

$Mg_2P_4O_{12}$, whereas only one line is observed in $Cu_2P_4O_{12}$ (in Raman). Similar splittings are observed in the other regions also. The characteristic IR absorption line of a cyclic P_4O_{12} ion (symmetric POP stretching) is observed as a doublet at 742 and 719 cm^{-1} in $Mg_2P_4O_{12}$, whereas only one line is observed for $Cu_2P_4O_{12}$ (at 730 cm^{-1}). The complete assignment of the observed frequencies is given in table 1. The frequencies of $Cu_2P_4O_{12}$ are also given in table 1 for comparison.

The splitting of different modes into several components indicates that the symmetry of the anion in $Mg_2P_4O_{12}$ is lower than that in $Cu_2P_4O_{12}$ which has D_{2d} symmetry. Thus it can be concluded that the symmetry of the P_4O_{12} ion in $Mg_2P_4O_{12}$ is S_4 .

The authors thank Prof. Bagieu-Beucher, CNRS, France, for providing the sample, and DST, New Delhi, for financial assistance.

6 May 1988; Revised 21 July 1988

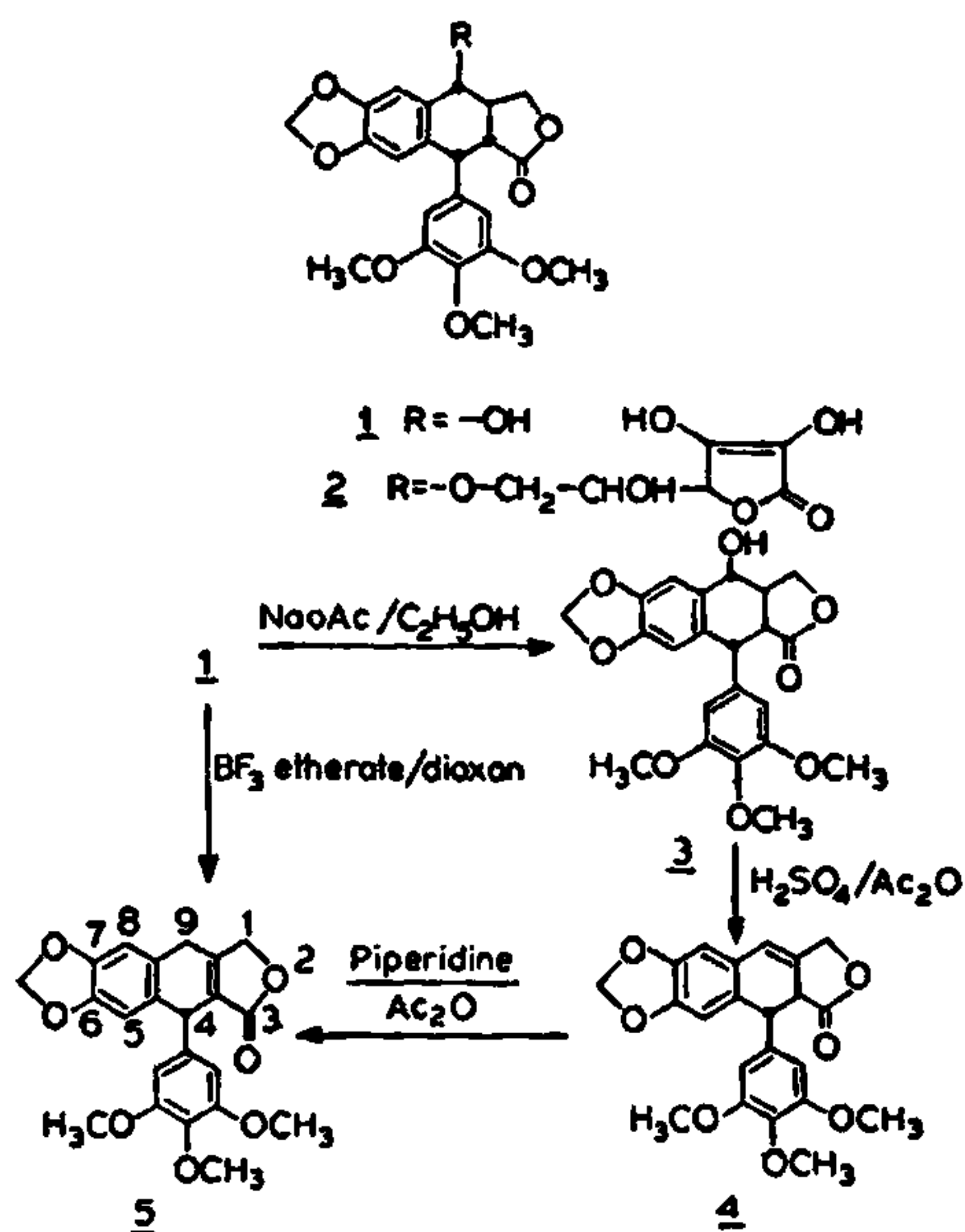
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A NEW ONE-STEP PREPARATION OF β -APOPICROPODOPHYLLIN FROM PODOPHYLLOTOXIN

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BETA-apopicropodophyllin was prepared in one-step in excellent yield by dehydration of podophyllotoxin (1) with boron trifluoride etherate in dioxan.

Podophyllotoxin (1) and several of its analogues and derivatives are cytostatic spindle poisons¹ and



antitumour agents, some at clinical level². 1 contains a *trans* fused highly strained γ -lactone system³, a feature that correlates with epimerization of 1 to its thermodynamically stable *cis* epimer picropodophyllin(3)⁴. β -Apopicropodophyllin (5), a dehydration product of 1, contains a *cis*-fused lactone system and acts as a much stronger antimitotic agent⁵; 5 was prepared previously by a three-step procedure⁶ (starting from 1 involving epimerization of 1 to 3, dehydration of 3 to α -apopicropodophyllin (4) and base-catalysed isomerization of 4 to 5) and also by a single-step procedure using *p*-toluensulphonyl chloride and pyridine⁷.

As reported earlier⁵ some of the ether derivatives of 1 were more biologically active than 1. It was envisaged that incorporating ascorbic acid in 1 through an ether linkage as in 2 might enhance the biological activity and therefore we decided to prepare the compound 2.

On stirring a mixture of 1 and ascorbic acid in the presence of borontrifluoride etherate in dioxan at room temperature and follow-up of the reaction, it was found that β -apopicropodophyllin (5) was the major product. When a mixture of 1 and ascorbic acid in dioxan was stirred no new product was obtained while only borontrifluoride etherate effected the dehydration of 1 with concomitant isomerization

to 5. The IR and PMR spectra are in accordance with the structure 5.

A mixture of 1 (0.5 g, 0.0012 mol) and borontrifluoride etherate (3 ml) in dry dioxan (15 ml) was stirred at room temperature for 15 h under N_2 atmosphere. Excess borontrifluoride etherate was removed under reduced pressure. After adding ice-cold water (30 ml) to the reaction mixture, the precipitated solid was extracted with diethyl ether (3 × 30 ml), ether extract washed with water (3 × 20 ml) and dried (Na_2SO_4). After evaporating the ether, the solid residue was column chromatographed (40 × 1 cm) using chloroform as the eluant. TLC monitored first fraction was separated, condensed to 5 ml and the petroleum ether (40–60°) was added when 5 was obtained as a white solid.

Yield 0.42 g (88%), m.p. 212–14° (lit. 214–15°)⁷. IR (nujol); 1760 (C=O), 1700 (C=C), 1600 cm^{-1} (aromatic C=C), PMR ($CDCl_3$): δ 3.75 (s, 11H, (OCH₃) and C₉-H), 4.8 (bs, 3H, C₁-H and C₄-H), 5.90 (s, 2H, O-CH₂-O), 6.30 (s, 2H, C₂-H and C₆-H) 6.60 (s, 1H, C₅-H), 6.70 (s, 1H, C₈-H).

28 March 1988

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HIGH PERFORMANCE LIQUID CHROMATOGRAPHIC ANALYSIS OF CERTAIN PHENOLS AND PHENOLIC ACIDS FROM PLANTS

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High performance liquid chromatography¹⁻³ (HPLC) is one of the most efficient among the recent analytical techniques of plant analysis. It is superior to other similar techniques like TLC, GLC, etc. in terms of the universality of application and reproducibility of results. A recent modification⁴, on line HPLC, combining the recording of UV-visible absorption spectra of individual eluate in MeOH with the presence of certain diagnostic reagents has revolutionized the easy identification of plant phenolics. The identification of phytotoxins and phytoalexins in plants under diseased conditions is an important aspect of phytochemical applications in plant pathology for which HPLC analysis is of great use. During our current work⁵ on the abnormal constituents of *Sorghum vulgare* affected by different fungi, we observed the presence of certain phenolic compounds responsible for offering resistance to microbial attack. To facilitate easy identification of these unusual phenolic compounds by HPLC it was necessary to keep the HPLC pattern for common plant phenols under standardized conditions. The HPLC data acquired for twenty phenolic or acidic phytochemicals using Shimadzu LC-6A liquid chromatograph are reported in this note. The test samples were either isolated from plant sources⁶ or procured from commercial firms.

Solutions were prepared in methanol and a concentration of 0.5–1 mg/ml was used. Both Zorbax C8 and Zorbax ODS (C18) reverse phase columns (4.6 mm i.d. × 25 cm) with 10% acetic acid:methanol (6:4) as mobile phase using a constant flow rate of 1 ml/min were employed. Pressures of $1 \times 100 \text{ kg F cm}^{-2}$ and $1.8 \times 100 \text{ kg F cm}^{-2}$ respectively and an ambient temperature were maintained. UV absorption was done at 280 nm. Concentrations were determined by area integration with an automatic integrator. The results are presented in tables 1 and 2. The lower detection limit was around 0.1 μg .

The results indicate that HPLC analysis can profitably be used for qualitative and quantitative analysis of common plant phenols and acids. The