REVIEW

Flavor of Cereal Products—A Review

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ABSTRACT

The review is focused on studies presenting quantitative data and odor activity values (ratio of concentration to odor threshold) of key odorants in bread (wheat and rye), toasted bread, puff pastries made with different fats, fragrant and nonfragrant rices, sweet corn, popcorn, and tortillas. The influence of raw materials, processing parameters, and storage conditions on the concentrations of key odorants and some data on flavor precursors and formation pathways of these compounds are discussed.

Heating of cereals leads to the formation of characteristic flavors attractive to the consumer. The flavors of bread, especially that of the baguette type, corn tortillas, popcorn, and aromatic rice are examples. It is, therefore, not surprising that numerous investigations have been performed to identify the volatiles that evoke the odor notes of bread in particular, but also of other heated cereals. Earlier reviews concerning the flavors of bread and rice have been published by Rothe (1974), Maga (1974, 1978, 1984), Grosch and Schieberle (1991), and Maarse (1991).

Progress in instrumental analysis, particularly high-resolution gas chromatography and mass spectrometry, has shown that the volatile fraction of heated cereals, like most other foods, consists of a multiplicity of compounds (Maarse et al 1994). However, recent studies have shown that only a small number of volatiles are of significance in determining the flavor (Grosch 1994).

The first approach undertaken to sort out the volatiles that contribute to an odor from those that do not, was the calculation of the ratio of concentration of the volatile compounds to their odor thresholds. Results were referred to as aroma values (Rothe and Thomas 1963), odor units (Guadagni et al 1966), or odor activity values (OAV) (Acree et al 1984). In this article, the term OAV is used.

Studies of aromatic rice, corn, tortillas, and sweet corn first identified many of the volatiles appearing in gas chromatograms and then, after quantification, the character-impact odorants were distinguished from the volatiles with low or no odor activity by calculation of OAV. This was, of course, very time-consuming work. In the 1980s, a new strategy of instrumental and sensory analysis was developed, allowing orientation of the identification experiments on volatiles that had a chance to contribute to the flavor of a food (Acree 1993; Grosch 1993, 1994; Schieberle 1995a).

In the new concept, the analysis of a food flavor starts with a screening of the potent odorants either by Charm analysis (Acree et al 1984) or by Aroma Extract Dilution Analysis (AEDA) (Ullrich and Grosch 1987). In both procedures, an extract obtained from the food is evaluated by gas chromatography-olfactometry (GCO). The extract is then diluted, usually as a series of 1:1 or 1:2 dilutions, and each dilution is analyzed again by GCO. In AEDA, the result obtained for each odor-active volatile compound is expressed as a flavor dilution (FD) factor, reflecting the ratio of the concentration of the odorant in the initial extract to its concentration in the most dilute extract in which an odor was detected by GCO. Consequently, the FD factor is a relative measure of odor potency and is proportional to the OAV of the compound in air. To indicate which of the compounds revealed by these techniques actually contributes to the aroma, quantitation of the odorants and calculation of OAV are the next steps in the analytical procedure (Grosch 1993, 1994; Schieberle 1995a).

This very effective methodology in flavor analysis has been applied to clarify the character-impact odorants of wheat and rye bread, puff pastries, and popcorn.

The main objectives of this review are to discuss the compounds that (on the basis of high OAV) are responsible for the distinct notes in the odor profiles of heated cereals.

BREAD

AEDA was applied to evaluate the potent odorants of wheat bread (baguette type) and rye bread. In these studies, the crust and crumb were analyzed separately (Table I) (Schieberle and Grosch 1987, 1991, 1994).

Crust Aroma

The pleasant aroma of wheat bread crust depends on the formation of roasty smelling compounds during the baking process, and also stability during storage. Two N-heterocyclics, 6-acetyltetrahydropyridine (no. 1 in Table I) and 2-acetyl-1-pyrroline (no. 2) had been proposed as character-impact odorants of the roasty note of the crust (Hunter et al 1969, Schieberle and Grosch 1985). However, the pyrroline (no. 2) that had been identified as a character-impact flavor compound of fragrant rices, showed the highest FD factor of the odorants identified in the crust, whereas the FD factor of no. 1 was relatively low (Table I). Quantitative measurements, which due to the instability of both odorants, were conducted as stable isotope dilution analysis (Schieberle and Grosch 1994), followed by a calculation of OAV (Table II). They confirmed the results of AEDA that the popcorn-like smelling 2-acetyl-1-pyrroline was the key odorant evoking the roasty note in the aroma profile of wheat bread crust.

The precursors of 6-acetyltetrahydropyridine (ACTPY) and 2-acetyl-pyroline (ACPY) have been clarified in model experiments (Schieberle 1990). According to the results shown in Table III, ACTPY was formed by a reaction of proline with 2-oxopropanal, a thermal degradation product of sugars. This reaction system also also provided ACPY, but in a much lower yield. Replacement of 2-oxopropanal by fructose inhibited the formation of ACPY. The higher amount of ACTPY formed in this model was due to the higher level of fructose when compared to that of 2-oxopropanal.

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Ornithine, an amino acid occurring in baker's yeast (Schieberle 1990), was then identified as the most effective precursor of the ACPY (Table III).

The different concentrations of 2-acetyl-1-pyrroline in wheat bread crust and crumb (Table II) might be explained by a burst of yeast cells induced by the high temperature in the crust. This might lead to a release of ornithine and the formation of ACPY. In contrast, the yeast cells are not disrupted at the lower temperature in the crumb and, consequently, no ornithine is available. This hypothesis is supported by the observation that only traces of the pyrroline were produced in the crumb, and the characteristic crust odor was lacking when the yeast was replaced by the leavening agent glucono-δ-lactone (Schieberle 1987). This hypothesis is also in agreement with the finding that toasting bread crumb produced ACPY in dependence on the amount of yeast used in the baking process (cf. Toasting).

ACPY disappeared very rapidly after baking (Table IV). This loss and the higher stability of odorants formed by lipid peroxidation, e.g., (E)-2-nonenal, is undoubtedly involved in the formation of the stale off-flavor perceivable after storage of wheat bread (Schieberle and Grosch 1992).

In contrast to wheat bread, rye bread crust was very low in ACPY and much higher in 3-methylbutanal, methional, and furanone no. 11 (Table II). Furthermore, the results of AEDA (Table I) also suggest that the concentrations of furanones no. 12 and 13, as well as those of acetic acid, are higher in the rye bread crust. These differences in the concentrations of potent odorants are most likely the cause for the differences in the overall odors of wheat and rye bread crust.

Wheat Bread Crumb

Because of high FD factors, 2-phenylethanol (no. 6), (E)-2-nonenal (no. 8), and (E,E)-2,4-decadienal (no. 9) were identified as the most potent odorants of wheat bread crumb (Table I).

Of the two aldehydes (nos. 8 and 9), which are known as autoxidation products of linoleic acid (Badings 1970), the concentration of (E)-2-nonenal was determined in wheat flour and in breads prepared with and without margarine. The results (Table V) indicate that compared to the concentration in the flour, the level of the aldehyde increased nearly 5-fold and 6.4-fold in the crumb and crust, respectively (bread A; Table V). However, a portion of the increase in the crust was caused by an oxidative breakdown of the fat used in the dough manufacturing, because the amount of (E)-2-nonenal decreased by 64% when the margarine was omitted (bread B; Table V).

To get an insight into the odorants responsible for the yeasty note in the flavor profile of the crumb, two breads were compared with different amounts of yeast used in the preparation of the doughs. While bread C was made using a liquid preferment and 1.5% yeast in the final dough, bread D was prepared using a soft dough preferment and 4.6% yeast in the final dough. The crumb of bread C was preferred in a hedonic sensory test because of its typical overall yeast-like aroma, (Gassenmeier and Schieberle 1995).

On the basis of a comparative AEDA of the two crumbs, the compounds listed in Table VI were considered responsible for the yeasty aroma (Gassenmeier and Schieberle 1995). Indeed, calculation of OAV (Table VI) suggested that the higher values of the flowery-yeasty 2-phenylethanol and of the malty, alcoholic 3-

TABLE I
Flavor Dilution (FD) Factors of Important Crust and Crumb Volatiles in Wheat and Rye Bread Flavor[a]

		Exponent *n* of FD-Factor 2^n			
		Wheat		Rye	
No.	Compound	Crust	Crumb	Crust	Crumb
1	6-Acetyltetrahydropyridine[b]	<3	<0	<3	<3
2	2-Acetyl-1-pyrroline	9	<3	<3	<3
3	3-Methylbutanal	7	<0	8	5
4	Methional	6	6	9	7
5	Phenylacetaldehyde	5	<3	6	9
6	2-Phenylethanol	<0	9	<0	<0
7	3-Methylbutanol	<0	5	<3	4
8	(E)-2-Nonenal	8	9	8	9
9	(E,E)-2,4-Decadienal	5	9	8	9
10	2-Ethyl-3,5-dimethylpyrazine	4	<3	6	<3
11	4-Hydroxy-2,5-dimethyl-3(2H)-furanone	7	<3	8	<3
12	3-Hydroxy-4,5-dimethyl-2(5H)-furanone	<0	<3	5	4
13	5-Ethyl-3-hydroxy-4-methyl-2(5H)-furanone	<3	<0	5	<0
14	Acetic acid	6	6	9	9
15	2- /3-Methylbutanoic acid	<0	<3	7	8

[a] Schieberle and Grosch (1987, 1991, 1994); Gassenmeier and Schieberle (1995).
[b] Mixture of the tautomers 6-acetyl-2,3,4,5- and 6-acetyl-1,2,3,4-tetrahydropyridine.

TABLE II
Concentration and Odor Activity Values (OAV) of Six Odorants in Wheat and Rye Bread Crust[a]

		Wheat Bread Crust		Rye Bread Crust	
Compound	No.[b]	(µg/kg)	OAV[c]	(µg/kg)	OAV[c]
6-Acetyltetrahydropyridine	1	58[d]	976	nd[e]	nd
2-Acetyl-1-pyrroline	2	19	950	0.8	40
3-Methylbutanal	3	1,406	469	3,295	1,098
Methional	4	51	510	480	4,800
(E)-2-Nonenal	8	56	560	45	450
4-Hydroxy-2,5-dimethyl-3(2H)-furanone	11	1,920	1,920	4,310	4,310

[a] Schieberle and Grosch (1994).
[b] From Table I.
[c] Calculated on the basis of odor thresholds in air.
[d] Only an approximate value, as a portion of no. 1 might be formed during isolation by simultaneous distillation and extraction (Schieberle 1995b).
[e] Not determined.

methylbutanol in combination with the lower OAV of the rancid, sweaty 2-/3-methylbutanoic acid were the main causes of the better flavor acceptance of crumb C.

Frasse et al (1993) showed that the two alcohols increase strongly during the fermentation of French bread doughs. The conditions (ratio of yeast to flour, time, temperature) leading to high yields of 2-phenylethanol and 3-methylbutanol in a preferment were elucidated by Gassenmeier and Schieberle (1995). Model studies were conducted in which the precursors of both alcohols, L-phenylalanine and L-leucine, were added to preferments. The results suggested that, during prefermentation, the two amino acids supplied by the flour are converted to a significant extent by the yeast by the Ehrlich pathway (Neubauer and Fromherz 1911) into the important crumb odorants 2-phenylethanol and 3-methylbutanol.

Addition of sourdough may improve the flavor of wheat bread crumb (Hansen and Hansen 1996). In particular, breads prepared by the addition of sourdough fermented with *Lactobacillus plantarum* plus the yeast *Saccharomyces cerevisiae* acquired the most aromatic odor and taste. In these breads the concentrations of 2-/3-methylbutanol and 2-phenylethanol were higher than in breads in which the yeast was omitted. The suggestion of Hansen and Hansen (1996) that the increase of the two alcohols might contribute to the more intense flavor of the sourdough-enriched bread crumb is in agreement with the results of Gassenmeier and Schieberle (1995).

TABLE III
Amounts (μg) of 2-Acetyltetrahydropyridine (ACTPY) and 2-Acetyl-1-pyrroline (ACPY) Formed in Models[a]

Reaction System[b]	ACTPY[c]	ACPY[c]
Proline plus 2-oxopropanal	160	41
Proline plus fructose	478	<0.3
Ornithine plus fructose	<0.3	53

[a] Schieberle 1990.
[b] Amino acid (4 mmol), dissolved in phosphate buffer (100 mL, 0.1 mol/L, pH 7.0) was boiled in the presence of 2-oxopropanal (0.1 mmol) or fructose (2 mmol), respectively.
[c] Amount (μg) after 2 hr.

TABLE IV
Loss of 2-Acetyl-1-pyrroline in the Crust During Storage of Wheat Bread at Room Temperature[a]

Storage Time (hr)	Level[b]	Loss (%)
0	19	0
3	9	47
24	4.4	77
96	2.1	89

[a] Schieberle and Grosch (1992).
[b] Concentration levels are expressed as μg/kg of crust (dry matter).

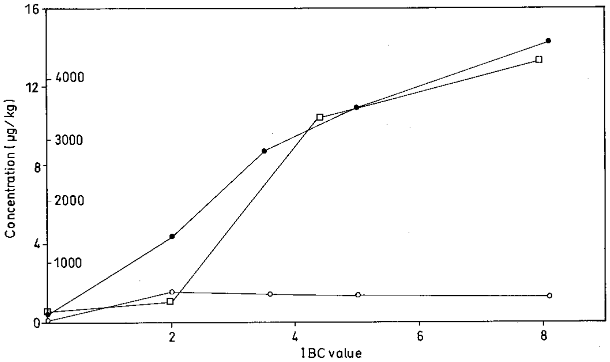

Fig. 1. Formation of three odorants depending on the intensity of the brown color (IBC value) of toasted wheat bread. 2-Acetyl-1-pyrroline (●), 6-acetyltetrahydropyridine (○), 4-hydroxy-2,5-dimethyl-3(2H)-furanone (□). IBC values were scored from 0 (unroasted) to 9 (strong brown) (Rychlik and Grosch 1996).

Toasting

A pleasant aroma characterized by the terms roasty, caramel-like, malty, and buttery, is formed when slices of wheat bread are toasted. The overall odor is very similar to that of wheat bread crust and it is, therefore, not surprising that the key odorants of medium-brown toasted bread slices (Table VII) also agreed with those of wheat bread crust (Table I). The concentrations of 2-acetyl-1-pyrroline, methional, (E)-2-nonenal, and 4-hydroxy-2,5-dimethyl-3(2H)-furanone differed at the most by a factor of two in the crust and in the medium-brown toasted crumb, respectively (Tables II and VII). The buttery note in the aroma profile of the toasted wheat bread was caused by 2,3-butanedione originating mainly from the flavored shortening used in dough preparation.

TABLE V
Level of (E)-2-Nonenal in Wheat Flour and Bread[a]

Wheat	Level[b]
Flour	18
Bread A[c]	
Crumb	94
Crust	115
Bread B[d]	
Crumb	97
Crust	62

[a] Schieberle and Grosch (1991).
[b] Concentration levels are expressed as μg/kg (dry matter).
[c] Bread formula: wheat flour (1 kg), water (550 mL), baker's yeast (60 g), surcrose (30 g), margarine (20 g), and salt (20 g).
[d] Margarine was omitted in the formula.

TABLE VI
Concentrations and Odor Activity Values (OAV) of Five Odorants in Wheat Bread Crumbs Prepared Using Preferments[a,b]

		Bread C		Bread D	
Compound	No.[c]	(mg/kg)	OAV	(mg/kg)	OAV
2-Phenylethanol	6	11.8	12	2.87	3
3-Methylbutanol	7	18.1	18	9.7	10
Ethyl octanoate		0.094	19	0.073	15
Butanoic acid		0.48	<1	0.91	<1
2-/3-Methylbutanoic acid	15	0.55	6	1.5	15

[a] Gassenmeier and Schieberle 1995.
[b] Bread formulas (kg): flour (C: 4.15, D: 4.9), water (C: 2.27, D: 2.825), salt (C, D: 0.11), yeast (C. 0.125, D: 0.325), preferment (C: 2.005 of I, D: 500 of II); preferment I: liquid suspension containing flour, water (1 kg each) and yeast (5 g) was incubated for 16 hr at 30°C; preferment II: soft dough consisting of flour (250 g), water (175 g) and yeast (75 g) was incubated as preferment I.
[c] From Table I.

TABLE VII
Concentration Levels and Odor Activity Values (OAV) of Odorants in Toasted Wheat Bread[a,b]

Compound	Level[c]	OAV[d]
2-Acetyl-1-pyrroline	8.8	1,205
(E)-2-Nonenal	174	328
2- and 3-Methylbutyric acid	1,750	318
4-Hydroxy-2,5-dimethyl-3(2H)-furanone	3,250	250
Methional	48	178
2,3-Butanedione	918	141

[a] Rychlik and Grosch (1996).
[b] Slices of wheat bread toasted to medium brown color.
[c] Expressed as μg/kg (dry matter).
[d] Calculated on the basis of odor threshold values in starch.

The levels of the odorants depended on the toasting conditions which are reflected by the intensity of the brown color (IBC value). The IBC value was scored on a scale from 0 (unroasted) to 10 (deep brown, nearly burnt) (Rychlik and Grosch 1996). As shown in Figure 1, the most important roasty odorant, 2-acetyl-1-pyrroline, increased continually until a maximum concentration of 14.4 µg/kg at an IBC value of 8 was reached. This was in contrast to 6-acetyltetrahydropyridine reaching only a low plateau of 1.5 µg/kg at an IBC value of 2 (Fig. 1). As in wheat bread crust, the pyridine was found to be less important for the roasty note than the pyrroline.

Figure 1 indicated that the formation of the caramel-like smelling 4-hydroxy-2,5-dimethyl-3(2H)-furanone was strong in the shortly toasted material, displayed by the lower IBC values of 2–4. At IBC values >4, the increase in the furanone was delayed, presumably due to its instability.

As shown in Table III, the amino acid ornithine supplied by baker's yeast was the most active precursor of 2-acetyl-1-pyrroline in wheat bread crust. Consequently, increasing the amount of yeast in the preparation of bread should enhance the amount of pyrroline in the toasting process. The data in Table VIII support this suggestion. The concentration of the pyrroline was very low in the bread prepared with a chemical leavening agent, but was strongly enhanced in toasted breads made by using increasing amounts of yeast in the dough.

PUFF PASTRY

The influence of added fat on the aroma of baked goods has been studied for puff pastries prepared from doughs containing either butter or margarine (Gassenmeier and Schieberle 1994a). Sweet, buttery, roasty notes (typical browned butter-like) were the most intense flavor impressions in butter pastries, while strawy, soapy, lard-like notes predominated when butter was replaced by a shortening.

On the basis of a comparative AEDA (Schieberle 1995a), seven odorants that appeared with a high FD factor in at least one of the two puff pastries were selected as indicators to establish the aroma differences caused by the fat type. Quantification and calculation of OAV (Table IX) showed that the metallic, musty smelling 4,5-epoxy-(E)-2-decenal and the fatty, green-smelling (E,Z)-2,4-decadienal, both formed during autoxidation of linoleic acid (Badings 1970, Gassenmeier and Schieberle 1994b), were by far the most important odorants of the margarine pastry. Also, in the butter pastry, both compounds belonged to the prominent odorants, but because the OAV were much lower than in the margarine pastry and were in the same range as those of both, the sweet, coconut-like smelling δ-decalactone and the caramel-like furanone, it was assumed that the latter two compounds are able to modify the overall odor impression into a sweet buttery note (Gassenmeier and Schieberle 1994a).

In the aroma of butter, 2,3-butanedione in addition to δ-decalactone, was identified as key aroma compound (Schieberle et al 1993). However, this odorant did not play a significant role in the aroma of the butter puff astry. It was assumed that the odorant was lost during the heating process, presumably by evaporation or by reactions with amino groups present in the dough (Gassenmeier and Schieberle 1994a).

To establish the source of precursors for the 2,4-decadienal isomers and for *trans*-epoxy-(E)-2-decenal, the amounts of the aldehydes before and after heating of a shortening sample containing 9.6% linoleic acid were determined (Schieberle and Gassenmeier 1995). As shown in Table X, heating the shortening for 7 min at 150°C led to a drastic increase in the amounts of the two odorants.

Because linoleic acid has been identified as precursor of the epoxydecenal, puff pastries were prepared with a sample of butter and with three shortenings (A–C in Table XI) differing in the linoleic acid content (Schieberle and Gassenmeier 1995). Determination of the epoxydecenal indicated (Table XI) that the concentration of this aldehyde was 7-fold higher in the pastry prepared with shortening A than in the butter pastry, although the linoleic acid was only 2.4-fold higher. In addition, a comparison of shortenings A–C in Table XI showed that the amount of epoxydecenal formed was not correlated with the linoleic acid concentration in the fat. In further experiments (Gassenmeier and Schieberle 1994b, Schieberle and Gassenmeier 1995), a good correlation was found between the amounts of hydroperoxides of linoleic acid present in the shortening and the epoxydecenal. It was shown that the 9- and 13-hydroperoxide isomers formed by the autoxidation of linoleic acid acted as precursors of the epoxide. The conclusion is that the

TABLE VIII
Amount of 2-Acetyl-1-pyrroline (ACPY) Formed During Toasting by Percentage of Yeast Used in the Baking Process[a]

Yeast (%)[b]	ACPY[c]
Without[d]	1.9
2	8.8
4	9.5
12	29.2
16	35.4

[a] Rychlik and Grosch (1996).

[b] In relation to the amount of flour.

[c] Expressed as µg/kg (dry matter) after toasting bread to medium brown.

[d] Bread prepared using a mixture of sodium hydrogen carbonate (3.8 g/100 g of flour) and sodium pyrophosphate (5 g/100 g of flour) as chemical leavening agents.

TABLE X
Amounts (mg/kg) of Two Aldehydes Contributing to the Aroma of Puff Pastries Before and After Heating of Shortening[a,b]

Odorant	Before	After
2,4-Decadienal[c]	0.22	21.3
trans-4,5-Epoxy-(E)-2-decenal	0.03	1.13

[a] Schieberle and Gassenmeier (1995).

[b] Shortening (10 g) heated for 7 min at 150°C under air in a closed vessel.

[c] Sum of (E,E)- and (E,Z)-geometric isomers.

TABLE IX
Concentration Levels and Odor Activity Values (OAV) of Seven Odorants in Puff Pastries Prepared with Butter or Margarine[a,b]

	Butter		Margarine	
Compound	Level[c]	OAV[d]	Level[c]	OAV[d]
(E,Z)-2,4-Decadienal	101	10	1,110	110
(E,E)-2,4-Decadienal	271	1.5	2,890	16
trans-4,5-Epoxy-(E)-2-decenal	38	29	268	206
δ-Decalactone	1,980	16	<10	<1
(Z)-2-Nonenal	1.6	<1	16	3.6
(E)-2-Nonenal	65	<1	64	<1
4-Hydroxy-2,5-dimethyl-3(2H)-furanone	290	12	360	15

[a] Gassenmeier and Schieberle (1994a).

[b] Puff-pastry prepared from 1 kg of flour and 1 kg of commercial sour cream butter or commercial nonaromatized baking margarine.

[c] Expressed as µg/kg.

[d] Calculated by using odor threshold values in sunflower oil.

formation of the epoxide, whose metallic, musty odor is not acceptable for most of the consumers, is inhibited when shortenings free of these hydroperoxides are used for the preparation of puff pastries.

COOKED RICE

A considerable number of different varieties of rices are grown throughout the world. Consumers from the industrialized countries seem to prefer the more bland nonfragrant varieties, whereas in South East Asia, India, and some Middle East countries, a number of more fragrant rices are highly favored and command higher prices than the nonfragrant varieties.

The flavor formed by the cooking of fragrant rice is described as popcorn-like (Buttery et al 1983a), which agrees with the finding that the popcorn-like smelling 2-acetyl-1-pyrroline was responsible for this odor note (Buttery and Ling 1982, Buttery et al 1983a).

The odorant was also detected in nonfragrant rice varieties, but its concentration was up to 100 times lower (Table XII). This difference was confirmed in a recent study on the volatiles of the two types of rice (Widjaja et al 1996).

Pandan leaves (*Pandanus amaryllifolius* Roxb., fragrant screw pine) are added during cooking to import aroma to nonfragrant rices. They contain 2-acetyl-1-pyrroline at concentrations 10 times higher than the fragrant rice varieties (Buttery et al 1983b).

Calculation of OAV revealed that, in addition to 2-acetyl-1-pyrroline, the aldehydes (E,E)-2,4-decadienal, nonanal, hexanal, octanal, and (E)-2-nonenal contribute to the flavor of cooked nonfragrant rice (Table XIII). Furthermore, decanal, and the phenolic flavor compounds 4-vinylguaiacol and 4-vinylphenol were present in amounts close to the odor thresholds (Table XIII).

According to Badings (1970), the formation of the aldehydes detected in cooked rice aroma can be explained by a peroxidation of lipids containing linoleic acid (nos. 2, 4, and 6 in Table XIII) or oleic acid (nos. 3, 5, and 7). The phenolic odorants no. 8 and 9 were produced by a thermal degradation of *p*-coumaric and ferulic acid whose concentrations differed significantly in the rice varieties (Widjaja et al 1996).

Buttery et al (1988) obtained the results presented in Table XIII by dynamic headspace analysis of a suspension of freshly cooked rice. Widjaja et al (1996) analyzed the volatiles isolated by simultaneous distillation-extraction during 1 hr of cooking rice. Widjaja et al (1996) found concentrations of the volatiles much higher than those listed in Table XIII. However, using OAVs (results not shown) calculated from threshold data presented in the literature, we were able to corroborate the data of Widjaja et al (1996) with the findings of Buttery et al (1988) that, in addition to 2-acetyl-1-pyrroline, only the aldehydes (E,E)-2,4-decadienal, hexanal, nonanal, and (E)-2-nonenal contribute to the aroma of cooked rice. However, the suggestion that 2-heptanone and 6-methyl-5-hepten-2-one participated in sweet floral and fruity notes as well as benzaldehyde in nutty notes (Widjaja et al 1996) has to be doubted, because the odor thresholds of these compounds in water are relatively high (Buttery et al 1988) and, consequently, the OAVs, calculated on the basis of the quantitative data presented by Widjaja et al (1996), do not surpass a value of one.

TABLE XI
Influence of Linoleic Acid Concentration in Butter and Shortenings on the Formation of *trans*-4,5-Epoxy-(E)-2-decenal in Puff Pastries[a]

Fat	Linoleic Acid (%)	Epoxydecenal (µg/kg of puff pastry)
Butter	4.0	38
Shortening		
A	9.6	268
B	16.1	135
C	48.5	183

[a] Schieberle and Gassenmeier (1995).

CORN PRODUCTS

Sweet Corn

The characteristic odor of dimethyl sulfide has been associated with sweet corn aroma (Bills and Keenan 1968) and, indeed, this odorant showed by far the highest OAV of the volatiles identified by dynamic headspace analysis in freshly cooked sweet corn (Table XIV) (Buttery et al 1994). The compound was absent in raw corn, but was formed during the cooking process. S-Methylmethionine occurring in raw corn has been proposed as the precursor (Bills and Keenan 1968). The amino acid is rapidly degraded at a temperature of 100°C to yield dimethyl sulfide and homoserine.

In addition to the odorants listed in Table XIV, the contribution of the highly volatile compounds hydrogen sulfide, methanethiol, and ethanethiol, which all have been identified in cooked sweet corn by Flora and Wiley (1974), have to be clarified. Being relatively potent odorants, they probably contribute to the total odor (Buttery et al 1994). Also, the significance of methional, which had been identified in sweet corn, is an open question (Buttery et al 1994). This aldehyde is very labile, so it was not possible to quantify this odorant by headspace analysis. However, precise results can be obtained by a stable isotope dilution assay as shown for bread crusts and toasted bread (Tables II and VII).

Popcorn

AEDA of freshly prepared popcorn indicated that 6-acetyltetrahydropyridine and 2-acetyl-1-pyrroline, also belonging to the character-impact odorants of wheat bread crust, (Tables I and II) mainly contributed to the characteristic smell of popcorn (Schieberle 1991). In addition, 2-propionyl-1-pyrroline eliciting a popcorn-like odor similar to that of acetyl homologue, was detected with a relatively high FD factor (Schieberle 1991).

TABLE XII
Amount of 2-Acetyl-1-pyrroline in Cooked Fragrant and Nonfragrant Rice Varieties[a]

Variety	Amount (µg/kg)[b]
Fragrant rice	
Malagkit	760
Basmati 370	610
Basmati 370	87
IR 841-76-1	560
Goolarah	691
YRF 9	670
Della	76
Jasmine	156
Nonfragrant rice	
Texas long grain	6
Lemont	4
Pelde	15

[a] Buttery et al (1986), Tanchotikul and Hsieh (1991), Widjaja et al (1996).
[b] After steam distillation continuous extraction.

TABLE XIII
Concentration Levels and Odor Activity Values (OAV) of Potent Odorants in Cooked California Long Grain Rice[a]

No.	Compound	Level[b]	OAV[c]
1	2-Acetyl-1-pyrroline	0.6	6
2	(E,E)-2,4-Decadienal	0.4	5.7
3	Nonanal	3	3
4	Hexanal	12	2
5	Octanal	0.9	1
6	(E)-2-Nonenal	0.1	1
7	Decanal	2	0.7
8	4-Vinylguaiacol	2	0.6
9	4-Vinylphenol	2	0.6

[a] Buttery et al (1988).
[b] Expressed in µg/kg of cooked rice (wet weight).
[c] Calculated on the basis of odor thresholds in water.

Quantitative measurements and calculation of OAVs were performed to examine the contribution of the three N-heterocyclics to the popcorn flavor (Schieberle 1995a). Acetylpyrazine was included in this experiment, although its FD factor was much lower than that of the three other odorants. However, on the basis of its popcorn-like odor note, the pyrazine had been proposed by Walradt et al (1970) as an important flavor compound of popcorn.

The results in Table XV established 6-acetyltetrahydropyridine (no. 1) followed by 2-acetyl-1-pyrroline (no. 2) and its homologue, 2-propionyl-1-pyrroline (no. 3), as the impact compounds of the roasty odor note of fresh popcorn, whereas acetylpyrazine (no. 4) did not contribute much to this odor note because its OAV was lower than those of the further roast odorants by factors of 364, 60, or 42, respectively.

In a sample prepared by popping the corn in a pan, much lower concentrations in particular of odorant no. 1 were obtained than in the fresh hot-air popped corn, whereas the concentration of no. 4 was higher (Table XV). Most likely, the longer heating time and, also the higher temperature during pan-popping, led to a degradation of the more labile no. 1 and favored the formation of the more stable pyrazine no. 4.

The flavor of popcorn is not stable. The decrease in the concentrations of nos. 1–3 during storage of popcorn for seven days (Table XV) is very well correlated with the decrease in the overall flavor quality.

Compared to no. 2, the concentration of no. 1 was much higher in popcorn than in wheat bread crust (Tables II and XV). This difference was undoubtedly due to the absence of ornithine, acting as precursor of no. 2 in wheat bread crust (Table III), as well as the presence of high amounts of free proline (155 mg/kg), the precursor of no. 1 in maize (Schieberle 1995b).

Corn Tortilla and Taco Shell

Recently, odorants causing the flavors of tortillas made from masa corn flour and of taco shells fried in oil were studied (Karahadian and Johnson 1993, Buttery and Ling 1995). A comparison of potent odorants (Table XVI) indicated that 2-aminoacetophenone showed the highest OAV in tortillas and was among the highest in taco shells. The odor quality of this ketone characterized by GCO agreed with the typical flavor impression of tortillas (Buttery and Ling 1995). According to Buttery and Ling (1994), 2-aminoacetophenone probably results from a breakdown of the amino acid tryptophane during the lime treatment of corn. In the presence of air, tryptophan can be oxidized to kynurenine, which is converted to 2-aminoacetophenone (Spacek 1954) under the alkaline conditions used during the preparation of masa.

Next to 2-aminoacetophenone, β-ionone, a breakdown product of β-carotene, was the most potent odorant of tortillas followed by 3-methylbutanal and 4-vinylguaiacol (Table XVI). In deep-fried taco shells, the odor quality of 2-aminoacetophenone is modified by (E,E)-2,4-decadienal smelling like fried fat and by the roasty and earthy odor notes of 2-acetyl-1-pyrroline and 2-ethyl-3,5-dimethylpyrazine.

CONCLUSIONS

Volatile compounds causing the characteristic odor notes in the aroma profiles of several heated cereals have been identified. Precise analytical methods have been developed for the quantitative determination of the typical odorants of some products to clearly demonstrate the influence of the raw materials, ingredients, parameters of processing, and storage conditions on the overall aroma of the final product.

TABLE XIV
Concentration Levels and Odor Activity Values (OAV) of Cooked Sweet Corn Volatiles[a,b]

Compound	Level[c]	OAV[d]
Dimethyl sulfide	760	2.5×10^3
Acetaldehyde	1700	113
Dimethyl trisulfide	<2	<100
4-Vinylguaiacol	110	37
2-Acetyl-1-pyrroline	2	20
2-Acetyl-2-thiazoline	6	6

[a] Buttery et al (1994).
[b] Fresh corn boiled for 10 min.
[c] Parts (mL) of compound per billion (10^9) parts of corn.
[d] Calculated on the basis of odor thresholds in water.

TABLE XVI
Selected Potent Odorants in Corn Tortillas and in Taco Shells[a]

Corn Tortilla[b]		Taco Shell[b]	
Compound	OAV[c]	Compound	OAV[c]
2-Aminoacetophenone	1,100	(E,E)-2,4-Decadienal	5,000
ß-Ionone	286	2-Aminoacetophenone	1,950
3-Methylbutanal	100	2-Acetyl-1-pyrroline	800
4-Vinylguaiacol	60	2-Ethyl-3,5-dimethylpyrazine	750
Hexanal	38	3-Methylbutanal	700
1-Octen-3-ol	10	(E)-2-Nonenal	625
2-Ethyl-3,5-dimethylpyrazine	10	Hexanal	400
4-Vinylphenol	6	6-Acetyltetrahydropyridine	230
(E)-2-Heptenal	6	Methional	200
α-Ionone	3	4-Vinylguaiacol	143

[a] Buttery and Ling (1995).
[b] Major brands purchased from local super markets.
[c] Odor activity values (OAV) calculated using odor thresholds in water.

TABLE XV
Concentration Levels and Odor Activity Values (OAV) of Four Roast Odorants in Fresh and Stored Hot-Air Popped Corn (HAP) and in Fresh Pan-Popped (PP) Corn[a]

		HAP Fresh[b]		Level[c] in Stored HAP [d]		PP Fresh[e]	
No.	Compound	Level[c]	OAV[f]	2 Days	7 Days	Level[c]	OAV[f]
1	6-Acetyltetrahydropyridine[g]	437	7,283	237	132	138	2,300
2	2-Acetyl-1-pyrroline	24	1,200	19	6	20	1,000
3	2-Propionyl-1-pyrroline	17	850	15	5	11	550
4	Acetylpyrazine	8	20	7	8	25	63

[a] Schieberle (1995b).
[b] Prepared using a hot-air corn-popper
[c] Expressed as µg/kg (dry matter).
[d] After cooling, the fresh HAP was sealed in polyethylene bags and stored in the dark at room temperature.
[e] Kernels popped in a surface-coated pan containing a small amount (5 g) of sunflower oil.
[f] Calculated using air thresholds of: 0.06 ng/L (no. 1), 0.02 ng/L (nos. 2 and 3), and 0.4 ng/L (no. 4).
[g] Sum of the tautomeric forms 6-acetyl-2,3,4,5- and 6-acetyl-1,2,3,4-tetrahydropyridine.

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