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FALCARINDIOL: AN ANTIFUNGAL POLYACETYLENE FROM *AEGOPODIUM PODAGRARIA*

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Acetylenic compounds occur in many plant species, and have often been shown to be toxic to bacteria, nematodes and mammals [1]. Although a few, e.g. capillin [2], safynol [3], wyerone [4] and its derivatives [5], have been shown to inhibit fungal growth, the antifungal activity of acetylenes from the Umbelliferae and their possible roles in resistance of plants to disease have received little attention.

I have now found antifungal activity in ground elder, *Aegopodium podagraria* L., in extracts of rhizomes, but especially in acetone extracts of young shoots. Two active compounds were isolated from the latter, and identified as falcarinol (**1**) (36 μg/g fresh tissue), and (**2**) (217 μg/g fresh tissue) by comparing their PMR, IR and UV spectra with previously published data [6], and by direct comparison (TLC and GLC) with authentic samples isolated during this work from *Daucus carota* L. [6, 7].

The antifungal properties of both compounds were assessed by measuring their effects on spore germination and subsequent germ-tube growth. In Butt slides, *Alternaria brassicicola* and *Septoria nodorum* were totally inhibited by falcarindiol at a concentration of 20 μg/ml. At 200 μg/ml falcarinol did not affect these fungi. The greater activity of the diol was confirmed in tests carried out using agar medium (Table 1), which indicated similar levels of activity to those shown by safynol [3] and wyerone [4].

These results show falcarindiol to be the major inhibitor *Aegopodium podagraria*. Its occurrence in shoots of this plant at a concentration of over 200 μg/g tissue is much greater than that shown to inhibit fungal growth *in vitro*. Falcarindiol also occurs in roots of *Daucus carota* [6],

Table 1. Activity of farcarinol and falcarindiol in spore germination tests. Germination (and germ tube length) as a percentage of control

	Farcarinol		Falcarindiol	
	100 ppm	10 ppm	100 ppm	10 ppm
Alternaria brassicicola	100 (50)	100 (63)	0	100(18)
Botrytis cinerea	100 (63)	100(100)	35(25)	100(75)
Septoria nodorum	54 (25)	100 (35)	0	48(10)
Uromyces fabae	34 (5)	100 (10)	0	0
Cladosporium cucumerinum	12 (5)	54 (5)	0	0
Colletotrichum lagenarium	0	0	0	0
Ascochyta fabae	100 (40)	100 (50)	0	100(40)
Glomerella cingulata	100 (34)	100 (50)	0	100(50)
Fusarium culmorum	100(100)	100(100)	0	100(75)
Aspergillus niger	100 (50)	100(100)	16(10)	100(20)

CH_2=CH.CHOH.(C≡C)$_2$.CHX.CH=CH.$(CH_2)_6$.Me

1 Falcarinol X = H

2 Flacarindiol X = OH

Apium graveolens L. [8], *Falcaria vulgaris* Bernh., *Oenanthe crocata* L. and *Opopanax chironium* Koch. [9]. These findings suggest that falcarindiol could play a part in protecting these species from fungal attack, and that the antimicrobial properties of other naturally occurring acetylenes should be investigated further.

EXPERIMENTAL

Isolation of **1** *and* **2**. Merck kieselgel 40 Art. 10180 Si gel was used for column chromatography and the presence of inhibitors in fractions was monitored by a *Cladosporium cucumerinum* TLC assay [10]. Merck fluorescent plates were used for TLC, and **1** and **2** were detected by their quenching properties under UV 254. Young shoots of *Aegopodium podagraria* (950 g fr. wt) were macerated and extracted by soaking × 3 in Me_2CO (2 l.) for 4 days. The residue from the combined extracts was divided, by eluting through a Si gel column with $CHCl_3$, into 2 active fractions. The first yielded falcarinol after purification by column chromatography (eluant *n*-C_6H_{14}–*iso*-Pr_2O–toluene, 2:1:1), followed by TLC (*n*-C_6H_{14}–*iso*-Pr_2O–toluene, 1:1:1, R_f 0.43). The second yielded falcarindiol after purification by column chromatography (*n*-C_6H_{14}–$CHCl_3$, 1:1), followed by TLC in 3 separate solvent systems (*iso*-Pr_2O–toluene, 1:1, R_f 0.35; *n*-C_6H_{14}–Me_2CO, 2:1, R_f 0.49; toluene–MeOH, 4:1, R_f 0.39).

Bioassay. Antifungal properties of **1** and **2** were assessed by 2 spore germination tests, using Butt slides [11] and impregnated agar plugs [12].

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