NOVEL PRENYLATED PTEROCARPANS FROM PHASEOLUS LUNATUS (LEGUMINOSAE)

S.A. Adesanya, M.J. O'Neill, I.R. Pantry and M.F. Roberts, Department of Pharmacognosy, The School of Pharmacy, University of London, 29-39 Brunswick Square, London WClN 1AX

Phaseolus species produce fungitoxic isoflavonoids in response to stress (O'Neill et al, 1983). Certain pterocarpanoid isoflavonoids are highly fungitoxic and may be potentially useful antifungal agents in horticulture or medicine. In the present study we have isolated 4 prenylated pterocarpans from an extract of P. lunatus. CuCl₂-treated seedlings were extracted with EtOH and fungitoxic substances in the extract were detected using a TLC-bioassay against Cladosporium cucumerinum. Chromatography over polyamide and silica gel yielded phaseollidin (1), $2-(\gamma\gamma-dimethylallyl)$ -phaseollidin (2) and two novel natural products (3) and (4), which were identified by their UV, MS and $^{1}\text{H-NMR}$ characteristics. Mass spectroscopy revealed (3) to be an isomer of (2) and ^{1}H -NMR spectroscopy confirmed the pterocarpan nature (Pachler and Underwood, 1967) and the presence of 2 isopentenyl chains. The B-ring substitution patterns for (3) and (2) were identical but the A-ring for (3) had two ortho coupled protons. The use of UV shift reagents (Ingham, 1982) indicated that a phenolic hydroxyl moiety was located at C-3. This compound was therefore characterised as 4-($\gamma\gamma$ dimethylallyl)-phaseollidin (3). The remaining pterocarpan (4) was identified as a 6a-hydroxy derivative by its dehydration in acid to form a pterocarpene (Ingham, 1982). Mass and ¹H-NMR spectroscopy indicated that the 6a-hydroxypterocarpan possessed two phenolic hydroxyls and two isopentenyl chains and enabled (4) to be characterised as $2-(\gamma\gamma \text{ dimethylallyl})-6a-hydroxy-phaseollidin.$ The occurrence of the pterocarpans in P. lunatus is of taxonomic interest. Phaseollidin (1) has been isolated from all Phaseolus species examined to date whereas diprenylated isoflavonoids have not previously been isolated from the genus. Compound (2) has been reported to occur only in the genus Erythrina (Kamat et al, 1981). Phaseollidin inhibits spore germination in \overline{C} . cucumerinum at 25 μ g ml⁻¹. The fungitoxic activities of the other pterocarpans isolated from P. lunatus deserve investigation.

$$\begin{array}{c} R^{1} \\ HO \\ R^{2} \\ R^{2} \\ R^{3} \\ R^{3} \\ R^{3} \\ R^{4} \\ R^{4} \\ R^{2} \\ R^{4} \\ R^{2} \\ R^{4} \\ R^{2} \\ R^{4} \\ R^{2} \\ R^{4} \\ R^{4} \\ R^{2} \\ R^{4} \\ R^{2} \\ R^{3} \\ R^{2} \\ R^{4} \\ R^{4} \\ R^{4} \\ R^{4} \\ R^{4} \\ R^{4} \\ R^{2} \\ R^{3} \\ R^{2} \\ R^{3} \\ R^{2} \\ R^{4} \\ R^$$

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