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Volatile Compounds of Selected Strawberry Varieties Analyzed by Purge-and-Trap Headspace GC-MS

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Six strawberry (*Fragaria* × *ananassa* Duch.) varieties, Senga Sengana, Jonsok, Polka, Korona, Bounty, and Honeoye, were studied in relation to composition of their volatile headspace compounds collected by dynamic purge-and-trap concentration. Also, the influence of cultivation technique on the volatile compounds was tested by comparing conventionally and organically cultivated strawberry varieties. In addition, the effect of geographical origin on strawberry volatiles was investigated. The emphasis of this study was lay in the industrial utilization of strawberry. A total of 52 different volatile compounds were determined from frozen strawberries grown in 1997 and 1998. In addition to individual compounds, total areas of chromatogram profiles were compared. The major esters were found to be methyl butanoate, ethyl butanoate, methyl hexanoate, and ethyl hexanoate. With the application of principal component analysis and analysis of variance to the data matrix, the varieties were classified into three groups. Var. Honeoye was most different from the others. Organic cultivation had no effect on strawberry volatiles.

KEYWORDS: **Organic cultivation; purge-and-trap; strawberry; varieties; volatile profiles**

INTRODUCTION

Strawberry (*Fragaria* × *ananassa* Duch.) is the most important cultivated berry in Finland. The annual yield of strawberries is ~15000 tons, of which >95% are sold in the fresh market. The fruit is grown mostly in the southern and eastern parts of the country between 60 and 64° N. The main strawberry variety used in the Finnish preservative industry, Senga Sengana, has been mainly imported. Alternatives for industrial product development and utilization would be beneficial. Recently, both consumers and the food industry have become more interested in organically cultivated agricultural products. However, the effect of organic cultivation on flavor or volatile aroma compounds in strawberry is not well investigated.

Over 350 volatile compounds have been identified in strawberries (*1*−*3*). The relationship between the aroma impact volatiles and strawberry varieties has been the subject of numerous investigations (*4*−*11*). Frozen Senga Sengana showed a higher amount of aroma compounds in comparison to Senga Litesse and Senga Gourmella (*10*). The production of acetaldehyde, ethanol, and ethyl acetate, for example, associated with off-flavor, are known to be affected by the variety (*12*). Ethyl esters are the major volatile compounds of strawberries at all ripening stages (*13*). Ethyl ester formation has also been found to be variety dependent (*14*). Agronomic and seasonal variations have been found to cause variation in the quantitative profile of strawberry volatiles (*3*). Genotype and growing conditions have been shown to cause changes to the key aroma compounds (*7*).

The headspace (HS) method of aroma compound analysis is a logical choice in analyses (*15*), but detection of the less volatile compounds of strawberries may cause problems (*6*, *16*). Dynamic headspace extraction applications have increased the number of strawberry volatiles identified to nearly 100 to date (*17*−*19*). The advantage of the dynamic headspace method compared to solvent extraction is its nondestructivity and capability to isolate volatiles in their natural form (*13*, *20*). Dynamic purge-and-trap collection combined with gas chromatography−mass spectrometry (GC-MS) has earlier been applied successfully to aroma profiling of strawberry varieties Oso Grande, Chandler, and Selva (*18*, *19*).

The aim of our two-year study was to compare the headspace composition of Senga Sengana, the most conventional raw material in the food industry, to that of other varieties which have potential for industrial use in the future. Our interest was to find new potential candidates for industrial processing purposes. The samples of strawberries were frozen after harvesting and thawed for analyses. In addition, differences between strawberries from organic or conventional cultivations were investigated. The influence of geographical origin on the volatiles of Senga Sengana was also studied.

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EXPERIMENTAL PROCEDURES

Strawberry Material. The fruit analyzed consisted of six conventionally farmed varieties: Senga Sengana, Jonsok, Korona, Polka, Honeoye, and Bounty. In addition, fruit of three organically cultivated (OR) varieties, Polka-OR, Honeoye-OR, and Jonsok-OR, were analyzed. The strawberries were grown by professional farmers in the Inner-Savo area of eastern Finland in 1997 and 1998 applying normal farming practice from second- and third-year bushes (*21*). The fruit was picked as decapped and ripened analogously at the later middle stage of the season by applying normal farming practice. A total of three subsamples (10 kg) from different farms ($n = 10$) were frozen and pooled after tunnel freezer (Pakkasmarja Ltd, Suonenjoki, Finland) for one sample lot. A final sample for analyses was 20 kg, simulating the typical raw material sample for industrial purposes. The farms were selected due to their similar growing conditions of fields such as soil, beds, fertilizers, and irrigation. EU Council Regulation (EEC 2092/91) was implemented in the organic cultivation at four farms. For investigation of the effect of the origin, Senga Sengana samples were collected in both eastern Finland (Senga-E) and southwestern Finland (Senga-SW). Two commercial Polish Senga Sengana batches, Senga-VP (received via Valio Ltd., Suonenjoki, Finland) and Senga-PP (received via Pakkasmarja Ltd.) were imported on the basis of practices in the Finnish food industry and investigated. Senga-VP was qualified as a class II type of strawberry based on EU Council Regulation (EEC 2200/96). All of the other strawberry samples represented class I. The strawberries were stored after tunnel-freezing at −20 °C in polyethylene bags for analyses.

Sample Preparation. Subsamples of 200 g of each strawberry sample lot were gently melted separately in a microwave oven in 600 mL beakers for 2 × 2.5 min at 30% power (AEG Micromat, Nürnberg, Germany) and shaken intermittently. The thawed fruit was homogenized in a beaker, covered with foil, and housed within a thermostated water bath (22 °C) for 25 min, after which time a 2 g sample was taken for analysis without delay. Three replicates from each subsample were prepared separately.

Reference Compounds. Ethyl butanoate, ethyl 2-methylbutanoate, methyl 2-methylbutanoate, methyl 3-methylbutanoate, methyl butanoate, methyl hexanoate, decanal, 2,4-hexadienal, 3-methylbutyl acetate, 2,3-pentanedione, 3-methyl-2-pentanone, and 3-methylbutanal were obtained from Sigma-Aldrich Chemie GmbH (Steinheim, Germany). 2-Pentanone, 2-hexanone, 2-heptanone, *trans*-2-hexenal, *cis*-3-hexenol, ethyl hexanoate, *n*-hexanal, benzaldehyde, butyl acetate, 3-methyl-2-butanone, butyl 3-methylbutanoate, methyl propionate, methyl octanoate, and methyl 3-methylbutanoate were obtained from Fluka Chemie AG (Buchs, Switzerland). 2-Heptanol was from Merck, and 3-methylbutyl 2-methylpropanoate and pentyl 2-methylpropanoate were obtained from Haarmann and Reimer GmbH (Teterboro, NJ).

Purge-and-Trap Isolation. Tekmar 3000 purge-and-trap equipment (Tekmar Co., Cincinnati, OH) was applied to dynamic headspace sampling (DHS) of volatile compounds. The strawberry sample (2 g) was equilibrated at the bottom of a prepurged headspace sampling tube (30 mL, 25 °C) for 3 min. The volatile compounds were purged with helium flush (440 mL) into the deactivated stainless steel column packed with 0.2 g of OV-1 and OV-25 liquid phase (1:1) (Chromatography Research Supplies Inc., Addison, IL) and cooled with CO_2 (−20 °C). The analytes were desorbed by backflushing via the deactivated transfer line (200 °C, 1.8 m × 1.6 mm i.d.) into a cryofocusing module (Tekmar Co.) and a DB-1 cryogenic trap (J&W Scientific, Folsom, CA; 20 cm × 0.32 mm i.d., $d_f = 0.25$ μm). The headspace sampling was controlled by Teklink v. 1.0 software (Tekmar Co).

GC-MS. GC-MS analysis was carried out with a QP5000 instrument (Shimadzu, Kyoto, Japan). The cryogenic trap was coupled to an analytical fused silica capillary column SPB-1701, 30 m × 0.25 mm i.d., $d_f = 0.25$ μm (Supelco Inc., Bellefonte, PA), with a direct connect capillary connector (Alltech Associates Inc., Deerfield, IL). The temperature program was as follows: 30 °C held for 8 min, then raised at 2 °C/min to 75 °C, at 10 °C/min to 100 °C, at 15 °C/min to 230 °C, and finally held for 5 min. The ionization energy was 70 eV, and the detection voltage was 1.30 kV. The compounds were monitored over the range m/z 40−310. The GC-MS system was controlled by Class 2.10 software (Shimadzu).

Table 1. Repeatability of Six Replicate HS-GC-MS Analyses: Average Relative Proportions and Cofficients of Variance (CV) for Selected Compounds in Headspace of Senga-E

compound	av relative proportion[a] (%)	CV %	av peak area[a]	CV %
ethyl pentanoate	0.07	17.6	947334	35.1
methyl 3-methylbutanoate	0.21	11.8	2784346	18.7
methyl pentanoate	0.21	15.2	2832002	15.9
pentyl acetate	0.25	17.3	3400418	26.2
ethyl 3-methylbutanoate	0.69	18.9	9382823	23.1
1-methylethyl butanoate	0.72	12.5	9873996	27.6
acetaldehyde	0.93	9.0	12630823	18.0
2-pentanone	3.91	13.6	52512545	14.1
2-heptanone	9.72	9.7	1.33E+08	22.1
methyl butanoate	13.91	14.7	1.87E+08	16.2
ethanol+acetone	14.84	13.7	2E+08	15.8
methyl hexanoate	16.62	16.4	2.26E+08	23.3
ethyl butanoate	20.75	9.4	2.81E+08	17.5
total	82.83		1.36E+09	

[a] Average of six subsamples.

Qualitative and Quantitative Analyses. Wiley spectral library (Shimadzu) and retention times of reference compounds were used for identification of the volatile compounds. All chromatographic peaks found in at least two of the total ion chromatograms (TIC) of the same sample lot were taken into account when the total area of peaks (100%) and relative proportions of the volatile compounds in the headspace of the samples were calculated. The critical limit for selecting the peaks for integration was a signal-to-noise ratio of three. Identification of the compounds was based on library spectra and on retention times and spectra of a reference compound when available. Identifications were compared with strawberry results published earlier (*1*, *3*, *4*, *10*, *18*, *19*, *22*−*24*). A total of 81 chromatograms (13 samples, 2 years, 3 replicates and repeatability tests) were processed.

Repeatability. Repeatability of the method was tested by analyzing six parallel, thawed subsamples of Senga-E strawberries. Every TIC peak found in at least five chromatograms was taken into account when the relative proportions of volatiles in the average headspace volume were calculated.

Statistical Analyses. Statistical analyses were performed using SPSS (SPSS 7.5.1, SPSS Inc. H, Chicago, IL). Significant differences in strawberry volatile composition were tested by one-way analysis of variance (ANOVA). Tukey's *t* test, a Tamhane test, and a nonparametric Mann−Whitney test were used for multiple comparison of sample lots of different varieties and four samples of Senga Sengana separately and annually. Differences between the sample lots of organic and normal cultivation practices were determined with an independent-samples *t* test. The effect of sample × year interaction on differences was also tested. The characterization of varieties was achieved by applying a principal component analysis (PCA) with standardization and cross-validation to the chromatographic data matrix using Unscrambler 7.5 (Camo ASA, Oslo, Norway).

RESULTS AND DISCUSSION

Repeatability. Repeatability of the dynamic HS-GC-MS method was determined with six strawberry subsamples of one sample lot, which were analyzed separately on different days. The results of averaged relative proportions and absolute areas of selected TIC peaks and coefficients of variation (CV%) obtained are shown in **Table 1**. CV% values were found to be <20% in the case of relative proportions. The variation was somewhat higher when the absolute peak areas were compared with each other. The variation was at the same level as that of Ibanez et al. (*25*) reached for absolute areas for the standard mixture with programmed temperature vaporizer GC injector. Compared to repeatability of purge-and-trap GC-MS results of Gomes da Silva et al. for strawberry (*19*), the variation in our

Table 2. HS-GC-MS Analysis of Strawberry Samples: Mean of Total Peak Areas and Number of Peaks Counted ($n = 3$)

	crop year 1997		crop year 1998	
sample	total peak area[a] (E+08)	total no. of peaks	total peak area[a] (E+08)	total no. of peaks
Senga	19.4bcd	37	12.6cde	33
Jonsok	26.5cd	36	7.16bc	25
Korona	7.16a	25	6.51bc	27
Polka	11.1abcd	36	4.07ab	24
Honeoye	6.66a	22	2.95a	15
Bounty	30.6d	34	7.35bc	24
Jonsok-OR	19.1bcd	26	12.2cde	28
Polka-OR	19.9bcd	31	7.17bc	25
Honeoye-OR	8.62ab	20	5.12ab	15
Senga-PP	10.3abc	33	10.6cd	34
Senga-VP	10.8abcd	28	19.2de	34
Senga-E	19.4bcd	31	15.5de	36
Senga-SW	11.6abcd	30	22.2e	33

[a] Significance of differences ($p < 0.05$) determined annually with multiple comparison are marked as a–d. Parameters marked with the same letter did not differ significantly from each other.

study was lower. As shown below, the purge-and-trap HS-GC-MS technique was reproducible enough to allow comparative comparison studies of the volatiles of different varieties.

Qualitative Analyses. A total of 52 different volatile compounds were analyzed in the headspace of melted and mashed strawberry samples. The number of volatiles is at the same level as previously extracted from strawberries by dynamic headspace technique (*13*, *22*). As we wanted to keep the sample preparation procedure identical with that in the sensory evaluation, no hard sample pretreatment, vacuum extraction, distillation, or heating was applied. In addition, stabilization time after gentle melting and before purging was kept the same as in the sensory analysis (25 min). The temperature of a sample during purging was also identical with that of quantitative sensory profiling (25 °C). Thus, the number of compounds detected was smaller than described before by the application of purge-and-trap to strawberry volatiles (*18*, *19*). The results of sensory analysis will be described in more detail in a separate publication.

Of all the peaks accepted for quantitative integration, only six were not identified. In addition, the resolution between ethanol and acetone was too low for proper quantitative measurement. When the results were calculated, they were considered as one response in the chromatograms. The main compounds identified were aliphatic straight-chain and branched esters.

Total Peak Area of GC Profiles. When the total peak areas for different samples were compared to each other as shown in **Table 2**, the differences between the years were high when compared with the difference between the samples in one year. The total area was higher in 1997 than in 1998 in every sample, except in Senga-VP and Senga-E. When all 13 samples from one year were combined into one group, the mean total area in 1997 was significantly higher than in 1998 ($F = 11.69$, $p < 0.001$). This was propably due to weather conditions. In Finland the summer of 1997 was warmer and drier than that of 1998, or than an average Finnish summer season, according to statistics of the Finnish Meteorological Institute. The rainfall in 1998 varied from 250 to 400 mm, where as average amount during the summer season is 180−220 mm. In addition, when the samples were divided into three groups according to variety, cultivation (normal vs organic), and origin (four Senga samples), the average total areas within groups were significantly higher in 1997 except in the case of origin. The significant differences ($p < 0.05$) between the samples determined annually with multiple comparison are also presented in **Table 2** as alphabetical codes. For example, Honeoye differed in both years from Senga and Jonsok. The number of volatile compounds taken into account for the profiles of different strawberry samples are listed also in **Table 2**. The total number of peaks was lowest in Honeoye in both years and highest in Senga Sengana.

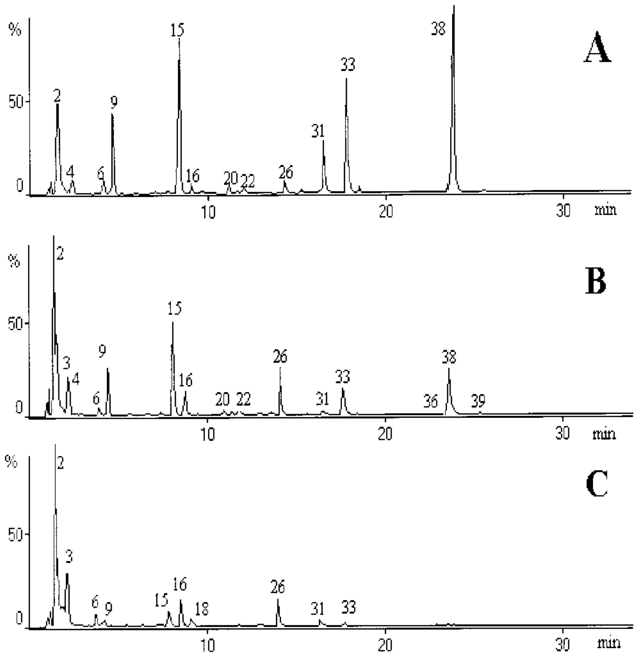

Figure 1. TIC for GC-MS analysis and relative intensities (percent) of volatile aroma compounds after purge-and-trap sampling of three strawberry varieties, Senga (A), Polka (B), and Honeoye (C), analyzed on an SPB-1701 column. The peak labels indicate the identification numbers in **Table 3**.

Variety Profiles. Figure 1 shows the TICs of GC-MS analysis of volatile aroma compounds of three strawberry varieties, Senga, Polka, and Honeoye (1997), analyzed with an SPB-1701 column using purge-and-trap sampling. The compounds in TICs having an average relative proportion $>1\%$ are coded with the identification numbers shown in **Table 3**. Variation in profiles of different genotypes of strawberry was obvious in both crop years. **Table 3** shows the average relative proportions of volatile compounds analyzed for each sample lot in three replicates. Methyl butanoate (**9**), ethyl butanoate (**15**), methyl hexanoate (**33**), and ethyl hexanoate (**38**) were the major compounds identified. These esters have also been found to be major volatile compounds of the dynamic headspace of fresh strawberries (*13*). The sum of the relative proportion of these esters was $>50\%$ in all samples except Honeyoe. This result supports the observation of Larsen (*14*) that ethyl ester formation is variety-dependent. Forney (*9*) found butanoates and hexanoates comprising $>80\%$ of total volatiles of fresh Annapolis, Kent, Micmac, and Cavendish, when in Honeoye they comprised only 50%. Perez (*13*) reported the ratio of methyl/ethyl esters is dependent on the variety. Our results show that the year effect was stronger than the variety effect in the case of Polka, for which the ratio of methyl/ethyl esters was 5 times higher in 1998 than in 1997. The proportion of unseparated ethanol + acetone (**2**) exceeded 10% in all varieties, and it was the highest peak in the profile of Honeoye.

The amounts of 3-methyl-2-butanone (**5**), 2-heptanone (**31**), methyl hexanoate (**33**), and ethyl hexanoate (**38**) in the profiles

Table 3. Volatile Compounds Analyzed in the Headspace of Strawberry Varieties: Mean of Relative Proportions ± Standard Deviation ($n = 3$) and Results of Analysis of Variance

ID	compound$^{\text{ident}}$	year	Senga	Jonsok	Korona	Polka	Honeoye	Bounty	variety^b	year^b	sample × year^b
1	acetaldehyde^{c,d}	1997	0.15 ± 0.03	0.30 ± 0.07	0.56 ± 0.05	0.49 ± 0.14	0.47 ± 0.19	0.35 ± 0.10	**	***	**
		1998	1.10 ± 0.19	1.84 ± 0.60	2.09 ± 0.26	2.35 ± 0.44	2.97 ± 0.60	2.73 ± 0.34	**		
2	ethanol + acetone^{c,d}	1997	11.22 ± 3.59	17.7 ± 2.28	21.5 ± 4.66	26.94 ± 4.00	49.20 ± 3.82	18.38 ± 6.30	***	*	*
		1998	16.63 ± 4.31	24.23 ± 4.06	22.5 ± 2.78	32.75 ± 4.34	42.34 ± 4.87	27.59 ± 3.94	***		
3	2,3-butanedione^{c,d}	1997	0.70 ± 0.49	0.92 ± 0.81	0.70 ± 0.34	4.25 ± 0.49	12.60 ± 1.43	3.91 ± 0.88	***	**	***
		1998	0.92 ± 0.42	1.79 ± 0.49	1.56 ± 0.39	3.52 ± 0.81	20.19 ± 2.57	1.74 ± 0.36	***		
4	ethyl acetate^{c,d}	1997	1.44 ± 0.30	1.96 ± 0.55	3.61 ± 0.99	2.50 ± 0.60	0.14 ± 0.06	0^a	***	***	***
		1998	0.91 ± 0.10	2.88 ± 1.07	2.05 ± 0.80	2.57 ± 0.93	4.69 ± 1.31	5.18 ± 1.39	**		
5	3-methyl-2-butanone^{d,e}	1997	0.09 ± 0.05	0.17 ± 0.08	0^a	0^a	0^a	0^a			
		1998	0.23 ± 0.14	0.14 ± 0.13	0^a	0^a	0^a	0^a			
6	2-pentanone^{c,d,e}	1997	1.47 ± 0.24	2.07 ± 0.45	0.96 ± 0.18	1.39 ± 0.12	3.24 ± 0.22	0.61 ± 0.20	***		***
		1998	4.34 ± 0.52	3.46 ± 1.54	1.01 ± 0.42	1.68 ± 0.57	0^a	1.18 ± 0.20	***		
7	ethyl propanoate^{c,d}	1997	0^a	0^a	0.28 ± 0.04	0.14 ± 0.14	0.75 ± 0.31	0^a	***	**	***
		1998	0^a	0^a	0.21 ± 0.19	0.20 ± 0.09	0^a	0^a			
8	1-butanol^{c,d}	1997	0^a	0^a	0.31 ± 0.06	0^a	0.58 ± 0.18	0^a	*	*	***
		1998	0^a	0^a	0.17 ± 0.06	0.15 ± 0.09	0.38 ± 0.08	0^a	*		
9	methyl butanoate^{c,d,e}	1997	5.51 ± 1.68	4.71 ± 1.23	15.78 ± 1.60	8.85 ± 2.65	1.58 ± 0.19	4.10 ± 1.25	***	***	**
		1998	12.23 ± 0.74	8.01 ± 3.90	17.55 ± 0.99	21.46 ± 5.52	1.77 ± 0.10	8.28 ± 1.09	***		
10	2-pentanol^{c,d}	1997	0.06 ± 0.05	0.05 ± 0.05	0^a	0.05 ± 0.04	0.36 ± 0.03	0.06 ± 0.02	***	***	***
		1998	0.10 ± 0.05	0^a	0^a	0^a	0^a	0^a	***		
11	2-hexanone^{c,d,e}	1997	0.14 ± 0.04	0.11 ± 0.04	0^a	0.6 ± 0.08	0.47 ± 0.09	0^a	***	**	*
		1998	0.13 ± 0.04	0.09 ± 0.08	0^a	0.80 ± 0.26	0.85 ± 0.22	0.10 ± 0.02	***		
12	3-methyl-2-pentanone^{d,e}	1997	0.18 ± 0.27	0.09 ± 0.02	0^a	0.18 ± 0.04	0.05 ± 0.03	0^a			
		1998	0.03 ± 0.00	0.12 ± 0.13	0^a	0.22 ± 0.05	0.23 ± 0.07	0^a	***		
13	methyl 2-methylbutanoate^{c,d,e}	1997	0.17 ± 0.05	0.23 ± 0.01	0.42 ± 0.08	0.77 ± 0.18	0.61 ± 0.17	0.32 ± 0.06	***		*
		1998	0.42 ± 0.45	0^a	0.22 ± 0.04	1.27 ± 0.57	0.35 ± 0.12	0.38 ± 0.04	**		
14	2-methyl-1-butanol^{c,d}	1997	0^a	0^a	0^a	0^a	0.43 ± 0.08	0^a	***	***	***
		1998	0^a	0^a	0^a	0^a	0^a	0^a			
15	ethyl butanoate^{c,d,e}	1997	15.30 ± 3.28	15.60 ± 3.37	24.52 ± 2.11	19.32 ± 1.40	5.32 ± 1.10	13.28 ± 1.69	***	*	**
		1998	20.55 ± 2.13	15.16 ± 8.13	15.21 ± 0.44	10.31 ± 4.84	3.45 ± 1.08	12.66 ± 1.03	**		
16	n-hexanal^{c,d,e}	1997	0.73 ± 0.27	0.84 ± 0.37	6.21 ± 1.28	4.90 ± 0.91	8.56 ± 0.15	2.77 ± 0.31	***	***	
		1998	1.74 ± 0.71	1.64 ± 0.78	6.95 ± 0.92	8.47 ± 1.45	12.29 ± 4.97	6.69 ± 0.16	***		
17	2-methyl-4-pentenal^{c,d}	1997	0^a	0.07 ± 0.06	0^a	0.47 ± 0.13	0^a	0.18 ± 0.15	***	***	***
		1998	0^a	0^a	0^a	0^a	0^a	0^a			
18	*n*-butyl acetate^{c,d,e}	1997	0.53 ± 0.13	0.49 ± 0.16	0.27 ± 0.43	0.73 ± 0.18	3.19 ± 0.17	0.25 ± 0.01	***		***
		1998	1.01 ± 0.07	0.94 ± 0.40	2.77 ± 0.14	0.79 ± 0.53	1.66 ± 0.47	0.84 ± 0.36	***		
19	methyl pentanoate^d	1997	0.14 ± 0.08	0.07 ± 0.02	0.46 ± 0.12	0.16 ± 0.11	0^a	0.12 ± 0.03	***		**
		1998	0.17 ± 0.08	0^a	0.37 ± 0.07	0.35 ± 0.04	0^a	0.20 ± 0.04	***		
20	1-methylethyl butanoate^{c,d}	1997	1.00 ± 0.26	1.02 ± 0.51	2.26 ± 0.71	1.06 ± 0.37	0^a	0.78 ± 0.15	***	***	
		1998	0.67 ± 0.10	0.13 ± 0.12	1.13 ± 0.39	0.51 ± 0.01	0^a	0.28 ± 0.08	***		
21	ethyl 2-methylbutanoate^{c,d,e}	1997	0.69 ± 0.25	1.38 ± 0.20	0.66 ± 0.05	1.01 ± 0.10	0^a	1.54 ± 0.35	***	***	***
		1998	0.16 ± 0.02	0.38 ± 0.36	0^a	0^a	0^a	0.52 ± 0.11	**		
22	ethyl 3-methylbutanoate^d	1997	1.30 ± 0.18	0.93 ± 0.02	0.91 ± 0.04	2.11 ± 0.11	0.88 ± 0.24	1.57 ± 0.32	***	***	**
		1998	0.56 ± 0.01	0.29 ± 0.25	0^a	0.71 ± 0.33	0.55 ± 0.17	0.63 ± 0.22	*		
23	*cis*-3-hexenal^{c,d,e}	1997	0^a	0^a	0^a	0.56 ± 0.27	0^a	0.35 ± 0.08	***	***	***
		1998	0^a	0^a	0^a	0^a	0^a	0^a			
25	3-methylbutyl acetate^{c,d,e}	1997	0.13 ± 0.09	0.08 ± 0.04	0^a	0^a	0^a	0^a	**		
		1998	0.16 ± 0.03	0.07 ± 0.06	0.19 ± 0.17	0^a	0^a	0^a	*		
26	*trans*-2-hexenal^{c,d,e}	1997	1.05 ± 0.43	1.69 ± 0.60	4.34 ± 0.82	8.52 ± 1.11	7.50 ± 1.09	5.44 ± 1.36	***		***
		1998	1.04 ± 0.29	1.96 ± 0.29	7.24 ± 1.52	4.33 ± 1.55	5.84 ± 1.29	5.48 ± 0.66	***		
27	5-methyl-2-hexanone^d	1997	0^a	0^a	0^a	0^a	0^a	0^a			*
		1998	0.11 ± 0.10	0^a	0^a	0^a	0^a	0^a	*		
28	propyl butanoate^{c,d}	1997	0.21 ± 0.18	0.12 ± 0.07	0.24 ± 0.10	0.21	0	0.1		***	
		1998	0.15 ± 0.13	0^a	0.07 ± 0.01	0^a	0^a	0^a	*		
29	ethyl pentanoate^{c,d}	1997	0.11 ± 0.04	0.11 ± 0.02	0.08 ± 0.08	0.56 ± 0.80	0^a	0.09 ± 0.04			
		1998	0.07 ± 0.04	0^a	0.04 ± 0.00	0^a	0^a	0^a	***		
31	2-heptanone^{c,d,e}	1997	6.09 ± 0.91	5.34 ± 0.68	0.87 ± 0.21	0.68 ± 0.21	2.20 ± 0.67	1.15 ± 0.14	***		*
		1998	7.41 ± 0.16	7.95 ± 2.54	0.42 ± 0.13	0.14 ± 0.14	2.46 ± 0.95	0.95 ± 0.35	***		
32	pentyl acetate^{c,d}	1997	0.13 ± 0.03	0.14 ± 0.03	0.13 ± 0.02	0.25 ± 0.08	0^a	0.10 ± 0.01	***	**	***
		1998	0.17 ± 0.19	0.27 ± 0.18	0.40 ± 0.04	0^a	0^a	0.27 ± 0.84	***		
33	methyl hexanoate^{c,d,e}	1997	16.91 ± 2.57	11.21 ± 0.81	7.42 ± 1.93	3.66 ± 3.14	1.14 ± 0.07	13.54 ± 1.07	***		
		1998	13.55 ± 1.71	15.00 ± 7.05	10.13 ± 0.98	5.71 ± 1.26	0^a	14.81 ± 3.05	***		
34	2-heptanol^{c,d,e}	1997	0.70 ± 0.12	0.97 ± 0.19	0^a	0.27 ± 0.15	0^a	0.36 ± 0.02	***	***	
		1998	0.46 ± 0.06	0.65 ± 0.41	0^a	0^a	0^a	0^a	***		
35	unknown^d	1997	0.03 ± 0.01	0.03 ± 0.01	0^a	0^a	0^a	0.03 ± 0.02	**	***	***
		1998	0^a	0^a	0^a	0^a	0^a	0^a			
36	benzaldehyde^{c,d,e}	1997	0.06 ± 0.01	0.05	0^a	1.58 ± 2.50	0.31 ± 0.13	0.06 ± 0.01			
		1998	0.07 ± 0.03	0^a	0^a	0^a	0^a	0^a	***		
37	butyl butanoate^{c,d}	1997	0.51 ± 0.19	1.13 ± 0.16	0.61 ± 0.52	0.17 ± 0.05	0.44 ± 0.42	0.18 ± 0.09	*		*
		1998	0.71 ± 0.30	0.46 ± 0.15	0.91 ± 0.50	0^a	0^a	0^a	***		
38	ethyl hexanoate^{c,d,e}	1997	31.79 ± 9.73	28.89 ± 6.35	4.26 ± 2.99	3.17 ± 5.00	0^a	28.03 ± 8.68	***	***	**
		1998	12.35 ± 7.28	11.79 ± 4.41	4.57 ± 0.40	0^a	0^a	8.30 ± 3.46	**		
39	octanal^{c,d}	1997	0.46 ± 0.53	0.12 ± 0.05	0^a	3.72 ± 6.15	0^a	0.17 ± 0.03			
		1998	0.20 ± 0.13	0.21 ± 0.13	0.11 ± 0.04	0^a	0^a	0.14 ± 0.08	*		

Table 3 (Continued)

ID	compound^{ident}	year	Senga	Jonsok	Korona	Polka	Honeoye	Bounty	variety^b	year^b	sample × year^b
40	hexyl acetate^{c,d}	1997	0.41 ± 0.29	0.62 ± 0.10	0^a	0.21 ± 0.23	0^a	0.85 ± 0.23	***		**
		1998	0.74 ± 0.35	0.51 ± 0.07	0.41 ± 0.17	0^a	0^a	0.30 ± 0.28	**		
41	*trans*-hex-2-enyl acetate^{c,d}	1997	0.31 ± 0.21	0.56 ± 0.03	0^a	0^a	0^a	0.56 ± 0.06	***		***
		1998	0.88 ± 0.50	0^a	0.36 ± 0.20	0^a	0^a	0.18 ± 0.19	**		
42	1-hexanol^{c,d}	1997	0^a	0^a	0^a	0^a	0^a	0.45 ± 0.31		***	***
		1998	0^a	0^a	1.37 ± 0.16	1.04 ± 0.53	0^a	0.58 ± 0.00	***		
43	1-methylethyl acetate^{c,d}	1997	0.00	0^a	0.18 ± 0.04	0.10 ± 0.01	0^a	0.02 ± 0.02	***	*	**
		1998	0^a	0^a	0^a	0.12 ± 0.15	0^a	0^a			
44	3-methyl-1-butanol^{c,d}	1997	0^a	0^a	0^a	0^a	0^a	0^a		***	***
		1998	0^a	0^a	0^a	0.36 ± 0.11	0^a	0^a	***		
45	unknown^d	1997	0^a	0^a	0^a	0.06 ± 0.07	0^a	0^a		**	***
		1998	0^a	0^a	0^a	0.20 ± 0.06	0^a	0^a	***		
46	6-methyl-5-hepten-2-one^d	1997	0.08 ± 0.08	0.12 ± 0.04	0^a	0^a	0^a	0.11 ± 0.04	**	***	***
		1998	0^a	0^a	0^a	0^a	0^a	0^a			
47	methyl 4-methyl-pentanoate^{c,d}	1997	0.15 ± 0.07	0.08 ± 0.10	0^a	0.29 ± 0.17	0^a	0^a	**	***	**
		1998	0^a	0^a	0^a	0^a	0^a	0^a			
48	unknown^d	1997	0.02 ± 0.02	0^a	0^a	0^a	0^a	0^a	*		**
		1998	0^a	0^a	0^a	0^a	0^a	0^a			
49	methyl propanoate^{c,d}	1997	0^a	0^a	0^a	0.10 ± 0.03	0^a	0^a	***	***	***
		1998	0^a	0^a	0^a	0^a	0^a	0^a			
50	methylethyl hexanoate^d	1997	0^a	0^a	0^a	0^a	0^a	0.16 ± 0.20			
		1998	0^a	0^a	0^a	0^a	0^a	0^a			

[a] Signal-to-noise ratio < 3. [b] Significant differences: *, $p < 0.05$; **, $p < 0.01$; ***, $p < 0.001$. [c] Reported also in refs *2*, *3*, and *18*. [d] Spectrum matched up to Wiley library. [e] Compared to t_R and mass spectrum of reference compound.

of Senga and Jonsok were higher than in Honeoye, Korona, and Polka. Methyl butanoate (**9**), methyl pentanoate (**19**), and 1-methylethyl butanoate (**20**) were typically highest in Korona and Polka. Ethyl propanoate (**7**) and 1-butanol (**8**) were identified only in Korona, Polka, and Honeoye.

Some compounds were detected only in 1997 and in some varieties. 2-Methyl-1-butanol (**14**) was found in Honeoye, whereas 2-methyl-4-pentenal (**17**) was detected only in Jonsok, Polka, and Bounty. 6-Methyl-5-hepten-2-one (**46**) and the unknown **35** were found in Senga, Jonsok, and Bounty, and methyl 4-methylpentanoate (**47**) was found in Senga, Jonsok, and Polka. Methyl propanoate (**49**) and *cis*-3-hexenal (**23**) were quantitated only in Polka, and methylethyl hexanoate (**50**) was found only in Bounty. 3-Methyl-2-butanone (**5**; *4*) and 3-methyl-2-pentanone (**12**; *24*) were not found in Korona and Polka. The great number of significant sample × year interactions in **Table 3** could be explained mainly by Polka and Bounty.

All of the compounds that had nonsignificant year × sample interaction ($p > 0.05$), but whose samples showed significant difference, were subjected to further statistical measures. At first, the years were combined into one data matrix, and then differences between varieties were tested using ANOVA. The final matrix consisted of compounds with a strong variety effect, such as 3-methyl-2-pentanone (**12**), *n*-hexanal (**16**), 1-methylethyl butanoate (**20**), 3-methylbutyl acetate (**25**), propyl butanoate (**28**), and methyl hexanoate (**33**). The amount of **20**, **25**, and **28** was significantly higher in Senga than in Honeoye. Senga and Jonsok had significantly more compound **25** than other varieties. Korona and Bounty differed significantly from Senga, Polka, and Honeoye in the case of 3-methyl-2-pentanone (**12**). The proportion of methyl hexanoate (**33**) was significantly lower in Honeoye than in all of the other varieties. The relationship between *n*-hexanal (**16**) and methyl hexanoate (**33**) in profiles is clear.

The biplots of PCA with a total of three dimensions, which takes all of the 52 compounds into account, are shown in **Figure 2**. The scores and loadings of both conventionally and organically cultivated varieties (-OR) from two years are presented. Three PCs explained the variance of data with 61%. The volatiles are labeled with the same identification numbers as in **Table 3**. The volatile compositions of Honeoye and Honeoye-OR were very similar and projected close to each other, but far away from other varieties, especially from Senga and Jonsok. This result is analogous to the total chromatogram area comparison described above.

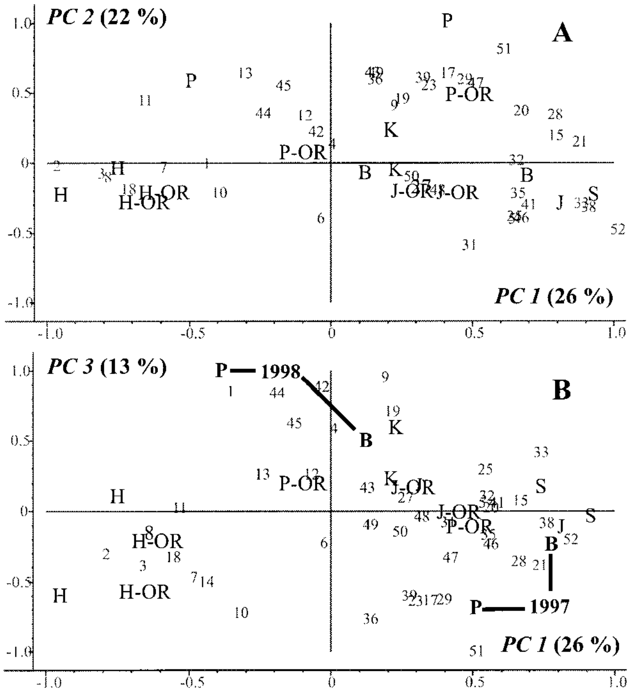

Figure 2. PCA biplots of volatile compounds in conventionally and organically cultivated strawberry varieties. PC 1 and PC 2 are shown in (A), and PC 1 and PC 3 are shown in (B). Three dimensions together explained 63% of the data variation. The volatiles are labeled with the same identification numbers as in **Table 3**.

The relationships between Honeoye variety and 2,3-butanedione (**3**), 1-butanol (**8**), 2-pentanol (**10**), and butyl acetate (**18**) are displayed in **Figure 2**. 3-Methyl-2-butanone (**5**), 3-methylbutyl acetate (**25**), methyl hexanoate (**33**), unknown (**35**), ethyl hexanoate (**38**), and *trans*-hex-2-enyl acetate (**41**) are close to

Table 4. Volatile Compounds Analyzed in the Headspace of Senga Sengana from Different Origins: Mean of Relative Proportions ± Standard Deviation ($n = 3$) and Results of Analysis of Variance

ID	compound	year	Senga-PP	Senga-VP	Senga-E	Senga-SW	origin^b	year^b	sample × year^b
1	acetaldehyde^{c,d}	1997	0.06 ± 0.01	0^a	0.22 ± 0.12	0.20 ± 0.17		***	***
		1998	0.20 ± 0.07	0.17 ± 0.06	0.93 ± 0.12	0.76 ± 0.04	***		
2	ethanol + acetone^{c,d}	1997	17.24 ± 1.99	17.26 ± 1.39	16.84 ± 5.58	15.15 ± 1.57			*
		1998	17.26 ± 1.82	26.03 ± 4.47	14.13 ± 0.94	12.97 ± 0.51	***		
3	2,3-butanedione^{c,d}	1997	0.44 ± 0.73	1.56 ± 0.29	1.62 ± 1.26	1.62 ± 0.96		***	***
		1998	1.33 ± 0.94	13.62 ± 3.29	0.48 ± 0.74	0.5 ± 0.47	*		
4	ethyl acetate^{c,d}	1997	1.91 ± 0.57	1.93 ± 0.80	1.78 ± 0.33	0.42 ± 0.48	*		***
		1998	1.89 ± 0.44	0^a	1.54 ± 0.97	2.20 ± 0.40	**		
5	3-methyl-2-butanone^{d,e}	1997	0^a	0^a	0^a	0^a			
		1998	0.17 ± 0.21	0^a	0.2 ± 0.3	0.05 ± 0.06			
6	2-pentanone^{c,d,e}	1997	4.14 ± 0.18	3.65 ± 0.98	1.83 ± 0.60	3.61 ± 0.14	**	*	***
		1998	3.96 ± 0.82	0.44 ± 0.2	3.91 ± 0.78	2.34 ± 0.51	***		
7	ethyl propanoate^{c,d}	1997	0^a	0^a	0.09 ± 0.08	0^a			***
		1998	0^a	0.14 ± 0.04	0^a	0.08 ± 0.08			
8	1-butanol^{c,d}	1997	0^a	0^a	0^a	0^a		***	***
		1998	0^a	0.16 ± 0.04	0^a	0^a			
9	methyl butanoate^{c,d,e}	1997	6.83 ± 0.75	5.84 ± 1.26	7.09 ± 0.96	10.98 ± 2.21	*		***
		1998	4.51 ± 0.07	3.40 ± 0.71	12.86 ± 2.69	7.54 ± 1.10	***		
10	2-pentanol^{c,d}	1997	0.17 ± 0.07	0.17 ± 0.06	0.14 ± 0.05	0.10 ± 0.10		*	
		1998	0.15 ± 0.06	0^a	0.13 ± 0.03	0.06 ± 0.03	**		
11	2-hexanone^{c,d,e}	1997	0.21 ± 0.02	0.16 ± 0.05	0.16 ± 0.04	0.08 ± 0.04	*	***	**
		1998	0.06 ± 0.02	0.04 ± 0.02	0.08 ± 0.01	0.08 ± 0.03			
12	3-methyl-2-pentanone^{d,e}	1997	0.07 ± 0.05	0^a	0^a	0^a	*		***
		1998	0^a	0.02 ± 0.02	0^a	0^a	*		
13	methyl 2-methylbutanoate^{c,d,e}	1997	0.28 ± 0.14	0.19 ± 0.04	0.30 ± 0.06	0.49 ± 0.03		*	
		1998	0.05 ± 0.05	0.30 ± 0.06	0.18 ± 0.015	0.23 ± 0.03	***		
14	2-methyl-1-butanol^{c,d}	1997	0.19 ± 0.16	0^a	0^a	0^a			
		1998	0.38 ± 0.30	0^a	0.25 ± 0.29	0^a			
15	ethyl butanoate^{c,d,e}	1997	16.67 ± 2.25	15.67 ± 1.22	22.42 ± 1.29	13.11 ± 2.39	**	*	***
		1998	17.10 ± 0.52	16.50 ± 1.05	19.58 ± 0.80	21.50 ± 2.87	*		
16	*n*-hexanal^{c,d,e}	1997	3.62 ± 0.45	5.19 ± 0.91	1.19 ± 0.30	1.76 ± 0.27	***		***
		1998	5.73 ± 1.89	2.25 ± 0.54	1.23 ± 0.38	0.80 ± 0.19	***		
17	2-methyl-4-pentenal^{c,d}	1997	0^a	0^a	0^a	0^a		***	***
		1998	0.37 ± 0.06	0.17 ± 0.06	0^a	0.09 ± 0.78	***		
18	*n*-butyl acetate^{c,d,e}	1997	1.01 ± 0.42	1.68 ± 0.29	0.51 ± 0.07	0.49 ± 0.04	***	**	***
		1998	1.50 ± 0.36	1.59 ± 0.14	1.50 ± 0.17	1.01 ± 0.08			
19	methyl pentanoate^{d}	1997	0.13 ± 0.05	0.14 ± 0.06	0.05 ± 0.04	0.16 ± 0.02			**
		1998	0.16 ± 0.02	0.13 ± 0.03	0.18 ± 0.03	0.11 ± 0.02	*		
20	1-methylethyl butanoate^{c,d}	1997	0.29 ± 0.04	0.49 ± 0.14	0.87 ± 0.34	1.15 ± 0.42	*	*	
		1998	0.19 ± 0.05	0.22 ± 0.16	0.71 ± 0.11	0.73 ± 0.20	**		
21	ethyl 2-methylbutanoate^{c,d,e}	1997	0.22 ± 0.02	0.30 ± 0.12	0.78 ± 0.31	0^a	**		***
		1998	0.06 ± 0.06	0.91 ± 0.18	0.10 ± 0.09	0.35 ± 0.02	***		
22	ethyl 3-methylbutanoate^{d}	1997	0.90 ± 0.18	1.01 ± 0.18	1.53 ± 0.16	0.34 ± 0.10	***		***
		1998	0.52 ± 0.04	0.13 ± 0.06	0.59 ± 0.12	0.99 ± 0.09	***		
23	*cis*-3-hexenal^{c,d,e}	1997	0.17 ± 0.10	1.46 ± 0.37	0^a	0.13 ± 0.12	***	*	***
		1998	0.59 ± 0.52	0.15 ± 0.07	0.12 ± 0.11	0^a			
24	unknown^{d}	1997	0^a	0^a	0^a	0^a		**	***
		1998	0.16 ± 0.08	0^a	0^a	0^a	**		
25	3-methylbutyl acetate^{c,d,e}	1997	0.31 ± 0.07	0^a	0.07 ± 0.04	0.16 ± 0.14	**		
		1998	0.12 ± 0.10	0.31 ± 0.38	0.19 ± 0.05	0.18 ± 0.09			
26	*trans*-2-hexenal^{c,d,e}	1997	3.15 ± 1.20	10.06 ± 1.58	1.22 ± 0.47	1.89 ± 0.44	***		***
		1998	8.97 ± 0.86	5.20 ± 0.23	1.01 ± 1.05	1.41 ± 0.24	***		
27	5-methyl-2-hexanone^{d}	1997	0^a	0^a	0^a	0^a		*	*
		1998	0^a	0^a	0.79 ± 0.62	0^a	*		
28	propyl butanoate^{c,d}	1997	0.23 ± 0.21	0.56 ± 0.39	0.07 ± 0.03	0.15 ± 0.03			
		1998	0.12 ± 0.02	0.13 ± 0.05	0.09 ± 0.02	0.13 ± 0.05			
29	ethyl pentanoate^{c,d}	1997	0.11 ± 0.04	0.07 ± 0.06	0.07 ± 0.03	0.21 ± 0.18			
		1998	0.09 ± 0.02	0.08 ± 0.01	0.08 ± 0.00	0.12 ± 0.03			
30	unknown^{d}	1997	0^a	0^a	0^a	0^a			
		1998	0^a	0^a	0.07 ± 0.07	0^a			
31	2-heptanone^{c,d,e}	1997	9.39 ± 0.95	8.95 ± 2.11	4.45 ± 0.56	11.59 ± 3.02	*		***
		1998	11.76 ± 2.52	1.20 ± 0.43	9.93 ± 1.26	7.09 ± 0.51	***		
32	pentyl acetate^{c,d}	1997	0.23 ± 0.05	0.16 ± 0.03	0.07 ± 0.03	0.15 ± 0.03	**	*	*
		1998	0.26 ± 0.11	0.15 ± 0.01	0.23 ± 0.03	0.16 ± 0.03			
33	methyl hexanoate^{c,d,e}	1997	13.90 ± 0.97	11.18 ± 0.55	12.97 ± 2.13	24.91 ± 6.29	**	*	***
		1998	8.88 ± 2.44	7.75 ± 2.22	15.31 ± 0.66	13.00 ± 0.66	**		
34	2-heptanol^{c,d,e}	1997	0.70 ± 0.27	0.61 ± 0.10	0.61 ± 0.08	0.51 ± 0.45			
		1998	0.45 ± 0.26	0.16 ± 0.03	0.66 ± 0.16	0.72 ± 0.13	*		
35	unknown^{d}	1997	0^a	0^a	0.04 ± 0.02	0^a	***		***
		1998	0^a	0.05 ± 0.02	0.01 ± 0.01	0^a	***		
36	benzaldehyde^{c,d,e}	1997	0.19 ± 0.05	0.14 ± 0.02	0.08 ± 0.04	0.08 ± 0.07	*	*	
		1998	0.13 ± 0.03	0.05 ± 0.03	0.07 ± 0.05	0.07 ± 0.03			
37	butyl butanoate^{c,d}	1997	0.29 ± 0.08	0.54 ± 0.10	0.31 ± 0.18	0.62 ± 0.69			
		1998	0.35 ± 0.05	0.16±+0.04	0.70 ± 0.35	0.65 ± 0.27			

Table 4 (Continued)

ID	compound	tear	Senga-PP	Senga-VP	Senga-E	Senga-SW	origin^b	year^b	sample × year^b
38	ethyl hexanoate^{c,d,e}	1997	15.13 ± 3.06	10.26 ± 2.86	22.44 ± 7.02	9.36 ± 8.49			**
		1998	11.90 ± 2.46	16.34 ± 4.17	11.38 ± 3.76	22.40 ± 3.80	*		
39	octanal^{c,d}	1997	0.34 ± 0.07	0.24 ± 0.06	0.03 ± 0.03	0.05 ± 0.04	***	***	***
		1998	0.11 ± 0.06	0.06 ± 0.03	0.10 ± 0.04	0.05 ± 0.05			
40	hexyl acetate^{c,d}	1997	0.91 ± 0.16	0.54 ± 0.30	0.15 ± 0.20	0.26 ± 0.24	*		**
		1998	0.51 ± 0.23	0.85 ± 0.32	0.36 ± 0.12	0.91 ± 0.05	*		
41	*trans*-hex-2-enyl acetate^{c,d}	1997	0.52 ± 0.02	0^a	0^a	0.27 ± 0.26	**	*	**
		1998	0^a	0.36 ± 0.14	0.32 ± 0.15	0.72 ± 0.25	**		

[a] Signal-to-noise ratio < 3. [b] Significant differences: *, $p < 0.05$; **, $p < 0.01$; ***, $p < 0.001$. [c] Reported also in refs *2*, *3*, and *18*. [d] Spectrum matched up to Wiley library. [e] Compared to t_R and mass spectrum of reference compound.

Senga and Jonsok. The year effect is shown in **Figure 2B** and demonstrated with Polka and Bounty samples. PC 3 is connected to crops, whereas PC 1 represents the varieties. Despite the weak change in coordinates of Honeoye, the distance of Honeoye to Senga and Jonsok was not dependent on a year. This phenomenon is shown in **Figure 2B** and **Table 3**, also. The differences in profiles analyzed by HS-GC-MS and classification of varieties into groups were similar to the previous study, where the same strawberries were analyzed with gas-phase FT-IR (*26*). Douillard divided 14 varieties into three clusters (*4*). Senga Sengana and Korona differed from each other as shown here in that study as well.

In conclusion, the profile of Jonsok was most similar to that of Senga Sengana. The sum of both the compounds and the relative proportions of esters were lowest in Honeoye. Polka, Korona, and Bounty were interesting and would have potential for industrial processing purposes. The relationships between HS-GC-MS profiles and sensory properties and contents of sugars and acids (*21*) of our strawberry sample material will be published separately.

Effect of Organic Cultivation. The total areas of volatiles in varieties cultivated organically were higher than in the conventionally cultivated ones (**Table 2**), except in Jonsok for 1997. However, the differences between total areas of conventionally and organically cultivated strawberry were not statistically significant within the varieties when samples were compared annually, as shown in **Table 2**. After the years were combined, Polka and Polka-OR differed at $p = 0.026$, but no difference between either Jonsok and Jonsok-OR or Honeoye and Honeoye-OR was found. The sample × year interaction was not significant ($F = 2.36$, $p > 0.05$). The number of volatiles forming the profiles was higher in the conventionally cultivated than in the corresponding organically cultivated fruit for the summer of 1997. In 1998 the difference between the cultivation techniques was not detected, as shown in **Table 2**. However, the total area of volatiles was due more to variety than to the type of cultivation. This can be seen in **Table 5** and **Figure 2**.

Table 5 summarizes all of those compounds that showed even a single significant difference, marked with asterisks, between conventionally and organically cultivated varieties in the pair-comparison t test. In addition, 3-methyl-2-butanone (**5**), unknown (**35**), and benzaldehyde (**36**) were detected only in Jonsok, hexyl acetate (**40**) was detected only in Polka, and unknown (**51**) was detected only in Polka-OR with no statistical difference. Otherwise, the profiles of organically cultivated varieties were very close to the corresponding conventionally grown ones shown in **Table 3**. In the case of Polka, differences between cultivation techniques existed mainly in 1998. The proportions of methyl and ethyl hexanoate (**33** and **38**) were higher in the organic than in the conventionally cultivated berries**.** The relative amount of methyl butanoate (**9**) in Polka-OR was as high as that of ethyl butanoate in Polka (**15**) and vice versa. Organically cultivated Honeoye contained a lower proportion of ethyl acetate (**4**) than any other Finnish strawberry sample analyzed in this status. Ethyl propanoate (**7**) was found to be at the same level in Jonsok-OR as in Korona and Polka, although it was lacking in the headspace of Jonsok. The proportion of ethyl butanoate (**15**) was highest in Jonsok-OR of year 1998, when all of the samples analyzed were taken into account. The relative amount of *trans*-2-hexenal (**26**) in Jonsok-OR was significantly lower than in Jonsok or in other samples except Senga-E. 4-Methyl-2-pentanol (**52**) was considered as a part of the profile in the case of Jonsok-OR. It was also integrated in Polka-OR samples from summer 1997.

When statistics were calculated after years had been combined together, some differences between samples became stronger. All statistical differences between samples with nonsignificant year × sample interaction were taken into account to draw conclusions for the effect of organic cultivation. There was more ethyl propanoate (**7**, $p < 0.01$) and 3-methyl-2-pentanone (**12**, $p < 0.001$) in Polka than in Polka-OR. Proportions of ethyl 2-methylbutanoate (**21**, $p < 0.05$), ethyl 3-methylbutanoate (**22**, $p < 0.05$), methyl hexanoate (**33**, $p < 0.05$), ethyl butanoate (**15**, $p < 0.01$), and 2-heptanone (**31**, $p < 0.01$) were higher in organically cultivated Polka. Ethyl butanoate (**15**, $p < 0.05$), 2-heptanol (**34**, $p < 0.05$), and *trans*-2-hexenal (**26**, $p < 0.01$) evaporated more from Jonsok than from Jonsok-OR. Ethyl 3-methylbutanoate (**22**, $p < 0.01$) and 4-methyl-2-pentanol (**52**, $p < 0.001$) were higher in organically cultivated Jonsok. In the case of Honeoye, ethyl butanoate (**15**) was higher in conventionally cultivated and methyl hexanoate (**33**) in organically cultivated berries.

The differences between organically and conventionally cultivated strawberries were most obvious in the variety Polka, but only in the case of 7 compounds of 49. Genotype had a stronger influence on the profiles of volatile compounds in strawberry than cultivation technique. This can be seen also in **Figure 2**. Jonsok and Jonsok-OR from both years are very close to each other in the PCA plot, as are also Honeoye and Honeoye-OR. In conclusion, the effect of organic cultivation was clearly weaker than the effect of variety.

Effect of Origin. This study was based on the industrial needs and utilization of strawberries. Raw material for products such as jams and jellies is normally a combination of fruit collected from different farmers and pooled before freezing. Our research interest was more in geographical origin and degrees of latitudes in Europe than in the effect of farming conditions. The Polish samples representing two quality classes were also selected on the basis of general practices in the Finnish food industry.

Table 5. Volatile Compounds That Showed a Significant Difference between Conventional and Organic Cultivation Techniques: Mean of Relative Proportions ($n = 3$; Differences Based on Independent-Samples *t* Test)

ID	compound	year	Polka	Polka-OR[b]	Honeoye	Honeoye-OR[b]	Jonsok	Jonsok-OR[b]
4	ethyl acetate[c,d]	1997	2.50	0.87	0.14	0[a]	1.96	0.7
		1998	2.57	3.22	4.69	0.85*	2.88	5.05
7	ethyl propanoate[c,d]	1997	0.14	0[a]	0.75	0.81	0[a]	0[a]
		1998	0.20	0[a]	0[a]	0[a]	0[a]	0.17*
8	1-butanol[c,d]	1997	0[a]	0[a]	0.57	0[a]*	0[a]	0[a]
		1998	0.15	0[a]	0.38	0.43*	0[a]	0[a]
9	methyl butanoate[c,d,e]	1997	8.85	9.66	1.58	0.99	4.71	7.74
		1998	21.46	10.60*	1.77	1.57	8.01	7.05
12	3-methyl-2-pentanone[d,e]	1997	0.18	0[a]	0.05	0[a]*	0.09	0[a]*
		1998	0.22	0.07	0.23	0*	0.12	0.12
14	2-methyl-1-butanol[c,d]	1997	0[a]	0[a]	0.43	0.19	0[a]	0[a]
		1998	0[a]	0.33*	0[a]	0[a]	0[a]	0[a]
15	ethyl butanoate[c,d,e]	1997	19.32	26.20	5.32	8.76	15.6	20.61
		1998	10.31	21.62*	3.45	5	15.16	28.62
16	*n*-hexanal[c,d,e]	1997	4.90	4.28	8.56	7.12	0.84	1.32
		1998	8.47	5.15*	12.29	8.32	1.64	1
19	methyl pentanoate[d]	1997	0.16	0.20	0[a]	0[a]	0.07	0[a]*
		1998	0.35	0.19*	0[a]	0[a]	0[a]	0[a]
20	1-methylethyl butanoate[c,d]	1997	1.06	2.40	0[a]	0[a]	1.02	0.87
		1998	0.51	0.42*	0[a]	0[a]	0.13	0.17
21	ethyl 2-methylbutanoate[c,d,e]	1997	1.01	1.14	0[a]	0[a]	1.38	0.85
		1998	0[a]	0.37***	0[a]	0[a]	0.38	0.88
22	ethyl 3-methylbutanoate[d]	1997	2.11	2.49	0.88	0.74	0.93	1.23
		1998	0.71	1.37*	0.55	0*	0.29	0.53
23	*cis*-3-hexenal[c,d,e]	1997	0.56	0.09*	0[a]	0[a]	0[a]	0[a]
		1998	0[a]	0[a]	0[a]	0[a]	0[a]	0[a]
26	*trans*-2-hexenal[c,d,e]	1997	8.52	7.10	7.5	6.69	1.69	1.3
		1998	4.33	4.09	5.84	6.57	1.96	0.63**
28	propyl butanoate[c,d]	1997	0.21	0.21	0[a]	0[a]	0.12	0.12
		1998	0[a]	0.05	0[a]	0[a]	0[a]	0.03**
31	2-heptanone[c,d,e]	1997	0.68	1.12	2.2	2.52	5.34	5.02
		1998	0.14	1.04**	2.46	3.01	7.95	5.18
32	pentyl acetate[c,d]	1997	0.24	0[a]*	0[a]	0[a]	0.14	0*
		1998	0[a]	0[a]	0[a]	0[a]	0.27	0.19
33	methyl hexanoate[c,d,e]	1997	3.66	5.74	1.13	1.32	11.21	13.15*
		1998	5.71	9.66*	0[a]	0.44	15	7.63
34	2-heptanol[c,d,e]	1997	0.27	0.25	0[a]	0[a]	0.97	0.51*
		1998	0[a]	0[a]	0[a]	0[a]	0.65	0.22
37	butyl butanoate[c,d]	1997	0.17	0.56	0.44	0.64	1.13	0.33
		1998	0[a]	0.13*	0[a]	0[a]	0.46	0.17*
38	ethyl hexanoate[c,d,e]	1997	3.17	10.76	0[a]	1.99	28.89	22.79
		1998	0[a]	6.19***	0[a]	0[a]	11.79	15.1
39	octanal[c,d]	1997	3.72	0.11	0[a]	0[a]	0.11	0[a]
		1998	0[a]	0[a]	0[a]	0[a]	0.22	0[a]***
42	1-hexanol[c,d]	1997	0[a]	0[a]	0[a]	0[a]	0[a]	0[a]
		1998	1.04	0[a]**	0[a]	0[a]	0[a]	0[a]
44	3-methyl-1-butanol[c,d]	1997	0[a]	0[a]	0[a]	0[a]	0[a]	0[a]
		1998	0.36	0[a]***	0[a]	0[a]	0[a]	0[a]
45	unknown[d]	1997	0.06	0[a]	0[a]	0[a]	0[a]	0[a]
		1998	0.20	0[a]***	0[a]	0[a]	0[a]	0[a]
46	6-methyl-5-hepten-2-one[d]	1997	0[a]	0[a]	0[a]	0[a]	0.12	0[a]***
		1998	0[a]	0[a]	0[a]	0[a]	0[a]	0[a]
47	methyl 4-methylpentanoate[c,d]	1997	0.29	0.13	0[a]	0[a]	0.08	0[a]**
		1998	0[a]	0[a]	0[a]	0[a]	0[a]	0[a]
49	methyl propanoate[c,d]	1997	0.10	0***	0[a]	0[a]	0[a]	0[a]
		1998	0[a]	0.06	0[a]	0[a]	0[a]	0[a]
52	4-methyl-2-pentanol[d]	1997	0[a]	0.30	0[a]	0[a]	0[a]	0.66*
		1998	0[a]	0[a]	0[a]	0[a]	0[a]	0.33

[a] Signal-to-noise ratio < 3. [b] Significant differences: *, $p < 0.05$; **, $p < 0.01$; ***, $p < 0.001$. [c] Reported also in refs *2*, *3*, and *18*. [d] Spectrum matched up to Wiley library. [e] Compared to t_R and mass spectrum of reference compound.

Unlike in other comparisons previously described, the year of cultivation itself did not show any effect ($p > 0.05$) on the mean total area of chromatogram of Senga Sengana grown in different areas of countries. However, the year × sample interaction was significant ($p < 0.01$), and the total areas diverged from each other depending on a season, as shown also in **Table 2**. **Table 4** shows the average relative percentages of volatile compounds analyzed from three replicates of Senga-VP, Senga-PP, Senga-E, and Senga-SW. Overall, the amounts of acetaldehyde (**1**) and 1-methylethyl butanoate (**20**) in profiles were higher in Finnish than in Polish samples. The profiles of Polish samples contained more butyl acetate (**18**) and octanal (**39**) than Finnish samples. As the unique cases, the high level of 2,3-butanedione (**3**) in Senga-VP (1998) and *trans*-2-hexenal (**26**) in Senga-VP (1997) and Senga-PP (1998) should be mentioned.

Significant differences between the samples, but nonsignificant year × sample interaction, were found in cases of 2-pentanol (**10**), methyl 3-methylbutanoate (**13**), 1-methylethyl butanoate (**20**), 3-methylbutyl acetate (**25**), and 2-heptanol (**34**).

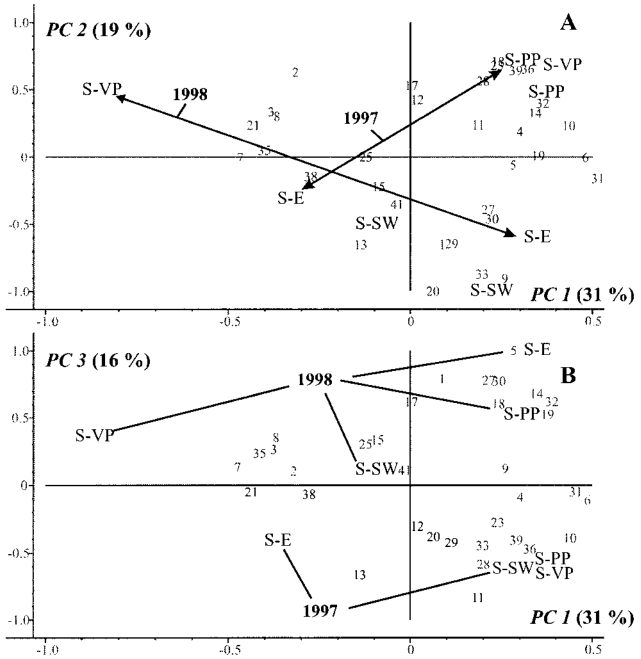

Figure 3. PCA biplots concerning effect of origin. PC 1 and PC2 are shown in (A), and PC1 and PC3 are shown in (B). Three dimensions together explain 66% of the data variation.

When years were combined in the same group, the significant difference between the samples was found only in the case of 1-methylethyl butanoate (**10**). Tukey's multiple comparison test pointed to the difference of Senga-VP and Senga-SW in 1997 and 1998 ($p < 0.05$). The relative proportion of 1-methylethyl butanoate was significantly higher in Finnish than in Polish strawberries in 1998 ($p < 0.05$).

The PCA biplots are shown in **Figure 3**, where explanation of variance was 66% with three PCs. The volatiles are labeled as in **Table 4**, and the mean values of samples for both years are presented. Finnish Senga samples were closer to each other than to Polish samples in both years. The biplot shows that Finnish strawberries are located close to methyl 2-methylbutanoate (**13**), 1-methylethyl butanoate (**20**), ethyl pentanoate (**29**), methyl hexanoate (**33**), and *trans*-hex-2-enyl acetate (**41**). Senga-PP had a strong connection to 2-methyl-1-butanol (**14**), butyl acetate (**18**), *cis*-3-hexenal (**23**), propyl butanoate (**28**), pentyl acetate (**32**), benzaldehyde (**36**), and octanal (**39**). Variation in Polish Senga-VP was higher than in other samples. Its projected locations were opposite to Senga-E in 1997 and 1998. In conclusion, the amount of volatiles was affected more pronouncedly by genotype than by different growing conditions in Europe.

ABBREVIATIONS USED

HS-GC, headspace gas chromatography; DHS, dynamic headspace; MS, mass spectrometry; TIC, total ion chromatogram; -OR, organically cultivated; H, Honeoye; S, Senga Sengana; J, Jonsok; B, Bounty; P, Polka; K, Korona; Senga-E, Senga Sengana grown in eastern Finland; Senga-SW, Senga Sengana grown in southwestern Finland; Senga-VP, Senga Sengana imported from Poland via Valio Hillotehdas Ltd. (Finland); Senga-PP, Senga Sengana imported from Poland via Pakkasmarja Ltd. (Finland); PCA, principal component analysis; PC, principal component.

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