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Effect of drying on the volatile constituents of thyme (*Thymus vulgaris* L.) and sage (*Salvia officinalis* L.)

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The losses of volatile constituents in herbs and spices depend mainly on drying parameters and biological characteristics of the plants. In the present study, two methods were applied in the analysis of the effect of drying on the aroma constituents of the widely used herbs thyme (*Thymus vulgaris* L.) and sage (*Salvia officinalis* L.). The volatile constituents of herbs (fresh, freeze-dried and oven-dried at 30°C and 60°C) were isolated by dynamic headspace and simultaneous distillation–extraction methods and analysed by capillary gas chromatography and coupled gas chromatography–mass spectrometry. In total, 68 compounds were identified in thyme and 44 in sage, and more than 100 components were screened quantitatively. A significant reduction in the amount of extracted volatiles was found only in the case of drying at 60°C, mainly as a result of the loss of non-oxygenated monoterpenes. The character of the changes of the headspace volatiles was more complex, especially for thyme, the content of aroma compounds being the highest when the herb was dried at 60°C. Some aroma assessment criteria (coefficient of efficiency C_e) are proposed on the basis of the results obtained.

INTRODUCTION

Volatile aroma compounds are the most sensitive components in the process of food drying. The effect of drying on the composition of volatile flavour constituents of various aromatic plants and vegetables has been the subject of numerous studies, which show that the changes in the concentrations of the volatile compounds during drying depend on several factors, such as the drying method and parameters that are characteristic of the product subjected to drying.

Huopalahti *et al.* (1985) found that the reduction of the flavour extract after drying of dill herb was significant (from 1·7 to 3·9 times in the case of freeze-drying, and from 6·7 to 11·2 times in the case of air-drying). The oven-dried and freeze-dried green leaves of young raspberry also had a markedly lower total content of volatiles compared with green frozen ones (Kirsi *et al.*, 1989). Kaminski *et al.* (1986) found that the losses in volatiles of carrots brought about by freeze-drying amounted to 69%, by hot air-drying to 75%, by fluidized bed drying to 81%, and by microwave hot air-drying to 84%. Most recently, the effect of convection (50°C), freeze- and sun-drying (in the shade) on the essential oil profile of thyme was analysed by Koller & Raghavan (1995), who concluded that the first two methods did not affect oil composition, whereas in the latter method most components were lost and the gas-chromatographic (GC) aroma profile was completely unbalanced in favour of a major compound, thymol.

However, other authors have found the changes in aroma and concentration of volatile constituents during drying to be less considerable. Thus, Pääkkönen *et al.* (1989) after careful panel testing failed to find significant differences in odour and taste intensities of air- and freeze-dried dill. In another study, the reduction in the total amount of the essential oil of sweet basil, marjoram and oregano during drying at room temperature was found to be 36–45%, 23–33% and 6–17%, respectively (Nykänen & Nykänen, 1987). Only slight quantitative changes of the flavour of parsley (Karawya *et al.*, 1980) and laurel (Skrubis, 1982) leaves were determined after drying. The similarity of air- and freeze-dried thyme and sage in GC odour tests was demonstrated by Koller (1988).

The method of analysis of volatile constituents is also very important. Leathy & Reineccius (1984) compared several methods for the isolation of volatile compounds from aqueous model systems and concluded that headspace (HS) is very dependent on the volatility of aroma

compounds, whereas simultaneous distillation–solvent extraction (SDE) gave very good recoveries. From the theoretical point of view, HS-GC analysis might be more easily correlated to the sensory analysis of aroma rather than GC analysis of the aroma concentrates from distillation or extraction with solvent (Aishima, 1982). Different methods of isolation were applied to investigate the effect of drying on the aroma changes in herbs and vegetables. When extraction (Huopalahti *et al.*, 1985; Nykänen & Nykänen, 1987) or SDE (Kirsi *et al.*, 1989, Kaminski *et al.*, 1986) were used, the changes in the total concentration of volatile compounds were determined. On the other hand, the use of the HS method (Koller, 1988) detects the changes of aroma compounds in the vapour phase, which can be better related to the sensory aroma profile of the product. The differences in percentage composition of volatile compounds in the samples obtained by different methods could be significant, as has been demonstrated in dill by Huopalahti *et al.* (1988). In general, HS samples are dominated by the more volatile components; steam-distilled concentrates also contain some higher boiling compounds, whereas extracts consist of both volatile and non-volatile fractions (Takeoka *et al.*, 1984). Jennings and Filsoof (1977) conclude that no single sampling system can be regarded as uniformly satisfactory, but that, depending on the sample and what the investigator wishes to study, one or another system may be superior. Therefore, Parliment (1986) suggests to consider several questions in determining the choice of sample preparation technique.

MATERIALS AND METHODS

Raw materials

Fresh thyme (*Thymus vulgaris* L.) and sage (*Salvia officinalis* L.) were collected from the open experimental garden of the Danish Royal University of Agriculture and Veterinary in Copenhagen in the second half of November. Only leaves were used for analyses. Fresh leaves were stored in the refrigerator at $4 \pm 2°C$ before isolation of volatile compounds; the rest of material was put for drying immediately after sorting. Leaves were not ground before isolation of volatiles.

Drying

Oven-drying was carried out at 30°C and 60°C at an air velocity of approximately 3·3 m s^{-1}. Freeze-drying was carried out in a Hetosicc CD204 dryer; the initial temperature was −50°C. The duration and final moisture of dried herbs together with the amounts used for analyses are presented in Table 1. The amounts of the herbs for SDE and HS analysis were calculated on the basis of the dry matter: i.e. dry matter content was equivalent in all samples, both fresh and dried by different methods.

Isolation and concentration of flavour compounds

For SDE analysis, volatile constituents from thyme and sage were simultaneously distilled and extracted in a Likens–Nickerson apparatus. Fresh, or an equivalent amount of dried, herbs (Table 1) were put into a 1 litre round-bottomed flask with 500 ml of distilled water and 2 ml of internal standard solution (4-methylpentan-1-ol 50 µl $litre^{-1}$ and damascenone 50 µl $litre^{-1}$ in water). Diethyl ether (25 ml, twice-distilled) was used for extraction. The distillation–extraction process was carried out for 1 h from the beginning of condensation of vapours on the walls of the condenser. The collected ether extracts were dried over anhydrous sodium sulphate (2 g), and samples were stored in the freezer at 18°C until further handling. Dried ether extracts were concentrated under a stream of nitrogen to 500 mg and analysed by GC. In order to determine the completeness of the recovery of the volatile compounds during 1 h of distillation, the residue was distilled for a further 1 h, and the extract obtained was analysed by GC. Only a few negligible peaks were detected by GC in the concentrated residue extract at the detection threshold used, demonstrating that all volatile oil was recovered in 1 h of distillation.

Dynamic HS was carried out using 9 g of fresh thyme and 10 g of sage or from an equivalent amount of dried herbs (Table 1) during 1·5 h at 42°C by purging with nitrogen at a flow rate of 10 ml min^{-1}. Internal standard (2 ml of 0·005%, v/v, 4-methylpentan-1-ol in water) were added and effluents were absorbed in the glass tubes with 300 mg of Porapak Q, mesh 50–80, which was carefully washed with diethyl ether prior to use. HS constituents were desorbed with twice-distilled

Table 1. Drying data

Herb	Thyme				Sage			
	Moisture (%)	Drying time (h)	Weight for analysis (g)		Moisture (%)	Drying time (h)	Weight for analysis (g)	
			SDE	HS			SDE	HS
Fresh	72·9		3·00	9·00	68·7		3·00	10·00
Oven-dried at 30°C	11·4	47	0·92	2·75	11·2	63	1·06	3·52
Oven-dried at 60°C	7·5	4	0·88	2·64	9·2	4	1·04	3·45
Freeze-dried	9·4	42	0·90	2·69	12·5	42	1·07	3·58

diethyl ether and concentrated to 200 mg just before GC analysis.

GC conditions

Volatile constituent concentrates were analysed on a Hewlett-Packard 5890A gas chromatograph using the following conditions: inlet, split 1:10; carrier gas, helium at a column flow rate of 1 ml min^{-1}; flame-ionization detection. Two columns were used: fused silica Carbowax 20M (BP20), 50 m×0·31 mm ID, 0·25 μm film thickness, with a temperature programme of 10 min at 60°C, 60°C to 190°C at 3°C min^{-1}, 190°C isothermal; and fused silica methylsilicone (HT5), 50 m×0·2 mm ID, 0·1 μm film thickness, with at temperature programme of 10 min at 50°C, 50°C to 250°C at 3°C min^{-1}, 250°C isothermal; the injected volume was 1 μl for the BP20 column and 0·5 μl for the HT5 column.

Gas chromatography–mass spectrometry

GC–MS was carried out on a HP 5890 instrument equipped with a 5970 Series mass selective detector in electron impact ionization mode at 70 eV, and the following GC parameters: inlet, split 1:10; carrier gas, helium at 2 ml min^{-1} column flow; column, fused silica DB-17, 30 m×0·25 mm ID, 0·25 μm film thickness; temperature programme, 50°C to 250°C increasing at 3°C min^{-1}, 250°C isothermal; injected volume, 1 μl. Before GC–MS analysis samples were stored in the freezer at −20°C.

Identification and quantitative evaluation

Identification of thyme and sage constituents was based mainly on the retention time data obtained on the two columns, and mass spectra. In addition, model mixtures of diluted pure reference chemicals were added to the samples to demonstrate enhancement of the relevant peaks. Finally, identification results were compared with data presented in the literature and were found to correspond well. Quantitative determination was made by using the internal standard.

Three SDE and four HS replicate analyses were carried out for every sample; the standard deviation as a percentage of the mean was between 1 and 8.

RESULTS AND DISCUSSION

Identification of volatile constituents

More than 100 volatiles isolated by SDE and HS methods were detected in thyme and sage by capillary GC and screened quantitatively. Compounds that were identified positively or tentatively (68 in thyme and 44 in sage) are listed in Table 2. All identified constituents have been already reported in the herbs analysed (Maarse & Visscher, 1989).

The peak areas of most of the compounds were negligible, therefore for further discussion only the quantitatively major compounds found in thyme and sage were considered, including the main aroma principles of both herbs (Heath, 1981). The concentrations of these constituents in arbitrary units are presented in Table 3 (thyme) and Table 4 (sage).

Constituents isolated by SDE

The changes in the total amount of volatiles isolated by the SDE method are shown Fig. 1(1). It is clear that the influence of oven-drying on the total amount of constituents isolated by SDE is similar for both thyme and sage. Quite similar concentrations of volatiles were determined in the herb, both fresh and oven-dried at 30°C. A 43% reduction in the total amount of compounds isolated by SDE was observed in oven-dried thyme at 60°C, and a 31% reduction in sage oven-dried at the same temperature as compared to fresh herb. It is worth mentioning that the weight of thyme during 4 h of drying at 60°C decreased 3·4 times, that of sage 3·1 times. Koller and Raghavan (1995) obtained very similar results with rosemary: 30% of essential oil was lost during air convection drying at 50°C. The total concentration of volatiles isolated by SDE in the freeze-dried sage was almost unchanged as compared with the fresh one and in thyme even increased, by approximately 20%. A considerable increase in the content of the major compound thymol, by 33%, was the main contribution to the total increase. It is difficult to explain this finding within the scope of the present study.

Some interesting observations could be made concerning the changes of individual flavour constituents. Most of the sage volatiles isolated by SDE did not undergo significant changes during oven-drying at 30°C and freeze-drying. The reduction in amounts of volatiles during oven-drying at 60°C depended on the volatility and chemical structure of the constituent. For instance, the concentration of myrcene was reduced 3·4 times, limonene 3 times, and β-pinene 2 times. On the other hand, the concentration of caryophyllene oxide remained nearly the same, and that of an unidentified compound (RT = 79:51) increased by approximately 38%. As this constituent was not identified, it is impossible to explain this finding.

The character of the changes of thyme constituents isolated by SDE is very similar to that of sage; however, some peculiarities should be noted. For instance, the amount of β-caryophyllene in the thyme oven-dried at 30°C and in the freeze-dried herb increased by 29% and 37%, respectively. Similar results were obtained in our previous study (Venskutonis *et al.*, 1996). The increase in the amount of β-caryophyllene during drying of sage is not so evident. Another tendency in the changes of volatiles is evident from the results obtained: the losses of non-oxygenated terpenes during oven-drying at 60°C were considerably higher than those of oxygenated

compounds, particularly terpene alcohols. Most likely, two reasons could be given for this tendency: the differences in the volatility and oxidation of some non-oxygenated compounds during drying.

HS constituents

The results of HS analysis also reveal some interesting peculiarities of the influence of drying on the aroma constituents (Tables 3 and 4 and Fig. 1(2)). The total content of the compounds absorbed on Porapack during dynamic HS purging of sage was the largest for the fresh herb, at a medium level in the freeze-dried herb, and lowest for the oven-dried herb. In case of oven-drying, the results were comparable for both drying temperatures: the total content of absorbed HS volatiles was 4·6 times lower for drying at 30°C and 3·7 times lower for drying at 60°C in comparison with fresh herb. The character of the changes of the individual constituents in HS was quite similar for all samples with a few exceptions. For instance, the concentration of unidentified compounds (RT = 7:92, 8:27) considerably increased in oven- (60°C) and freeze-dried sage and thyme. In the chromatograms of the HS concentrates from the fresh herb, the peaks of these compounds were not detected or were negligible. The relevant peaks in SDE-GC profiles of thyme were not detected at all, and only negligible concentrations of these compounds were found in sage samples isolated by SDE. It is also worth noting that in HS concentrates of thyme the largest concentration of such compounds was obtained from the herb oven-dried at 60°C, whereas in sage it was from the freeze-dried sample. These constituents could be volatile products of the thermal and/or enzymatic degradation of some compounds during sample preparation and/or drying; however, it is difficult to determine the true reason of this finding within the scope of the present study.

Table 2. Volatile constituents identified in thyme and sage

Constituent[a]	Identified in thyme	Identified in sage
1. *cis*-Hex-3-en-1-ol	RT, MS, Co-I	NI
2. Tricyclene	RT, MS, Co-I	RT, Co-I
3. α-Thujene	RT, MS	RT
4. α-Pinene	RT, MS, Co-I	RT, MS, Co-I
5. Camphene	RT, MS, Co-I	RT, MS, Co-I
6. Sabinene	RT, MS, Co-I	RT, Co-I
7. Oct-1-en-3-ol	RT, MS, Co-I	NI
8. β-Pinene	RT, MS, Co-I	RT, MS, Co-I
9. Myrcene	RT, MS, Co-I	RT, MS, Co-I
10. Octan-3-ol	RT, MS, Co-I	NI
11. α-Phellandrene	RT, MS, Co-I	RT, Co-I
12. δ-3-Carene	RT, MS	RT, Co-I
13. α-Terpinene	RT, MS, Co-I	RT, Co-I
14. *p*-Cymene	RT, MS, Co-I	RT, MS, Co-I
15. Limonene	RT, MS, Co-I	RT, MS, Co-I
16. β-Phellandrene	RT, MS, Co-I	RT, MS, Co-I
17. 1,8-Cineole	RT, MS, Co-I	RT, MS, Co-I
18. *cis*-β-Ocimene	RT, MS, Co-I	RT, MS, Co-I
19. *trans*-β-Ocimene	RT, Co-I	RT, Co-I
20. γ-Terpinene	RT, MS, Co-I	RT, Co-I
21. *trans*-Sabinene hydrate	RT, MS	RT, Co-I
22. Terpinolene	RT, MS, Co-I	RT, Co-I
23. Linalool	RT, MS, Co-I	RT, MS, Co-I
24. α-Thujone	RT, Co-I	RT, MS, Co-I
25. *cis*-Sabinene hydrate	MS	RT, Co-I
26. β-Thujone	NI	RT, MS, Co-I
27. Camphor	RT, MS, Co-I	RT, MS, Co-I
28. Isopulegol	NI	RT, Co-I
29. Menthone	RT	RT
30. Isoborneol	RT, MS, Co-I	RT, Co-I
31. Isomenthone	RT	NI
32. Borneol	RT, MS, Co-I	RT, MS, Co-I
33. Terpinen-4-ol	RT, MS, Co-I	RT, MS, Co-I
34. *p*-Cymen-8-ol	MS	NI
35. α-Terpineol	RT, MS, Co-I	RT, MS, Co-I
36. *cis*-Dihydrocarvone	MS	RT, Co-I
37. Methylchavicol	RT, MS, Co-I	RT, MS, Co-I
38. Citronellol	RT, Co-I	NI
39. Nerol	RT, MS, Co-I	RT, Co-I
40. Thymol methyl ether	RT, MS	NI
41. Neral	RT, Co-I	NI
42. Carvone	NI	RT, MS
43. Carvacrol methyl ether	RT, MS	NI
44. Geraniol	RT, MS, Co-I	RT, Co-I
45. Linalyl acetate	RT, Co-I	RT, Co-I
46. Geranial	RT, Co-I	RT, Co-I
47. Bornyl acetate	RT, MS, Co-I	RT, MS, Co-I
48. Isobornyl acetate	NI	RT, MS
49. Thymol	RT, MS, Co-I	RT, MS, Co-I
50. Carvacrol	RT, MS, Co-I	NI
51. Thymyl acetate	RT, MS	NI
52. Eugenol	RT, Co-I	NI
53. Geranyl acetate	RT, MS, Co-I	NI
54. β-Elemene	NI	NI
55. β-Caryophyllene	RT, MS, Co-I	RT, MS, Co-I
56. α-Ionone	RT, Co-I	NI
57. [*cis*]-α-*trans*-Bergamotene	MS	NI
58. α-Humulene	RT, MS, Co-I	RT, MS, Co-I
59. *allo*-Aromadendrene	RT	NI
60. γ-Muurolene	MS	NI
61. Germacrene D	MS	NI
62. β-Ionone	RT, Co-I	NI
63. α-Muurolene	MS	NI
64. β-Bisabolene	MS	NI
65. γ-Cadinene	MS	NI
66. δ-Cadinene	MS	NI
67. *cis*-Nerolidol	RT, Co-I	NI
68. *trans*-Calamenene	MS	NI
69. *trans*-Nerolidol	RT, Co-I	NI
70. Caryophyllene oxide	MS	RT, Co-I
71. Viridiflorol	NI	RT, MS
72. γ-Eudesmol	MS	NI
73. T-Cadinol	MS	NI
74. Farnesol[b]	RT	NI

[a]Constituents are listed in order of elution from HT5 column.
[b]Structure of isomer unknown.
RT, identification confirmed on BP20; MS, identification confirmed by GC–MS; Co-I, identification confirmed by co-injection of an authentic compound; NI, not identified.

Some differences in the concentration of HS aroma constituents between the sage oven-dried at 30°C and 60°C can also be pointed out. The slightly higher total amount of HS volatiles collected from the herb oven-dried at 60°C than from the herb dried at 30°C can be explained mainly by the increase of a few compounds (namely, α- and β-thujones, 1,8-cineole, β-pinene), whilst the concentration of most of the rest of constituents was found to be considerably lower (e.g. *trans*-hex-2-enal, β-caryophyllene, α-humulene).

The character of the changes in the composition of the HS volatiles determined in thyme was completely different. The total amount of purged volatiles was the highest for thyme oven-dried at 60°C: it was 4·2 times higher than in the fresh herb, 19·4 times higher than in the herb oven-dried at 30°C, and 12·9 times higher than in the freeze-dried herb (Table 3 and Fig. 1(2)). Although panel testing of the samples was not performed in this study, it was evident that the intensity of odour of the thyme oven-dried at 60°C was much

Table 3. Composition (in arbitrary units) of the main constituents of thyme in extracts (SDE) and headspace (HS)

Compound	Distillation–extraction (SDE)				Headspace (HS)			
	Fresh herb	Dried herb			Fresh herb	Dried herb		
		30°C	60°C	Freeze-dried		30°C	60°C	Freeze-dried
Not identified (RT = 7:95)	—	—	—	—	—	0·04	0·41	0·18
α-Thujene	5·05	4·78	2·40	5·32	0·68	0·09	2·16	0·10
α-Pinene	3·70	3·68	2·11	3·99	0·46	0·06	1·46	0·07
Camphene	1·96	1·90	1·10	2·12	0·26	0·04	1·07	0·06
1-Octen-3-ol	3·89	3·79	2·25	4·15	0·08	0·04	1·46	0·06
β-Pinene	1·26	1·20	0·71	1·31	0·13	0·02	0·51	0·02
Myrcene	6·61	6·12	2·76	7·01	0·61	0·14	2·85	0·16
α-Terpinene	3·40	3·25	1·68	3·80	0·31	0·08	1·58	0·10
p-Cymene	82·70	80·50	37·00	87·96	10·66	1·87	38·88	2·04
Limonene	1·74	1·65	0·60	1·69	0·17	0·03	0·74	0·03
1,8-Cineole	3·21	3·04	2·17	3·24	0·26	0·02	1·54	0·04
γ-Terpinene	21·20	20·20	8·24	22·03	1·53	0·59	9·40	0·78
trans-Sabinene hydrate	2·47	3·42	2·49	3·17	0·08	0·03	1·42	0·06
Linalool	9·47	9·08	6·10	10·41	0·14	0·05	2·40	0·10
Borneol	3·20	3·12	2·32	3·68	0·03	0·02	0·62	0·05
Terpinen-4-ol	2·35	1·67	1·23	2·42	0·02		0·11	0·01
Thymol	137·20	134·00	87·70	182·00	0·45	0·11	3·66	0·25
Carvacrol	8·43	8·60	5·33	11·29	—	—	0·17	—
β-Caryophyllene	5·87	7·57	4·66	8·06	0·39	0·08	0·76	0·13
Total (including compounds not listed in table)	321·72	317·01	183·16	388·33	17·98	3·92	76·14	5·90

Table 4. Composition (in arbitrary units) of the main sage constituents in extracts (SDE) and headspace (HS)

Compound	Distillation–extraction (SDE)				Headspace (HS)			
	Fresh herb	Dried herb			Fresh herb	Dried herb		
		30°C	60°C	Freeze-dried		30°C	60°C	Freeze-dried
Not identified (RT = 7:92)	0·10	0·03	0·19	0·16	0·01	0·02	0·48	0·80
trans-Hex-2-enal	2·42	2·60	0·61	2·34	1·90	0·66	0·36	1·87
α-Pinene	3·08	2·76	1·70	3·01	1·08	0·21	0·28	0·68
Camphene	5·45	4·86	3·00	5·42	1·70	0·35	0·45	1·09
β-Pinene	7·29	6·63	3·64	6·08	2·46	0·40	0·61	1·39
Myrcene	2·82	2·50	0·82	2·61	0·93	0·13	0·32	0·50
Limonene	2·40	2·30	0·81	2·43	0·72	0·11	0·25	0·40
1,8-Cineole	22·45	22·79	16·70	24·06	6·28	1·19	1·39	3·22
γ-Terpinene	1·04	1·11	0·75	1·10	0·09	0·04	0·12	0·06
α-Thujone	137·50	138·10	90·03	137·20	32·34	5·68	7·77	18·15
β-Thujone	9·02	9·26	5·53	9·16	2·20	0·37	0·55	1·23
Camphor	32·34	35·30	26·57	36·90	3·97	1·40	1·08	3·27
Isopulegol	2·17	2·02	1·52	1·92	0·19	0·06	0·05	0·15
Isoborneol	2·45	2·54	1·86	2·63	0·10	0·10	0·04	0·19
Terpinen-4-ol	1·14	1·10	0·73	1·08	0·06	0·02	0·02	0·05
β-Caryophyllene	9·47	9·91	7·11	8·89	0·81	0·46	0·14	1·13
α-Humulene	11·50	11·57	8·54	9·88	0·69	0·40	0·12	0·96
Viridiflorol	9·87	9·68	9·19	9·01	0·05	0·03	0·01	0·06
Total (including compounds not listed in the table)	274·94	278·43	191·02	276·65	56·94	12·35	15·24	31·93

stronger in comparison with the fresh herb, dried at 30°C and the freeze-dried herb. It means that the influence of drying method on the release of flavour compounds can be very individual for a particular herb. For instance, the amount of volatiles in HS of fresh, oven-dried (30°C) and freeze-dried sage significantly exceeds that of thyme; however, when oven-drying at 60°C was applied, the intensity of aroma release from thyme was 'activated' 4·2 times (compared with fresh herb) in terms of the total increase in HS volatiles collected during purging with nitrogen.

Because the conditions of analysis were identical for all HS runs and the water contents in the relevant thyme and sage samples were also comparable (Table 1), the reasons for significant differences in HS concentrations could lie in the botanical structure. It should be said that the changes in HS concentration above a particular herb (thyme or sage) were not dependent on its moisture content (Tables 1, 3 and 4). Therefore, it could be supposed that thyme leaves undergo significant changes in their botanical structure during drying at a high temperature (60°C in our case). From this point of view, sage leaves could be considered as 'more resistant' to the effect of drying at higher temperatures. It seems that the changes in HS after drying are individual for each particular plant, even those belonging to the same family. For instance, Koller and Raghavan (1995) found that the total GC area of rosemary HS volatiles after air convection drying at 50°C was decreased only by 14%, whereas microwave drying at 600 W caused a significantly bigger reduction (2·4 times). It is known that

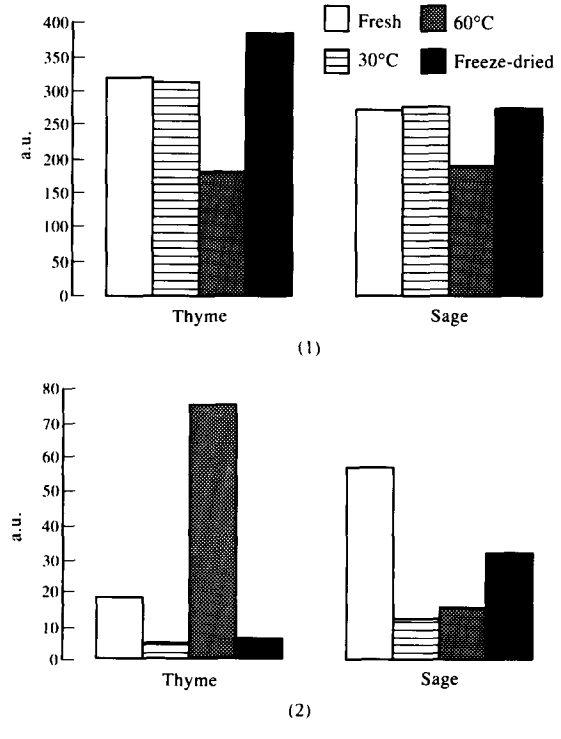

Fig. 1. Changes in the total content of volatile constituents in thyme and sage during drying, in arbitrary units (a.u.): (1) isolated by SDE; (2) isolated by dynamic HS.

labiatae synthesize and store essential oils in glandular hairs or trichomes (Hay & Svoboda, 1993). The essential oils in sage and thyme are formed and released from capitate and peltate trichomes that are very similar in structure; however, the formation of glandular hairs in sage (Croteau *et al.*, 1981) can be different from that in thyme (Yamamura *et al.*, 1989). It should also be emphasized that the leaves of thyme (small in-curled, 2–5 mm long) and sage (oval to lanceolate, 5–7·5 cm long, surface covered with fine short hairs) are very different (Heath, 1981).

Comparison of SDE and HS results

In terms of aroma, every volatile constituent of herb can be assessed by three main parameters: total concentration of the constituent, its content in HS vapours and odour threshold value. Most likely, the concentration of a particular constituent in HS vapours depends on the botanical structure of the particles that store the essential oils in the plant and the physicochemical properties of this constituent. When the concentration of a particular constituent in the HS is compared with its odour threshold value, the extent of the contribution of this compound to the formation of the aroma can be measured. However, the main purpose of this study was to compare the composition of volatiles isolated by SDE (the total amount in the herb) with that determined by HS (outside the herb). It is reasonable to raise a point about the applicability of such a comparison by using dynamic HS instead of static one. Therefore, it should be emphasized that such a comparison was based on the percentage amounts of the individual constituents in SDE and HS. Most likely, relative amounts of the volatile compounds in static HS samples would not considerably differ from the dynamic HS when the purging time is short. Therefore, the relative concentration of a particular constituent determined by dynamic HS can be considered as a certain derivative of the concentration of this constituent in static HS within a definite period of time (in this case the purging time was 1·5 h).

The results obtained show that the percentage composition of volatile compounds in the concentrates obtained by SDE and HS is completely different. The differences also depend on the treatment used, particularly the drying method. These differences in the case of thyme are demonstrated in Fig. 2. For instance, the major compound, thymol, in the concentrate obtained by SDE constitutes 42–48%, while in HS only 2·5–4·8%. Such volatile compounds as *p*-cymene, γ-terpinene and myrcene prevail in HS vapours of thyme. Therefore, the ratio of the percentage amount of an individual compound in HS to that in SDE could be of some interest. Such a ratio could be used as a specific coefficient of efficiency (C_e) for a particular constituent in an aromatic herb. To some extent, it would represent the level of the participation of the compound in the creation of the odour. However, it should be emphasized that C_e must be

clearly distinguished from the aroma index and/or charm value, i.e. the parameters that directly relate to the sensory characteristics of a particular compound (odour threshold value, aroma quality). For instance, the comparatively small C_e of thymol in thyme shows that the relative amount of this compound in the essential oil ('inside' the herb, 'passive' state) is much higher than in the headspace ('outside' the herb, 'active' state).

The percentage concentrations of some major volatile constituents of thyme and sage and their C_e values are given in Table 5. It is interesting to note that, for some compounds, the coefficients are different in thyme and sage. For instance, the C_e of β-caryophyllene in fresh thyme is 2·8 times higher than that in fresh sage. The absolute concentration (in arbitrary units) of β-caryophyllene in SDE and HS samples of fresh thyme was lower than in fresh sage by 1·6 and 2·1 times, respectively. However, the total amount of volatiles in the HS of fresh sage was 3·2 times higher than that of fresh thyme, and therefore the percentage content of β-caryophyllene in sage HS was lower than that in thyme HS.

C_e values were also calculated for dried herb. The changes in C_e for some constituents of thyme and sage after drying are shown in Fig. 3. It can be seen that the

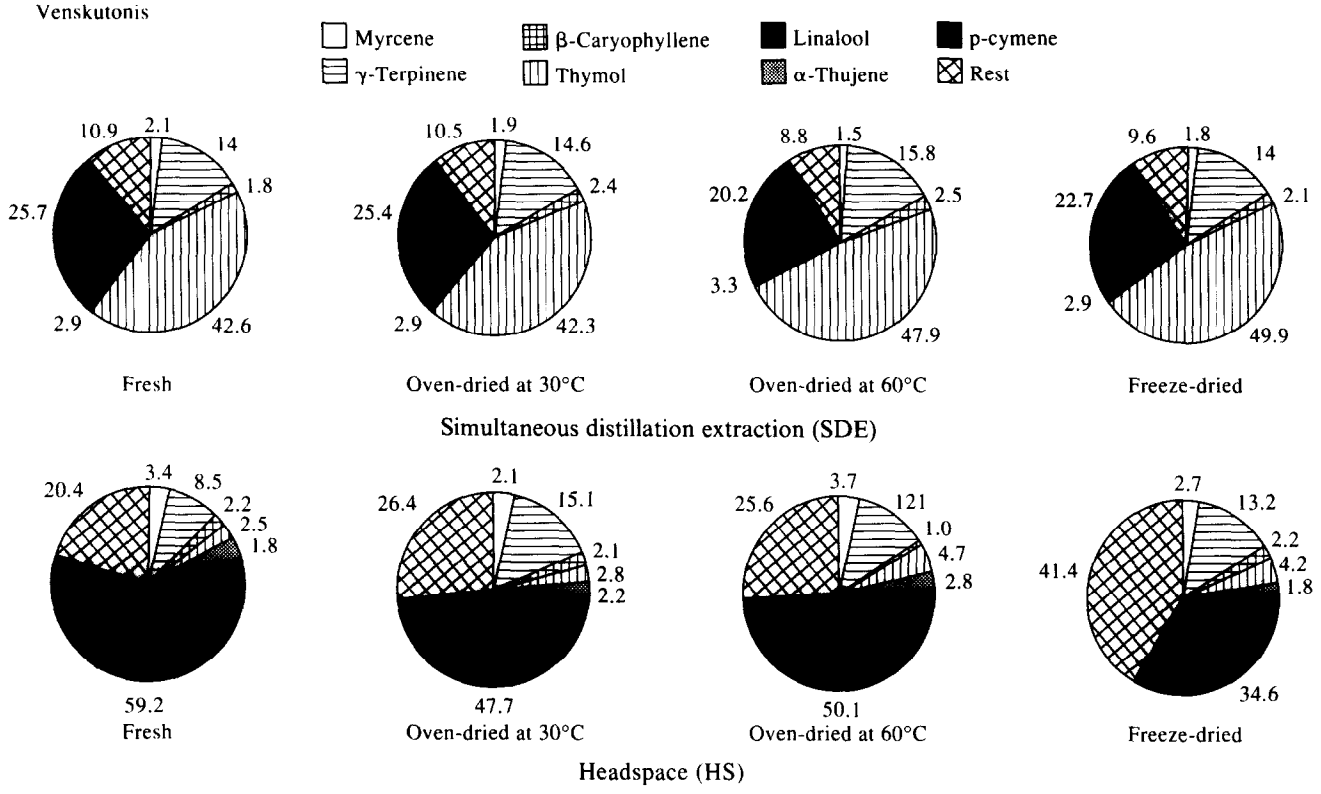

Fig. 2. Changes in the percentage content of the main constituents in thyme isolated by SDE (top row) and HS (bottom row) during drying.

Table 5. Percentage content of volatile compounds and their coefficients of efficiency (C_e) in fresh thyme and sage

Compound	Thyme			Sage		
	SDE	HS	C_e	SDE	HS	C_e
α-Pinene	1·15	2·55	2·22	1·12	1·90	1·70
Camphene	0·61	1·42	2·33	1·98	2·99	1·51
β-Pinene	0·39	0·74	1·90	2·65	4·32	1·63
Myrcene	2·05	3·40	1·66	1·03	1·64	1·59
1,8-Cineole	1·00	1·46	1·46	8·16	11·0	31·35
γ-Terpinene	6·59	8·53	1·29	0·38	0·17	0·45
p-Cymene	25·71	59·2	82·31			
α-Thujone				50·01	56·80	1·14
β-Thujone				3·28	3·86	1·18
Camphor				11·76	6·98	0·59
Linalool	2·94	0·79	0·27			
Thymol	42·65	2·50	0·06			
β-Caryophyllene	1·82	2·15	1·18	3·44	1·43	0·42
α-Humulene				4·18	1·22	0·29

changes in C_e depend on the chemical structure of the constituent and its origin (i.e. these changes were different for thyme and sage). For instance, the C_e for linalool (polar compound) in thyme increased significantly after oven-drying at 60°C, whereas that for β-caryophyllene (apolar compound) was reduced several-fold. The C_e of ψαρθωπђθλλενε ιν τђθμε αλσω δεψρεασεδ αφτερ δρθινγ ατ ≷°Ψ ανδ φρεεζεδρθινγ∴ χђιλε τђε C_e of the same compound in sage increased considerably when the same methods of drying were applied. The considerable variability of C_e, depending both on the chemical properties of the volatile constituent and on its origin, demonstrates the complexity of the effect of drying on the equilibrium between aroma compounds in the essential oil storing particles of the plant and HS vapours. For instance, the percentage composition of constituents in the total essential oil isolated by SDE can undergo insignificant changes during drying, whereas the composition of the relevant HS volatiles can change considerably. Certainly, it is possible to predict that the larger the changes that occur in HS composition, the more unbalanced will be the aroma obtained after drying compared with the fresh herb. However, this study cannot provide the answers to many questions arising, and the subject needs further investigation.

CONCLUSIONS

1. The effect of oven-drying (30°C) and freeze-drying on the total content of volatile compounds isolated by SDE was insignificant; the losses at 60°C were 43% in thyme and 31% in sage.
2. The changes in the concentrations of volatiles in HS differed significantly for thyme and sage and were dependent on the method and the drying temperature.
3. The extensive release of volatiles from thyme dried at 60°C indicates that the biological structure of the oil gland trichomes of this plant was strongly affected.
4. The ratio of the percentage content of the individual compounds in HS to that in SDE (coefficient of efficiency, C_e) can be of some interest in assessing changes of the equilibrium between the relative contents of volatile compounds in essential oil storing particles and HS vapours.

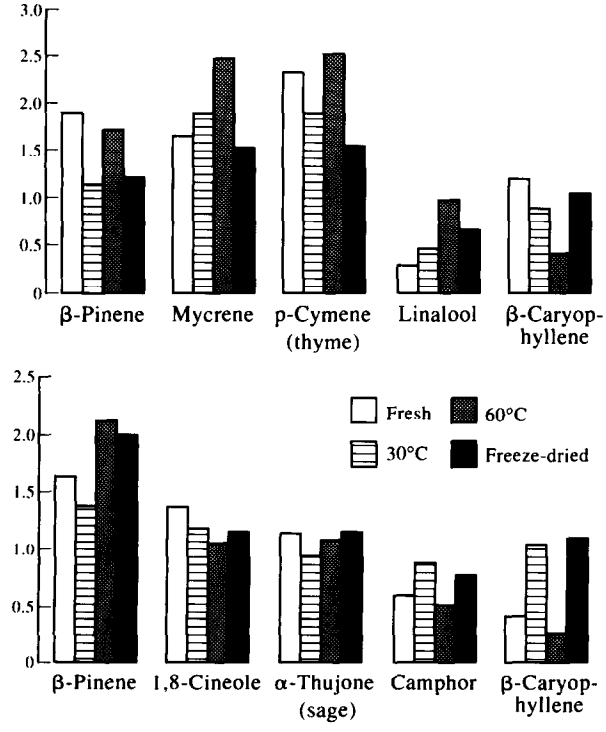

Fig. 3. Changes in the coefficients of efficiency (C_e) of some thyme and sage volatile constituents during drying.

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