzoic acid was larger, if no further purification of the chloro acid was performed. If desired, however, the acid may be purified via its sodium salt, which is sparingly soluble in cold sodium hydroxide solution.

A suspension of 15 g of 4-chloro-3,5-dinitrobenzoic acid in 60 ml of 33 % dimethylamine in alcohol was heated in a closed vessel at 100° for 4 hours. The solution was then evaporated to a small volume. By addition of hydrochloric acid yellow crystals of 4-dimethylamino-3,5-dinitrobenzoic acid separated. Yield 14 g, with a melting point of 210–220°. The crude product was dissolved in the minimum amount of hot alcohol and the solution filtered. By cooling large orange-yellow crystals separated. Yield 11 g + 1 g from the mother liquor, *i. e.* 77 %. M. p. 248°.

which further amounts of the *epi*-form could be isolated.

$C_{24}H_{26}O_8$ (442.5)
Calc. OCH_3 14.0 Found OCH_3 14.0

Epi-pinoresinol. *Epi*-pinoresinol diacetate (1.0 g) was dissolved in hot ethanol (25 ml) and potassium hydroxide (0.5 g) in water (0.5 ml) was added. The potassium salt precipitated at once. After cooling, it was collected on a filter, washed with ethanol, acetone and ether, dissolved in a small amount of water, and precipitated with acetic acid. The *epi*-pinoresinol (0.6 g) was recrystallized twice from ethanol. M. p. 140.5–141.5°. $[\alpha]_D^{20} + 126^\circ$ (Chloroform, $c = 2$).

$C_{20}H_{22}O_6$ (358.4)
Calc. OCH_3 17.3 Found OCH_3 17.2

A small amount of *epi*-pinoresinol was methylated with dimethyl sulfate and alkali. The dimethyl ether was isolated and recrystallized from ethanol. The melting point of the substance was 129–130°, alone or as admixture of pure *epi*-pinoresinol dimethyl ether, kindly supplied by Dr. J. Gripenberg.

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