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THE TAXONOMIC SIGNIFICANCE OF LEAF FLAVONOIDS IN WEST MALAYSIAN DICRANOPTERIS TAXA (GLEICHENIACEAE)

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SUMMARY

A survey of leaf flavonoids in *Dicranopteris curranii, D. pubigera* and some varieties of *D. linearis* have shown that major flavonoids are flavonols and flavones with glycosidic combination at the 4'-, 3- and/or 7-positions. It is remarkable that each species and each variety of *D. linearis* is distinguished by at least one different flavonol or flavone.

INTRODUCTION

The flavonoid and *C*-glycosylxanthones based on 1,3,6,7-tetrahydroxyxanthone contents of *Dicranopteris linearis* (Burm.) Underw. and *D. pectinata* (Willd.) Underw. have been studied (Wallace et al., 1983). Two species, *D. pubigera* (Blume) Nakai and *D. curranii* Copel., and four varieties of *D. linearis*, i.e. var. *linearis*, var. *alternans* (Mett.) Holttum, var. *montana* Holttum, and var. *subpectinata*. (Christ) Holttum, from this genus were not chemically investigated earlier. In this study the detailed flavonoid chemistry of these six taxa is reported.

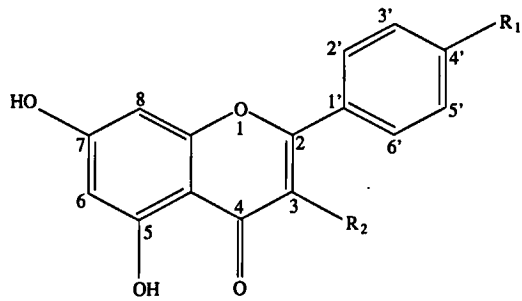
MATERIALS AND METHODS

Fresh specimens were collected from various localities in West Malaysia from June to December, 1993. Voucher specimens were deposited in the Universiti Pertanian Malaysia herbarium. Fresh leaves were exhaustively extracted with 80% methanol. The methanolic extract was evaporated under reduced pressure. Two-dimensional chromatograms of the concentrated extracts were run on Whatman No. 1 paper in BAW (4:1:5) and 15% acetic acid. Individual flavonoid glycosides were separated by paper chromatography on Whatman 3MM paper using standard procedures (Markham, 1982; Harborne, 1989). Standard procedures for the identification of flavonoid glycosides were applied, using standards where available (Harborne, 1967; Mabry et al., 1970).

Table 1. Flavonoid identification in the pinnae of *Dicranopteris* and its varieties.

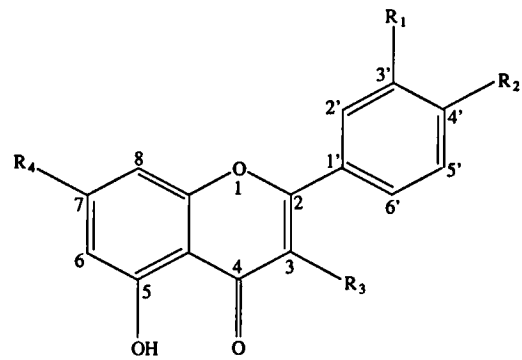
No.	Flavonoid glycosides Km: Kaempferol Qu: Quercetin Ap: Apigenin Lu: Luteolin	Colour(s) in UV / UV+NH_3	Rf_s in				UV spectrum in			
			BAW	H_2O	15%	PhOH	80% MeOH	+NaOAc	+H_3BO_3	+NaOH
1.	Qu-7-OMe-3-rhamnoside	Dk / Yg	74	38	55	63	344.8, 265	272.4	344.6	345.8 (dec.)
2.	Qu-3-arabinoside	Dk / Y	51	37	56	52	350.2, 257.2	268.8	369.4	373.8
3.	Qu-7-OMe-3-arabinoside	Dk / Yg	56	45	65	54	343.2, 266	273	351	355.8 (dec.)
4.	Km-3-glucoside	Dk / Y	76	27	51	62	355, 256	271.4	374	379
5.	Qu-3-rhamnoside	Dk / Y	77	38	52	64	350, 262.6	269	362	374
6.	Km-4'-OMe-7-arabinoside	Dk / Y	65	44	06	50	355.5, 267 sh, 257	271.5	384.5	393 (dec.)
7.	Km-4'-OMe-7-glucoside	Dk / Dk	58	31	51	61	346.5, 291 sh, 265	267.5	349.5	370 (dec.)
8.	Km-3-OMe-7-glucoside	Dk / Yg	78	29	51	78	348.5, 295 sh, 265	272.5	352.5	371.5
9.	Km-3-arabinoside	Dk / Yg	76	29	41	87	352, 315.5, 264	272	334.1	370.5
10.	Km-4'-OMe-3-glucoside	Dk / Dk	60	33	56	47	349, 263	270	355	396.5
11.	Km-3-OMe-7-rhamnosylarabinoside	Dk / Y	80	37	46	83	343.5, 264	272.5	346	363
12.	Qu-7-arabinoside	Y / Y	38	68	14	23	366.8, 272	279	369.6	378.6
13.	Qu-3-glucoside	Dk / Y	59	41	53	49	354, 282.5, 257.5	272	373	492.5
14.	Km-3-rhamnoside	Dk / Y	80	38	51	74	343.5, 264.5	272	346.5	390
15.	Km-3,7-diglucoside	Dk / Yg	63	61	61	53	350, 266.5	267.5	351.5	398
16.	Km-3,4'-OMe-7-arabinoside	Dk / Dk	77	30	43	66	350, 270	272	352	394.5
17.	Km-3-OMe-7,4'-diglucoside	Dk / Dk	66	61	66	55	350, 271	273	351.5	347.5 (dec.)
18.	Km-3,7-diarabinoside	Dk / Yg	64	35	64	61	346.5, 293 sh, 267	270	350	371
19.	Qu-3-xylosylglucoside	Dk / Y	78	39	51	76	363.5, 257	271	366	379.5
20.	Qu-3-OMe-7-glucoside	Dk / Yg	57	48	66	69	345.5, 288, 265.5	272	390	393
21.	Qu-3-rutinoside	Dk / Y	81	29	47	64	349, 264 sh, 256	270.5	379	367.5
22.	Km-3,4'-diglucoside	Dk / Dk	72	24	43	56	350.5, 293, 266	273.5	351.5	387.5
23.	Qu-7-OMe-3-xylosylglucoside	Dk / Yg	83	47	50	73	347.5, 263.5	271.5	352	379.5
24.	Km-4'-arabinosylglucoside	Dk / Dk	87	38	55	79	344, 264	271	347	390
25.	Ap-7-rhamnoside	Dk / Y	79	39	55	62	344.4, 264	271.6	346.2	348.8
26.	Lu-7-glucoside	Dk / Yg	76	39	49	67	342, 269	274	350	395.5
27.	Lu-3'-OMe-7-rhamnoside	Dk / Yg	78	27	53	64	344, 264, 292.5	272.5	344	379.5

Colours: Dk = dark; Y = yellow; Yg = yellow-green — BAW = butanol-acetic acid-water; PhOH - saturated phenol in water — sh = shoulder.



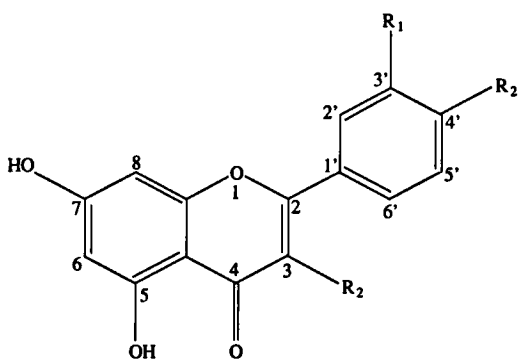
I

$R_1 = R_2 = OH$: Kaempferol (= Km)
$R_1 = OH$; $R_2 = OMe$: Isokaempferide (= Km-3-OMe)
$R_1 = OMe$; $R_2 = OH$: Kaempferide (= Km-4'-OMe)
$R_1 = R_2 = OMe$: Ermanin (= Km-3,4'-diOMe)



II

$R_1 = R_2 = R_3 = R_4 = OH$: Quercetin (= Qu)
$R_1 = R_2 = R_3 = OH$; $R_4 = OMe$: Rhamnetin (= Qu-7-OMe)
$R_1 = OMe$; $R_2 = R_3 = R_4 = OH$: Isorhamnetin (= Qu-3'-OMe)



III

$R_1 = H$; $R_2 = OH$: Apigenin (= Ap)
$R_1 = R_2 = OH$: Luteolin (= Lu)
$R_1 = OMe$; $R_2 = OH$: Chrysoeriol (= Lu-3'-OMe)

Fig. 1. Flavonoids detected in Malaysian *Dicranopteris* taxa.

Table 2. Flavonoid distribution in the pinnae of *Dicranopteris* species and its varieties.

Taxon Collector number Locality	Flavonoid *O*-glycosides																										
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27
D. curranii Copel. *Umi Kalsom 296* Cameron Highland, Pahang, W Malaysia	–	–	–	–	–	o	o	o	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
D. pubigera (Blume) Nakai *Umi Kalsom 288* Cameron Highland, Pahang, W Malaysia	–	–	–	+	–	–	–	–	–	–	–	–	+	–	o	+	+	+	–	–	–	–	–	–	–	–	–
D. linearis (Burm.) Underw.																											
var. *linearis* *Umi Kalsom 279* Hutan Simpan Mata Air, Perlis, W Malaysia	–	–	–	o	–	–	–	–	–	–	+	+	+	o	–	–	–	–	–	–	–	–	–	–	–	–	+
var. *alternans* (Mett.) Holttum *Umi Kalsom 317* Gunung Ledang, Johor, W Malaysia	–	–	–	o	–	–	–	–	–	–	–	–	+	–	–	–	–	–	+	+	+	–	+	–	–	–	–
var. *montana* Holttum *Umi Kalsom 273* Fraser's Hill, Pahang, W Malaysia	–	–	–	–	–	–	–	–	+	–	–	+	–	–	–	–	–	–	–	–	–	–	–	–	–	+	–
var. *subpectinata* (Christ) Holttum *Umi Kalsom 297* Cameron Highland, Pahang, W Malaysia	+	+	+	+	+	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	+	–	–	–

o = major compounds, + = minor compounds

RESULTS AND DISCUSSION

Two-dimensional paper chromatograms of 80% methanolic extracts of *Dicranopteris* species and varieties showed that flavonols and flavone *O*-glycosides were major components of leaf flavonoids. Subsequent analysis of the isolated flavonols and flavone *O*-glycosides were carried out by chemical and spectroscopic means and 27 glycosides were obtained (Table 1 and Fig. 1). Their distribution is given in Table 2. Previous workers (Wallace et al., 1983) studied *D. linearis* from Hawaii and found a different flavonoid pattern. They found quercetin-3-glucoside, kaempferol-3-glucoside, quercetin-3-rutinoside, quercetin-3-rhamnoside, and kaempferol-3-rhamnoside, but they found kaempferol-3-rutinoside as well. The differences in flavonoid patterns between *D. linearis* from Malaysia and Hawaii suggest geographical variation. *Dicranopteris curranii* yielded a very simple profile consisting of three compounds (see Table 2). *Dicranopteris pubigera* yielded six flavonol glycosides (Table 2).

From a chemotaxonomic view, it is remarkable that each taxon of *Dicranopteris* possesses at least one flavonoid not present in the other investigated taxa. Thus quercetin-3-xylosylglucoside, quercetin-3-methyl ether-7-glucoside, quercetin-3-rutinoside, quercetin-7-methyl ether-3-xylosylglucoside, and kaempferol-4'-arabinosylglucoside were observed only in *D. linearis* var. *alternans*, apigenin-7-rhamnoside only in *D. linearis* var. *subpectinata*, kaempferol-3-methyl ether-7-rhamnosylarabinoside, luteolin-3'-methyl ether-7-rhamnoside, kaempferol-3-rhamnoside and quercetin-7-arabinoside in *D. linearis* var. *linearis* and luteolin-7-glucoside only in *D. linearis* var. *montana*. *Dicranopteris curranii* had compounds 6–8 as a taxon-characteristic flavonoid; *D. pubigera* produced compounds 15–18 which were not detected in the other taxa. The taxa of *Dicranopteris* studied are difficult to distinguish because of the similarity in pinnae morphology. The results presented here suggest that flavonoid patterns of pinnae may be useful characters for classification in *Dicranopteris*.

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