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Phytochemical studies on the heartwoods and barks of African and Australian species of Acacia

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SUMMARY

The phytochemistry of the heartwoods of ten species of *Acacia* native to Southern Africa, representing the series *Gummiferae* and *Vulgares*, is correlated with that of some 400 Australian species examined in a recent study.

Examination by paper chromatography of these heartwoods reveals the presence of the same relatively rare type of 5-deoxyflavonoids common to species from both Australia and Southern Africa.

RÉSUMÉ

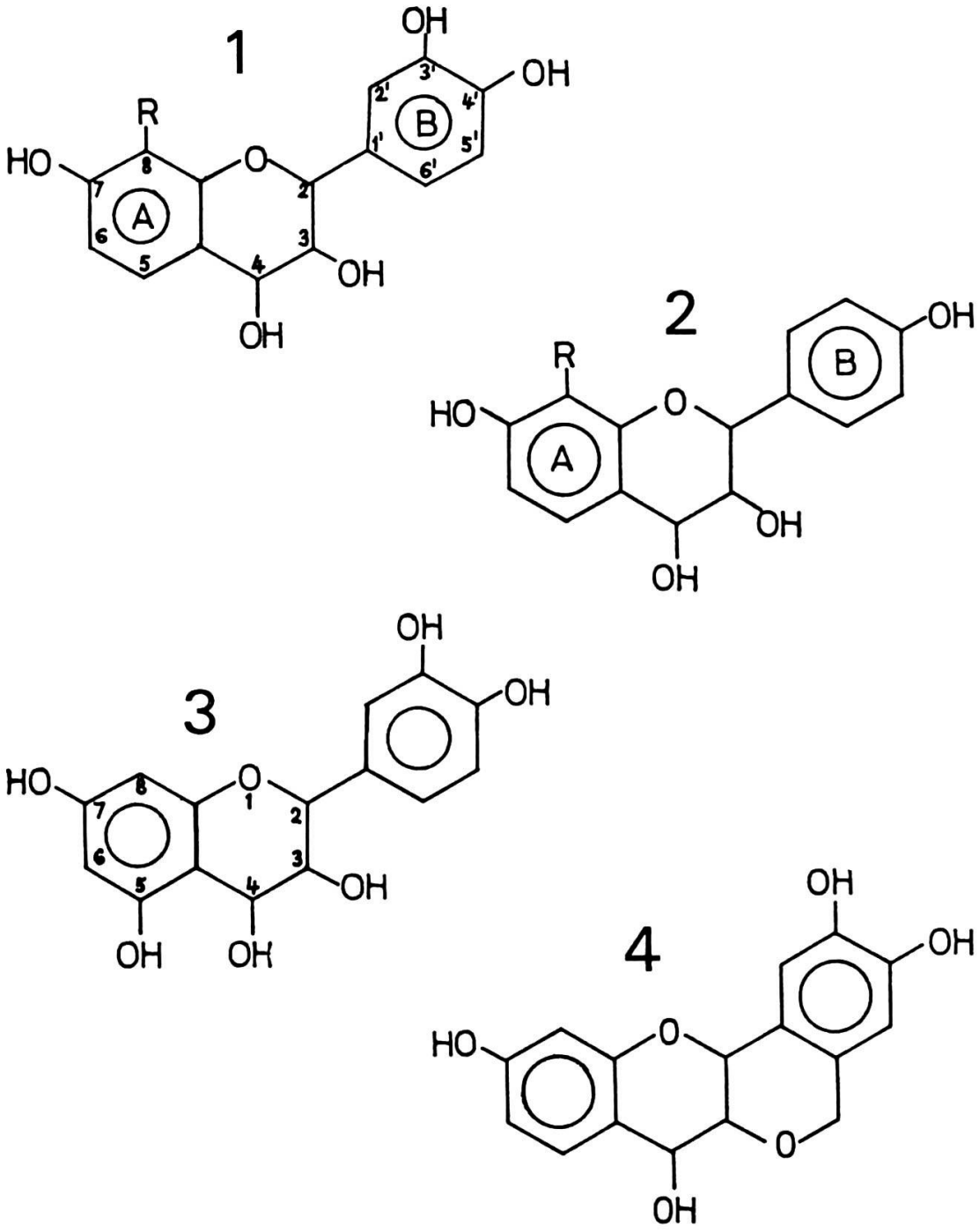
La phytochimie des bois de cœur de dix espèces d'*Acacia* indigènes de l'Afrique du Sud et faisant partie des séries *Gummiferae* et *Vulgares* est comparée à celle de quelque 400 espèces australiennes qui avaient fait l'objet d'une étude récente.

Un examen au moyen de papiers chromatographiques de ces bois de cœur démontre la présence du même type assez rare de 5-désoxyflavonoïdes dans les espèces australiennes et sud-africaines.

Introduction

The commercial importance of *Acacia mearnsii* De Wild. (black wattle) in the leather, paper pulping and wood adhesive industries has led to a great deal of work on tannins extracted from the heartwood and bark of this and closely-related *Acacia*. The principal condensed tannins found in this genus are leucoanthocyanidins, a class of "reduced" flavonoids. For the most part these tannins are related to and associated with 5-deoxyflavonoids which differ structurally from those occurring in other higher plants. Examination by paper chromatography of these heartwoods reveals their presence in species from Australia and Southern Africa, but to date only a relatively small number of African species have been examined.

Our earlier phytochemical surveys dealt with the flavonoid content of heartwoods and barks of some 400 species of the 700 *Acacia* principally native to Australia (Tindale & Roux, 1969; 1974). Arbitrary subdivision of these species on a chemical basis into two main groups based on analogues of the pairs mollisacacidin (Formula 1, R = H) (3′, 4′, 7-trihydroxy) and guibourtacacidin (Formula 2, R = H) (4′, 7-dihydroxy) on the one hand, and melacacidin (Formula 1, R = OH) (3′, 4′, 7,



Formula 1. — R = H, mollisacacidin; R = OH, melacacidin.
Formula 2. — R = H, guibourtacacidin; R = OH, teracacidin.
Formula 3. — Leucocyanidin.
Formula 4. — Peltogynol.

8-tetrahydroxy) and teracacidin (Formula 2, R = OH) (4′, 7, 8-trihydroxy) on the other, followed from this study.

The presence of resorcinol-type 5-deoxyflavonoids as represented by mollisacacidin and guibourtacacidin (Formulae 1 and 2, R = H) and their analogues in *Acacia* species represents a loss mutation in evolution since the universal flavonoid precursor carries an oxygen substituent in the 5-position (as, for example, in Formula 3, leucocyanidin) (cf. Harborne & al., 1971). Presumption that subsequent 8-hydroxylation or 8-methoxylation to form melacacidin and teracacidin analogues (Formulae 1 and 2, R = OH or OMe) represents further evolutionary change amongst *Acacia*, led to considerations of the most likely phyletic lines within the genus *Acacia*.

African species

These studies have now been extended to include ten species native to Southern Africa. These bipinnate species (Table 1) belong to the *Gummiferae* and *Vulgares* according to G. Bentham's classification of the genus *Acacia* (Bentham, 1875), but according to J. Vassal's recent classification (Table 1, Vassal, 1969-72), they would be placed in subgenus *Acacia* subsection *Uniseriae* and subgenus *Aculeiferum* respectively.

Table 1. — Flavonoid patterns of heartwoods of *Acacia* species native to Africa. Arranged according to G. Bentham's classification (1875).

Group	*Species*	*Flavonoid Pattern*	*Type of Inflorescence*
Gummiferae [1]			
	Acacia karroo	3′, 4′,7	capitate [3]
	A. luederitzii		
	var. *luederitzii*	3′, 4′, 7 + 4′, 7	capitate [4]
	var. *retinens*	3′, 4′, 7 + 4′, 7	capitate [4]
	A. nilotica subsp. *kraussiana*	3′, 4′, 7	capitate [3]
	A. reficiens subsp. *reficiens*	3′, 4′, 7 + 4′, 7	capitate [4]
Vulgares [2]			
Subseries *Gerontogeae Spiciflorae*			
A. *Triacanthae*	*A. senegal*		
	var. *leiorachis*	3′, 4′, 7, 8	spicate [3]
	var. *rostrata*	3′, 4′, 7, 8	spicate [3]
B. *Diacanthae*	*A. burkei*	4′, 7, 8	spicate [5]
	A. erubescens	4′, 7, 8	spicate [3]
	A. galpinii	4′, 7, 8	spicate [5]
	A. nigrescens	3′, 4′, 7, 8	spicate [6]
	A. welwitschii	3′, 4′, 7	spicate [3]

[1] According to J. Vassal's classification all of these species in the *Gummiferae* would be placed in subgenus *Acacia* subsection *Uniseriae*.

[2] According to J. Vassal's classification all of these species in the *Vulgares* would be placed in subgenus *Aculeiferum*.

[3] (Roux, 1974).

[4] (Du Preez, 1971; Du Preez & al., 1970).

[5] (Malan, 1973).

[6] (Fourie, 1971; Fourie & al., 1972).

Ser. *Gummiferae* Bentham [1] which is strongly represented in Africa, is characterized by the following features: bipinnate foliage, several or all stipules spinescent and sometimes enlarged to form "ant-galls", the absence of prickles on the stems, capitate or spicate inflorescences, mostly colporate pollen and albuminous or exalbuminous seeds (Vassal, 1969-72: 15). The four African species studied have capitate inflorescences and all have heartwoods with flavonoids featuring resorcinol A-ring analogues (Formulae 1 and 2, R = H). In *Acacia karroo* Hayne and *A. nilotica* (L.) Delile subsp. *kraussiana* (Bentham) Brenan mollisacacidin (Formula 1, R = H) is present in the heartwoods, whereas guibourtacacidin (Formula 2, R = H) occurs in *A. luederitzii* Engler var. *luederitzii* and var. *retinens* (Sim) J. Ross & Brenan. On the basis of previous work (Tindale & Roux, 1974) such chemical content reflects relatively primitive enzymic systems amongst *Acacia* spp. We have also obtained results from material collected in Australia for two species which occur in Asia, but are naturalized in Australia, viz. *A. nilotica* (L.) Delile subsp. *indica* (L.) Willd. and *A. farnesiana* (L.) Willd. In the former species which is native to Asia, we have recorded mollisacacidin-melacacidin in the heartwood, whereas mollisacacidin or guibourtacacidin (and in one instance teracacidin) occur in the latter species. According to Vassal's classification all of the above species belong to subgenus *Acacia* subsection *Uniseriae* except *A. farnesiana* which is a member of subsection *Pluriseriae* and is believed to have been introduced from tropical America to Asia, Africa and Australia at an early date in their colonizations.

Less than ten species of the *Gummiferae* occur in Australia, all being confined to the tropical regions except *A. farnesiana*. Mollisacacidin is present in the heartwoods of three native Australian species, viz. *A. suberosa* A. Cunn. ex Benth., *A. pallidifolia* Tindale and *A. calcigera* Tindale (Tindale & Roux, 1974).

In the *Vulgares* which are also strongly represented in Africa, six native species with spicate inflorescences have been examined (Table 1). Five species, viz. *A. burkei* Bentham, *A. erubescens* Welw. ex Oliver, *A. galpinii* Burtt-Davy, *A. nigrescens* Oliver and *A. senegal* (L.) Willd. var. *leiorachis* Brenan and var. *rostrata* Brenan, have heartwoods featuring flavonoids with pyrogallol A-ring nuclei (Formulae 1 and 2, R = OH) in their heartwoods, but *A. welwitschii* Oliver has flavonoids with resorcinol A-ring analogues. Our record of mollisacacidin in the latter species is one of the very rare exceptions for a species of *Acacia* with spicate inflorescences, so that it is hoped to check this result with other wood samples. Vassal (1969-72: 14) has summarized the features of his new subgenus *Aculeiferum* which is equivalent to ser. *Vulgares* Benth. Some of the more important features of this group which is unrepresented in Australia, are as follows: bipinnate foliage, non-spinescent stipules, infrapetiolar or infrastipular prickles, capitate or spicate inflorescences, porate or very rarely moderately colporate pollen and exalbuminous seeds. Although based on a limited study, the chemical content of heartwoods amongst the *Vulgares* (mainly pyrogallol A-ring flavonoids: Formulae 1 and 2, R = OH) suggests that they are generally more advanced than those members of the *Gummiferae* (exclusively resorcinol A-ring flavonoids: Formulae 1 and 2, R = H) examined.

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[1] *Acacia albida* Delile placed by Vassal in the genus *Faidherbia* is excluded here from the definition of *Gummiferae*.

Australian species

The majority of the 700 Australian species of *Acacia* belong to the series *Phyllodineae*, *Botryocephalae* and *Pulchellae* in Bentham's classification. Recently these three series have been grouped by Vassal (1969-72: 16) under his subgenus *Heterophyllum* which is absent from Africa except for *A. heterophylla* (Lam.) Willd. of Reunion and Mauritius. However, Brenan (1959: 50-51), has recorded seventeen Australian species which have become naturalized in that region.

Both the *Botryocephalae* and *Pulchellae* are characterized by bipinnate foliage, whereas phyllodes are present in the *Phyllodineae*, although bipinnate foliage does persist in adult plants of several species of the *Uninerves Racemosae* which are believed to be closely allied to the *Botryocephalae* (Tindale & Roux, 1974). Bentham's three series are characterized by capitate or spicate inflorescences, the absence of prickles on the stems, stipules often absent or in a few species the stipules or branchlets spinescent, colporate or very rarely porate pollen and rarely albuminous seeds.

In the *Botryocephalae*, an endemic Eastern Australian group of about 32 bipinnate species with capitate inflorescences, either mollisacacidin or guibourtacacidin has been recorded for all taxa except *A. jonesii* F. Muell. & Maiden which has not been examined yet. Unlike members of the *Gummiferae* the stipules are absent or very small, but never spinescent.

In the other small Australian group with bipinnate foliage, the *Pulchellae*, both melacacidin and mollisacacidin have been recorded for species with capitate inflorescences (Tindale & Roux, 1974), although it has been difficult to obtain data about the hydroxylation patterns due to the small amount of heartwood in their stems. Both melacacidin and cyanidin occur in a sample of *A. drummondii* Lindl., one of the few members of this group with spicate inflorescences. In the *Pulchellae* which are almost confined to the south-western region of Western Australia, stipules are absent or small and setaceous but non-spinescent, although in *A. pulchella* R. Br. and its allies spines are present.

Amongst the *Phyllodineae* which occur predominantly in Australia, although a few species are found in South East Asia, the Pacific Islands and the Mascarenes, species bearing capitate inflorescences have heartwoods with either pyrogallol A-ring nuclei or resorcinol A-ring analogues. In addition three Australian species have peltogynoid content (Formula 4 and analogues, compounds related to mollisacacidin Formula 1, R = H) in their purple heartwoods (Tindale & Roux, 1974), but none has been found yet in African species of *Acacia*. On the other hand there is a very marked correlation between species with spicate inflorescences and heartwoods with flavonoids featuring pyrogallol A-ring nuclei. An examination of about 100 species in the *Juliflorae*, a phyllodinous group characterized by spicate inflorescences, has shown the presence of melacacidin or teracacidin or complex mixtures with mollisacacidin and guibourtacacidin. Only two exceptions have been found, viz. *A. dorothea* Maiden (which has very short spikes and is considered to be more closely allied to the *Uninerves Racemosae*) and an undescribed species in the *A. whitei*-group. The *Juliflorae* are considered to be an advanced group both chemically and morphologically.

Conclusions

Although only a small number of species from Southern Africa in the *Gummiferae* and *Vulgares* have been examined to date, it is of great interest that the same relatively rare type of 5-deoxyflavonoids occurs in their heartwoods as in the 400 Australian species examined in our previous surveys (Tindale & Roux, 1969; 1974), although so far no species with peltogynoid content have been found in the African taxa.

Amongst the species from Southern Africa all of the 4 taxa of the *Gummiferae* in our survey have capitate inflorescences and heartwoods with flavonoids of the resorcinol A-ring group (mollisacacidin and guibourtacacidin). No members of this series with spicate inflorescences were studied. On the other hand 6 members of the *Vulgares* with spicate inflorescences were examined and with one exception (i.e. *A. welwitschii*) all had heartwood with pyrogallol A-ring flavonoids (melacacidin and teracacidin). No material of species in this series with capitate inflorescences was available for study.

The Australian species with capitate inflorescences may have heartwoods with either group of flavonoids, but all the *Botryocephalae* as well as a high percentage of the *Gummiferae* and the *Phyllodineae Uninerves Racemosae* and *Phyllodineae Brunioideae* belong to the resorcinol A-ring group and are considered to be more primitive according to the chemical evidence. On the other hand the *Phyllodineae Plurinerves* (with rare exceptions in the *Dimidiatae*) and the *A. salicina-A. frumentacea-A. graffiana* group in the *Uninerves Racemosae* belong to the pyrogallol A-ring group. Members of the *Pulchellae* with capitate inflorescenses as well as the *Phyllodineae* (*Pungentes*, *Calamiformes* and *Uninerves*) belong to either the resorcinol A-ring or pyrogallol A-ring groups. However, there is a strong correlation between species with spicate inflorescences and heartwoods with pyrogallol A-ring flavonoids, although rare exceptions have been noted. This was revealed in a study of about 100 members of the *Phyllodineae Juliflorae* and one species of the *Pulchellae* with spicate inflorescences (i.e. *A. drummondii* Lindl.). Three species of the *Phyllodineae* with capitate inflorescences revealed a peltogynoid content in their heartwoods. According to Bentham's classification all were considered to be relatively primitive.

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