

The carvone and dillapiole content of dill fruits by gas chromatography without preliminary distillation

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Cold hexane extracts of sixteen specimens of dried dill fruit were examined for their content of carvone and dillapiole by gas chromatography. Dillapiole was absent from "European dill" (even Indian grown), and present in "Indian dill" (including European grown) in about twice the weight of carvone. These two forms of dill are otherwise less distinct than the forms of fennel which are referred to one species.

Growing fruits of European dill, *Anethum graveolens* L., have been observed to produce a 'specific level' of carvone some time before they are ripe (Betts, 1965). Developing fennel fruits were not found to have 'specific levels' of anethole and fenchone (Betts, 1968a), although in mature fruits the proportions of these constituents were found to be reasonably constant for three forms of fennel (Betts, 1968b). Sixteen dried dill fruits of various origins have now been examined by gas-liquid chromatography after cold solvent extraction, to assess the proportion of the terpenoid (+)-carvone to dillapiole, should the latter aromatic substance be present. When found, dillapiole exceeded the amount of carvone in the fruits, even those grown in England. Dillapiole-free dill was found from many geographical sources, including India.

EXPERIMENTAL

Drug material and its extraction. Specimens of dried dill fruit were obtained from the sources indicated in Table 1, where they are also described. Extraction was as previously described (Betts, 1968b) but using n-hexane containing the two paraffins n-icosane and n-tetracosane as internal standards for the test oil constituents carvone and dillapiole respectively.

Gas chromatography was as previously described (Betts, 1968a, b) on a 15% Carbowax 20M column, but at 190° to enable the dillapiole to emerge within 20 min, t_r relative to tetracosane being 0.81. Carvone emerged within 6 min under these conditions, t_r relative to eicosane being 0.49. The identity of the carvone and dillapiole peaks was confirmed on a column of silicone elastomer E301, on which the paraffins are not suitable as standards owing to their very long retention times.

RESULTS AND DISCUSSION

As with fennel (Betts, 1968b), wide variations were noted in the content of the constituents of the essential oils of different dill fruits (Table 2), these bearing no

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Table 1. *Origin and description of dill fruits*

Reference letter and source	Size (length × width)	Colour	Form	Av. wt in mg of 100 cremocarps
A Retail grocer's proprietary pack	4.5 × 2.5 mm	Grey-brown, buff wings and ridges	Ovoid, rounded cremocarps and mericarps	665
B "Peucedanum sowa" (1897) Pharm. Soc. Museum	5.0 × 2.5 mm	Pale buff-brown lighter wings and ridges	Ovoid-lanceolate rounded cremocarps and mericarps	560
C Madras (Lalah and Sons) India	5.0 × 2.5 mm	Grey-brown, buff wings and ridges	Ovoid, rounded cremocarps and mericarps	550
D "European dill" Stock drug at School of Pharmacy	6.0 × 3.0 mm	Brown, light buff wings and ridges	Mostly flattened mericarps, ovoid	525
E "Indian dill" Stock drug at School of Pharmacy	4.5 × 2.5 mm	Pale brown, lighter wings and ridges	Ovoid-lanceolate, rounded cremocarps and mericarps	515
F Olomouc, Czechoslovakia "A. graveolens"	4.5 × 3.0 mm	Dull brown, paler wings	Ovoid, flat mericarps	400
G Myddelton House, School drug garden, England	5.0 × 2.5 mm	Dark brown, paler wings and ridges	Ovoid, flat, mostly mericarps	395
H Wisconsin, U.S.A. "A. graveolens"	4.5 × 2.5 mm	Dark brown, paler wings	Ovoid-lanceolate, fairly flat mericarps	365
J "Anethum graveolens" Pharm. Soc. Museum	4.0 × 2.5 mm	Grey-brown, paler wings	Ovoid-rounded, fairly flat mericarps	355
K Iasi, Rumania "A. graveolens"	4.0 × 2.5 mm	Brown, pale distinct wings and ridges	Ovoid, fairly flat mericarps	330
L Kaunas, U.S.S.R. "A. graveolens"	4.0 × 2.5 mm	Dull brown, paler wings	Ovoid-rounded, flat, curled mericarps	330
M Jammu, India "A. graveolens"	5.0 × 2.5 mm	Grey-brown, paler wings	Lanceolate, flat, twisted mericarps	300
N Essen, Germany "A. graveolens"	4.5 × 2.0 mm	Light brown, paler wings and ridges	Ovoid, flat, very thin mericarps	295
P Istanbul, Turkey "A. graveolens"	4.5 × 2.5 mm	Grey-brown, paler wings and ridges	Ovoid-lanceolate, rounded, mostly mericarps	295
Q Jammu, India "Anethum sowa"	3.0 × 1.5 mm	Grey-brown paler wings and ridges	Pyriform cremocarps and mericarps	265
R Grown from Q at Myddelton House, School drug garden	4.5 × 1.5 mm	Grey-brown, paler wings and ridges	Pyriform, thin mericarps	(80) unripe

Specimens F, H, K, L, N and P were from Botanical Gardens. M and Q were kindly sent by Dr. C. K. Atal of the Regional Research Laboratory, Jammu, India; and C was supplied by P. Mittulaul Lalah & Sons of Madras, India at the kind request of Dr. J. S. Pruthi of the Central Agmark Laboratory, Nagpur.

relation to the weights of the fruits. However, the various specimens fell into two groups; with or without dillapiole. The first group represents "Indian dill" whilst the second group is "European dill" without necessarily implying geographic origin. Apart from one example in each group (D and Q-R being grown from Q) the Indian dill was heavier than the European dill, weighing over 500 mg/100 fruits (cremocarps) against the 400 mg or less of the latter. Although the carvone content of 100 fruits was similar over part of the range exhibited by the two groups, the assay on fruit

Table 2. Essential oil constituents of dill specimens

Reference (see Table 1)	mg/100 fruits (= cremocarps)		Ratio w/w dillapiole: carvone	mg/g fruit wt	
	Carvone	Dillapiole		Carvone	Carvone + dillapiole
B	5.0	9.2	1.8	9	25
A	4.7	7.9	1.7	7	19
E	3.3	4.3	1.3	6	15
C	3.0	6.7	2.2	6	18
R	2.5	4.1	1.6	7	unripe 22
Q	1.8	4.0	2.2		
G	8.2			21	
L	6.5			20	
K	6.2			19	
F	5.3			13	
D	5.3			10	
J	4.8			14	
M	4.4			15	
N	3.9			13	
P	3.9			13	
H	3.7			10	

weight was accordingly distinctive, being 10 mg/g or above for European dill, but less than this for Indian dill. When present, dillapiole occurred in about twice the weight of carvone (except for specimen E), so that the combined content of carvone and dillapiole was equal to, or greater than, the carvone content of the best European dill on a weight basis.

Dill is not an easy plant to grow, often dying before all its fruits are ripe, and some specimens contained many small fruits which were not used in this work. However, the low weight Indian dill Q was not unripe, for it germinated well, unlike many dills. It provided specimen R which showed that the presence of dillapiole is not specific to dill grown in India. Conversely, European dill grown in India (M) is dillapiole free. Plants grown from Q were virtually indistinguishable from European dill plants, so that the validity of the taxon *Anethum sowa* Roxb. for Indian dill appears to rest on slight differences in fruit shape and the presence of dillapiole, although the "*A. graveolens*" fruit of Khafagy & Mnajed (1968) contained dillapiole. The bitter and sweet forms of fennel are much more distinct (Betts, 1968a) yet are referred to as one species.

The carvone content of European dill grown at Myddelton House corresponded to the level per 100 fruits observed in fresh, ripe material (Betts, 1965). As with fennel, it was possible to examine individual fruits (Betts, 1968b) of a specimen suspected to be mixed because of a dillapiole: carvone ratio of only 0.3. This came from another English school of pharmacy labelled "European dill", and contained some Indian dill.

Although terpene hydrocarbon peaks were observed, their evaluation would have required the gas chromatograph to be run at a lower temperature, and these substances have been observed to decrease during storage of dill (Kalitzki, 1954) which consists of thin structures with a large surface area. The values for Museum specimen B do not suggest any loss of the other essential oil constituents.

Dillapiole is less volatile than carvone and probably more soluble in the aqueous condensate from steam distillation. Nevertheless, dillapiole forms a considerable proportion of Indian dill oil, [19% recorded by Chakravati & Bhattacharya (1954) and about 27% by Khafagy & Mnajed (1968)] though contributing little to the odour.

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