

A NEW FLAVONO-LIGNAN FROM HYDNOCARPUS WIGHTIANA

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(Received in UK 30 May 1973; accepted for publication 13 July 1973)

Chemical examination of the seed hulls of Hydnocarpus wightiana (Flacourtiaceae) has led to the isolation of a new $C_{15} + C_9$ compound which we have named hydnocarpin. It had m.p. $262-64^\circ$ and mol. formula $C_{25}H_{20}O_9$ (M^+ 464). It answered Mg/HCl and $FeCl_3$ colour reactions, λ_{max}^{MeOH} 270 and 335 nm (Inf1). ν_{max}^{KBr} 3450, 1639, 1282, 1156 cm^{-1} . Acetylation of hydnocarpin yielded a tetraacetate m.p. $196-98^\circ$; ν_{max}^{KBr} 1754, 1724, 1639 cm^{-1} . NMR ($CDCl_3$, 60MHz): δ 7.63-6.66 (9Ar-H), 4.97 (d, $J = 7.5$ Hz, 1H), 4.50-4.18 (m, 3H), 3.85 (s, OCH_3), 2.44 (3H) and 2.35 (6H) (Ar-O-COCH₃), 2.05 (3H, aliphatic-OCOCH₃). Methylation with dimethyl sulphate and K_2CO_3 in acetone gave a tetra methyl ether m.p. $146-48^\circ$; ν_{max}^{KBr} 3571, 1639 cm^{-1} which could be acetylated to form a methyl ether acetate m.p. $173-75^\circ$; (M^+ 548), ν_{max}^{KBr} 1639 cm^{-1} .

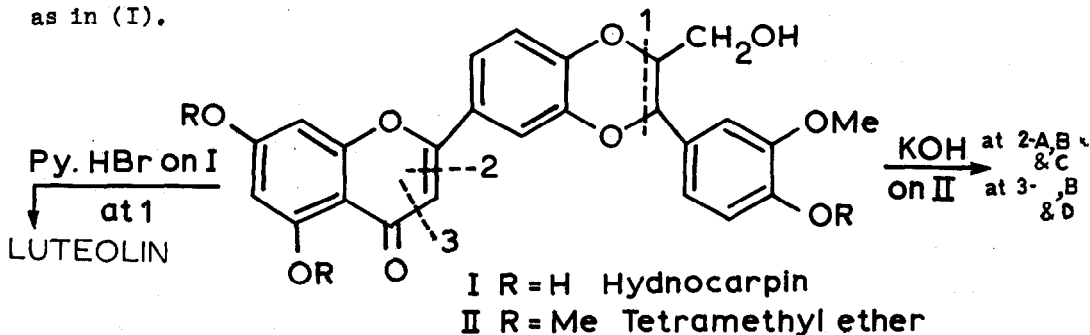
Fission of the above tetramethyl ether with absolute alcoholic KOH yielded a mixture of 2 products which could be separated as neutral (A + B) and acid (C) components. A & B were identified as phloracetophenone dimethyl ether and ohloroglucinol dimethyl ether. C Had m.p. $210-12^\circ$; λ_{max}^{MeOH} 280 nm, ν_{max}^{KBr} 3597, 1695 cm^{-1} . It formed a methyl ester m.p. $110-12^\circ$; which underwent acetylation to yield a methyl ester acetate m.p. $125-27^\circ$ (M^+ 402). Degradation of the tetramethyl ether with aqueous alcoholic KOH yielded another neutral product (D) in good amount in addition to A, B & C. It had m.p. $165-66^\circ$, ν_{max}^{KBr} 3590, 1685 cm^{-1} . It yielded an acetate m.p. $115-16^\circ$.

It was clear that C and D represented the side phenyl part of the flavonoid with a C_9 unit attached. Compound C was a benzoic acid derivative and D the corresponding acetophenone. This relationship was confirmed by treating compound D with I_2 and pyridine whereby it was converted into C.

Hydnocarpin, when heated with Py. HBr yielded luteolin, as the C_{15} part and from the water soluble portion of the products after methylation veratrol could be isolated, indicating that the other part would be a C_6-C_3 unit involved in ether linkage with the 3',4' positions of luteolin.

It was now clear that Hydnocarpin was a flavono-lignan. The only known compound of this type was silymarin¹. A comparison of their properties, particularly mass spectra, confirmed their close relationship, the former being a derivative of luteolin and the latter of taxifolin. Hydnocarpin methyl ether acetate had significant peaks at m/e 548, 312, 284, 236 (base peak), 194, 193, 177. Hydnocarpin itself had mass peaks at m/e 180 (coniferyl alcohol), 162, 138, 124.

Hydnocarpin may be considered to result from an oxidative coupling of a flavone unit (luteolin) with coniferyl alcohol. Based on analogy with silymarin and also on reactivity considerations hydnocarpin could be represented as in (I).



ACKNOWLEDGMENT: One of the authors (K.R.R.) wishes to express his gratitude to Indian Council of Agricultural Research (India) for the financial assistance.

Reference:

1. Pelter and Hansel, Tetrahedron Letters, 1968, 2911.