Aroma Volatiles of Blanched Green Peas (*Pisum sativum* L.)

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The volatiles of blanched green peas representing a range of genotypes and pea sizes were collected by the dynamic headspace technique. A total of 47 compounds were detected repeatedly in the pea headspace. Thirteen of these have not been reported in green peas previously. The majority of the constituents were degradation products of fatty acids, especially saturated and monounsaturated six-carbon aldehydes, ketones, alcohols, and their ester derivatives. Three 3-alkylmethoxypyrazines were identified. A fourth methoxypyrazine, identified as either 5- or 6-methyl-3-isopropyl-2-methoxypyrazine, has not been found in green peas previously. Significant differences were detected among genotypes in the concentration levels of 21 compounds. Pea size influenced the content of 17 compounds significantly. Potential ways to improve the green pea aroma by technical and breeding measures are discussed.

Keywords: *Pisum sativum; green peas; volatiles; flavor; dynamic headspace*

INTRODUCTION

Frozen green peas (*Pisum sativum* L.) are produced commercially for human consumption. In Denmark, the peas are harvested and vined mechanically, followed by blanching, freezing, and finally grading according to size. Green peas are traditionally served either cold in salad bars or hot as a side dish. In a parallel study by Bech et al. (1997), consumers rated pea flavor as the most important attribute of green pea quality. It is therefore relevant to focus on the parameters influencing the flavor quality of green peas. An attempt to improve the flavor profile may include development of new varieties with a more desirable aroma composition combined with steps to avoid formation of undesirable volatiles during harvest, vining, blanching, and storage. These goals imply knowledge of qualitative and quantitative differences in the aroma composition among genotypes and of the origin and organoleptic impact of each single volatile.

Information in the literature concerning qualitative and quantitative data of the aroma content in blanched green peas is scarce. Identification and quantification of the headspace composition of blanched green peas using dynamic headspace adsorption have not been carried out previously to our knowledge. Shipton et al. (1969), however, isolated a number of volatiles from blanched ruptured green peas by distillation and vacuum sublimation. Quantification of the volatiles in unblanched peas has been performed only on macerated material, and only as rough estimates, that is, large peak, small peak, etc. (Shipton et al., 1969; Murray et al., 1976). Murray and Whitfield (1975) identified and quantified three methoxypyrazines in the juice of unblanched peas using the dynamic headspace adsorption technique. Their studies suggested that three 3-alkyl-2-methoxypyrazines contribute significantly to the characteristic green pea aroma despite the very low concentration of these compounds in the headspace (Murray et al., 1970, 1976; Murray and Whitfield, 1975). Several studies point out the degradation products of the fatty acids as being responsible for the haylike off-odor often experienced in peas (Bengtsson et al., 1967; Murray et al., 1976; Williams et al., 1986).

In this part of an extensive research program focusing on the qualitative aspects of green peas (Bech et al., 1997), we aim to (1) identify the volatiles emitted from blanched green peas after 15 months of storage at −24 °C, (2) detect the influence of pea size and genotype on the aroma composition, and (3) evaluate by GC-sniffing the significant contributors to the aroma profile.

MATERIALS AND METHODS

Materials. Green peas (*P. sativum* L. var. medullare Alef.), commercially grown in Denmark, were harvested, vined, blanched in water (93 °C) for 1.5 min, individually frozen in a fluid-bed freezer, and size graded at a commercial pea production plant using conventional industrial methods. The size gradings were as follows: 0 (6−7.5 mm), 1 (7.5−8.2 mm), 2 (8.2−8.75 mm), 3 (8.75−10.2 mm), and 4 (≥10.2 mm). Ten genetic selections were studied: 24 (sizes 2, 3, and 4); 23 (sizes 2, 3, and 4); 20 (sizes 2, 3, and 4); 05 (sizes 2, 3, and 4); 08 (sizes 2 and 3); 03 (sizes 1, 2, and 3); 09 (sizes 1 and 3); 30 (sizes 0, 1, and 2); 07 (size 1); and 04 (size 3). Each sample of peas was stored in standard retail polyethylene bags at −24 °C for ∼15 months.

Dynamic Headspace Sampling. For collection of headspace volatiles, 100 g of frozen peas was placed single-layered in an aluminum foil tray (17 × 17 × 2 cm) at room temperature for 30 min and then transferred to an 0.89 L open reaction vessel for 90 min. A four-flange lid without stoppers was

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mounted on the vessel during this period. The temperature in the reaction vessel was kept constant at 18 °C by immersion in a temperature-regulated water bath. Subsequently, the vessel was closed airtight with Teflon stoppers mounted with Teflon tubing (3.2 mm o.d.) and purged for 15 min with purified helium (45 mL/min). Dynamic headspace adsorption was performed for the following 1 h on 100 mg Porapack Q 50−80 mesh (Waters Inc., Milford, MA) inserted between two desiloxanized glass wool plugs in glass tubes (4 mm i.d., length = 180 mm).

The Porapak adsorption columns were eluted with double-distilled pentane (HPLC grade) into 300 μL microvials. For quantitative estimations, 10 μL of 4-methyl-1-pentanol (Aldrich, Steinheim, Germany, 82.1 ng/μL pentane) was transferred with a Hamilton syringe to the glass vial prior to careful evaporation of excess solvent under nitrogen flow to a final volume of 50 μL. Pyridine was used as standard for quantitation of nitrogen-containing compounds.

The equipment was purified and tested for impurities between each sampling using the following procedure: The reaction vessel and the lid were scoured with running hot tap water for 5 min followed by rinsing in distilled water and air-drying at 100 °C. After cooling, the inner surfaces of the vessel were rinsed in pentane (distilled HPLC grade). Tubings, stoppers, and Teflon connectors were also rinsed in pentane after each sampling. Prior to transfer of the peas to the vessel, the entire purge and trap system was checked for contaminants: the empty vessel was purged with helium for 15 min followed by collection of volatiles for 1 h using the method described above. When the entire purge gas sample was free of contaminants, the peas were transferred to the vessel. Helium was prefiltered through activated charcoal to remove contaminants. After use, the Porapack columns were regenerated with 20 mL of pentane. The last 300 μL of the rinsing eluate was concentrated to 50 μL and tested for impurities.

Analysis of Volatiles. Gas chromatography was performed on a Shimadzu 14A equipped with a Chrompack (Middelburg, The Netherlands) WCOT fused silica capillary column (50 m, 0.25 mm i.d., DF = 0.2 μm liquid phase: CP-WAX 52CB). Helium was applied as carrier gas with a flow rate of 1.1 mL/min and 110 kPa column head pressure. The oven temperature was kept at 30 °C for 1.5 min, programmed to 120 °C at 3 °C/min and further to 220 °C at 10 °C/min, followed by constant temperature for 3.5 min. The injector temperature was 200 °C and the FID detector temperature 220 °C. One microliter of each sample was injected onto the GC column in splitless mode (splitless purge time = 45 s). Identification of compounds was performed by GC/MS (mass spectrometer: JEOL-JMS AX 505W, JEOL Ltd., Akishima, Tokyo 196, Japan). Selected ion monitoring (SIM) was carried out on an SSQ 710 Finnigan Mat with 70 eV of ionization voltage. GC conditions were as described above. Compounds suggested by the MS database were verified by comparison of the retention times and MS spectra of authentic reference compounds.

Quantification of methoxypyrazines took place from 500 g pea samples, using the method described above. These compounds were quantified on a Shimadzu flame thermoionic detector (FTD-14). Detector hydrogen flow was 3 mL/min and air flow 120 mL/min. Other GC parameters were identical to those listed above.

GC-Sniffing. The organoleptic evaluation of single aroma compounds was performed by GC-sniffing. Four judges noted descriptors induced by the compounds eluting from the GC column. An SGE OSS-2 splitter system with air humidifier in the sniff insert was mounted on a Shimadzu 14A. Columns and GC setup were as described above. The split flow to the GC detector and sniff insert was 1:3 in the initial training evaluations. However, in the subsequent experiments published here, the column was mounted directly on the sniff insert to increase the concentration levels of volatiles guided to the sniff insert. The GC sniffing sessions were performed in duplicate by each judge.

Experimental Design and Statistics. An analysis on genotype effects on the aroma profile was performed using data for size 3 peas. The genotypes 03, 05, 08, 09, 20, 23, and 24 were used in a completely randomized block design with replicates as blocks and genotypes as treatments.

An analysis of genotype and size effects was caried out in an analysis of variance including main effects of replication, size, and genotype, together with a size−variety interaction effect. The test was performed on four genetic selections (05, 20, 23, and 24) and three pea sizes (2, 3, and 4). Approximate 95% level least significant difference (LSD) values were computed for each compound by the use of the average number of nonmissing observations per size−variety combination. For compounds without missing values this is the true 95% LSD value. If the averages for two genotype−size combinations differed more than the 95% LSD value, they were categorized as significantly different at the 5% level.

A small number of observations were recorded as "low detection threshold" when obviously present but below the level of plus three standard errors of the GC detector noise level from the baseline average. In those cases, an estimated fixed "low value" based on the GC threshold value for each compound was inserted. If the replications of a size−variety combination were all recorded as low detection threshold values, the error degrees of freedom were decreased by the number of (nonmissing) replications. All comparisons were carried out in triplicate.

RESULTS AND DISCUSSION

Identification of Aroma Compounds. A total of 47 compounds were detected repeatedly in the pea headspace (Table 1). Forty-two of these were identified by both MS and comparison of retention times of unknown compounds with those of compounds suggested by the MS database (Table 1).

The majority of the constituents were degradation products of fatty acids, especially saturated and monounsaturated six-carbon aldehydes, ketones, alcohols, and their ester derivatives (Table 1). Fatty acid degradation may be either enzymatic or caused by autoxidation. Two compounds, that is, 2-pentylfuran, a well-known lipid autoxidation product (Ho and Chen, 1994), and (*Z*)-3-hexenyl acetate, have not been isolated from peas previously.

A number of monoterpenes were isolated: α-pinene, *β*-pinene, sabinene, 3-carene, myrcene, limonene, (*Z*)-*β*-ocimene, and (*E*)-*β*-ocimene. These compounds are frequent constituents of the essential oil and headspace of flowers and leaves but have not been reported in fresh or blanched green peas previously (Nijssen et al., 1996). There has been some speculation concerning the origin of other monoterpenes and monoterpenoids isolated from peas (Murray et al., 1976); apart from being potential products of endogenous isoprenoid biosynthesis, members of this group may be products of carotenoid degradation. Murray et al. (1976) reported cineole in green peas and suggested that this terpenoid and other stable structures were adsorbed from the soil. A likely derivative of carotenoids, 6-methyl-5-hepten-2-one (Buttery, 1981), was isolated in the present study. This compound has not been reported in green peas before.

Two sulfur-containing compounds, dipropyl disulfide and methyl propyl disulfide, are most likely induced by thermal impact during blanching. They have not been reported in green peas previously but are well-known character impact compounds in onion (Buttery, 1981).

Four methoxypyrazines were detected in the headspace. The concentration levels of 3-isopropyl-2-methoxypyrazine, 3-*sec*-butyl-2-methoxypyrazine, and 3-isobutyl-2-methoxypyrazine were all below the sensitivity level of the MS, and they were therefore identified by

Table 1. Volatiles Isolated from the Headspace of Thawed Green Peas by Dynamic Headspace Technique [Tests for Differences among Variety and Size Means Are Based on a 4 × 3 (Genotype × Size) Balanced Analysis of Variance]

isolated compd[a]	Kovats index	suggested origin of compd[c]	olfactory descriptors repeatedly associated with peak	av content, ng/100 g/h	STD	genotype effects	size effects	interaction genotype × size
ethyl acetate	886			nq[d]		nq	nq	nq
ethanol	926			nq		nq	nq	nq
2-methylbutanal[b]	963	AAD/TH		289.6	126.6	*	**	*
α-pinene	1017	TE		5.7	3.7	ns[e]	*	ns
methyl 3-methylbutanoate	1020			16.6	8.6	**	**	***
ethyl 3-methylbutanoate	1071			nq		nq	nq	nq
hexanal	1081	FA	green, strong	1514.0	536.7	***	**	ns
β-pinene	1102	TE		nq		nq	nq	nq
3-pentanol	1107	FA		16.0	7.0	***	ns	ns
sabinene	1117	TE		21.0	10.5	***	***	***
3-carene	1145	TE		53.8	21.6	***	***	***
1-penten-3-ol	1158	FA		10.7	5.6	*	*	ns
myrcene	1162	TE		nq		nq	nq	nq
heptanal	1184	FA		39.4	16.5	**	***	***
limonene	1194	TE		84.8	204.8	*	ns	*
2-methylbutanol	1199	AAD/TH		(18.6)[f]	(5.4)	***	*	*
3-methylbutanol	1199	AAD/TH		(18.6)[f]	(5.4)	***	*	*
(*E*)-2-hexenal	1216	FA		nq		nq	nq	nq
methyl propyl disulfide	1225	AAD/TH		nq		nq	nq	nq
2-pentylfuran[b]	1227	FA		15.5	4.9	***	ns	*
(*Z*)-*β*−ocimene	1232	TE		nq		nq	nq	nq
1-pentanol	1245	FA		25.6	9.7	ns	ns	ns
(*E*)-*β*-ocimene	1246	TE		nq		nq	nq	nq
3-octanone	1249	FA		nq		nq	nq	nq
unknown (94, 119, 134, 67, 44)	1253			45.2	59.9	ns	ns	ns
hexyl acetate	1269	FA	sweet, perfume	26.9	8.4	**	ns	ns
unknown (136, 121, 93, 91, 79, 77)	1276			18.0	23.7	**	**	***
octanal	1284	FA	orange, sweet	12.4	10.4	ns	ns	ns
1-octen-3-one	1296	FA	mushroom strong	nq		nq	nq	nq
(*Z*)-3-hexenyl acetate	1312	FA		166.4	50.5	***	***	**
(*E*)-2-heptenal	1320	FA		49.8	17.7	**	*	ns
unknown (43, 57, 71, 99, 86, 128)	1330			4.2	2.0	**	*	*
6-methyl-5-hepten-2-one	1338	TE		9.4	5.3	ns	ns	ns
hexanol	1348	FA		104.0	26.6	***	ns	ns
dipropyl disulfide	1375	AAD/TH	sulfurous sour	32.5	65.6	**	*	***
(*Z*)-3-hexen-1-ol	1379	FA		101.9	28.9	***	ns	ns
nonanal	1391	FA		20.9	26.5	ns	ns	ns
(*E*)-2-hexenol	1404	FA		nq	nq	nq	nq	
(*E*)-2-octenal[b]	1419	FA		nq	nq	nq	nq	
3-isopropyl-2-methoxypyrazine	1429	MP	pea pod, bell pepper, blanched peas	0.03	0.14	ns	ns	ns
5- or 6-methyl-3-isopropyl-2-methoxypyrazine	1440	MP	dry grass, spruce	0.15	0.07	**	*	*
1-octen-3-ol	1444	FA		38.25	15.9	ns	**	ns
heptanol	1451	FA		nq		nq	nq	nq
(*E*,*E*)-2,4,heptadienal	1485	FA		nq		nq	nq	nq
3-*sec*-butyl-2-methoxypyrazine	1494	MP	green	0.04	0.03	ns	ns	ns
3-isobutyl-2-methoxypyrazine	1519	MP	green, peas, bell pepper	<0.01		nq	nq	nq
octanol	1548	FA		4.3	2.3	ns	ns	ns

[a] MS spectra and GC retention times were consistent with those of reference compounds unless otherwise noted. MS spectra of unknown compounds are listed in parentheses with descending intensities. [b] Tentative identification. The mass spectrum was consistent with published data. [c] AAD, amino acid derivative; FA, fatty acid breakdown product or derivative of these; MP, methoxypyrazines, biosynthesis unknown; TE, terpenoids or breakdown product of these; TH, secondary compounds, produced during blanching. [d] nq, not quantified. [e] ns, nonsignificant: *, $P < 0.05$; **, $P < 0.01$; ***, $P < 0.001$. [f] 2- and 3-methylbutanol were quantified as one peak.

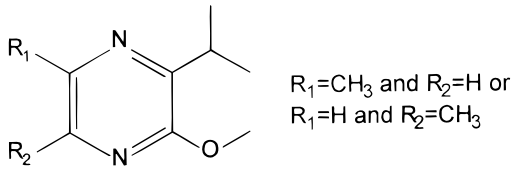

Figure 1. Stuctures of 5- and 6-methyl-3-isopropyl-2-methoxypyrazine, one of which was present as the major methoxypyrazine in all pea samples.

SIM and compared with spectra and retention indices of original compounds. The fourth methoxypyrazine, 5- or 6-methyl-3-isopropyl-2-methoxypyrazine (Figure 1), was present in significantly higher amounts than the former three (Table 1) and could therefore be analyzed in full scan mode. Synthesis of 5- and 6-methyl-3-isopropyl-2-methoxypyrazine isomers according to the methods described by Karmas and Spoerri (1952) and Seifert et al. (1970) followed by GC/MS analysis showed that the spectra of the isomer with the lowest retention time were identical to those of the unknown methoxypyrazine. We have not been able to determine which of the two isomers has the lowest retention time. Neither the 5- or 6-methyl-3-isopropyl-2-methoxypyrazine isomer has been identified in peas previously, but the 5-methyl isomer has been reported in several other vegetables (Takken et al., 1975).

Genotype and Size Effects on the Aroma Composition. A total of 31 compounds were quantified (Table 1). Significant genotype differences were observed for 21 compounds, whereas pea size influenced the concentration levels of 17 compounds significantly. Interaction between genotype and size effects was observed in 12 cases (Table 1). The concentration levels of the remainder 16 compounds were too close to the noise level of the GC-FID to be quantified accurately. The accuracy of the experimental method and reproduc-

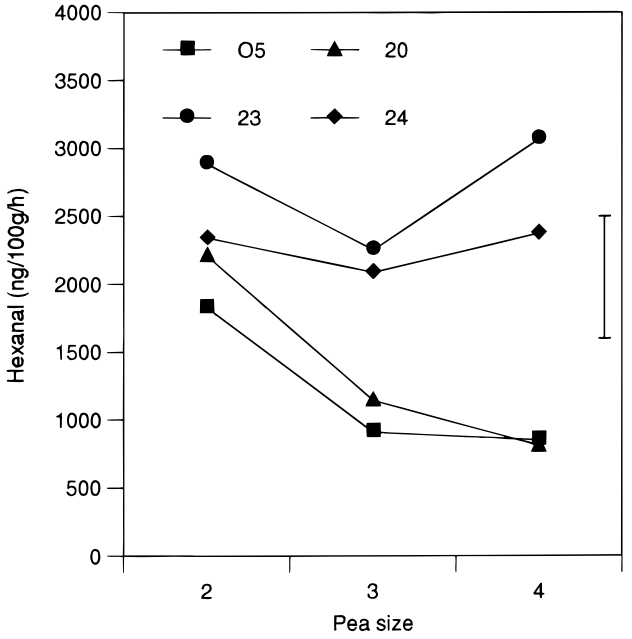

Figure 2. Hexanal concentrations in the headspace of four genotypes (05, 20, 23, and 24) represented in three sizes (2, 3, and 4). Vertical bar represents LSD (900).

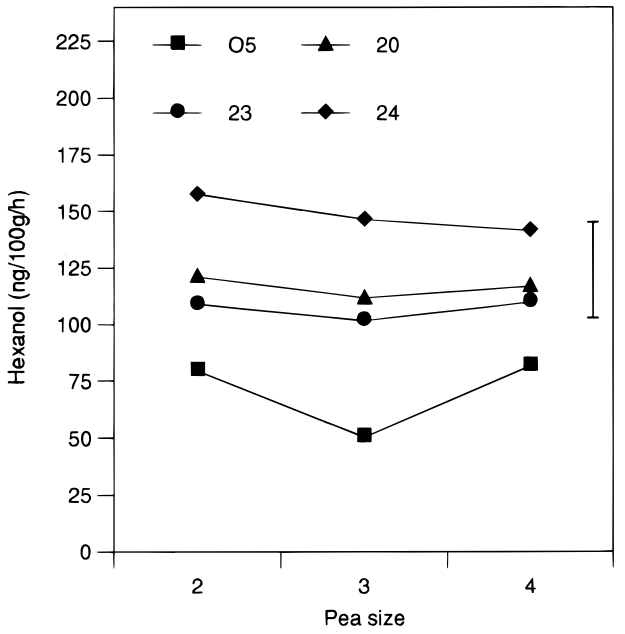

Figure 3. Hexanol concentrations in the headspace of four genotypes (05, 20, 23, and 24) represented in three size gradings (2, 3, and 4). Vertical bar represents LSD (46).

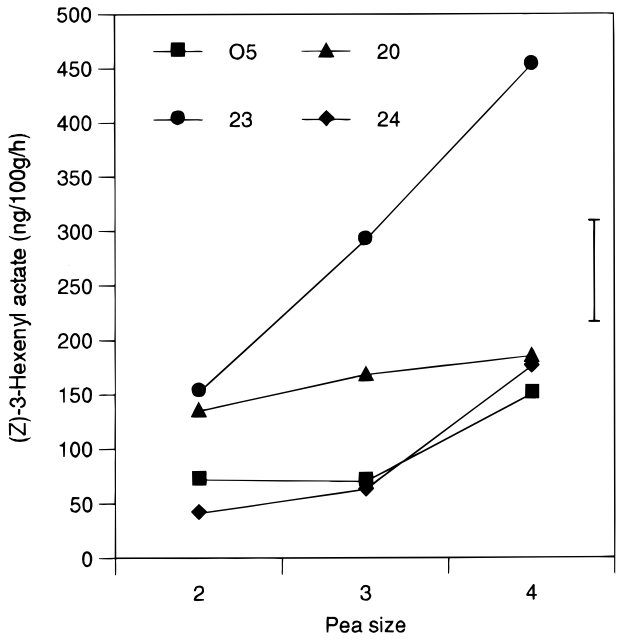

Figure 4. (*Z*)-3-Hexenyl acetate concentrations in the headspace of four genotypes (05, 20, 23, and 24) represented in three size gradings (2, 3, and 4). Vertical bar represents LSD (87).

ibility of the quantitative experimental results were determined by performing repeated measurements on samples taken from the same batch of peas. The coefficients of variation (CV) varied from 1.5 to 9.8% on non-nitrogen compounds and from 70.1 to 78.7% for the extreme low concentrations of methoxypyrazines.

Hexanal comprised on average 55% of the trapped volatile mass (Table 1). Clear differences were observed in the concentration levels of hexanal among genotypes ranging from 591 ng/100 g/h in genotype 93 to 2252 ng in 23 (size 3 samples). The hexanal content decreased significantly with pea size in some selections, whereas others showed no significant differences in hexanal levels among size gradings (Figure 2). The observed higher hexanal level in small peas observed in two selections is in accordance with findings by Bengtson et al. (1967), who concluded that off-odor caused by hexanal develops more readily in small peas than in larger ones. They suggested that this difference was caused by the fact that small peas are more tender and therefore more exposed to mechanical damage, that is, fractures in the skin tissue. The same authors showed that the hexanal development indeed takes place in the testa as opposed to in the cotyledons and that the skin comprises a higher fraction of the total pea mass in small peas than in larger ones (Bengtson et al., 1967). The lack of size effect on hexanal content, observed in two of four selections in the present study (Figure 2), suggests that the susceptibility of size 3 and 4 peas to mechanical damage varies significantly among selections. Size 3 is the most common pea size in commercial products.

Hexanol, which is most likely formed from hexanal by alcohol dehydrogenase, was among the most abundant compounds in the headspace (Table 1). The concentration of hexanol in size 3 peas varied significantly among genotypes from 50 ng/100 g/h in genotype 53 to 146 ng in 24. Pea size did not influence the hexanol concentration level significantly (Figure 3).

The contents of two other major compounds originating from the fatty acid breakdown group, (*Z*)-3-hexenyl acetate and (*Z*)-3-hexenol, increased with pea size in all genotypes (Figures 4 and 5). (*Z*)-3-Hexenol is emitted from most green plant tissues and is known as "leaf alcohol". The increase in (*Z*)-3-hexenyl acetate and (*Z*)-3-hexenol concentrations reflects the influence of differences in the average development stage or age of the maturing seed as demonstrated in an experiment where concentration levels of aroma compounds at different harvest dates in the same field were compared. The level of (*Z*)-3-hexenyl acetate increased from 30.8 to 83.0 ng/100 g/h 3 days later and to 199.8 ng/100 g/h when the harvest was delayed another 2 days. The corresponding concentrations for (*Z*)-3-hexenol were 60.5, 174.7, and 269.7 ng/100 g/h, respectively. Tenderometer

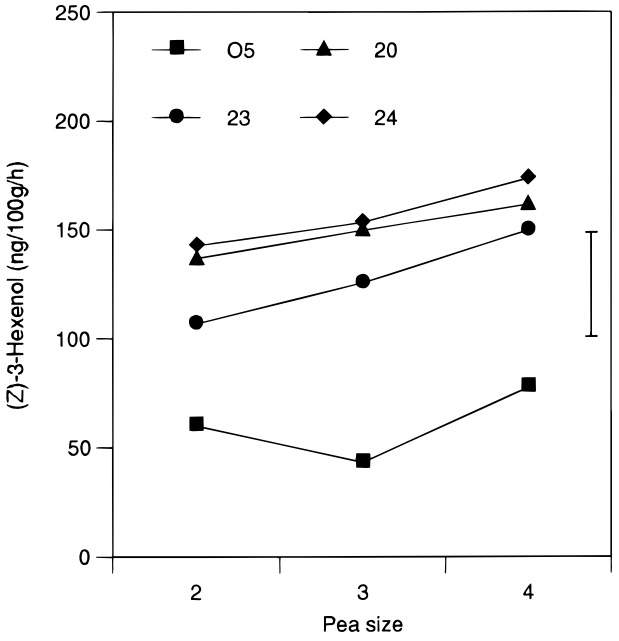

Figure 5. (*Z*)-3-Hexenol concentrations in the headspace of four genotypes (05, 20, 23, and 24) represented in three size gradings (2, 3, and 4). Vertical bar represents LSD (49).

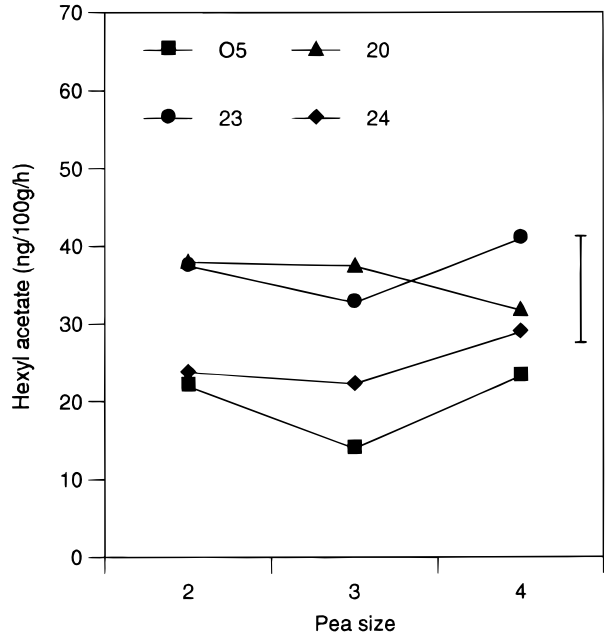

Figure 6. Hexyl acetate concentrations in the headspace of four genotypes (05, 20, 23, and 24) represented in three sizes (2, 3, and 4). Vertical bar represents LSD (14).

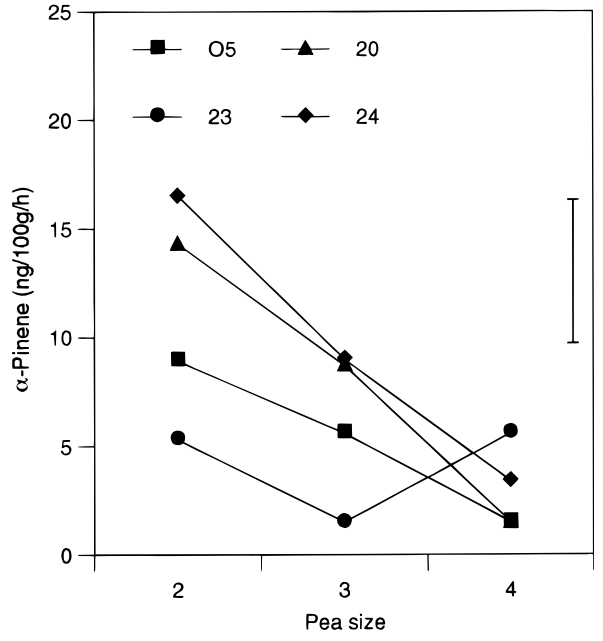

Figure 7. α-Pinene concentrations in the headspace of four genotypes (05, 20, 23, and 24) represented in three size gradings (2, 3, and 4). Vertical bar represents LSD (7).

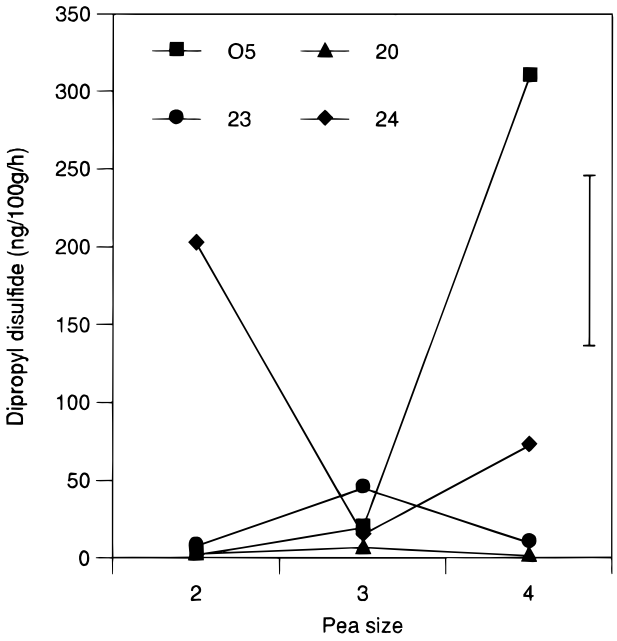

Figure 8. Dipropyl disulfide concentrations in the headspace of four genotypes (05, 20, 23, and 24) represented in three size gradings (2, 3, and 4). Vertical bar represents LSD (110).

readings on the 3 days were 86, 141, and 156. The concentration level of both compounds varied significantly among genotypes (Table 1; Figures 4 and 5).

Significant genotype effects were also detected for hexyl acetate (Figure 6 and Table 1), but no differences among pea sizes were observed. The concentration level ranged from 13 ng/100 g/h in genotype 53 to 41 ng/100 g/h in genotype 23. Octanal, yet another fatty acid breakdown product, showed no significant differences in concentration levels among genotypes or pea sizes.

Several genotype and size effects were detected among the terpenes (Table 1), an example being α-pinene, which was correlated negatively with pea size in most genotypes (Figure 7).

Dipropyl disulfide showed large variations among genotypes and in some cases also among sizes within genotypes and among replicates (Figure 8). Some genotypes had generally low dipropyl disulfide levels, for example, genotypes 20 and 23 (Figure 8), whereas others showed extreme differences among pea sizes, for example, genotypes 24 and 05 (Figure 8).

The concentration of 5- or 6-methyl-3-isopropyl-2-methoxypyrazine varied significantly among genotypes and sizes (Figure 9). Two genotypes, however, showed no differences among pea sizes, whereas genotypes 23 and 5 emitted more 5- or 6-methyl-3-isopropyl-2-methoxypyrazine from size 4 peas than from sizes 2 and 3 (Figure 9). The 3-isobutyl-2methoxypyrazine could not be quantified even by the nitrogen sensitive GC-NPD

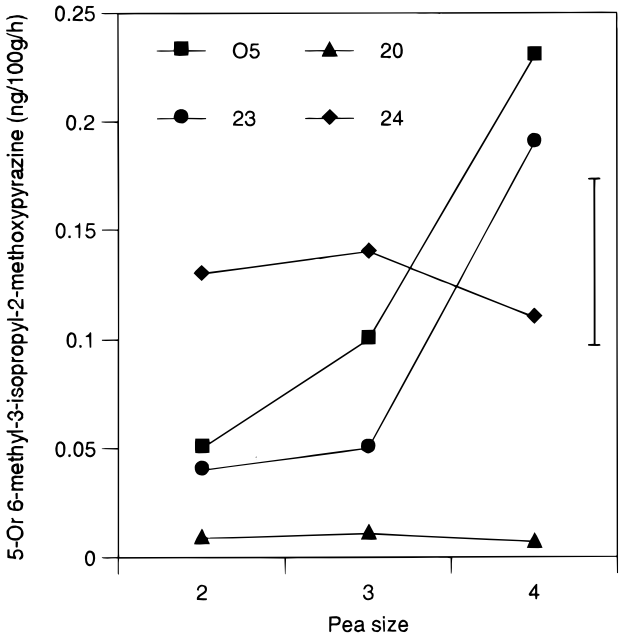

Figure 9. 5- or 6-methyl-3-isopropyl-2-methoxypyrazine concentrations in the headspace of four genotypes (05, 20, 23, and 24) represented in three size gradings (2, 3, and 4). Vertical bar represents LSD (0.075).

detector. No significant differences in 3-isopropyl-2-methoxypyrazine or 3-*sec*-butyl-2-methoxypyrazine content could be detected among genotypes or pea sizes (Table 1).

GC-Sniff Evaluation of Aroma Compounds. The GC-sniff method is used here to determine which compounds contribute to the aroma profile with a high degree of certainty. The well-known drawback of this method is the loss synergistic effects among volatiles. This has to be taken into account when results from GC-sniffing experiments are evaluated.

Hexanal contributed, according to the GC-sniff test, with a "green, strong" tone to the pea aroma (Table 1). Hexanal has been suggested to be among the most important contributors to off-odor in peas (Bengtson and Bosund, 1964; Williams et al., 1986), and it is used as an indicator for oxidative deterioration in foods in general (Ho and Chen, 1994). The contribution of this compound to the odor or off-odor of peas has, however, been subject to some debate: off-odor development is of major significance for the quality of peas, and several studies have pointed at a range of degradation products of fatty acids as the cause for off-odor. Bengtson et al. (1967) observed that the off-odor was correlated positively to hexanal concentration level. Addition of hexanal to samples of fresh peas resulted in off-flavor sensation, although the character was somewhat different from that of stored peas. Williams et al. (1986) demonstrated that addition of lipoxygenase to blanched samples of the English green garden pea caused significant off-flavor development. Murray et al. (1976) concluded that off-odor in unblanched peas is caused by breakdown of unsaturated lipids. They could not attribute the off-odor to a single compound but suggested that off-odor in peas was caused largely by a number of unsaturated carbonyls. In contrast to Bengtson et al. (1967), Murray et al. (1976) observed little significance of hexanal to the odor. The relative size of the hexanal peak in the study by Murray et al. (1976) was low compared to that in the present study. Although Murray et al. (1976) solely indicated relative contents of the aroma volatiles, that is, large peak, small peak, etc., they reported the hexanal/hexanol ratio to be 1: 200, whereas the ratio was 15:1 in our study (Table 1). The low hexanal content in the samples of Murray et al. (1976) may account for the reported insignificant contribution of this compound to the odor of peas.

The GC-sniff test indicated no strong odors in the hexanol elution area. Murray et al. (1976) reported hexanol to be the dominating compound quantitatively and suggested that it contributed to the green haylike off-odor in peas. The relative hexanol levels in the samples of Murray et al. (1976) were, as mentioned above, much higher than in the present study.

Other consistent GC-sniff descriptors in the group comprising degradation products of fatty acids were "sweet and perfumelike" for hexyl acetate, "orange, sweet" for octanal, and "mushroom, strong" for 1-octen-3-one (Table 1). The latter and 1-octen-3-ol are character impact compounds in mushrooms (Pyysalo and Suihko, 1976; Buttery, 1981). None of these compounds have previously been reported as significant contributors to the aroma of peas.

The sniff-test indicated that dipropyl disulfide was responsible for the "sulfurous or sour" onionlike aroma which was characteristic for some of the blanched pea samples. This compound is a well-known contributor to the aroma of onion (Kimura et al., 1990). Green peas have a delicate taste when served mixed with lightly fried onions. It is therefore possible that dipropyl disulfide is desirable for the flavor of green peas in certain concentrations. This is further investigated in a sensory panel evaluation comparing peas with distinctly different levels of dipropyl disulfide.

The methoxypyrazines induced distinct responses in the GC-sniff test, with descriptors such as "pea pod", "bell pepper", "blanched peas", "peas", and "spruce". This is consistent with previous studies finding 3-isopropyl-2-methoxypyrazine, 3-*sec*-butyl-2-methoxypyrazine, and 3-isobutyl-2-methoxypyrazine to be among the most potent aroma compounds in green peas (Murray and Whitfield, 1975; Murray et al., 1976) and other vegetables, for example, bell pepper (Buttery, 1981). The odor in the elution area of 5- or 6-methylisopropyl-2-methoxypyrazine was described as "dry grass and spruce". In the literature this compound has previously been described as "strongly green" and "green bean-like" (Takken et al., 1975).

Optimization of the Aroma Profile. The compounds influencing the aroma profile significantly seem to be grouped in two main categories: (1) the fatty acid breakdown products, which contribute to the pea aroma with "strong, green", "perfume, sweet", "orange, sweet", and "mushroom" odors as determined by the GC-sniff test, and according to other studies also to the off-odor development, and (2) the methoxypyrazines, responsible for the characteristic pea aroma also associated with bell pepper. Attempts to improve the flavor of peas should include regulation of the concentration levels of compounds in these groups.

The relationship between the concentration levels of fatty acid breakdown products and the flavor quality is, however, not a simple one: a moderate formation is beneficial to the flavor, but high levels are categorized as undesirable off-flavor by taste panels (Murray et al., 1976). This balance may be achieved by manipulating

one or several of the parameters influencing the formation of these products, which takes place during two phases: (1) in the preblanching period from harvest and vining to blanching at the production plant and (2) during storage. The preblanching enzymatic oxidation of fatty acids may be very rapid due to testal damage and lack of enzyme inhibition combined with relatively high temperatures during harvest and transport. Makower and Ward (1950) and Pendlington (1961) showed that the off-odor appears within hours after mechanical bruising during harvest and vining, causing low scores in test panel ratings compared to hand-podded peas. The production of fatty acid breakdown products during these phases may therefore be reduced by shortening the time span from harvest to blanching and freezing. Furthermore, the temperature in this period may be controlled to influence the speed of off-odor formation. The formation of fatty acid breakdown products during the storage period may take place either enzymatically or by autoxidation. The former depends on the efficiency of enzyme inhibition during blanching and by the storage conditions. Halpin and Lee (1987) observed no significant changes in flavor scores of peas after 9 months of storage at −23 °C if blanching took place at temperatures between 71 and 96 °C. In contrast, peas blanched at 60 °C showed significantly lower flavor scores after 9 months of storage. This difference could be attributed to a significantly higher lipoxygenase activity in peas blanched at 60 °C. Lipoxygenase activity in blanched peas apparently increased slightly during storage (Halpin and Lee, 1987). Accordingly, Martens (1986) blanched batches of wrinkle-seeded vining peas at 85−90 °C for 2−4 min and evaluated several sensory parameters after 1−2 weeks and after 52 weeks of storage at −20 °C. No significant changes in flavor ratings within the categories "sweet flavor", "fruity flavor", "earthy flavor", or "off-flavor" were noted by the sensory panel comparing samples from the two storage intervals. Williams et al. (1986) demonstrated that the aroma of the English green garden peas changed significantly in unblanched samples during 2 months of storage, whereas blanching (130 s at 83 °C) and storage for 12 months at −18 °C caused no detectable changes in the aroma. These conditions are similar to those applied in the present study, that is, blanching at 93 °C for 90 s and storage for 15 months at −24 °C. Information in the literature concerning the inactivation of enzymes in peas by blanching shows some variation in thermal stability of the enzymes. Williams et al. (1986) found that when English green garden peas were blanched in one layer, lipoxygenase was inactivated after 3 min at 83 °C. Peroxidase was significantly more heat stable than lipoxygenase, whereas catalase was readily inactivated at relatively low temperatures. Antis and Friend (1974) isolated four lipoxygenase isozymes from pea seedlings. These were all inactivated by boiling, which, however, is an undesirable treatment of green peas prior to freezing. Reynolds (1982) purified three lipoxygenase isozymes from pea seeds, which differed significantly in thermal stability. All isozymes were inactivated after blanching at 80 °C for 5 min, whereas some activity was retained for all three after incubation at 60 °C for 40 min. These results together indicate that it is possible to control enzyme activity and thus off-odor development during the postblanching phase by adjusting the blanching parameters.

An attempt to regulate the aroma quality of green peas by influencing the level of the character impact 3-alkyl-methoxypyrazines by breeding measures seems feasible at least in the case of 5- or 6-methyl-3-isopropyl-2-methoxypyrazine. Higher concentrations of the remaining three methoxypyrazines should be collected in each trapping session to exclude the influence of noise from the detector in the quantification. This will enable detection of any differences in the 3-alkylmethoxypyrazine content among genotypes.

The aim of the work presented in this paper was primarily to identify and quantify the composition of volatiles in a range of green pea genotypes each represented by a number of pea sizes. This investigation is now being continued in a study comparing the objective aroma data of an extensive number of pea samples with aroma evaluations by a sensory panel. In this way we hope to evaluate in detail which volatiles are significant contributors to the aroma of green peas.

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