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Dihydrocinnamic acids in *Pteridium aquilinum*

J. Méndez [1]

Consejo Superior de Investigaciones Cientificas, Apartado 122, E-15780 Santiago de Compostela, Spain

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Abstract

Dihydro-*p*-coumaric (phloretic) and dihydroferulic acids have been identified in *Pteridium aquilinum*. Whereas the latter has been located in cyanogenic and acyanogenic plants, the first has only been detected in cyanogenic forms.

Keywords: Pteridaceae; Bracken fern; 4-Hydroxyphenyl propionic acid; Phloretic acid; 3-Hydroxy,4-methoxyphenyl propionic acid; Dihydroferulic acid

1. Introduction

Common bracken *(Pteridium aquilinum* L. Kuhn) is one of the most widely distributed vascular plants.

The use of its rhizomes and fronds as food appears to have been widespread. Croziers have been recommended as a substitute for asparagus in England, France and particularly in Japan where they are regarded as a delicacy (Fletcher & Kirkwood, 1979). In this latter country, young croziers are consumed fresh, canned, dried or pickled; they have been regularly imported from China, USSR and more recently from Spain. However, some shipments from NW Spain have been rejected, due to their strong bitter taste. Therefore, a general screening for polymorphism of cyanogenesis in bracken fern from NW Spain was carried out.

2. Materials and methods

Cyanogenic (350 g) and acyanogenic (240 g) croziers were collected in Foncuberta (Orense) and in San Martiño Fontecada (Coruña) in April and May. respectively. Both were homogenized with a 2% $NaHCO_3$ solution. The filtrates were acidified to pH 3.0 and extracted with ether (3×). The ether fractions were dried, filtered, concentrated in vacuo and chromatographed on Whatman 3 MM paper in toluene–HOAc–water (4:1:5). The chromatograms were observed under UV light and two absorbing bands; (Rf 0.11–0.15 and 0.42–0.48) were eluted with methanol (3×). The eluates of the second band were chromatographically purified in isopropanol–ammonia–water (10:1:1). The eluates of both bands co-chromatographed with phloretic and dihydroferulic acids in 8 solvents. Their UV maxima in MeOH showed bathochromic shifts after addition of KOH, suggesting the presence of free phenolic hydroxyls.

3. Results and discussion

In plants, with and without cyanogenic character, several spots were observed in the chromatograms when sprayed with diazotized sulfanilic acid and identified as *p*-coumaric, ferulic, *p*-hydroxybenzoic and vanillic acids, previously found in this weed (Bohn & Tryon, 1967). In addition, two UV-absorbing compounds with identical chromogenic reactions, but with Rf values higher than those of *p*-coumaric and ferulic acids, in most solvents, were detected. Both compounds co-chromatographed in 8 solvents with synthetic dihydro-*p*-coumaric (phloretic) and dihydroferulic acids and their UV spectra in

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Table 1
Rf values (100×) and UV-data of phloretic and dihydroferulic acids from *Pteridium aquilinum*

Solvents	Unknown	Both	Phloretic acid	Unknown	Both	Dihydroferulic acid
TAW	47	47	45	49	45	48
IAW	78	77	78	42	40	40
HOAc	11	10	10	76	78	77
TFF	54	54	57	62	64	62
BAcA	36	40	36	60	61	61
CM	32	32	33	57	57	58
DAc	49	51	52	52	51	48
AcCA	92	89	90	89	91	92
Max nm						
MeOH	278, 286		279, 287	282		282
KOH	241, 294		242, 295	244, 295		246, 291

TAW, toluene–acetic acid–water (4:1:5, upper layer); IAW, iso-propanol–ammonia–water (10:1:1); HOAc, 2% acetic acid; TFF, toluene–ethyl formate–formic acid (5:4:1); BAcA, bencene–ethyl acetate–acetic acid (50:5:2); CM, chloroform–methanol (9:1); DAc, dibutyl ether–ethyl acetate (88:12); AcCA, ethyl acetate–chloroform–acetic acid (15:5:1).

MeOH and in the presence of KOH were indistinguishable from those of both synthetic acids (Table 1).

Whereas both acids are widely found in sheep rumen (Chesson, Stewart, & Wallace, 1982) and horse urine (Chapman, Chapman, & Clark, 1970), and dihydroferulic acid in cow urine (Suemitsu, Fujita, Yoshimura, & Kondo, 1969) these phenylpropanoids are of rather narrow distribution in the plant kingdom. Thus, dihydroferulic acid has been reported in *Zea mays* var. *indentata* (Gramineae) (Sakata & Yamagata, 1980), *Shorea robusta* (Dipterocarpaceae) (Saha & Ganguly, 1979) and *Bulbophyllum vaginatum* (Orchidaceae) (Leong, Harrison, & Powell, 1999). Free phloretic acid was found in male flowers of *Cucurbita pepo* (Cucurbitaceae) (Itokawa, Oshida, Ikuta, Inatomi, & Adachi, 1982), in brined olive drupes (Owen et al., 2003), in the xylem sap of apple trees (Grochowska, 1967), and its bound form in the leaves of apple (Miidla & Savisaar, 1977).

In *P. aquilinum* these acids are reported for the first time, but phloretic acid occurs exclusively in cyanogenic plants, whereas dihydroferulic acid was present in both cyanogenic and acyanogenic forms. Nevertheless, neither a connection with the bitter taste nor a correlation of cyanogenesis with 4-hydroxyphenyl propionic acid content were further investigated.

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