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SHORT COMMUNICATION

FLAVONOL GLYCOSIDE VARIATION IN FENNEL, *FOENICULUM VULGARE*

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Abstract—The occurrence of quercetin 3-arabinoside in the leaves of *Foeniculum vulgare* has been confirmed and three other flavonol glycosides, kaempferol 3-arabinoside, kaempferol 3-glucuronide and quercetin 3-glucuronide, were identified. A survey of natural populations of fennel showed that they could be divided into two chemical races; a third of the sample contained only the 3-glucuronides, while the remainder contained all four glycosides.

INTRODUCTION

IN SPITE of wide use of fennel, *Foeniculum vulgare* Miller, in flavouring and spices, little is known of its flavonoids. The only report is of a quercetin 3-arabinoside in the leaves; the substance isolated differed in m.p. from other known 3-arabinosides and was therefore named foeniculin.[1] A recent widespread survey of members of the Umbelliferae for their flavonoids[2] showed that kaempferol and quercetin were very common in leaves and flowers, but that they mainly occurred as the 3-glucosides or 3-rutinosides. The 3-arabinoside of fennel therefore seemed to be an unusual taxonomic character in the family and worthy of further study.

RESULTS

Fennel plants, grown from spontaneous seed collected in Italy, were first examined for flavonols and no quercetin 3-arabinoside could be detected. Instead, another unusual class of glycosides were discovered, namely the 3-glucuronides of kaempferol and quercetin. This class of glycoside is uncommon in higher plants and has not previously been reported in the Umbelliferae. Traces of a third glycoside were present, but, from R_f data, this was either quercetin 3-glucoside or 3-galactoside.

In order to resolve the apparent discrepancy with previous work,[1] three other fennel plants were examined, one collected from the Avon Gorge, Bristol, and two from herbarium sheets. All three samples were identical in their flavonoid pattern, as revealed by two-dimensional chromatography, and showed two additional components to those present in the Italian material. These were identified as quercetin and kaempferol 3-arabinosides. A survey of 15 additional herbarium specimens, of plants collected in different parts of Europe, confirmed the presence of two chemical races in fennel. All samples uniformly contained the pair of 3-glucuronides (in equal amounts), while two thirds had the pair of 3-arabinosides

[1] T. OHTA and T. MIYAZAKI, *J. Pharm. Soc. Japan* **76**, 323 (1959).
[2] R. K. CROWDEN, J. B. HARBORNE and V. H. HEYWOOD, *Phytochem.* **8**, 1963 (1969).

(again in equal amounts) as additional components. Quercetin 3-arabinoside does, therefore, occur in fennel but it is not invariably present. Its distribution, from the present limited survey, does not appear to be correlated either with subspecies divisions or with geographical distribution.

The presence of flavonol glycoside races in this species is not surprising in view of its known morphological heterogeneity[3] and that considerable variations occur in the essential oil fraction of the seeds.[4-6] Intraspecific variation in flavonol glycosides has only been reported infrequently; the present case exemplifies once again the importance of examining several populations of a plant species in order to allow for such variations.

EXPERIMENTAL

Plant sources. Two fresh samples were of plants grown in this University from spontaneous seed collected in Italy and of plants collected from the Avon gorge, Bristol. Herbarium samples were obtained from the collections of this University and that of the University of Leicester.

Separation and identification of flavonoids. Crushed leaf of *F. vulgare* was extracted with 70% EtOH and the concentrated extract was chromatographed in *n*-BuOH–HOAc–H_2O (4:1:5) (BAW) and the flavonoid bands so separated were purified by successive chromatography on paper in appropriate solvents (see Ref. 7). Flavonol glycosides were identified by chromatographic comparison in five solvents with authentic markers, by acid hydrolysis to the respective aglycones and sugars, and by u.v. spectral analysis. Authentic quercetin 3-glucuronide was obtained from leaves of *Bielschmiedia miersii*.[8]

Flavonol survey. Small samples of fennel from herbarium sheets were surveyed by two-dimensional paper chromatographs in BAW and 15% HOAc. Dried papers were dipped in 5% alcoholic $AlCl_3$, when flavonols all appeared as bright yellow green fluorescent spots. This procedure increased the sensitivity of detection severalfold and also allowed the proper detection of kaempferol 3-arabinoside, which was obscured by a blue fluorescing cinnamic acid component on untreated papers. Typical R_fs ($\times 100$, in BAW and 15% HOAc respectively) were as follows: quercetin 3-glucuronide (39,40); quercetin 3-arabinoside (54,27); kaempferol 3-arabinoside (70,37); kaempferol 3-glucuronide (57,46); quercetin 3-galactoside (?) (58,41). The quercetin 3-arabinoside (foeniculin) differed significantly in R_f from values reported for avicularin, quercetin 3-α-arabinofuranoside (70,31).

Results of Survey

Arabinoside positive races (no. refers to analysis no. on herbarium slip): H101, Anglesey, 1947; H102, Hythe, 1885; H106, St. Marys Scillies, 1952; H108, Istra Jugoslavia, 1963; H109, Calvi, Corsica, 1966; H110, Garrigne, France, 1969; H113, Aylestone, Leicester, 1948; H116, Avon Gorge, Bristol, 1969 (fresh) (collected by J.B.H.); H117, Brownhills, Warwick, no date; H118, unknown source; H119, Gottingen, 1970; H120, Essen, 1970; H122, Essen, 1970 (var. *dulce*).

Arabinoside negative races: H103, Goata, Jugoslavia, 1964 (subsp. *piperitum*); H107, Aberdovey, Wales, 1956; H111, West Norfolk, 1950; H112, Rothley, Leics., 1965; H115, Italian Riviera, 1969 (fresh, from seed collected in 1968 by Miss Moglia); H121, Essen, 1970 (subsp. *piperitum*). (Nos. H101–114 were from the University of Leicester Herbarium).

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