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DISTRIBUTION OF MYRISTICIN IN SEEDS OF THE UMBELLIFERAE

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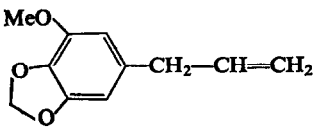
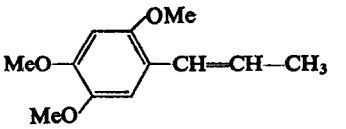
Abstract—Seeds of 100 species from fifty genera of the Umbelliferae were surveyed for the psychotropic aromatic ether myristicin. It was found for the first time in the tribe Caucalideae, in *Daucus glochidiatus*, *Pseudorlaya pumila* and *P. minuscula*. Its presence in the tribes Peucedaneae (three genera) and Apieae (eight genera) was confirmed. Variation within species was noted in that it occurred in seed of both the cultivated parsnip *Pastinaca sativa* and the cultivated fennel (*Foeniculum vulgare*) but was absent from wild collections of these species. The only genus where it occurred regularly was *Oenanthe* (in all of five species examined). It could not be detected in any other of the Umbelliferae tribes nor in the related family, Araliaceae, and thus appears to be rare as a seed constituent.

INTRODUCTION

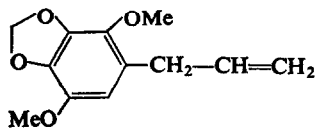
RECENT interest in the natural occurrence of the aromatic ether myristicin (I) has been stimulated by the report[1] that it may be a psychotropic substance in man, having a hallucinogenic activity similar to that of the synthetic psychomimetic 3-methoxy-4,5-methylenedioxyamphetamine. Although first isolated from the nutmeg *Myristica fragrans* (Myristicaceae),[2] it has been found most frequently in leaf oils of members of the Umbelliferae. Thus, Shulgin[1] lists ten genera of the family as containing it and points out the presence of the related asarone (II) in carrot seed oil.[3] More recently, myristicin has been detected as a minor constituent of carrot root oil[4] and its absence from commercial seed oil confirmed.[5] Other



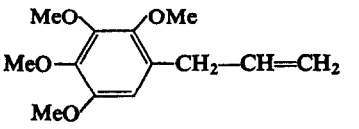
Myristicin (I)



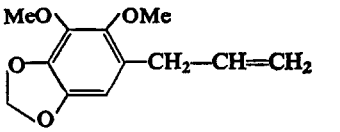
Asarone (II)



Parsleyapiole (III)



Allyltetramethoxybenzene (IV)



Dillapiole (V)

[1] A. T. SHULGIN, *Nature* **210**, 380 (1966).
[2] F. W. SEMMLER, *Chem. Ber.* **23**, 103 (1890); **24**, 3818 (1891).
[3] T. ASAHINA and T. TSUKAMOTO, *Chem. Zentral.* **I**, 1843 (1927).
[4] R. G. BUTTERY, R. M. SEIFERT, D. G. GUADAGNI, D. R. BLACK and L. C. LING, *J. Agr. Food Chem.* **16**, 1009 (1968).
[5] R. M. SEIFERT, R. G. BUTTERY and L. LING, *J. Sci. Food Agr.* **19**, 383 (1968).

related compounds include apiole (III) and 1-allyl-2,3,4,5-tetramethoxybenzene (IV), which accompany myristicin in parsley seed,[6] and dillapiole (V), present in dill, *Anethum graveolens*.[7]

In connexion with a concerted micro- and macro-molecular chemotaxonomic survey[8] of the Umbelliferae, we have now examined seeds of representative species of the whole family to see how widespread myristicin and related compounds are. Seeds were chosen for study since they were more accessible than fresh leaf samples and it was hoped that seed occurrences might be correlated, at least to some extent, with presence of myristicin in leaf and stem.

RESULTS

133 powdered seed samples, representing some 100 species of umbellifer drawn from fifty genera were surveyed for myristicin by TLC on silica gel in benzene of ether extracts, using a vanillin–H_2SO_4 spray for detection purposes. With this reagent, propenyl phenolic ethers (e.g. I) give brown yellow colours, whereas the isomeric allyl benzenes (e.g. II) give pink-red colours. Myristicin, when present, also appeared as a dark violet absorbing spot under short u.v. light and its occurrence was confirmed, in the case of new records in the family, by co-chromatography in four other solvents and by spectral comparison. The occurrence of apiole was similarly confirmed. The method used, unlike the more conventional steam distillation procedure, failed to show the presence of aromatic ethers if present in bound form and indeed the substance asarone (II) could not be detected in carrot seed, although large quantities of this material were used for extraction.

The results of the survey (Table 1) showed that myristicin was present in twenty-three and apiole in ten seed samples of the 133 examined. Previously only recorded in seed of parsley, celery, dill and *Oenanthe stolonifera*,[1] myristicin has now been found in a number of new sources. In general, the results on seeds are indeed correlated with previous reports of myristicin in leaf oils (*Levisticum*, *Foeniculum*) or root oils (*Pastinaca*). It is interesting that in both parsnip *Pastinaca sativa* and fennel *Foeniculum vulgare*, myristicin occurs in cultivated forms but not in wild seed collections. One effect of cultivation on both these plants seems to have been the accumulation of myristicin in the seed. Other examples are, of course, known in which the secondary constituent content has been altered in a wild plant species as a result of human selection. The reason why these two umbellifer species should produce hallucinogenic compound in cultivation, but not in the wild, however, remains obscure.

Taxonomically, the most significant results are three new records in species outside the two tribes, the Peucedaneae and Apieae, which were already known to contain myristicin. These three taxa, *Daucus glochidiatus* and two *Pseudorlaya* species (Table 1), are all in the tribe Caucalideae sensu Bentham,[9] or in the Dauceae of Engler and Prantl.[10] Careful search of all relevant species gave negative results so that the present three records of myristicin adds useful confirmation to the generally accepted view that the genus *Pseudorlaya* is closely related to that of *Daucus*. Within the Caucalideae group, myristicin is clearly uncommon but it is nevertheless sufficiently frequent (in three species of two genera in a total of fifty to seventy species in ten genera) to be of value in the multivariate numerical approach to the taxonomy of the group, which is in progress.

[6] H. WAGNER and J. HÖLZL, *Deutsche Apotheker-Zeitung* **108**, 1620 (1968).
[7] G. CIAMINCIAN and P. SILBER, *Chem. Ber.* **29**, 1799 (1896).
[8] R. K. CROWDEN, J. B. HARBORNE and V. H. HEYWOOD, *Phytochem.*, in press.
[9] G. BENTHAM, in *Genera Plantarum* (by G. BENTHAM and J. D. HOOKER), **1**, 859 (1867).
[10] O. DRUDE, in *Die natürlichen Pflanzenfamilien* (edited by A. ENGLER and K. PRANTL), **3 (8)**, 63 (1897–8).

TABLE 1. OCCURRENCES OF MYRISTICIN AND RELATED COMPOUNDS IN THE UMBELLIFERAE

Tribe and genus	Distribution of myristicin: Previous records	Distribution of myristicin: This paper
Apieae		
Apium	In leaf of celery, *A. graveolens*	Not detected in seed of celery (three varieties) or of *A. inundatum*, *A. crassipes* and *A. nodiflorum*
Anethum	In leaf and seed of dill, *A. graveolens*	In seed of *A. sowa*, Indian dill, accompanied by apiole
Crithmum	In leaf of *C. maritimum;* apiole in root	Absent from seed, but apiole is present
Foeniculum	In leaf of fennel, *F. vulgare*	Not detected in seed of wild collections, but present with apiole in cultivated form (var. *dulce*)
Petroselinum	In leaf and fruit, with apiole, of parsley, *P. crispum*	Confirmed in seed of five cultivated forms; apiole sometimes present as well
Pimpinella	None	In seed of *P. anisum*
Oenanthe	In *O. stolonifera* fruits	In seed, together with apiole, of *O. aquatica*, *O. crocata*, *O. pimpinelloides* and *O. silaifolia*
Ridolfia	In flower oil of *R. segetum*	Not detected in seed
Peucedaneae		
Levisticum	None	In seed, with apiole, of *L. officinale*
Ligusticum	Dillapiole in fruit of *L. scoticum* L.	
Pastinaca	In roots of parsnip, *P. sativa*	In seeds of four parsnip varieties but absent from four wild collections
Phellandrium	In *P. aquaticum* leaf	
Dauceae		
Daucus	In root of cultivated *D. carota;* asarone in seed	Absent from seed of both cultivated and wild *D. carota* and from seven other species. Present in seed of *D. glochidiatus* (Labill.) Fischer & C. A. Meyer
Pseudorlaya	None	In seed of *P. pumila* (L.) Grande and of *P. minuscula* (Pau) Laínz, the only known species

Within the Umbelliferae as a whole, myristicin seems to be rare as a seed character; it could not, incidentally, be detected in seeds of the related family Araliaceae. While the present survey suggests that seed occurrence is related to presence in other organs, this has yet to be proved. For this reason a more extensive survey of leaf and root oils is now in progress.

EXPERIMENTAL

Plant Sources

Seed samples were mainly of spontaneous origin, supplied by various botanic gardens and by collectors. The Caucalideae material was from the Phytochemical Unit collection, which has been taxonomically verified (cf. Ref. 8). Authentic myristicin was isolated from commercial nutmeg and apiole from parsley seed. The cultivated varieties of carrot, parsnip, celery and parsley examined were those listed in Messrs. Sutton's 1969 seed catalogue.

Methods of Identification

About 5 g of each seed sample was ground to a fine powder with sand and soaked in ether for at least 4 hr. The extract was spotted ($\times$ 10) on a silica gel plate, which was then developed with benzene. The dried plate was sprayed with vanillin in ethanolic H_2SO_4 and heated for 10 min at 105°. Myristicin and apiole appeared

as brown spots at R_f 0·50 and 0·39 respectively. Thymol (pink R_f 0·32), eugenol (brown R_f 0·20) and isoeugenol (red R_f 0·29) were all run as markers. A number of unidentified mauve and blue spots also showed up in many seed extracts. Those near the origin were probably furanocoumarins, since they could be detected as fluorescent blue spots on untreated plates. None of the mobile mauve and blue reacting constituents was aromatic in character, since they did not appear as blue purple absorbing spots under short u.v. light and they did not have any significant u.v. absorption above 230 nm.

Myristicin and apiole were identified by co-chromatography with authentic markers in benzene (R_fs 0·50, 0·39), toluene (0·49, 0·39), 10% $CHCl_3$ in benzene (0·55, 0·44) and 20% light petroleum (b.p. 40–60°) in benzene (0·46, 0·37). They were also identified by u.v. spectroscopy, after purification on silica gel successively with benzene, toluene and 10% $CHCl_3$/benzene. Myristicin had λ_{max} 278 and 285 nm, unchanged by alkali addition; apiole showed a broad band with λ_{max} 280 nm. The isomers apiole (parsley apiole, III) and dill-apiole (V) could not be separated by TLC and the identification of apiole in the present studies may refer to either or both isomers. The presence of myristicin in *Pseudorlaya pumila* was confirmed by mass spectroscopy (mol. wt. found 192; required 192).

Negative Records

Myristicin was not detected in seeds of following plants: Scandiceae subtribe Scandicineae, *Anthriscus* (3 spp.), *Chaerophyllum* (3 spp.), *Cuminum cyminum*, *Molopospermum peloponnesiacum*, *Myrrhis odorata*, *Myrrhoides nodosa* (*Physocaulis nodosa*), *Scandix iberica;* Scandiceae subtribe Caucalineae, *Astrodaucus* (2 spp.), *Caucalis platycarpos*, *Chaetosciadium trichospermum*, *Orlaya* (3 spp.), *Lisaea heterocarpa*, *Torilis* (5 spp.), *Turgenia latifolia;* Coriandreae, *Coriandrum melphitense*, *Bifora radians;* Smyrnieae, *Cachrys* (2 spp.), *Conium maculatum*, *Heptaptera triquetra*, *Smyrnium* (2 spp.), *Smyrniopsis armena;* Apieae, *Apium* (3 spp.), *Athamanta macedonica*, *Falcaria vulgaris*, *Pimpinella serbica*, *Portenschlagiella ramosissima;* Peucedaneae *Ferula* (3 spp.), *Heracleum* (2 spp.), *Opopanax* (2 spp.), *Peucedanum* (3 spp.), *Prangos* (2 spp.),; Laserpitieae, *Elaeoselinum lagascae*, *Melanoselinum decipiens*, *Laserpitium* (12 spp.), *Thapsia* (2 spp.); Dauceae, *Daucus* (10 spp.), *Artedia squamata;* Araliaceae, *Acanthopanax pentaphyllum*, *Aralia spinosa*, *Hedera helix*.

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