

UMTATIN AND RELATED CHROMONES FROM THE HEARTWOOD OF

PTAEROXYLON OBLIQUUM

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We have already described the occurrence in the heartwood of the African sneezewood, Ptaeroxylon obliquum, of a number of coumarins (1) and of chromones (2). It is now clear that this source is especially rich in chromones, and this communication deals with the structure of umtatin and related compounds. Those chromones certainly known to contain a benzoxepin ring system will be described separately: in all, thirteen chromones have been characterised so far.

In addition to heteropeucenin 7-methyl ether Ib, we have now identified the parent compound, heteropeucenin Ia, $C_{15}H_{16}O_4$, m.p. 195° , and the dimethyl ether Ic, $C_{17}H_{20}O_4$, m.p. $153-155^{\circ}$, neither of which has been recognised as a natural product before. The structures follow from analytical and spectroscopic evidence together with the methylation of heteropeucenin first to the 7-methyl ether and then to the dimethyl ether. Peucenin (3), $C_{15}H_{16}O_4$, m.p. 215° , with structure IIa, was also found and characterised by conversion into the 7-methyl ether IIb, m.p. 109° , different from Ib but having nearly the same nuclear magnetic resonance spectrum. Other workers (4,5) have noted peucenin in Ptaeroxylon heartwoods.

The availability of peucenin has enabled us to re-investigate the validity in this series of the Gibbs test for phenols having the para position free. This test has not given reliable results mainly because green colours are often developed instead of the normal blue. The response is common amongst chelated phenols including salicylaldehyde, but is usually regarded as a negative indication. We have adopted the use of sodium hydrogen carbonate buffers and watched the development of a clear green colour visually or as an absorption band near 700 μ . If the response is positive, a strong colour develops during 30 minutes and continues to increase in intensity; if negative, either no such absorption appears or it is weak, gives a

brownish colour, and gradually fades. Peucenin, its 7-methyl ether, and salicylaldehyde give positive responses of this kind, while heteropeucenin and its derivatives give negative responses. The use of the pyridine-borate buffer technique (6) is possible but gives less definite results and is less convenient.

Umtatin, $C_{15}H_{12}O_5$, m.p. 178° , $[\alpha]_D^{21} -56.3$ (c, 0.15 in $CHCl_3$), has structure IIIa. The ultraviolet spectrum is that of a chromone derived from phloroglucinol, and the compound gives a purplish ferric reaction and a positive Gibbs test. Mild acetylation yielded the mono-acetate IIIb which was soluble enough in deuteriochloroform to allow a good nuclear magnetic resonance spectrum to be obtained. This showed the presence of one benzenoid proton (τ 3.7), one chelated hydroxyl proton (τ -2.5) and one proton at position 3 on the pyrone ring (τ 3.8). Three-proton bands appeared at τ 8.26 and τ 7.85 corresponding to olefinic methyl and acetyl methyl groups, respectively. Two-proton bands appropriate to the methylene protons of the vinyl and acetoxymethyl systems appeared close together near τ 5. Multiplets at τ 4.7 (one proton) and 6.9 (two protons) formed an ABX system as expected for the three protons of the hydrofuran ring.

Structure IIIa for umtatin was further established as follows. Hydrogenation of the acetate gave a dihydro-derivative lacking the properties of an isopropenyl substituent but exhibiting a six-proton doublet at τ 9.0 due to an isopropyl group. Interaction of umtatin with methanesulphonyl chloride in pyridine supplied the related 2-chloromethylchromone derivative IIIc which, reduced by zinc in acetic acid, afforded the 2-methylchromone IIIId the protons of the new methyl group resonating at τ 7.69. Hot hydriodic acid induced in IIIId a Wessely-Moser rearrangement of the chromone ring and, in the hydrofuran ring, an allylic fission followed by ring closure leading to isoheteropeucenin IV, in poor yield, but identical with an authentic specimen and giving a negative Gibbs test.

2-Hydroxymethylchromones may be regarded as vinylogous α -ketols and in alkaline solution are presumably converted by hydrolysis into true α -ketols. Hence they strongly reduce Fehlings reagent whereas 2-methylchromones are unable to do so in the absence of any other reducing group. For example, umtatin IIIa rapidly reduces Fehlings reagent in conditions under which the related 2-methylchromone IIIId is inert. Peucenin and heteropeucenin and their ethers are also without action on Fehlings reagent, and we have found the test a most useful one.

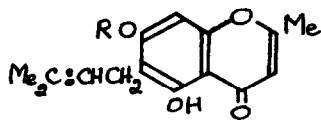
Ptaerochromenol Va, $C_{15}H_{14}O_5$, m.p. 176° , with the general properties of a 5-hydroxychromone, is a 2,2-dimethylchromone derivative exhibiting at τ 8.6 a six-proton band due to the two

methyl groups and at τ 3.47 and 4.51 doublets ($J = 10$ c.p.s.) due to the olefinic protons. The presence of a 2-hydroxymethylchromone arrangement was indicated by the ready reduction of Fehlings reagent and supported by the n.m.r. spectrum (of the derived mono-acetate Vb) which included a methylenic band at τ 5.1 similar to that given by umtatin acetate IIIb. The angular annelation was suggested by the near identity of the ultraviolet spectrum of ptaerochromenol with that of alloptaeroxylin Vc and the negative Gibbs test. Confirmation of structure Va was obtained by treating ptaerochromenol with methanesulphonyl chloride in pyridine and then with zinc in acetic acid, a sequence giving alloptaeroxylin Vc identical with an authentic specimen.

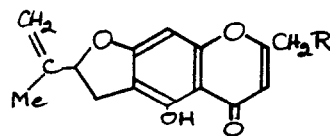
Ptaerocyclin, $C_{15}H_{14}O_7$, m.p. 266° , has not been obtained in quantities large enough to allow a complete structural investigation, but expression VI will serve to summarise our present knowledge. The compound is optically active and has the spectroscopic properties of a 7-alkoxy-5-hydroxy-2-methylchromone. It does not reduce Fehlings reagent but gives a positive Gibbs test. It contains one benzenoid proton (τ 3.55) but resists hydrogenation so no olefinic system is present. Since it is attacked by periodic acid it should be a 1,2-glycol, but we have been unable to identify any fission product. In deuteriodimethyl sulphoxide the compound exhibits two hydroxylic proton resonances removed by deuterium oxide: one, a singlet (τ 4.7), corresponding to a tertiary alcoholic function; the other, a doublet (τ 4.42), to a secondary alcoholic function. The latter function also accounts for a doublet at τ 6.40 which changes to a singlet on deuteration and corresponds to the methine proton. There are two AB quartets, one centered at τ 6.23, the other at 6.05, and both seem to originate from methylene groups attached to oxygen atoms in rigid cyclic systems. The last proton to be accounted for resonates at τ 4.65 and must therefore be attached to a carbon atom carrying at least one oxygen atom. There are no clear indications of dihedral couplings, and this fact excludes many structures that would otherwise be possible. In structure VI the stereochemistry of the secondary alcoholic function can be such that the dihedral angle formed with the benzylic proton is near to 90° and so unlikely to give rise to a sizable coupling constant. Moreover, the bicyclic system is rigid and the benzylic proton can be held almost exactly in the plane of the aromatic system thus accounting for the low field at which it resonates.



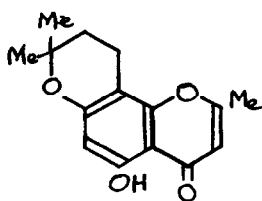
Ia; $R^1=R^2=H$
 Ib; $R^1=Me, R^2=H$
 Ic; $R^1=R^2=Me$



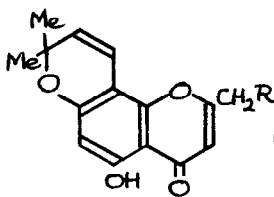
IIa; $R=H$
 IIb; $R=Me$



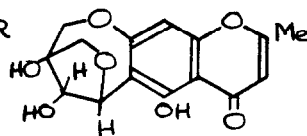
IIIa; $R=OH$
 IIIb; $R=OAc$
 IIIc; $R=Cl$
 IIId; $R=H$



IV



Va; $R=OH$
 Vb; $R=OAc$
 Vc; $R=H$



VI

References

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