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PLANT GROWTH INHIBITING PROPERTIES OF PLUMIERIDE FROM *PLUMERIA OBTUSIFOLIA**

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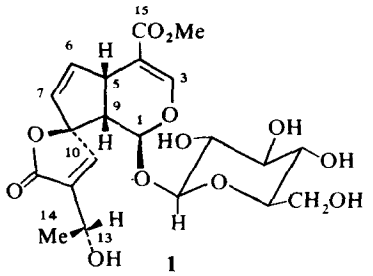
Key Word Index—*Plumeria obtusifolia*; Apocynaceae; plant growth inhibitor; iridoid glucosides.

INTRODUCTION

As part of a program involving Vietnamese plants of biological and medical interest, we investigated the bark of *Plumeria obtusifolia* (Apocynaceae) used in Vietnamese folk medicine as an antiphlogistic. We now wish to report the isolation of a constituent with significant plant growth inhibiting activity which was shown to be identical with the iridoid glycoside plumieride (**1**).



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RESULTS

The residue of a methanol extract of dried powdered bark, after addition of water, was extracted with ether benzene (1:1) followed by *n*-butanol. Evaporation of the *n*-butanol phase gave a residue which was chromatographed over Si gel. Elution with $CHCl_3$–MeOH (9:1) yielded crystals (1%), mp 156–158°, inhibiting the gibberellin-induced growth in different bioassays.

Only in the negative ion MS did the compound show [1, 2] a molecular ion at *m/e* 470 ($C_{21}H_{26}O_{12}$, M^-) whereas the high resolution positive ion spectrum was characterized by prominent fragment ions at *m/e* 308 ($C_{15}H_{16}O_7$, $M^+ - C_6H_{10}O_5$) and 291 ($C_{15}H_{15}O_6$, $M^+ - C_6H_{11}O_6$), both suggesting a $C_6H_{11}O_6$ sugar side chain moiety with cleavage of the aglycone-O bond in the latter case. Thus, the ion at *m/e* 308 indicated the elemental composition of the aglycone undergoing further stepwise loss of $2H_2O$ (*m/e* 272, $C_{15}H_{12}O_5$), CO_2 (*m/e* 228, $C_{14}H_{12}O_3$) or CO_2Me (*m/e* 213, $C_{13}H_9O_3$). The 100 MHz ^1H NMR spectrum (pyridine-d_5, TMS as internal standard) showed signals at δ 7.85 (*s*, 3-H), 7.57 (*s*, 10-H), 6.43 (*dd*, $J = 6$, $J' = 2$ Hz, 6-H), 5.55 (*d*, $J = 6$ Hz, 7-H), 5.39 (*dd*, $J = 5.5$, $J' = 2$ Hz, 5-H), 5.27 (*d*, $J = 7$ Hz, 1-H), 4.95 (*d*, $J = 7$ Hz, 13-H), 3.9–4.4 (7 glucose protons), 3.65 (methyl ester-H_3), 3.01 (*dd*, $J = 7$, $J' = 5.5$ Hz, 9-H) and 1.60 (*d*, $J = 7$ Hz, 14-H_3). Hydrolysis, catalysed by 5% HCl, gave β-glucose (confirmed by TLC comparison with an authentic sample) and a highly unstable aglycone moiety. These results, together with further IR and UV data, suggested the inhibitor as plumieride (**1**) also isolated from other *Plumeria* species [3, 4], the structure of which has been established by Schmid *et al.* [4]. Final proof was obtained by direct comparison with an authentic specimen (mp, mmp, IR).

The plant growth inhibiting activity of plumieride was investigated in the dwarf pea (Figs. 1 and 2) as well as dwarf maize and dwarf rice bioassays. The mode of counteracting the gibberellin effect has been found to be quite similar in these three bioassays. Plumieride shows a slight inhibition of wheat seedling growth whereas even high concentrations (up to 10^{-4} M) caused no effect to the auxin (IAA) stimulated growth of wheat coleoptile sections. Thus, the plant growth inhibiting activity of **1** seems to be restricted to interfering with gibberellin-induced growth. The growth inhibiting properties of plumieride reported here are in accordance with similar effects of other unsaturated lactones isolated from higher plants [5].

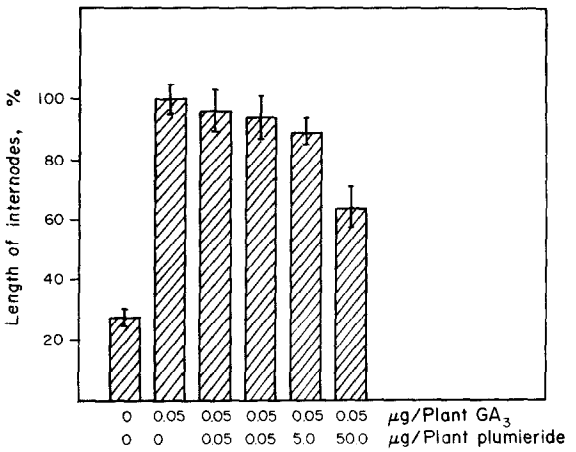

Fig. 1. Inhibition of GA_3-stimulated growth of dwarf peas (cv Meteor) by simultaneously applied plumieride.

EXPERIMENTAL

Air-dried powdered bark (50 g) of *Plumeria obtusifolia* L., collected near Hanoi, was extracted exhaustively with MeOH in a Soxhlet. The soln was concd to dryness and the residue, after addition of H_2O, extracted 5× with Et_2O–C_6H_6 (1:1) to remove pigments and lipids. Upon further extraction with

* Part 3 in the series "Natural Products from Vietnamese Plants". For Part 2 see Adam, G., Huong, H. Th. and Khoi, N. H. (1978) *Phytochemistry* **17**, 1802.

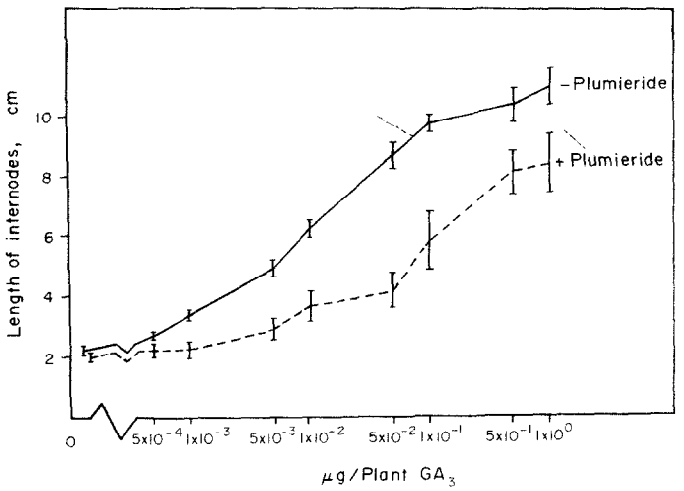

Fig. 2. Influence of plumieride (50 μg/plant) on GA_3 stimulation of dwarf pea growth.

n-BuOH (10 ml, 6 ×), the organic phase was dried, giving after concn a residue which was chromatographed over Si gel. The progress of the separation was followed by TLC on Si gel (Merck) ($CHCl_3$–MeOH, 8:2; detection with vanillin–phosphoric acid 10 min at 110°). Elution with $CHCl_3$–MeOH (9:1) yielded plumieride (**1**), after repeated crystallization from EtOH and MeOH (0.5 g), mp 156–158° (monohydrate), $[\alpha]_D^{25}$ −115.5° (H_2O) (lit. [4] mp 156–158°, $[\alpha]_D$ −119°).

Gibberellin bioassays with dwarf peas (cv Meteor), dwarf maize (d_5 mutant), dwarf rice (cv Tan-ginbozu) and the inhibitor bioassays, using wheat seedlings or wheat coleoptile sections, were carried out as described earlier [6–8].

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