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ANTHOCYANINS OF THE MELASTOMATACEAE, MYRTACEAE AND SOME ALLIED FAMILIES

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Key Word Index—Melastomataceae; Myrtaceae; Lecythidaceae; Myrtiflorae; acylated anthocyanins; malvidin-3-(*p*-coumarylrutinoside)-5-glucoside.

Abstract—Acylated anthocyanins were found to be abundant in the Melastomataceae but were not found in closely allied families. Their distribution may help in placing *Memecylon*. Anthocyanins of *Barringtonia* support the separation of the Lecythidaceae from the Myrtiflorae.

INTRODUCTION

Several naturally occurring anthocyanins have been shown to exist as glycosyl esters, containing one or more moles of caffeic, *p*-coumaric, or ferulic acid. Although the exact position of the acyl group on the sugar residue is difficult to establish and remains to be determined in most cases, the existence of the acyl group can be detected quite early in the process of extracting and identifying an anthocyanin. Deacylation and identification of resultant anthocyanin is readily carried out. Accordingly, it is possible to look for and at least partially identify such pigments in a reasonably large number of specimens. Although acylated anthocyanins have been recognized as characteristically present in certain taxa (Labiatae and Solanaceae) [1], no attempt appears to have been made to discover the limit of their distribution in the Tubiflorae or among any other plant group. One apparently isolated occurrence reported is that of malvidin-3-(*p*-coumarylglucoside)-5-glucoside in *Tibouchina semidecandral* [2]. This paper describes an investigation of the frequency of acylated anthocyanins in the Melastomataceae and in allied families. Cyanic flowers or fruit were studied from species in most families that have been included in the order Myrtiflorae according to the main systems of classification.

RESULTS AND DISCUSSION

Results obtained for flower or fruit pigments of 82 species are given in the accompanying table. Published results for several other species have not been included; however they serve to strengthen the correlation described below.

Most anthocyanins were known compounds, samples of which were on hand for direct comparison. Acylated anthocyanins were recognized initially by R_f values in relation to available anthocyanins with the same aglycone and by their lability to hydrolysis in acid media. Confirmation was obtained from the short-wavelength contribution to the UV spectrum, and by mild basic hydrolysis of the acyl linkage giving a different, identifiable, anthocyanin.

A practical problem was that many of these plants were small forest herbs from which little material could be obtained, and it was not always possible to obtain anthocyanins free from glycosyl esters of the same phenolic acids that occur in the acylated anthocyanins. Thus, after basic hydrolysis, the anthocyanin could be readily identified, but the identity of the liberated acid remained ambiguous. The extent to which the anthocyanins were identified is indicated by the names used in the table.

The most striking feature of the results is that acylated anthocyanins are evidently abundant in the Melastomataceae, occurring here in 24 out of 31 species, are almost certainly absent in the Myrtaceae, the other major family of the order (and the one with which it has closest affinity), and are probably absent from all the other families as well. The compounds thus show a discrete distribution at the family level. As this also appears to hold true in the Tubiflorae, and as there are several records of acylated anthocyanins from species in families other than those mentioned here, it seems likely that the presence of acyl residues in anthocyanins has more systematic value in this group of plants than the glycosidic or methylation pattern.

Results for two species of *Memecylon* support the proposed separation of the Memecyloideae as a separate family [3] but are of limited value because non-acylated anthocyanins do occur in the Melastomataceae. From herbarium annotations it seems that flower colour of some species is very like that of some Melastomataceae with acylated pigments, but fresh material of these has not so far been obtained.

Some other aspects of the anthocyanin structures are of interest. Malvidin was more common in the Melastomataceae (67%) than among the other species (48%). This appears to parallel the occurrence of highly alkylated ellagic acid derivatives in the Melastomataceae [4].

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Table 1. Anthocyanins in some members of the Myrtiflorae

Family and species	Cyanic part	Compounds identified	Source or voucher
MYRTACEAE: Myrtoideae			
Eugenia aquea Burm.	fr	Cy-3-glucoside	8763
E. malaccensis L.	fl	Mv-3,5-diglucoside	SBG
Feijoa sellowiana Berg.	fl	Cy-3-glucoside	SBG
Lophomyrtus bullata (Sol. ex A. Cunn.) Burret	fr	Cy-3-glucoside	AU
L. obcordata (Raoul.) Burret	fr	Cy-3-glucoside	AU
Neomyrtus pedunculata (Hook f.) Allan	fr	Cy-3-glucoside	AU
Psidium guajavica L.	fr	Cy-3-glucoside	—
Rhodomyrtus tomentosa Wight	fl	Mv-3-glucoside	—
Leptospermoideae			
Beaufortia squarrosa Schau.	fl	Pg, Pn-3,5-diglucosides	KP
Callistemon phoenicious Lindl.	fl	Cy-3-glucosides	KP
C. lanceolatus Sweet	fl	Cy-3-glucoside	—
Calothamnus oldfieldii F. Muell.	fl	Pn, Cy-3-glucosides; Cy-3,5-diglucoside	KP
C. quadrificus R. Br.	fl	Cy-3-glucoside	KP
C. torulosa Schau.	fl	Cy-3-glucoside	KP
C. villosa R. Br.	fl	Pg, Pn, Cy-3-glucosides	KP
C. gilesii F. Muell.	fl	Cy-3,5-diglucoside	KP
Eucalyptus caesia Benth.	fl	Cy-3-glucoside	KP
E. macrocarpa Hook.	fl	Cy glycoside	KP
Hypocalymma robustum Endl.	fl	Mv-3,5-diglucoside	KP
Kunzea baxterii (Klotz.) Schau.	fl	Cy, Dp-3-glucosides	KP
K. jocunda Diels	fl	Mv-3,5-diglucoside	KP
Leptospermum erubescens Schau.	fl	Mv-3,5-diglucoside	KP
L. flavescens Sm.	fl	Cy-3-glucoside	16288
L. scoparium Forst.	fl	Cy, Pn-3-glucoside	AU
L. seriaceum Labill.	fl	Mv-3,5-diglucoside	KP
Melaleuca nesophila F. Muell.	fl	Mv-3,5-diglucoside	KP
M. steedmani C. A. Gardn.	fl	Cy-3,5-diglucoside	KP
Meterosideros excelsa Sol.*	fl	Cy, Pn, Mv-3-glucoside	AU
M. fulgens Sol.	fl	Cy, Dp-3-glucosides	—
M. kermadecensis W. R. B. Oliver	fl	Pn, Pn, Cy-3-glucosides Pn Mv-3,5-diglucosides	AU
Scholtzia capitata F. Muell.	fl	Cy-3-glucoside; Cy-3,5-diglucoside	KP
S. parviflora F. Muell.	fl	Cy-3-glucoside; Cy-3,5-diglucoside	KP
CHAMELAUCIAE			
Chamelaucium uncinatum Schau.	fl	Dp-3-glucoside; Dp glycosides	KP
Darwinia citriodora (Endl.) Benth.	fl	Pg, Cy-3,5-diglucosides	KP
D. oldfieldii Benth.	fl	Cy-3,5-diglucoside	KP
Pileanthus pendunculatus Endl.	fl	Dp-3-glucoside: Dp rhamnoside	KP
Thryptomene denticulata (F. Muell.) Benth.	fl	Cy-3-glucoside; Mv-3,5-diglucoside	KP
T. maisonervii F. Muell	fl	Cy-3-glucoside; Dp rhamnoside	KP
Verticordia monadelpha Turcz.	fl	Cy, Dp-3,5-diglucosides	KP
V. picta Endl.	fl	Cy-3,5-diglucoside; Cy glycoside	KP
LECYTHIDACEAE			
Barringtonia macrostachya Kurz.	fl	Cy, Dp-3-sambubiosides	001310
B. racemosa Roxb.	fl	Cy, Dp-3-sambubiosides	04605
Couropita guinensis Hook.	fl	Cy, Dp-3-glucosides	SBG
RHIZOPHORACEAE			
Gynotroches axillaris Bl.	fr	Cy-3-glucoside	8627
LYTHRACEAE			
Lagerstroemia indica L.	fl	Dp, Pt, Mv-3-glucosides	SBG
L. speciosa (L.) Pers.	fl	Pn, Mv-3,5-diglucosides	12083
PUNICACEAE			
Punica granatum St Lag.*	fl	Pg-3,5-diglucoside	—

Table 1. Anthocyanins in some members of the Myrtiflorae

Family and species	Cyanic part	Compounds identified	Source or voucher
COMBRETACEAE			
Lumnitzera littorea (Jack) Voight	fl	Pg, Pn, Cy-3-glucosides: Pg, Pn-3,5-diglucosides	8600
Quisqualis indica L.	fl	Cy-3-glucoside	16122
Terminalia catappa L.	fr	Cy-3-glucoside	4080
MELASTOMATACEAE: Melastomatoideae			
Dissotis rotundifolia Benth.	fl	Mv-3,5-diglucoside	SBG
Melastoma malabathricum L.	fl	Mv-3,5-diglucoside	—
M. sanguineum Sims	fl	Mv-3,5-diglucoside; Cy-3-glucoside	005241
Oritrephes grandiflora Ridl.	fl	Cy-3-glucoside	
Osbeckia perakensis Ridl.	fl	Mv-3-(acylglucoside)-5-glucoside	18327
Oxyspora hispida Ridl.	infl	Mv-3-(*p*-coumarylrutinoside)-5-glucoside	15396
Phyllagathis elliptica	fl	acylated Mv glucoside	—
P. rotundifolia Bl.	fl	Mv-3-acylglucoside-5-glucoside	1353
P. scortechinii Ridl.	fl	acylated Pn glycoside	—
P. tuberculata King	fl	Mv-3-(*p*-coumarylglucoside)-5-glucoside	006675
Sarcopyramis nepalensis Wall.	fl	Mv-3,5-diglucoside; acylated Mv glycoside	7919
Sonerila argentea	fl	acylated Mv diglycoside	
S. erecta Jack.	fl	acylated Pn, Mv glycosides	9113
S. heterostemon Naud.	fl	acylated Mv glycosides	13380
S. rudis Stapf	fl	acylated Mv glycosides	4598
S. prostrata Ridl.	fl	acylated Mv glycosides	06239
Anplectrum pallens Geddes	fr	acylated Dp-3,5-diglucoside	—
A. divaricatum Triana	fr	acylated Cy, Dp-3,5-diglucosides	005995
Dissochaeta celebica Bl.	fr	Dp-3-(*p*-coumarylglucoside)-5-glucoside	
D. bracteata Bl.	fr	Dp, Mv-3-(acylglucoside)-5-glucoside	7674
Marumia reticulata Ridl.	fl	Mv-3-acylglucoside-5-glucoside	—
M. nemorosa (Bl.) Flor.	fl	Mv-3-acylglucoside-5-glucoside	—
Medinilla hasseltii Bl.	fr	Pg-3-(acylglucoside)-5-glucoside	9017
M. schortechinii King	infl	Pg-3-(*p*-coumarylglucoside)-5-glucoside	15954
M. heteroanthera King	fl	Pg-3-(acylglucoside)-5-glucoside	—
Driessenia glandulifera Cogn.	infl	acylated Cy diglycoside	—
Clidemia hirta Don	fr	acylated Dp-3,5-diglucoside	—
Tibouchina semidecandra Cogn.*	fl	Mv-3-(*p*-coumarylglucoside)-5-glucoside	AU
Pternandra coerulescens Jack	fr	acylated Mv glycoside	15656
ASTRONIOIDEAE			
Astronia smilacifolia Triana	fl	acylated Mv-3-diglycoside-5-glycoside	
MEMECYLOIDEAE			
Memcylon amplexicaule Roxb.	fr	Cy-3,5-diglucoside	5099
M. caeruleum Jack	fl	Mv-3,5-diglucoside	16376

Abbreviations: fl, flowers; fr, fruit; infl, inflorescence; SBG, Singapore Botanic Gardens; AU, University of Auckland campus; KP, King's Part Botanic Garden. * Species for which results have been reported previously [8].

The most common glycosidic pattern was the 3-glucoside or the 3,5-diglucoside. The 3-sambubiosides found in *Barringtonia* were not detected in any of the other families, a result of some interest because Cronquist [5] considers that the Lecythidaceae do not belong in the Myrtalean alliance but constitute a separate order, whose affinities probably lie with the Malvales. Sambubiose occurs in both anthocyanins and flavonol glycosides of various species of *Hibiscus* [6] and is a sufficiently rare sugar to be rated as evidence for affinity between these two groups.

EXPERIMENTAL

Plant material was collected from forest or other habitats in Peninsular Malaysia, Kinabalu National Park in Sabah, and from named collections in the University of Auckland, New Zealand, and in King's Park Botanic Garden, Perth, Australia. Voucher specimens of some species collected in the wild were deposited in the herbarium of the University of Malaya (KLU), and the aquisition numbers of these are given in the table. Extraction, purification and identification of anthocyanins and hydrolysis products were carried out according to standard methods [7]. Samples of acylated anthocyanins were treated with 1N NaOH at 28° under N_2 for 10 min. The soln was then acidified with HCl, dried *in vacuo*, and the anthocyanin taken up in absolute EtOH. Any traces of NaCl present in soln did not interfere significantly with identification of the anthocyanin.

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