The Content and Composition of Aroma Compounds in Three Different Cultivars of Dill, *Anethum graveolens* L.

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Gehalt und Zusammensetzung der Aromastoffe in drei Abarten vom Dill, *Anethum graveolens* L.

Zusammenfassung. Der Gehalt und die Zusammensetzung der Aromastoffe in drei Züchtungen von Dill, Dura Sv, Dukat OE und Mammut WW, wurden zwei Jahre lang an zwei Orten in Finnland während der frühen Stufe der Reife (vor der Knospen-Formation) studiert. Die Aromastoffe wurden durch Lösungsmittelextrahierung isoliert und die konzentrierten Extrakte mit Capillar-GC-MS analysiert. Zwischen den drei Sorten wurden große Unterschiede im Gehalt des Gesamtaromas festgestellt. Der Aromagehalt von Dura (2200 mg/kg frischer Dill, 1,1% der Trockensubstanz) war zwei- bis dreimal höher als bei den anderen Sorten. Obwohl 22 Aromastoffe identifiziert wurden wurde der Gehalt von nur fünf Hauptkomponenten, α-Phellandren, 3,6-Dimethyl-2,3,3a,4,5,7a-hexahydrobenzofuran, β-Phellandren, Limonen und p-Cymen, in den drei Sorten miteinander verglichen. In allen Sorten waren α-Phellandren und das Benzofuranoid die Hauptkomponente. Ihre Gehalte waren am höchsten in der Sorte Dura (680 und 1110 mg/kg frischer Dill). Die Auswahl der Sorten ist das beste Mittel, die Qualität des Dills zu verbessern.

Summary. The content and composition of aroma compounds in the three dill cultivars Dura Sv, Dukat OE and Mammut WW at an early stage of maturity (before bud formation) were studied during two seasons at two different localities in Finland. The aroma compounds were isolated by solvent extraction and the concentrated extracts were analysed by capillary GC-MS. Great differences in the total aroma content were found between the three cultivars. Dura gave the best results (2,200 mg/kg fresh weight, 1.1% of dry weight), 2- to 3-fold compared with the two other cultivars. Although 22 aroma compounds were identified the amounts of only five main components α-phellandrene, 3,6-dimethyl-2,3,3a,4,5,7a-hexahydrobenzofuran, β-phellandrene, limonene and p-cymene were compared in the three cultivars. They composed of 70–90% of the total aroma compounds. In all cultivars α-phellandrene and the benzofuranoid were the major components. Their contents were highest in the Dura cultivar (680 and 1,110 mg/kg of fresh dill, respectively). The selection of cultivars is the best way to improve the quality of the dill herb.

Introduction

It is well known that the dill (*Anethum graveolens* L.) herb and seed are used for their flavour as condiments or ingredients in foodstuffs in a number of different forms, e.g. fresh, dried, essential oil or oleoresin [1]. The herb or weed consists of the fresh aerial part of the plant including stalks, leaves and fruits. The quality of the dill herb and seed depends upon their essential oil content and composition. Dill seed is characterized by a high content of carvone and limonene [2–6], whilst the herb contains, in addition to carvone and limonene, significant amounts of α-phellandrene and 3,6-dimethyl-2,3,3a,4,5,7a-hexahydrobenzofuran [7–13]. However, the contents of these main components have been found to vary according to geographical origin [3, 14, 15], harvesting time, i.e. the state of maturity [13–22], and growth conditions [23–27]. Also the isolation procedure may affect the oil content and composition [11, 28, 29].

On the other hand, only a few studies have been carried out concerning the differences between dill types or cultivars grown under the same conditions as to their essential oil content and composition. Embong et al. [5] found different seed oil compositions in two dill types grown under identical conditions. Also Chubey and Dorrell [24] observed that two existing cultivars and strains of dill harvested when mature gave oils with greatly different yields and qualities.

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Z Lebensm Unters Forsch (1985) 181:92–96

The aim of the present study was to find out whether there are differences in the aroma contents and compositions in the three cultivars of the dill herb before bud formation, at an early stage of maturity at which the plant is mostly utilized in Finland. The work is a part of a larger research project carried out to promote domestic herb plant farming. The dill was grown at two different localities, Sahalahti and Viikki, during two consecutive years using the normal farming practice. The dill crops and other results of the farming experiments will be published as a separate report.

Experimental

Materials

The studied dill (*Anethum graveolens* L.) cultivars were "Dura" Sv, "Dukat" OE and "Mammut" WW, which are commercially available in Finland. The dill was grown at two different localities at Sahalahti (61°29′ N.lat.) near the city of Tampere and at Viikki (60°15′ N.lat.) near the city of Helsinki).

The dill was harvested at the same stage of maturity before bud formation [16], packed into polyethylene bags, frozen and stored −20 °C. Samples were analysed as soon as possible, but at least within two weeks [30].

Isolation of Aroma Compounds

Aroma compounds were isolated by extracting 45 g of chopped frozen dill for 6 h with 350 ml of a mixture of redistilled n-pentane/diethyl ether (1 + 2, v/v) by using a modified Soxhlet technique as described by Huopalahti et al. [11]. The extract was concentrated to the volume of 25 ml.

Gas Chromatography and Mass Spectrometry

The quantitative gas-chromatographic determinations were performed on a Varian 3700 gas chromatograph equipped with a flame ionization detector connected to a Hewlett Packard 3388A integrator. A fused-silica capillary column (25 M × 0.32 mm i.d. film thickness 0.20 μm) coated with OV-351 was used for the separations. The oven temperature was programmed at the rate of 2 °C/min from 70 to 230 °C after an isothermal period of 2 min. The flow rate of carrier gas (helium) was 1.3 ml/min.

The quantitative estimations of aroma compounds were performed using linalool as the internal standard. In the calculation of the total aroma content 50 peaks were summed up. The quantitative values were not corrected by the gas-chromatographic calibration factors [31]. The presented values are mean values from duplicate determinations.

The aroma compounds were identified on a VG Analytical 7070E mass spectrometer with an ion-source energy of 70 eV.

Results and Discussion

Table 1 shows the total aroma content of the three dill cultivars grown at two different localities during the years of 1983 and 1984. The herb was harvested before bud formation, the average growth period being 43 days. The experimental fields represented different soil types, but the farming practice and fertilization were similar. In all cases the Dura cultivar gave the best yield, the total aroma content calculated on fresh dill weight basis, being about two- to three-fold compared with that of Dukat and Mammut cultivars. The values found for Dukat and Mammut were each year at about the same levels. However, the total aroma content of all cultivars differed greatly in two consecutive years, the values found in 1984 being much lower than those in 1983, with the exception of Dura grown at Sahalahti (Table 1). The total aroma content of the Dura cultivar calculated as percentage of the dry matter varied at Viikki from 1.1% in 1983 to 0.57% in 1984, but was about 1.0% in both years at Sahalahti. This cultivar also gave the best crop each year [32].

Mammut was the reference cultivar in our earlier studies. Thus at Sahalahti the total aroma content of the Mammut cultivar varied from 0.16% to 0.42% of dry matter in the experiments carried out during the years of 1979–1981 [14], whereas in the present work it was in the range of 0.38–0.70% (Table 1). The variation during the six-year period is over four-fold and depends mainly on variation of the growth conditions.

Comparison of the values of the total aroma content in the dill herb with those of essential oil content reported in the literature is difficult because of the different methods of isolation and determination. How-

Table 1. The total aroma content of the three dill cultivars grown at two different localities in 1983 and 1984

Cultivar	The total aroma content							
	Sahalahti				Viikki			
	1983		1984		1983		1984	
	mg/kg[a]	%[b]	mg/kg[a]	%[b]	mg/kg[a]	%[b]	mg/kg[a]	%[b]
Dura Sv	1,470	1.14	1,490	1.02	2,170	1.06	556	0.57
Dukat OE	790	0.68	478	0.38	867	0.62	272	0.26
Mammut WW	817	0.70	492	0.38	1,270	0.84	214	0.24

[a] mg/kg of fresh dill
[b] % of dry weight

Table 2. Amounts of some aroma compounds in the three dill cultivars grown at Sahalahti and Viikki in 1983 and 1984

Compound	Concentration, mg/kg of fresh dill											
	Sahalahti						Viikki					
	Dura		Dukat		Mammut		Dura		Dukat		Mammut	
	1983	1984	1983	1984	1983	1984	1983	1984	1983	1984	1983	1984
α-Phellandrene	669	629	388	248	422	300	681	133	374	89	639	30
3,6-Dimethyl-2,3,3a, 4,5,7a-hexahydro-benzofuran	499	578	205	114	180	79	1,110	167	325	69	396	41
β-Phellandrene	102	92	57	36	64	40	120	44	54	21	97	19
Limonene	39	33	21	13	24	15	51	15	21	7	37	7
p-Cymene	10	15	11	6	10	5	16	19	8	8	8	11

ever, in our studies the correlation between the total aroma content determined by GC of the solvent extract and the essential oil content found by steam distillation by the method of Clevenger [33] was very good ($r = 0.97$, $n = 6$). Moreover, there were great variations in the maturity stages of the plants studied by different authors. The only available data covering a complete growing season of dill were given in two investigations [20, 21]. El-Gengaihi and Hornok [21] found values for the essential oil content of the dill herb at a very early stage of maturity during the start of stem growth (41 days) and during the start of umbel growth (48 days) 0.24% and 0.46% of fresh weight, respectively. On the other hand, Zlatev [20] reported the essential oil content in dill at appearance of stalks from 0.68% to 1.4% of dry matter in the spring and summer sowed plants, respectively. Leaves in both cultivars studied gave the greatest part of the oil. However, the oil content of dill increased very rapidly during the development of the plant, the umbels being the most important oil producing organs [cf. also 13, 16].

In other studies concerning the oil content of the dill herb no information about its maturity stage was given. The data from various countries varied from 0.16% to 1.5% of dry weight [2, 3, 34].

Against this background the values found here for the total aroma content of the Dura cultivar were rather high.

Although 50 components could be separated by capillary GC of the dill herb extract, among which 22 were identified [cf. 11, 16], only five main compounds were chosen to facilitate the comparison of their amounts in the three cultivars (Table 2). In most cases they represent nearly 70–90% of the total aroma content. Moreover, their sensory characteristics apparently strongly affect the overall aroma quality of the dill herb at the growth stage before bud formation [31].

α-Phellandrene was the major component of all the three cultivars at Sahalahti in 1983 and 1984 and of Dukat and Mammut cultivars at Viikki, with the exception of Mammut in 1984. The exceptionally low value given for α-phellandrene in the 1984 Mammut crop of Viikki was obviously due to an insect infestation. At Sahalahti the amount of α-phellandrene was highest in the Dura cultivar, about 650 mg/kg of fresh weight, in both years, whilst it was approximately half of that in Dukat and Mammut. At Viikki the α-phellandrene content was at a similar high level in 1983 in the Dura and Mammut cultivars as in the Dura cultivar at Sahalahti. But in 1984 the α-phellandrene content of all cultivars at Viikki was rather low (90–130 mg/kg). It was, however, at the same concentration level (90 mg/kg) as found earlier by Schreier et al. [12] in the fresh German dill herb. If we take into account the value 50 mg/kg found earlier for α-phellandrene in the Mamut cultivar [31], we can see that the variation range of the α-phellandrene content within and between the different dill cultivars is broad.

On the other hand, the relative amount of α-phellandrene was comparatively constant, 40–60% of the total aroma content of dill at Sahalahti and 30–50% at Viikki in both years. These figures are in accordance with our earlier findings [14, 16]. Moreover, Ihloff [19] noticed that the typical odour and flavour of the herb oil derived from dill at an early stage of maturity is due to its high content of phellandrene. Using diene value determination he found 63–67% of phellandrene in the herb oil. If also the amount of β-phellandrene (6–8%) in the total aroma content is taken into consideration, our values for the total phellandrene are near the range presented by Ihloff [19].

β-Phellandrene concentration in mg/kg of fresh weight was highest in the Dura cultivar at both localities, Sahalahti and Viikki, during the two-year period. The maximum value 100–120 mg/kg was four to six times higher than the value found earlier by Schreier

et al. [12] in the German dill herb and by Huopalahti [31] in the Mammut cultivar. Unfortunately there are no studies about odour threshold concentration and sensory characteristics of β-phellandrene.

3,6-Dimethyl-2,3,3a,4,5,7a-hexahydrobenzofuran has evidently a very important odour impact on dill at its early stage of maturity, because of its dill-like, floral and herbaceous odour and high odour value [31]. Therefore its high concentration in the fresh dill herb is of major importance. Table 2 shows that the concentration of the benzofuranoid was next to highest in most cases. Its concentration was highest in the Dura cultivar in each year both at Sahalahti (499 mg/kg in 1983 and 578 mg/kg in 1984) and Viikki (1,110 mg/kg in 1983 and 167 mg/kg in 1984). There were no great differences in the amounts of the benzofuranoid in the Dukat and Mammut cultivars. The fluctuation in the concentration of the compound was not as great at Sahalahti as at Viikki. The lowest values found in this study were at about the same level as given by Schreier et al. [12] in the German dill herb and by Huopalahti [31] in the Mammut cultivar.

The proportion of the benzofuranoid varied in the different cultivars at Sahalahti in 1983 from 22% to 34% and during 1984 from 16% to 39%, whilst the values at Viikki were from 31% to 51% and from 19% to 30%, respectively. The lowest values were found in the Mammut cultivars and the highest ones in the Dura cultivars.

Huopalahti and Linko [16] have shown previously that the relative amount of the benzofuranoid increased remarkably at an early stage of maturity of the Mammut cultivar, reaching its peak of 31% at the flowering stage and being 16% before bud formation. The same high benzofuranoid percentage at the beginning of flowering and the following rapid decrease was found by Porter et al. [13] and Kernoczi et al. [22]. Its share was, however, higher in leaves than in stems or umbels. This indicates that the biosynthesis of 3,6-dimethyl-2,3,3a,4,5,7a-hexahydrobenzofuran starts at an early stage of plant development increasing towards the beginning of flowering.

Limonene has an lemon-like odour [35]. Table 2 shows that the limonene content was highest (39–51 mg/kg) in the Dura cultivar, but did not deviate much from that of the two other cultivars at two locations in each year. Its relative amount was quite similar, 2.5–3% in the all cultivars, which corresponds well with our earlier work with the Mammut cultivar (3.5% [16]). The percentage of limonene increased at flowering and later stages of plant development [13, 16].

It has been reported that p-cymene has a typical odour reminiscent of carrot [35]. In the present study the p-cymene content of the dill herb was from 5 to 19 mg/kg of fresh weight in the different cultivars. Both limonene and p-cymene were present in the three dill cultivars distinctly above their threshold concentrations in water [31].

Only in some of the samples traces (<0.1%) of carvone were found. This confirms that dill had been harvested at about the same stage of maturity. The carvone content of the dill herb has been shown to increase rapidly from the beginning of its flowering [13, 16, 22].

Measurable quantities of thymol (1–18 mg/kg) and myristicin (1–25 mg/kg) were also found in the different dill cultivars.

According to the sensory evaluation of dill herb constituents, it was found that besides 3,6-dimethyl-2,3,3a,4,5,7a-hexahydrobenzofuran also α-phellandrene, limonene, p-cymene and *cis*-3-hexen-1-ol greatly contribute to the over all aroma of the herb [31]. In the present study these components, excluding *cis*-3-hexen-1-ol existed in highest concentrations in the Dura cultivar indicating its superior quality.

On the basis of the results presented it can be concluded that selection and breeding are probably the best way to obtain the optimal total aroma content and the best quality for the dill herb before bud formation.

Acknowledgement. The author thanks Eila Kesälahti for her technical assistance and Suomen Akatemia for the financial support.

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Received January 25, 1985

Accepted February 20, 1985