Fungus Pigments. XXV* Penioflavin

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In a paper [1] describing the chromatographic separation of the compounds from the chloroform soluble part of the extract of wood attacked by the fungus *Peniophora sanguinea* Bres. mention was made of a yellow fraction preceding the red pigments. Further purification of this fraction gave a yellow crystalline compound for which the name penioflavin is proposed. Penioflavin is probably identical with the yellow compound described by v. Massow.[2]

Penioflavin has the composition $C_{21}H_{16}O_6$ and gives a diacetate ($C_{25}H_{20}O_8$) and a dimethyl ether ($C_{23}H_{20}O_6$), both colourless. Two hydroxyl groups in penioflavin are thus indicated. One of them is strongly chelated (δ 12.70). Further information obtainable from the ^{1}H NMR spectrum of penioflavin is the presence of two methoxyl groups (δ 3.78 and 4.02) and an aldehyde group (δ 9.52). That the aldehyde group is aromatic and chelated follows from the IR spectra (ν 1630 cm^{-1} in penioflavin, 1690 cm^{-1} and 1695 cm^{-1} in the dimethyl ether and the diacetate, respectively). The aromatic region of the ^{1}H NMR spectra of penioflavin, the dimethyl ether and the diacetate, all contain two singlets, one proton each and a five-proton slightly broadened singlet, evidently due to a monosubstituted phenyl group.

The part of the penioflavin molecule not accounted for by these results corresponds to $C_{12}O$. To this the two hydrogens and the six substituents should be attached. The simplest ring systems which fulfil these requirements are dibenzofuran and the three isomeric naphthofurans. Biogenetic considerations, taking particularly into account the co-occurrence with peniosanguin (*1* or *2*),[3] strongly favor a dibenzofuran structure for penioflavin. Using similar biogenetic considerations the substituents can be located as in *3*, with *4* as a less likely alternative.

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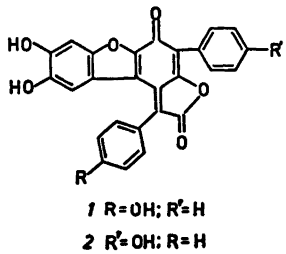
However, an X-ray analysis of the diacetate showed that this has the structure *5* [4] and hence the correct structure of penioflavin is *4*.

It is thus evident that penioflavin is not a degradation (and methylation) product of peniosanguin (*1* or *2*), as structure *3* would have implied. However, peniosanguin and penioflavin can, at least formally, be derived from a common 2,5-diphenylbenzoquinone precursor (*6* or its equivalent), with the formation of the new carbon-carbon bond taking place at opposite quinone carbonyls as indicated in Scheme 1. This hypothesis, if correct, lends some support for *1* rather than *2* as the structure of peniosanguin.

Experimental. Melting points were determined by means of a Kofler melting point microscope and are uncorrected. Spectra were obtained using the following instruments: UV spectra on a Beckman DK-2, IR spectra on a PE-700, ^{1}H NMR spectra on a Jeol PMX60 and mass spectra on a PE 270B. Elemental analyses were carried out by Ilse Beetz, Microanalytisches Laboratorium, Kronach, German Federal Republic.

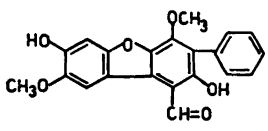
Isolation of penioflavin. The combined foreruns from the chromatography of the pigments produced by *Peniophora sanguinea* [1] were rechromatographed on Silica-gel with chloroform as eluent. From the fractions, which on TLC showed a single yellow spot, *penioflavin* was obtained as yellow crystals with a double m.p. 206/215 °C. Anal. $C_{21}H_{16}O_6$: C, H. UV (EtOH) λ_{max} (log ε): 266 (4.56), 298 (4.36), 314sh (4.21), 372 (3.81) nm; λ_{min}(log ε): 234 (4.20), 281 (4.16), 333 (3.46) nm. IR (KBr): 3320, 1630, 1470, 1440, 1355, 1340, 1280, 1140, 1040 cm^{-1}. ^{1}H NMR (60 MHz; $CDCl_3$): δ 3.78 (3 H, s), 4.02 (3 H, s), 5.96 (1 H, s), 7.20 (1 H, s), 7.44 (5 H, s), 7.62 (1 H, s), 9.52 (1 H, s), 12.70 (1 H, s). MS [70 eV; *m/e* (% rel int.)]: 364 (100, M$^+$), 349 (25), 317 (19), 289 (22).

Penioflavin dimethyl ether. To penioflavin (30 mg) dissolved in dimethyl formamide was added methyl iodide (0.5 ml) and K_2CO_3. The mixture was stirred overnight at room temperature giving a colourless solution. Water was then added and the stirring continued, to allow the excess methyl iodide to evaporate. The white crystalline precipitate was further

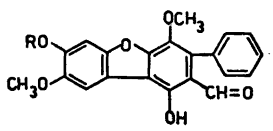


1 R=OH; R'=H

2 R'=OH; R=H

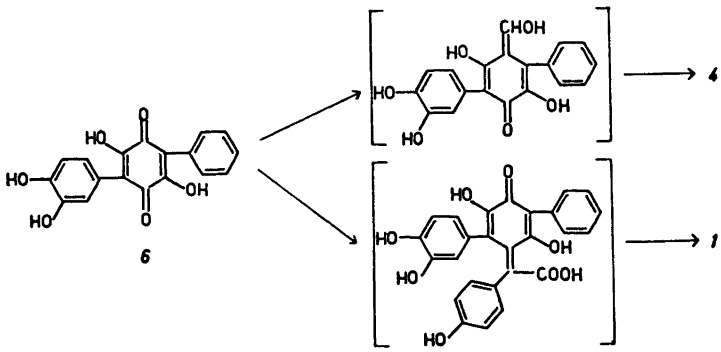


3



4 R=H

5 R=Ac



Scheme 1.

purified by TLC ($CHCl_3$ as eluent) and recrystallised from $CHCl_3$/light petroleum, m.p. 154–157 °C. Anal. $C_{33}H_{20}O_6$: C, H. UV (EtOH) λ_{max}(log ε): 263 (4.58), 308 (4.23) nm; λ_{min} (log ε): 233 (4.25), 299 (4.20) nm. IR (KBr): 1690, 1590, 1475, 1340, 1275, 1220, 1125, 1040 cm^{-1}. ^1H NMR (60 MHz, $CDCl_3$): δ 3.90 (3 H, s), 4.02 (6 H, s), 4.13 (3 H, s), 7.19 (1 H, s), 7.36 (5 H, s), 7.58 (1 H, s), 9.84 (1 H, s). MS [70 eV; *m/e* (% rel. int.)]: 392 (100 ,M^+), 377 (15), 362 (35), 347 (13), 346 (23), 345 (10), 331 (9), 188.5 (15), 181 (14).

Penioflavin acetate (5). Penioflavin (30 mg) was allowed to stand one day with acetic anhydride (2 ml) to which a drop of pyridine had been added. Ice was then added to the stirred colourless solution. The precipitate was recrystallised from dichloromethane/light petroleum. M.p. 228–230 °C. Anal. $C_{25}H_{20}O_8$: C, H. UV (EtOH) λ_{max}(log ε): 264 (4.45), 309 (3.88), 320sh (3.82) nm; λ_{min}(log ε): 234 (4.20), 300 (3.83) nm. IR (KBr): 1765, 1595, 1470, 1440, 1345, 1285, 1225, 1200, 1125, 1040 cm^{-1}. ^1H NMR (60 MHz, $CDCl_3$): δ 2.38 (3 H, s), 2.56 (3 H, s), 3.95 (6 H, s), 7.38 (1 H, s), 7.47 (6 H, s), 9.63 (1 H, s). MS [70 eV; (% rel. int.)]: 448 (4, M^+), 406 (31), 364 (100), 349 (14), 317 (10), 289 (10), 43 (13).

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4. Hiltunen, L. and Niinistö, L. *Personal communication.*

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