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ARTICLE

Quantitation of Key Peanut Aroma Compounds in Raw Peanuts and Pan-Roasted Peanut Meal. Aroma Reconstitution and Comparison with Commercial Peanut Products

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By means of stable isotope dilution assays (SIDA), 26 odor-active compounds, previously characterized by GC−olfactometry (GC-O), were quantitated in raw peanuts, and the concentrations of 38 odorants were determined in pan-roasted peanut meal. On the basis of the quantitative data and odor thresholds determined in vegetable oil, the odor activity values (OAVs) of the most important aroma compounds in raw as well as in pan-roasted peanut meal were calculated. 3-Isopropyl-2-methoxypyrazine, acetic acid, and 3-(methylthio)propanal showed the highest OAVs in raw peanuts, whereas methanethiol, 2,3-pentanedione, 3-(methylthio)propanal, and 2- and 3-methylbutanal as well as the intensely popcorn-like smelling 2-acetyl-1-pyrroline revealed the highest OAV in the pan-roasted peanut meal. Aroma recombination studies confirmed the importance, in particular, of methanethiol and of lipid degradation products in the characteristic aroma of the freshly roasted peanut material. To evaluate additive effects on the overall aroma, the concentrations of eight pyrazines, previously not detected by GC-O among the odor-active volatiles, were additionally quantitated in the pan-roasted peanut meal. A sensory experiment in which the eight pyrazines were added to the recombinate clearly revealed that these volatiles did not show an impact on the overall aroma. Finally, selected odorants were quantitated in commercial peanut products to confirm their important role in peanut aroma.

KEYWORDS: Stable isotope dilution assay; aroma recombinate; peanut butter; pyrazines; methanethiol

INTRODUCTION

The identification of the volatile compounds present in raw and roasted peanuts has been the topic of several studies over the past 40 years. However, systematic investigations aimed at characterizing the most odor-active compounds, for example, by applying the concept of "molecular sensory science" (*1*, *2*), have only scarcely been performed. To close this gap, the aroma-active volatiles in organically grown raw West African peanuts and in ground, pan-roasted meal produced therefrom have recently been identified (*3*). The results indicated 3-isopropyl-2-methoxypyrazine (earthy, pea-like), 3-isobutyl-2-methoxypyrazine (bell pepper-like), and *trans*-4,5-epoxy-(*E*)-2-decenal (metallic) as important odorants in the raw nuts, whereas 2-acetyl-1-pyrroline (popcorn-like, roasty) and 4-hydroxy-2,5-dimethyl-3(2*H*)-furanone (caramel-like) elicited the highest flavor dilution (FD) factors in a pan-roasted meal produced therefrom (*3*).

Brown et al. (*4*) were the first to determine the concentrations of some aliphatic aldehydes and ketones in Spanish and runner peanuts. Other groups suggested aldehydes and pyrazines as the main contributors to the pleasant roasty note of roasted peanuts on the basis of the quantitative data obtained (*5*, *6*). However, although pyrazines show extreme differences in their odor thresholds (*7*), studies were usually focused on pyrazines with high odor thresholds rather than on pyrazines showing extremely low odor thresholds, such as 2,3-diethyl-5-methylpyrazine.

Schirack et al. (*8*) recently performed a comprehensive quantitative study on several key volatiles and showed that phenylacetaldehyde, guaiacol (2-methoxyphenol), (*E*,*E*)-2,4-decadienal, and 4-hydroxy-2,5-dimethyl-3(2*H*)-furanone contributed with high odor activities to the overall aroma of microwave-blanched peanuts.

For the quantitation of trace odorants, a stable isotope dilution assay (SIDA) is the method of choice in particular to compensate losses during the workup procedure (*1*). However, up to now, this analytical approach has not been used in peanut flavor research. In addition, almost no data on the quantitative differences in the key aroma compounds between raw and roasted peanuts of the same batch are currently available.

Therefore, the aims of this study were (i) to quantify the most important odorants in raw peanuts and pan-roasted peanut meal, (ii) to quantify some of the key odor-active compounds in several peanut products, and (iii) to prove the contribution of pyrazines and other compounds to the overall aroma of roasted peanuts by means of aroma recombination studies.

MATERIALS AND METHODS

Peanuts. Raw peanuts from West Africa (Cameroon) were purchased from Orkos (Souci-Bouy, France). Ground pan-roasted peanut meal was

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produced as reported recently (*3*). Removal of the seed coat was not carried out because preliminary studies had shown that constituents of the skin did not contain key aroma compounds. Prior to use, the peanuts were deshelled, frozen in liquid nitrogen, and stored at −25 °C.

Different commercial peanuts or peanut products, respectively, were obtained from the local trade: roasted peanuts (Virginia type, imported and roasted in shell by Nut-Work, Hamburg, Germany), peanut oil (cold pressed from roasted seeds, mildly refined; purchased in a local store), and American peanut butter (John B. Sanfilippo & Son, Inc.) (Elgin, IL). Peanut butter and peanut oil were stored at −25 °C prior to analysis.

Chemicals. The reference compounds used in the quantitation experiments were purchased from commercial sources or were synthesized as recently reported (*3*).

Propanal and TLC plates silica gel 60 (with fluorescent indicator F_{254}; 20 × 20 cm size, 0.25 mm layer thickness on glass support, with concentration zone) were obtained from VWR (Darmstadt, Germany). [$^2H_3$]-Methyllithium−lithium iodide complex in anhydrous diethyl ether (10 mmol), ethylmagnesium bromide (1.0 mol/L in tetrahydrofuran), anhydrous tetrahydrofuran, and methanethiol as well as 2,5-dimethylpyrazine, 2,6-dimethylpyrazine, 2,3-dimethylpyrazine, 2-ethyl-3-methylpyrazine, and 2-ethyl-5- and 2-ethyl-6-methylpyrazine were purchased from Sigma-Aldrich (Taufkirchen, Germany). 1,4-Diazine (pyrazine) was from Alfa Aesar (Karlsruhe, Germany). Argon and liquid nitrogen were obtained from Linde (Munich, Germany). Diethyl ether and pentane were each freshly distilled using a Vigreux column (150 cm × 3 cm) prior to use.

Synthesis of 2-Ethyl-3,5-dimethylpyrazine and 2-Ethyl-3,6-dimethylpyrazine. Because 2-ethyl-3,5- and 2-ethyl-3,6-dimethylpyrazine are commercially available only as mixture of both isomers, each single isomer was synthesized as follows:

A solution of 2,6-dimethylpyrazine (2.16 g, 20 mmol) in anhydrous tetrahydrofuran (or a solution of 2,5-dimethylpyrazine; 2.16 g, 20 mmol) was slowly dropped into a stirred solution of ethylmagnesium bromide kept in an atmosphere of argon and was then refluxed for 2 h. After cooling to room temperature, the suspension was carefully treated with distilled water (20 mL) and extracted with diethyl ether (3 × 50 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated to ∼20 mL on a Vigreux column. To isolate the target compounds, aliquots (1 mL) were applied onto TLC plates and developed with pentane/diethyl ether (7:3; v/v) as the mobile phase. The UV-active area (R_f range = 0.3−0.4) was isolated and extracted with diethyl ether (50 mL). After filtration, the solution was concentrated to a final volume of ∼5 mL by means of a Vigreux column. The purity of the compounds was checked following the protocol described earlier (*9*).

2-Ethyl-3,5-dimethylpyrazine: MS-EI, *m*/*z* (%) 135 (100), 136 (84), 56 (34), 108 (16); MS-CI, *m*/*z* (%) 137 (100), 65 (18), 138 (12).

2-Ethyl-3,6-dimethylpyrazine: MS-EI, *m*/*z* (%) 135 (100), 136 (98), 42 (81), 56 (65), 108 (63); MS-CI, *m*/*z* (%) 137 (100), 138 (12).

Synthesis of Isotopically Labeled Internal Standards. [$^2H_3$]-*Trimethylpyrazine*. [$^2H_3$]-Trimethylpyrazine was synthesized according to a method reported by Wagner et al. (*7*) with some modifications. A solution of 2,5-dimethylpyrazine (0.54 g, 5 mmol) was slowly dropped into a solution of [$^2H_3$]-methyllithium−lithium iodide complex in anhydrous diethyl ether (20 mL, 10 mmol) and was refluxed for 1 h. After cooling to room temperature, brine was added to the reaction mixture and the aqueous phase was extracted with diethyl ether (3 × 50 mL). The organic extracts were combined, dried over anhydrous Na_2SO_4, and, after filtration, concentrated to ∼15 mL. Isolation of the target compound was done by TLC on silica gel 60 as reported above. The purified extracts were combined and concentrated to ∼5 mL by means of a Vigreux column.

MS-EI, *m*/*z* (%) 125 (100), 42 (90), 126 (50); MS-CI, *m*/*z* (%) 126 (100), 127 (8).

[$^2H_3$]-*Methylpyrazine*. [$^2H_3$]-Methylpyrazine was synthesized as reported above for [$^2H_3$]-trimethylpyrazine, but starting from a solution of pyrazine in diethyl ether (0.4 g, 5 mmol) and [$^2H_3$]-methyllithium−lithium iodide complex in anhydrous diethyl ether (20 mL, 10 mmol). Isolation was performed as described above.

MS-EI, *m*/*z* (%) 97 (100), 40 (60), 70 (55), 53 (30), 69 (20), 98 (18); MS-CI, *m*/*z* (%) 98 (100), 99 (5).

The following isotopically labeled internal standards were synthesized according to the literature cited: [$^{13}C_4$]-2,3-butanedione (*9*); [$^{13}C_2$]-2,3-pentanedione and [$^2H_3$]-dimethylpyrazine (2,3-, 2,6-, and 2,5-isomers) (*10*); [$^2H_{2-5}$]-hexanal and [$^2H_2$]-(*E*,*E*)-2,4-nonadienal (*11*); [$^2H_{2-4}$]-1-octen-3-one (*12*); [$^2H_{2-5}$]-2-acetyl-1-pyrroline (*13*); [$^2H_6$]-dimethyl trisulfide (*14*); [$^2H_{2-7}$]-2-propionyl-1-pyrroline and [$^2H_{2-6}$]-2-acetyltetrahydropyridine (*15*); [$^2H_3$]-2-ethyl-3,6-dimethylpyrazine, [$^2H_3$]-2-ethyl-3,5-dimethylpyrazine, [$^2H_3$]-2,3-diethyl-5-methylpyrazine, [$^2H_4$]-2-acetyl-2-thiazoline, and [$^2H_3$]-2-methoxyphenol (*16*); [$^2H_3$]-3-isopropyl-2-methoxypyrazine (*17*); [$^2H_2$]-2-furfurylthiol and [$^2H_3$]-3-(methylthio)propanal (*18*); [$^2H_3$]-3-(*sec*-butyl)-2-methoxypyrazine (*19*); [$^2H_3$]-3-isobutyl-2-methoxypyrazine (*20*); [$^2H_2$]-(*E*)-2-nonenal, [$^2H_4$]-(*E*,*E*)-2,4-decadienal, and [$^2H_2$]-2-methylbutanal (*21*); [$^2H_2$]-(*E*)-2-decenal and [$^2H_2$]-(*Z*)-2-decenal (*22*); [$^2H_2$]-butanoic acid (*23*); [$^{13}C_2$]-phenylacetaldehyde (*24*); [$^2H_2$]-3-methylbutanoic acid (*25*); [$^2H_4$]-*trans*-4,5-epoxy-(*E*)-2-decenal (*26*); [$^{13}C_2$]-4-hydroxy-2,5-dimethyl-3(2*H*)-furanone (*27*); [$^{13}C_2$]-3-hydroxy-4,5-dimethyl-2(5*H*)-furanone (*28*); [$^2H_3$]-4-vinylphenol (*29*); [$^2H_3$]-4-vinyl-2-methoxyphenol and [$^2H_3$]-4-hydroxy-3-methoxybenzaldehyde (*30*); [$^2H_3$]-2-acetylpyrazine (*31*); and [$^2H_4$]-octanal (*32*).

Determination of the concentrations of the synthesized labeled compounds was performed as previously described (*33*).

[$^{13}C_2$]-Acetaldehyde, [$^{13}C_2$]-phenylacetic acid, and [$^2H_3$]-acetic acid were from Sigma-Aldrich. [$^2H_3$]-Methanethiol was synthesized prior to use, and its concentration was determined as described earlier (*25*).

Quantitation by Stable Isotope Dilution Assays (SIDA). Aliquots of the samples (5−150 g) (depending on the amounts of the analyte determined in preliminary experiments) were suspended in diethyl ether, and defined amounts of the isotopically labeled standards were added in ethereal solution. The amount of the solvent used for extraction was chosen as previously described (*3*). For extraction of the volatiles from raw or commercially available roasted peanuts, these were frozen in liquid nitrogen and ground by means of a commercial blender (Privileg, Fürth, Germany). The suspension was vigorously stirred at room temperature for 4 h to obtain equilibrium between the standard and the analyte. After extraction, the solid residues were filtered off and washed twice with the solvent, and the combined solvent extracts were dried over anhydrous Na_2SO_4 and finally submitted to a SAFE distillation to separate the nonvolatile compounds (*34*). The peanut oil was used for SAFE distillation after dilution with diethyl ether (1:2; v/v). The distillates obtained were concentrated to a final volume of ∼200 μL at 38 °C by means of a Vigreux column (60 cm × 1 cm) followed by microdistillation (*35*).

Quantitation of 2-Acetyltetrahydropyridine and 2-Acetyl-1-pyrroline. Freshly pan-roasted peanut meal (100 g) was suspended in water (600 mL), and, after the addition of the internal standards [$^2H_{2-6}$]-2-acetyltetrahydropyridine (3 μg) and [$^2H_{2-5}$]-2-acetyl-1-pyrroline (3 μg), the suspension was continuously steam-distilled and extracted with diethyl ether in an apparatus according to the method of Likens and Nickerson (*36*) for 2 h. The extract was dried over anhydrous Na_2SO_4, concentrated to ∼300 μL, and analyzed by two-dimensional gas chromatography−mass spectrometry.

High-Resolution Gas Chromatography−Mass Spectrometry (HRGC-MS). HRGC-MS was performed for the analysis of 2- and 3-methylbutanoic acid, acetic acid, and eight non-odor-active pyrazines (**Tables 1** and **2**). For this purpose, a Varian GC 3800 gas chromatograph (Varian, Darmstadt, Germany) was coupled to an ion trap mass spectrometer Saturn 2000 (Varian) in combination with the capillary column FFAP (30 m × 0.32 mm, 0.25 μm film thickness) (J&W Scientific, Folsom, CA) or a PTA-5 (30 m × 0.32 mm, 0.5 μm film thickness) (Supelco, Bellefonte, PA), respectively.

Monitoring of the selected ions for the aroma-active compounds (**Table 2**) was carried out in the MS-CI mode using methanol as the reactant gas. Samples were injected automatically by using a Combi PAL autosampler (CTC Analytics, Zwingen, Switzerland). The following temperature programs were used: FFAP (40 °C held for 2 min, then raised at 4 °C/min to 110 °C, at 6 °C/min to 180 °C, and finally at 15 °C/min to 230 °C) and PTA-5 (40 °C held for 2 min, then raised at 6 °C/min to 180 °C, and finally at 100 °C/min to 240 °C).

Quantitation of the Non-Odor-Active Pyrazines. Methylpyrazine, the three isomers of dimethylpyrazine, and 2-ethyl-5- and 2-ethyl-6-methylpyrazine were first separated on an FFAP capillary as described above. Because trimethylpyrazine and 2-ethyl-3-methylpyrazine coeluted as one peak on this stationary phase (**Figure 1A**), a new strategy was developed to determine the single abundances of both compounds. Among the stationary phases tested, the PTA-5 was the most successful in separating

Table 1. Mass Traces of Selected Non-Odor-Active Pyrazines and the Respective Labeled Isotopologues and Response Factors Used in Their Quantitation by Means of Stable Isotope Dilution Assays

		mass trace[a] (*m*/*z*)		
pyrazine	labeled standard	analyte	internal standard	response factor[b]
methylpyrazine	[$^2H_3$]-methylpyrazine	95	98	1.00
2,5-dimethylpyrazine	[$^2H_3$]-2,3-dimethylpyrazine	109	112	0.88
2,6-dimethylpyrazine	[$^2H_3$]-2,3-dimethylpyrazine	109	112	0.85
2,3-dimethylpyrazine	[$^2H_3$]-2,3-dimethylpyrazine	109	112	1.00
2-ethyl-5-methylpyrazine	[$^2H_3$]-trimethylpyrazine	123	126	0.84
2-ethyl-6-methylpyrazine	[$^2H_3$]-trimethylpyrazine	123	126	0.91
2-ethyl-3-methylpyrazine	[$^2H_3$]-trimethylpyrazine	123	126	1.00
trimethylpyrazine	[$^2H_3$]-trimethylpyrazine	123	126	0.99

[a] Mass trace obtained by MS-CI. [b] MS response factor.

Table 2. Isotopically Labeled Standards, Selected Ions, and Response Factors Used in the Stable Isotope Dilution Assays

		mass trace[a] (*m*/*z*)		response factor[b]
odorant	labeled standard	analyte	internal standard	
methanethiol[c]	[$^2H_3$]-methanethiol	49	52	0.99
2-methylbutanal	[$^2H_2$]-2-methylbutanal	87	89	0.99
3-methylbutanal	[$^2H_2$]-2-methylbutanal	87	89	0.97
2,3-butandione	[$^{13}C_4$]-2,3-butandione	87	91	0.93
2,3-pentandione	[$^{13}C_2$]-2,3-pentandione	101	103	0.97
hexanal	[$^2H_{2-5}$]-hexanal	101	103−106	0.88
1-octen-3-one	[$^2H_{2-4}$]-1-octen-3-one	127	129−131	0.77
octanal	[$^2H_4$]-octanal	129	133	1.00
2-acetyl-1-pyrroline	[$^2H_{2-5}$]-2-acetyl-1-pyrroline	112	114−117	0.93
dimethyl trisulfide	[$^2H_6$]-dimethyl trisulfide	127	133	0.99
2-propionyl-1-pyrroline	[$^2H_{2-7}$]-2-propionyl-1-pyrroline	126	128−133	0.98
2-ethyl-3,6-dimethylpyrazine	[$^2H_3$]-2-ethyl-3,6-dimethylpyrazine	137	140	0.71
2-ethyl-3,5-dimethylpyrazine	[$^2H_3$]-2-ethyl-3,5-dimethylpyrazine	137	140	0.87
3-isopropyl-2-methoxypyrazine	[$^2H_3$]-3-isopropyl-2-methoxypyrazine	153	156	0.85
furfurylthiol	[$^2H_2$]-2-furfurylthiol	115	117	1.00
3-(methylthio)propanal	[$^2H_3$]-3-(methylthio)propanal	105	108	0.90
acetic acid[d]	[$^2H_3$]-acetic acid	61	64	0.75
2,3-diethyl-5-methylpyrazine	[$^2H_3$]-2,3-diethyl-5-methylpyrazine	151	154	0.72
3-(*sec*-butyl)-2-methoxypyrazine	[$^2H_3$]-3-(*sec*-butyl)-2-methoxypyrazine	167	170	0.91
3-isobutyl-2-methoxypyrazine	[$^2H_3$]-3-isobutyl-2-methoxypyrazine	167	170	0.91
(*Z*)-2-nonenal	[$^2H_2$]-(*E*)-2-nonenal	141	143	0.99
(*E*)-2-nonenal	[$^2H_2$]-(*E*)-2-nonenal	141	143	0.99
2-acetyltetrahydropyridine	[$^2H_{2-6}$]-2-acetyltetrahydropyridine	126	128−132	0.99
2-acetylpyrazine	[$^2H_3$]-2-acetylpyrazine	123	126	1.00
(*Z*)-2-decenal	[$^2H_2$]-(*Z*)-2-decenal	155	157	0.88
(*E*)-2-decenal	[$^2H_2$]-(*E*)-2-decenal	155	157	0.90
butanoic acid	[$^2H_2$]-butanoic acid	89	91	0.86
phenylacetaldehyde	[$^{13}C_2$]-phenylacetaldehyde	121	123	1.00
2-methylbutanoic acid[d,e]	[$^2H_2$]-3-methylbutanoic acid	103	105	0.94
3-methylbutanoic acid[d,e]	[$^2H_2$]-3-methylbutanoic acid	103	105	0.94
(*E*,*E*)-2,4-nonadienal	[$^2H_2$]-(*E*,*E*)-2,4-nonadienal	139	141	0.66
2-acetyl-2-thiazoline	[$^2H_4$]-2-acetyl-2-thiazoline	130	134	0.86
(*E*,*E*)-2,4-decadienal	[$^2H_{3-5}$]-(*E*,*E*)-2,4-decadienal	153	156−158	0.84
2-methoxyphenol	[$^2H_3$]-2-methoxyphenol	125	128	1.00
trans-4,5-epoxy-(*E*)-2-decenal	[$^2H_4$]-*trans*-4,5-epoxy-(*E*)-2-decenal	139	143	0.95
4-hydroxy-2,5-dimethyl-3(2*H*)-furanone	[$^{13}C_2$]-4-hydroxy-2,5-dimethyl-3(2*H*)-furanone	129	131	0.93
3-hydroxy-4,5-dimethyl-2(5H)-furanone	[$^{13}C_2$]-3-hydroxy-4,5-dimethyl-2(5H)-furanone	129	131	0.99
4-vinyl-2-methoxyphenol	[$^2H_3$]- 4-vinyl-2-methoxyphenol	151	154	0.97
4-vinylphenol	[$^2H_3$]-4-vinylphenol	121	124	0.88
4-hydroxy-3-methoxybenzaldehyde	[$^2H_3$]-4-hydroxy-3-methoxybenzaldehyde	153	156	0.98
phenylacetic acid	[$^{13}C_2$]-phenylacetic acid	137	139	0.80

[a] Mass traces used for peak area evaluation of analyte and standard, respectively (MS-CI). [b] MS response factor. [c] Quantitation was performed by headspace-GC-MS. [d] Quantitation was performed by GC-MS. [e] Differentiation of 2- and 3-methylbutanoic acid was performed as described in (*33*).

2-ethyl-3-methylpyrazine from all other pyrazines (**Figure 1B**). The amount of trimethylpyrazine was, thus, calculated as the difference between the sum of the concentrations of trimethylpyrazine and 2-ethyl-3-methylpyrazine determined on the FFAP and the concentration of 2-ethyl-3-methylpyrazine singly determined on the PTA-5 column.

Two-Dimensional Gas Chromatography−Mass Spectrometry (2D-HRGC-MS). With the exceptions of acetic acid, 2- and 3-methylbutanoic acid, and methanethiol, the 41 compounds listed in **Table 2** were quantitated by means of a 2D-HRGC-MS system using the FFAP column in the first dimension, and either an OV-1701 column (30 m × 0.32 mm, 0.25 μm

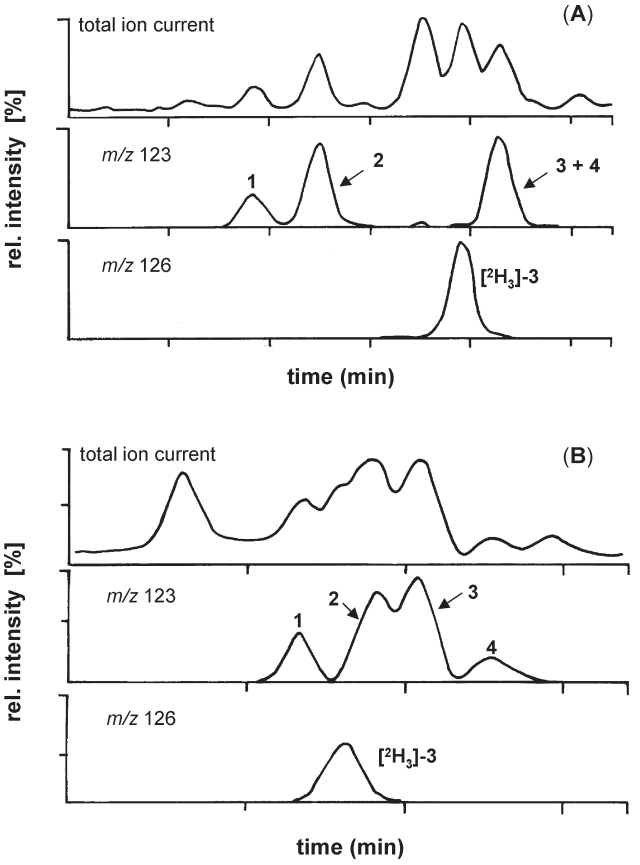

Figure 1. Mass chromatograms of 2-ethyl-5-methylpyrazine (**1**), 2-ethyl-6-methylpyrazine (**2**), trimethylpyrazine (**3**), and 2-ethyl-3-methylpyrazine (**4**; both isomers in sum) on an FFAP capillary column (**A**) as well as quantitation of 2-ethyl-3-methylpyrazine (**4**) on a PTA-5 capillary column (**B**) by means of stable isotope dilution assay using [$^2H_3$]-trimethylpyrazine ([$^2H_3$]-**3**) as internal standard.

film thickness) (J&W Scientific) or the PTA-5 column in the second dimension. The two-dimensional HRGC-MS system consisted of a Trace GC (Thermo Scientific, Dreieich, Germany) coupled to a GC 3800 by means of an uncoated and deactivated fused silica transfer line (0.32 mm i.d,) held at 250 °C and, finally, to an ion trap mass spectrometer Saturn 2100 (Varian). Methanol was used as the reactant gas. Heart-cuts were done by means of the moving capillary stream switching system (MCSS) (Fisons Instruments, Mainz, Germany), and selected portions of the eluate of the first dimension (FFAP column) were transferred to the second dimension (OV-1701 or PTA-5, respectively). The application of the samples and the temperature programs were performed as described above for the GC-MS system; for the OV-1701 column the same temperature program was used as for the PTA-5 column.

For the analysis of 2-acetyltetrahydropyridine, the PTA-5 capillary column was used in the second GC.

Quantitation of Methanethiol. Methanethiol was determined by SIDA of static headspace samples. For this purpose, the ground, freshly roasted peanut meal (20 g) was filled in headspace vials (volume = 120 mL) and sealed with an airtight septum. A defined volume of the labeled compound (corresponding to a total amount of 1.4 μg of [$^2H_3$]-methanethiol) was injected into the headspace vials with a gastight syringe. After equilibration (40 °C; 30 min) with permanent shaking, aliquots of the headspace (5 mL) were withdrawn and analyzed by means of headspace GC-MS as previously described by Guth and Grosch for stewed beef (*25*).

Determination of MS Calibration Factors. Calibration factors were determined by analyzing mixtures of known amounts of the labeled and unlabeled compounds in three different mass ratios (3:1, 1:1, 1:3) by GC-MS. The factors calculated are summarized in **Tables 1** and **2**.

Determination of Odor Thresholds. For the calculation of odor activity values (OAVs), odor thresholds in oil were used. The odor thresholds were determined in vegetable oil following a recently published protocol (*37*).

Aroma Profile Analysis. The sensory evaluation of the aroma models and the pan-roasted peanut meal was performed by 10 assessors recruited from the German Research Center for Food Chemistry. The assessors were regularly trained in orthonasal odor perception as previously described (*37*). Characteristic aroma descriptors, determined in preliminary sensory experiments, were used for the evaluation. Each descriptor was represented by the odor of a reference compound dissolved in sunflower oil at a concentration 100-fold above the respective odor threshold. The aroma models and the freshly, pan-roasted peanut meal were evaluated by rating the overall intensity on the basis of a seven-point linear scale (0, 0.5, 1.0, 1.5, ..., with 0 = not perceivable, 0.5 = weak, 1 = weakly perceivable, 1.5 = perceivable, 2 = moderately perceivable, and 3 = strongly perceivable). The following compounds given in parentheses were chosen for the respective odor attributes: popcorn-like, roasty (2-acetyl-1-pyrroline); buttery (2,3-butandione); fatty, deep-fried ((*E*,*E*)-2,4-decadienal); earthy (2,3-diethyl-5-methylpyrazine); metallic (*trans*-4,5-epoxy-(*E*)-2-decenal); sulfury, burnt (2-furfurylthiol); seasoning-like, spicy (3-hydroxy-4,5-dimethyl-2-(5*H*)-furanone, sotolone); caramel-like (4-hydroxy-2,5-dimethyl-3-(2*H*)-furanone); earthy, pea-like (3-isopropyl-2-methoxypyrazine); sulfury (methanethiol); malty (3-methylbutanal); cooked potato-like (3-(methylthio)propanal); honey-like (phenylacetaldehyde); and clove-like, smoky (4-vinyl-2-methoxyphenol).

Aroma Recombination Experiments. For aroma recombination, the following aroma models were prepared on the basis of the quantitative data obtained for the roasted peanut meal: To simulate the peanut matrix, the model system consisted of a mixture of peanut solids (starch and protein) and sunflower oil, in which the aroma-active compounds were dissolved in the concentrations analyzed in the respective sample. A weight ratio of 48:52 between oil and protein/starch (solids) was chosen, because this represents the ratio analyzed in the pan-roasted peanut meal. For preparation of the protein/starch matrix, raw peanuts were subsequently extracted with the following solvents of different polarities: pentane, diethyl ether, and dichloromethane (24 h each). The residue was suspended in water, stirred for 30 min, and finally freeze-dried. After the extraction/freeze-drying process had been repeated, an odorless powder was obtained.

The following mixture of 25 aroma compounds was prepared in sunflower oil (48 g) for the aroma **model I**: 4-vinylphenol (780 μg), acetic acid (300 μg), phenylacetic acid (240 μg), phenylacetaldehyde (240 μg), 4-vinyl-2-methoxyphenol (200 μg), 4-hydroxy-2,5-dimethyl-3(2*H*)-furanone (200 μg), 2-methylbutanal (97 μg), 3-methylbutanal (64 μg), 2-ethyl-3,6-dimethylpyrazine (20 μg), 2,3-butandione (9.0 μg), 2,3-pentanedione (8.3 μg), 3-(methylthio)propanal (4.0 μg), 2-ethyl-3,5-dimethylpyrazine (2.3 μg), 2,3-diethyl-5-methylpyrazine (1.3 μg), 2-acetyl-1-pyrroline (0.9 μg), 2-furfurylthiol (0.9 μg), 2-acetyltetrahydropyridine (0.7 μg), 2-acetylpyrazine (0.40 μg), 2-methoxyphenol (0.40 μg), 2-propionyl-1-pyrroline (0.40 μg), 3-hydroxy-4,5-dimethyl-2(5*H*)-furanone (0.40 μg), 3-isopropyl-2-methoxypyrazine (0.25 μg), 2-acetyl-2-thiazoline (0.20 μg), 3-isobutyl-2-methoxypyrazine (0.08 μg), and 3-(*sec*-butyl)-2-methoxypyrazine (0.025 μg). After addition of the deodorized peanut solids (52 g), the mixture was vigorously shaken and left for 1 h for equilibration.

The mixture contained methanethiol and all odorants showing OAVs >1 (**Table 7**), except six aldehydes derived from lipid peroxidation. In addition, five compounds were used showing OAVs <1, but might show additive effects due to their odor qualities, for example, 2-acetylpyrazine (roasty), 2-methoxyphenol and 4-vinylphenol (phenolic), and 3-isobutyl- and 3-(*sec*-butyl)-2-methoxypyrazine (earthy).

For the preparation of aroma **model II**, the following seven aldehydes were additionally added to model I: (*E*,*E*)-2,4-decadienal (87 μg), hexanal (84 μg), (*E*)-2-decenal (+(*Z*)-2-decenal) (27 μg), *trans*-4,5-epoxy-(*E*)-2-decenal (9.7 μg), octanal (14 μg), (*E*)-2-nonenal (+(*Z*)-2-nonenal) (6 μg), and (*E*,*E*)-2,4-nonadienal (3.2 μg). Furthermore, methanethiol (11 μg) was added.

Addition Experiment. To evaluate possible additive effects of eight non-odor-active pyrazines, previously not detected by GC−olfactometry (GC-O) (*3*) (**Table 1**), to the overall aroma of roasted peanuts, a triangle test (*37*) was carried out. For this purpose, the pyrazines were added in the concentrations analyzed in the roasted peanut meal to aroma model II, obtaining aroma model III. This model was evaluated in comparison to model II (without the added pyrazines) in a triangle test, and the assessors were asked to identify the sample that differed from the other two samples. The statistical significance was calculated as described earlier (*38*).

Table 3. Concentrations of 26 Important Aroma Compounds in Raw Peanuts[a]

aroma compound	concn[b] (μg/kg)
acetic acid	9176
hexanal	2734
phenylacetic acid	109
phenylacetaldehyde	103
3-methylbutanoic acid	55
butanoic acid	37
2-methylbutanoic acid	21
4-vinyl-2-methoxyphenol	21
(*E*)-2-nonenal	19
trans-4,5-epoxy-(*E*)-2-decenal	18
2-methylbutanal	17
4-vinylphenol	16
4-hydroxy-2,5-dimethyl-3(2*H*)-furanone	15
3-methylbutanal	14
3-(methylthio)propanal	8.6
3-isopropyl-2-methoxypyrazine	6.2
2,3-pentanedione	6.1
(*E*,*E*)-2,4-decadienal	5.8
(*E*)-2-decenal	5.1
(*E*,*E*)-2,4-nonadienal	2.4
2-methoxyphenol	1.2
3-hydroxy-4,5-dimethyl-2(5*H*)-furanone	1.2
(*Z*)-2-nonenal	0.90
3-(*sec*-butyl)-2-methoxypyrazine	0.64
3-isobutyl-2-methoxypyrazine	0.42
1-octen-3-one	0.22

[a] Compounds were selected on the basis of previous GC-O results (*3*). [b] Mean values of triplicates, differing not more than ±10%.

RESULTS AND DISCUSSION

Quantitation of the Odorants in the Raw Peanuts and the Pan-Roasted Peanut Meal Produced Therefrom. Twenty six important odorants previously identified in raw peanuts and 38 key aroma compounds previously characterized in pan-roasted peanut meal (*3*) were quantitated by means of SIDAs.

The results obtained for the raw peanuts showed that acetic acid was the most abundant odorant (9176 μg/kg) (**Table 3**), followed by hexanal (2734 μg/kg), phenylacetic acid (109 μg/kg), phenylacetaldehyde (103 μg/kg), 3-methylbutanoic acid (55 μg/kg), butanoic acid (37 μg/kg), and 2-methylbutanoic acid (21 μg/kg). Many compounds, however, were present in only trace amounts, for example, 3-isopropyl-2-methoxypyrazine (6.2 μg/kg), 3-(*sec*-butyl)-2-methoxypyrazine (0.64 μg/kg), and 3-isobutyl-2-methoxypyrazine (0.42 μg/kg) as well as 1-octen-3-one (0.22 μg/kg).

Quantitation of the aroma-active compounds in the pan-roasted peanut meal revealed quite high concentrations for 4-vinylphenol (7814 μg/kg) (**Table 4**), acetic acid (3035 μg/kg), phenylacetic acid (2363 μg/kg), and phenylacetaldehyde (2427 μg/kg). In addition, further compounds were found in high concentrations, for example, 4-vinyl-2-methoxypyrazine, 4-hydroxy-2,5-dimethyl-3(2*H*)-furanone, 2-methylbutanal, (*E*,*E*)-2,4-decadienal, hexanal, and 3-methylbutanal. The pyrazines 2-ethyl-3,6- and 2-ethyl-3,5-dimethylpyrazine as well as 2,3-diethyl-5-methylpyrazine were found in concentrations of 196, 23, and 13 μg/kg, respectively. These compounds were quantitated only in the pan-roasted peanut meal because they had not been perceived during GC-O of raw peanuts (*3*). Among the roasty (popcorn-like) smelling compounds, 2-acetyl-1-pyrroline was found with the highest concentration of 8.9 μg/kg, whereas the other roasty-smelling odorants occurred in lower amounts: 2-acetylpyrazine (4.2 μg/kg), 2-propionyl-1-pyrroline (3.7 μg/kg), and 2-acetyl-2-thiazoline (1.9 μg/kg).

Obviously due to a reaction with other volatiles during concentration of the SAFE distillate, the labile 2-acetyltetrahydropyridine was difficult to quantitate in the SAFE distillate. Therefore, both 2-acetyl-1-pyrroline and 2-acetyltetrahydropyridine were quantified in a separate experiment using a simultaneous steam distillation extraction (SDE). The concentrations amounted to 16.8 and 13.0 μg/kg, respectively. In comparison to the concentrations determined in the SAFE distillate, the amount of 2-acetyl-1-pyrroline was much higher. Because both odorants have previously been identified as degradation products of the amino acid proline when heated in the presence of carbohydrates (*39*), an additional formation during SDE could be expected. By comparing the amounts of 2-acetyl-1-pyrroline determined in an SDE extract (16.8 μg/kg) with those found by the more careful SAFE distillation (8.9 μg/kg), it was assumed that also the amount of 2-acetyltetrahydropyridine was 47% lower as compared to the concentration determined in the SDE extract (13.9 μg/kg). Thus, the concentration of 2-acetyltetrahydropyridine in the peanut meal was estimated to be 7.4 μg/kg.

To indicate which odorants are formed to a remarkable extent during roasting, the concentrations in raw and roasted peanuts were compared. It became evident that only a certain set of odorants (**Table 5**) was clearly increased during roasting. In particular, the concentrations of the Strecker aldehydes 2- and 3-methylbutanal as well as of phenylacetaldehyde considerably increased during roasting, whereas the concentration of 3-(methylthio)propanal

Table 4. Concentrations of 38 Important Aroma Compounds in Pan-Roasted Peanut Meal[a]

aroma compound	concn[b] (μg/kg)
4-vinylphenol	7814
acetic acid	3035
phenylacetic acid	2363
phenylacetaldehyde	2427
4-vinyl-2-methoxyphenol	2017
4-hydroxy-2,5-dimethyl-3(2*H*)-furanone	1953
2-methylbutanal	971
(*E*,*E*)-2,4-decadienal	868
hexanal	838
3-methylbutanal	637
(*E*)-2-decenal	270
2-ethyl-3,6-dimethylpyrazine	196
octanal	143
methanethiol	113
trans-4,5-epoxy-(*E*)-2-decenal	96
2,3-butanedione	90
2,3-pentanedione	83
(*E*)-2-nonenal	60
3-(methylthio)propanal	40
4-hydroxy-3-methoxybenzaldehyde	34
(*E*,*E*)-2,4-nonadienal	32
2-ethyl-3,5-dimethylpyrazine	23
(*Z*)-2-nonenal	14
2,3-diethyl-5-methylpyrazine	13
(*Z*)-2-decenal	12
2-acetyl-1-pyrroline	8.9
2-furfurylthiol	8.8
2-acetyltetrahydropyridine	7.4
2-acetylpyrazine	4.2
2-methoxyphenol	4.1
2-propionyl-1-pyrroline	3.7
3-hydroxy-4,5-dimethyl-3(2*H*)-furanone	3.7
1-octen-3-one	1.3
3-isopropyl-2-methoxypyrazine	2.4
2-acetyl-2-thiazoline	1.9
dimethyl trisulfide	1.4
3-(*sec*-butyl)-2-methoxypyrazine	0.28
3-isobutyl-2-methoxypyrazine	0.76

[a] Compounds were selected on the basis of previous GC-O results (*3*). [b] Mean values of triplicates, differing not more than ±10%.

Table 5. Selected Aroma Compounds Showing Clear Changes in Their Concentrations between Raw Peanuts (RP) and the Roasted Peanut Meal (RPM) Produced Therefrom

odorant	concn[a] (μg/kg) RP	RPM
phenylacetaldehyde	103	2427
3-methylbutanal	17	637
2-methylbutanal	14	971
3-(methylthio)propanal	8.6	39
4-hydroxy-2,5-dimethyl-3(2*H*)-furanone	15	1953
2,3-pentanedione	6.1	83
trans-4,5-epoxy-(*E*)-2-decenal	18	96
(*E*,*E*)-2,4-decadienal	5.8	868
(*E*,*E*)-2,4-nonadienal	2.4	32
acetic acid	9176	3035
hexanal	2734	838
3-isopropyl-2-methoxypyrazine	6.2	2.4

[a] Mean values of triplicates, differing not more than ±10%.

was only moderately increased. It is known from model studies (*40*) that these aldehydes are generated from their parent free amino acids when these are reacted with α-dicarbonyl compounds, which may stem from carbohydrate degradation.

4-Hydroxy-2,5-dimethyl-3(2*H*)-furanone and 2,3-pentanedione were both much increased after roasting. From various model experiments it is known that 4-hydroxy-2,5-dimethyl-3(2*H*)-furanone is either formed by dehydration of reducing monosaccharides, preferably fructose-1,6-biphosphate (*41*), or formed in a reaction of 2-hydroxyacetone and 2-oxopropanal, two well-known carbohydrate degradation products (*42*).

2,3-Pentanedione might also be generated from carbohydrate degradation, but currently its origin is not yet clarified. By application of the so-called Carbon Modul Labeling (CAMOLA) approach, it was previously found that the homologous 2,3-butanedione can be formed by an aldol condensation of formaldehyde and hydroxypropanone (*43*). A similar reaction of acetaldehyde (formed by a Strecker degradation of alanine) and hydroxypropanone (probably formed by a degradation of carbohydrates) may lead to the generation of 2,3-pentanedione.

Furthermore, an increase in the concentrations of three lipid peroxidation products could be observed. It was much pronounced for (*E*,*E*)-2,4-decadienal, which is a well-known degradation product of linoleic acid formed via the 9-hydroperoxide, and can subsequently be oxidized into *trans*-4,5-epoxy-(*E*)-2-decenal (*44*). In contrast, acetic acid, hexanal, and 3-isopropyl-2-methoxypyrazine decreased after roasting.

Calculation of OAVs. To get a deeper insight into the contribution of the quantitated odorants to the overall aroma of raw and roasted peanuts, the OAVs (ratio of concentration to odor threshold) were calculated for each odorant. Because peanuts contain a high amount of fat (48%), sunflower oil was chosen as an appropriate matrix for threshold determination. For most compounds, odor thresholds, previously determined by our group, were used (*37*, *45*).

The calculation showed that in raw peanuts only 11 of the 26 compounds quantitated were present in concentrations above their odor thresholds (**Table 6**). Among them, 3-isopropyl-2-methoxypyrazine showed the highest OAV of 90, followed by acetic acid, 3-(methylthio)propanal, 2,3-pentanedione, and hexanal, suggesting a major impact of these odorants on the overall aroma of raw peanuts.

In the pan-roasted peanut meal, 27 of the 38 compounds quantitated showed OAV ≥ 1 (**Table 7**). By far the highest OAV was calculated for methanethiol followed by 2,3-pentanedione and

Table 6. Orthonasal Odor Thresholds (OTs) and Odor Activity Values (OAVs) of Key Odorants in Raw Peanuts

aroma compound	OAV[a]	OT[b] (μg/kg)	ref[c]
3-isopropyl-2-methoxypyrazine	90	0.07	*22*
acetic acid	74	124	*46*
3-(methylthio)propanal	43	0.2	*47*
2,3-pentanedione	21	0.3	*48*
hexanal	10	276	*46*
3-methylbutanal	3	5.4	*47*
3-methylbutanoic acid	3	22	*46*
2-methylbutanal	2	10	*49*
(*E*,*E*)-2,4-nonadienal	2	1.5	*48*
phenylacetaldehyde	1	83[d]	
trans-4,5-epoxy-(*E*)-2-decenal	1	25[d]	

[a] OAV calculated by dividing the concentration (**Table 3**) by the odor threshold. [b] Odor threshold determined in sunflower oil. [c] Reference for odor threshold. [d] Unpublished data.

the Strecker aldehydes 3-(methylthio)propanal, 3-methylbutanal, and 2-methylbutanal. 2-Acetyl-1-pyrroline can be suggested as the main contributor to the roasty (popcorn-like) note of roasted peanuts due to its OAV of 89, whereas the other roasty-smelling compounds, such as 2-propionyl-1-pyrroline, 2-acetyltetrahydropyridine, and 2-acetyl-2-thiazoline, showed lower OAVs. However, because the odor qualities of these four compounds were similar, additive effects on the flavor intensity can be assumed. Among the pyrazines, 3-isopropyl-2-methoxypyrazine showed the highest OAV of 35 followed by 2,3-diethyl-5-methylpyrazine. By contrast, 2-ethyl-3,5-dimethylpyrazine and 2-ethyl-3,6-dimethylpyrazine showed much lower OAVs of 3 and 1, respectively.

Aroma Recombination Studies. The calculation of OAVs shows the aroma potency of a single compound in a given matrix, but this approach is not able to address interactions occurring at the human odorant receptors with other odorants when presented together. To address this challenge, aroma recombination studies were performed.

The first aroma model (model I) containing most of the key aroma compounds quantitated in the roasted peanut material, but from which all odorants eliciting fatty and green odors were left out, revealed an intense roasty aroma somewhat resembling that of rye bread crust (**Figure 2A**), and the panel indeed described the overall aroma as roasty and bread-crust like, respectively.

By comparison of the overall odor of this model with a sample of freshly roasted peanuts, clear differences could be detected. Therefore, a new attempt was made to mimic the aroma of freshly roasted peanuts. For this purpose, model I was spiked with the seven lipid peroxidation compounds quantitated (**Table 3**) and, additionally, with methanethiol. In this model assigned as model II, the sensory panel found a much better agreement of the overall odor in comparison with the real peanut sample (**Figure 2B**), and the sensory panel could clearly recognize the aroma of freshly roasted peanuts in the recombinate. Thus, methanethiol and the lipid peroxidation products were proven to be of great importance for the overall aroma of roasted peanuts. Because no key odorant singly elicited an odor resembling the roasted peanut aroma, it can be suggested that a unique mixture of the key aroma compounds in their natural concentration conveys the impression of roasted peanuts. This mixture can be assigned as the combinatorial code of peanut aroma able to interact with the right receptors in the human olfactory bulb.

Quantitation of Eight Non-Odor-Active Pyrazines in Pan-Roasted Peanut Meal. In the literature, it is often discussed that the entire group of nutty-smelling pyrazines contributes to the overall aroma of nuts and to roasted peanuts in particular. To prove the contribution of some further pyrazines previously not

Table 7. Odor Activity Values (OAVs) of 38 Aroma Compounds in Pan-Roasted Peanut Meal and Their Orthonasal Odor Thresholds (OTs)

aroma compound	OT[a] (μg/kg)	OAV[b]	ref[c]
methanethiol	0.06	1889	*12*
2,3-pentanedione	0.3	286	*48*
3-(methylthio)propanal	0.2	200	*47*
3-methylbutanal	5.4	118	*47*
2-methylbutanal	10	97	*49*
2-acetyl-1-pyrroline	0.1	89	*54*
4-hydroxy-2,5-dimethyl-3(2*H*)-furanone	25	78	*47*
4-vinyl-2-methoxyphenol	50	40	*54*
2-propionyl-1-pyrroline	0.1	37	*48*
3-isopropyl-2-methoxypyrazine	0.07	35	*22*
phenylacetaldehyde	83[d]	29	
2,3-diethyl-5-methylpyrazine	0.5	27	*49*
acetic acid	124	24	*46*
2-furfurylthiol	0.4	22	*54*
(*E*,*E*)-2,4-nonadienal	1.5	22	*48*
2,3-butandione	10	10	*48*
phenylacetic acid	360	7	*55*
2-acetyltetrahydropyridine	1.2[d]	6	
(*E*,*E*)-2,4-decadienal	180	5	*56*
trans-4,5-epoxy-(*E*)-2-decenal	25[d]	4	
hexanal	276	3	*46*
octanal	51.5	3	*46*
(*Z*)-2-nonenal	4.5	3	*21*
2-ethyl-3,5-dimethylpyrazine	7.5[d]	3	
3-hydroxy-4,5-dimethyl-3(2*H*)-furanone	1.6[d]	2	
2-acetyl-2-thiazoline	1.8	1	*50*
2-ethyl-3,6-dimethylpyrazine	166[d]	1	
dimethyl trisulfide	2.3	<1	*12*
3-(*sec*-butyl)-2-methoxypyrazine	0.5	<1	*47*
4-hydroxy-3-methoxybenzaldehyde	181	<1	*22*
(*Z*)-2-decenal	50	<1	*48*
2-acetylpyrazine	10	<1	*54*
2-methoxyphenol	16	<1	*46*
1-octen-3-one	10	<1	*21*
3-isobutyl-2-methoxypyrazine	0.8	<1	*49*
(*E*)-2-decenal	3220	<1	*48*
(*E*)-2-nonenal	900	<1	*21*
4-vinylphenol	14720[d]	<1	

[a] Odor threshold determined in sunflower oil. [b] Odor activity value calculated by dividing the concentration (**Table 3**) by the odor threshold. [c] Reference used. [d] Unpublished data.

detected among the odor-active pyrazines by aroma extract dilution analysis (AEDA) (*3*) to the overall aroma of roasted peanuts, eight pyrazines were quantitated by means of SIDA in the pan-roasted peanut meal. Among them, 2,5-dimethylpyrazine (760 μg/kg) and methylpyrazine (442 μg/kg) were found with the highest amounts (**Table 8**). Trimethylpyrazine and 2-ethyl-6-methylpyrazine were analyzed in concentrations of 262 and 210 μg/kg, respectively. The other pyrazines were detected in somewhat lower concentrations. Because the odor thresholds of these compounds in oil are extremely high, for example, 27000 μg/kg for 2-methylpyrazine (*50*), 8000 μg/kg for 2,6-dimethylpyrazine (*51*), 2600 μg/kg for 2,5-dimethylpyrazine (*52*), and 297 μg/kg for trimethylpyrazine (*53*), it could be assumed that these compounds would not contribute to the overall aroma of roasted peanuts. Despite this, possible additive effects caused by these compounds cannot be excluded. Therefore, the role of these pyrazines in the overall roasted peanut flavor was investigated by means of aroma recombination studies.

For this purpose, a third sensory experiment was carried out. Model II, prepared without the addition of the eight pyrazines and representing the overall peanut aroma, was used as reference. Its overall sensory impression was compared to that of model III, to which all eight pyrazines were added. The results showed that the sensory panel was not able to detect a difference between

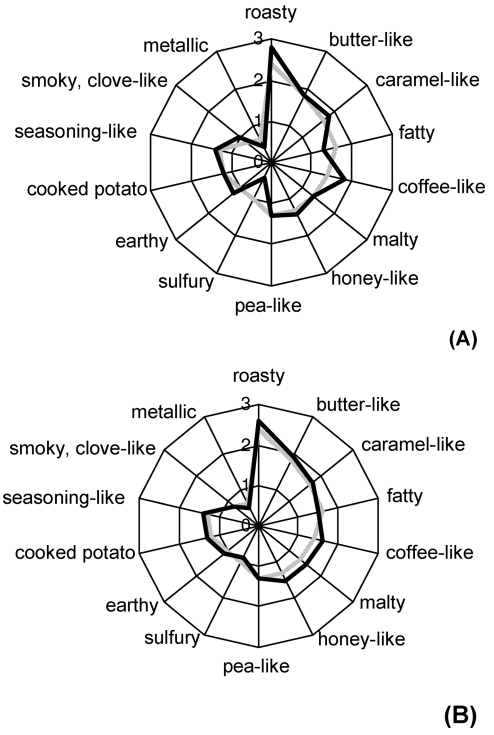

Figure 2. (**A**) Aroma profile analysis of pan-roasted peanut meal (gray line) and aroma model I (black line). (**B**) Aroma profile analysis of pan-roasted peanut meal (gray line) and aroma model II (black line).

Table 8. Concentrations of Non-Odor-Active Pyrazines in Pan-Roasted Peanut Meal

pyrazine	concn[a] (μg/kg)
2,5-dimethylpyrazine	760
methylpyrazine	442
trimethylpyrazine	262
2-ethyl-6-methylpyrazine	210
2,6-dimethylpyrazine	89
2-ethyl-5-methylpyrazine	81
2,3-dimethylpyrazine	69
2-ethyl-3-methylpyrazine	40

[a] Mean values of triplicates, differing not more than ±10%.

models II and III, because only 5 of 13 panelists (significance value α (%) > 5.0) were able to recognize the deviating mixture (data not shown). This result clearly shows that the pyrazines, which were not detectable by GC-O (*3*), do not contribute to the overall aroma of the roasted peanuts, and, thus, additive effects could be ruled out for the group of these pyrazines.

Quantitation of Selected Odorants in Commercial Peanut Products. The model procedure used for roasting of the peanuts may result in concentrations of odorants differing from those of intact roasted peanuts or commercial peanut products, respectively. To get a first insight into the differences in the concentrations as compared to commercial products, 13 key aroma compounds detected in the roasted peanut meal were selected and quantitated in intact roasted Virginia peanuts, a commercial peanut butter, and a commercial peanut oil processed from roasted peanuts, respectively.

In general, the data obtained for the Virginia peanuts (VP; **Table 9**) were in good correlation with the results of the pan-roasted peanuts meal (PRP; **Table 9**), although some differences could be observed. For example, the higher concentrations of the amino acid degradation products 2- and 3-methylbutanal as well as phenylacetaldehyde in the pan-roasted material are undoubtedly

Table 9. Comparison of the Concentrations of Selected Odorants in the Pan-Roasted Peanut Meal (PRP) with Commercial Peanut Products: Virginia Peanuts (VP), Peanut Butter (PB), and Peanut Oil (PO)

odorant	concn[a] (μg/kg)			
	PRP	VP[b]	PB	PO[c]
(*E*,*E*)-2,4-decadienal	868	649	909	257
hexanal	838	273	506	1778
(*E*,*E*)-2,4-nonadienal	32	81	17	10
phenylacetaldehyde	2427	943	397	355
2-methylbutanal	971	123	715	127
3-methylbutanal	637	57	204	82
4-hydroxy-2,5-dimethyl-3(2*H*)-furanone	1953	113	62	52
2,3-pentanedione	83	44	42	11
2-acetyl-1-pyrroline	8.9	5.2	11	0.1
2-ethyl-3,6-dimethylpyrazine	196	141	557	57
2-ethyl-3,5-dimethylpyrazine	24	65	115	28
2,3-diethyl-5-methylpyrazine	13	13	38	4.8
3-isopropyl-2-methoxypyrazine	2.4	5.4	3.1	0.5

[a] Mean values of triplicates, differing not more than ±10%. [b] Commercial peanuts roasted in shell. [c] Produced from roasted peanuts.

caused by the higher temperatures in the pan-roasting process. The same trend was found for the caramel-like-smelling 4-hydroxy-2,5-dimethyl-3(2*H*)-furanone, the roasty 2-acetyl-1-pyrroline, and the buttery 2,3-pentanedione. The pyrazines, however, were quite similar in their concentrations, although differences may also be caused by the different varieties used.

In the peanut butter (PB; **Table 9**), the highest amount of alkylpyrazines was measured, which was by a factor of ~3 higher than in the commercially roasted peanuts or the pan-roasted nuts. In the peanut oil (PO; **Table 9**), in particular, 2-acetyl-1-pyrroline and the Strecker aldehydes were low, whereas hexanal was highest.

The somewhat higher concentrations of the lipid peroxidation products (*E*,*E*)-2,4-decadienal and (*E*,*E*)-2,4-nonadienal in the roasted peanut meal might be a result of the stronger roasting procedure in the pan compared to the industrial in-shell roasting procedure. Nevertheless, the sensory evaluation of the aroma of the pan-roasted peanut meal and industrially roasted Virginia peanuts showed great similarities, and no fatty off-note could be observed in the pan-roasted peanut meal (data not shown).

In peanut butter, the concentrations of lipid-derived compounds were quite similar to those in the pan-roasted material (PRP). However, the Strecker aldehydes as well as the caramel-like-smelling 4-hydroxy-2,5-dimethyl-3(2*H*)-furanone were much lower than in the PRP.

In peanut oil, the concentrations of most odorants, except hexanal, were significantly lower than in the other samples. Whereas (*E*,*E*)-2,4-decadienal and (*E*,*E*)-2,4-nonadienal seemed to be partially removed after the refining step, it may be postulated that hexanal must have been newly generated during storage. However, no green off-flavor was perceivable in this sample.

2-Acetyl-1-pyrroline, 2-ethyl-3,5- and 2-ethyl-3,6-dimethylpyrazine, and 2,3-diethyl-5-methylpyrazine as well as the Strecker aldehydes 2- and 3-methylbutanal were found in the highest abundances in peanut butter. Thus, it can be assumed that these thermally induced compounds are further generated during the commercial processing steps, for example, grinding or milling.

In summary, the data suggested that the commercial roasting process and the model roasting in the pan obviously generate the same key odorants and a similar overall aroma, although differences between varieties could not be taken into account in this study.

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