Wightianone–Palmitic Acid, a Clathrate from *Calophyllum wightianum*

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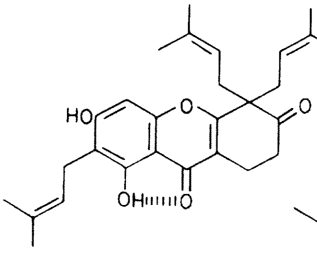
Summary The heartwood of *Calophyllum wightianum* T. Anders gives, upon extraction with benzene, a clathrate composed of 4 moles of wightianone (**1**), a new member of the rare tetrahydroxanthone series of phenols, and 1 mole of fatty acid, mainly palmitic.

FROM the heartwood of *Calophyllum wightianum* T. Anders (Guttiferae) benzene extracts a yellow phenol, wightianone, which seemed to fit none of the common categories of heartwood phenols. Moreover, the ^{1}H n.m.r. spectrum required the presence of 40 protons whereas accurate mass measurements indicated a molecular ion *m/e* 450·2493 incompatible with any molecular formula in the series $C_xH_{40}O_y$. After many attempts at further purification by chromatography and crystallisation we noted that a six-proton singlet at δ 1·25 varied slightly in relative intensity. This band was therefore assumed to be intrusive in its entirety and the pigment was assigned the molecular formula $C_{28}H_{34}O_5$ and eventually the structure (**1**). Because material was very limited the only reaction studied in detail was hydrogenation, which furnished a hexahydro-derivative assigned the molecular formula $C_{28}H_{40}O_5$ from n.m.r. and mass spectral results on the assumption that intrusive protons were no longer present.

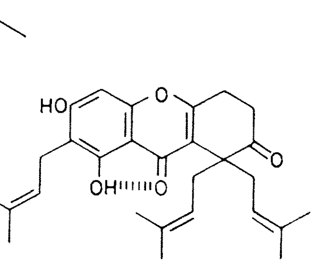
The usual evidence readily established the presence of one chelated and one rather acidic phenolic proton along with one carbonyl group (ν_{max} 1700 cm^{-1}; ^{13}C n.m.r. δ 212 p.p.m. in the hexahydro-derivative), as in a saturated acyclic ketone or a cyclohexanone system, and another carbonyl group in a highly conjugated and/or hydrogen bonded situation (ν_{max} 1645 cm^{-1}; ^{13}C n.m.r. δ 181·4 p.p.m. in the hexahydro-derivative). These results pointed to a 5,7-dihydroxychromone nucleus and this was confirmed by the u.v. spectrum (λ_{max} 230, 258, 300, and 330 nm) and general correspondence with chromones related to peucenin.[1,2]

Three prenyl substituents were disclosed by mass spectroscopic losses of C_5H_9, C_4H_6, and C_4H_8 fragments from the molecular ion to give the strongest peaks in the spectrum;[3] the ^{1}H n.m.r. spectrum showed the requisite bands for

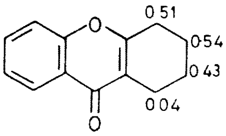
3 vinylic protons and 6 vinylic methyl groups together with bands for 3 methylene groups only one of which was attached to aryl carbon (benzylic methylene resonance at δ 3·48) This leaves one vacant aromatic position between two oxygen atoms (ArH, δ 6 34) but does not indicate which one A strong positive Gibbs test[2,4] requires a free position *para* to the hydroxy group and so orientates the phenolic system in (**1**)



(1)



(2)



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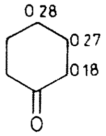

(4)

The other two prenyl groups are attached to sp^3 carbon but the methylene resonances, though at two different fields (δ 3 16 and 2 70), cannot indicate two different methylene groups The splitting patterns and double irradiation experiments show that each 2-proton band consists of one resonance from each methylene group *i e* there are two *identical* spin systems $-CH_AH_BCH_X{=}C<$ (J_{AX} 7 7, J_{BX} 8 5, and J_{AB} 13 5 Hz) superimposed and therefore two prenyl groups identically situated

The ^1H n m r evidence (in $CDCl_3$) finally shows that the remaining protons belong to the grouping CH_2CH_2 attached at each end to sp^2 carbon This leaves only one carbon atom unassigned, and the two equivalent prenyl groups must be attached to it, the splitting pattern being a consequence of diastereotopicity Assembly of these structural features leads only to structures (**1**) and (**2**) Because material was very limited, we sought to distinguish between these structures by the aromatic solvent shift method using benzene,[5] which caused the ring methylene resonances to move upfield and almost to the same position so that the original two triplets became a somewhat broadened singlet Relevant shifts for tetrahydroxanthone[6] (**3**) and cyclohexanone (**4**) are shown in the diagrams, assuming solvent shifts to be approximately additive, we now expect solvent shifts for structure (**1**) of 0 61 and 0 31 p p m and for structure (**2**) of 0 72 and 0 78 p p m The pigment actually suffers shifts of 0 59 and 0 29 p p m and therefore has structure (**1**)

The intrusive 6-proton singlet seemed likely to originate from a long chain of methylene groups and there is, just clear of the noise, a triplet at δ 0 88 that could be ascribed to a terminal methyl group while a similar triplet at δ 2 37 suggested methylene attached to sp^2 carbon and so the presence of a fatty acid A rough determination of the methyl–methylene ratio gave for the acid a size between dodecanoic and stearic acids Since conventional means had failed to separate the pigment from the acid, the pigment was dissolved in warm methanol saturated with urea so that, when this crystallised first, it would tend to take the acid with it as a clathrate[7] Two successive treatments reduced the intrusive band to a relative intensity of about 1 proton but losses were too great for the separation to be completed

The acid recovered from the urea crystallizate was found by methylation (CH_2H_2) and g l c analysis to be palmitic with a little myristic The original pigment had had m p 167 °C whereas the 'acid-free' pigment melted at *ca.* 130 °C, a fall of *ca* 35 °C showing that the original pigment was itself an inclusion compound This was then reconstituted by crystallising the 'pure' pigment with authentic palmitic acid and had m p 160 °C and was otherwise indistinguishable from the original material except that the intrusive band was somewhat stronger (clathrates are seldom perfectly stoicheiometric) Relative proton intensities showed the pigment and acid to be in the molar ratio 4 : 1, as are many similar inclusion compounds between deoxycholeic acid and fatty acids[7] It is also interesting that this one crystallises in long regular hexagonal prisms as do the urea clathrates

A pigment named zeyloxanthonone and assigned structure (**2**) has been reported in a related plant, *Calophyllum zeylanicum*[8] No evidence was advanced for the orientation of the aromatic part and clathrate formation has not been discussed It is therefore possible that the two pigments are identical

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