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Comparison of the Key Aroma Compounds in Organically Grown, Raw West-African Peanuts (*Arachis hypogaea*) and in Ground, Pan-Roasted Meal Produced Thereof

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Application of an aroma extract dilution analysis on an aroma distillate prepared from organically grown, raw West-African peanuts (Cameroon) revealed 36 odor-active areas in the flavor dilution (FD) factor range of 1 to 2048. The identification experiments, which were all performed by using the respective reference chemicals, revealed 2-isopropyl-3-methoxypyrazine (earthy, pea-like), 2-isobutyl-3-methoxypyrazine (bell pepper-like, earthy), and *trans*-4,5-epoxy-(*E*)-2-decenal (metallic) with the highest FD factors among the 36 aroma compounds identified. The two last mentioned odorants and another set of 22 further odorants were identified for the first time in raw peanuts. A comparative aroma extract dilution analysis applied on distillates prepared from either the raw peanuts or ground peanut meal roasted in a pan showed 52 odor-active areas in the FD factor range of 8 to 2048 in the roasted nut material. The identification experiments in combination with the FD factors revealed that among them, 2-acetyl-1-pyrroline and 4-hydroxy-2,5-dimethyl-3-(2*H*)-furanone showed the most significant contribution to the overall aroma, followed by 1-octen-3-one, 2-isopropyl-3-methoxypyrazine, (*E*,*E*)-2,4-decadienal, and *trans*-4,5-epoxy-(*E*)-2-decenal. As a further result, 20 aroma compounds were newly identified in roasted peanuts, such as 2-propionyl-1-pyrroline and 2-acetyltetrahydropyridine (both popcorn-like). In particular, 2-acetyl-1-pyrroline and 4-hydroxy-2,5-dimethyl-3(2*H*)-furanone showed the most pronounced increase after roasting.

KEYWORDS: Peanut aroma; *trans*-4,5-epoxy-(*E*)-2-decenal; 2-acetyl-1-pyrroline; 2-propionyl-1-pyrroline; 2-acetyl-1,4,5,6-tetrahydropyridine; 2-acetyl-3,4,5,6-tetrahydropyridine

INTRODUCTION

Peanuts (*Arachis hypogaea*) belong to the most important oilseeds with an annual worldwide production of 36.4 million metric tons in 2004 (*1*). Most of the peanut crop originates from China, India, West Africa (Nigeria), and the United States. Raw, boiled or roasted peanuts are important food crops in Africa and Southeast Asia, whereas in Europe peanuts are mainly consumed as snacks.

The identification of volatile compounds in either raw or roasted peanuts has been a research topic for more than 40 years, and, up to now, over 300 volatile compounds were identified in roasted peanuts, while about 70 volatile components were reported in raw peanuts (*2*). Pattee et al. (*3*) as well as Brown et al. (*4*) were among the first to analyze the volatiles of raw peanuts. The latter authors identified and quantified in particular carbonyl compounds, and suggested that hexanal and octanal are responsible for the legume-like aroma of raw peanuts (*4*). Later on, Fischer and Grosch (*5*) identified the pea-like 2-isopropyl-3-methoxypyrazine in raw peanut and confirmed its significant contribution to the legume-like aroma by means of sensory analyses.

During roasting of peanuts, a pleasant aroma is generated changing the overall pea-like flavor into an attractive roasty, nut-like aroma. One of the first attempts to analyze the volatiles of roasted peanuts was done by Mason et al. (*6, 7*). These authors identified several alkylpyrazines as well as Strecker aldehydes, such as 2- and 3-methylbutanal and phenylacetaldehyde, in an extract of roasted peanuts and postulated phenylacetaldehyde as an important odorant for the sweet odor and pyrazines for the roasty and nutty aroma. In the same year, Brown et al. (*8*) reported acetic acid, butanoic acid and methylbutanoic acid as well as lipid peroxidation products, such as 2,4-decadienal as additional volatiles. Johnson et al. (*9, 10*) identified 46 additional peanut volatile components, among them many pyrazines. In a comprehensive study, Walradt et al. (*11*)

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then reported 142 volatiles in roasted peanuts, among them phenols (e.g., 4-vinylphenol, 2-methoxyphenol, 2-methoxy-4-vinylphenol), terpenes (β-pinene, limonene, α-terpineol), and sulfur compounds like 3-(methylthio)-propionaldehyde. Investigations of Buckholz et al. (*12*) and Ho et al. (*13*) were later on focused on the quantitative determination of roasted peanut volatiles. Their results suggested several pyrazines as major contributors to the peanut flavor. Recently, Didzbalis et al. (*14*) suggested ethyl 2-methylbutanoate and ethyl 3-methylbutanoate to be responsible for a fruity and fermented off-flavor detectable in raw and in roasted peanuts. These authors also reported the identification of 4-hydroxy-2,5-dimethyl-3(2*H*)-furanone as a previously unknown aroma compound in roasted peanuts.

Although numerous investigations on the volatiles of raw and roasted peanuts have been performed so far, most of the studies did not investigate the aroma contribution of single odorants to the overall flavor, e.g., by using a combination of analytical methods with human sensory perception during the analytical steps applied. Dilution to odor threshold techniques, such as the aroma extract dilution analysis (AEDA), are well-accepted approaches in the separation of odor-active compounds from the bulk of odorless food volatiles (*15*). Matsui et al. (*16*) were the first to apply this method on a commercial oil processed from roasted peanuts. As a result, in particular, ethyl 2-methylbutanoate, 2,5-ethyl-3-dimethylpyrazine, 2,3-diethyl-5-methylpyrazine, (*Z*)-2-nonenal, (*E*,*E*)-2,4-decadienal, and (*E*)-β-damascenone were suggested as key odorants. However, since quite large dilution steps (1:10) were used in the AEDA to narrow down the set of volatiles to the most odor-active ones, the relative importance of each odorant did not become obvious.

To investigate a burnt stale and floral off-flavor caused by microwave blanching, AEDA has also recently been applied on the aroma of peanuts (*17*). On the basis of higher FD factors in the blanched peanuts, guaiacol and phenylacetaldehyde were suggested as the odorants responsible for the off-odor. In roasted peanuts, 4-hydroxy-2,5-dimethyl-3(2*H*)-furanone, 2-ethyl-3,5-dimethylpyrazine, and nonanal, followed by phenylacetaldehyde, acetophenone, 3-ethyl-2,5-dimethylpyrazine, (*E*,*E*)-2,4-decadienal, decanoic acid, 4-acetoxy-2,5-dimethyl-3(2*H*)-furanone, and methyl cinnamate were suggested as important odorants (*17*). However, several compounds judged as important in the roasted peanuts were only tentatively identified.

It is without doubt that the roasting procedure is the key factor in generating the characteristic aroma of roasted peanuts. However, studies comparing the key aroma compounds in raw and roasted peanuts from the same batch on the basis of dilution to odor thresholds methods are scarcely available. Such data are needed to evaluate which odorants are just transferred from the raw nuts into the roasted nuts, and which are aroma compounds formed from certain flavor precursors occurring in the raw peanuts. Such data could be used, for instance, in sensory directed breeding trials or in optimizing the yields of desired odorants during roasting. Therefore, the aim of the present investigation was to compare the most important odorants in raw and in ground, then roasted peanuts by application of aroma extract dilution analyses. To analyze the peanut material as fresh as possible, organically grown nuts, still able to germinate, were used, and a laboratory method for thermal processing was applied.

MATERIAL AND METHODS

Materials. Raw peanuts from West Africa (Cameroon; crop 2007) were purchased from Orkos (Souci-Bouy, France). The nuts were organically grown on a farm and transported to Germany by air freight. The nuts (average length, 15 mm; average diameter, 8 mm) were still able to germinate. The shell was immediately removed, and the nuts were stored at −25 °C prior to use. Immediately before grinding, the seed coats were peeled off, the nuts were frozen in liquid nitrogen, and then powdered by means of a commercial blender (Privileg, Fürth, Germany).

To obtain the roasted peanut material, raw ground peanuts (200 g) were roasted in a frying pan under permanent stirring until a characteristic roasty odor was generated (≈11 min). Sensory panel tests showed that the material elicited an odor very similar to that of commercially roasted peanuts. Although intact peanuts are commonly roasted in the production of commercial samples, this model procedure provided freshly roasted material under defined conditions, whenever needed for analytical purposes. Although several studies (*18*) have shown that grinding before roasting may cause enzymatic lipid oxidation, no lipid-type off-odor was detected in the roast and ground material.

Reference Odorants. The following reference odorants were obtained from the sources given in parentheses: 2-acetylpyridine, 2-acetylthiazole, 2-acetyl-2-thiazoline, butanoic acid, 1,8-cineole, (*E*,*E*)-2,4-decadienal, (*E*)-2-decenal, 2,3-diethyl-5-methylpyrazine, dimethyl trisulfide, 2-ethyl-3,5-dimethylpyrazine, 2-ethyl-3,6-dimethylpyrazine, (*E*)-2-heptenal, hexanal, 3-hydroxy-4,5-dimethyl-2-(5*H*)-furanone, 3-hydroxy-2-methylpyran-4-one, 4-hydroxy-2,5-dimethyl-3-(2*H*)-furanone, 2-isopropyl-3-methoxypyrazine, 2-isobutyl-3-methoxypyrazine, (*R*/*S*)-2-methylbutanal, (*R*/*S*)-2-methylbutanoic acid, 3-methylbutanoic acid, 3-(methylthio)-propanal, (*R*,*S*)-γ-lactone, (*E*)-2-nonenal, octanal, 1-octen-3-one, 2,3-pentandione, phenylacetaldehyde, phenylacetic acid, 2,3,5-trimethylpyrazine, and (*E*)-2-undecenal (Sigma-Aldrich Chemie, Taufkirchen, Germany). Acetic acid, 4-hydroxy-3-methoxybenzaldehyde, and 2,3-butandione (VWR International, Darmstadt, Germany). 3-Methylbutanal, 4-vinyl-2-methoxyphenol, and 4-vinylphenol (Lancaster, Mühlheim, Germany), 2-methoxyphenol (Serva, Heidelberg, Germany), and nonanal (Roth, Karlsruhe, Germany). (*Z*)-4-Heptenal was a gift from Symrise (Holzminden, Germany).

The following reference odorants were synthesized according to the literature cited: 2-acetyl-1-pyrroline and 2-propionyl-1-pyrroline (*19*), 2-acetyltetrahydropyridine (*20*), 2-ethenyl-3,5-dimethylpyrazine (*21*), (*Z*)-2-nonenal (*22*), *trans*-4,5-epoxy-(*E*)-2-decenal (*23*), and 4-mercapto-4-methyl-2-pentanone (*24*).

Isolation of the Volatiles. Ground raw or the roasted peanut material (150 g), respectively, was extracted with diethyl ether (1 L) by vigorous stirring at room temperature for 30 min. The mixture was filtered, and the residue was washed twice with diethyl ether (300 mL). The combined organic phases were dried over anhydrous sodium sulfate and concentrated to about 500 mL at 38 °C using a Vigreux column (60 cm × 1 cm), and the volatiles were isolated using the solvent-assisted flavor evaporation (SAFE) technique (*25*). The distillate obtained was finally concentrated to 200 μL using a microdistillation apparatus at 38 °C (*19*).

High Resolution Gas Chromatography-Olfactometry (HRGC-O). HRGC-O was performed by means of a Trace GC Ultra (Thermo Electron Corporation, Dreieich, Germany) using the following fused silica capillaries: FFAP and DB-5 (both 30 m × 0.32 mm, 0.25 μm film thickness) (J & W Scientific, Folsom, CA). The samples were applied by the cool-on-column technique at 40 °C using helium at a flow rate of 2.5 mL/min as the carrier gas. For the FFAP capillary, the initial temperature of 40 °C was held for 2 min, then raised at 4 °C/min to 110 °C, then at 6 °C/min to 180 °C and finally at 15 °C/min to 230 °C. For the DB-5 capillary, the initial temperature of 40 °C was held for 2 min, then raised at 6 °C/min to 170 °C and finally at 20 °C/min to 240 °C.

For HRGC-O, the effluent was split 1:1 by volume at the end of the capillary by means of an Y-type splitter and two deactivated fused silica capillaries (50 cm × 0.25 mm). One part was directed to the flame ionization detector (FID) held at 250 °C, and the other part to a heated sniffing-port (200 °C). Calculation of linear retention indices (RI) was done by using a series of *n*-alkanes as described previously (*19*).

Aroma Extract Dilution Analysis (AEDA). In a first approach, the chromatogram of the undiluted samples was evaluated by four sniffers to eliminate potential gaps in detecting odor-active regions.

Following, the FD factors of the odor-active compounds were determined by diluting the extract stepwise 1:1 (v:v) with diethyl ether and by analyzing each dilution by HRGC-O. This was done by three experienced panelists, and the results were averaged (*16*). By definition, the FD factor obtained for each single odorant in the AEDA is equal to the highest dilution in which the odorant could be perceived at the sniffing-port.

High Resolution Gas Chromatography−Mass Spectrometry (HRGC−MS). For compound identification, mass spectra were generated by means of a sector field mass spectrometer type MAT 95 S (Finnigan, Bremen, Germany) in the electron impact mode (MS-EI) at 70 eV using the capillaries and temperature programs described above.

Two Dimensional-High Resolution Gas Chromatography-Olfactometry−Mass Spectrometry (TD-HRGC-O−MS). To obtain unequivocal mass spectra, in some cases two dimensional-HRGC-O−MS was performed using the Moving Column Stream Switching system (MCSS) (Fisons Instruments, Mainz, Germany). Capillary FFAP, installed in the first gas chromatograph (Fisons Instruments, type Mega 2-Series), was connected to the MCSS, system and the carrier gas flow was trapped with liquid nitrogen (−80 °C). The MCSS system was connected to an FID and the first sniffing-port by a Y-type splitter, and by a heated transfer line to the second GC, which was equipped with the capillary DB-5. The end of the second capillary was coupled to an ion trap mass spectrometer (ITD 800, Finnigan) and a sniffing-port via a Y-type splitter to allow a simultaneous olfactory detection while mass spectra were recorded.

Static Headspace Olfactometry (SH-O). Freshly roasted peanut material (20 g) was filled in headspace vials (volume 120 mL) and subsequently sealed with a septum. The samples were equilibrated at 40 °C for 30 min. Six vessels were prepared, and decreasing headspace volumes (10 mL, 5 mL, 2.5 mL, 1.25 mL, 0.6 mL, and 0.3 mL) were withdrawn with a gastight syringe for GC-O. The samples were analyzed as follows: Starting with the largest volume (10 mL), the respective headspace volume was injected into a gas chromatograph (Trace GC Ultra), equipped with a cold-trap unit. During the injection, air was released through a pressure control valve while the aroma compounds were cryofocused on an uncoated fused-silica capillary (i.d. = 0.53 mm) held at −150 °C using liquid nitrogen. Then, the cold-trap was heated to 250 °C for 5 min (heating rate of 15 °C/min), and the volatiles were transferred onto the fused silica capillary column (30 m × 0.25 mm; 0.25 μm film thickness) (J & W Scientific). A temperature of 0 °C was held for 3 min, then the temperature was raised at 6 °C/min to 60 °C and further at 15 °C/min to 240 °C (held for 5 min, isothermally). Helium at a flow rate of 1.2 mL was used as carrier gas. At the end of the column, the effluent was transferred to an FID, a sniffing-port, and an ion trap mass spectrometer (Saturn 2100 T; Varian, Darmstadt, Germany).

The portion of the carrier gas flow leading to each detector was adjustable by a flow control unit. For GC-O analysis, the odorants were led to the sniffing-port and the FID. For the identification experiments, odorants were detected by both, their characteristic odor and their mass spectra. Spectra were generated in the chemical ionization mode (CI-mode) with an ionization energy of 70 eV and methanol as the reagent gas.

RESULTS AND DISCUSSION

Identification of Odor-Active Constituents in Raw Peanuts. Volatiles were isolated by immediate solvent extraction of raw peanuts ground in liquid nitrogen, followed by high-vacuum distillation. The distillate obtained exhibited the typical green, pea-like aroma of raw peanuts, when a drop of the ethereal solution was sniffed on a strip of filter paper. Application of GC-O to the original distillate revealed 36 aroma-active areas among which two compounds with pea-like, bell pepper-like and earthy odors showed a very high intensity. Also another compound with an intense metallic aroma showed a quite intense odor. After sniffing of serial dilutions, compound **18** exhibiting a pea-like, earthy flavor was detected with the highest FD factor of 2048 among the 36 odor-active areas, followed by compound **26** with a bell pepper-like, earthy odor, and compound **46** with a green, metallic odor, both of which showed FD factors of 512.

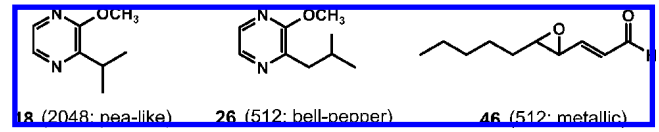

Figure 1. Structures of the most odor-active volatiles in raw peanuts (numbering refers to **Table 1**).

To identify the compounds responsible for the perceived odors, first, the retention indices of the odor-active areas were determined on two different stationary GC phases. A comparison with data of ≈1000 food odorants available in an in-house database suggested certain structures for each odorant. Next, the distillate was fractionated on silica gel using pentane/diethyl ether mixtures of increasing polarity (*19*). In the single fractions obtained, the odorants were again located by GC-O and the mass spectra were recorded using either HRGC−MS or the two dimensional-HRGC-O−MS approach. The MS data obtained were first cross-checked against the data available in the database, but finally, the structure was confirmed by comparing the analytical and sensory attributes with those of the respective reference compounds. This procedure was necessary, because several trace odorants coeluted with volatiles present in high amounts and, thus, without fractionation incorrect identifications would have occurred. Following this procedure, all odorants detected by GC-O could be identified. The three most odor-active odorants in raw peanuts were characterized as 2-isopropyl-3-methoxypyrazine (**18**), 2-isobutyl-3-methoxypyrazine (**26**), and *trans*-4,5-epoxy-(*E*)-2-decenal (**46**) (**Figure 1**). Both the 2-isobutyl-3-methoxypyrazine and the *trans*-4,5-epoxy-(*E*)-2-decenal are reported in this study for the first time as aroma constituents of raw peanuts. With somewhat lower FD factors, acetic acid (**22**, FD 128), 2- and 3-methylbutanoic acid (**38**, FD 128) as well as butanoic acid (**36**, FD 32) were identified as further odorants exhibiting pungent, sweaty and rancid odor qualities, respectively (**Table 1**). Additionally, the smoky 2-methoxyphenol (**44**, FD 64), the caramel-like 4-hydroxy-2,5-dimethyl-3-(2*H*)-furanone (**48**, FD 32), and the seasoning-like smelling 3-hydroxy-4,5-dimethyl-2-(5*H*)-furanone (**49**, FD 32) are suggested as potential contributors to the overall aroma of raw peanuts. Altogether, 36 odorants could be identified. Among them, 24 aroma compounds not only were evaluated for their aroma contribution but also were characterized for the first time as volatile constituents of raw peanuts.

Odor-Active Constituents in the Ground Roasted Peanut Meal. Freshly roasted peanuts are known to lose their attractive aroma during storage. Thus, in order to get freshly roasted material, raw peanuts were ground and roasted in a pan until the characteristic roasty odor of freshly roasted peanuts was generated. Although this procedure might lead to the enzymatic formation of lipid degradation products (*18*), a sensory evaluation of the material by a panel of trained assessors did not give a hint on any lipid derived off-odor. Parameters for the generation of a "representative" aroma were selected in preliminary experiments by comparing the overall flavor to that of a commercially available sample of roasted, then ground peanuts.

An aroma distillate obtained by solvent extraction of the roasted material followed by a distillation step fully represented the typical aroma of roasted peanuts.

Table 1. Most Odor-Active Compounds (FD ≥ 16 in at Least One Sample) in Aroma Distillates Isolated from Raw Peanuts and Roasted Peanut Meal

			RI on[c]		FD factor[d]		earlier reported as volatile constituent[e]	
no.	odorant[a]	odor quality[b]	FFAP	DB-5	raw	roasted	raw	roasted
1	3-methylbutanal	malty	913	650	2	64		*26*
2	2-methylbutanal[f]	malty	927	665	2	32		
3	2,3-butandione	butter-like	980	542	2	64		*11*
4	2,3-pentandione	butter-like	1058	705	1	32		*11*
5	hexanal	green	1079	803	8	32	*3, 26*	*11*
6	(*Z*)-3-hexenal	green, apple-like	1140	800	8	<1		
7	1,8-cineol	eucalyptus-like	1191	1033	8	16		
8	(*Z*)-4-heptenal	fishy	1235	900	<1	16		
9	octanal	citrus-like, fatty	1281	1003	4	64	*26*	*11*
10	1-octen-3-one	mushroom-like	1296	978	32	1024		
11	(*E*)-2-heptenal	fatty, green	1311	958	<1	32		*26*
12	2-acetyl-1-pyrroline	roasty, popcorn-like	1325	922	16	2048		
13	dimethyl trisulfide	sulfury	1365	968	8	16		*14*
14	4-mercapto-4-methyl-2-pentanone[g]	catty	1367	942	<1	16		
15	nonanal	citrus-like, fatty	1388	1103	4	64	*26*	*14*
16	2,3,5-trimethylpyrazine	earthy	1391	1003	<1	32		*27*
17	2-propionyl-1-pyrroline	roasty, popcorn-like	1408	1025	<1	512		
18	2-isopropyl-3-methoxypyrazine	pea-like, earthy	1428	1083	2048	1024	*5*	
19	2-ethyl-3,6-dimethylpyrazine	roasted potato, earthy	1432	1071	<1	64		*27*
20	2-ethyl-3,5-dimethylpyrazine	roasted potato, earthy	1447	1076	<1	16		*11*
21	3-(methylthio)-propanal	cooked-potato	1449	908	16	256		*27*
22	acetic acid	pungent	1463	600	128	16	*28*	*28*
23	2,3-diethyl-5-methylpyrazine	potato, roasty	1480	1151	<1	128		*11*
24	2-(sec-butyl)-3-methoxypyrazine	earthy	1491	1161	32	32		
25	(*Z*)-2-nonenal	fatty, leaf-like	1498	1147	16	128	*26*	*26*
26	2-isobutyl-3-methoxypyrazine	bell pepper-like, earthy	1520	1179	512	256		
27	(*E*)-2-nonenal	fatty	1523	1161	32	256	*26*	*26*
28	2-acetyl-(1,4,5,6)- and (3,4,5,6)-tetrahydropyridine	roasty, popcorn-like	1548	1061 + 1142	<1	256		
29	2-ethenyl-3,5-dimethylpyrazine	earthy	1553	1099	<1	128		
30	2-ethenyl-3-ethyl-5-methylpyrazine	musty, earthy	1582	1180	<1	64		
31	2-acetylpyridine	roasty	1587	1030	<1	64		*11*
32	(*Z*)-2-decenal	fatty	1606	1253	8	128	*26*	*26*
33	2-acetylpyrazine	roasty	1617	1020	<1	16		*11*
34	(*E*)-2-decenal	fatty	1633	1266	4	16	*26*	*26*
35	2-acetylthiazole	roasty	1635	1018	<1	16		
36	butanoic acid	sweaty	1636	821	32	8		*15*
37	phenylacetaldehyde	honey-like	1641	1048	4	256		*7*
38	2- and 3-methylbutanoic acid[f]	sweaty, rancid	1673	879	128	32		*11*
39	(*E*,*E*)-2,4-nonadienal	fatty	1696	1216	32	256	*26*	*26*
40	(*E*)-2-undecenal	tallowy, fatty	1737	1361	4	64	*4*	*4*
41	2-acetyl-2-thiazoline	roasty	1749	1105	<1	32		
42	(*E*,*Z*)-2,4-decadienal	fatty	1752	1296	<1	64		*29*
43	(*E*,*E*)-2,4-decadienal	deep-fried	1798	1321	32	1024	*26*	*29*
44	2-methoxyphenol	smoky	1855	1088	64	128		*11*
45	3-hydroxy-2-methylpyran-4-one	caramel-like	1978	1108	<1	16		*14*
46	*trans*-4,5-epoxy-(*E*)-2-decenal[g]	metallic, green	2000	1382	512	1024		
47	γ-nonalactone[f]	coconut-like	2018	1368	16	128		
48	4-hydroxy-2,5-dimethyl-3-(2*H*)-furanone	caramel-like	2039	1069	32	2048		*15*
49	3-hydroxy-4,5-dimethyl-2-(5*H*)-furanone[g]	seasoning-like	2191	1108	32	64		
50	2-methoxy-4-vinylphenol	smoky, clove-like	2200	1314	8	64		*11*
51	4-vinylphenol	spicy, phenolic	2400	1239	2	128		*11*
52	phenylacetic acid	honey-like	2544	1272	8	256		
53	4-hydroxy-3-methoxy-benzaldehyde	vanilla-like	2610	1404	4	32		

[a] The compound was identified by comparing its mass spectra (MS-EI, MS-CI), retention indices on capillaries FFAP and DB-5 as well as the odor quality and the odor intensity perceived during sniffing with data of reference compounds. [b] Odor quality perceived at the sniffing-port. [c] Retention index. [d] Flavor dilution factor determined by AEDA on capillary FFAP. [e] The compound was earlier reported as volatile compound in raw or roasted peanuts in the given reference. [f] Stereochemistry was not determined. Odor qualities are given for the racemate. [g] No unequivocal mass spectrum was obtained. Identification is based on the remaining criteria given in footnote[a].

Application of the AEDA to the distillate revealed a total of 52 odor-active areas in the FD factor range of 8 to 2048. The odor-active compounds responsible for the odors detected during GC-O were all subsequently identified following the procedure described above.

The odor-active areas **12** and **48** exhibiting an intense roasty or caramel-like odor note, respectively, at the highest FD factor of 2048 were identified as 2-acetyl-1-pyrroline and 4-hydroxy-2,5-dimethyl-3-(2*H*)-furanone (**Figure 2**). With a somewhat lower FD factor of 1024, 1-octene-3-one (**10**, mushroom-like), 2-isopropyl-3-methoxypyrazine (**18**, pea-like, earthy), (*E*,*E*)-2,4-decadienal (**43**, deep-fried), and *trans*-4,5-epoxy-(*E*)-2-decenal (**46**, metallic, green) are also likely to contribute to the overall aroma of roasted peanuts. The results of the AEDA in combination with the identification experiments revealed the roasty smelling 2-propionyl-1-pyrroline (**17**), 3-(methylthio)-propanal (**21**, cooked potato-like), 2-isobutyl-3-methoxy-pyrazine (**26**, bell pepper, earthy), (*E*)-2-nonenal (**27**, fatty), 2-acetyl-tetrahydropyridine (**28**, roasty, popcorn), phenylacetaldehyde (**37**, honey-like), (*E*,*E*)-2,4-nonadienal (**39**, fatty), and phenylacetic acid (**52**, honey-like) as additional aroma contributors. For compound **28**, both tautomers, the 2-acetyl-1,4,5,6-tetrahydropyridine and the 2-acetyl-3,4,5,6-tetrahydropyridine could be identified on the nonpolar stationary GC phase. Although

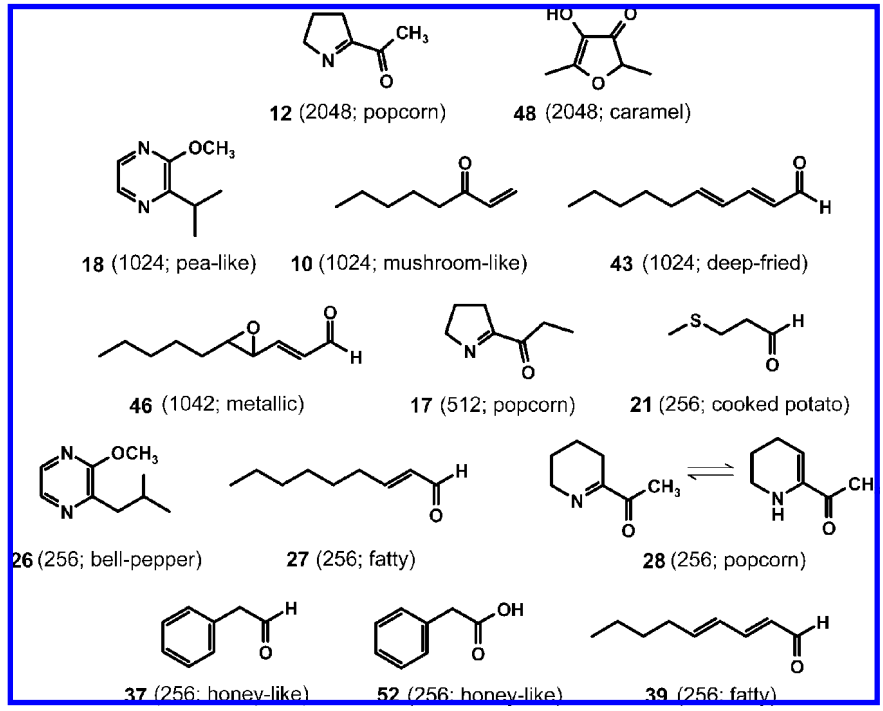

Figure 2. Structures of the most odor-active volatiles identified in roasted peanut meal (numbering refers to **Table 1**).

Table 2. Important Odorants in the Headspace of Roasted Peanut Meal

compound	odor quality	RI[a] on DB-5	vol[b] (mL)	FD[c]
dimethyl sulfide	cabbage-like	453	10	1
acetaldehyde	pungent	350	2.5	4
2,3-butandione	butter-like	517	2.5	4
propionaldehyde	pungent	436	2.5	4
methylpropanal	malty	486	1.25	8
2-methylbutanal	malty	639	0.6	16
3-methylbutanal	malty	628	0.6	16
methanethiol	sulfury	357	0.3	32

[a] Retention index. [b] Smallest headspace volume in which the odorant was perceived. [c] The relative FD factor was calculated by dividing the highest volume analyzed (10 mL) by the smallest volume in which the odorant was detected.

the correct name of the compound is 6-acetyl-2,3,4,5-tetrahydropyridine, the 2-acetyl-nomenclature was kept, since this name was used for 40 years in the literature. In total, 52 odorants were identified in the roasted peanut material, of which ≈20 are reported in this study for the first time as aroma compounds of roasted peanuts (**Table 1**).

The procedure used for the isolation of the volatiles discriminates highly volatile compounds, because these may be lost during solvent evaporation. To overcome this gap, GC-O was applied on static headspace samples using a series of decreasing gas volumes above the freshly roasted nut material.

In a sample of 0.3 mL, only one odor-active compound was detected (**Table 2**). The identification experiments revealed methanethiol to be responsible for the intense sulfury odor detected at RI 357. By increasing the headspace volume to 0.6 mL, besides methanethiol the two malty smelling aldehydes 2- and 3-methylbutanal were additionally detectable, followed by the malty smelling methylpropanal in a headspace volume of 1.25 mL (**Table 2**). As compared to the results of the AEDA (**Table 1**), four compounds, namely methanethiol, acetaldehyde, propanal, and dimethyl sulfide were identified as further odorants in roasted peanuts.

Changes Induced by the Roasting Procedure. A comparison of the FD factors determined for the same odorants in both the raw and the roasted nuts allows insights into compounds

Table 3. Peanut Aroma Compounds Showing Higher FD Factors after Roasting

		FD factor in	
odorant	odor quality	raw	roasted peanuts
2-acetyl-1-pyrroline	popcorn-like	16	2048
4-hydroxy-2,5-dimethyl-3(2*H*)-furanone	caramel-like	32	2048
(*E*,*E*)-2,4-decadienal	deep-fried	32	1024
1-octen-3-one	mushroom-like	32	1024
3-(methylthio)-propanal	potato	16	256
phenylacetaldehyde	honey-like	4	256
(*E*,*E*)-2,4-nonadienal	fatty	32	256
γ-nonalactone	coconut-like	16	128
4-vinylphenol	spicy, phenolic	16	128
3-methylbutanal	malty	2	64
2-methylbutanal	malty	2	32

which are formed from odorless precursors during roasting, since FD factors are linearly correlated with concentrations in air (*16*).

The most obvious changes in FD factors occurred for 2-acetyl-1-pyrroline (*12*) and 4-hydroxy-2,5-dimethyl-3(2*H*)-furanone (**48**), both of which showed significantly higher FD factors in the roasted sample (**Table 3**). Previous studies have shown that 2-acetyl-1-pyrroline is generated from the amino acid proline and reducing carbohydrates via 1-pyrroline and 2-oxopropanal as the key intermediates (*30, 31*). Although the amounts of free amino acids in peanuts were not yet determined, it can be assumed that compound **12** is formed from a reaction of proline and reducing carbohydrates during roasting. Two further popcorn-like smelling odorants, namely 2-propionyl-1-pyrroline (**17**) and 2-acetyl-tetrahydropyridine (**28**), which both were identified for the first time as constituents of roasted peanuts, were previously reported to be generated also from proline and the carbohydrate degradation products hydroxypropanone and 2-oxobutanal, respectively (*31, 32*).

Hexoses are known to generate 4-hydroxy-2,5-dimethyl-3(2*H*)-furanone (**48**) upon thermal treatment, with rhamnose and fructose-1,6-biphosphate being the most efficient precursors (*33*). 2,4-Dihydroxy-2,5-dimethyl-3(2*H*)-furanone has previously been confirmed as the key intermediate in the generation of **48** (*34*).

It can, thus, be assumed that **48** is generated during the thermal treatment of the nuts by carbohydrate degradation.

Higher FD factors in the roasted nuts were also observed for the Strecker aldehydes 2- and 3-methylbutanal (**1** and **2**) as well as for 3-(methylthio)-propanal (**21**) and phenylacetaldehyde (**37**) suggesting that the degradation of free amino acids via a Strecker-type reaction plays an important role in peanut aroma generation.

Interestingly, some odorants like 1-octen-3-one (**10**), (*Z*)-2-nonenal (**25**), (*E*)-2-nonenal (**27**), (*Z*)-2-decenal (**32**), (*E,E*)-2,4-nonadienal (**39**), and (*E,E*)-2,4-decadienal (**43**), known to be formed during peroxidation of unsaturated fatty acids, also showed a clear increase during roasting. Since peanut oil is quite rich in linoleic acid, lipid peroxidation products also seem to contribute to the desired aroma of roasted peanuts. However, as previously shown by us in a study on puff-pastries (*35*), a thermal treatment of products containing quite high amounts of unsaturated fatty acids will only lead to volatile formation, if the intermediate hydroperoxides are already preformed in the fats used. Thus, it may be assumed that the respective hydroperoxides were already present in the raw peanuts and are degraded into the oxo-compounds during roasting.

In total, 17 odorants were only detected in the roasted, but not in the raw peanuts, and, in addition, 25 further aroma compounds increased in their concentrations during roasting. However, some compounds, like 2-isopropyl-3-methoxypyrazine (**18**), 2-isobutyl-3-methoxypyrazine (**26**), *trans*-4,5-epoxy-(*E*)-2-decenal (**48**), and 3-hydroxy-4,5-dimethyl-3-(2*H*)-furanone (**49**), remained unchanged. These compounds are, thus, suggested to be metabolites of the raw peanut seeds. In addition, these odorants are not lost to a significant degree during the roasting procedure. On the other hand, acetic acid (**22**), butanoic acid (**36**), and 2- and 3-methylbutanoic acid (**38**), which are also constituents of the raw peanuts, are significantly reduced during roasting.

These investigations confirmed, in particular, the importance of 2-isopropyl-3-methoxypyrazine (**18**) for the pea-like aroma of raw peanuts as reported previously (*5*). However, since further methoxypyrazines, like 2-isobutyl-3-methoxypyrazine (**26**), and 2-(*sec*-butyl)-3-methoxypyrazine (**24**) were identified here, these might add to the intensity of the pea-like aroma. The latter two methoxypyrazines have been reported before in other legumes, such as peas (*Pisum sativum*) and French beans (*Phaseolus vulgaris*) together with **18**, and their formation is suggested to follow an enzymatic route involving free amino acid metabolization (*36*).

trans-4,5-Epoxy-(*E*)-2-decenal is also reported for the first time in raw peanuts. It is known to be formed by a degradation of linoleic acid hydroperoxides during thermal food treatment (*35*). However, since its FD factor did not increase during roasting of peanuts, a biochemical pathway is possibly involved in its formation in peanuts.

The alkylpyrazines 2-ethyl-3,6-dimethylpyrazine (**19**), 2-ethyl-3,5-dimethylpyrazine (**20**), and 2,3-diethyl-5-methylpyrazine (**23**) have previously not been reported as key contributors to peanut aroma, although many other pyrazines have been reported to occur in roasted peanuts. The reason for this is possibly due to the fact that the above-mentioned pyrazines have very low odor thresholds (*37*) and are, thus, only detected if GC-O is applied. On the other hand, 2-methylpyrazine, 2,5-dimethylpyrazine, and 2-ethyl-5-(or 6)-methylpyrazine, which have been proposed as odorants responsible for the roasted peanut flavor in previous investigations (*6, 14*), were not detected as aroma-active compounds in our study, most likely because their high odor thresholds (*37*) make these compounds unlikely to be important odorants of roasted peanuts.

A comparison of the results with data recently obtained by applying AEDA on roasted peanuts (*17*) shows that our study confirms the importance of 4-hydroxy-2,5-dimethyl-3(2*H*)-furanone (**48**), (*E*,*E*)-2,4-decadienal (**43**), phenylacetaldehyde (*37*), and—with somewhat lower FD factors—nonanal (**15**), 2-ethyl-3,6-dimethylpyrazine (**19**) and 2-ethyl-3,5-dimethylpyrazine (**20**) to the overall flavor of roasted peanuts. However, compounds such as acetophenone, decanoic acid, 4-acetoxy-2,5-dimethyl-3(2*H*)-furanone, and methyl cinnamate, which have been reported with high FD factors (*17*), were not detected as aroma-active compounds in our study. These differences might be explained by the different peanut varieties used in both studies, or by the different roasting procedure applied.

To confirm the contribution of the investigated odor-active compounds to the overall flavor of raw and roasted peanut meal, quantitative data are, however, necessary. Therefore, the results of this study will be taken as a basis for further investigations on the aroma compounds of peanuts based on the molecular sensory science concept.

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