Differences in Key Odorants of Handmade Juice of Yellow-Flesh Peaches (*Prunus persica* L.) Induced by the Workup Procedure

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Application of aroma extract dilution analysis (AEDA) on a flavor extract isolated from a freshly prepared, enzyme-inactivated peach juice using solvent extraction and high-vacuum distillation (extract I) revealed 24 odor-active regions in the gas chromatogram. Flavor dilution (FD) factors ranged from 4 to 512. The highest FD factors were determined for β-damascenone (cooked-apple-like) and γ-decalactone (peach-like). Cooking of peaches for 2 h in an apparatus equipped for simultaneous steam distillation/extraction (extract II) yielded an overall more intense aroma extract (extract II). By AEDA, 30 odorants were detected in the FD-factor region of 4−16384 and were subsequently identified. The results revealed that in extract II, besides the two above-mentioned aroma compounds, both had FD factors of 16 384; δ-decalactone, γ-dodecalactone additionally, and 6-dodeceno-γ-lactone contributed with very high FD factors (FD 8192) to the overall aroma. In general, the thermal treatment led to the formation of 15 new odorants which were not detected in I. Furthermore, the lactones and β-damascenone were significantly increased in II, thereby indicating their generation from precursors in the fresh juice.

Keywords: *Peach aroma; aroma extract dilution analysis; β-damascenone; γ-decalactone; δ-decalactone; flavor precursor*

INTRODUCTION

Due to their attractive aroma, fruits of the tree *Prunus persica* L., peaches, are widely consumed either as fresh fruit, canned fruit, and processed juice.

Sevenants and Jennings (1966, 1971) were the first to investigate the composition of the volatile fraction of fresh peaches. They identified 24 compounds in an extract prepared from 7 tons of peach fruits and proposed that in particular lactones as well as α-pyrone and 6-pentyl-α-pyrone were characteristic odorants in the peach flesh. Do et al. (1969) identified a homologous series of γ-lactones (γ-penta- to γ-dodecalactone) as well as certain δ-lactones as volatile peach constituents. Also, Broderick (1966), Spencer et al. (1978), Narein et al. (1990), and Rizzolo et al. (1995) suggested a key role of lactones, especially of the peach-like smelling γ-decalactone, for the overall peach flavor.

Recently, Horvat et al. (1990) quantified the predominant peach volatiles and approximated their flavor contribution based on a calculation of odor units (ratio of concentration to odor threshold). Their results confirmed γ-decalactone as a key peach aroma compound and proposed hexanal, (*E*)-2-hexenal, and linalol as other impact aroma compounds in the fresh peach fruit.

Fischer et al. (1992) and Fischer (1995) applied high-resolution gas chromatography/olfactometry on a flavor extract of peaches. On the basis of their identification experiments, γ-decalactone, γ-jasmolactone, γ-octalactone, dihydro-β-ionone, β-damascenone, (*Z*)-3-hexenal, and (*E*)-2-hexenal were proposed as the key odorants.

A comparative aroma extract dilution analysis (cAEDA; cf. review by Schieberle, 1995) is a useful tool to estimate quantitative changes in the entire set of aroma-active volatiles of a given food induced by, e.g., thermal processing. However, no such approach aimed at clarifying the influence of a thermal treatment on peach aroma has been reported in the literature.

The aim of the following investigation was, therefore, to gain insight into changes in key peach odorants induced by heating and applying the cAEDA on extracts obtained from either a fresh, handmade peach juice or the respective cooked peach flesh.

EXPERIMENTAL PROCEDURES

Materials. Full ripe yellow-flesh peaches (*Prunus persica* L.) cv. Redcap were purchased at a local market.

Chemicals. The following reference aroma compounds were obtained commercially: nos. **1**, **3**, **7**, **8**, **11**−**13**, **15**, **17**, **20**, **21**, **23**, **24**, **I**−**IV**, **VII**−**XIII** (Aldrich, Steinheim, Germany); no. **4** (Lancaster, Mühlheim, Germany); nos. **9** and **10** (Alfa-Products, Karlsruhe, Germany); nos. **18** and **14** were gifts from Dragoco (Holzminden, Germany) and Haarmann & Reimer (Holzminden, Germany), respectively. The following compounds were synthesized closely following the procedures reported in the literature given in parentheses: no. **2** (Schieberle and Hofmann, 1997), no. **6** (Ullrich and Grosch, 1988), no. **16** (Schieberle and Grosch, 1991) and no. **22** (Widder et al., 1991). (*Z*)-Hex-3-enyl acetate (no. **5**) was prepared by reacting (*Z*)-3-hexenol (Aldrich, Steinheim, Germany) in the presence of an excess of acetic acid and trace amounts of concentrated sulfuric acid.

Isolation of the Volatiles from Fresh Peach Juice (Extract I). Full ripe peaches were halfed and freed from the stone. Then, to inhibit enzymic reactions (Buttery et al., 1987), the flesh (250 g) was immediately homogenized by means of an Ultraturrax (Jahnke und Kunkel, Hohenstaufen, Germany) in an aqueous saturated $CaCl_2$ solution (300 mL). The fruit

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Table 1. Most Odor-Active Volatiles (FD ≥ 4) in an Extract Prepared from Fresh Peach Juice

no.	odorant[a]	odor quality[b]	RI FFAP	RI SE-54	FD factor[c]
1	butan-2,3-dione	buttery	987		4
2	(*Z*)-3-hexenal	green, apple-like	1147	793	32
3	(*E*)-2-hexenal	green, banana-like	1215	853	32
4	1-octen-3-one	mushroom-like	1288	980	16
5	(*Z*)-3-hexenyl acetate	fruity	1321	1007	16
6	(*Z*)-1,5-octadien-3-one	geranium-like	1360	984	4
7	acetic acid	sour, vinegar-like	1451		16
8	(*E*)-2-nonenal	tallowy, fatty	1527	1160	32
9	(*Z*)-2-nonenal	tallowy, fatty	1532	1095	4
10	(*E*,*Z*)-2,6-nonadienal	cucumber-like	1573	1155	4
11	butanoic acid	sweaty	1614	820	4
12	2- and 3-methylbutanoic acid	sweaty	1655	874	4
13	γ-hexalactone	coconut-like, fruity	1698	1080	4
14	β-damascenone	cooked apple-like	1805	1390	512
15	γ-octalactone	coconut-like	1911	1259	16
16	4,5-epoxy-(*E*)-2-decenal	metallic	1995	1362	64
17	γ-decalactone	peach-like	2140	1472	512
18	γ-jasmolactone	peach-like	2176	1443	32
19	6-pentyl-α-pyrone	coconut-like	2176	1450	16
20	δ-decalactone	coconut-like	2194	1493	64
21	γ-dodecalactone	fruity	2370	1677	32
22	6-dodeceno-γ-lactone	fruity	2389	1655	16
23	phenylacetic acid	honey-like	2550	1263	4
24	vanillin	vanilla-like	2569	1400	4

[a] The compound was identified by comparing it with the reference compound on the basis of the following criteria: retention index (RI) on two HRGC stationary phases given in the table, mass spectra obtained by MS(EI) and MS(CI), and odor quality and odor intensity perceived at the sniffing port. [b] Odor quality perceived at the sniffing port. [c] Flavor dilution (FD) factor determined in the extract of the volatiles. Analyses were performed by two assessors in duplicate. The data differed by fewer than two FD factors.

suspension was subsequently extracted with diethyl ether (6 times, total volume 600 mL), the organic layer was separated, dried over Na_2SO_4, and finally concentrated to 100 mL at 38 °C by using a Vigreux column (60 cm × 1 cm i.d.). The volatiles were isolated by sublimation in vacuo as reported previously (Sen et al., 1991). For aroma extract dilution analysis (AEDA), this distillate was concentrated to 200 μL.

Isolation of the Volatiles Formed during Cooking of Peach Juice (Extract II). Fresh peaches (250 g) were freed from the stone, halfed, diced, and immediately suspended in a 1 L vessel containing boiling water (300 mL), which was connected to an apparatus for simultaneous steam distillation/extraction. Using peroxide-free diethyl ether (50 mL) as the organic solvent, distillation was performed for 3 h. For AEDA, the extract was dried over Na_2SO_4 and concentrated to 200 μL by distilling off the solvent at 38 °C.

High-Resolution Gas Chromatography (HRGC)/Mass Spectrometry (MS). HRGC was performed by means of a type 8000 gas chromatograph (Fisons Instruments, Mainz, Germany) by using the following capillary: FFAP (30 m × 0.32 mm fused silica column; free fatty acid phase, 0.25 μm; J&W Scientific, Fisons Instruments, Mainz, Germany) and SE-54 (30 m × 0.32 mm fused silica column DB-5; 0.25 μm; J&W Scientific, Fisons Instruments, Mainz, Germany). The samples were applied by the cold on-column injection technique at 35 °C. After 2 min, the temperature of the oven was raised at 40 °C/min to 60 °C for FFAP and to 50 °C for SE-54. The temperature of the oven was raised at 4 °C/min to 230 °C and held for 10 min. The flow of the helium carrier gas was 2.3 mL/min. Linear retention indices (RI) were calculated using *n*-alkanes as the reference. MS analysis was performed by means of an MS 95 S (Finnigan, Bremen, Germany) in tandem with the capillaries described above. Mass spectra in the electron impact mode (MS/EI) were generated at 70 eV and in the chemical ionization mode (MS/CI) at 115 eV with isobutane as the reagent gas.

Aroma Extract Dilution Analysis (AEDA). The flavor dilution (FD) factors of the odor-active compounds were determined by HRGC/olfactometry of serial dilutions using the aroma extract dilution analysis (AEDA) approach (cf. Schieberle, 1995). The following dilution series were evaluated by sniffing: The original aroma extract (200 μL) of either the fresh

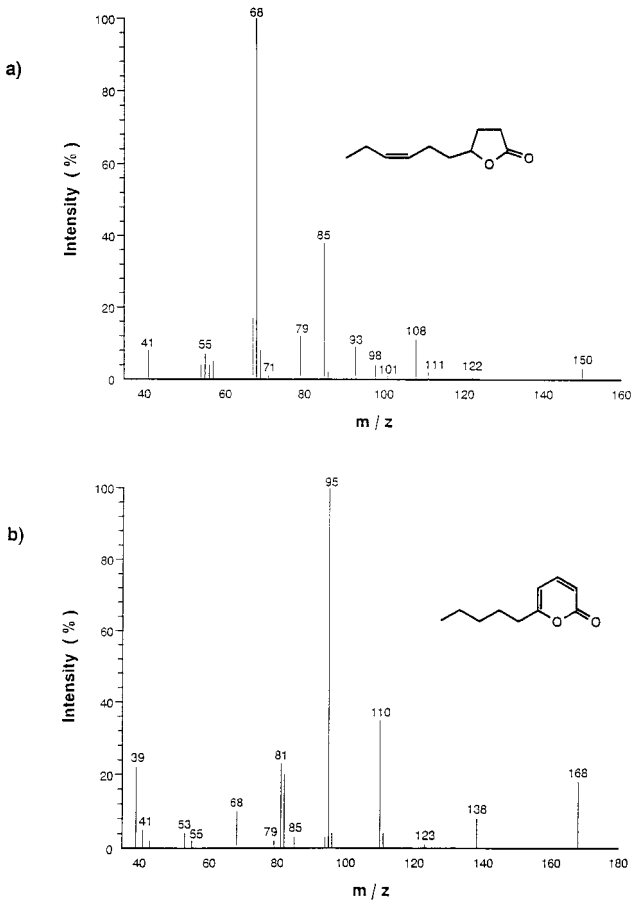

Figure 1. Mass spectrum (EI) of (a) γ-jasmolactone and (b) 6-pentyl-α-pyrone.

or the thermally treated juice prepared from ripe peaches (250 g) was stepwise diluted with diethyl ether (1 + 1). HRGC/Olfactometry was performed with aliquots (0.5 μL) of the diluted extracts. At the end of the capillary, the effluent was

Table 2. Most Odor-Active Volatiles (FD ≤ 4) in an Extract Prepared by Simultaneous Steam Distillation/Extraction of Peach Slices

			RI		
no.	odorant[a]	odor quality[b]	FFAP	SE-54	FD-factor[c]
1	butan-2,3-dione	buttery	987	<700	128
I	octanal	tallowy, citrus-like	1277	1002	4
4	1-octen-3-one	mushroom-like	1288	980	128
II	nonanal	tallowy	1381	1107	8
III	2-octenal	green, fatty	1400	1056	4
IV	2-decanone	fatty, fruity	1405	1191	128
V	methional	cooked potato-like	1448	902	16
VI	unknown	fatty	1459	1260	4
8	(*E*)-2-nonenal	tallowy, fatty	1527	1160	128
VII	linalol	flowery, tea-like	1534	1100	128
10	(*E*,*Z*)-2,6-nonadienal	cucumber-like	1573	1155	32
VIII	phenylacetaldehyde	flowery, honey-like	1638	1040	16
12	2- and 3-methylbutanoic acid	sweaty	1655	874	512
IX	(*E*,*E*)-2,4-nonadienal	fatty, waxy	1690	1211	32
X	(*E*,*E*)-2,4-decadienal	fatty, waxy	1800	1314	128
14	β-damascenone	cooked apple-like	1805	1390	16384
XI	2-methoxyphenol	smoky	1860	1087	32
15	γ-octalactone	coconut-like	1911	1259	128
16	4,5-epoxy-(*E*)-2-decenal	metallic	1995	1362	128
XII	γ-nonalactone	fruity	2019	1360	8
17	γ-decalactone	peach-like	2140	1472	16384
XIII	eugenol	clove-like	2153	1357	8
18	γ-jasmolactone	peach-like	2176	1443	512
19	6-pentyl-α-pyrone[d]	coconut-like	2176	1450	128[d]
20	δ-decalactone	coconut-like	2194	1493	8192
XIV	unknown	soapy	2288		1024
21	γ-dodecalactone	fruity	2370	1677	8192
22	6-dodeceno-γ-lactone	fruity	2389	1655	8192
XV	unknown	sweet	2431	1300	8
23	phenylacetic acid	honey-like	2550	1263	64
24	vanillin	vanilla-like	2569	1400	64

[a] The compound was identified by comparing it with the reference compound on the basis of the following criteria: retention index (RI) on two HRGC stationary phases given in the table, mass spectra obtained by MS(EI) and MS(CI), and odor quality and odor intensity perceived at the sniffing port. [b] Odor quality perceived at the sniffing port. [c] Flavor dilution (FD) factor determined in the extract of the volatiles. Analyses were performed by two assessors in duplicate. The data differed by fewer than two FD factors. [d] The FD factors were determined on a SE-54 capillary.

split 1:1 (by vol.) into an FID and a sniffing port device using deactivated but uncoated fused silica capillaries (50 cm × 0.32 mm). The FID and the sniffing port were held at 200 °C.

RESULTS

Aroma Extract Dilution Analysis of Fresh Peach Juice. To inhibit enzymic odorant degradation/formation, the fruits were homogenized in saturated $CaCl_2$ solution (Buttery et al., 1987; Fischer et al., 1992). The volatiles were isolated by solvent extraction, followed by high-vacuum distillation at 25 °C and 10^{-4} bar. An overall sensory evaluation of the flavor distillate obtained revealed the typical green, fruity, flowery aroma impression of fresh peaches.

Application of HRGC/olfactometry on this aroma extract resulted in the detection of 24 odor-active compounds, which were first described in their odor quality and then ranked in their flavor impact by evaluating the GC eluates of serial dilutions. This AEDA revealed two compounds with the highest FD factors among the 24 odor-active compounds, eliciting cooked-apple-like and a peach-like odor, respectively. Comparison of their retention indices on two capillary columns (SE-54, FFAP), their mass spectra, as well as their odor quality with those of synthetic reference compounds led to the identification of β-damascenone and γ-decalactone. These appear to be responsible for the aroma impressions. The results of further identification experiments are summarized in Table 1. The data show that 4,5-epoxy-(*E*)-2-decenal (**16**; Table 1) and δ-decalactone (**20**) are additional important peach odorants contributing with somewhat lower odor activities to the overall aroma of the extract.

Compounds **18** and **19** coeluted on the FFAP column. Separation of the flavor extract on an SE-54 column allowed the separation of both odorants, which, based on their mass spectra (Figure 1a,b), were identified as γ-jasmolactone (**18**) and 6-pentyl-α-pyrone (**19**). The AEDA performed on the SE-54 column suggested that both compounds contributed to the same extent to the overall aroma, because their FD factors determined on the SE-54 column were nearly identical.

Aroma Extract Dilution Analysis of the SDE Extract. Cooking of the peaches during simultaneous steam distillation generated an overall more intense flavor extract. To gain insight into the reason for these flavor changes, sliced peaches were immediately suspended in boiling water and the volatiles either present or formed were isolated by simultaneous steam distillation extraction. Application of the AEDA on the concentrated extract revealed 31 odor-active regions in the gas chromatogram. The results of the AEDA in combination with the identification experiments are summarized in Table 2. As found in the extract of the fresh peaches (extract I), β-damascenone (no. **14**; Table 2) and γ-decalactone (no. **17**; Table 2) appeared with the highest FD factors. As further key odorants, δ-decalactone (no. **20**; Table 2), γ-dodecalactone (no. **21**) and 6-dodeceno-γ-lactone (no. **22**) were identified, all of which also contributed to the fresh peach aroma (cf.

Table 3. Important Peach Odorants Showing Most Significant Differences in Their FD Factors between Fresh (Extract I) and Cooked Peach Material (Extract II)

odorant[a]	odor quality[b]	FD factor[c] I	FD factor[c] II
γ-decalactone	peach-like	512	16384
β-damascenone	cooked apple-like	512	16384
δ-decalactone	coconut-like	64	8192
γ-dodecalactone	fruity	32	8192
6-dodeceno-γ-lactone	fruity	16	8192
γ-jasmolactone	peach-like	32	512
6-pentyl-α-pyrone	coconut-like	16	128

Table 1). However, 15 compounds (marked with a letter in Table 2) were newly formed during cooking of the peach flesh. Among them, due to a relatively high FD factor (FD ≥ 128), in particular, 2-decanone (no. **IV**), linalol (no. **VII**), (*E*,*E*)-2,4-decadienal (no. **X**), and an unknown compound (no. **XIV**), eliciting a soapy odor note, are of special interest. On the other hand, eight compounds, namely, (*Z*)-3- (no. **2**; Table 1) and (*E*)-2-hexenal (no. **3**), (*Z*)-3-hexenyl acetate (no. **5**), (*Z*)-1,5-octadiene-3-one (no. **6**), (*Z*)-3-nonenal (no. **9**), γ-hexalactone (no. **13**), acetic acid (no. **7**), and butanoic acid (no. **11**), contributing to fresh peach odor (cf. Table 1), did not appear among the odorants of the thermally treated peaches. Although, in particular for (*Z*)-3-hexenal, a degradation of the odorants during the distillation procedure might be assumed, in the case of the two acids, their low steam volatility might be the reason for their disappearance in the extract from the cooked peaches.

CONCLUSIONS

The aroma extract dilution analyses were performed on the basis of the same weight of peaches (250 g); the extracts were concentrated to the same degree (200 μL); and the same amounts of the flavor extract had been used for HRGC (0.5 μL). On the basis of these prerequisites, changes in the FD factors do give insight into changes in the concentrations of single odorants (comparative AEDA; cf. Schieberle, 1995).

A comparison of the FD factors of the key odorants in extracts I and II demonstrated that significant changes in the FD factors were induced by thermal processing (Table 3). For example, heating of the juice led to an increase of the amounts of γ-decalactone and β-damascenone by a factor of 32. Furthermore, other lactones such as δ-decalactone, γ-dodecalactone, or 6-dodeceno-γ-lactone showed somewhat lower FD factors from the extract of fresh peaches, increased factors of 128, 256, or 512, respectively. These changes are well in line with the more intense sweet, peach-like odor of extract II.

Furthermore, these data indicate that obviously high amounts of lactone precursors are present in the fresh fruit material liberating these odorants upon thermal processing. Heating of the fruit juice, however, also led to the formation of new odorants, which were lacking in extract I. For example, besides an unknown soapy smelling compound, linalol, 2-decanone, (*E*,*E*)-2,4-decadienal, (*E*,*E*)-2,4-nonadienal, 2-methoxyphenol, methional, and phenylacetaldehyde were detected exclusively in II. On the other hand, (*Z*)-3-hexenal and (*E*)-2-hexenal were completely degraded by heating of the fruits, reflected by the loss of the overall green odornote after processing.

LITERATURE CITED

Broderick A. What is important in peach flavor? *Am. Perfum. Cosmet.* **1966**, *81*, 43−45.

Buttery, R. G.; Terahnishi, R.; Ling, L. C.; Flath, R. A.; Stern, D. J. Fresh tomato volatiles: a quantitative study. *J. Agric. Food Chem.* **1987**, *35*, 540−544.

Do, J. Y.; Salunkhe, D. K.; Olson, L. E. Isolation, identification and comparison of the volatiles of peach fruits as related to harvest maturity and artificial ripening. *J. Food Sci.* **1969**, *34*, 618−621.

Fischer, N.; Hammerschmidt, F.-J.; Brunke, E.-J. Occurrence of the γ-jasmolactone as a constituent of peach flavour. In *Progress in flavour precursor studies;* Schreier, P., Winterhalter, P., Eds.; Allured Publishing Corp.: Carol Stream, IL, 1992; pp 287−294.

Fischer, N. On the combination of sensorial and instrumental techniques in analytical aroma research (in German). *Aroma allgemein* **1995**, 132−145.

Horvat, R. J.; Chapman, G. W.; Robertson, J. A.; Meredith, F. I.; Scorza, R.; Callahan, A. M.; Morgens, P. Comparison of the volatile compounds from several commercial peach cultivars. *J. Agric. Food Chem.* **1990**, *38*, 234−237.

Jennings, W. G.; Sevenants, M. R. Volatile components of peach. *J. Food Sci.* **1964**, *29*, 796−801.

Narain, N.; Hsieh, T. C.-Y.; Johson, C. E. Dynamic headspace concentration and gas chromatography of volatile flavor components in peach. *J. Food Sci.* **1990**, *55*, 1303−1307.

Rizzolo, A.; Lombardi, P.; Vanoli, C.; Polesello, A. Use of capillary gas chromatography/sensory analysis as an additional tool for sampling technique comparison in peach aroma analysis. *J. High Resolut. Chromatogr.* **1995**, *18*, 309−314.

Schieberle, P. New developments in methods for analysis of volatile flavor compounds and their precursors. In *Characterization of food: emerging methods;* Goankar, A., Ed.; Elsevier: Amsterdam, 1995; 403−431.

Schieberle, P.; Grosch, W. Potent odorants of wheat bread crumb—Differences to the crust and effect of a longer dough fermentation. *Z. Lebensm. Unters. Forsch.* **1991**, *192*, 130−135.

Schieberle, P.; Hofmann, T. Evaluation of the character impact odorants in fresh strawberry juice by quantitative measurements and sensory studies on model mixtures. *J. Agric. Food Chem.* **1997**, *45*, 227−232.

Sen, A.; Laskawy, G.; Schieberle, P.; Grosch, W. Quantitative determination of β-damascenone in foods using a stable isotope dilution assay. *J. Agric. Food Chem.* **1991**, *39*, 757−759.

Sevenants, M. R.; Jennings, W. G. Volatile components of peach II. *J. Food Sci.* **1966**, *31*, 81−86.

Sevenants, M. R.; Jennings, W. G. A research note: Occurrence of 6-pentyl-α-pyrone in peach essence. *J. Food Sci.* **1971**, *36*, 536.

Spencer, M. D.; Pangborn, R. M.; Jennings, W. G. Gas chromatographic and sensory analysis of volatiles from cling peaches. *J. Agric. Food Chem.* **1978**, *26*, 725−732.

Ullrich, F.; Grosch, W. Identification of the most intense odor compounds formed during autoxidation of methyl linolenate at room temperature. *J. Am. Oil Chem. Soc.* **1988**, *65*, 1313−1317.

Widder, S.; Sen, A.; Grosch, W. Changes in the flavour of butter oil during storage—Identification of the potent odorants. *Z. Lebensm. Unters. Forsch.* **1991**, *193*, 32−35.

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