Primary Odorants in Popcorn

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Application of an aroma extract dilution analysis to freshly prepared popcorn revealed 23 odorants among which 2-acetyl-1-pyrroline (roasty, popcorn-like), (*E,E*)-2,4-decadienal (fatty), 2-furfurylthiol (coffee-like), and 4-vinyl-2-methoxyphenol (spicy) predominated with the highest FD factors (odor activities). Further potent flavor compounds showing roasty odors were 2-acetyltetrahydropyridine and 2-propionyl-1-pyrroline. The latter compound showed a very low odor threshold of 0.02 ng/L (air), which was in the same magnitude as that reported for the 2-acetyl-1-pyrroline homologue. Sensory analysis of homologues 2-butanoyl- and 2-hexanoyl-1-pyrroline revealed that a longer alkyl side chain canceled the roasty flavor note and increased the odor thresholds by a factor of 10^5.

INTRODUCTION

The characteristic sweet-roasty flavor note of heat-processed cereal foods (e.g., bread, crackers, cooked basmati rice) is often described as "popcorn-like", and it seems likely that the compounds responsible for this odor impression are also present in popcorn. Up to now only one investigation on the volatile compounds in popcorn has been reported (Walradt et al., 1970). The authors identified a total of 58 volatiles in an extract of microwave-popped corn. Among them and on the basis of its popcorn-like odor note, acetylpyrazine was proposed as an important flavor compound.

Volatile compounds, which contribute significantly to a food flavor, can be localized in the capillary gas chromatogram of food extracts and evaluated on the basis of their odor activities by methods using gas chromatography–olfactometry (GC/O) [cf. review by Grosch (1990)]. One such procedure called aroma extract dilution analysis (AEDA) helped focusing on the identification of the important odorants in bread crust (Schieberle and Grosch, 1987), boiled beef (Gasser and Grosch, 1988), lemon oil (Schieberle and Grosch, 1988), and lime honey (Blank et al., 1989).

This study was undertaken to identify the odorants with the highest odor activities in an extract of freshly prepared popcorn.

MATERIALS AND METHODS

Popcorn. Corn (80 g; Purity Foods, Okemos, MI) was popped by using a commercial hot-air corn popper (PP 105, IMEX Corp.).

Chemicals. Pure samples of the compounds in Table II were obtained commercially: **1** (Sigma, Munich, FRG), **2**, **7**, and **16** (Aldrich, Steinheim, FRG), **5a** and **13b** (Alfa, Karlsruhe, FRG), **9** and **23** (Merck, Darmstadt, FRG), **19** (Lancaster, Eastgate, Morecombe, England).

4 and **13a** were gifts from Dr. R. Emberger (Haarmann and Reimer, Holzminden, FRG) and **8a**, **8b**, and **22** from Dr. I. Flament (Firmenich, Geneva, Switzerland). The following compounds were synthesized according to the literature cited: 4,5-epoxy-(*E*)-2-decenal (Schieberle and Grosch, 1991], 2-acetyl-1-pyrroline (Buttery et al., 1982), 2-acetyl-1,4,5,6-tetrahydropyridine (Büchi and Wüst, 1971), (*Z*)-2-nonenal (Ullrich and Grosch, 1988).

Synthesis. *2-Propionyl-1-pyrroline [1-(Azacyclopent-1-en-2-yl)-1-propanone].* In a first step 2-propionylpyrrole was synthesized from pyrrylmagnesium iodide and propionyl chloride (Oddo, 1910). Hydrogenation and partial reoxidation of the pyrrole derivative were then performed according to the method described by Buttery et al. (1982) for the related 2-acetyl-1-pyrroline with some modifications: 2-propionylpyrrole (20 mmol) was dissolved in methanol (30 mL) and, after addition of rhodium on alumina (0.8 g) as catalyst, hydrogenated in an autoclave (Type III; Roth, Karlsruhe, FRG) for 20 h at 1000 Pa. The solution of the 2-(1-hydroxypropyl)pyrrolidine obtained was filtered over Celite, freed from the solvent, and then dissolved in toluene (60 mL) which was presaturated with nitrogen. After addition of silver carbonate on Celite (100 mmol) as oxidation catalyst (Fetizon and Golfier, 1968), the suspension was stirred and refluxed for 60 min. The solution was filtered over Celite and chromatographed on two water-cooled columns (20 cm × 1.8 cm) packed with a slurry of silica gel in pentane. The toluene was eluted with 60 mL of pentane, followed by 60 mL of pentane/diethyl ether (95:5 v/v). The title compound was eluted with 150 mL of pentane/diethyl ether (7:3 v/v) and then purified by preparative GLC. ^{1}H NMR (CD_2Cl_2; numbering of carbon atoms refers to Figure 2) δ 1.08 (t, J = 7.3 Hz, 3 H, C-7), 1.91 (quint., 2 H, C-2), 2.7 (m, 2 H, C-3), 2.91 (quart., J = 7.3 Hz, 2 H, C-6), 4.07 (m, 2 H, C-1). The GC and mass spectral data are summarized in Table I.

2-Butanoyl-1-pyrroline [1-(azacyclopent-1-en-2-yl)-1-butanone] and 2-hexanoyl-1-pyrroline [1-(azacyclopent-1-en-2-yl)-1-hexanone] were prepared analogously to 2-propionyl-1-pyrroline as described above: pyrrylmagnesium iodide was reacted with either butanoyl chloride or hexanoyl chloride, and the 2-substituted pyrrole derivatives obtained were subsequently hydrogenated and partially reoxidized, yielding the title compounds. After purification by preparative GLC, the structures were confirmed by ^{1}H NMR measurements: 2-butanoyl-1-pyrroline δ 0.97 (t, 3 H), 1.62 (sext, 2 H), 1.90 (quint., 2 H), 2.68 (m, 2 H), 2.86 (t, 2 H), 4.05 (m, 2 H); 2-hexanoyl-1-pyrroline δ 0.92 (t, 3 H), 1.40 (m, 4 H), 1.80 (m, 2 H), 1.91 (quint., 2 H), 2.7 (m, 2 H), 2.84 (t, 2 H), 4.06 (m, 2 H). The GC and mass spectral data are reported in Table I.

Isolation of the Popcorn Volatiles. Freshly prepared popcorn (600 g) was immediately frozen in liquid nitrogen and finely powdered by grinding in a Waring Blender. The powder was soaked overnight in dichloromethane (6 L) and then extracted in six Soxhlet apparatus for 8 h. The combined extracts were concentrated on a Vigreux column (100 cm × 2 cm) to about 150 mL and the volatiles isolated by sublimation in vacuo as recently described (Sen et al., 1991). The extract was concentrated to 200 µL by distilling off the solvent on a Vigreux column (60 cm × 1 cm) followed by microdistillation (Bemelmans, 1979).

Column Chromatography. The volatiles obtained from 1.2 kg of popcorn were fractionated at 10–12 °C on a water-cooled column (20 cm × 1 cm) packed with a slurry of silica gel in pentane/diethyl ether (95:5 v/v). Stepwise elution was performed with 25 mL of pentane/diethyl ether (95:5 v/v; fraction A), 50 mL of pentane/diethyl ether (85:15 v/v; fraction B), 45 mL of pentane/diethyl ether (7:3 v/v; fraction C), and 150 mL of diethyl ether (fraction D).

GAS CHROMATOGRAPHY

Preparative GLC. The SE-54 column (3 m × 2 mm stainless steel column packed with Silicone SE-54 (3% w/w) on Chro-

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Table I. Retention Indices, Mass Spectral Data, and Odor Threshold Values of Homologues 1-(Azacyclopent-1-en-2-yl)-1-alkyl Ketones

compound	RI on capillary		MS (EI) *m/z* (%)	odor threshold, ng/L (air)
	SE-54	OV-1701		
2-acetyl-1-pyrroline [1-(azacyclopent-1-en-2-yl)-1-ethanone]	921	1002	41 (100), 43 (100), 83 (60), 68 (39), 69 (36), 111 (35)	0.02
2-propionyl-1-pyrroline [1-(azacyclopent-1-en-2-yl)-1-propanone]	1024	1104	57 (100), 41 (90), 97 (72), 69 (62), 68 (26), 96 (24), 125 (8), 124 (4)	0.02
2-butanoyl-1-pyrroline [1-(azacyclopent-1-en-2-yl)-1-butanone]	1118	1207	69 (100), 41 (92), 43 (65), 97 (42), 96 (35), 111 (18), 124 (12), 83 (10), 139 (8)	>2000
2-hexanoyl-1-pyrroline [1-(azacyclopent-1-en-2-yl)-1-hexanone]	1319	1410	69 (100), 41 (90), 43 (64), 97 (42), 96 (38), 82 (20), 110 (12), 124 (12), 138 (12), 167 (8)	>2000

mosorb G AW DMCS (100–120 mesh)) was used with the following temperature program: after 2 min at 50 °C, the temperature was raised by 6 °C/min to 230 °C and then kept at 230 °C for 10 min. The compounds were condensed into cooling traps by using an outlet split ratio of 1:12 (by volume) as previously described (Schieberle et al., 1987).

HRGC/MS was performed with a Carlo Erba gas chromatograph (Type Mega 5160) using the capillaries SE-54 and OV-1701 (Schieberle et al., 1987). In addition, the capillary CP-wax for amines (30 m × 0.32 mm fused silica column, Chrompack, Müllheim, Germany) and the capillary FFAP (30 m × 0.32 mm fused silica capillary, Fa. ICT, Frankfurt, Germany) were used. The samples were applied by the on-column injection technique at 35 °C. The temperature of the oven was raised by 40 °C/min to 50 °C (60 °C for CP-wax and FFAP), held 2 min isothermally, and then raised by 4 °C/min to 240 °C. Retention data of the compounds are presented as retention indices (RI) calculated from the retention times of alkanes by using a program for cubic spline interpolation (Halang et al., 1979).

MS analyses were performed with an MS 8230 (Finnigan, Bremen, Germany) in tandem with the capillaries described above. Mass spectra in the electron impact mode [MS(EI)] were generated at 70 eV and in the chemical ionization mode [MS(CI)] at 115 eV with isobutane as reagent gas.

Proton magnetic resonance spectra (^{1}H NMR) were recorded in CD_2Cl_2 solution with a Bruker AM 360 spectrometer operating at 360 MHz.

Aroma Extract Dilution Analysis (AEDA); Approximation of Odor Threshold Values. The FD factors of the odorants were determined by an AEDA (Ullrich and Grosch, 1987; Schieberle and Grosch, 1987) of the following dilution series: The original extract (200 μL) from 600 g of popcorn was stepwise (1:1) diluted by addition of diethyl ether. Aliquots were analyzed by using the capillary SE-54. Odor thresholds were approximated by an olfactometric method (Ullrich and Grosch, 1987) using (*E*)-2-decenal instead of hexanal as internal standard (Blank et al., 1989). HRGC was performed on the capillary SE-54.

RESULTS

The volatiles from 600 g of freshly popped corn were isolated by solvent extraction and sublimation in vacuo and the most important odorants evaluated by AEDA. The FD chromatogram (Figure 1) from the volatile fraction displayed 23 odorants in the FD factor range 8–512 of which compounds **3** (roasty) and **20** (fatty) followed by **2** (roasty, coffee-like) and **19** (spicy) showed the highest FD factors. The results of the identification experiments obtained from an extract of 1.2 kg of popcorn are summarized in Table II. The data reveal that 2-acetyl-1-pyrroline (**3**), (*E,E*)-2,4-decadienal (**20**), 2-furfurylthiol (**2**), and 4-vinyl-2-methoxyphenol (**19**) were the most important odorants in popcorn.

In the elution range of compounds **5**, **6**, and **11** further roasty, popcorn-like odors were perceived. In fraction C of the extract of the volatiles, compounds **6** and **11** were identified as tautomers of 2-acetyltetrahydropyridine (Schieberle, 1990). The mass spectrum of compound **5b** is shown in Figure 2. The fragment ions of the MS(EI)

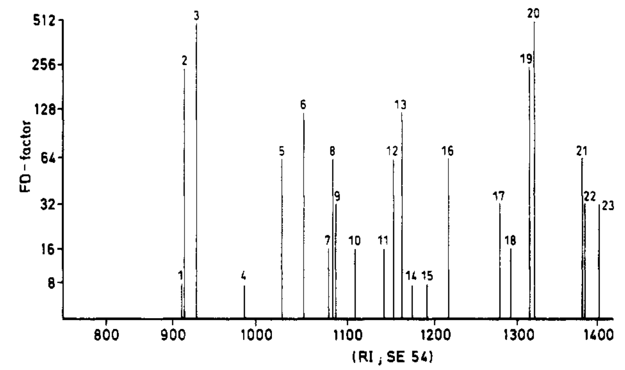


Figure 1. FD chromatogram of the odorants of an extract from freshly prepared popcorn.

(*m/z* 69, pyrroline ring; *m/z* 57, $CH_3CH_2C{=}O$; *m/z* 97, $M^+ - C{=}O$) were in agreement with the data given in Table I for the synthetic 2-propionyl-1-pyrroline. The compound smelled intensely roasty and showed a low odor threshold of 0.02 ng/L (air) (Table I). A comparison of the odor thresholds of further 1-pyrroline derivatives (Table I) showed that the values depended very strongly on the length of the carbon chain. While 2-acetyl- and 2-propionyl-1-pyrroline had extremely low odor thresholds, those of 2-butanoyl- and 2-hexanoyl-1-pyrroline were more than 10^5-fold higher.

On column SE-54 2-propionyl-1-pyrroline coeluted with the roast-smelling odorant acetylpyrazine. Sniffing of serial dilutions of the extract on an OV-1701 capillary which separated both compounds (cf. Table II) showed FD factors of 4 and 64 for acetylpyrazine and 2-propionyl-1-pyrroline, respectively, and indicated the latter compound to be mainly responsible for the roasty odor impression perceived on the SE-54 column. This might be explained by differences in their odor thresholds from that of acetylpyrazine (0.4 ng/L, air) being 20-fold higher than that of 2-propionyl-1-pyrroline.

The results of the further identification experiments (Table II) indicated that (*Z*)-2-nonenal, (*E,Z*)-2,4-nonadienal, 4,5-epoxy-(*E*)-2-decenal, 2,5-dimethyl-3-ethylpyrazine, and 2,3-dimethyl-6-ethylpyrazine as well as (*E*)-2-nonenal and 2,3-diethyl-5-methylpyrazine, on the basis of their FD factors, were additional important odorants.

DISCUSSION

The results indicated that 2-acetyl-1-pyrroline, (*E,E*)-2,4-decadienal, 2-furfurylthiol, and 4-vinyl-2-methoxyphenol were the most important odorants in fresh popcorn. 2-Acetyl-1-pyrroline was reported as character impact compound for the roasty, popcorn-like odor note of cooked rice (Buttery et al., 1982) and bread crust (Schieberle and Grosch, 1985). The compound was shown to be formed during bread processing from a reaction of the amino acids

Table II. Primary Odorants (FD Factor ≥ 8) in Popcorn

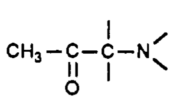
no.	compound[a]	fraction[b]	RI on SE-54	RI on OV-1701	odor description[c]	FD factor
1	methional	C	908	1029	cooked potato	8
2	2-furfurylthiol[d]	A	912	983	roasty, coffee-like	256
3	2-acetyl-1-pyrroline	D	921	1002	roasty, popcorn-like	512
4	1-octen-2-one	B	980	1058	mushroom-like	8
5a	acetylpyrazine	D	1023	1118	roasty, popcorn-like	4
5b	2-propionyl-1-pyrroline	C	1024	1104	roasty, popcorn-like	64
6	2-acetyltetrahydropyridine	C	1049	1433[e]	roasty, popcorn-like	128
7	2,5-dimethyl-4-hydroxy-2*H*-furan-3-one (furaneol)	acidic[g]	1080	1979[f]	caramel-like	16
8a	2,5-dimethyl-3-ethylpyrazine	D	1082	1136	potato-like	64
8b	2,3-dimethyl-6-ethylpyrazine	D	1084	1146		
9	2-methoxyphenol	B	1091	1221	sweet, burnt	32
10	unknown		1109		potato-like, roasty	16
11	2-acetyltetrahydropyridine	C	1145	1655[e]	roasty, popcorn-like	16
12	(*Z*)-2-nonenal	B	1147	1241	green, tallowy	64
13a	2,3-diethyl-5-methylpyrazine	D	1158	1218	potato-like	64
13b	(*E*)-2-nonenal	B	1161	1258	green, tallowy	
14	unknown		1178		sulfurous	8
15	2,4-nonadienal	B	1192	1339	fatty, waxy	8
16	(*E*,*E*)-2,4-nonadienal	B	1216	1339	fatty, waxy	64
17	unknown		1280		hydrolyzed protein	32
18	(*E*,*Z*)-2,4-decadienal	B	1296	1410	fatty, waxy	16
19	4-vinyl-2-methoxyphenol	B/C	1315	1473	spicy, clove-like	256
20	(*E*,*E*)-2,4-decadienal	B	1318	1434	fatty, fried fat	512
21	4,5-epoxy-(*E*)-2-decenal	B/C	1381	1538	metallic	64
22	(*E*)-β-damascenone[d]	B	1389	1498	cooked apple	32
23	vanillin	acidic[g]	1403	1577[f]	vanilla-like	32

[a] The compound was identified by comparing it with the reference substance on the basis of the following criteria: RI on the two capillaries given in the table, mass spectra obtained by MS(EI) and MS(CI), and odor quality perceived at the sniffing port. [b] Fraction in which most of the compound appeared after separation of the volatiles by column chromatography. [c] Odor description assigned during AEDA. [d] To get enough material for the identification experiments, the compound was enriched from an extract obtained by simultaneous steam distillation extraction of 4 kg of popcorn. [e] The RI was determined on capillary CP-wax for amines. [f] The RI was determined on capillary FFAP. [g] The acidic volatiles were isolated by treatment of the ethereal extract with an aqueous sodium bicarbonte solution (0.1 mol/L).

proline and ornithine with the sugar degradation product 2-oxopropanal (Schieberle, 1990). It seems likely that the popping process affords a similar reaction within the maize kernel.

(*E*,*E*)-2,4-Decadienal has been characterized as a peroxidation product of linoleic acid [review by Grosch (1987)], the major fatty acid among the lipids occurring in maize oil (Wessels, 1981). 4-Vinyl-2-methoxyphenol was shown to be formed as the main product of a thermally induced decarboxylation of ferulic acid (Fiddler et al., 1967). This acid is present in corn in amounts of about 8 mg/kg (Steinke and Paulson, 1964). As precursors of 2-furfurylthiol in foods, e.g., meat, cysteine or glutathione and ribose have been proposed (Grosch et al., 1990).

Besides 2-acetyl-1-pyrroline, the tautomers of 2-acetyltetrahydropyridine and 2-propionyl-1-pyrroline were responsible for the roasty odor note of popcorn. Folkes and Gramshaw (1981) speculated that heterocyclics with the structural feature



where the nitrogen atom and the adjacent carbon atom form part of a ring structure, exhibit roasty or cracker-like odors. 2-Propionyl-1-pyrroline, which has not been previously reported among the food flavors, fits very well into this proposal, although its alkyl side chain is one carbon atom longer. In contrast, 2-butanoyl-1-pyrroline and 2-hexanoyl-1-pyrroline did not smell roasty and showed very high odor thresholds. These data clearly indicate that the longer alkyl side chains do not fit a receptor molecule to stimulate a roasty, popcorn-like odor impression.

Acetylpyrazine, earlier reported as an important odorant

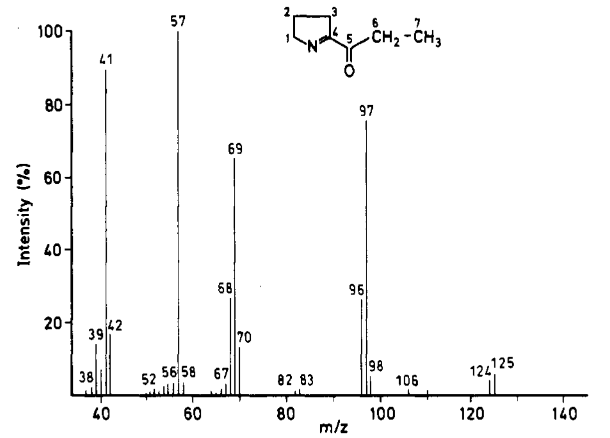


Figure 2. Mass spectrum [MS(EI)] of compound **5b** isolated from 4 kg of popcorn.

in popcorn (Walradt et al., 1970), contributed only with a very low FD factor to the overall flavor.

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Registry No. 1, 3268-49-3; **2**, 98-02-2; **3**, 99583-29-6; **4**, 4312-99-6; **5a**, 22047-25-2; **5b**, 133447-37-7; **6**, 25343-57-1; **7**, 3658-77-3; **8a**, 13360-65-1; **8b**, 15707-34-3; **9**, 90-05-1; **11**, 27300-27-2; **12**, 60784-31-8; **13a**, 18138-04-0; **13b**, 18829-56-6; **15**, 6750-03-4; **16**, 5910-87-2; **18**, 2363-88-4; **19**, 7786-61-0; **20**, 25152-84-5; **21**, 73528-44-6; **22**, 23726-93-4; **23**, 121-33-5; 2-butanoyl-1-pyrroline, 133447-38-8; 2-hexanoyl-1-pyrroline, 133447-39-9; 2-propionylpyrrole, 1073-26-3; 2-(1-hydroxypropyl)pyrrolidine, 100869-02-1; pyrrylmagnesium iodide, 66202-47-9; butanoyl chloride, 141-75-3; hexanoyl chloride, 142-61-0; propionyl chloride, 79-03-8.