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ANTHOCYANINS OF SOME MALAYSIAN MEMBERS OF THE GESNERIACEAE

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Key Word Index—Gesneriaceae; Cyrtandriodeae; anthocyanine; malvidin 3-arabinosylglucoside-5-glucoside; chemotaxonomy.

Abstract—The occurrence of 'normal' 3-hydroxylated anthocyanins in 8 Malaysian species of the Gesneriaceae supports the important chemotaxonomic results for this family. New compounds found in *Chirita*, *Didissandra* and *Didymocarpus* are the 3-arabinosylglucoside-5-glucosides of cyanidin and malidin, pigments which may have some systematic value.

INTRODUCTION

INTEREST in the anthocyanins of the Gesneriaceae has centred on the rare 3-desoxyanthocyanins, since the distribution of these has provided a positive contribution to taxonomy of the family. The pigment studies by Harborne[1] completely support the recent division of the family by Burtt[2] into subfamilies Gesnerioideae (mostly American species) and Cyrtandroideae (mostly Asian or African species). However the family consists of some 1200 species and is predominantly tropical, while the 46 species examined for their anthocyanins have been brought into cultivation in temperate localities, some as popular indoor plants. Evidently it would be desirable to increase the proportion of the family studied as well as to overcome any possible selection factor in the sample already covered. Although some 160 species have been reported for the Malayan peninsula,[3] many are of limited distribution or are recorded from forest areas now cleared, or have insignificant or acyanic flowers. Results reported here are for 8 species, all belonging to the Cyrtandroideae.

RESULTS AND DISCUSSION

All the aglycones identified were of the commonly occurring 3-hydroxylated type, thus supporting the limitation of 3-desoxyanthocyanins to the Gesnerioideae. The species-richness of the tropical rainforest ecosystem is accompanied by a high degree of infra-specific variation, the extent of this being of obvious relevance to any phytochemical studies. Variation was particularly noticeable among forest herbs that occupy a series of discrete and disjunct habitats, e.g. peat soil on mountain ridges. The results given in Table 1 refer to the specimens that were richest in anthocyanins, but *Didymocarpus crinita* in particular

[1] J. B. HARBORNE, *Phytochem.* **5**, 589 (1966).
[2] B. L. BURTT, *Notes Roy. Botan. Garden Edinb.* **24**, 205 (1962).
[3] H. N. RIDLEY, *Flora of the Malay Peninsula*, Crown Agents for the Colonies, London (1922).

had a wide range of flower colour, including acyanic forms, while the variety with foliar anthocyanin was seen in one locality only. Some collections of *Aeschynanthus obconicus* contained cyanidin-3-sambubioside in addition to the previously reported pelargonidin pigment,[1] but on the other hand the occurrence of different pigments in the corolla and clyx of *A. parvifolius* was a completely consistent feature.

TABLE 1. ANTHOCYANINS OF SOME MALAYSIAN GESNERADS

Species	No.*	Plant organ	Compounds†
Trichosporeae			
Aeschynanthus longicalyx	8089	Flower	Pg-3-sambubioside
A. obconica	14999	Flower	Pg- and Cy-3-sambubioside
A. parvifolius	6719	Corcolla	Pg-3-sambubioside
		Calyx	Cy-3-sambubioside
Didymocarpeae			
Chirita calignosa	5708	Flower	Mv-3-arabinosylglucoside-5-glucoside
Didissandra filicina	7750	Flower	Mv-3-arabinosylglucoside-5-glucoside; Mv-3,5-diglucoside
Didymocarpus atrosanguineum	14294	Flower	Cy-3-sambubioside; Cy glycoside
D. crinita	6613	Flower	Mv-3-arabinosylglucoside-5-glucoside
		Leaf	Cy-3-arabinosylglucoside-5-glucoside; Cy glycoside
Paraboea cordata	4193	Flower	Mv-3,5-diglucoside

* From specimens deposited in the Herbarium of the Division of Botany, School of Biological Sciences, University of Malaya, Kuala Lumpur.

† Abreviations: Cy, cyanidin; Mv, malvidin; Pg, pelargonidin.

In most cases a strong band of high mobility was seen in the first preparative chromatogram, but after elution and re-chromatographing this became identical to one of the lower-R_f components. This suggested that the anthocyanins were initially present in combination with a highly labile substituent but this was not investigated further.

TABLE 2. R_f VALUES OF NEW ANTHOCYANINS AND RELATED GLYCOSIDES*

Compound	R_f (× 100) in†			
	1% HCl	HOAc–HCl	BAW	BuHCl
Malvidin-3-glucoside	12	38	25	31
Malvidin-3,5-diglucoside	21	54	15	12
Malvidin-3-arabinosylglucoside-5-glucoside	45	78	22	14
Cyanidin-3-arabinosylglucoside-5-glucoside	39	60	15	05

* Determined at 28°, resulting in higher values than usually recorded.

† Solvents: 1% HCl, 12 N HCl–H_2O (3:97); HOAc–HCl, HOAc–H_2O–12 N HCl (15:82:3); BAW, *n*-BuOH–HOAc–H_2O (4:1:5); BuHCl, *n*-BuOH–2 N HCl (1:1).

Didymocarpus crinita was the best source of a new glycoside of malvidin. This had the spectrum and fluorescence of a 3,5-diglycoside and upon partial hydrolysis gave malvidin-3,5-diglucoside, malvidin-3-glucoside and malvidin-5-glucoside. Sugars obtained on total hydrolysis were glucose and arabinose in the approximate mole ratio of 2:1. Assuming,

from the structures of known anthocyanins, that the disaccharyl entity is attached at the 3-position then the compound must be a malvidin-3-arabinosylglucoside-5-glucoside. Leaves of *D. crinita* also yielded two cyanidin glycosides but in insufficient quantity for detailed investigation. From the R_f values (Table 2), it seems probable that one of these is cyanidin-3-arabinosylglucoside-5-glucoside.

Although arabinose not uncommonly occurs in direct combination with phenolic groups, this appears to be the first case of it being found in combination with other sugars in phenolic glycosides. The occurrence of xylosylglucosides (sambubiosides) has already been noted as a feature of the Cyrtandroideae[1] and it appears that the arabinosylglucosides may also be common in this subfamily. As the former are rare and the latter so far unknown from other sources, it seems likely that the chemotaxonomic value of the anthocyanin aglycones in the Gesneriaceae may be accompanied by a clear distinction in glycosidic type.

EXPERIMENTAL

Plant material was collected from forest areas or limestone hills in West Malaysia. Isolation and identification of anthocyanins was by the usual methods.[4] Authentic samples of anthocyanidins and sugars came from commercial sources and anthocyanins were isolated by the author from sources in which they had been identified completely.[5]

[4] J. B. HARBORNE, *Comparative Biochemistry of the Flavonoids*, Academic Press, London (1967).
[5] J. B. LOWRY, *Malaysian J. Sci.* **1**, 133 (1972).