Tableau. 3. Spectres de RMN (δ ppm)* in DMSO

	2′ 6′	2‴ 6‴	5′	3‴ 5‴	6″	8″	8	6	3	3″
Putraflavone (3′-8″) (1)	7,90 *d* J = 2Hz	7,50 *d*	6,70	6,70	6,40 *s*	—	6,40	6,20 *d* J = 2Hz	6,70	7,20
Composé *Tmesipteris*	7,99 *m* J = 9Hz	7,59 *d* J = 9Hz	7,12 *d* J = 9Hz	6,70 *d* J = 9Hz	6,37 *s*	—	6,45 *d* J = 2,5Hz	6,20 *d* J = 2,5Hz	[6,81 *s*	6,76 *s*]
Robustaflavone (3′-6″) (2)	7,87 *d*, 7,94 *d* J = 2Hz, J = 2,9Hz	7,97 *d* J = 9Hz	7,09 *d* J = 9Hz	7,03 *d* J = 9Hz	—	6,68 *s*	6,52 *d* J = 2Hz	6,23 *d* J = 2Hz	[6,80 *s*	6,80 *s*]

*Déplacements chimiques par rapport au TMS.

d'un échantillon d'herbier [3] nous montre l'homogénéité biochimique de l'ordre des Psilotales, homogénéité déjà soulignée par Caldicott *et al.* [4] après étude de la cutine des deux genres.

Il convient de noter en outre que, parmi l'ensemble des Ptéridophytes, une telle définition flavonique se rencontre également chez les Selaginellales (Lycopsida) [3, 5, 6]. Ce résultat mérite attention puisque des auteurs comme Baker [7], Campbell [8] et Scott [9] ont, sur des critères classiques, proposé précisément d'inclure les genres *Psilotum* et *Tmesipteris* dans les Lycopsida. Il semble, pour notre part, que cette analogie de composition révèle l'expression d'un caractère ancestral, et traduit plus un élément de filiation qu'un caractère de parenté étroite. L'ensemble des considérations phylogénétiques concernant les divers taxons précédemment cités sera envisagé prochainement, à la lumière notamment de données nouvelles relatives aux Isoetales.

PARTIE EXPERIMENTALE

Tmesipteris tannensis a été récolté en Nouvelle Zélande. 30 g de frondes séches ont été hydrolysées par fraction de 3 g suivant la technique utilisée au laboratoire [10] et les flavonoïdes sont récupérés par extraction éthérée. Après évaporation de Et_2O, le résidu est repris par H_2O bouillante. La filtration sur verre fritté n°4 permet l'élimination des substances lipophiles. Après refroidissement et acidification par HCl, on procède à une nouvelle extraction par Et_2O. Après évaporation du solvant, le résidu repris par MeOH est chromatographié sur CM de silice (Merck, solvant C_6H_6–EtOAc–HOAc 10:3:2). La bande inférieure majeure, récupérée et éluée par le MeOH, est à nouveau chromatographiée à l'aide du système polyamide Macherey Nagel DC6, solvant C_6H_6–MeEtCO–MeOH, 6:2:2; la bande inférieure, après récupération, est chromatographiée sur colonne de polyamide Macherey Nagel SC6 suivant la technique antérieurement décrite [11]. Le composé inconnu est récupéré dans les deux dernières fractions (n°5 et 6). Les valeurs de R_f (Tableaux 1 et 2) ont été comparées à celles d'un échantillon d'amentoflavone extrait de *Psilotum*.

Remerciements—Nous remercions vivement Monsieur le Professeur Brownlie, Université de Canterbury, Nouvelle Zélande, pour la récolte et l'envoi de l'échantillon de *Tmesipteris*.

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INDUCED PTEROCARPANS OF *PSOPHOCARPUS TETRAGONOLOBUS*

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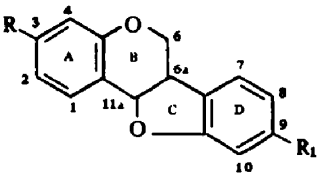
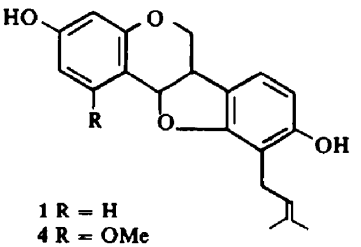
Key Word Index—*Psophocarpus tetragonolobus*; Leguminosae; winged bean; pterocarpan; antifungal.

Among the numerous phenolic compounds induced in immature winged bean pods inoculated with spore suspensions of *Botrytis cinerea* or *B. fabae* are 3 which inhibit *Cladosporium cucumerinum*. Two of these inhibitory compounds were also induced by the action of $CuCl_2$ solution on winged bean leaves.

The first compound, (M^+ 324, $C_{20}H_{20}O_4$) had PMR, UV and MS identical to phaseollidin [1, 2] (**1**). The



2 R = OH, R_1 = OMe
3 R = OMe, R_1 = OH



1 R = H
4 R = OMe

TLC R_f was identical to that of an authentic sample in 3 solvent systems. The PMR spectrum of the second compound (M^+ 270, $C_{16}H_{14}O_4$, $[\alpha]_D^{18}$ −201°, in $CHCl_3$) showed the complex pattern characteristic of the heterocyclic ring protons in pterocarpans [3] and analysis of the chemical shifts and splittings of the signals for the aromatic ring protons supported substitution at C-3 and C-9, as expected on biogenetic grounds. The close similarity of the PMR and UV spectra to those of medicarpin (**2**) ($[\alpha]_D^{20}$ −229.5° [4], $[\alpha]_D^{22}$ −226° [5], both in $CHCl_3$) suggested that the two compounds might be isomeric. On hydrogenation in EtOH over Pd/C an isoflavan (M^+ 272) was produced, the MS of which showed retro-Diels–Alder fragmentation yielding major peaks at *m/e* 136 and 137 (the latter representing an hydroxymethoxytropylium ion, or arising from H transfer to *m/e* 136). The presence of these fragments confirms that a OMe group is attached to ring A. The pterocarpan is therefore considered to be 9-hydroxy-3-methoxypterocarpan (**3**), which has already been synthesised [6], but has not yet been reported as a natural product.

The third compound (M^+ 354, $C_{21}H_{22}O_5$, $[\alpha]_D^{18}$ −225°, in $CHCl_3$) was identified by PMR [3] as a pterocarpan containing one OMe and one isopentenyl group. The presence of 4 aromatic protons showed that both of the OH groups required to complete the molecular formula must be phenolic. Hydrogenation of this pterocarpan gave an isoflavan (M^+ 358) which cleaved in the mass spectrometer by both retro-Diels–Alder pathways [7] giving fragments *m/e* 153 (100%), 206 (31%) and 205 (18%). The pterocarpan therefore has the OMe group attached to ring A and the isopentenyl group to ring D; in addition each of these rings bears one OH group. The PMR resonance at 7.3–7.5 δ, apparently characteristic of H-1 in pterocarpans [1, 3] was missing in this case, indicating substitution at C-1. The doublets at 6.98 and 6.37 δ (J = 8 Hz) can therefore be assigned to H-7 and H-8 (cf. phaseollidin [1] (**1**), 6.93 and 6.36 δ). Further evidence for substitution at C-1 is provided by the broad singlet at 6.08 δ, representing the two A-ring protons. The equivalence of their chemical shifts must result from substitution at C-1 and C-3, since only in this case do the protons experience an equal degree of shielding by the oxy-substituents. In pterocarpans unsubstituted at C-1 but with oxy-substituents at C-2 and C-3, H-1 is less shielded than H-4, and examples [8] show a chemical shift difference of 0.44–0.50 δ between H-1 and H-4.

It remains to be established whether the substituent at C-1 in the new pterocarpan is OH or OMe; a negative Gibbs test favours the latter, and structure (**4**) is consequently indicated for this compound.

EXPERIMENTAL

Seed of *Psophocarpus tetragonolobus* (L) D.C. was supplied by Highlands Agriculture Experiment Station, Aiyura, Papua New Guinea. PMR spectra were recorded at 60 MHz. Immature pods were opened along the sutures, the seeds removed and the exposed tissue inoculated with drops of aq. spore suspension (5×10^5 spores/ml) of *Botrytis cinerea* or *B. fabae*. After 24 hr incubation at 21° the drops of spore suspension were replaced by H_2O. After a further 24 hr the infected tissue was macerated in MeOH. The macerate was filtered and evapd to yield a residue which, combined with the spore suspension, was partitioned between $CHCl_3$ and H_2O. The $CHCl_3$ phase contained compounds (**1**) (**3**) and (**4**) which were isolated by TLC (Si gel, $CHCl_3$–EtOH, 97:3, then hexane–EtOAc, 3:1). Leaves were cut into strips and floated on 10^{-3} M aq. $CuCl_2$. After 72 hr the leaves were macerated in MeOH. The filtered macerate was evapd and the resulting residue was dissolved in $CHCl_3$ previously shaken with the $CuCl_2$ soln. Phenolic compounds were separated from the $CHCl_3$ by extraction with 1% aq. NaOH and recovered by acidification with HCl. Compounds (**1**) and (**4**) were isolated by TLC as above, in yields of 67 and 52 mg/kg fr. wt respectively.

Spectroscopic data. (**3**), λ_{max}^{EtOH} nm (log ε): 283 *sh* (3.78), 286 (3.82), 292 *sh* (3.63). PMR ($CDCl_3$, δ): 7.45 (*d*, J = 8 Hz, H-1), 7.1 (*br. d*, J = 8 Hz, H-7), 6.66 (*q*, J = 8, 2.5 Hz, H-2), 6.4 (*m*, H-4, H-8, H-10), 5.52 (*d*, J = 7 Hz, H-11a), 4.24 (*m*. H-6 eq.), 3.8 (*s*, —OMe). (**4**), λ_{max}^{EtOH} nm (log ε): 284 (3.52). PMR ($CDCl_3$, δ): 6.98 (*d*, J = 8 Hz, H-7), 6.37 (*d*, J = 8 Hz, H-8), 6.08 (*br.s*, H-2, H-4), 5.6 (*d*, J = 7 Hz, H-11a), 5.36 (*m*, isopentenyl CH), 4.2 (*m*, H-6 eq.), 3.87 (*s*, —OMe), 3.4 (*m*, isopentenyl CH_2), 1.75, 1.79 (*s*, *s*, isopentenyl Me's).

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