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A FURTHER SURVEY OF FERNS FOR CINNAMIC AND BENZOIC ACIDS*

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Abstract—Forty-six species or varieties of ferns have been examined for phenolic acids. Of widespread occurrence are *p*-coumaric, caffeic, and ferulic acids as well as the correspondingly substituted benzoic acids.

RESULTS AND DISCUSSION

IN THE first paper in this series[1] an examination of forty-six ferns for phenolic acids was reported. *p*-Coumaric acid, caffeic acid, and ferulic acid were widely encountered as were the correspondingly substituted benzoic acids. The current study represents an extension of the survey made possible by the availability of new sources of plants. Added to the list are forty-six ferns representing one new family, two new tribes within the Polypodiaceae, two new varieties of *Pteridium aquilinum*, and an additional 18 genera. The results are recorded in Table 1.

Examination of the results of this survey again point to the widespread occurrence of *p*-coumaric acid, caffeic acid, ferulic acid, *p*-hydroxybenzoic acid, protocatechuic acid, and vanillic acid which we referred to earlier[1] as the "basic complement" of phenolic acids in ferns. Of much more limited distribution are sinapic acid *o*-coumaric acid, salicylic acid, gentisic acid, and syringic acid. A compilation of the results of the two surveys is given in Table 2. The three ferns mentioned in the paper by Ibrahim, Towers and Gibbs[2] were not included due to the incompleteness of their study.

A small number of ferns, from this as well as the earlier study, did not yield any detectable cinnamic acid or benzoic acid derivatives by the chromatographic method used. This may reflect a concentration below that observable by the procedure and does not necessarily suggest that these organisms lack the ability to elaborate phenolic compounds. It is also possible that the analyses were performed at a time in the plant's life when the phenolic acid concentration was at a minimum. The variability of phenolic acid content in ferns was demonstrated recently in our laboratory.[3]

It is clear from the results that most ferns possess the enzymatic machinery necessary to synthesize the more common cinnamic and benzoic acids. The sporadic occurrence of sinapic acid and *o*-coumaric acid, however, raises a very interesting question concerning their biosynthesis. Does the small number of ferns which contain these acids possess unique enzyme systems (*o*-hydroxylation in the case of *o*-coumaric acid; and 5-hydroxylation followed

* Part V in the series "Phenolic Compounds in Ferns".

[1] B. A. BOHM and R. M. TRYON, *Can. J. Botany* **45**, 585 (1967).
[2] R. K. IBRAHIM, G. H. N. TOWERS and R. D. GIBBS, *J. Linn. Soc., Botany* **58**, 223 (1962).
[3] A. D. M. GLASS and B. A. BOHM, *Phytochem.* **8**, 371 (1969).

TABLE 1. CINNAMIC AND BENZOIC ACIDS IN SOME FERNS

	*	PAC		CAF		FER		SIN		HBA		PRO		VAN	
	Source	a	b	a	b	a	b	a	b	a	b	a	b	a	b
Ophioglossaceae—															
Botrychium multifidum J. G. Gmelin	BC	+	+	+	+	+	+	−	−	+	+	−	−	+	+
B. virginianum Swartz	BC	+	+	+	+	−	−	−	−	+	+	−	−	−	−
Gleicheniaceae—															
Dicranopteris emarginata (Brack.) Robinson	HI	+	+	+	+	+	+	−	−	+	+	+	+	+	−
Hymenophyllaceae—															
Hymenophyllum barbatum V. den Bosch	MI	+	−	+	+	−	−	−	−	+	−	−	−	−	−
Mecodium recurvum (Gaud.) Copel.	HI	+	+	+	+	−	−	−	−	+	+	−	+	−	+
M. wrightii (V. den Bosch.) Copel.	QC	+	+	+	+	+	+	−	−	+	+	+	+	+	+
Vandenboschia cyrtotheca (Hilleb.) Copel.	MI	+	+	−	−	−	−	−	−	+	+	−	−	+	+
V. davalliodes (Gaud.) Copel.	HI	−	−	−	−	−	−	−	−	−	−	−	−	−	−
Gonocommus minutus (Blume) V. den Bosch.	MI	−	−	−	−	−	−	−	−	−	−	−	−	−	−
Cyatheaceae—															
Cyathea fauriei (Christ.) Copel.	TOK	+	+	+	+	+	−	−	−	+	+	+	+	+	−
C. hancockii Copel.	TOK	+	+	+	+	+	+	−	−	+	+	+	+	−	−
C. metteniana (Hance) Christ. et Tard.	TOK	+	+	+	+	+	+	−	−	+	+	+	+	+	−
C. podophylla Hook	TOK	+	+	+	+	+	+	−	−	+	+	+	+	−	−
Polypodiaceae—															
Woodsieae															
Woodsia oregana D. C. Eaton	BC	+	+	+	−	+	−	−	−	+	+	+	−	−	+
Dryopterideae															
Ctenitis decomposita (R. Br.) Copel.	UBC	+	+	+	+	−	+	−	−	+	+	+	−	+	−
Dryopteris austriaca (Jacq.) Woynar.	BC	+	+	+	−	+	+	−	−	+	+	+	−	+	+
D. felix-mas (L.) Schott.	BC	+	+	+	+	+	+	−	−	+	+	+	−	+	+
Gymnocarpium dryopteris (L.) Newm.	BC	−	+	−	−	−	−	−	−	−	+	−	−	−	−
Lastrea globulifera Brack.	HI	−	+	+	+	+	+	−	−	−	−	−	+	−	−
Polystichum andersonii Hopkins	UBC	−	+	−	−	−	+	−	−	−	+	−	−	−	−
P. lonchitis (L.) Roth	BC	+	+	−	−	−	−	−	−	+	+	−	−	+	−
Thelypteris phegopteris Slossen	BC	+	+	−	−	+	+	−	−	+	+	−	−	+	−
Asplenieae—															
Asplenium unilaterale Lamarck	HI	−	+	+	+	−	+	−	−	−	+	−	−	−	−
Blechneae—															
Blechnum brasiliense Desv. var. *crispum* hort.	TOK	+	+	+	−	−	−	−	−	+	+	−	−	−	−
B. discolor (Forst.) Keys	TOK	−	−	+	−	−	−	−	−	−	−	−	−	−	−
B. orientale L.	TOK	−	+	+	+	−	−	−	−	−	+	−	+	−	−
B. spicant (L.) Roth.	BC	+	+	+	+	+	+	−	−	+	+	+	+	+	+
Doodia dives Kunze	TOK	−	−	−	+	−	−	−	−	−	−	−	−	−	−
Sadleria hillebrandii Robinson	HI	−	+	+	+	−	−	−	−	−	−	−	−	−	−
S. cyatheoides Kaulf.	HI	+	+	+	+	+	+	−	+	+	+	+	+	+	+
Woodwardia orientalis S.W. var. *formosana* Ros.	TOK	−	−	−	−	−	−	−	−	−	−	−	−	−	−
W. unigemmata (Makina) Nakei	TOK	−	−	−	−	−	−	−	−	−	−	−	−	−	−
Dennstaedteiae—															
Dennstaedtia wilfordii (Moore) Koidz.	UBC	+	+	+	+	+	+	−	−	+	+	+	−	+	+
Microlepia setosa (Smith) Alston	HI	−	+	+	+	−	+	−	+	−	+	−	−	−	+
Gymnogrammeae—															
Coniogramma pilosa (Brack.) Hier	UBC	+	+	+	+	+	+	−	−	+	+	−	−	−	−
Cryptogramma crispa (L.) R. Br.	BC	+	+	+	+	+	+	−	−	+	+	+	+	+	+
Hemionitis arifolia (Burm.) Moore	UBC	+	+	+	+	+	+	−	−	+	+	+	+	+	−
Pelleae rotundifolia Hook	UBC	+	+	+	−	−	+	−	−	−	+	−	−	−	−
Adiantum pedatum L.	BC	+	+	+	+	+	−	−	−	+	+	+	−	+	−
Pterideae—															
Pteridium aquilinum Kuhn var. *aquilinum*	KEW	+	+	+	+	+	+	−	−	+	+	−	−	+	+
P. aquilinum Kuhn var. *decomposita*	HI	+	+	+	+	+	+	−	−	+	+	−	−	+	+
Pteris longifolia L.	UBC	+	+	+	+	+	+	+	+	+	+	+	+	+	+

TABLE 1.—*continued*

	* Source	PAC a	PAC b	CAF a	CAF b	FER a	FER b	SIN a	SIN b	HBA a	HBA b	PRO a	PRO b	VAN a	VAN b
Davallieae—															
Nephrolepis cordifolia (L.) Presl	HI	+	+	+	+	+	+	−	+	−	+	−	+	+	+
Polypodieae—															
Phlebotium sp.	UBC	+	+	+	+	+	+	−	−	+	+	+	+	+	+
Pleopeltis thunbergiana Kaulf.	HI	+	+	+	+	−	−	−	−	+	+	+	+	−	−
Polypodium glycyrrhiza D. C. Eaton	BC	+	+	+	+	−	−	−	−	+	+	+	+	+	+

* Source of material: British Columbia (BC); University of British Columbia Greenhouses (UBC); Maui, Hawaiian Islands (MI); Hawaii, Hawaiian Islands (HI); Queen Charlotte Islands, British Columbia (QC); University of Tokyo Botanical Gardens (TOK); Kew Gardens (KEW).

Explanation of symbols: PCA, *p*-coumaric acid; CAF, caffeic acid; FER, ferulic acid; SIN, sinapic acid; HBA, *p*-hydroxybenzoic acid; PRO, protocatechuic acid; VAN, vanillic acid; a, acidic hydrolysis; b, basic hydrolysis; +, present; −, absent.

TABLE 2. A COMPILATION OF THE RESULTS OF THE FIRST AND PRESENT FERN SURVEYS FOR PHENOLIC ACIDS

Phenolic acid	First survey	Second survey	Total	Percent*
p-Coumaric	40	40	80	87
Caffeic	43	37	80	87
Ferulic	39	29	68	74
Sinapic	2	4	6	7
o-Coumaric	2	0	2	2
p-Hydroxybenzoic	34	38	72	78
Protocatechuic	27	24	51	56
Vanillic	42	26	68	74
Gentisic	1	0	1	1
Salicylic	1	0	1	1
Syringic	1	0	1	1

* Calculated as percent of 92 species examined. Four varieties of *Pteridium aquilinum* are counted as species for the purpose of this calculation.

by methylation in the case of sinapic acid) or do the products arise through the functioning of relatively un-specific enzymes which also catalyze earlier steps in the cinnamic acid pathway?

In their study of the distribution of the syringyl function in plants Ibrahim and coworkers[2] observed a somewhat more consistent appearance of sinapic acid in angiosperms than they did in the other major plant groups examined. A reasonably clearcut chemical line could be drawn between angiosperms and gymnosperms based upon their observations, even though a few exceptions did occur. In non-seed plants (14 species tested), however, only a species of *Selaginella* had sinapic acid. The three ferns tested had no sinapic acid. Our combined results (Table 2) show that sinapic acid does occur occasionally in the Pteridophyta.

MATERIALS AND METHODS

British Columbia ferns were collected by the authors during the summer of 1967. Ferns from Hawaii were collected by the second author in mid-December 1967 in Hawaii Volcanoes National Park. Dr. T. M. C. Taylor, formerly of this Department, supplied the filmy ferns from Hawaii and the ferns from Maui. *Mecodium wrightii*, from the Queen Charlotte Islands, was collected by Dr. W. B. Schofield of this Department. Plants from the University of Tokyo Botanical Garden and from Kew Gardens were supplied through the generosity of the directors of these institutions. Plant material was either extracted with boiling ethanol in the field or airmailed to Vancouver and extracted immediately. Plants sent by airmail were wrapped in wet tissue paper and sealed into plastic bags. Details of the extraction, hydrolysis, and chromatographic procedures are to be found in the original survey.[1]

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