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FLAVONOID PATTERNS AND PHYTOGEOGRAPHY: THE GENUS *RHODODENDRON* SECTION *VIREYA*

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Key Word Index—*Rhododendron*; Ericaceae; flavonoid pattern; flavonols; phytogeography; chemotaxonomy.

Abstract—A survey of leaf hydrolysates of 52 species in section *Vireya* of *Rhododendron* showed that the flavonols kaempferol, quercetin and myricetin were commonly present. However, other more characteristic *Rhododendron* flavonol derivatives were either rare (caryatin, azaleatin) or absent (gossypetin). A study of the glycosides in four representative species showed that quercetin and kaempferol were present as the 3-rhamnoside, 3-glucoside, 3-galactoside or 3-rutinoside. The pattern in section *Vireya* is thus simpler than that in other *Rhododendron* species. This is in keeping with its geographical isolation, most species being endemic to the mountains of the Malesian-Australian region.

INTRODUCTION

Previous investigations of flavonoids in the ornamentally important genus *Rhododendron* have centred on the species from Southeast Asia, which were collected and brought to Europe by Forrest, Kingdon-Ward and others. In a major survey of some 206 species, subspecies and cultivars, the frequencies of different flavonoid constituents were recorded and some correlations with taxonomy noted [1]. In addition to the more common flavonoid constituents (kaempferol, quercetin, myricetin, proanthocyanidins, dihydroflavonols), the leaves contained several rarer and more distinctive components. In particular, the yellow flavonol pigment gossypetin was widely recorded in 76% of the taxa, while the 5-*O*-methylated flavonols azaleatin and caryatin were found in 34% and 10% of the taxa respectively. These same compounds were also found, together with anthocyanins, in the flowers [2]. The leaves of some 18 North American species belonging to the subgenus *Pentanthera* have similarly been surveyed. The pattern was broadly similar

Table 1. Distribution of flavonoids in *Rhododendron* section *Vireya*

Subsection and species of *Rhododendron*	Edinburgh accession no.	My	Qu	Km	Az	Ca	Go	DHF
Pseudovireya								
R. retusum (Bl.) Benn.	672708	–	+	+	–	–	–	–
Phaeovireya								
R. beyerinckianum Koord	Stoner 7	+	+	–	–	–	–	–
R. dianthosmum Sleum.	613133	+	+	–	–	–	–	–
R. hooglandii Sleum.	671320	+	+	+	–	–	–	–
R. konori Becc.	681335	–	+	+	–	–	–	–
R. leptanthum F. Muell.	Black 132	–	+	–	–	–	–	–
R. phaeochitum F. Muell.	650269	–	+	–	–	–	–	–
R. rarum Schltr.	614238	–	+	–	–	–	–	+
R. superbum Sleum.	741177	+	+	–	–	–	–	–
Malayovireya								
R. acuminatum Hook. f.	762737 801263	+	+	+	–	–	–	+
R. durionifolium Becc.	762621	+	+	+	–	–	–	–
R. micromalayanum Sleum.	672554	–	+	+	–	–	–	–
Albovireya								
R. yelliottii Warb.	662231	+	+	–	–	–	–	–
Solenovireya								
R. jasminiflorum Hook. f.	Woods 581	+	+	+	+	–	–	–
R. orbiculatum Ridl.	672464	–	+	–	–	–	–	–
R. pneumonanthum Sleum.	672550	–	+	+	–	–	–	–
R. stapfianum Hemsl. ex Prain	801292	+	–	–	–	–	–	–
R. suaveolens Sleum.	762848	–	+	+	+	–	–	–

Table 1. (*Contd.*)

Subsection and species of *Rhododendron*	Edinburgh accession no.	My	Qu	Km	Az	Ca	Go	DHF
Vireya								
R. aurigeranum Sleum.	Woods 40	+	+	−	−	−	−	−
R. abietifolium Sleum.	801268	+	+	−	−	−	−	−
R. bagobonum Copel. f.	801147	−	+	+	−	−	−	−
R. brookeanum Low ex Lindl.	773344 690955	−	+	+	−	−	−	−
R. buxifolium Low ex Hook. f.	762764	+	+	−	−	−	−	−
R. crassifolium Stapf	672545 792889	−	+	+	−	−	−	+
R. christi Foerster	682541	−	+	−	+	−	−	−
R. christianna Sleum.	Woods 2231	−	+	+	+	+	−	−
R. culminicolum F. Muell. var. *rubicola*		+	+	−	−	−	−	+
R. gracilentum F. Muell.	Woods 1855	−	+	+	−	−	−	−
R. inconspicuum JJS	Black 1334	−	+	−	−	−	−	+
R. intranervatum Sleum.	622876	−	+	−	−	−	−	−
R. javanicum Reinw.	Woods 1053 730741	−	+	+	+	−	−	+
R. laetum JJS	670214	−	+	−	−	−	−	−
R. lanceolatum Ridl.	781729	+	+	+	−	−	−	+
R. leucogigas Sleum.	613136	−	+	−	−	−	−	−
R. macgregoriae F. Muell.	614242	−	+	−	+	+	−	−
R. meijeri Argent, Lamb & Phillips	801358	−	+	+	+	−	−	−
R. nervulosum Sleum. var. *exuberans*	801299	−	+	−	−	−	−	−
R. niewenhuisii JJS	781725	−	+	+	−	−	−	−
R. planecostatum Sleum.	801296	−	−	+	−	−	−	−
R. polyanthemum Sleum.	801253	−	+	−	−	−	−	−
R. praetervisum Sleum.	792879	+	+	−	−	−	−	−
R. robinsonii Ridl.	731358	−	+	−	−	−	−	−
R. rugosum Low ex Hook. f.	762747	+	+	−	−	−	−	−
R. stenophyllum Hook. f.	672546	−	+	+	−	−	−	−
R. vandeursenii Sleum.	681064	+	+	−	−	−	−	−
R. womersleyi Sleum.	762046	+	−	+	−	−	−	−
R. wrightianum Koord. var. *cyclopense* J.J.S.	670477	−	+	+	−	−	−	−
R. youngii Argent	762115	+	+	−	+	−	−	−
R. zoelleri Warb.	Woods 1895	−	+	+	−	−	−	−
Unclassified								
R. kawakamii	710098	−	+	+	−	−	−	−
R. limentodes	781723	−	+	+	−	−	−	−
R. searleanum	741176	−	+	−	−	−	−	−

Key: My, myricetin; Qu, quercetin; Km, kaempferol; Az, azaleatin; Ca, caryatin, Go, gossypetin; DHF, dihydroflavonol (usually dihydroquercetin).

Table 2. Percentage frequencies of flavonoid characters in leaves of *Rhododendron* species of different geographical origin

Flavonoid character	Frequency (as % species) in China, Burma, India, etc.	New Guinea, Papua, etc.	North American
Quercetin	100	94	100
Myricetin	51	35	35
Kaempferol	23	44	82
Azaleatin	34	15	12
Caryatin	10	4	12
Gossypetin	76	0	0
Dihydroflavonols	68	13	18
Size of species sample	206	52	18

to Asian species, although gossypetin was not found and 5-*O*-methylated flavonols had a low frequency [3].

In order to complete a flavonoid study of the genus *Rhododendron*, the section *Vireya*, a monophyletic group of 300 species restricted in their occurrence to the Malesian-Australian region, needs to be included. Over half these species are endemic to Papuasia and because they mainly grow in inaccessible mountain regions, they have only been recently collected and investigated [4]. Only one species, *R. lochae* from Queensland, had been examined earlier [1]. The present paper records an investigation of 52 such species for leaf flavonoids. Some of these results have been mentioned briefly in a symposium proceedings [5].

RESULTS

The results of surveying *Vireya* species for flavonoid aglycones in the leaf are presented in Table 1, where the taxa are arranged in subsections, following the taxonomic studies of G. Argent [unpublished results]. The patterns are compared with those of other *Rhododendron* species in Table 2. The major flavonols are kaempferol, quercetin and myricetin, as in Southeastern Asian species, but myricetin has a lower frequency and kaempferol a higher frequency. Gossypetin (8-hydroxyquercetin) is notably absent, while azaleatin (5-methylquercetin) occurs in eight and caryatin (3,5-dimethylquercetin) in two species. Dihydroflavonols are present but in much fewer species (13% compared to 68%).

From patterns of spots on two-dimensional chromatograms of leaf extracts, it appears that the glycosidic complexity of the flavonols present in species of section *Vireya* is less than in other species. Only two to three glycosides of any given flavonol were present, whereas in the Asian species four or five glycosides could often be detected [1]. Detailed examination of the glycosides in four representative species confirmed this point. Thus, *R. bagobonum* was found to contain rutin (quercetin 3-rhamnosylglucoside), *R. javanicum* kaempferol 3-rhamnoside and an azaleatin 3-diglycoside, *R. pneumonanthum* rutin and quercetin 3-glucoside and *R. crassifolium* the 3-glucosides and 3-galactosides of kaempferol and quercetin.

There are no obvious correlations between flavonoid occurrences and subsectional classification (see Table 1). This is not surprising in view of the general uniformity within section *Vireya*, apart from the variation in floral characters [4].

DISCUSSION

According to Stevens [4], species of section *Vireya*, while separated from other *Rhododendron* taxa on the basis of seed and indumentum characters, are most distinctive in their geography (mostly high mountain regions of Malesia-Australia) and their highly developed floral types. According to the flavonoid chemistry now revealed (Table 2), they have a simpler pattern of compounds than Southeastern Asian species. Several characteristic *Rhododendron* constituents occur less frequently (e.g. azaleatin), while gossypetin is completely lost.

In other sections of *Rhododendron*, the occurrence of gossypetin in the leaves is correlated with its presence in flowers, where it contributes to yellow flower colour. The disappearance of gossypetin from the leaves of section *Vireya* species suggests it may well be absent from the flowers, although this has still to be established experimentally. If this is so, then its absence from the leaves may be associated with changes in pollinating vectors. Certainly, section *Vireya* flowers are morphologically distinct from the flowers of other *Rhododendron*, reflecting their pollination mainly by birds, sphingid moths and butterflies [4]. Pollinators and flower types are probably different in Southeastern Asian species, although their pollination biology has not yet been studied in as great a detail.

The most striking feature of the present results is the correlation with phytogeography. It is most noticeable that the differences in flavonoid patterns between species of Southeastern Asia and those of Malesia-Australia are very similar to those between species of Southeastern Asia and North America (Table 2). This fact and the nature of the changes in flavonoid chemistry would most readily be interpreted if the genus *Rhododendron* had originated in Southeastern Asia, in central China or the Himalayan regions, and radiated out from such a centre. The plants of Borneo, Papua and New Guinea could then be regarded as one series of more recently evolved species, while those of North America would be another. Such speculation, however, depends heavily on the morphological and anatomical evidence and at present, there seems to be little agreement among taxonomists about evolutionary trends within the genus [6]. The simplification in flavonoid chemistry with advancement could, however, be readily fitted into our general view of evolving pathways of flavonoid synthesis within the angiosperms [7].

EXPERIMENTAL

Plant material. Freshly dried leaves were supplied from the living collection of *Rhododendron* species growing at Edinburgh Botanic Garden. Herbarium specimens have been deposited there for reference purposes.

Flavonoid analyses. These were carried out by standard procedures, as described earlier.

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