Evaluation of Flavor Characteristic Compounds in Dill Herb Essential Oil by Sensory Analysis and Gas Chromatography

Jorge A. Pino,*,[†] Arístides Rosado,[‡] Isabel Goire,[§] and Elda Roncal[†]

Food Industry Research Institute, Carretera Guatao Km 3.5, La Habana 19200, Cuba, Scientific Research National Center, Havana, Cuba, and Perfumery and Soap Industry "Suchel", Havana, Cuba

Oils obtained from different growth stages of dill were categorized into three groups by a quality rating test of their aromas. The aroma of oil corresponding to 50% fruit formation was the most favored. According to the odor assessment of each volatile compound by the sniffing method of gas chromatography, α-phellandrene, 3,9-epoxy-1-*p*-menthene, myristicin, β-myrcene, and (*Z*)-dihydrocarvone were the preferred components, while (*E*)-dihydrocarvone and elemicin were the least favored. A regression equation, which included myristicin and elemicin, could explain the differences among the five kinds of oil.

Keywords: *Dill oil; flavor; sensory analysis; GC*

INTRODUCTION

Dill, *Anethum graveolens* L., is an important condiment crop from which both herb and seed have been extensively used in all kinds of flavoring including those for baking mixes, sauces, salads, and seafoods. In the food industry, the herb and seed have been largely replaced by dill oil obtained by steam distillation from freshly cut, entire herbs including stalks, leaves, and fruits or from separated mature seeds. The two oils differ in composition: seed oil is characterized by a high content of carvone and limonene (Guenther, 1950; Koedam et al., 1979), while the herb oil contains, in addition, significant amounts of α-phellandrene and 3,9-epoxy-1-*p*-menthene (Schreier et al., 1981; Lawrence, 1980), both considered among the most important odorants of dill herb (Blank and Grosch, 1991). The contents of these main components have been found to vary according to geographical origin, harvesting time, growth conditions, and isolation procedure (Koedam et al., 1979; Huopalahti and Linko, 1983; Huopalahti, 1984).

The aim of the present study was to determine whether there are differences in the composition of the essential oils from dill herb at different growth stages and to identify the odor characteristic compounds produced by dill herb grown in Cuba.

MATERIALS AND METHODS

Materials. Dill herb was harvested at the "Suchel" Experimental Agricultural Station at different growth stages: 100% flowering, lower than 50% fruit formation, 50% fruit formation, and 100% fruit formation.

Sample Preparation. Essential oils from four different growth stages were obtained by atmospheric steam distillation (60 kg in each case). In addition, a fifth sample of an old oil (10 years old) was prepared.

Gas Chromatography. Analyses were conducted with a Pye Unicam 204 instrument equipped with a flame ionization detector and a SPB-1 fused silica column (30 m × 0.25 mm i.d., film thickness 0.25 μm). The column was temperature programmed from 50 to 200 °C at 4 °C/min and held at the final temperature until the chromatogram was complete. Carrier gas (hydrogen) flow rate was 0.6 mL/min, and injector and detector temperatures were 220 and 250 °C, respectively. The samples were injected in the split mode with a 1:20 split ratio.

Gas Chromatography–Mass Spectrometry. Analyses were performed on a Unicam Automass 20 equipped with a BP-17 fused silica column (30 m × 0.25 mm i.d., film thickness 0.25 μm). The column was temperature programmed from 80 to 220 °C at 4 °C/min and held at the final temperature until the chromatogram was complete. Carrier gas (helium) flow rate was 0.8 mL/min. Mass spectra were recorded at 70 eV.

Identities of compounds were established by comparing mass spectra with those of authentic reference substances or with the Wiley/NBS mass spectral data base. Furthermore, identities were checked on the basis of retention data with reference substances.

Quantitative estimations were made by relating individual peak areas to the total area of the reconstructed ion chromatogram (obtained by recording the total ion current from the injected sample in the GC–MS system, without involving calibration factors).

Sensory Evaluation. *Odor Assessment.* The sniffing method of GC (Guadagni et al., 1966) was used to describe the characteristic odor of each volatile compound of dill herb oil by well-trained panelists. Samples were injected into a GC with the parameters described earlier. Effluent from the column was split at a ratio of 1:1.

Quality Rating Test. The five essential oils were evaluated by a 4-point quality scale (4, very good; 1, uncharacteristic) according to five well-trained panelists using the sniffing method (Larmond, 1977).

Statistical Analysis. The numerical sensory scores were submitted to analysis of variance and Duncan's test. The percentage composition of volatile compounds was subjected to arc-sine transformation for correlation and stepwise linear regression, using the SPSS computer package (SPSS, 1987).

RESULTS AND DISCUSSION

The quality sensory scores for the five kinds of dill herb oil were examined by analysis of variance. The result (Table 1A) showed that the *F* value was significant at the 1% level. Since a significant difference was found among the samples, Duncan's test (Snedecor, 1956) was used to further process the data. The result (Table 1B) indicated that the aroma of 50% fruit formation dill herb attained the largest sensory score among the samples, while that of old oil was the smallest; the other three samples were not significantly different at the 5% level.

[†] Food Industry Research Institute.

[‡] Scientific Research National Center.

[§] Perfumery and Soap Industry "Suchel".

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Table 1

(A) Analysis of Variance for the Different Kinds of Dill Herb Oil

source of variance	df	SS	S^2	F
among samples	4	8.6	2.15	10.75[a]
among judges	20	4.0	0.20	
total	24	12.6	0.52	

(B) Result of Duncan's Test for the Different Kinds of Dill Herb Oil[b]

100% flowering	<50% fruit formation	50% fruit formation	100% fruit formation	old oil
b	b	a	b	c

[a] Significantly different at the 1% level. [b] Samples with different letters were significantly different at the 5% level.

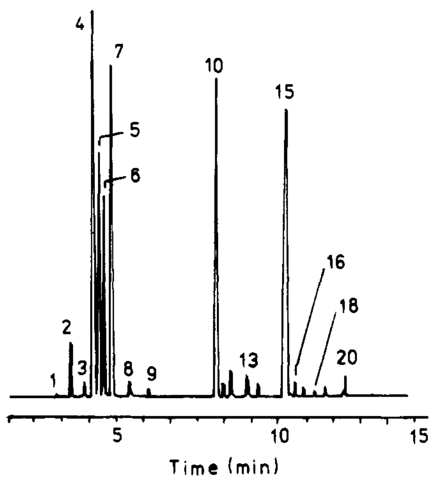

Figure 1. Reconstructed chromatogram of 50% fruit formation dill herb oil.

Table 2. Odor Assessment of Volatile Compounds of Dill Herb Oil

peak no.[a]	compound	odor description
1	α-thujene	warm-resinous
2	α-pinene	pine-like
3	β-myrcene	fragrant, fresh
4	α-phellandrene	dill-like, fragrant, fresh
5	limonene	citrus-like, fresh
6	β-phellandrene	fragrant, fresh
7	*p*-cymene	citrusy, fresh
8	α-terpinene	lemony-citrusy
9	α,*p*-dimethylstyrene	sour
10	3,9-epoxy-1-*p*-methene	dill-like, floral, fragrant
11	*trans*-dihydrocarvone	caraway-like, sour
12	sabinol	woody, sour
13	3,9-epoxy-*p*-cymene[b]	sour
14	*cis*-dihydrocarvone	cooling, fresh, minty
15	carvone	caraway-like, cooling
16	isopiperitenone[b]	minty
17	thymol	spicy
18	elemicin[b]	woody, sour
19	dillapiol	warm-woody
20	myristicin	nutmeg-like, fragrant

[a] Peak numbers refer to Figure 1. [b] Not previously reported as dill herb volatile compound.

Figure 1 shows the reconstructed chromatogram obtained by recording the total ion current of the 50% fruit formation dill herb oil, while the identities and aroma description of each volatile compound by GC odor assessment are given in Table 2. Among the 20 compounds, peaks 4 (α-phellandrene) and 10 (3,9-epoxy-1-*p*-menthene) gave the best aromas. On the other hand, five compounds, i.e., peaks 8, 11–13, and 18, were found to possess a sour aroma and were not considered to be characteristic of dill herb oil. Of these compounds, 3,9-epoxy-*p*-cymene and elemicin were identified for the first time in dill herb oil (Pino et al., 1994).

Table 3. Percentage Compositions of Various Kinds of Dill Herb Oil

peak no.[a]	100% flowering	<50% fruit formation	50% fruit formation	100% fruit formation	old oil
1	0.25	0.36	1.06	0.86	0.54
2	3.12	3.42	3.17	2.64	2.45
3	1.27	1.25	1.56	0.96	0.64
4	20.55	20.15	24.88	18.18	9.62
5	14.17	14.52	11.92	11.80	13.59
6	9.73	9.24	8.21	7.32	6.62
7	9.14	8.39	13.38	13.64	20.35
8	0.37	0.19	0.34	0.34	0.29
9	0.19	0.17	0.18	0.30	0.11
10	13.64	13.81	14.85	12.44	11.30
11	0.46	0.36	0.29	0.65	3.92
12	0.40	0.49	0.50	0.56	0.79
13	0.54	0.56	0.34	0.80	0.50
14	0.74	0.79	0.99	0.72	0.13
15	14.18	14.49	14.50	19.58	15.56
16	0.45	0.43	0.40	1.58	1.84
17	0.25	0.16	0.16	0.62	0.30
18	0.16	0.10	0.05	0.16	0.22
19	0.88	0.64	0.31	0.05	0.14
20	0.10	0.11	0.20	0.10	nd[b]

[a] Numbers refer to Figure 1 and Table 2. [b] Not detected.

Table 3 shows the percentage composition of the five kinds of dill herb oil. The composition of the old oil was the most different. This is not unexpected, because the contents of α-phellandrene (peak 4) and 3,9-epoxy-1-*p*-menthene (peak 10) that contribute to the preferred aroma were the lowest among all of the samples, while the amounts of peaks 11, 12, and 18, which contribute to the sour aroma, were the highest. Consequently, the aroma of the old oil was the least favored.

With regard to the composition of the old oil, the following remark should be made. In this sample, a striking difference in the *trans*-dihydrocarvone: *cis*-dihydrocarvone ratio was observed, in comparison with the others. As both stereoisomeric dihydrocarvones probably make different important contributions to the characteristic dill herb aroma, it seems very probable that the different ratio of these compounds can have a marked influence on the quality of dill herb oil. Both dihydrocarvones had been found to be the subject of isomerization in dill seed oil (Koedam et al., 1979).

Correlations among the volatile compounds of dill herb oil are given in Table 4. In general, the correlation between pairs of components was very high in all cases. For instance, α-phellandrene (peak 4) had a significant negative correlation with peaks 7, 11, 12, and 18. This result indicates a high level of mutual effect among volatiles during sensory evaluation. That is, compounds associated with preferred aroma show a strong correlation with others that contribute to the sour aroma.

Correlations between the sensory scores and the amounts of volatile compounds of dill herb are shown in Table 5. Seven compounds were found to be at 5% significance level, i.e., peaks 3, 4, 10, 14, and 20 with positive correlations and peaks 11 and 18 with negative ones. This result indicates that the richer the oil is in β-myrcene, α-phellandrene, 3,9-epoxy-1-*p*-menthene, *cis*-dihydrocarvone, and myristicin, the more favored the aroma. However, the opposite is true for *trans*-dihydrocarvone and elemicin.

To gain more insight into the characteristic compounds of dill herb oil, stepwise linear regression analysis was used (Draper and Smith, 1981). The practical purpose in searching for such relations is the possibility of using instrumental techniques, e.g. GC,

Table 4. Correlation Matrix of Volatile Compounds of Dill Herb Oil[a]

peak no.	peak no. 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
1	1	−0.22	0.22	0.29	−0.95	−0.52	0.36	0.32	0.36	0.20	−0.17	0.16	−0.12	0.51	0.42	0.16	0.27	−0.43	−0.72	0.51
2		1	0.84	0.78	0.36	0.87	−0.86	−0.34	−0.05	0.87	−0.71	−0.79	−0.36	0.40	−0.61	−0.95	−0.67	−0.78	0.74	0.77
3			1	0.97	−0.11	0.70	−0.69	0.12	0.14	0.99	−0.85	−0.82	−0.46	0.81	−0.46	−0.92	−0.52	−0.92	0.50	0.94
4				1	−0.25	0.66	−0.73	0.18	0.37	0.96	−0.94	−0.86	−0.26	0.87	−0.25	−0.84	−0.31	−0.89	0.41	0.96
5					1	0.53	−0.34	−0.52	−0.56	−0.08	0.21	−0.10	−0.11	−0.54	−0.61	−0.27	−0.52	0.25	0.72	−0.42
6						1	−0.92	−0.07	0.02	0.71	−0.69	−0.89	−0.17	0.38	−0.58	−0.89	−0.51	−0.46	0.94	0.46
7							1	0.15	−0.33	−0.70	0.83	0.93	−0.09	−0.42	0.29	0.81	0.27	0.54	−0.77	−0.55
8								1	0.35	0.04	−0.21	−0.19	0.01	0.62	0.21	0.08	0.36	0.12	−0.08	0.19
9									1	0.10	−0.60	−0.40	0.73	0.47	0.76	0.07	0.75	−0.13	−0.22	0.35
10										1	−0.83	−0.80	−0.48	0.77	−0.49	−0.93	−0.56	−0.93	0.51	0.93
11											1	0.93	−0.06	−0.82	0.03	0.74	0.05	0.74	−0.43	−0.86
12												1	0.02	−0.70	0.27	0.84	0.23	0.61	−0.72	−0.71
13													1	−0.22	0.82	0.48	0.86	0.45	−0.25	−0.34
14														1	−0.04	−0.58	−0.05	−0.68	0.17	0.88
15															1	0.68	0.97	0.32	−0.71	−0.18
16																1	0.69	0.78	−0.77	−0.74
17																	1	0.48	−0.59	−0.28
18																		1	−0.22	−0.94
19																			1	0.19
20																				1

[a] If $r > 0.88$ or $r < -0.88$, then significant at the 5% level.

Table 5. Correlation Coefficient between Sensory Score and Volatile Compound Concentration

peak no.	r^a	peak no.	r^a
1	0.39	11	−0.95
2	0.69	12	−0.82
3	0.92	13	−0.15
4	0.99	14	0.89
5	−0.37	15	−0.09
6	0.56	16	−0.75
7	−0.69	17	−0.17
8	0.21	18	−0.88
9	0.49	19	0.28
10	0.91	20	0.97

[a] If $r > 0.88$ or $r < -0.88$, then significant at the 5% level.

Table 6. Summary of Multiple Linear Regression Analysis

regression eq	R^2	SE	F
$S = 2.07 + 7.35X_{20} - 1.22X_{18}$	1.00	5.5×10^{-9}	170.65[a]

[a] Significant at the 1% level.

to supplement or replace sensory testing in the quality classification of dill herb oil. The result is given in Table 6. Two volatile compounds, i.e., elemicin (peak 18) and myristicin (peak 20), were selected in the model. The multiple correlation coefficient (R^2) is 1.00, which means that this model can explain 100% of the differences between the essential oils. The partial R^2 of these two compounds indicates that myristicin ($R^2 = 0.94$) is the critical contributor to this equation. This compound has been characterized as an important odorant in dill herb flavor (Huopalahti, 1986; Blank and Grosch, 1991).

To measure how well the calculated scores agree with the experimental scores, three new samples of dill herb oil were evaluated. Their sensory scores were 2.0, 3.2, and 4.0, and the fitted scores by the model equation were 2.3, 3.4, and 3.7, respectively. Thus, the fitted scores using the GC data are as accurate and representative as the experimental scores determined by the sensory test panel members. The scope of this study precluded the repetition of the experiments with the new samples.

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