Tetrahedron Letters No.41, pp. 3665-3668, 1965. Pergamon Press Ltd.
Printed in Great Britain.

THE STRUCTURE OF HINOKIRESINOL

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(Received 11 August 1965)

The wood of Chamaecyparis obtusa Sieb. et Zucc. has previously been investigated by many workers and the occurrence of hinokinin, hinokiol, and hinokione in the neutral part of the ether extracts of the wood has been reported by Yoshiki and Ishiguro[1] and Fukui and Chikamori[2]. The acidic part of them has now been investigated and a new phenolic compound, named hinokiresinol, $C_{17}H_{16}O_2$, m.p. 102-103°, has been isolated from it.

The present paper deals with the elucidation of the structure (I) for hinokiresinol.

The molecular formula of hinokiresinol was supported by a mass spectral determination of the dimethyl ether mentioned below, which showed a strong peak at 280 m/e.

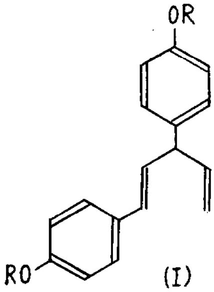
Hinokiresinol, positive ferric chloride and Millon's tests, showed infrared absorption bands at 3340 and 1250 cm^{-1} (phenolic OH) and gave the following derivatives: dimethyl ether, $C_{19}H_{20}O_2$, m.p. 64°, $[\alpha]_D$ 8.4°, dibenzoate, $C_{31}H_{24}O_4$, m.p. 127°, $[\alpha]_D$ -6.5°, diacetate, $C_{21}H_{20}O_4$, b.p.

197°/0.1 mm., $[\alpha]_D$ 0.7°, and diphenylurethane, $C_{31}H_{26}O_4N_2$, m.p. 160°, $[\alpha]_D$ 8.6°. Therefore, both oxygen atoms in hinokiresinol must be present as hydroxyl groups.

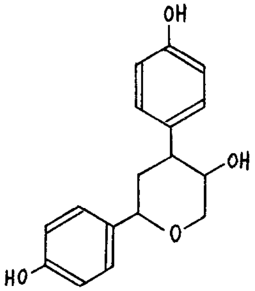
Hinokiresinol possessed two ethylenic double bonds, since it absorbed two moles of hydrogen by hydrogenation over Adams' catalyst in alcohol to give a tetrahydro compound, which was characterized as its dibenzoate, $C_{31}H_{28}O_4$, m.p. 65°. Hinokiresinol showed the ultraviolet absorption at 264 $m\mu$ (log ε 4.3) with a shoulder at 300 $m\mu$ in alcohol, whilst the tetrahydro compound showed absorption at 280 $m\mu$ (log ε 3.5) in alcohol or at 295 $m\mu$ (log ε 3.8) in aqueous alkali. These observations and the absorption bands in the infrared at 967 cm^{-1} indicated that one of the double bonds was a trans double bond, conjugated with an aromatic nucleus. The second double bond was shown to be a vinyl group by bands in the infrared at 919 and 1002 cm^{-1}, each one proton peak at τ 4.89(d), 4.83(d), and 3.86-4.09(m) in the n.m.r. of the dibenzoate (II), and peaks at τ 9.19(t) and 8.37(q) for one ethyl group in the n.m.r. of the tetrahydro dibenzoate. Further the presence of the group $-CH=CH_2$ was established by the liberation of formaldehyde on ozonolysis of the diacetate (III).

On ozonolysis of the diacetate (III), followed by oxidation with silver oxide in aqueous hydroxide solution, p-hydroxybenzoic acid and p-hydroxyphenylacetic acid were afforded. p-Hydroxybenzoic acid was also obtained in good yield by oxidation of the diacetate (III) with potassium permanganate in acetic acid at 70°, followed by treatment with alkali.

These results indicating the structure I for hinokiresinol were further supported by the synthesis of dimethyl ether of tetrahydrohinokiresinol.



(I) R=H
(II) $R=COC_6H_5$
(III) $R=COCH_3$



(IV)

Thus, β-(p-methoxyphenyl)-ethylbromide was converted to Grignard reagent, followed by reaction with p-methoxypropiophenone in benzene. The product, b.p. 150-160°/0.1 mm, on catalytic hydrogenation afforded a pale yellow oil, which, after purification by chromatography on silica gel was proved to be identical with a specimen derived from the natural hinokiresinol by a comparison of their infrared spectra.

This compound is supposed to be correlated biogenetically to sugiresinol (IV), which was isolated by Funaoka and his co-workers$^{3)}$ from the wood of *Cryptomeria japonica* and has recently been shown by Kai$^{4)}$ to have the structure (IV).

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