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THE OCCURRENCE OF FLAVONOL ARABINOSIDES IN THE EPACRIDACEAE

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Key Word Index—*Epacris*; *Cyathodes*; Epacridaceae; foeniculin; avicularin; flavonol-3-arabinosides; chemotaxonomy.

Abstract—Foeniculin (quercetin-3-arabinoside) has been detected in 26 species of Epacridaceae. The structural analogues of myricetin and kaempferol have also been observed. Avicularin cooccurred with foeniculin in one species.

INTRODUCTION

Four different quercetin-3-arabinosides have been reported in the angiosperms [1]. One of these, avicularin (3-α-L-arabofuranoside), is of widespread occurrence, whilst the other three, guaijaverin (3-α-L-arabopyranoside), polystachoside (3-β-L-arabinoside) and foeniculin (configuration unknown), are each known only from a single species.

Table 1. The occurrence of flavonol arabinosides (foeniculin analogues) in the Epacridaceae

Plant species	3-arabinoside of My	Qu	Km†
Subfamily Epacrideae			
Archeria comberi Melville	a	L,P	L,P
Dracophyllum minimum F. Muell.	a	P	a
Epacris acuminata Benth.	a	L,P	P
E. corymbiflora Hook. f.	a	L	a
E. impressa Labill.	a	L,P	L
E. lanuginosa Labill.	L	L,P	a
E. marginata Melville	L	L	a
E. virgata Hook f.	a	L	a
Prionotes cerinthoides (Labill.) R.Br.	a	L,P	P
Richea procera (F. Muell.) F. Muell.	a	L,P	L,P
*R. scoparia** Hook. f.	L	L,P	L,P
Sprengelia incarnata Sm.	a	L,P	L
Subfamily Styphelieae			
Acrotriche serrulata (Labill.) R.Br.	L	L	a
Astroloma humifusum (Cav.) R.Br.	a	a	a
A. pinifolium (R. Br.) Benth.	L	a	a
Brachyloma daphnoides (Sm.) Benth.	a	L,P	a
Cyathodes dealbata R.Br.	L,P,Fr	L	a
C. glauca Labill.	a	L	a
C. parvifolia R.Br.	L	L,Fr	a
C. petiolaris (D.C.) Druce	Fr	L,Fr	a
Leucopogon australis R.Br.	a	L	a
L. ericoides (Sm.) R.Br.	a	a	a
L. hookeri Sond.	a	L,P,Fr	L,P
L. lanceolatus (Sm.) R.Br.	a	a	a
Lissanthe sapida R. Br.	a	L,P,Fr	L,P,Fr
L. strigosa (Sm.) R.Br.	a	L,P,Fr	a
Monotoca empetrifolia R.Br.	L,P	L,P,Fr	a
Styphelia adscendens R.Br.	a	a	a
Trochocarpa cunninghamii (D.C.) W. M. Curtis	L	L,P	a
T. gunnii (Hook. f.) Benth.	a	L	a

*avicularin cooccurs with foeniculin in the corolla and the leaves.
† Key: L = leaves, P = petals and stamens, Fr = fruit, a = absent.

RESULTS AND DISCUSSION

In an earlier survey of anthocyanins in the Epacridaceae [2], the characteristic glycosides were identified as 3-arabinosides and 3-galactosides. During a survey of flavonols, these same sugars were identified amongst the 3-glycosides of quercetin, myricetin and kaempferol. Further examination using cochromatography, indicated that the epacrid quercetin-3-arabinoside was structurally different from avicularin isolated from leaves of *Rhododendron indicum* (Ericaceae). R_f data of the epacrid pigment suggested that it might in fact be foeniculin, and this was confirmed by cochromatography of an authentic reference isolated from leaves of *Foeniculum vulgare* (Umbelliferae) [3]. Neither authentic foeniculin nor the epacrid pigment was hydrolyzed by α- and β-glycosidase (yeast extract and emulsin, respectively), again suggesting the two compounds are identical. By way of comparison polystachoside and avicularin are hydrolyzed by α- and β-glycosidase, respectively [1], but the reaction of guaijaverin is unknown.

In contrast to its apparent rarity elsewhere in the plant kingdom, foeniculin is widespread in the Epacridaceae and is present in the majority of species studied (26/30). It is seldom present as the dominant pigment but it occurs in significant quantities in many species. Myricetin and kaempferol 3-arabinosides are also present (10/30 and 9/30, respectively) (Table 1), and are assumed to be structural analogues of foeniculin. Of the two, the kaempferol derivative has been recorded elsewhere [3], but the myricetin derivative has not previously been reported.

The more familiar arabinoside of quercetin, avicularin, also occurs in the Epacridaceae but is apparently rare. However, its routine detection by PC is difficult due to overlapping by kaempferol 3-arabinoside (foeniculin analogue) and its actual occurrence may be more widespread than is reported here. Confident identification has been made in only one species, *Richea scoparia*, where it is present in relatively high concentration.

EXPERIMENTAL

Plant material. Fresh material was used throughout the investigation. Flowers, leaves and fruit were examined from all species of the sub family Slyphelieae, but only flowers and leaves were examined from species of the sub family Epacrideae. All species were obtained from their native habitat in Tasmania or from mainland Australia. Voucher specimens have been placed in the Botany Department Herbarium, University of Tasmania.

Table 2. R_f data (× 100) for flavonol arabinosides

	BAW	15% AcOH	H_2O	PhOH
foeniculin	61	27	6	50
avicularin	73	31	8	54
My 3 arabinoside (foeniculin analogue)	41	18	3	23
My 3 arabinoside (avicularin analogue)	58	25	6	24
Km 3 arabinoside (foeniculin analogue)	73	35	7	76
Qu 3 galactoside	56	36	8	50

Pigment identification and distribution. 2D-PC was used in the general survey of species, and routine identification of pigments was based on R_f and colour reactions. Standard chromatographic and spectral procedures were used in the determination of basic flavonol structure. Specific identification of foeniculin, the analogous kaempferol arabinoside and avicularin was made using cochromatography with authentic references (from *Foeniculum vulgare* and *Rhododendron indicum*). Myricetin arabinoside (avicularin type) (Table 2) was obtained from leaves of *Daboecia cantabrica* (Ericaceae). Rigorous R_f data (Table 2) was obtained using 50 μl of a solution (OD = 1.0) of the purified pigment. Enzyme hydrolyses were carried out for avicularin, foeniculin (epacrid pigment) and authentic foeniculin as follows: 1 mg of pigment was used with 1 mg of enzyme in 1 ml of buffer (acetate buffer, pH 5 for β-glycosidase and phosphate buffer pH 6.8 for α-glycosidase). The activity of the enzymes was verified using avicularin (β-glycosidase) and maltose (α-glycosidase) as test substrates.

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