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The Structure of Cephalochromin

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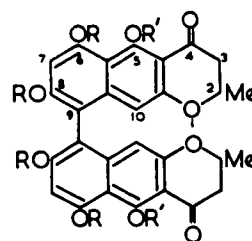
THE fungus *Cephalosporium* sp. (P.R.L. 2070) produces, in copious amounts, a yellow pigment which on continuous extraction with n-hexane yields orange crystals, $C_{29}H_{22}O_{10}$, m.p. $> 300^\circ$, $[\alpha]_D = 510^\circ$ (in $CHCl_3$). We suggest the name cephalochromin and structure (I) for this compound.

Cephalochromin has six hydroxyl groups [cf. (II)], two of which are strongly hydrogen bonded to carbonyl groups [tetra-acetate (III), tetrabenzoate (IV)]. Its i.r. spectrum has strong bands at 3100 (free OH), 2900 (broad, chelated OH), 1648, 1636, and 1590 cm^{-1} , the last three due to a hydrogen-bonded carbonyl group and aromatic frequencies found in binaphthyl systems. The compound easily yields a diphenylhydrazone, and the carbonyl functions can be reduced to methylenes with zinc and hydrochloric acid. It cannot be hydrogenated at room temperature and pressure over Raney nickel or platinum oxide.

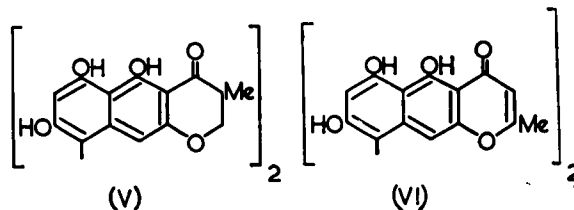
The u.v. spectrum of the compound [λ_{max} . (in EtOH) 234, 270, 295, 329, and 418 $m\mu$] is very similar to that of 4,5,4',5'-tetrahydroxy-1,1'-dinaphthyl,¹ and almost identical with that of ustilaginoidin A.² The presence of a binaphthyl skeleton is further confirmed by the detection of small amounts of perylene on fusion of the pigment with zinc and zinc chloride.^{3,4}

The n.m.r. spectrum (tetramethylsilane as standard; $\delta = 0$) of cephalochromin exhibits signals at 1.32 p.p.m. (δ) (doublet, 6 protons, 2 methyl groups), 2.64 p.p.m. (doublet, 4 protons at positions 3), 4.5 p.p.m. (multiplet, 2 protons at positions 2), 5.90 and 6.48 p.p.m. (singlets, 2 aromatic protons each), and 9.28 and 14.44 p.p.m. (singlets, 2 protons each from the phenolic hydroxyls at positions 6 and 5, respectively). Superimposed on the 6.48 p.p.m. signal was a broader signal (2 protons) centred at near 6.5 p.p.m., due to the phenolic protons at positions 8. The signals due to the phenolic protons were located by deuteration, methylation, and acetylation experiments. The signal at 14.44 p.p.m. is due to a very strongly hydrogen-bonded proton similar, for example, to the phenolic proton in 6-acetyl-2-chloro-

3,5-dimethoxyphenol,⁵ whereas that at 9.3 p.p.m. is also due to a chelated proton, but not as strongly hydrogen bonded as the former. The third type of phenolic proton appears to be almost free of hydrogen bonding, and gives a similar signal to that obtained from 2,2'-dihydroxy-1,1'-binaphthyl. The signals due to the aromatic protons are compatible only with a structure where these are in different environments.



- (I); R=R'=H
 (II); R=R'=Me
 (III); R=Ac, R'=H
 (IV); R=Bz, R'=H



The above considerations can lead to only two possible structures, (I) and (V), for cephalochromin. Structure (I) is indicated since ustilaginoidin A² (VI) is obtained on boiling cephalochromin under reflux with iodine and potassium acetate in acetic acid.⁶ Also, the "Birch acetate rule"⁷ can apply only to (I).

Whereas Allport and Bu'Lock⁸ have obtained 5-hydroxy-2-methylchromanone from a fungus, we believe this to be the first instance where the more complex dinaphthodihydropyranone system has been described. Further, its behaviour towards oxidising agents, to be later described more fully, is entirely compatible with the results and views of the above workers.

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¹ Allport and Bu'Lock, *J.*, 1958, 4090.

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³ Read, Shu, Vining, and Haskins, *Canad. J. Chem.*, 1959, 37, 731.

⁴ Read and Vining, *Chem. and Ind.*, 1963, 1239.

⁵ Arison, Wendler, Taub, Hoffsommer, Kuo, Slates, and Trenner, *J. Amer. Chem. Soc.*, 1963, 85, 627.

⁶ Geissman, *Austral. J. Chem.*, 1958, 11, 376.

⁷ Birch and Donovan, *Austral. J. Chem.*, 1953, 6, 373.

⁸ Allport and Bu'Lock, *J.*, 1960, 654.

