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Coffee Roasting and Aroma Formation: Application of Different Time−Temperature Conditions

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The impact of time−temperature combinations of roasting processes on the kinetics of aroma formation in coffee was investigated. The development of 16 aroma compounds and the physical properties of coffee beans was followed in a commercial horizontal drum roasting process and in laboratory scale fluidizing-bed roasting processes at high temperature-short time and low temperature-long time conditions. All trials were run to an equal roast end point as defined by the lightness of coffee beans. In addition, the effect of excessive roasting on aroma composition was studied. Compared to low temperature-long time roasting, high temperature-short time roasting resulted in considerable differences in the physical properties and kinetics of aroma formation. Excessive roasting generally led to decreasing or stable amounts of volatile substances, except for hexanal, pyridine, and dimethyl trisulfide, whose concentrations continued to increase during over-roasting. When the drum roaster and the fluidizing bed roaster were operated in the so-called temperature profile mode, that is, along the identical development of coffee bean temperature over roasting time, the kinetics of aroma generation were similar in both processes.

KEYWORDS: Coffee; roasting; solid phase microextraction; aroma formation; degree of roast

INTRODUCTION

In the processing chain from the ripe coffee cherry to roasted coffee, roasting presents the most important step, whose main objective is to produce the desired aroma and taste. Furthermore bean color turns to brown or even black, and brittleness is greatly increased so that grinding and extraction become possible. High temperatures of beyond 200 °C are required for the roasting process. Green coffee beans exhibit exceptional hardness due to unusually thick cell walls and a lack of intracellular spaces. Consequently, they may be regarded as an aggregation of microreactor units that support a considerable pressure build-up during roasting. Theoretical values of internal pressure of up to 16 bars after roasting have been calculated (*1*–*4*). Despite the high pressure conditions during roasting, no evidence of cell wall disruption was observed in scanning electron microscopy (*4*), which is probably due to the fact that at high temperature coffee cell walls change from a glassy state to the more elastic rubbery state, which also allows the considerable volume increase during roasting (*4, 5*). Fundamental changes in the microfibril network of cell walls and the formation of an intracellular pore structure were described (*4, 6*).

Physical and chemical properties of roasted coffee are highly influenced by process conditions during roasting, in particular by the time−temperature conditions within the coffee bean as a function of heat transfer. Heat transfers by contact, conduction, radiation, and convection. Although all types of heat transfer take place during roasting, convection is most effective and most appropriate for uniform roasting. Almost exclusive convective heat transfer is achieved by fluidizing-bed roasting, which allows fast roasting and results in low density, high yield coffee (*7*). Traditional horizontal drum roasting involves more conductive heat transfer and is slower. Fast roasting is reported to yield more soluble solids, less degradation of chlorogenic acids, less burnt flavor, and lower loss of volatiles (*8*). Fast roasted coffee is generally suspected to be more affected by lipid oxidation due to higher oil migration from the bean core to the surface (*9*), and there are concerns about organoleptical properties of fast roasted coffee (*10*). Sivetz (*11*), however, reported increased flavor and aroma in fast roasted coffee.

The state of a roasted coffee bean as influenced by the roasting conditions is described in terms of the degree of roast. There are various possibilities to define the degree of roast, i.e., color development, roast loss, organic roast loss, and water content. Indirect determination methods for the degree of roast by ratios of free amino acids (*12*), alkylpyrazines (*13*), and content of chlorogenic acids (*10*) have also been proposed. Of these methods, color of coffee bean or ground coffee is the most frequently used indicator. As bean color intensity is correlated to the final roasting temperature (*10, 11*), temperature measurements also are applied. However, Schenker (*4*) carried out a

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Table 1. Process Parameters of Roasting Trials and Product Properties

	laboratory scale (fluidizing-bed roaster)					production scale
			profile			
	HTST	LTLT	step 1	step 2	step 3	drum roasting
	process parameters					
hot air temperature [° C]	260	228	180	180 → 232 (linear)	232	n. a.[a]
roasting time [s]	160	660	180	360	360	1170
hot air velocity [m/s]	3	3	3	3	3	
	product properties ($n = 3$)					
lightness [L^*]	21.05 ± 0.15	21.00 ± 0.16			20.78 ± 0.16	21.00 ± 0.16
roast loss [g/100 g wb]	16.64 ± 0.02	17.05 ± 0.05			17.66 ± 0.03	n. a.
organic roast loss [g/100 g wb]	8.54 ± 0.13	9.24 ± 0.04			10.10 ± 0.12	n. a
density [g/cm^3]	0.548 ± 0.001	0.588 ± 0.002			0.584 ± 0.005	0.592 ± 0.002
water content [g/100 g wb]	1.30 ± 0.02	1.57 ± 0.01			1.73 ± 0.02	1.79 ± 0.40

[a] n.a.: not available.

series of roasting trials on a production scale with various temperature profiles, which did not result in a direct relationship between degree of roast and final product temperature. He concluded that data on final bean temperature are of limited value as they differ in the function of raw material and process conditions. Recently, new approaches for online determination of roast degree during the roasting process have been investigated. Dorfner et al. (*14*) analyzed roaster gases directly by laser mass spectrometry, reported evolution of several aroma components during roasting, and postulated a multivariate statistics model to monitor the degree of roast. An approach using a chemosensor array was chosen by Hofmann et al. (*15*). They identified 2-furfurylalcohol and hydroxy-2-propanone as possible marker substances to monitor the course of roasting. Though literature frequently refers to an optimum degree of roast, a concise definition of it is usually not given because of its complexity, and to date, no clear and universally accepted definition exists. It is obvious that an optimum degree of roast is in particular a function of green coffee origin, intended coffee brewing method, and personal taste preferences.

From the several hundred volatile compounds identified in coffee, around 30 have been identified as aroma impact compounds (*16–19*). Various authors described the formation of aroma compounds during roasting. Holscher and Steinhart (*20*) compared *Arabica* and *Robusta* coffees and provided data on the evolution of methanethiol, dimethyl sulfide, 2,3-butanedione, 2,3-pentanedione, methylpropanal, 2/3-methylbutanal, methylacetate, and 2-methylfuran as a function of the degree of roast. The development upon roasting was similar, but concentration differences between the two coffee varieties were found. Grosch (*21*) investigated the formation of 2-furfurylthiol. He concluded that it is formed by reactions of cysteine with arabinose and reported on substantial amounts of 2-furfurylthiol being linked by disulfide bonds to other components of roasted coffee. A masking effect by odorants formed in the later stages of roasting, covering the sweet earthy notes, was found by Gretsch et al. (*22*). The authors correlated global sensory attributes with relative composition of aroma compounds at various degrees of roast. Mayer et al. (*23*) investigated the influence of the degree of roast on concentrations of aroma impact compounds in three coffee varieties. However, detailed specifications on the applied roasting process and determination of color values were not given. Several different roasting processes were assessed in terms of flavor formation by Schenker et al. (*24*). He found that most aroma compounds exhibited the highest increase in concentration at the medium stage of dehydration and pleaded for the precise control of roasting time and temperature in order to reach specific flavor profiles.

Numerous publications appeared on the nature of reactions leading to roasted coffee flavor (for an overview, see Flament (*25*), Reineccius (*26*), and Shibamoto (*27*)). Despite the high value of insights into possible reaction mechanisms resulting from model systems, it must be taken into account that such model systems simulate reaction conditions within a coffee bean only to a limited extent. Model systems are usually heated mixtures of precursor substances in solution, which are in contrast to the low moisture content within coffee beans. It was shown that, depending on water content of the reaction mixtures, fundamentally different reaction pathways might be followed, for example, in the reaction of glucose with L-proline (*28*). For these reasons, new approaches for model reactions involving extracted coffee bean shells were developed for in-bean roasting experiments (*29*). However, in view of the complexity of coffee roasting, experiments with real green coffee beans on standard roasting equipment under well controlled conditions are still the most efficient way to gain insight into the kinetics of coffee flavor generation.

The aim of the present study was to investigate the evolution of aroma compounds during roasting with different time−temperature conditions and to compare experimental results from a laboratory scale fluidizing-bed process to those from a traditional production scale horizontal drum roasting process. For this purpose, a commercial single origin coffee traditionally roasted in a drum roaster was chosen as a model, and time−temperature conditions were established on the laboratory roaster to achieve the same color of roasted coffee. Furthermore, the question whether these time−temperature conditions lead to equivalent coffees in terms of aroma and physical properties was investigated.

MATERIALS AND METHODS

Roasting Process and Process Characterization. *Raw Material.* Washed green *Coffea arabica Tip.* variety from Sumatra (Mandheling, S-795, Kartika 1) was supplied by Rast Ltd. (Ebikon, Switzerland). The moisture content of green coffee was 10.04 g/100 g wb.

Roasting Trials. At the production scale, coffee was roasted using a G-45 drum roaster (Probat Ltd., Emmerich, Germany) with a batch size of 20 kg. At the laboratory scale, batches of 100 g of green beans were roasted using a fluidizing-bed hot-air laboratory roaster (G. W. Barth AG, Freiberg/Neckar, Germany), which was described in detail by Schenker (*4*) and Geiger et al. (*30*). Two isothermal programs, i.e., high temperature-short time (HTST) and low temperature-long time (LTLT), and one temperature profile program (Profile) were carried

Table 2. Roasting Times for Intermittent Sampling of Coffee Beans for Aroma Analysis

roasting process	roasting time [s]							
HTST	30	70	100	130	145	160[a]	200	
LTLT	120	240	420	600	660[a]	720	840	1140
profile	375	510	630	780	900[a]	1200		
drum roasting	180	360	540	660	780	900	1170[a]	

[a] Corresponds to targeted roasting end point with lightness $L^* = 21$.

out. Coffees were roasted to a target roast degree with lightness $L^* = 21$, where 100 means white and 0 means black.

Process parameters and roasted coffee properties are described in **Table 1**. For aroma analysis, samples were taken at different roasting times during drum roasting (**Table 2**). At the laboratory scale, batches were roasted during different roasting times according to **Table 2**. Color measurement and gravimetrical determination of moisture content were carried out using the methods described in Baggenstoss et al. (*31*). Bean core temperature in the laboratory roaster was recorded during roasting by placing thermocouples (Type K, 0.5 mm, Thermocoax Ltd., Surèsnes, France) into drilled holes in the green coffee beans.

Density. For the determination of coffee bean density, a displacement method was used, as described by Schenker (*6*). A stainless steel wire basket with and without 30 g of coffee beans was immersed in peanut oil, and the weight difference corresponded to the weight of oil displaced by coffee beans. Using a density of 910 kg m^{-3} for peanut oil at 25 °C, coffee bean density could be determined. Air bubbles between coffee beans had to be removed by moving the basket up and down, but care had to be taken not to overextend weight measuring time, in order to prevent oil from penetrating into the pores of coffee beans.

Aroma Analysis. *Chemicals.* Stable isotope labeled standards were obtained from Sigma-Aldrich St. Louis, MO, USA ([$^2H_3$]-methanethiol), Dr. Ehrenstorfer GmbH, Augsburg, Germany ([$^2H_6$]-dimethyl sulfide, [$^2H_5$]-pyridine, and [$^2H_2$]-3-methylbutanal), Witega Laboratorien, Berlin, Germany ([$^2H_3$]-4-vinylguaiacol), AromaLAB, Munich, Germany ([$^{13}C_4$]-2,3-butanedione, [$^{13}C_2$]-2,3-pentanedione, [$^2H_2$]-methylpropanal, and [$^2H_6$]-3-mercapto-3-methylbutyl formate), Cambridge Isotope Laboratories Inc., Andover MA, USA ([$^2H_3$]-*N*-methylpyrrole), and Toronto Research Chemicals, North York, Canada ([$^2H_2$]-2-furfurylthiol and [$^2H_{9-10}$]-2,3,5-trimethylpyrazine). [$^2H_2$]-hexanal (*32*) and [$^2H_6$]-dimethyl trisulfide (*33*) were synthesized at Nestlé Research Center (Lausanne, Switzerland).

SPME-GC-MS Analysis and Quantification of Coffee Aroma Compounds. Roasted coffee was analyzed immediately after roasting. Sample preparation was carried out in triplicate. Quantitative analysis of aroma compounds was done using an adapted method as described in ref *31*. Freshly roasted coffee was ground using a grain mill (Buehler-Miag 4000, Milano, Italy) at level 3. Then ground coffee was weighed in a 100 mL flask and suspended in boiling water (5% total solids for compounds **1**, **2**, **4**, **5**, **9**, **15**, and **16**; 1% total solids for compounds **3**, **6**−**8**, and **10**−**14**; see **Table 3**). The suspension was stirred for 10 min, while the flask was kept closed. The flask was then cooled under cold water, and the coffee solution was spiked with definite amounts of isotopically labeled standards (**Table 3**). The coffee solution was subsequently stirred for another 10 min, and 7 mL were transferred to 20 mL headspace vials.

Coffee aroma compounds were sampled with solid phase microextraction at 40 °C for 10 min using a Supelco 50/30 μm StableFlex DVB/CAR/PDMS fiber (Supelco, Buchs, Switzerland). Injection was carried out at 240 °C in the splitless mode with a splitless time of 240 s. Compounds **3**, **6**−**8**, and **10**−**14** were separated on a 60 m × 0.25 mm × 0.25 μm ZB-Wax column (Phenomenex, Aschaffenburg, Germany) using a Fisons 8000 Series gas chromatograph (Thermo Electron, Allschwil, Switzerland) with the following temperature program: 40 °C (6 min), 4 °C/min, 120 °C (0 min), 40 °C/min, and 240 °C (5 min). The gas chromatograph was coupled to a quadrupole mass spectrometer SSQ710 (Finnigan MAT, San Jose, California), where mass spectra were recorded in the single ion monitoring (SIM) mode using electron ionization and an ionization potential of 70 eV. Compound **1** was separated and quantified using the same setup with the following temperature program: 40 °C (6 min), 40 °C/min, and 240 °C (5 min). Compounds **2**, **4**, **5**, **9**, **15**, and **16** were separated on a 60 m × 0.25 mm × 0.25 μm ZB-1701 column (Phenomenex, Aschaffenburg, Germany) in a 2000 series TRACE GC gas chromatograph (Thermo Quest CE Instruments, Milano, Italy) with 40 °C (6 min), 4 °C/min, 120 °C (0 min), 40 °C/min, and 240 °C (5 min) as the temperature program. The GC was coupled to a TSQ triple quadrupole mass spectrometer (Finnigan MAT, San Jose, California) with Q1 operating in the RF-only mode. Spectra were recorded in single ion monitoring mode. Electron ionization with an ionization potential of 70 eV was used. All SPME-GC-MS measurements were run in triplicate.

Table 3. Analytes and Standards Used in GC-MS Analyses

analyte (A)	selected ion (*m*/*z*) of A	internal standard (IS)	selected ion (*m*/*z*) of IS
methanethiol (**1**)	48	[$^2H_3$]-**1**	51
dimethyl sulfide (**2**)	47	[$^2H_6$]-**2**	50
dimethyl trisulfide (**3**)	126	[$^2H_6$]-**3**	132
3-mercapto-3-methylbutyl formate (**4**)	102	[$^2H_6$]-**4**	108
2-furfurylthiol (**5**)	114	[$^2H_2$]-**5**	116
methylpropanal (**6**)	72	[$^2H_7$]-**6**	79
2-methylbutanal (**7**)	86	[$^2H_2$]-**8**	88
3-methylbutanal (**8**)	71	[$^2H_2$]-**8**	73
hexanal (**9**)	56	[$^2H_2$]-**9**	58
2,3-butanedione (**10**)	43	[$^{13}C_4$]-**10**	45
2,3-pentanedione (**11**)	100	[$^{13}C_2$]-**11**	102
N-methylpyrrole (**12**)	81	[$^2H_3$]-**12**	84
pyridine (**13**)	79	[$^2H_5$]-**13**	84
4-vinylguaiacol (**14**)	150	[$^2H_3$]-**14**	153
2,3,5-trimethylpyrazine (**15**)	122	[$^2H_{9/10}$]-**15**	131 + 132
2-ethyl-3,5-dimethylpyrazine (**16**)	135	[$^2H_{9/10}$]-**15**	131 + 132

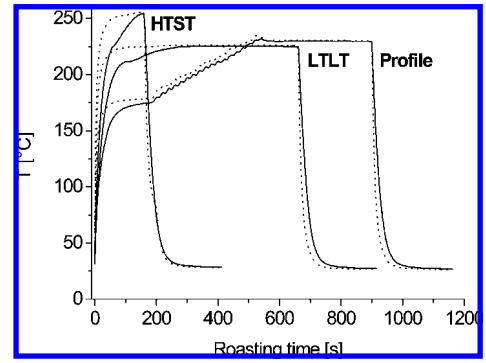

Figure 1. Evolution of bean core (—) and bulk (···) temperature during roasting with the fluidizing bed hot-air laboratory roaster.

Statistical Analysis. Student's *t*-test was applied to the results with a level of significance of 95%.

RESULTS AND DISCUSSION

Evolution of Physical Properties during Roasting. Bulk and bean core temperatures during roasting with the laboratory scale roaster are displayed in **Figure 1**. Although bean core temperature rapidly converged to bulk temperature, a small difference between the two remained, and the temperature of incoming hot air was never attained. Bean temperature measurement in the commercial drum roaster was not possible, but it is supposed that bean core temperature evolution took place in a way similar to that in the profile roasting process, although temperature increase was probably slower. The development of the physical properties of coffee during roasting strongly depended on the applied temperature and roasting time (**Figures 2**–**4**). High temperature roasting lead to lower density, higher bean volume, less roast loss, and lower moisture content compared to roasting processes at lower temperature. These results are in agreement with findings from other authors (*4, 34*).

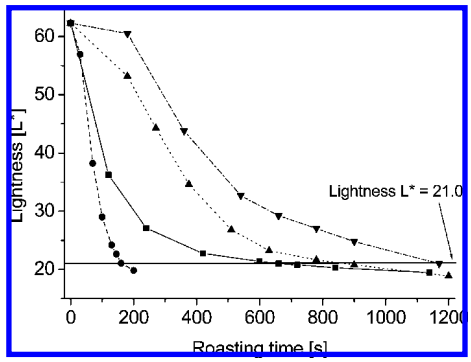

Figure 2. Evolution of the lightness of coffee beans during different roasting processes (LTLT, ■; HTST, ●; profile, ▲; drum roasting, ▼).

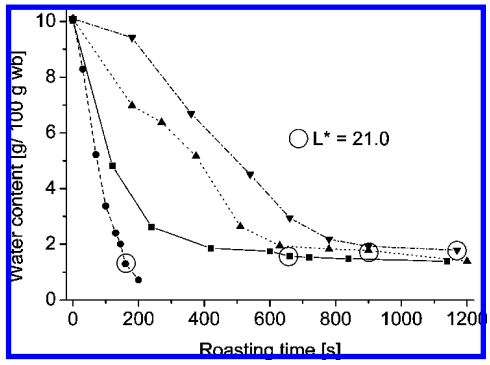

Figure 3. Evolution of the water content of coffee beans during different roasting processes (LTLT, ■; HTST, ●; profile, ▲; drum roasting, ▼).

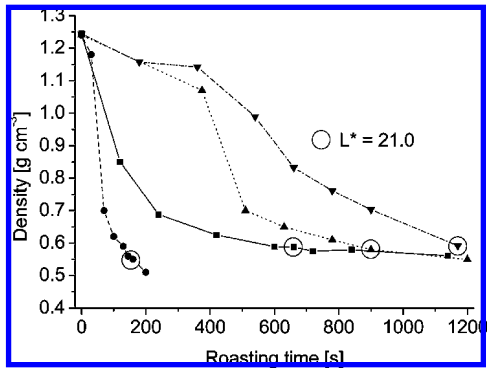

Figure 4. Evolution of the density of coffee beans during different roasting processes (LTLT, ■; HTST, ●; profile, ▲; drum roasting, ▼).

However, Geiger et al. (*30*) established mass balance during similar HTST and LTLT processes and found higher water content after HTST roasting than after LTLT. In those tests, initial water content of green coffee was considerably lower, which may have led to different water evaporation kinetics. Compared to the classical drum roasting process, the laboratory scale fluidizing-bed processes were faster with regard to moisture loss, color development, and evolution of coffee bean density. Evolution of these properties during profile and drum roasting was similar, but because of the obviously faster temperature increase in profile roasting, the development of roasting parameters was slightly faster. Use in the profile roast of an initially lower air temperature that subsequently rose more slowly probably would have produced bean temperature behavior more similar to that for the drum roast and thus would have provided an even better basis for comparing these two roasts.

Evolution of Aroma Compounds during Roasting with Different Time−Temperature Conditions. The following graphic presentations show the development of aroma compounds over roasting time. The development of aroma compounds was also plotted as a function of L^*-values. In order to increase the clarity of these latter presentations, an inverse and logarithmic scale was selected. This change of scale does not stipulate any physical meaning.

Sulfur Compounds. Sulfur compounds are among the most important aroma compounds in coffee. Methanethiol, dimethyl trisulfide, 3-mercapto-3-methylbutyl formate, and especially 2-furfurylthiol were cited as being impact compounds of coffee aroma (*16, 17*). It is generally thought that sulfur-containing amino acids act as the sulfur source for aroma compounds during roasting (*35–37*). Methanethiol is believed to result from the pyrolysis of methionine (*36*), and it is likely that dimethyl sulfide and dimethyl trisulfide are further oxidation and disproportionation products of the same reaction sequence (*38*). It could also be that *S*-methylmethionine, which is known to occur in flowering plants as an intermediate, could serve as a precursor for dimethyl sulfide. For these reasons, formation kinetics of these compounds should be at least partly related to each other.

The development of sulfur compounds during roasting is presented in **Figure 5**. Concentrations at $L^* = 21$ are shown in **Table 4**. The sulfides and methanethiol exhibited a large increase during the first stages of roasting. Methanethiol formation seemed to be favored by higher temperatures since the HTST process resulted in highest methanethiol concentration. Degradation took place at the end of HTST roasting, while during the other roasting processes, decrease of methanethiol concentration was not observed. In contrast, formation of dimethyl sulfide was faster with regard to the evolution of lightness, and maximum concentration was higher when low temperature was applied. The fact that in drum roasting, where temperature increase within coffee beans was slow, dimethyl sulfide formation started also very early, suggests that the required activation energy is low, and hence, reaction mechanisms involving radical species are probably predominant. Decrease of dimethyl sulfide concentration was observed toward the end of the roasting process.

Dimethyl trisulfide exhibited biphasic behavior. During all four roasting processes, a relatively fast increase was observed during the first stages, followed by decrease through medium roast degree. Two additional measuring points were determined in the case of profile roasting (after 180 and 270 s roasting time) in order to make the early increase visible. Toward the end of the roasting process, distinct reincrease was observed.

Formation of 3-mercapto-3-methylbutyl formate obviously required high activation energy since formation started late in the roasting process. The onset of formation was observed at L^* values between 40 and 30, which corresponded to roasting times of around 30 s at 260 °C (LTLT) and 120 s at 228 °C (LTLT), and to bean core temperatures of 212 °C (LTLT) and 194 °C (HTST). A maximum value was then quickly achieved followed by a fast degradation. During HTST roasting, at the roasting end point, 3-mercapto-3-methylbutyl formate concentration was around twice as high as that in the other roasting processes. 2-Furfurylthiol concentration increased continuously during the roasting process depending on temperature, and no decrease was observed, which is in agreement with results from other authors (*4, 22, 23, 37*). The constant increase of 2-furfurylthiol during roasting suggests the existence of a large pool of precursor compounds. As in the case of 3-mercapto-3-methylbutyl formate, a certain onset temperature was necessary in order to initiate formation. At $L^* = 21$, significantly higher

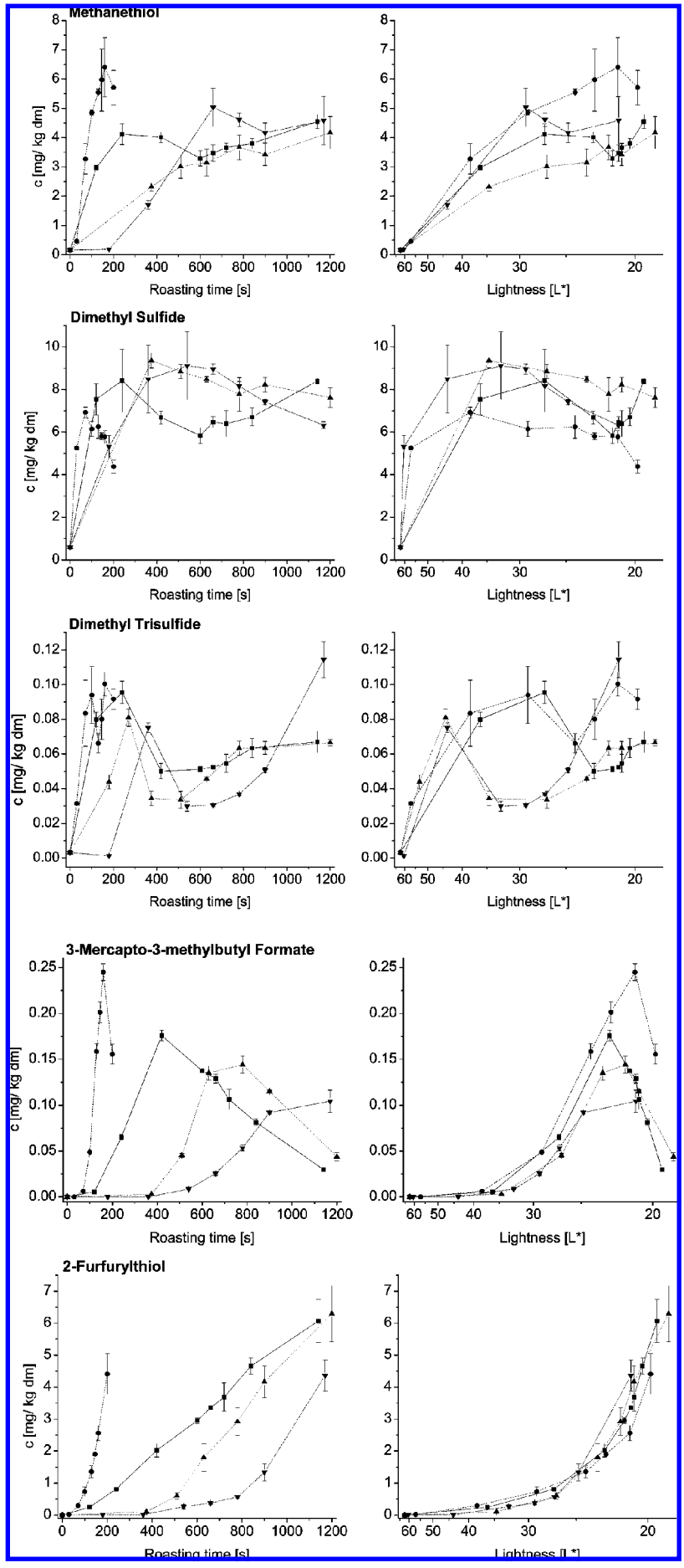
Methanethiol
c [mg/ kg dm]
Roasting time [s]
Lightness [L*]
Dimethyl Sulfide
c [mg/ kg dm]
Roasting time [s]
Lightness [L*]
Dimethyl Trisulfide
c [mg/ kg dm]
Roasting time [s]
Lightness [L*]
3-Mercapto-3-methylbutyl Formate
c [mg/ kg dm]
Roasting time [s]
Lightness [L*]
2-Furfurylthiol
c [mg/ kg dm]
Roasting time [s]
Lightness [L*]

Figure 5

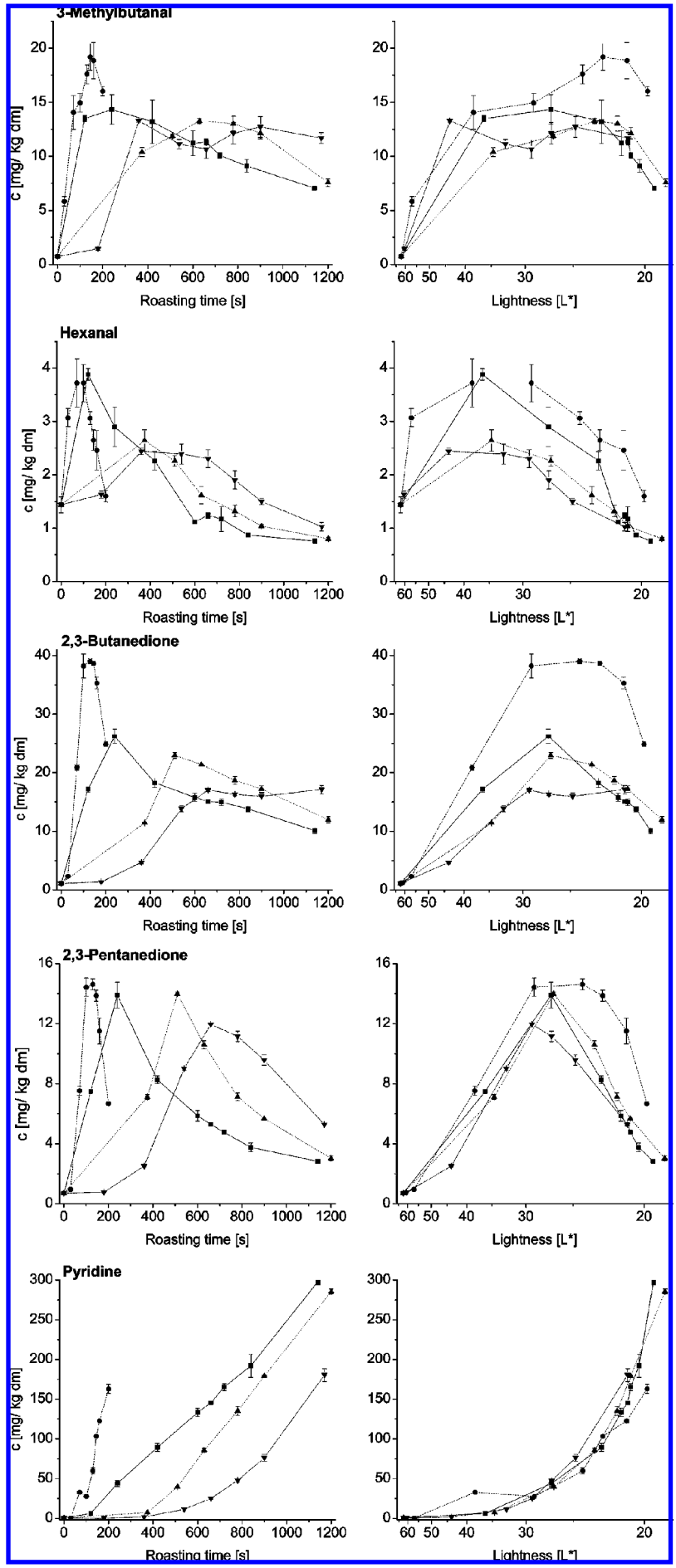
3-Methylbutanal
Hexanal
2,3-Butanedione
2,3-Pentanedione
Pyridine
c [mg/ kg dm]
Roasting time [s]
Lightness [L*]

Figure 5

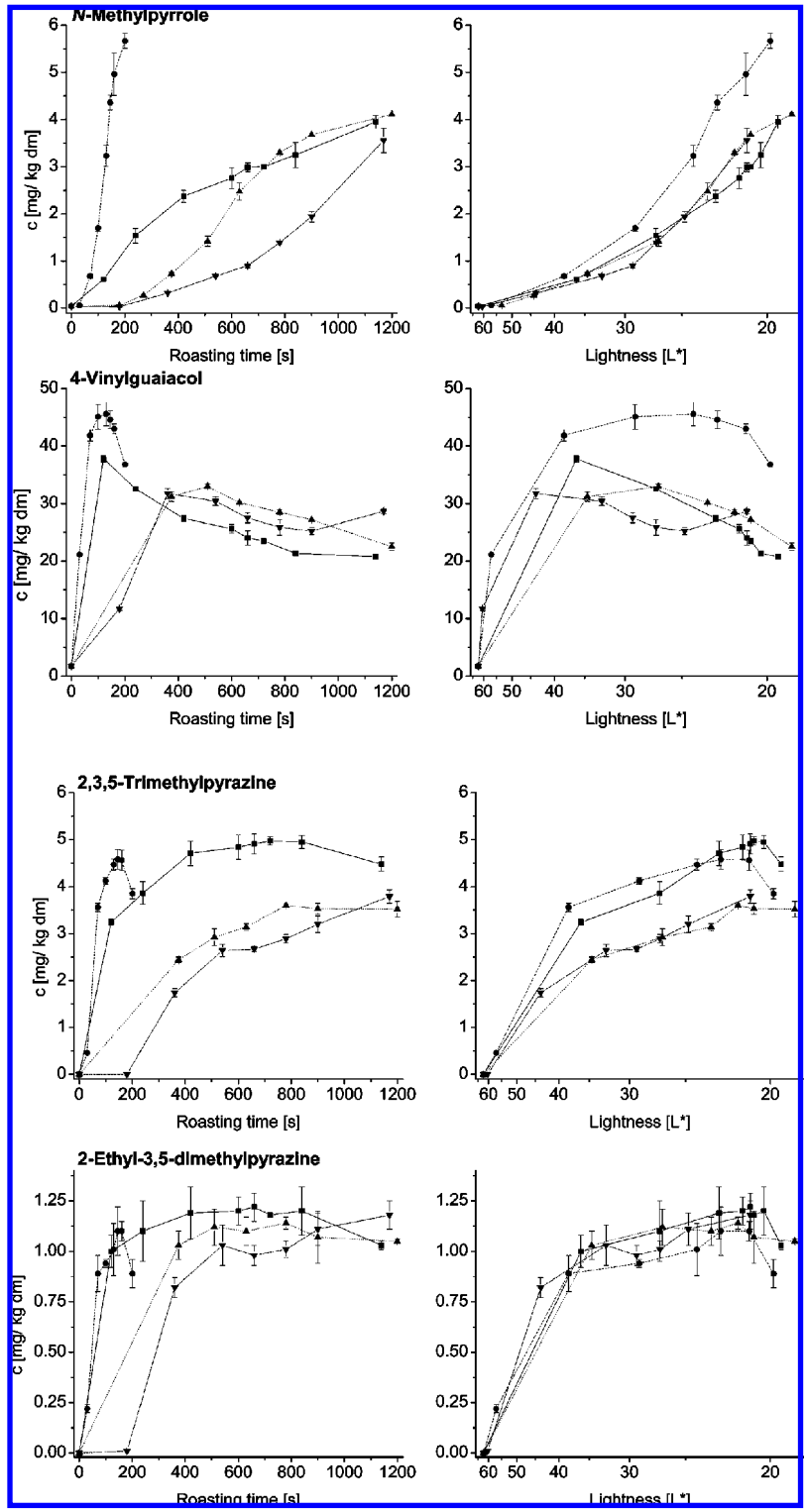

Figure 5. Evolution of selected coffee aroma compounds during roasting as a function of time and lightness (LTLT, ■; HTST, ●; profile, ▲; drum roasting, ▼).

amounts of 2-furfurylthiol were found in the low temperature-long time roasting processes (LTLT, profile, and drum roasting) compared to that in the HTST roast.

Aldehydes and α-Diketones. Strecker aldehydes such as methylpropanal, 2-methylbutanal, and 3-methylbutanal are regarded to be products of decarboxylative transamination of amino acids with subsequent addition of water and breakdown into aminoacetone and the corresponding Strecker aldehyde (*39*).

The development of aldehydes and α-diketones during roasting is shown in **Figure 5** (methylpropanal and 2-methylbutanal are not shown). Concentrations at $L^* = 21$ are displayed in **Table 4**. Their behavior upon roasting is similar. A fast increase during the first stages of roasting is followed by decreasing concentration toward higher degrees of roast. This is in agreement with other studies (*20, 23, 40*). Formation of the three Strecker aldehydes in the beginning of the roasting process seemed to be slightly favored by high temperature, and at lightness $L^* = 21$, 2- and 3-methylbutanal concentration in HTST roasted coffee was significantly higher than in the long-time roasts, with the exception of 2-methylbutanal in profile

Table 4. Influence of Time−Temperature Conditions on Concentration of Aroma Compounds after Roasting ($L^* = 21$)[a]

aroma compound	Roasting process			
	LTLT [mg/kg dm]	HTST [mg/kg dm]	profile [mg/kg dm]	drum roasting [mg/kg dm]
methanethiol	3.5 ± 0.3a	6.4 ± 1.0b	3.4 ± 0.4a	4.6 ± 0.8a,b
dimethyl sulfide	6.5 ± 0.3a	5.8 ± 0.3b	8.2 ± 0.4c	6.3 ± 0.2a,b
dimethyl trisulfide	0.053 ± 0.001a	0.10 ± 0.01b	0.064 ± 0.004c	0.11 ± 0.01b
3-mercapto-3-methylbutyl formate	0.129 ± 0.005a	0.24 ± 0.01b	0.115 ± 0.002c	0.10 ± 0.01a,c
2-furfurylthiol	3.35 ± 0.03a	2.6 ± 0.2b	4.2 ± 0.5a	4.4 ± 0.5a
methylpropanal	20.2 ± 0.9a	23.1 ± 2.2a	n.a.	14.0 ± 1.1b
2-methylbutanal	18.7 ± 0.2a	24.4 ± 2.0b	21.7 ± 0.7b	19.2 ± 1.1a
3-methylbutanal	11.3 ± 0.3a	18.9 ± 1.7b	12.1 ± 0.5a	11.7 ± 0.5a
hexanal	1.24 ± 0.05a	2.5 ± 0.4b	1.04 ± 0.03c	1.03 ± 0.08c
2,3-butanedione	15.1 ± 0.1a	35.3 ± 1.0b	17.2 ± 0.5c	17.1 ± 0.7c
2,3-pentanedione	5.29 ± 0.08a	11.5 ± 0.9b	5.67 ± 0.08c	5.28 ± 0.01a
N-methylpyrrole	2.99 ± 0.09a	5.0 ± 0.4b	3.7 ± 0.2c	3.6 ± 0.3a,c
pyridine	145.7 ± 0.7a	122.6 ± 2.5b	179.3 ± 1.1c	180.6 ± 8.1c
4-vinylguaiacol	24.0 ± 1.2a	43.0 ± 0.8b	27.18 ± 0.06c	28.7 ± 0.5d
2,3,5-trimethylpyrazine	4.9 ± 0.2a	4.6 ± 0.2a	3.5 ± 0.1b	3.8 ± 0.1b
2-ethyl-3,5-dimethylpyrazine	1.22 ± 0.07a	1.10 ± 0.05a	1.1 ± 0.1a	1.18 ± 0.07a

[a] Different letters indicate statistically significant differences ($p < 0.05$). n.a.: data not available.

roasting, where its concentration was lower than that for HTST roasting but not significantly so at the $p < 0.05$ level. Hexanal is not formed by the Maillard reaction but results from the oxidation of lipids (*25*). Considerable amounts of hexanal were found in green coffee (around 1.5 mg/kg dm). Temperatures of nearly 220 °C were necessary to further increase its concentration. The extent of formation and maximum concentration depended on roasting temperature (HTST and LTLT, 3.5−4.0 mg/kg dm; profile and drum roasting, which exhibited lower product temperatures before hexanal peak concentration was attained, ca. 2.5 mg/kg dm). Peak concentration of hexanal was attained at L^* values between 40 and 30, then degradation of hexanal was observed. At $L^* = 21$, hexanal concentration was significantly higher in HTST roasted coffee than in LTLT roasted coffee. Profile and drum roasting both resulted in significantly lower hexanal concentrations than those in the two isothermal roasting processes.

Various possible formation pathways for the α-diketones 2,3-butanedione, and 2,3-pentanedione have been suggested. From model systems of glucose with alanine, Yaylayan and Keyhani (*41*) concluded that 2,3-butanedione is formed by a single pathway involving glucose carbon atoms only, while in model systems with glucose and glycine, formation via C_3/C_3 and C_2/C_4 cleavage was possible. Formation of 2,3-pentanedione was observed involving glucose carbons only (10%) and via the incorporation of C2′-C3′ atoms of alanine to a C_3 carbon unit from glucose. In a model experiment under roasting conditions and using the carbohydrate module labeling approach, Schieberle et al. (*42*) showed that in the reaction of glucose and proline, 87% of the resulting 2,3-butanedione emerged from a C_3/C_1 recombination of glucose, 13% from a C_2/C_2 recombination, while none of the 2,3-butanedione was formed from the intact carbohydrate. This was in accordance with a proposed reaction mechanism involving aldol condensation of acetaldehyde with hydroxyacetaldehyde and hydroxyacetone (*43*). A second model with formaldehyde and hydroxypropanone also led to the formation of 2,3-butanedione (*42*). Other reaction pathways were proposed, involving the 1-deoxyglycosone (*44*) and sugar fragmentation followed by intramolecular condensation (*43*). In addition, 2,3-pentanedione was cited to be the main volatile thermal degradation product of 4-hydroxy-2,5-dimethyl-3(2H)-furanone (*25*). Formation of 2,3-butanedione required a certain activation energy and was clearly accelerated by high roasting temperature. During HTST roasting, a maximum concentration of almost 40 mg/kg dm was attained and remained constant during a period of 45 s. Then fast degradation was observed. With lower temperature roasting processes, the evolution of 2,3-butanedione was similar, but less rapid with lower maximum concentrations. 2,3-Pentanedione formation and elimination followed a similar pattern as in the case of 2,3-butanedione, but differences in maximum concentration were low, and evolution as a function of lightness was similar for all time−temperature profiles applied. This is an indication that, in contrast to 2,3-butanedione, the formation of 2,3-pentanedione seems to be substrate limited and less dependent on roasting time and temperature. It is therefore assumed that 2,3-pentanedione does not result from the same sugar fragments as 2,3-butanedione and that the formation and degradation pathways are different. Formation of 2,3-pentanedione from the reaction of 2,3-butanedione with formaldehyde with subsequent loss of water, proposed by Weenen and Apeldoorn (*44*) as linked to formation of 2,3-butanedione, is therefore not corroborated in the case of coffee roasting.

At roasting end point with lightness $L^* = 21$, HTST roasted coffee exhibited double the amount of 2,3-butanedione and 2,3-pentanedione as for all other roasts. However, degradation of both diketones was very fast at the end of HTST roasting, and concentrations similar to those resulting from the long time processes would have been obtained by extending the HTST process by 30 to 40 s, with only minor change in roasted coffee lightness (**Figure 2**).

Heterocyclic and Phenolic Compounds. Heterocycles and phenolic compounds are typical roasting products, resulting from the Maillard reaction (pyrazines), thermal decomposition of ferulic acid (guaiacols), and trigonelline degradation (pyridine, *N*-methylpyrrole). In model reaction systems, pyridine and *N*-methylpyrrole were also produced from classical Maillard reaction mixtures consisting of amino acids and glucose/sucrose (*25*). Among the examined heterocyclic and phenolic compounds, only 2-ethyl-3,5-dimethylpyrazine and 4-vinylguaiacol are of key importance for coffee aroma.

Figure 5 shows the development of heterocyclic compounds during roasting, and concentrations at $L^* = 21$ are presented in **Table 4**. Formation kinetics of pyridine were found to be very similar to those of 2-furfurylthiol. High temperature was needed to initiate reactions leading to pyridine, and once formation began, pyridine concentration continuously rose during roasting. Impact of roasting time was higher than the effect of temperature, and at $L^* = 21$, the highest pyridine concentrations were found in profile and

drum roasting. Formation of *N*-methylpyrrole was observed at roasting temperatures of around 170 °C, and the rate of formation increased with increasing temperature. For better comparison between profile and drum roasting, *N*-methylpyrrole concentration was measured at two additional points during the first stage of profile roasting (180 and 270 s roasting time). In contrast to pyridine, the reactions seemed to be much more temperature-dependent, and consequently, the highest amount at $L^* = 21$ was found after HTST roasting.

2,3,5-Trimethylpyrazine and 2-ethyl-3,5-dimethylpyrazine both exhibited relatively fast increase in the beginning of the roasting process. At darker degrees of roast, a slight decrease was observed for HTST roasting, while in the other processes, concentration increase leveled off. In the case of LTLT roasting, degradation was observed when coffees were over-roasted. Similar observations were made by Gretsch et al. (*22*), however, for relatively light roasts only (roasting temperature of 230 °C during max. 9 minutes). At roasting end point with $L^* = 21$, the amount of 2,3,5-trimethylpyrazine was significantly higher in LTLT and HTST roasted coffees compared to that in the drum and profile roastings, while no significant differences were observed in concentrations of 2-ethyl-3,5-dimethylpyrazine.

Formation of 4-vinylguaiacol immediately started in the beginning of the roasting process, which suggests low activation energy and hence the involvement of a radical reaction pathway. Evolution of 4-vinylguaiacol during roasting was highly dependent on temperature. The isothermal processes with very fast increase of bean core temperature both resulted in high formation rates during the first stage of roasting, while profile and drum roasting processes led to slower increase of 4-vinylguaiacol. After attaining maximum concentration, which was higher with increasing roasting temperature, elimination occurred. At the end of the roasting process ($L^* = 21$), HTST roasting yielded by far the highest concentration of 4-vinylguaiacol. Dorfner et al. (*45*) found the same evolution of 4-vinylguaiacol during roasting and established a two-channel model for the degradation of 5-feruloylquinic acid during coffee roasting. In the first, endothermic roasting stage, formation of 4-vinylguaiacol is predominant because of low activation energy. Once exothermic roasting conditions are attained, 4-vinylguaiacol degrades yielding guaiacol, which then degrades to phenol.

Effect of Excessive Roasting on Aroma Compounds. To determine the effect of excessive roasting beyond usual degrees of roast on the formation and degradation of aroma compounds, the profile roasting process was extended to 20, 25, 30, 35, and 40 min, i.e., after completing the temperature step, coffee beans were kept for 11, 16, 21, 26, and 34 min, respectively, at 232 °C. Lightness L^* of the resulting coffee beans was 18.9, 18.5, 18.2, 17.7, and 17.6, respectively. Trends and final concentration after 40 min of roasting time are shown in **Table 5**. For many of the investigated aroma compounds, degradation exceeded formation, and decreasing amounts were found in coffee roasted for excessive periods. 3-Mercapto-3-methylbutyl formate, as the most extreme example, degraded to zero concentration after 40 min of roasting time. Other compounds, such as the Strecker aldehydes (methylpropanal, 2-methylbutanal, and 3-methylbutanal) and the α-diketones (2,3-butanedione and 2,3-pentanedione) were also degraded, but decrease seemed to level off at a certain concentration, whereas 4-vinylguaiacol exhibited a steady decrease throughout excessive roasting. 2-Furfurylthiol concentration increased until 25 min of roasting time, but then the concentration decreased. Dimethyl sulfide concentration also decreased, albeit slowly. Concentration of pyridine increased throughout 40 min of roasting, whereas the increase of *N*-methylpyrrole decelerated and leveled off after 35 min of roasting. Dimethyl trisulfide, which already exhibited increasing concentration toward the end of roasting to normal degrees of roast, increased further at excessive conditions. Hexanal revealed minimum concentration after 20 min of roasting time, then increased steadily during the next 20 min. 2,3,5-Trimethylpyrazine and 2-ethyl-3,5-dimethylpyrazine remained at stable concentration during 35 min of roasting and then slowly decreased.

Table 5. Effect of Over-Roasting in Profile Roasting on Aroma Compounds

compound	behavior upon excessive roasting	concentration after 40 min of roasting ($n = 1$) [mg/kg dm]
methanethiol	n.a.[a]	n.a.
dimethyl sulfide	slightly decreasing	7.0
dimethyl trisulfide	steadily increasing	0.14
3-mercapto-3-methylbutyl formate	decreasing to 0 mg/kg dm	n.d.[b]
2-furfurylthiol	increasing until 25 min, then decreasing	4.6
methylpropanal	decreasing, leveling off after 35 min	8.5
2-methylbutanal	decreasing, leveling off after 35 min	4.6
3-methylbutanal	decreasing, leveling off after 35 min	3.3
hexanal	decreasing until 20 min, then increasing	1.8
2,3-butanedione	decreasing, leveling off after 35 min	6.5
2,3-pentanedione	decreasing, leveling off after 35 min	1.2
N-methylpyrrole	increasing, leveling off after 35 min	5.0
pyridine	increasing	586
4-vinylguaiacol	decreasing	9.4
2,3,5-trimethylpyrazine	stable, decreasing after 35 min	3.2
2-ethyl-3,5-dimethylpyrazine	stable, decreasing after 35 min	0.9

[a] n.a.: results not available. [b] n.d.: not detected.

Relationship between Color Development, Physical Changes, and Aroma Formation. The results obtained from this study showed that attaining the same coffee bean color (which is most frequently referred to as the degree of roast) using different time−temperature conditions during roasting does not necessarily mean that coffees are equivalent in terms of aroma and physical properties. High speed roasting with high hot air temperature led to different formation and elimination kinetics and in many cases to different concentrations of aroma compounds at roast color $L^* = 21$ (**Table 4**). The same observations applied for the evolution of physical properties such as density, roast loss, and water content (**Table 1**). Similar results were obtained by Schenker (*4*). Aroma compounds whose concentrations peaked and then decreased at medium degrees of roast, degraded rapidly near the end of HTST roasts. Thus for HTST roasts, small increases in roasting time would have reduced their concentration to levels similar to or lower than those attained in the longer roasts and would have reduced L^* only slightly. However, small increases in HTST roast time would not have produced pyridine and 2-furfurylthiol levels equal to those produced by the longer roasts. It is highly probable that the different time−temperature profiles applied

do not only result in differences with regard to aroma compounds but also to flavor in general.

Using a time−temperature profile on the laboratory scale fluidizing-bed roaster, which approximated the temperature profile in a traditional drum roaster, similar results were obtained for physical properties and aroma formation in the resulting coffees. Temperature increase in the first stage of roasting was still faster in profile roasting than in drum roasting. Even better accord would be expected if a lower rate of temperature rise had been used during the profile roast. It is therefore possible to transfer roasting conditions of a traditional horizontal drum roaster to a fluidizing-bed system, but roasting time would not be reduced, if the roaster wants to produce a coffee with similar flavor properties.

The degree of roast is ultimately a question of definition, and the definition should depend on the specific requirements. In industrial practice, where constant quality of green coffee is roasted on the same roasting equipment, color measurement is surely an adequate, fast, and simple method for determining the degree of roast. However, if coffee of equal sensory quality is intended to be produced with different roasting processes, more details about the roasting processes are needed. An exhaustive list of important physical values for reports on coffee roasting was proposed by Eggers and Pietsch (*7*). The more physical and chemical parameters taken into account for the definition of a degree of roast, the more precise its determination and the better the transferability from one roasting process to another. In addition, an ideal definition of a degree of roast should also be independent from variations in raw material. Concentrations and ratios of different reaction products and remaining amounts of green coffee precursors (amino acids, chlorogenic acids, etc.) are potentially well suited indicators; however, their analysis is usually too complex for industrial practice.

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LITERATURE CITED

(1) Barbera, C. E. Gas-Volumetric Method for the Determination of the Internal Non Odorous Atmosphere of Coffee Beans. In 3rd International Scientific Colloquium on Coffee, Trieste, Italy, 1967; Association Scientifique Internationale pour le Café: Paris, France; pp 436−442.

(2) Clarke, R. J.; Macrae, R. *Coffee. Volume 2: Technology*; Elsevier Science Publishers Ltd.: Essex, 1987.

(3) Radtke, R., Das Problem der CO2-Desorption von Röstkaffee unter dem Gesichtspunkt einer neuen Packstoffentwicklung. In 7th International Scientific Colloquium on Coffee, Hamburg, Germany; Association Scientifique Internationale pour le Café: Paris, France, 1975.

(4) Schenker, S. Investigations on the Hot Air Roasting of Coffee Beans. Dissertation No. 13620, Eidgenoessische Technische Hochschule Zuerich (ETH), Switzerland, 2000.

(5) Geiger, R. Development of Coffee Bean Structure during Roasting: Investigations on Resistance and Driving forces. Dissertation No. 15430, Eidgenoessische Technische Hochschule Zuerich (ETH), Switzerland, 2004.

(6) Schenker, S.; Handschin, S.; Frey, B.; Perren, R.; Escher, F. Pore structure of coffee beans affected by roasting conditions. *J. Food Sci.* **2000**, *65* (3), 452–457.

(7) Eggers, R.; Pietsch, A. Technology I: Roasting. In *Coffee: Recent Developments*; Clarke, R. J., Vitzthum, O. G., Eds. Blackwell Science Ltd.: London, 2001; pp 90−107.

(8) Nagaraju, V. D.; Murthy, C. T.; Ramalakshmi, K.; Rao, P. N. S. Studies on roasting of coffee beans in a spouted bed. *J. Food Eng.* **1997**, *31* (2), 263–270.

(9) Puhlmann, R.; Habel, G. Examinations to test the grinding behavior of roasted coffee. *Lebensmittelindustrie* **1989**, *36* (4), 161–163.

(10) Illy, A.; Viani, R. *Espresso Coffee: the Chemistry of Quality*; Academic Press Limited: London, 1995.

(11) Sivetz, M. Growth in Use of Automated Fluid Bed Roasting of Coffee Beans. In 14th International Scientific Colloquium on Coffee, San Francisco, CA; Association Scientifique Internationale pour le Café: Paris, France, 1991; pp 313−318.

(12) Nehring, U. P.; Maier, H. G. Indirect Determination of the Degree of Roast in Coffee. *Z. Lebensm.-Unters. Forsch.* **1992**, *195* (1), 39–42.

(13) Hashim, L.; Chaveron, H. Use of methylpyrazine ratios to monitor the coffee roasting. *Food Res. Int.* **1995**, *28* (6), 619–623.

(14) Dorfner, R.; Ferge, T.; Yeretzian, C.; Kettrup, A.; Zimmermann, R. Laser mass spectrometry as on-line sensor for industrial process analysis: Process control of coffee roasting. *Anal. Chem.* **2004**, *76* (5), 1386–1402.

(15) Hofmann, T.; Bock, J.; Heinert, L.; Kohl, C. D.; Schieberle, P. Development of selective Chemosensors for the On-Line Monitoring of Coffee Roasting by SOMMSA and COTA Technology. In Heteroatomic Aroma Compounds; ACS Symposium Series 826; American Chemical Society: Washington DC, 2002; pp 336−352.

(16) Blank, I.; Sen, A.; Grosch, W. Potent Odorants of the Roasted Powder and Brew of Arabica Coffee. *Z. Lebensm.-Unters. Forsch.* **1992**, *195* (3), 239–245.

(17) Czerny, M.; Mayer, F.; Grosch, W. Sensory study on the character impact odorants of roasted Arabica coffee. *J. Agric. Food Chem.* **1999**, *47* (2), 695–699.

(18) Czerny, M.; Wagner, R.; Grosch, W. Detection of odor-active ethenylalkylpyrazines in roasted coffee. *J. Agric. Food Chem.* **1996**, *44* (10), 3268–3272.

(19) Semmelroch, P.; Grosch, W. Studies on character impact odorants of coffee brews. *J. Agric. Food Chem.* **1996**, *44* (2), 537–543.

(20) Holscher, W.; Steinhart, H. Investigation of Roasted Coffee Freshness with an Improved Headspace Technique. *Z. Lebensm.-Unters. Forsch.* **1992**, *195* (1), 33–38.

(21) Grosch, W. Key Odorants of Roasted Coffee: Evaluation, Release, Formation. In 18th International Scientific Colloquium on Coffee, Helsinki, Finland; Association Scientifique Internationale pour le Café: Paris, France, 1999; pp 17−26.

(22) Gretsch, C.; Sarrazin, C.; Liardon, R. Evolution of Coffee Aroma Characteristics during Roasting. In 18th International Scientific Colloquium on Coffee, Helsinki, Finland; Association Scientifique Internationale pour le Café: Paris, France, 1999; pp 27−34.

(23) Mayer, F.; Czerny, M.; Grosch, W. Influence of provenance and roast degree on the composition of potent odorants in Arabica coffees. *Eur. Food Res. Technol.* **1999**, *209* (3−4), 242–250.

(24) Schenker, S.; Heinemann, C.; Huber, M.; Pompizzi, R.; Perren, R.; Escher, F. Impact of roasting conditions on the formation of aroma compounds in coffee beans. *J. Food Sci.* **2002**, *67* (1), 60–66.

(25) Flament, I. *Coffee Flavor Chemistry*; John Wiley & Sons Limited: Chichester, England, 2002.

(26) Reineccius, G. A. The Maillard reaction and coffee flavor. In 16th International Scientific Colloquium on Coffee, Kyoto, Japan; Association Scientifique Internationale pour le Café: Paris, France, 1995; pp 249−257.

(27) Shibamoto, T. An overview of coffee aroma and flavour chemistry. In 14th International Scientific Colloquium on Coffee, San Francisco, CA; Association Scientifique Internationale pour le Café: Paris, France, 1991; pp 107−116.

(28) Schieberle, P. The Carbon Module Labeling (CAMOLA) technique - A useful tool for identifying transient intermediates in the formation of Maillard-type target molecules. *Ann. N. Y. Acad. Sci.* **2005**, *1043*, 236–248.

(29) Muller, C.; Hofmann, T. Screening of raw coffee for thiol binding site precursors using "in bean" model roasting experiments. *J. Agric. Food Chem.* **2005**, *53* (7), 2623–2629.

(30) Geiger, R.; Perren, R.; Kuenzli, R.; Escher, F. Carbon dioxide evolution and moisture evaporation during roasting of coffee beans. *J. Food Sci.* **2005**, *70* (2), E124–E130.

(31) Baggenstoss, J.; Poisson, L.; Luethi, R.; Perren, R.; Escher, F. Influence of water quench cooling on degassing and aroma stability of roasted coffee. *J. Agric. Food Chem.* **2007**, *55* (16), 6685–6691.

(32) Lin, J. M.; Welti, D. H.; Vera, F. A.; Fay, L. B.; Blank, I. Synthesis of deuterated volatile lipid degradation products to be used as internal standards in isotope dilution assays. 1. Aldehydes. *J. Agric. Food Chem.* **1999**, *47* (7), 2813–2821.

(33) Milo, C.; Grosch, W. Changes in the odorants of boiled salmon and cod as affected by the storage of the raw material. *J. Agric. Food Chem.* **1996**, *44* (8), 2366–2371.

(34) Ortola, M. D.; Londono, L.; Gutierrez, C. L.; Chiralt, A. Influence of roasting temperature on physicochemical properties of different coffees. *Food Sci. Technol. Int.* **1998**, *4* (1), 59 66.

(35) Holscher, W.; Vitzthum, O. G.; Steinhart, H. Prenyl alcohol source for odorants in roasted coffee. *J. Agric. Food Chem.* **1992**, *40* (4), 655–658.

(36) Merritt, C.; Robertson, D. H.; McAdoo, D. J. The relationship of volatile compounds in roasted coffee to their precursors. In 4th International Scientific Colloquium on Coffee, Amsterdam, Netherlands; Association Scientifique Internationale pour le Café: Paris, France, 1969; pp 144−148.

(37) Stahl, H. D.; Parliment, T. H. Generation of furfuryl mercaptan in cysteine-ribose model systems in relation to roasted coffee aroma. In 15th International Scientific Colloquium on Coffee, Montpellier, France; Association Scientifique Internationale pour le Café: Paris, France, 1993; pp 607−615.

(38) Parliment, T. H.; Kolor, M. G.; Rizzo, D. J. Volatile Components of Limburger Cheese. *J. Agric. Food Chem.* **1982**, *30* (6), 1006–1008.

(39) Grosch, W. Chemistry III: Volatile Compounds. In *Coffee: Recent Developments*; Clarke, R. J. , Vitzthum, O. G., Eds. Blackwell Science Ltd.: London, 2001; pp 67−89.

(40) Yeretzian, C.; Jordan, A.; Badoud, R.; Lindinger, W. From the green bean to the cup of coffee: investigating coffee roasting by on-line monitoring of volatiles. *Eur. Food Res. Technol.* **2002**, *214* (2), 92–104.

(41) Yaylayan, V. A.; Keyhani, A. Origin of 2,3-pentanedione and 2,3-butanedione in D-glucose/L-alanine maillard model systems. *J. Agric. Food Chem.* **1999**, *47* (8), 3280–3284.

(42) Schieberle, P.; Fischer, R.; Hofmann, T. The Carbohydrate Module Labelling Technique - A Useful Tool to Clarify Formation Pathways of Aroma Compounds Formed in Maillard-Type Reactions. In *Flavour Research at the Dawn of the Twenty-First Century*; LeQuere, J. L., Etievant, P. X., Eds.; Lavoisier: London, 2003; pp 447−452.

(43) Hofmann, T. Characterisation of intense odorants in carbohydrate/cysteine model reactions and evaluation of their formation. A contribution to the Maillard reaction. Dissertation, Technical University, Munich, Germany, 1995.

(44) Weenen, H.; Apeldoorn, W. Carbohydrate cleavage in the Maillard reaction. In *Flavour Science - Recent Developments*; Taylor, A. J., Mottram, D. S., Eds.; The Royal Society of Chemistry: Cambridge, 1996; pp 211−216.

(45) Dorfner, R.; Ferge, T.; Kettrup, A.; Zimmermann, R.; Yeretzian, C. Real-time monitoring of 4-vinylguaiacol, guaiacol, and phenol during coffee roasting by resonant laser ionization time-of-flight mass spectrometry. *J. Agric. Food Chem.* **2003**, *51* (19), 5768–5773.

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