# FURANOCOUMARINS IN SEEDS OF WILD AND CULTIVATED PARSNIP

## MAY R. BERENBAUM, ARTHUR R. ZANGERL and JAMES K. NITAO

Department of Entomology, 320 Morrill Hall, University of Illinois at Urbana-Champaign, 505 S. Goodwin, Urbana, Il 61801, U.S.A.

(Received 11 January 1984)

Key Word Index—Pastinaca sativa; Umbelliferae; parsnip; chemotaxonomy; furanocoumarins; imperatorin; bergapten; isopimpinellin; xanthotoxin; sphondin.

Abstract—The furanocoumarin content of ripe seeds of seven cultivars of *Pastinaca sativa* was compared to that of ripe seeds from a naturalized population in central Illinois. Five furanocoumarins were identified and quantified in the intact seeds. While seeds of wild and cultivated plants contain furanocoumarin components in identical proportions, seeds from wild plants contain almost three times the quantity of furanocoumarins on a dry weight basis as do seeds of cultivars.

#### INTRODUCTION

The edible parsnip, Pastinaca sativa L. (Umbelliferae), has been cultivated for its edible taproot since Roman times. Native to Eurasia, P. sativa was introduced into North America in 1609 with the first European settlement at Jamestown, Virginia. By 1818, it had become extensively naturalized throughout eastern North America [1] and today remains one of the most abundant weeds of roadsides and waste places. In some areas, the wild parsnip is regarded as a noxious weed, due to its photosensitizing properties. Contact with aerial parts of the plant, particularly foliage and flowers, in the presence of sunlight induces blistering, erythema and, eventually, dark persistent pigmentation in the affected area ('parsnip dermatitis') [2]. The phototoxicity of P. sativa is the result of UV-mediated photobinding between epidermal DNA and the furanocoumarins present in the plant [3]. Furanocoumarins also display phototoxic properties toward bacteria, fungi, protozoans and insects [4-7].

It has been suggested that one consequence of crop plant domestication is the deliberate or inadvertent selection for reduced levels of secondary compounds that are distasteful or toxic. Insofar as many of these chemicals are involved in the defense of plants against their enemies, the reduction due to artificial selection in these defenses may account at least in part for the increased susceptibility of crop plants to herbivores and pathogens. While phytochemical changes due to artificial selection and domestication have frequently been documented, changes in plant chemistry associated with escape from cultivation are little known. In this study, a part of a larger study to determine genetic and environmental determinants of furanocoumarin distribution and abundance in *Pastinaca sativa*, we examined the furanocoumarin content of the ripe seeds of wild and domestic parsnip.

We collected ripe seeds from a roadside population approximately 1 acre in extent (0.4 hectares) in Champaign County, IL. Ten seeds were collected from the primary umbel of each of 20 plants selected at random in the population. Seeds from seven cultivars of *P. sativa* were obtained from various commercial seed companies; ten seeds of each cultivar were analysed for furano-coumarin content and composition. An ethanolic extract of each seed was separated and quantified by HPLC.

Table 1. Furanocoumarin composition of seeds of cultivars and wild plants of Pastinaca sativa (values are percentage of total)

	Imperatorin (4)	Bergapten (1)	Isopimpinellin (2)	Xanthotoxin (3)	Sphondin (5)	No. of seeds
All American (Joseph Harris Co., NY)	39.7	17.7	10.8	29.1	2.8	10
Fullback Short Thick (J. W. Jung Seed Co., WI)	39.8	15.7	7.5	36.1	0.8	10
Hollow Crown Improved (Stokes Seeds Ltd., NY)	45.2	15.0	10.8	26.7	2.2	10
Harris Model (Joseph Harris Co., NY)	41.1	15.8	11.4	28.6	3.1	10
Gladiator (Thompson & Morgan Inc., NY)	48.1	18.2	6.0	25.0	2.6	10
Offenham (Thompson & Morgan Inc., NY)	43.8	19.1	5.8	27.3	3.9	10
Tender & True	34.0	18.8	6.4	34.0	6.8	10
(Thompson & Morgan Inc., NY)						
Cultivars mean	41.7	17.2	8.4	29.6	3.2	70
(range)	(34.0-48.1)	(15.0-19.1)	(5.8-11.4)	(26.7-36.1)	(0.8-6.8)	
Wild plants mean	42.1	16.6	9.7	28.7	2.9	200
(range)	(24.3-50.0)	(8.7–22.6)	(5.3–16.9)	(20.3–40.7)	(0.3–9.6)	

1810 Short Reports

1 R = OMe,  $R^1 = H$ 

 $2 R = R^1 = OMe$ 

3  $R^1 = OMe$ , R = H

4 R<sup>1</sup> = OCH<sub>2</sub>CH = CMe<sub>2</sub>, R = H

#### RESULTS AND DISCUSSION

There are few if any qualitative differences in the composition of furanocoumarins in the seeds of cultivated and wild P. sativa. All seeds surveyed, both wild and cultivated, contain the same five furanocoumarins (1-5) and no significant differences in relative concentrations of these constituents were found between wild and cultivated P. sativa (Wilcoxon 2-sample test) (Table 1). Imperatorin (4) is the major constituent in the majority of individual plants in the wild population and is a major constituent in all of the cultivars. Quantitatively, however, there is a striking difference between the wild plants and the cultivars. The average furanocoumarin content of a wild seed—37.92  $\pm$  2.43  $\mu$ g/seed, with a range of 17.0-60.1  $\mu$ g/seed (comprising approximately 1% of the dry weight of the seed)—is almost three times greater than that of the seed of a cultivar  $(13.74 \pm 0.96 \,\mu\text{g/seed})$ , with a range of 8.5–22.2  $\mu$ g/seed). This difference is highly significant (P < 0.001, Wilcoxon 2-sample test).

The differences observed between seeds of wild and cultivated plants may be due either to an increase in concentration in plants that escape cultivation or to a decrease in plants that are under continuous cultivation. It is improbable that reduction of furanocoumarins in seeds of cultivars per se was an objective of artificial selection since furanocoumarins in seeds are sequestered in oil tubes (vittae) and thus are not involved with contact photosensitization. It is more likely that there was selection, deliberate or otherwise, to reduce the furanocoumarin content of edible parts and of foliage in order to reduce the risks of handling and the probability of photosensitization. Reduction in the furanocoumarin content of cultivar seeds may have been an incidental consequence of selection for reduced furanocoumarin content of leaves and roots. Umbellifers grown commercially for seed are treated routinely with insecticides for aphids, Lygus and other seed-feeding insect pests [8]; the increase in the concentration of furanocoumarins in seeds of plants escaped from cultivation may well result from increased selection pressure by herbivores.

Whether this increase in furanocoumarin content represents a reversion to a 'wild' state is difficult to determine since many of the plants growing 'wild' even in the area of indigeneity have also escaped from cultivation. Concentrations in seeds in the wild population examined here are comparable to those reported for wild populations of *P. sativa* in Europe [9-11]. In that furanocoumarins are insecticidal and fungicidal, this level of furanocoumarin production may result from selection imposed by the herbivores and pathogens of *P. sativa* in natural populations.

## **EXPERIMENTAL**

Intact seeds were placed singly in sealed test tubes and extracted with EtOH at 100° for 30 min. The samples were then evaporated to dryness and redissolved in EtOAc for injection in a Waters M-45 HPLC. The separation was performed at 500 psi on a normal phase silica column (10 cm × 5 mm) with a solvent consisting of cyclohexane-isopropyl ether-n-amyl alcohol (15:4:1). Detection was by UV absorbance (254 nm). Quantification was by peak area integration with a Hewlett-Packard 3390A Integrator. Furanocoumarins in parsnip seed were separated as follows at a flow rate of 1.5 ml/min: imperatorin, 2.7 min; bergapten, 3.02 min; isopimpinellin, 3.64 min; xanthotoxin, 4.10 min; and sphondin, 5.50 min.

Acknowledgements—We thank R. Larson for helpful discussion. This work was supported by NSF BSR 8214723.

# REFERENCES

- Nuttall, T. (1818) in Classica Botanica Americana (Exan, J., ed.) Vol. 1, p. 312. Hafner, New York.
- Soine, T. O., Abu-Shady, H. and DiGangi, F. E. (1956) J. Am. Pharm. Assoc. 45, 426.
- 3. Musajo, L., Bordin, P., Caporale, G., Maraciana, S. and Rigatti, G. (1967) Photochem. Photobiol. 6, 711.
- Fowlks, W. L., Griffiths, D. G. and Oginsky, E. L. (1958) Nature 181, 571.
- Chakraborty, D. P., Das Gupta, A. and Bose, P. K. (1957) Ann. Biochem. Exp. Med. 17, 59.
- Young, A. R. and Barth, J. (1982) Photochem. Photobiol. 35, 83
- 7. Berenbaum, M. (1978) Science 201, 532.
- 8. Gray, D. and Steckel, J. R. A. (1983) J. Hortic. Sci. 58, 73.
- 9. Beyrich, T. (1966) Pharmazie 21, 365.
- 10. Simsova, J. and Blazek, Z. (1966) Cesk. Farm. 16, 22.
- 11. Orlov, Y. and Sirenko, L. Y. (1969) Rastit. Resur. 5, 445.