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AN EXTENDED PHYTOCHEMICAL SURVEY OF AUSTRALIAN SPECIES OF *ACACIA*: CHEMOTAXONOMIC AND PHYLOGENETIC ASPECTS

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Abstract—An earlier phytochemical survey of the flavonoid content of heartwoods and barks of *Acacia* species is extended to a much wider range distributed throughout the Australian continent, and representing most sections and subsections of the genus. Flavonoids with pyrogallol (7,8-hydroxy) A-ring nuclei almost exclusively populate the heartwoods of most species constituting subsections of the Plurinerves and Juliflorae, while resorcinol (7-hydroxy) A-ring analogues are similarly represented under the Brunioideae, Uninerves—subsection Racemosae and the Botryocephaleae. Individual representation of both hydroxylation patterns, or their mixtures in heartwoods, are present amongst the Continuae, and under many subsections of the Pungentes, Calamiformes and Uninerves. A small group, *A. peuce* (Continuae), *A. carnei* (Pungentes) and *A. crombei* (Uninerves) show close chemical relationships, being sharply differentiated by the peltogynoid content of their purple heartwoods. This renders them unique amongst the Mimosaceae. Evolutionary trends amongst taxa are discussed on the basis of morphological and chemical correlations.

INTRODUCTION

TINDALE and Roux,[1] in the first extensive chemical study of the heartwoods and barks of *Acacia* species native to Australia, showed a basic subdivision of heartwood flavonoids into four groups, depending on variations in their phenolic hydroxyl pattern. Thus, amongst heartwood flavonoids, the pair 7,3′,4′-trihydroxy and 7,4′-dihydroxy were usually associated and accompanied by related (7,3′,4′,5′-tetrahydroxy) or identical (7,3′,4′-trihydroxy) analogues in the barks. This situation contrasted with similar B-ring variation in the pair 7,8,3′,4′-tetrahydroxy and 7,8,4′-trihydroxy, whose analogues often existed independently in heartwoods, and were absent from their associated barks.

Subsequently variations, representing selective *O*-methylation of these substitution patterns, were demonstrated by du Preez and Roux[2] and by Drewes and Isley[3] through isolation of 8-*O*-methylflavan-3,4-diols from *A. cultriformis* and 3-*O*-methylflavonols from *A. mearnsii* respectively. Clark-Lewis and Porter[4] recently confirmed their wider distribution in Australian *Acacia* species.

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[1] TINDALE, M. D. and ROUX, D. G. (1969) *Phytochemistry* **8**, 1713.
[2] DU PREEZ, I. C. and ROUX, D. G. (1970) *J. Chem. Soc.* **C**, 1800.
[3] DREWES, S. E. and ISLEY, A. H. (1969) *Phytochemistry* **8**, 1039.
[4] CLARK-LEWIS, J. W. and PORTER, L. J. (1972) *Australian J. Chem.* **25**, 1943.

Chemotaxonomic inferences drawn from our previous study,[1] and recently extended to include a small number of newly-examined species from the arid zones of Australia,[4] are presently re-examined for some 400 *Acacia* species, of which about 275 show clearly-defined heartwood content.

RESULTS AND DISCUSSION

Chemical aspects

Our extended assessment of the distribution of hydroxylation patterns of flavonoids from the heartwoods of *Acacia* spp. mostly endemic to Australia (Table 1) suggests that chemical differentiation should be sought mainly between analogues of the pairs mollisacacidin (**1**, R=H) (7,3′,4′-trihydroxy) and guibourtacacidin (**2**, R=H) (7,4′-dihydroxy) on the one hand, and melacacidin (**1**, R=OH) (7,8,3′,4′-tetrahydroxy) and teracacidin (**2**, R=OH) (7,8,4′-trihydroxy) on the other. This follows from the invariable association of the minor 7,4′-dihydroxy pattern, where present, with the predominant 7,3′,4′-trihydroxy analogues in the same heartwoods. Similar association of the minor 7,8,4′-trihydroxy group with the equally predominant 7,8,3′,4′-tetrahydroxy group is less frequent, but their individual occurrence in heartwoods of species falling under identical subsections and sections of the genus, apparently affords similar support.

TABLE 1. FLAVONOID PATTERNS OF HEARTWOODS OF *Acacia* SPECIES MOSTLY ENDEMIC TO AUSTRALIA

Section Subsection Species	Flavonoid pattern	Section Subsection Species	Flavonoid pattern
Phyllodineae			
		V: Brunioideae	
II: Continuae		*A. brunioides*	7,3′,4′ + 7,4′
A. continuae	7,8,3′,4′	spp. *gordonii*	
A. peuce	peltogynoids (7,3′,4′)	*A. cedriodes*	7,3′,4′ + 8-OMe
III: Pungentes		*A. gittinsii*	7,3′,4′
(ii) Plurinerves		*A. minutifolia*	7,3′,4′
A. colletioides	7,8,3′,4′	*A. resinocostata*	7,3′,4′
var *nyssophylla*		*A. ruppii*	7,3′,4′
A. colletioides	7,8,3′,4′	VI: Uninerves	
A. comans	7,3′,4′	(ii) Armatae	
A. lanigera	7,8,3′,4′	*A. armata*	7,8,3′,4 + 8-OMe
A. trinervata	7,8,3′,4′ (+8-OMe)	*A. armata*	7,8,3′,4 + 8-OMe
(iii) Uninerves		x *A. dodonaeifolia*	
A. carnei	peltogynoids (7,3′,4′)	(iii) Triangulares	
A. genistifolia	7,8,4′	*A. hubbardiana*	7,3′,4′
A. maitlandii	7,8,3′,4′	*A. sp. aff. orbifolia*	7,3′,4′ *or* 7,8,4′
A. prainii	7,8,3′,4′	(iv) Brevifoliae	
A. rupicola	7,8,3′,4′	*A. acinacea*	7,8,3′,4′
A. siculiformis	7,8,3′,4′	*A. camptoclada*	7,8,3′,4′
A. tetragonophylla	7,3′,4′ (+7,4′)	*A. imbricata*	7,8,3′,4′ + 7,8,4′
IV: Calamiformes		*A. lineata*	7,8,3′,4′ + 7,3′,4′
(ii) Plurinerves		*A. meissneri*	7,3′,4′ + 7,4′
A. dielsii	7,3′,4′	*A. merrallii*	7,3′,4′
A. euthycarpa	7,3′,4′	*A. uncinata*	7,3′,4′
A. fragilis	7,3′,4′	(v) Angustifoliae	
A. havilandii	7,3′,4′ + 7,8,3′,4′	*A. crombei*	peltogynoids (7,3′,4′)
A. leptoneura	7,3′,4′ + 7,4′	*A. dodonaeifolia*	7,8,3′,4′
A. menzelii	7,8,3′,4′	*A. ensifolia*	7,8,4
A. rigens	7,8,3′,4′	*A. howitti*	7,8,3′,4′ + 8-OMe
A. sowdenii	7,8,3′,4′	*A. leprosa*	7,8,3′,4′ (+7,3′,4′)
A. wilhelmiana	7,8,3′,4′	*A. microcarpa*	7,3′,4′
(iii) Uninerves		*A. montana*	7,8,3′,4′
A. calamifolia	7,3′,4′	*A. pruinocarpa*	7,8,4′ (+8-OMe)
A. gracilifolia	7,8,3′,4′	*A. saxatilis*	7,3′,4′ + 8-OMe
A. juncifolia	7,8,3′,4′	*A. vernicifluа*	7,8,3′,4′
A. pilligaensis	7,3′,4′ + 7,4′	*A. victoriae*	7,8,4′ (+8-OMe or 7,4′)
A. quadrilateralis	7,8,3′,4′	*A. yirrkallensis*	7,3′,4′

TABLE 1. (*continued*)

Section Subsection Species	Flavonoid pattern
(vi) Racemosae	
A. adunca	7,3',4'
A. amoena	7,3',4'
A. argyrophylla	7,3',4'
A. bancroftii	7,2',4'
A. barringtonensis	7,3',4'
A. beckleri	7,3',4'
A. betchei	7,3',4'
A. boormanii	7,3',4'
A. brachybotrya	7,3',4'
A. buxifolia	7,3',4' (+7,4')
A. caesiella	7,3',4'
A. chalkeri	7,3',4'
A. chrysella	7,3',4'
A. clunies-rossiae	7,3',4'
A. cultriformis	7,3',4' (+8-OMe)
A. cultriformis x. *A. decora*	7,3',4' + 8-OMe
A. decora	7,3',4'
A. difformis	7,3',4'
A. falcata	7,3',4'
A. falciformis	7,3',4'
A. fimbriata	7,3',4'
A. flocktoniae	7,3',4' + 7,4'
A. gillii	7,3',4'
A. gladiiformis	7,3',4'
A. hakeoides	7,3',4'
A. hamiltoniana	7,3',4'
A. jucunda	7,3',4'
A. kettlewelliae	7,3',4'
A. kybeanensis	7,3',4'
A. linearifolia	7,3',4'
A. linifolia	7,3',4' + 7,4'
A. lucasii	7,3',4'
A. mabellae	7,3',4' + 7,4'
A. mcgillivrayi	7,3',4' + 7,4'
A. mckieana	7,3',4'
A. mcnuttiana	7,3',4'
A. microbotrya	7,3',4'
A. neriifolia	7,3',4'
A. notabilis	7,3',4'
A. obliquinervia	7,3',4' (+7,4')
A. obtusata	7,3',4'
A. penninervis	7,3',4' (+7,4')
A. sp. nov. aff. *penninervis*	7,3',4'
A. pravissima	7,3',4'
A. prominens	7,3',4'
A. pubicosta	7,3',4'
A. pustula	7,3',4'
A. pycnantha	7,3',4'
A. quornensis	7,3',4'
A. retinoides	7,3',4'
A. rivalis	7,3',4'
A. rubida	7,3',4'
A. saliciformis	7,3',4'
A. subulata	7,3',4'
A. vestita	7,3',4'
A. wattsiana	7,3',4'
Groups of *A. salicina*—*A. graffiana*—*A. frumentacea*	
Group of *A. frumentacea*	
A. frumentacea	7,8,3',4'
Group of *A. graffiana*	
A. blakelyi	7,8,3',4'
A. graffiana	7,8,3',4'
A. iteaphylla	7,8,3',4'
Group of *A. salicina*	
A. ligulata	7,8,3',4' (+7,3',4')
A. rostellifera	7,8,3',4'
A. salicina	7,8,3',4' (+7,3',4')
A. sp. aff. *salicina*	7,8,3',4' (+7?,3',4')
A. sclerosperma	7,8,3',4' (+7,3',4')
VII: Plurinerves	
(ii) Triangulares	
A. deltoidea	
(iii) Brevifoliae	7,3',4' + 7,8,3',4'
A. monticola	
A. translucens	7,8,3',4'
(iv) Oligoneurae	7,3',4'
A. baeuerlenii	
A. cognata	7,8,3',4'
A. dawsonii	7,8,3',4' + 8-OMe
A. elliptica	7,8,3',4'
A. estrophiolata	7,8,3',4'
A. ptychoclada	7,8,3',4' (+8-OMe)
A. simsii	7,8,3',4'
A. subporosa	7,8,3',4'
A. trineura	7,8,3',4' (+8-OMe)
(v) Microneurae	7,8,3',4'
A. argyrodendron	7,8,3',4'
A. calcicola	7,8,3',4'
A. cambagei	7,8,3',4' (+7,8,4' +8-OMe)
A. cana	7,8,3',4' (+7,3',4')
A. coriacea	7,8,3',4'
A. georginae	7,8,3',4' +7,3',4'
A. farinosa	7,8,3',4'
A. homalophylla	7,8,3',4'
A. loderi	7,8,3',4'
A. osswaldii	7,8,3',4'
A. pendula	7,8,3',4'
A. sessiliceps	7,8,3',4' (+8-OMe)
A. stenophylla	7,8,3',4' (+7,8,4' +8-OMe)
A. viscidula	7,8,3',4'
(vi) Nervosae	
A. complanata	7,8,3',4' (+8-OMe)
A. cyclops	7,8,3',4'
A. excelsa	7,8,3',4'
A. frigrescens	7,8,3',4'
A. harpophylla	7,8,3',4'
A. imblexa	7,8,3',4'
A. ixiophylla	7,8,3',4' (+8-OMe)
A. melanoxylon	7,8,3',4' + 8-OMe
A. sclerophylla	7,8,3',4' (+8-OMe)
(vii) Dimidiatae	
A. bakeri	7,8,3',4'
A. binervata	7,3',4'
A. dineura	7,3',4'
A. flavescens	7,8,3',4' (+7,3',4' + 8-OMe)
A. platycarpa	7,8,3',4' (+7,8,4')
A. retivenia	7,3',4' (+7,8,3',4')
A. rothii	7,3',4'
VIII: Juliflorae	
(i) Continuae	
A. triptera	7,8,3',4' (+8-OMe)
(iii) Rigidulae	
A. argyraea	7,8,3',4' (+7,8,4')
A. chisholmii	7,8,3',4' (+7,8,4' + 8-OMe)
A. dacrydioides	7,8,4'
A. leptophleba	7,8,3',4'
A. limbata	7,8,3',4' + 7,3',4'
A. linarioides	7,8,3',4'
A. lysiphloia	7,8,3',4'
A. mountfordiae	7,8,3',4'
A. pubifolia	7,8,4' (+8-OMe)
A. pycnostachya	7,8,3',4' + 8-OMe
A. stipuligera	7,8,4'
A. subtilinervis	7,8,3',4'

TABLE I. *(continued)*

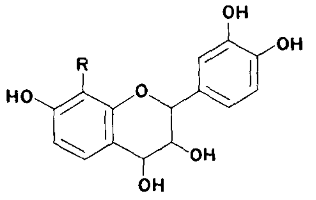
Section Subsection Species	Flavonoid pattern
(iv) Tetramerae	
A. alpina	7,8,3',4'
A. floribunda	7,8,3',4'
A. longifolia var. *longifolia*	7,8,3',4'
A. longissima	7,8,3',4'
A. mucronata var. *dissitiflora*	7,8,3',4'
A. neurophylla	7,8,3',4'
A. obtusifolia	7,8,3',4'
A. orites	7,8,4'
A. whitei	7,8,4' + 8-OMe
(v) Stenophyllae	
A. aneura var. *aneura*	7,8,3',4' (+8-OMe)
A. aneura var. *latifolia*	7,8,3',4' (+7,8,4' + 8-OMe)
A. aprepta	7,8,3',4' + 8-OMe
A. brachystachya	7,8,3',4' (+7,8,4')
A. burkittii	7,8,3',4'
A. cibaria	7,8,3',4'
A. citriodora	7,8,3',4' + 7,3',4'
A. clivicola	7,8,3',4' (+8-OMe)
A. cuthbertsonii	7,8,3',4'
A. cyperophylla	7,8,3',4' (+8-OMe + 7,3',4')
A. filifolia var. *compressa*	7,8,3',4' + 7,3',4'
A. grasbyi	7,8,3',4'
A. hilliana	7,8,3',4' (+7,3',4')
A. hynesiana	7,8,3',4'
A. kempeana	7,8,3',4'
A. merinthophora	7,8,3',4' + 8-OMe
A. multispicata	7,8,3',4'
A. ramulosa	7,8,3',4'
A. resinomarginea	7,8,3',4'
A. tenuissima	7,8,3',4' + 7,8,4' + 7,3',4' + 7,4'
A. wanyu	7,8,3',4'
(vi) Falcatae	
A. acuminata	7,8,3',4'
A. adsurgens	7,8,3',4' (+8-OMe)
A. ancistrocarpa	7,8,3',4' (+7,3',4')
A. aulacocarpa	7,8,3',4' (+7,8,4' + 8-OMe)
A. blakei	7,8,3',4' + 8-OMe
A. bulgaensis	7,8,3',4'
A. burrowii	7,8,4' (+8-OMe)
A. calyculata	7,8,3',4'
A. cheelii	7,8,3',4'
A. cowleana	7,8,3',4' (+7,3',4')
A. crassa	7,8,3',4'
A. crassicarpa	7,8,3',4' (+8-OMe)
A. crassifrugis	7,8,3',4'
A. cunninghamii forma "A"	7,8,3',4'
A. cunninghamii forma "B"	7,8,3',4'
A. sp. aff. *cunninghamii*	7,8,3',4' (+7,8,4')
A. difficilis	7,8,3',4' + 7,8,4' (+7,3',4' + 7,4')
A. diphylla	7,8,3',4'
A. doratoxylon	7,8,3',4' (+8-OMe)
A. doratoxylon var. *angustifolia*	7,8,3',4' + 8-OMe
A. sp. aff. *doratoxylon*	7,3',4' + 8-OMe
A. eriopoda	7,8,4'
A. glaucescens	7,8,3',4' + 8-OMe
A. granitica	7,8,3',4' + 8-OMe
A. hammondii	7,8,3',4' + 7,8,4' (+7,3',4' + 7,4')
A. hemsleyi	7,8,3',4'
A. julifera	7,8,4'
A. lasiocalyx	7,8,3',4'
A. leiocalyx	7,8,3',4' (+8-OMe)
A. leptocarpa	7,8,3',4' + 7,8,4' (+7,3',4' + 7,4')
A. leptostachya	7,8,3',4' (+7,3',4' + 8-OMe)
A. longispicata	7,8,3',4'
A. maidenii	7,8,4'
A. plectocarpa	7,8,3',4'
A. polystachya	7,8,3',4'
A. proxima	7,8,4'
A. quadrimarginea	7,8,3',4'
A. shirleyi	7,8,4' (+7,8,3',4' + 8-OMe)
A. signata	7,8,3',4'
A. sparsiflora	7,8,3',4' + 8-OMe
A. stereophylla	7,8,3',4'
A. stowardii	7,8,3',4'
A. torulosa	7,8,4' (+7,8,3',4' + 7,3',4' + 7,4' + 8-OMe)
A. tropica	7,8,4'
A. tumida	7,8,4' (+8-OMe)
(vi) Dimidiatae	
A. dimidiata	7,8,3',4'
A. holosericea	7,8,3',4' + 7,3',4'
A. humifusa	7,8,3',4' + 7,3',4' + 7,8,4'
A. mangium	7,8,4'
A. pellita	7,8,3',4'
(vii) Uninerves	
A. dorothea	7,3',4' + 7,4'
<u>Bipinnatae</u>	
Botryocephaleae	
A. baileyana	7,3',4'
A. cardiophylla	7,3',4'
A. chrysotricha	7,3',4'
A. constablei	7,3',4'
A. dealbata ssp. *dealbata*	7,3',4'
A. dealbata ssp. *subalpina*	7,3',4'
A. deanei ssp. *deanei*	7,3',4' (+7,4')
A. deanei ssp. *paucijuga*	7,3',4'
A. decurrens	7,3',4'
A. elata	7,3',4'
A. filicifolia	7,3',4'
A. fulva	7,3',4'
A. glaucocarpa	7,3',4'
A. irrorata ssp. *irrorata*	7,3',4'
A. irrorata ssp. *velutinella*	7,3',4'
A. latisepala	7,3',4'
A. leptoclada	7,3',4
A. leucoclada ssp. *argentifolia*	7,3',4
A. leucoclada ssp. *leucoclada*	7,3',4'
A. loroloba	7,3',4'
A. mearnsii	7,3',4'
A. mollifolia	7,3',4'
A. muellerana	7,3',4'
A. nano-dealbata	7,3',4'
A. o'shanesii	7,3',4'
A. parramattensis	7,3',4'

TABLE 1. (*continued*)

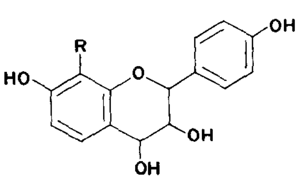
Section Subsection Species	Flavonoid pattern	Section Subsection Species	Flavonoid pattern
A. parvipinnula	7,3′,4′	Pulchellae	
A. polybotrya	7,3′,4′	*A. lasiocarpa* ssp. *lasiocarpa*	7,8,3′,4′
A. pubescens	7,3′,4′		
A. schinoides	7,3′,4′	*A. megacephala*	7,3′,4′
A. silvestris	7,3′,4′	Gummiferae	
A. spectabilis	7,3′,4′	*A. calcigera*	7,3′,4′
A. storyi	7,3′,4′	*A. farnesiana*	7,3′,4′
A. terminalis (syn. *A. botrycephala*)	7,3′,4′ (+7,4′)	*A. farnesiana*	7,8,4′
		A. pallidifolia	7,3′,4′
A. trachyphloia	7,3′,4′	*A. suberosa*	7,3′,4′

Arranged according to a slightly adapted form of the classification of Maiden and Betche[5] (1916) which is a later modification of Bentham's[6] scheme (1864). Hydroxylation patterns in parentheses are those which occur occasionally, but which are not representative of all samples.

The 8-*O*-methyl ethers of melacacidin and teracacidin (**1**, **2**, R=OMe) almost invariably accompany both these flavonoid species (**1**, **2**, R=OH) (Table 1). Exceptions do, however, exist, as exemplified by their association with mollisacacidin (**1**, R=H) and guibourtacacidin (**2**, R=H) in *A. cultriformis.*[2] The foregoing, nevertheless, suggests that *O*-methylation represents the final step in the biogenesis of 8-*O*-methyl ethers, and that their presence or absence is unlikely to be of taxonomic significance. Similar deduction seems possible from perusal of Table 1.



(**1**)



(**2**)

The most significant recent advance in the chemistry of components of *Acacia* heartwoods has been the isolation of peltogynoids (Table 2, **3**–**7**), 5-hydroxypeltogynoids (**8, 9**) as well as their flavonoid analogues (**10**–**15**) from the heartwoods of three species, *A. peuce*, *A. carnei* and *A. crombei* by Brandt, Ferreira and Roux.[7–9] The above groups are represented by the predominant components (+)-2,3-*trans*-3,4-*trans*- and (+)-2,3-*trans*-3,4-*cis*-peltogynols (**3**, **4**), (−)-2,3-*cis*-3,4-*cis*-peltogynol (**5**), (+)-2,3-*trans*-peltogynone (**6**) and its chalcone analogue (**7**),[9] (−)-crombenin (**8**), a new type of peltogynoid having also the unusual 5-hydroxylation[8] and (+)-crombeone (**9**), a 5-hydroxypeltogynone.[7] The most notable amongst the flavonoid analogues (**10**–**15**) is optically active (+)-3-*O*-methylfustin (**12**). The peltogynoids **5**, **7**–**9** and the optically active flavonoid **12** represent novel compounds. The predominant peltogynols (**3**, **4**), and also fisetin (**13**) are alone common

[5] MAIDEN, J. H. and BETCHE, E. (1916) *A Census of New South Wales Plants*, p. 89, Government Printer, Sydney

[6] BENTHAM, G. and MUELLER, F. (1864) *Flora Australiensis*, p. 301, Lovell Reeve, London.

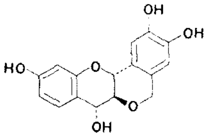
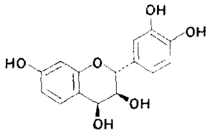
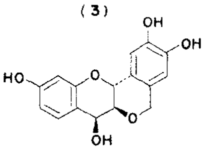
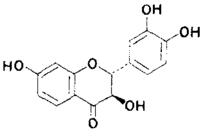
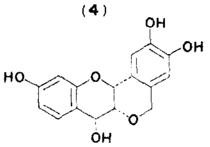
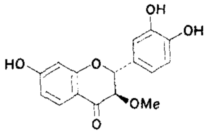
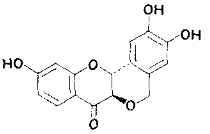
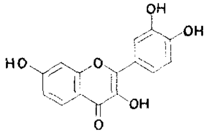
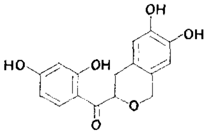
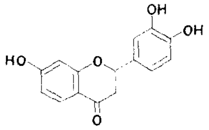
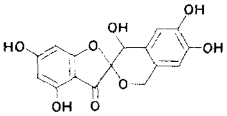
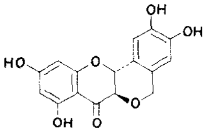
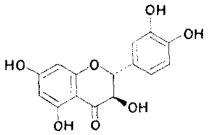
[7] BRANDT, E. V., FERREIRA, D. and ROUX, D. G. (1971) *Chem. Commun.* 116.

[8] BRANDT, E. V., FERREIRA, D. and ROUX, D. G. (1972) *J.C.S. Chem. Commun.* 392.

[9] BRANDT, E. V., FERREIRA, D. and ROUX, D. G. unpublished work.

to all three species. The remaining peltogynoids and flavonoids have a more limited distribution, but are nevertheless often very prominent components, e.g. crombeone (**9**) in both *A. crombei* and *A. carnei*.

TABLE 2. DISTRIBUTION OF PELTOGYNOIDS AND FLAVONOIDS AMONGST THE HEARTWOODS OF *Acacia crombei*, *A. carnei* AND *A. peuce*

Peltogynoids	*A. crombei*	*A. carnei*	*A. peuce*	Flavonoids	*A. crombei*	*A. carnei*	*A. peuce*
 (3)	✓	✓	✓	 (10)	✓		
 (4)	✓	✓	✓	 (11)		✓	
 (5)			✓	 (12)		✓	✓
 (6)		✓		 (13)	✓	✓	✓
 (7)		✓		 (14)			✓
 (8)	✓		✓				
 (9)	✓	✓		 (15)		✓	

Variations within species

Variations between species as exemplified in Tables 1 and 2, even if broadly interpreted, must be considered in relation to significant variations within species as previously demonstrated for *A. cultriformis*.[2] Thus *A. tetragonophylla* exhibits the presence of mollisacacidin

(**1**, R=H) in six specimens, but is accompanied by high concentrations of guibourtacacidins (**2**, R=H) in five others; by high concentrations of 8-*O*-methyl ethers in one, and by a combination of these variations in three. From the total of seventeen specimens of *A. tetragonophylla* examined, two gave "anomalous" hydroxylation patterns 7,8,4′ and 7,4′; 7,8,3′,4′ and 8-OMe compared with those cited above. Such variability was, however, relatively rare (*A. salicina* and *A. leptostachya* are other examples), contrasting with many instances, e.g. *A. burkittii* (7 specimens), *A. coriacea* (10) and *A. monticola* (8), where consistent results were obtained from all specimens of many different origins.

Chemotaxonomic Correlations

Arbitrary subdivision of species on a chemical basis into two main groups as suggested above, namely mollisacacidin (**1**, R = H) + guibourtacacidin (**2**, R = H) series (7,3′,4′-trihydroxy + 7,4′-dihydroxy analogues) and melacacidin (**1**, R=OH) + teracacidin (**2**, R=OH) series (7,8,3′,4′-tetrahydroxy + 7,8,4′-trihydroxy series), permits the following observations.

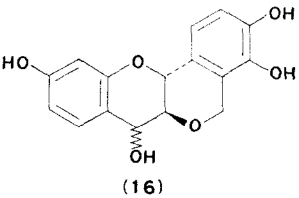
Melacacidin + teracacidin analogues populate almost exclusively the heartwoods of species under Section VII, Plurinerves [i.e. Subsections: (iii) Brevifoliae, (iv) Oligoneurae, (v) Microneurae and (vi) Nervosae] and under Section VIII, Juliflorae [i.e. Subsections: (i) Continuae, (iii) Rigidulae, (iv) Tetramerae, (v) Stenophyllae, (vi) Falcatae and (vii) Dimidiatae] (see Table 1). A number of exceptions are represented amongst the above, namely under Plurinerves, Subsection (vii) Dimidiatae, where the main chemical subdivisions are both represented individually in species or mixed; and under the Juliflorae, Subsections (v) Stenophyllae and (vi) Falcatae where mollisacacidin occasionally accompanies melacacidin.

Mollisacacidin–guibourtacacidin analogues on the other hand are distributed almost exclusively under the Botryocephaleae as shown before;[1] in the rather limited number of Brunioideae examined and perhaps somewhat surprisingly under a single Subsection, (vi) Racemosae of the Uninerves, with the notable exception of the differentiated *A. salicina*–*A. graffiana*–*A. frumentacea* groups (see Table 1). Isolated occurrence of mollisacacidin in a single species, *A. dorothea* under the Juliflorae, (vii) Uninerves is notable, but requires conformation. Amongst the otherwise uniformly mollisacacidin-containing Racemosae (52 species examined), the teracacidin-containing heartwood of *A. pruinocarpa* (3 specimens examined) and *A. ensifolia* (1 specimen examined) drew attention to the anomalous position of these species in the Uninerves Racemosae. On chemical and morphological grounds both taxa should be placed in the Uninerves Angustifoliae next to *A. victoriae* which has the same type of false racemose inflorescences as well as similar broad, flat, thin legumes with almost orbicular, horizontally placed seeds. These two species may provide a link with the differentiated groups of *A. salicina*, *A. graffiana* and *A. frumentacea* presently placed with the Racemosae, although with predominantly melacacidin content (see Table 1).

A third category of heartwood composition is represented by the "admixed" group of mollisacacidin (7,3′,4′-trihydroxy)-melacacidin (7,8,3′,4′-tetrahydroxy) and their associated guibourtinidin (7,4′-dihydroxy) and teracacidin (7,8,4′-trihydroxy) analogues. Species which reflect such "admixtures" are mainly grouped under the Sections: II Continuae, III Pungentes [Subsections: (ii) Plurinerves and (iii) Uninerves], IV Calamiformes [Subsections: (ii) Plurinerves and (iii) Uninerves] and VI Uninerves [Subsections: (iii) Triangulares, (iv) Brevifoliae and (v) Angustifoliae]. The *A. salicina*–*A. graffiana*–*A. frumentacea* groups classed under the Racemosae, show slight evidence of being a "mixed" group, but with emphasis on melacacidin as common denominator, and also as the main heartwood component of constituent species. The remaining Sections of the genus *Acacia*, namely Puchellae and Gumniferae (two and four species respectively of each) show evidence of representing "mixed" groups of species.

The distribution of peltogynoids, at present confined to three species, *A. peuce*, *A. carnei* and *A. crombei* (Table 2), as members of a large genus of the Mimosaceae, is unusual, also since compounds of this class have hitherto been regarded as restricted to the heartwoods of a number of species of the Caesalpiniaceae, namely *Peltogyne porphyrocardia*,[10-12] *P. pubescens*,[10,12] *P. venosa*,[10,12] *Trachylobium verrucosum*,[10,13] *Colophospermum mopane*,[11,12] *Gonniorrhacis marginata*[14] and *Distemonanthus benthamianus*.[15] Peltogynols (**3**, **4**), which represent the major components common to all three *Acacia* species (Scheme 2), are structurally related to mollisacacidin (**1**, R=H). Indeed, one of these, *A. crombei*, contains (+)-2,3-*trans*-3,4-*cis*-mollisacacidin (**10**), and all contain heartwood flavonoids (**10**–**15**) based on the phenolic 7,3′,4′-trihydroxyl pattern as represented by mollisacacidin. The peltogynoids crombenin (**8**) and crombeone (**9**) are similarly related[7,8] to the associated dihydroflavonol (+)-taxifolin (**15**), in all possessing a 3,5,7,3′,4′-hydroxylation pattern; the 5-OH group is otherwise rare in *Acacia* flavonoids. Parallel associations of peltogynoids and flavonoids exist amongst the Caesalpiniaceae.

Accordingly the presumed ability of enzymic systems to elaborate conventional flavonoid compounds by the introduction of the equivalent of a methylene group during D-ring cyclization, might be regarded as an "advanced" characteristic related to that previously found amongst closely related genera (*Colophospermum* under subfamily Caesalpinoideae Group 4, *Gonniorrhacis*, *Peltogyne* and *Trachylobium* under subfamily Caesalpinoideae Group 2 and *Distemonanthus* under Group 1)[16,17] of the Caesalpiniaceae. However, one point of distinction persists, considering that in the heartwoods of all the above genera of the Caesalpiniaceae D-ring formation leads to two alternative B-ring substitution patterns, represented by the analogues of the peltogynols (**1**–**3**) and those of the mopanols (**16**),[11,12,14,15] while in the single genus of the Mimosaceae only analogues of the former type (**1**–**3**) are represented. The above chemical relationships might in time assist in elucidating problems of phylogeny and taxonomy which undoubtedly exist amongst the Leguminales (see Ref. 16).



(**16**)

While the chemistry of the three peltogynoid-containing *Acacia* heartwoods suggests their close mutual relationship, these species are located under separate Sections of the

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[10] ROBINSON, G. M. and ROBINSON, R. (1935) *J. Chem. Soc.* 744.

[11] DREWES, S. E. and ROUX, D. G. (1966) *J. Chem. Soc.* **C**, 1644.

[12] DREWES, S. E. and ROUX, D. G. (1967) *J. Chem. Soc.* **C**, 1407.

[13] VAN DER MERWE, J. P., FERREIRA, D., BRANDT, E. V. and ROUX, D. G. (1972) *J.C.S. Chem. Commun.* 521.

[14] GOTTLIEB, O. R. and RÉGO DE SOUSA, J. (1972) *Phytochemistry*, **11**, 2841.

[15] KING, F. E., KING, T. J. and STOKES, P. J. (1954) *J. Chem. Soc.* 4587.

[16] HEYWOOD, V. H. (1971) in *Chemotaxonomy of the Leguminosae* (HARBORNE, J. B., BOULTER, D. and TURNER, B. L., eds.), pp. 1–29. Academic Press, New York.

[17] HUTCHINSON, J. (1964) *The Genera of Flowering Plants*, Vol. I. Clarendon Press, Oxford.

genus, namely II Continuae (*A. peuce*), III Pungentes, (iii) Uninerves (*A. carnei*) and VI Uninerves, (v) Angustifoliae (*A. crombei*). However, this observation could be regarded as being partly in line with the established distribution of the proposed basis of chemical subdivision (7,3′,4′-trihydroxy and 7,8,3′,4′-tetrahydroxy) throughout many Sections of the *Acacia*. It should be noted, however, that the peltogynoids lack an 8-hydroxy group which predominates in other species in the sub-divisions in which they occur.

Origins, relationships and evolutionary trends

The absence of the 5-hydroxyl group characterizes almost all flavonoid analogues present in the heartwoods of the *Acacia*, but is also generally characteristic of the Leguminosae.[18] According to current theory based on acetate (or malonate) synthesis of the phloroglucinol A-ring, the universal flavonoid precursor carries an oxygen substituent in the 5-position, and this is presumably removed during the final stages of biosynthesis.[18] The presence of resorcinol-type 5-deoxyflavonoids, as represented by mollisacacidin and guibourtacacidin (**1**, **2**, R=H) and their analogues in *Acacia* species, thus represents a loss mutation in evolution.[18] The presumption that subsequent 8-hydroxylation or 8-methoxylation to form melacacidin and teracacidin analogues (**1**, **2**, R=OH) represents further evolutionary change amongst *Acacia*, leads to the following considerations.

Bipinnate species. The Botryocephaleae, a group of 32 Eastern Australian species with bipinnate leaves developing no phyllodes and round inflorescences, are the most primitive both morphologically and chemically. Of the 29 species examined, all contain mollisacacidin (**1**, R=H) and its analogues, and in 2 taxa guibourtacacidin (**2**, R=H) is also present. No members of the Botryocephaleae are native to Western Australia, but are concentrated in New South Wales, South-Eastern Queensland, Victoria, Tasmania and to a lesser extent in South Australia. The centre of distribution appears to be New South Wales which has the largest number of species.

In the Pulchellae, which is almost confined to Western Australia and is especially common in the South-West, both mollisacacidin (**1**, R=H) and melacacidin (**1**, R=OH) are present, but insufficient species have been examined to enable reliable conclusions. The Pulchellae may have been derived from the Botryocephaleae. The inflorescences in most species are round, but in a few species spicate. However, except in one species, no phyllodes are formed, the bipinnate foliage persisting throughout the life of the plant.

In the Gummiferae four species have mollisacacidin but there is one record of teracacidin in *A. farnesiana*. Here it would be desirable to examine more material.

Phyllodinous species. The Brunioideae are considered primitive as they belong to the mollisacacidin series (**1**, R=H), but more should be examined for confirmation of this statement. In the Calamiformes and Pungentes both mollisacacidin (**1**, R=H) and melacacidin (**1**, R=OH) are recorded, but insufficient species have been studied. Teracacidin (**2**, R=OH) is present in one species of the Pungentes (iii) Uninerves and peltogynol (**3**) and its analogues in another. Only two species of the Continuae have been studied, one with peltogynol (**3**) and the other with melacacidin (**1**, R=OH).

The group of 55 species of the Uninerves (vi) Racemosae is considered to be primitive as all species belong to the mollisacacidin (**1**, R=H) series and bipinnate foliage persists with the foliage in the mature trees or shrubs of a few species. They were probably derived

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[18] HARBORNE, J. B. (1971) in *Chemotaxonomy of the Leguminosae* (HARBORNE, J. B., BOULTER, D. and TURNER, B. L., eds.), p. 43, Academic Press, New York.

from the Botryocephaleae. All except five of these species are native to Eastern Australia, which probably represents the centre of origin of the Australian species of *Acacia*. Under the Uninerves (vi) Racemosae is also a group of 9 species native to Western Australia and the inland regions of Australia recording melacacidin (**1**, R=OH) and melacacidin–mollisacacidin. These species in the *A. salicina*—*A. graffiana*—*A. frumentacea* groups are considered to be more advanced. In the Subsections (ii) Armatae, (iii) Triangulares, (iv) Brevifoliae and (v) Angustifoliae of the Uninerves both melacacidin (**1**, R=OH) and mollisacacidin (**1**, R=H) as well as melacacidin–mollisacacidin, teracacidin (**2**, R=OH) and peltogynol (**3**) have been recorded.

Thirty-four species of the Plurinerves [(iii) Brevifoliae, (iv) Oligoneurae, (v) Microneurae and (vi) Nervosae] belong to the melacacidin (**1**, R=OH) series, mollisacacidin being only recorded in *A. translucens*. In the Plurinerves (vii) Dimidiatae both mollisacacidin (**1**, R=H) and melacacidin (**1**, R=H) are recorded. The Plurinerves are considered to be more advanced chemically (increased emphasis on 8-hydroxylation) and also morphologically than the Uninerves.

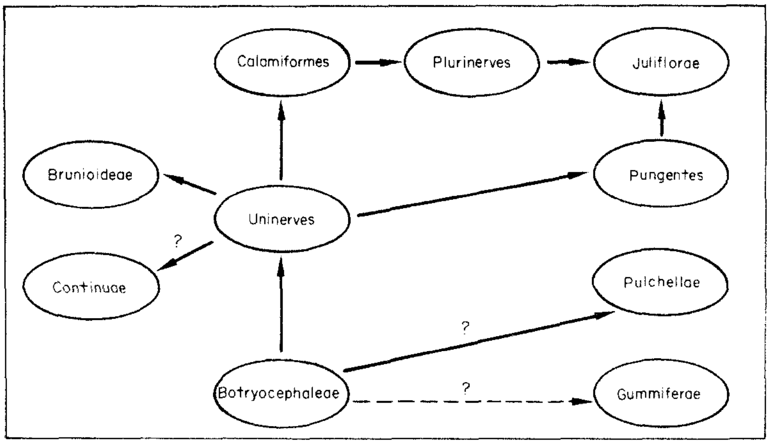

Fig. 1. Possible evolutionary trends amongst the *Acacia*.

The Juliflorae are regarded as the most highly evolved both morphologically and chemically. They are characterized by phyllodes, and are the only Australian group of species with spike-like inflorescences, except a few members of the Pulchellae. A fairly high percentage of the taxa, except in the Subsection (iv) Tetramerae, are native to tropical Northern Australia. Either melacacidin (**1**, R=OH) or teracacidin (**2**, R=OH) is recorded in the 80 species examined. Complex chemical associations such as melacacidin–mollisacacidin–teracacidin–guibourtacacidin or melacacidin–teracacidin are represented in single heartwoods especially in tropical species. In Subsection (vii) Uninerves *A. dorothea* has mollisacacidin + guibourtacacidin, this species having some morphological similarity with the Uninerves (vi) Racemosae especially the 1-nerved flattened phyllodes which resemble those of *A. rubida*. The inflorescences of *A. dorothea* are, however, very shortly spicate but not orbicular as in the Uninerves (vi) Racemosae, although chemical similarities apparently underlie the above individual morphological affinity. The most likely phyletic lines within the genus *Acacia* based on the above information are summarized in Fig. 1.

EXPERIMENTAL

Materials. Voucher specimens of all specimens examined are kept in the National Herbarium NSW. Voucher numbers can be had on request to either author.

Examination and generation of anthocyanidins from heartwood extracts. Chromatographic methods for the extraction and identification of components were those described previously.[1] The 8-*O*-methyl ethers of mollisacacidin and teracacidin were recognized by this high R_f values in a 3 N HCl–90% (w/w) formic acid (1:1, v/v) mixture.[2] The 3-*O*-methyl derivatives of flavonols lacking a 5-OH group were recognized by their blue fluoresence under UV light,[3,4] and by their position of 2-way chromatograms relative to the brilliantly yellow–green fluorescing related flavonols (lacking a 5-OH group), including their partial mobility in 2% AcOH.

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