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CONCERNING HYPOPHYLLANTHIN

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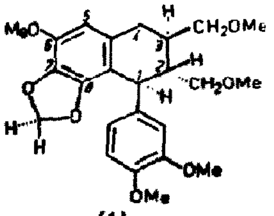
Abstract: The structure (1) for hypophyllanthin was confirmed by X-ray crystallography.

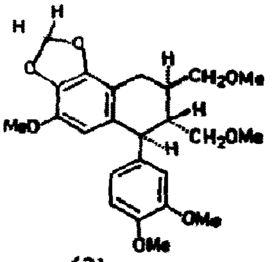
We have proposed[1] earlier structure (1) for hypophyllanthin, a constituent of Phyllanthus niruri Linn, based on ^{1}H n.m.r. and mass spectral data. In particular the double resonance experiments clearly indicated that irradiation of the benzylic protons (δ 2.70, $C_{(4)}$-H) caused a 21% increase in the integrated intensity of the proton (δ 6.34, $C_{(5)}$-H) while no enhancement of the signal intensity was observed when the doubly benzylic proton (δ 4.1, $C_{(1)}$-H) was irradiated. Further, the methylenedioxy protons appeared as a pair of doublets at δ, 5.62 and 5.70, indicating their unsymmetrical nature and also their location in ring-A. This was reconfirmed from a study of its 270 MHz spectrum.

Recently[2] an alternative structure (2) was postulated for hypophyllanthin, based on the analysis of the ^{13}C n.m.r. of aryltetralins. The revised structure appeared to be untenable since this structure does not explain our N.O.E.results, as observed[3] in other systems. Further the assignment of carbon resonances of hypophyllanthin, in particular of the ring-A carbons, appear to be based on erroneous assumptions. In view of this controversy, we reinvestigated this problem and determined the crystal structure of hypophyllanthin via X-ray crystallography.

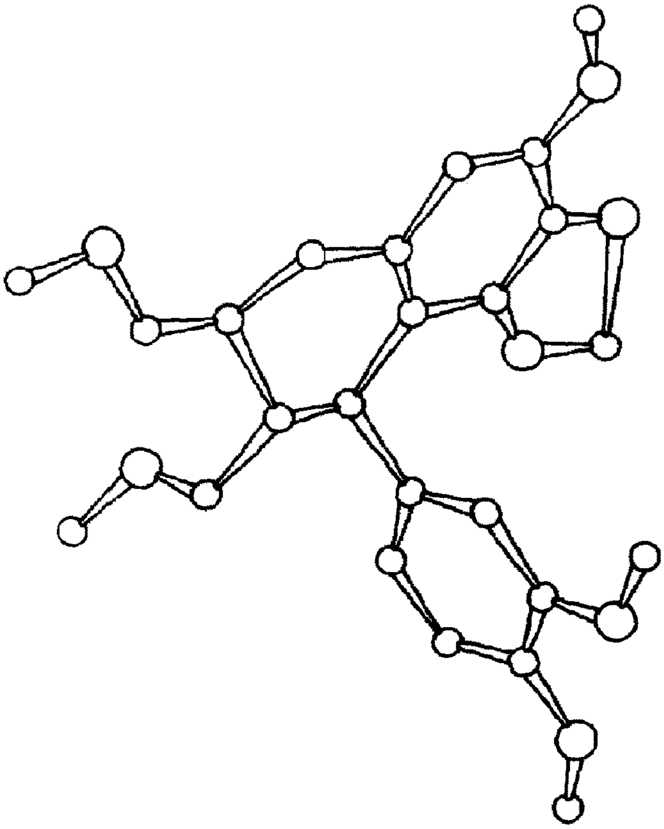
The colourless crystals of hypophyllanthin used for X-ray studies were orthorhombic and belong to space group $P2_12_12_1$. The unit cell parameters are a = 5.730 (1), b = 13.542 (1) and c = 29.431 (5) Å with four molecules in the unit cell. A total of 1923 reflections were collected on a CAD-4 diffractometer (λ= 1.542 Å, $\omega/2\theta$ scan) out of which 1245 were judged as significant $[\,|F_{obs}| \geqslant 2\sigma(|F_{obs}|)\,]$. The direct method programme MULTAN-78[4] was used for the structure determination. The E-map calculated with the set of phases having highest psi zero figure of merit revealed a stereochemically meaningful fragment of seven atoms. The structure was developed from this by repeating Karle recycling procedure[5] three times, the final E-map contained all the thirtyone non-hydrogen atoms (fig.1). The R-factor at the present stage of refinement of positional and isotropic thermal parameters of non-hydrogen atoms using block diagonal least squares method is 10.6%. The X-ray crystallographic results are in conformity with the structure proposed[1] via ^{1}H n.m.r. and mass spectral data.



(1)



(2)



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