

## Sensory and Chemical Changes in Tomato Sauces during Storage

PASCALE LANDY,\* CLAIRE BOUCON, GONNIE M. KOOYMAN,  
PIETER A. D. MUSTERS, ED A. E. ROSING, TEUN DE JOODE, JAN LAAN, AND  
PETER G. M. HARING

Unilever Research Vlaardingen, Olivier van Noortlaan 120, 3133 AT Vlaardingen, The Netherlands

The present work aimed to identify the key odorants of tomato sauces responsible for the flavor change during storage. Products made from paste or canned tomatoes were stored at 25 and 40 °C. Sensory properties and quantification of the key odorants were measured and correlated. Significant sensory changes appeared after 1 and 3 months at 25 °C in the respective dice and paste sauces ( $p < 0.01$ ). The dice sauce was characterized by a steep loss of the sensory quality during the early storage and then by identical changes within the same time span at 25 and 40 °C. In the paste sauce the sensory deterioration was slower than for the dice sauce and occurred more extensively at 40 °C than at 25 °C. Correlation between sensory and instrumental data revealed that the source of sensory changes should be (*E,E*)-deca-2,4-dienal in the dice sauce. The sensory change in the paste sauce could be due to acetaldehyde, methylpropanal, 3-methylbutanal, oct-1-en-3-one, 3-methylbutanoic acid, deca-2,4-dienal, 2-methoxyphenol, and  $\beta$ -damascenone.

**KEYWORDS:** Flavor analysis; sensory analysis; storage; tomato sauce

### INTRODUCTION

Flavor and its stability are major issues in food products as quality indices. Thus, a consumer's preference is largely based upon such performances. The flavor of tomato-based products represents an important attribute besides their color, nutritive value, and consistency (*1*). The most important odorants causing the aroma of fresh and processed tomatoes have been extensively studied and reviewed (*2–7*). During paste manufacturing (breaking, concentration, and pasteurization) many volatiles are lost by evaporation, while many other compounds are formed at this stage from lipoxygenase activity, breakdown of sugars, carotenoid co-oxidation, and Maillard reaction processes (*1, 8*).

During storage tomato sauces tend to change color from red to orange, develop off-flavors, and lose flavor strength even when the food product is in a frozen state (*9*). To our knowledge, only a few works have been published on the change in tomato volatiles during storage. Large amounts of dimethyl sulfide were formed in tomato juice stored in plain tin cans, and generally carbonyl concentration decreased while alcohols increased (*10*). Coulibaly et al. (*11*) reported for tomato juice stored in enameled cans an increase in furfural, benzaldehyde,  $\alpha$ -terpineol, and 6-methyl-5-hepten-2-one, whereas phenylethanol and benzyl alcohol were found to be lost. In basil-flavored tomato sauce heat-induced sulfur compounds were not affected by different storage temperatures, whereas the terpenic compounds of the basil flavor were extensively lost (*12*). However, no study was

undertaken to evaluate the impact of such chemical observations on the sensory quality change of tomato products during storage.

The aims of the present research were (i) to evaluate and describe the sensory changes in sauces made from canned diced tomatoes or tomato paste during storage at 25 and 40 °C in glass jars, (ii) to characterize and quantify the potent odorants of the sauce aroma, (iii) to compare the sensory and instrumental analyses between both storage regimes and between both sauces, and (iv) to identify the odorants responsible for the tomato flavor instability during storage through correlation between sensory and instrumental data sets.

### MATERIALS AND METHODS

**Tomato Sauce Preparation.** Hot break tomato paste (40%) (Conesa, Badajoz, Spain) was diluted with water (60%). Canned diced tomatoes in water (Copaïs Canning Industry S.A., Athens, Greece) were drained before use. The paste and dice sauces contained 0.5% salt and 1% refined soybean oil (van den Berg Foods, Rotterdam, The Netherlands). After mixing of the ingredients, the pH was adjusted to 4.4 with NaOH solution (30 mol/L). The sauces were cooked for 20 min at 95 °C. The cooked sauces were then filled hot into glass jars (720 g), capped, and pasteurized in a rotary retort apparatus (97 °C for 10 min) with liquid water.

**Storage Trial.** Normal storage was carried out at 25 °C and the accelerated storage at 40 °C in the absence of light. Sampling time points for the dice sauce were 0.5, 1, 1.5, 2, 3, 4, 6, 8, 12, and 18 months at 25 °C and 1, 2, 3, 4, 5, 6, 7, 8, 10, 12, 14, and 16 weeks at 40 °C. For the paste sauce the sampling time points were more spaced, that is, 0.5, 1, 2, 3, 4, 6, 8, 12, and 18 months at 25 °C and 1, 2, 4, 6,

\* Address correspondence to this author at INRA, 17 rue Sully, 21065 Dijon Cedex, France (fax 33 3 80 69 30 86; e-mail plandyfr@yahoo.fr).

8, 10, 12, 14, and 16 weeks at 40 °C. For each time/temperature combination some glass jars were taken out and frozen for later aroma and sensory analyses.

**Chemicals.** The isotope-labeled compounds [1,2-<sup>13</sup>C<sub>2</sub>]acetaldehyde, [<sup>2</sup>H<sub>3</sub>]methyl iodide, and [<sup>2</sup>H<sub>6</sub>]acetone were purchased from Cambridge Isotope Laboratories, Inc. (Andover, MA). All other compounds were purchased from Aldrich (Steinheim, Germany) except for β-damascenone, which came from Firmenich (Geneva, Switzerland).

The isotope-labeled compounds [<sup>2</sup>H<sub>6</sub>]dimethyl trisulfide, [<sup>2</sup>H<sub>4</sub>]-(*E,E*)-deca-2,4-dienal, and [<sup>13</sup>C<sub>2</sub>]-4-hydroxy-2,5-dimethyl-3(*2H*)-furanone were gifts of Peter Schieberle.

The registered trade name of 4-hydroxy-2,5-dimethyl-3(*2H*)-furanone, Furaneol, is used throughout the text for simplification.

**Syntheses.** The following labeled internal standards were synthesized according to the cited literature: [6,7-<sup>2</sup>H<sub>4</sub>]-oct-1-en-3-one (*13*), 3-([<sup>2</sup>H<sub>3</sub>]-methylthio)propanal or methional (*14*), 3-methyl[<sup>2</sup>H<sub>2</sub>]butanoic acid (*15*), and [<sup>13</sup>C<sub>2</sub>]-β-damascenone (*16*).

*2*-[<sup>2</sup>H<sub>3</sub>]-Methoxyphenol (*Guaiacol*). Catechol was benzylated with benzyl bromide, and the monobenzyl ether was purified by column chromatography. This product was then treated with [<sup>2</sup>H<sub>3</sub>]methyl iodide, purified again by column chromatography, and subsequently hydrogenated to remove the benzyl group.

**Isolation of the Tomato Volatiles.** Tomato sauce (100 g) was extracted three times with a total volume of 300 mL of dichloromethane. A high-vacuum distillation was performed to separate the volatiles from the nonvolatile residues, that is, mainly tomato pigments and oil (*17*). The solvent extract was fractionated into the neutral/basic and acidic volatiles with sodium carbonate (0.5 mol/L, 300 mL). The resulting basic aqueous phase was acidified with HCl (3 mol/L) until approximately pH 2 and extracted twice with 100 mL of dichloromethane. Both fractions were concentrated on Vigreux and Bemelmans columns to 200 μL.

**Screening of the Key Aroma Compounds.** For the neutral/basic and acidic fractions, the stepwise flavor dilution factors (FD factors) were determined by aroma extract concentration analysis (*18*).

The screening of potent highly volatile compounds was performed by static headspace dilution analysis (*19*). Tomato sauce (10 g) introduced into a headspace vessel (250 mL) was heated at 40 °C for 20 min. Stepwise volumes of headspace from 0.1 to 10 mL were analyzed by gas chromatography–olfactometry (GC-O).

**Gas Chromatography—Olfactometry Conditions.** GC-O analyses were performed in duplicate from solvent extracts and gas headspace samples at different FD factors.

Solvent extracts (0.5 μL) were injected into an Agilent gas chromatograph (model 6890, Agilent, Avondale, PA) equipped with a flame ionization detector at 250 °C and a sniffing port at 250 °C. Separation was performed on a CP-FFAP column (25 m × 0.32 mm, 0.3 μm) for the acidic fraction, and on both the free fatty acid phase and a CP-Sil 8 CB column for the neutral/basic fraction (60 m × 0.32 mm, 0.25 μm) (Chrompack, Middelburg, The Netherlands). The samples were applied by using the on-column injection technique at 40 °C. After 2 min at 40 °C, the oven temperature was raised at 40 °C/min to 60 °C, held for 2 min isothermally, and raised at 6 °C/min to 250 °C for 15 min. The constant flow of the carrier gas helium was 1.5 mL/min. Effluents were split 1:1 (v/v) at the end of the capillary between the FID and the sniffing port.

Headspace samples (0.1–10 mL) were injected into a Chrompack gas chromatograph (model 9001, Chrompack) equipped with a flame ionization detector at 250 °C, a sniffing port at 250 °C (1:1, v/v), and a PTI/TCT unit (model 4001, Chrompack). The desorption time and temperature in a silylated glass liner were, respectively, 15 min and 250 °C. The carrier gas helium at a flow of 20 mL/min swept the gas sample into the trap (CP-Sil 8 CB, 1 m × 0.53 mm, 5.0 μm) (Chrompack), where the volatiles were cryofocused at –120 °C with liquid nitrogen for 1 min. The cryotrap was rapidly heated to 255 °C, and the volatiles were injected into the GC. The capillary column used was a CP-Sil 8 CB (60 m × 0.32 mm, 1 μm) (Chrompack). After 5 min at 0 °C, the oven temperature was raised at 6 °C/min to 150 °C and then at 20 °C/min to 250 °C for 15 min. The pressure of the carrier gas helium was 100 kPa.

**Quantification by Standard Addition Method.** The standard addition method was used to quantify acetaldehyde, dimethyl sulfide, methylpropanal, and 3-methylbutanal (*20*). This method consists of adding the analyte in a known amount. The sauces (20 g) were spiked with 100 μL of aqueous standard solutions and mixed for 1 h at room temperature. An aliquot of 2 g of sauce was placed into 10-mL vials, kept at room temperature for 24 h, and stirred at 40 °C for 30 min for equilibration before analysis. A headspace sample (1 mL) was injected into a CE Instruments gas chromatograph (ThermoQuest, Rodano, Italy) equipped with a PTV injector at 200 °C isothermally and a flame ionization detector at 275 °C. The capillary column was a CP-Sil 5 CB (25 m × 0.53 mm, 5.0 μm) (Chrompack). The helium carrier gas flow was 8 mL/min. After 10 min at 0 °C, the oven temperature was raised to 50 °C at 5 °C/min, then raised to 250 °C at 40 °C/min, and held at 250 °C for 10 min.

Four different additions into the sauce were performed. Indeed, the final peak area in analyte, that is, analyte initially present plus added analyte, was adjusted to obtain approximately 1.5, 2, 3, and 5 times the initial analyte peak area (without addition). Each addition in compound was analyzed in triplicate. The linear regression of the plots representing the concentration of the analyte added into the product as a function of its peak area gave correlation coefficient values >0.97. The percentage of variation varied from 5 to 20%.

**Quantification by Solvent Extraction/Stable Isotope Dilution Assays (SIDA).** Solvent extraction and SIDA methods were applied to quantify dimethyl trisulfide, methional, and Furaneol (*21*). Response factors were determined according to the method of Sen et al. (*21*). Sauces were spiked with known amounts of labeled internal standards and stirred for 1 h. All of the samples were at least analyzed in duplicate. The percentage of variation varied from 2 to 10%.

**Quantification by Solid Phase Microextraction (SPME)/Stable Isotope Dilution Assays.** SPME and SIDA methods were applied for quantification of oct-1-en-3-one, methional, 3-methylbutanoic acid, (*E,E*)-deca-2,4-dienal, 2-methoxyphenol, and (*E*)-β-damascenone. Response factors were determined according to the method of Sen et al. (*21*). Samples of dice or paste sauce (40 g) were mixed with 40 g of a saturated NaCl solution and then spiked with 0.1–60 μg of labeled internal standard solutions. After mixing, aliquots of 12.5 g were poured into 20-mL vials and thermostated for 5 min at 40 °C. An SPME fiber (65 μm polydimethylsiloxane/divinylbenzene) (Supelco, Bellefonte, PA) was exposed to the sample for extraction of the volatiles for 30 min at 40 °C. The volatiles were desorbed for 5 min into the GC injector at 260 °C isothermally in splitless mode. All of the samples were at least analyzed in duplicate. The percentage of variation varied from 0.5 to 10%.

**Gas Chromatography—Mass Spectrometry (GC-MS).** MS analyses were performed with a 6890 Agilent gas chromatograph coupled with an Agilent mass spectrometer (5973 model). All of the samples were injected in a cool injector system (CIS-4, Gerstel, Mulheim an der Ruhr, Germany). The helium flow rate was held constant at 1 mL/min.

**GC-O Solvent Extracts and Headspace Gas.** The same GC-MS conditions were used for solvent extracts (1 μL) and headspace gas (1 mL). The liner temperature was raised from 30 to 40 °C at 1 °C/min, held for 2 min, and raised to 250 °C at 2 °C/min for 3 min. The capillary columns and oven conditions were the same as for the GC-O experiments. The electronic impact ionization conditions were as follows: electron energy, 70 eV; scan range, 29–350 *m/z*; scan speed, 3 scans/s; interface temperature, 250 °C; source temperature, 230 °C.

**Solvent Extracts for Odorant Quantification.** The quantification of dimethyl trisulfide, methional, and Furaneol was performed by two-dimensional gas chromatography (two 6890 Agilent gas chromatographs) in the electron impact ionization full scan mode. The two capillaries used in combination were a CP-Sil 8 CB (60 m × 0.32 mm, 1 μm) (Chrompack) as the precolumn and a CP-Sil 19 CB (60 m × 0.32 mm, 0.25 μm) as the main column. The samples (5 μL) were injected at 20 °C, and then the injector system temperature was raised at 6 °C/min to 250 °C for 10 min. The retention time ranges transferred on the main column were determined by injection of reference compounds. The electron impact ionization conditions were as fol-

lows: electron energy, 70 eV; interface temperature, 260 °C; source temperature, 230 °C.

**SPME Extracts.** Two methods, A and B, were applied to quantify the odorants, method A for 3-methylbutanoic acid, guaiacol, and  $\beta$ -damascenone and method B for oct-1-en-3-one and (*E,E*)-deca-2,4-dienal.

Method A used a CP-Wax 58 CB column (25 m  $\times$  0.25 mm, 0.2  $\mu$ m) (Chrompack). After 5 min at 40 °C, the oven temperature was raised to 250 °C at 2.5 °C/min and held at 250 °C for 10 min. The electron impact ionization/single ion monitoring conditions were as follows: electron energy, 70 eV; interface temperature, 250 °C; source temperature, 230 °C.

Method B used a CP-Sil 5 column (30 m  $\times$  0.25 mm, 1  $\mu$ m) (Chrompack). The oven temperature was raised from 0 to 250 °C at 2.5 °C/min and held at 250 °C for 10 min. The positive chemical ionization/single ion monitoring conditions were as follows: reagent gas, methane (1 mL/min); interface temperature, 250 °C; source temperature, 250 °C.

**Sensory Analysis. Discriminative Methods.** For the duo-trio test, the left product was the reference product (at  $t = 0$ ) and coded as such. The middle and right products were numerically coded samples of which one was the reference and the other the test product with a given storage temperature–time combination. The panelists were asked to identify which numerically coded product was identical to the reference. The panelists evaluated each duo-trio test twice. For the triangle test, products A and B to be differentiated were offered according to the following combinations: AAB, ABA, BAA, BBA, BAB, and ABB. The three given products were numerically coded. The panelists had to select which of the three samples was different from the others.

**Descriptive Method.** The spectrum method was applied with a trained panel consisting of 12 women from 30 to 50 years old. For the attribute generation reference ( $t = 0$ ) and stored products (1, 2, and 3 months at 40 °C and 2 months at 25 °C) were tasted by the panelists. Fifteen aroma descriptors and four taste descriptors were hence generated. The panel selected standard food products or pure chemicals in solution as references to describe qualitatively and quantitatively each attribute. The references were especially used for the training sessions. The quantitative reference used during the scoring sessions was a sour solution: citric acid at 3.0 g/L; malic acid at 1.0 g/L; ascorbic acid at 0.1 g/L; tartaric acid at 0.25 g/L. This solution was 3 times diluted to get a second reference of lower intensity. The respective intensities of the two sour solutions were fixed at 6 and 13. Additional training and monitoring sessions were organized to get the panelists familiar with the products, the 15-point scale, and the reference solutions.

Data acquisition was performed with FIZZ software (Biosystems, Couternon, France). A balanced Latin-square design was used to order randomly the offers for each panelist to escape from a sensory carry-over effect. All of the tomato sauce samples were presented in duplicate to the panelists under normal daylight conditions and tested at 60 °C without any host food.

**Statistics.** Statistical Analysis Systems software (SAS Institute Inc., Cary, NC) was used to perform analyses of variance (ANOVA) and principal component analyses (PCA) from the sensory data. A one-way ANOVA was applied to compare the scores of the dice and paste sauces at  $t = 0$ . The Student–Newman–Keuls test was chosen for the multiple comparison of means. The Pearson correlation coefficients between sensory and instrumental data were calculated with the CORR procedure (SAS). Partial least-squares (PLS) models were calculated from SAS for prediction of the sensory attribute scores from the key aroma compound concentration (22).

## RESULTS AND DISCUSSION

**Sensory Discriminative Test.** The first step to understanding tomato flavor instability during storage was to confirm the significant change in the overall flavor during time with duo-trio tests. The flavor difference between products at  $t = 0$  and after 1 month of storage at 25 °C from dice and paste sauces was significant at 0.1 and 10% levels, respectively (Table 1). Those first results revealed that the sensory changes occurred

**Table 1.** Difference Test Results Performed from Tomato Dice and Paste Sauces

conditions	sauce <sup>a</sup>		
	dice	paste	
$t = 0$	1 month/25 °C <sup>b</sup>	≠*****	≠**
$t = 0$	3 months/25 °C <sup>b</sup>	NT	≠*****
$t = 0$	0.5 month/40 °C <sup>b</sup>	NT	=
$t = 0$	1 month/40 °C <sup>b</sup>	NT	≠*****
1 month/25 °C	1 month/40 °C <sup>c</sup>	=	≠*
3 months/25 °C	3 months/40 °C <sup>c</sup>	=	≠***
3 months/25 °C	1 month/40 °C <sup>c</sup>	=	=

<sup>a</sup> =, products not significantly different ( $p > 0.20$ ); ≠, products significantly different at (\*) 20%, (\*\*) 10%, (\*\*\*) 5%, (\*\*\*\*) 1%, and (\*\*\*\*\*). 0.1% significance level. NT, not tested. <sup>b</sup> Duo-trio test. <sup>c</sup> Triangle test.

**Table 2.** Intensities of the Sensory Attributes Corresponding to the Tomato Dice and Paste Sauces at  $t = 0$

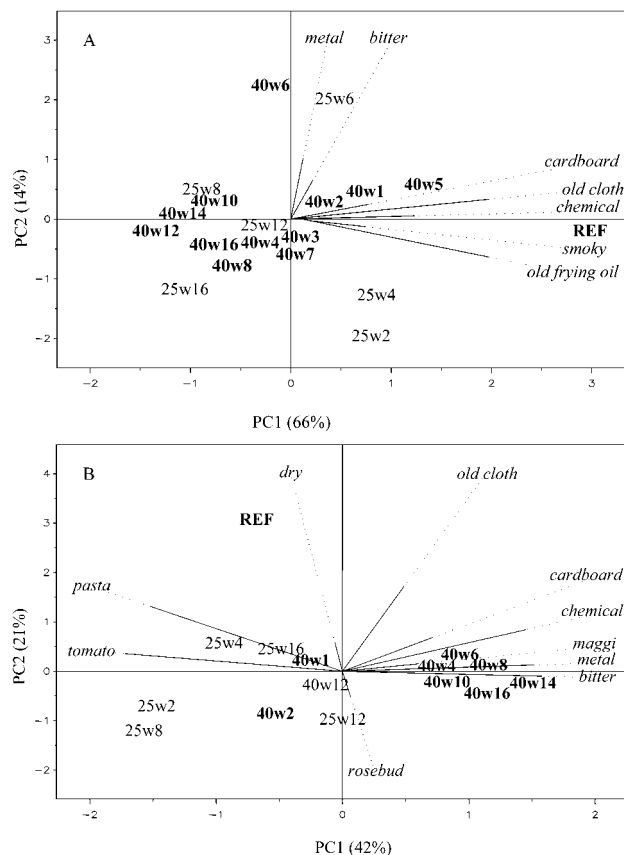
sensory attribute	dice sauce	paste sauce <sup>a</sup>
malty	3.2	4.4
old frying oil	4.3	0.4*
dry	3.1	3.7
chemical	3.2	1.5*
smoky	1.2	0.5*
green	0.7	1.3
old cloth	4.9	2.0*
cardboard	3.0	1.7
earthy	2.5	1.9
pasta	2.6	2.2
sweet	1.9	5.7*
sour	8.4	6.5*
salt	7.0	5.1*
applesauce	0.1	5.4*
rosebud	1.1	3.8*
maggi	0.8	0.5
tomato	3.9	5.8*
metal	2.5	2.9
bitter	2.3	2.5

<sup>a</sup> An asterisk indicates that the attribute intensity was significantly different between dice and paste sauces at the 5% level.

at different rates in the dice and paste sauces and were likely to be faster in the dice sauce. With regard to the fast flavor change in the dice sauce, no further difference test was performed with products stored at 25 or 40 °C. For paste sauce, the samples stored for 3 months at 25 °C presented a flavor significantly different from the reference at the 1% level. During storage at 40 °C the flavor degradation of the paste sauce appeared also to be drastic between 2 and 4 weeks: after 2 weeks at 40 °C, no significant difference was reported, whereas after 4 weeks, the significance level recorded was 0.1%.

The triangle test results were performed between stored products and aimed at giving a time trend of the flavor behavior during storage (Table 1). In the dice sauce, the overall flavor change did not seem to be different at 25 and 40 °C because the flavor was similar after 1 month at both temperatures and the same after 3 months. Conversely, in the paste sauce, the flavor tends to change differently at 25 and 40 °C for equal storage times. A deeper insight into the behavior of tomato sauces during storage was realized by a sensory descriptive method used to characterize qualitatively and quantitatively the flavor degradation of tomato sauces during storage.

**Descriptive Sensory Analysis at  $t = 0$ .** At  $t = 0$  the dice and paste sauces presented different sensory characteristics (Table 2). Some of the attributes with significantly different intensities ( $p < 0.05$ ) varied to a large extent between the dice



**Figure 1.** PCA biplot of the descriptive sensory analysis of the tomato dice (A) and paste (B) sauces stored for 4 months at 25 and 40 °C. Significant sensory attributes are indicated in italics. Codes of the stored samples indicate first the storage temperature, 25 or 40, for, respectively, 25 or 40 °C, and second the storage duration given in weeks after the letter w. The reference sample ( $t = 0$ ) is coded REF.

and paste sauces. Thus, the dice sauce was characterized by high scores in the descriptors *old frying oil*, *old cloth*, and *sour* and by low scores in the descriptors *apple sauce*, *rosebud*, and *sweet*; the paste sauce was characterized conversely. Those six attributes explained the sensory profile difference between the dice- and paste-based products.

**Descriptive Sensory Analysis during Storage.** The PCA biplots of the dice and paste sauces presented in **Figure 1** aimed at visualizing the attributes with significant time trend at 25 and 40 °C and also at explaining the sensory differences between stored samples. The scores of the attributes with a clear and significant change ( $p < 0.05$ ) during storage are given in **Tables 3** and **4** and reveal to what extent the sensory profile changed with time. Those sensory data were obtained from products stored for 4 months at 25 and 40 °C.

The attributes used to build the PCA plots for the dice and paste sauces are those given in **Tables 3** and **4**, that is, with a clear and significant score change over time. The PCA plot of the dice product was characterized by a clear shift between the reference ( $t = 0$  or REF) and the stored samples at both temperatures, from right to left (**Figure 1A**). The reference was defined by high scores in *old frying oil*, *old cloth*, *cardboard*, and *chemical*. No sensory attribute with clear increasing intensity seems to represent the stored dice samples. The presence of a fast flavor degradation in the dice sauce during the early stage of the storage was confirmed by the duo-trio test results: the overall difference between products at  $t = 0$  and  $t = 1$  month at 25 °C was significant at the 0.1% level (**Table 1**).

**Table 3.** Scores of the Attributes Varying Significantly during the Storage of the Tomato Dice Sauce for 4 Months at 25 and 40 °C<sup>a</sup>

attribute	$t = 0$	40 °C		25 °C	
		1 month	4 months	1 month	4 months
old frying oil	4.3 <sup>a</sup>	2.7 <sup>b</sup>	2.9 <sup>b</sup>	3.7 <sup>c</sup>	2.5 <sup>b</sup>
chemical	3.2 <sup>a</sup>	2.0 <sup>bc</sup>	1.8 <sup>c</sup>	2.5 <sup>b</sup>	2.5 <sup>b</sup>
smoky	1.2 <sup>a</sup>	0.8 <sup>ab</sup>	0.6 <sup>b</sup>	0.5 <sup>b</sup>	0.4 <sup>b</sup>
old cloth	4.9 <sup>a</sup>	3.5 <sup>b</sup>	3.0 <sup>bc</sup>	3.7 <sup>b</sup>	2.6 <sup>c</sup>
cardboard	3.0 <sup>a</sup>	2.6 <sup>b</sup>	2.0 <sup>b</sup>	2.4 <sup>b</sup>	2.1 <sup>b</sup>
metal	2.5 <sup>a</sup>	2.1 <sup>a</sup>	2.4 <sup>a</sup>	2.3 <sup>a</sup>	2.2 <sup>a</sup>
bitter	2.3 <sup>a</sup>	2.1 <sup>ab</sup>	2.2 <sup>ab</sup>	1.9 <sup>ab</sup>	1.6 <sup>b</sup>

<sup>a</sup> Scores with different letters are significantly different at the 5% level. Some of the attributes did not vary significantly within the selected sensory data but for some time points they did vary.

**Table 4.** Scores of the Attributes Varying Significantly during the Storage of the Tomato Paste Sauce for 4 Months at 25 and 40 °C<sup>a</sup>

attribute	$t = 0$	40 °C		25 °C	
		1 month	4 months	1 months	4 months
dry	3.7 <sup>ab</sup>	3.5 <sup>ab</sup>	3.4 <sup>ab</sup>	3.2 <sup>b</sup>	4.0 <sup>a</sup>
chemical	1.5 <sup>a</sup>	1.5 <sup>a</sup>	1.5 <sup>a</sup>	1.3 <sup>ab</sup>	1.0 <sup>b</sup>
old cloth	2.0 <sup>a</sup>	1.3 <sup>b</sup>	1.3 <sup>b</sup>	1.5 <sup>b</sup>	1.5 <sup>b</sup>
cardboard	1.7 <sup>a</sup>	1.4 <sup>a</sup>	1.6 <sup>a</sup>	1.3 <sup>a</sup>	1.8 <sup>a</sup>
pasta	2.2 <sup>a</sup>	1.4 <sup>b</sup>	1.2 <sup>b</sup>	1.8 <sup>c</sup>	1.3 <sup>b</sup>
rosebud	3.8 <sup>a</sup>	4.3 <sup>a</sup>	4.2 <sup>a</sup>	4.2 <sup>a</sup>	4.3 <sup>a</sup>
maggi	0.5 <sup>ab</sup>	0.7 <sup>a</sup>	0.5 <sup>ab</sup>	0.4 <sup>b</sup>	0.6 <sup>ab</sup>
tomato	5.8 <sup>a</sup>	5.6 <sup>ab</sup>	5.0 <sup>b</sup>	5.8 <sup>a</sup>	5.9 <sup>a</sup>
metal	2.9 <sup>ab</sup>	3.5 <sup>b</sup>	3.2 <sup>ab</sup>	2.7 <sup>a</sup>	2.7 <sup>a</sup>
bitter	2.5 <sup>a</sup>	2.9 <sup>a</sup>	2.8 <sup>a</sup>	2.5 <sup>a</sup>	2.7 <sup>a</sup>

<sup>a</sup> Scores with different letters are significantly different at the 5% level. Some of the attributes did not vary significantly within the selected sensory data, but for some time points they did vary.

A slight time trend was observed: the longer the dice sauce was stored at both temperatures, the more the samples were located in the negative part of PC1, for example, samples with the codes 40w12, 40w14, 40w16, 25w8, and 25w16. In addition, the storage temperature did not seem to affect the sensory quality of the dice sauce; the samples stored at 25 and 40 °C were placed together on the PCA biplot. This result was confirmed by the triangle test results, which reported no significant difference between products stored at 25 and 40 °C for 1 or 3 months (**Table 1**).

For the paste sauce the reference sample (REF) fell within all of the products stored at 25 °C and the products stored at 40 °C until 8 weeks (**Figure 1B**). Basically the attributes *tomato* and *pasta* were representative of this first sample group. The paste samples from 6 to 14 weeks at 40 °C were characterized by the attributes *chemical*, *bitter*, and *metal*. Hence, in the presence of tomato paste, the sensory change between the reference and stored samples was occurring after a longer period of time at both temperatures than in the dice sauce. As for the dice sauce, the duo-trio test confirmed the general observations of the PCA plots: the paste sauce was significantly different from the reference after 3 months at 25 °C ( $p < 0.01$ ), instead of 1 month for the dice sauce ( $p < 0.001$ ) (**Table 1**).

In the paste sauce the effects of the storage temperature on the sensory changes were found to be very different at 25 and 40 °C. The sensory deterioration of the paste sauce was higher at 40 °C than at 25 °C, whereas in the case of the dice sauce it was similar at both temperatures. The triangle tests performed from the paste sauce confirmed that from 1 month the sensory qualities at 25 and 40 °C became different (**Table 1**).

**Table 5.** Aroma Extract Concentration Analysis and Static Headspace Dilution Analysis of Tomato Dice and Paste Sauces

compound <sup>a</sup>	odor description <sup>b</sup>	identification method <sup>c</sup>	RI on		FD factor <sup>d</sup>	
			CP-Sil 8	FFAP	dice sauce	paste sauce
acetaldehyde	fruity	SHDA	<600		1	9
methanethiol	sulfury, cabbage	SHDA	<600		1	1
dimethyl sulfide	cabbage	SHDA	<600		9	9
2-methylpropanal	chocolat	SHDA	<600		1	3
butane-2,3-dione	buttery	SHDA	<600			1
3-methylbutanal	chocolat	SHDA	663		3	9
hexanal	green, grassy	NBF	807	1080	75	5
butanoic acid	sweaty	ACF		1617	20	
(Z)-3-hexenol	green, grassy	NBF	865		20	
2- and 3-methylbutanoic acid <sup>e</sup>	sweaty	ACF		1655	250	250
methional	potato	NBF	919	1457	1000	1000
oct-1-en-3-one	mushroom	NBF	984	1300	250	250
dimethyl trisulfide	alliaceous	NBF	986	1375	250	75
octanal	citrus-like	NBF	1011		20	5
phenylacetaldehyde	honey-like	NBF	1061	1673	75	75
Furaneol	caramel-like	ACF		2064	250	250
2-methoxyphenol	medicinal	ACF		1862	250	
linalool/nonanal <sup>e</sup>	floral	NBF	1105		5	20
p-mentha-1,5-dien-8-ol <sup>f</sup>	floral	NBF	1190		20	75
unknown	minty, fresh	NBF		1730	75	75
5-ethyl-3-hydroxy-4-methylfuran-2(5H)-one (abhexon)	bouillon-like	ACF		2307	5	5
unknown	pen-like	NBF	1312		1000	1000
(E,E)-deca-2,4-dienal	oily	NBF	1337		1000	20
unknown	floral	NBF	1381	1839	5	
(E)- $\beta$ -damascenone	floral	NBF	1400	1852	1000	1000

<sup>a</sup> Compounds identified from their retention index on the stationary phases used (FFAP and CP-Sil 8), their mass spectrum obtained by MS, and odor description. <sup>b</sup> Odor description perceived at the sniffing port. <sup>c</sup> Method or fraction used to identify the compounds: static headspace dilution analysis (SHDA), neutral/basic fraction (NBF), or acidic fraction (ACF). NBF and ACF are obtained from aroma extract concentration analysis (AECA). <sup>d</sup> Flavor dilution factor (FD factor) determined from extracts or gas volumes injected for GC-O. The indicated FD factors are the highest ones determined from the two stationary columns. <sup>e</sup> Stereochemistry not determined. <sup>f</sup> Tentative identification.

Eckerle et al. (23) also reported from canned tomato paste a development of bitter note intensity as the product deteriorated during storage. The Maillard reaction was assumed to be responsible for this bitter off-note. Generally, in both sauces the increase or decrease in attribute scores appeared to occur to a low extent, that is, <2 units. For instance, the most drastic time trend concerned the attributes *old frying oil* and *old cloth* in the dice sauce (Table 3) or *pasta* in the paste sauce (Table 4).

Furthermore, triangle tests from dice and paste sauces also showed that the flavor did not change significantly between 3 and 12 months of storage at 25 °C. Consequently, most of the sensory changes occurred in the early stage of storage.

**Attributes Affecting Sensory Changes.** Because (i) PC1 explained most of the total variance and (ii) a clear time trend of the scores was shown only along PC1, this component contained the main sensory changes over time. From the PCA the resulting factor patterns were used to determine the attributes that contributed the most to the sensory changes over storage. The selected attributes presented loadings with highest absolute values, that is, values >0.70. The so-called key attributes were *old frying oil*, *old cloth*, and *cardboard* for the dice sauce and *pasta*, *rosebud*, and *bitter* for the paste sauce. Those attributes exhibited during time the highest variation in intensity and participated also in the sensory profile difference between the dice and paste sauces. Attributes found in the literature describing cooked pasta products are *nutty*, *musty*, *moldy*, *cardboard*, and *vegetable* (24). The latter are considered to be explanatory regarding the general descriptor *pasta*.

**Identification of the Key Aroma Compounds.** Aroma compounds detected in dice and paste sauces by the complementary methods static headspace dilution analysis (SHDA) and

aroma extract concentration analysis (AECA) are presented in Table 5. The key odorants identified by SHDA are dimethyl sulfide and 3-methylbutanal in both dice and paste sauces. In the paste sauce made from a more processed raw material, two additional low boiling point odorants appeared to be potent, acetaldehyde and 2-methylpropanal. Acetaldehyde, dimethyl sulfide, methylpropanal, and 3-methylbutanal are responsible for the cooked tomato flavor perceived when the sauces are nasally assessed.

From the results of AECA the criterium for the potent odorant selection was an FD factor  $\geq 250$ . Consequently, the important middle/low volatile compounds in dice and paste sauces were the following: 3-methylbutanoic acid, methional, oct-1-en-3-one, dimethyl trisulfide, Furaneol, 2-methoxyphenol, (E,E)-deca-2,4-dienal, and (E)- $\beta$ -damascenone. Together with acetaldehyde, dimethyl sulfide, 2-methylpropanal, and 3-methylbutanal, the latter were quantified in the dice and paste sauces at  $t = 0$  and during storage. The small qualitative differences between the flavor of the dice and paste sauces may be interpreted by the application of heat treatment for the production of the canned diced tomatoes.

No new key compound was detected instrumentally in dice and paste sauces stored for 4 months at 40 °C. No new sensory attribute was generated sensorily by the trained panelists from smelling and tasting of stored sauces. Hence, the quality change of tomato sauces during storage seemed to be mainly due to degradation of some key aroma compounds and formation of others already present at  $t = 0$ . Those chemical modifications were not at the origin of the generation of attributes specific to stored products.

All of the key compounds identified from dice and paste sauces were also detected as important in the literature (3–7,

**Table 6.** Concentration<sup>a</sup> (Micrograms per Kilogram) of the Key Aroma Compounds Quantified in Tomato Dice and Paste Sauces

compound	sauce	t = 0	storage at 40 °C				storage at 25 °C <sup>b</sup>	
			1 month	2 months	3 months	4 months	6 months	12 months
acetaldehyde	dice	613.2	613.2	613.2	613.2	613.2	613.2	613.2
	paste	1199.7	1571.3	1571.3	1571.3	1571.3	1039.7	1039.7
dimethyl sulfide	dice	3830.3	3830.3	3830.3	3830.3	3830.3	3830.3	3830.3
	paste	7488.1	7488.1	7488.1	7488.1	7488.1	7488.1	7488.1
methylpropanal	dice	nd <sup>c</sup>	nd	nd	nd	nd	nd	nd
	paste	31.6	51.1	67.0		78.4	31.6	54.9
3-methylbutanal	dice	28.0	28.0	28.0	28.0	28.0	28.0	28.0
	paste	62.8	101.8	101.8	101.8	101.8	62.8	62.8
oct-1-en-3-one	dice	1.4		0.6	0.7	0.5	1.4	1.0
	paste	1.7	1.2	1.2	1.0	1.0	1.8	1.6
dimethyl trisulfide	dice	1.1		1.5	1.2	0.7	0.8	0.9 <sup>b</sup>
	paste	0.7	0.9	0.5	0.4	0.7	0.4	0.5 <sup>b</sup>
methional	dice	51.4		72.5	54.4	53.3	61.8	64.5 <sup>b</sup>
	paste	89.7	81.3	77.6	67.5	84.6	59.7	66.1 <sup>b</sup>
3-methylbutanoic acid	dice	1427.0	1698.0	1693.0	1934.0	2141.0	1562.0	1653.0
	paste	1139	1378	1509	1664	1749	1230	1408
<i>(E,E)</i> -deca-2,4-dienal	dice	11.0	5.3	4.4	2.7	3.1	3.0	3.5
	paste	4.1	2.4	2.2	1.7	1.7	2.0	<2.0
2-methoxyphenol	dice	23.8	23.9	22.2	24.1	23.9	23.0	27.7
	paste	2.3	2.6	2.9	3.3	3.5	2.6	2.7
<i>(E)</i> - $\beta$ -damascenone	dice	30.0	32.7	25.8	31.7	27.0	27.8	31.8
	paste	14.5	19.4	22.5	24.7	26.2	16.0	18.1
Furaneol	dice	196.3		176.1	168.2	349.7	157.8	174.8 <sup>b</sup>
	paste	855.7	689.7	649.7		557.7	488.2	409.8

<sup>a</sup> Concentrations are the mean of at least duplicates. <sup>b</sup> Data determined after a storage of 18 months at 25 °C. <sup>c</sup> nd, not detected.

25, 26). However, odorants from processed tomato products such as acetic acid, 1-nitro-2-phenylethane, sotolon, and eugenol were not detected or reported as potent in the present work. Several factors may explain this discrepancy, that is, the tomato variety and processing and storage conditions of the raw materials. Another possible reason is the screening method of the potent aroma volatiles. Buttery et al. (5, 6) and Krumbein and Aueswald (25) used Tenax trapping for the volatile isolation, whereas Guth and Grosch and Langlois et al. (7, 26) applied solvent extraction coupled with dilution techniques. Odor activity values (OAVs) were calculated in the cited literature to select the key compounds. The advantage of OAVs is to take into account the odor threshold in water of the volatiles and to compensate for losses during isolation and concentration steps (19). Guth and Grosch (7) compared the odorants selected with highest FD factors and those reported with highest OAVs. With the exception of acetic and 3-/2-methylbutyric acid, both odorant lists were in agreement.

The approach considered in the present work was to rely on the aroma compounds with highest FD factors and to integrate them into a sensory analysis concept in order to obtain which of the chemical compounds explained most of the sensory change during storage.

**Comparison in Key Odorant Concentration between the Reference Samples (t = 0).** The quantitative data obtained by standard addition and stable isotope dilution assays are given in Table 6 for the dice and paste sauces, respectively. In the headspace above the product, the quantity of compounds was too low to allow quantification of all the compounds by static headspace. Static headspace was used to quantify the most volatile compounds and solvent extraction/SPME the low/middle volatile compounds.

At t = 0 acetaldehyde, dimethyl sulfide, 3-methylbutanoic acid, and Furaneol were the most abundant compounds in both dice and paste sauces. Three key odorants, methylpropanal, 3-methylbutanal, and methional, were in higher concentration in the paste sauce than in the dice sauce. Three other compounds present in marked higher concentration in the dice sauce than

in the paste sauce were *(E,E)*-deca-2,4-dienal, 2-methoxyphenol, and *(E)*- $\beta$ -damascenone.

Six of the key odorants, acetaldehyde, dimethyl sulfide, methylpropanal, 3-methylbutanal, methional, and Furaneol were mainly generated during heat treatment or storage. The formation of acetaldehyde, 2-methylpropanal, 3-methylbutanal, and methional was due to nonenzymatic Strecker degradation (27, 28). Different chemical pathways seem to lead to the production of dimethyl sulfide, that is, from *S*-methylmethionine sulfonium salt (29) or from methional degradation (30–32). The higher level of Furaneol in paste sauce than in dice sauce should be caused by sugar degradation and Maillard reaction employing hexoses or 6-deoxy sugars with amino acids during heat treatment (33, 34).

Deca-2,4-dienal is produced by the oxidation of linoleic acid (35). The marked lower level of this unsaturated compound in the paste sauce is explained by its extensive degradation into *trans*-4,5-epoxy-*(E)*-decenal and hexanal during paste production (36). The unsaturated aldehyde *(E,E)*-deca-2,4-dienal produces mouthfeel properties by smoothing out harsh, acidic type notes of tomato juice and diluted paste in the range of 2.5–10 ppb.

The compounds 2-methoxyphenol and *(E)*- $\beta$ -damascenone are formed respectively in fruits from lignin and carotenoid degradation (27). Braell et al. (37) reported that hydrolysis of glycosides could also yield *(E)*- $\beta$ -damascenone. The lower level of 2-methoxyphenol and *(E)*- $\beta$ -damascenone in the paste sauce can be explained by further reactions during processing steps.

**Changes in Key Odorant Concentration during Storage.**  
*Dice Sauce.* Acetaldehyde, dimethyl sulfide, methylpropanal, 3-methylbutanal, 2-methoxyphenol, and *(E)*- $\beta$ -damascenone were essentially unchanged in the dice sauce during storage at 25 and 40 °C (Table 6).

The level of deca-2,4-dienal and oct-1-en-3-one decreased to a pronounced extent after 4 months at 40 °C compared to dimethyl trisulfide. Oxidative reactions are likely to be the source of the loss of deca-2,4-dienal, oct-1-en-3-one, and dimethyl trisulfide. The latter is also likely to undergo disproportionation reactions.

**Table 7.** Correlation<sup>a</sup> Coefficients between Sensory Score and Key Odorant Content in the Tomato Dice and Paste Sauces

compound	dice sauce			paste sauce		
	old frying oil	old cloth	cardboard	pasta	rosebud	bitter
acetaldehyde				-0.85**	0.92**	0.86**
methylpropanal				-0.89**	0.90**	0.72**
3-methylbutanal				-0.93**	0.98**	0.82**
oct-1-en-3-one	0.10	0.42	0.19	0.85**	-0.94**	-0.72**
dimethyl trisulfide	0.08	-0.05	0.41	0.28	-0.06	0.26
methional	-0.53	-0.57*	-0.31	0.41	-0.32	0.24
3-methylbutanoic acid	-0.25	-0.48	-0.42	-0.86**	0.88**	0.59
( <i>E,E</i> )-deca-2,4-dienal	0.92**	0.97**	0.89**	0.90**	-0.87**	-0.39
2-methoxyphenol	0.43	0.45	0.29	-0.79**	0.80**	0.45
$\beta$ -damascenone	0.32	0.51	0.55*	-0.89**	0.90**	0.64*
Furaneol	-0.38	-0.29	-0.66*	0.65	-0.54	-0.07

<sup>a</sup> Significant correlations ( $n = 9-14$ ): \*,  $p < 0.05$ ; \*\*,  $p < 0.01$ .

The dice sauce samples showed a marked increase in Furaneol and 3-methylbutanoic acid after 4 months at 40 °C, whereas methional formation was small but significant. The rise in 3-methylbutanoic acid together with a constant level in 3-methylbutanal could confirm the work done by Hofmann et al. (38). They showed that the acids were not significantly formed by oxidation of the aldehyde but through a new oxygen-dependent formation pathway of the Strecker reaction as a function of the reaction parameters.

Generally the time trend observed at 40 °C in the dice sauce, that is, increase or decrease of a compound, was also present at 25 °C but less pronounced. However, the strong instability of deca-2,4-dienal was still reported at 25 °C. For Furaneol different chemical mechanisms in the dice product seem to occur during normal and accelerated storages. Hence, at 40 °C, the caramel-like smelling furanone was mostly generated by Maillard-type reactions and at low temperature (25 °C), its breakdown represented the major pathway.

**Paste Sauce.** Only the amount of dimethyl sulfide remained at a constant level during paste sauce storage at 25 and 40 °C (Table 6).

Conversely, in the dice sauce Furaneol was lost at both 25 and 40 °C. It is likely that during the tomato paste processing most of the Furaneol precursors have already reacted. Methional exhibited a decrease as for Furaneol. The Strecker aldehyde is likely to undergo oxidation into sulfoxide and/or degradation in methanethiol. This mechanism is assumed to dominate at 25 °C because the methional decrease was more important at 25 °C than at 40 °C, at which the Strecker reaction could occur and compensate for the methional loss. The other Strecker reaction products, acetaldehyde, methylpropanal, 3-methylbutanal, and 3-methylbutanoic acid, presented an increase at 40 °C.

In the dice sauce (*E*)- $\beta$ -damascenone and 2-methoxyphenol were rather stable, whereas in the paste sauce they could be still formed from their respective precursors. As in the dice sauce, oct-1-en-3-one, dimethyl trisulfide, and (*E,E*)-deca-2,4-dienal showed a decrease of their concentration.

The comparison of quantitative data between dice and paste sauces during storage clearly shows how different or similar are the chemical stabilities of both tomato products and hence explains the variations in storage performance between products made from more or less processed raw materials.

**Relationship between Sensory and Chemical Analyses.** The study of relationships between sensory and chemical data was performed from key odorant concentrations and descriptor scores when both varied significantly over storage time. The attributes *malty*, *green*, *earthy*, *sweet*, *sour*, *salt*, and *applesauce* were thus

not included. Similarly, acetaldehyde, dimethyl sulfide, methylpropanal, and 3-methylbutanal were not considered for the dice sauce, and only dimethyl sulfide was removed in the case of the paste sauce. Two complementary methods were used to establish relationships between sensory and instrumental data, that is, correlation between both data sets and prediction of the sensory scores from the odorant concentrations with the partial least-squares (PLS) regression method. The correlation coefficient measures the strength of the linear relationship between pairs of variables. PLS regression allows the descriptor scores to be predicted from the key odorant concentrations or predictor variables. As a multivariate method, the PLS method provides a more global picture of the variation of an attribute as a function of the different compounds. The PLS models for paste and dice sauces included four factors and explained ~95% of the total variability in the sensory data. Data sets at both storage temperatures, 25 and 40 °C, were used for both methods.

**Dice Sauce.** The correlation coefficients between key odorants and attributes for the dice sauce are shown in Table 7. A strong and significant positive correlation was found between (*E,E*)-deca-2,4-dienal and the three key attributes of this sauce, that is, *old frying oil*, *old cloth*, and *cardboard*. The PLS model developed for the dice sauce explained >97.7% of the variance for each individual descriptor (Table 8). The same key odorant, that is, (*E,E*)-deca-2,4-dienal, was revealed as a major contributor of the variations of *old frying oil*, *old cloth*, and *cardboard*. The attributes *old frying oil*, *old cloth*, and *cardboard* being the key attributes of the sensory changes in the dice sauce during storage, (*E,E*)-deca-2,4-dienal is mainly responsible for the change in the sensory quality of the dice sauce. This result is not causal as (*E,E*)-deca-2,4-dienal is described in the literature as giving a negative rancid/oily note at a concentration >10 ppb (2). Consequently, as the dice sauce is stored, the decreasing level of (*E,E*)-deca-2,4-dienal induces a more desirable flavor, less *old frying oil*, *old cloth*, and *cardboard*.

**Paste Sauce.** More key odorants presented significant positive and negative correlations for each attribute (Table 7). This is explained by the presence of three more components, acetaldehyde, methylpropanal, and 3-methylbutanal, and also by the higher concentration in the paste sauce of some odorants such as methional, 3-methylbutanoic acid,  $\beta$ -damascenone, and Furaneol. The key attribute *pasta* of the paste sauce was positively correlated with oct-1-en-3-one and (*E,E*)-deca-2,4-dienal, which can be related to the characteristics *musty*, *vegetable*, and *cardboard* of cooked pasta (24). *Pasta* was also negatively correlated with acetaldehyde, methylpropanal, 3-methylbutanal, 3-methylbutanoic acid, 2-methoxyphenol, and  $\beta$ -damascenone, which are compounds characterized by *fruity*,

**Table 8.** Coefficients Obtained by Partial Least Squares for the Prediction of the Attribute Scores of the Tomato Dice and Paste Sauces from the Key Odorant Concentrations

compound	dice sauce			paste sauce		
	old frying oil	old cloth	cardboard	pasta	rosebud	bitter
acetaldehyde				-0.29	0.30	0.49
methylpropanal				-0.11	0.06	0.17
3-methylbutanal				-0.30	0.33	0.44
oct-1-en-3-one	-0.175	0.015	-0.116	0.14	-0.18	-0.21
dimethyl trisulfide	0.022	-0.057	0.138	0.13	0.14	-0.11
methional	-0.310	-0.297	-0.203	0.24	-0.22	-0.04
3-methylbutanoic acid	-0.028	-0.152	-0.097	0.00	0.00	-0.05
( <i>E,E</i> )-deca-2,4-dienal	0.847	0.791	0.726	0.13	-0.18	0.04
$\beta$ -damascenone	-0.338	-0.261	-0.202	0.11	-0.11	-0.25
2-methoxyphenol	0.165	0.135	0.090	-0.06	0.04	0.05
Furaneol	-0.217	-0.119	-0.305	0.02	-0.05	0.26
% variance explained	99.44	99.31	99.75	99.73	99.31	98.57

**Table 9.** Correlation<sup>a</sup> Coefficients between the Key Odorant Concentrations in the Tomato Paste Sauce

compound	acet-aldehyde	methylpropanal	3-methylbutanal	oct-1-en-3-one	dimethyl trisulfide	methional	3-methylbutanoic acid	deca-2,4-dienal	2-methoxyphenol	$\beta$ -damascenone
acetaldehyde	1.00									
methylpropanal	<b>0.74**</b>	1.00								
3-methylbutanal	<b>0.97**</b>	<b>0.83**</b>	1.00							
oct-1-en-3-one	<b>-0.92**</b>	<b>-0.92**</b>	<b>-0.96**</b>	1.00						
dimethyl trisulfide	0.32	-0.16	0.19	-0.13	1.00					
methional	0.30	-0.13	0.09	-0.08	<b>0.76**</b>	1.00				
3-methylbutanoic acid	<b>0.71**</b>	<b>0.98**</b>	<b>0.80**</b>	<b>-0.91**</b>	-0.17	-0.17	1.00			
( <i>E,E</i> )-deca-2,4-dienal	-0.37	<b>-0.78**</b>	<b>-0.57*</b>	<b>0.63*</b>	0.48	<b>0.65*</b>	<b>-0.82**</b>	1.00		
2-methoxyphenol	<b>0.65**</b>	<b>0.93**</b>	<b>0.75**</b>	<b>-0.87**</b>	-0.20	-0.16	<b>0.98**</b>	<b>-0.80**</b>	1.00	
$\beta$ -damascenone	<b>0.80**</b>	<b>0.98**</b>	<b>0.88**</b>	<b>-0.95**</b>	-0.11	-0.09	<b>0.98**</b>	<b>-0.77**</b>	<b>0.96**</b>	1.00
Furaneol	0.107	-0.413	-0.103	0.180	0.501	<b>0.756</b>	-0.485	<b>0.828</b>	-0.498	-0.39

<sup>a</sup> Significant correlations ( $n = 9-13$ ): \*,  $p < 0.05$ ; \*\*,  $p < 0.01$ .

malty, sweaty, smoky, and floral notes. The same key odorants were highly correlated to the second key attribute *rosebud*, but with the opposite sign, which is explained by the internal correlation between the two attributes. The third key attribute of the paste sauce, *bitter*, showed a positive correlation with acetaldehyde, methylpropanal, 3-methylbutanal, and  $\beta$ -damascenone and a negative and strong correlation with oct-1-en-3-one. The cause of the *bitter* score increase during storage would be expected from the formation of nonvolatile bitter-tasting compounds during Maillard reaction and not from volatile aroma compounds. Thus, the high correlation between *bitter* and aroma compounds is likely to be just causal.

The coefficients obtained from the PLS regression for the paste sauce are given in **Table 8**. The percentage of variance explained for each descriptor varied between 84.9 and 99.7%. For the key attribute *pasta*, the odorants revealed as major contributors in the PLS model were three Strecker aldehydes, acetaldehyde, 3-methylbutanal, and methional. Although highly correlated to the *pasta* attribute, key odorants such as oct-1-en-3-one and (*E,E*)-deca-2,4-dienal do not present a strong coefficient in the PLS model (**Tables 7 and 8**). This might be explained by the high internal correlation between the two compounds. Because of this correlation the coefficient of each separate compound is decreased in the PLS model. **Table 9** reports the correlation coefficients between all of the key odorants and reveals many such high correlations. Most differences between simple linear correlation and PLS models can thus be explained by the presence of strong internal correlations between key odorants.

As for *pasta*, the variation in *rosebud* scores was strongly predicted by the concentrations of acetaldehyde, 3-methylbu-

tanal, and methional (**Table 8**). The PLS model of *rosebud* exhibited coefficients of the same order of magnitude as for *pasta* but with the opposite sign.

The *bitter* note was mostly predicted from the potent odorants acetaldehyde and 3-methylbutanal and to a lesser extent by 2-methoxyphenol and Furaneol (**Table 8**).

The search for internal correlation between key odorants in the dice sauce showed only two significant correlations, between 3-methylbutanoic acid and oct-1-en-3-one ( $R = -0.87$ ) and between 2-methoxyphenol and  $\beta$ -damascenone ( $R = 0.68$ ). In addition, (*E,E*)-deca-2,4-dienal was identified from the correlation and PLS methods as the compound responsible for the flavor change in the dice sauce during storage. In the paste sauce, due to internal correlations between compounds, the PLS model cannot confirm the findings of the simple correlations and points out rather causal relationships between attributes and compounds. In the paste sauce the key odorants contributing strongly to the PLS models are to be used as predictive molecules of the flavor change during storage.

The performed difference tests enabled the reporting of the occurrence during storage of a faster significant flavor change in the dice sauce than in the paste sauce. The use of descriptive sensory analysis gave a better understanding of the flavor differences occurring during storage between the dice and paste sauces. Hence, special care should be taken for the dice sauce in the early storage because of its steep degradation relative to the  $t = 0$  samples and due to the attributes *old frying oil*, *old cloth*, and *cardboard*, whereas for the paste sauce the temperature effect became a critical factor of the storage performance after 1 month because of a more extensive sensory change at higher temperature. The *pasta*, *rosebud*, and *bitter* attributes



were mainly responsible for the sensory quality loss of the paste sauce. The different behaviors of the two sauces with regard to the storage temperatures means that the changes in the balance between aroma compounds formed and aroma compounds disappearing at higher temperature result significantly in a different quality of the paste sauce but not in the case of the dice sauce. The chemistry behind this observation could be due to the greater involvement of the Maillard reaction in the paste sauce than in the dice sauce.

The compound contributing strongly to the aroma instability of the dice sauce during storage should be (*E,E*)-deca-2,4-dienal. In the paste sauce the chemical source of sensory changes was more complex. Hence, the statistical relationships found between sensory and instrumental data were more likely to be causal. The key odorants found to be contributing to the quality change of the paste sauce aroma could be acetaldehyde, methylpropanal, 3-methylbutanal, oct-1-en-3-one, 3-methylbutanoic acid, deca-2,4-dienal, 2-methoxyphenol, and  $\beta$ -damascenone.

#### ACKNOWLEDGMENT

We gratefully acknowledge Peter Schieberle for the gift of the isotope-labeled compounds, dimethyl trisulfide, deca-2,4-dienal, and Furanol.

#### LITERATURE CITED

- Thakur, B. R.; Singh, R. K.; Nelson, P. E. Quality attributes of processed tomato products: a review. *Food Rev. Int.* **1996**, *12*, 375–401.
- Kazeniak, S. J.; Hall, R. M. Flavor chemistry of tomato volatiles. *J. Food Sci.* **1970**, *35*, 519–530.
- Buttery, R. G.; Seifert, R. M.; Guadagni, D. G.; Ling, L. C. Characterization of additional volatile components of tomato. *J. Agric. Food Chem.* **1971**, *19*, 524–529.
- Petro-Turza, M. Flavor of tomato and tomato products. *Food Rev. Int.* **1986**, *2*, 311–353.
- Buttery, R. G.; Teranishi, R.; Ling, L. C.; Turnbaugh, J. G. Quantitative and sensory studies on tomato paste volatiles. *J. Agric. Food Chem.* **1990**, *38*, 336–340.
- Buttery, R. G.; Teranishi, R.; Flath, R. A.; Ling, L. C. Identification of additional tomato paste volatiles. *J. Agric. Food Chem.* **1990**, *38*, 792–795.
- Guth, H.; Grosch, W. Evaluation of important odorants in foods by dilution techniques. In *Flavor Chemistry—Thirty Years of Progress*; Teranishi, R., Wick, E. L., Hornstein, I., Eds.; Kluwer Academic/Plenum Publishers: New York, 1999; pp 377–386.
- Hayes, W. A.; Smith, P. G.; Morris, A. E. J. The production and quality of tomato concentrates. *Crit. Rev. Food Sci. Nutr.* **1998**, *38*, 537–564.
- Hylton, R.; Bhatia, U. Storage stable tomato-based sauce. U.S. Patent 4,840,806, 1989.
- Nelson, P. E.; Hoff, J. E. Tomato volatiles: Effect of variety, processing and storage time. *J. Food Sci.* **1969**, *34*, 53–56.
- Coulibaly, Y.; Seck, S.; Crouzet, J. Evolution des constituants volatils au cours du stockage du jus de tomate. Role de l'acide ascorbique et des pigments (Changes of tomato juice volatile components during storage. Role of ascorbic acid and carotenoid pigments). *Ann. Technol. Agric.* **1979**, *28*, 17–30.
- Ghizzoni, C.; Del Popolo, F.; Porretta, S. Characterization of the volatile fraction of some processed tomato sauces. In *Pasta Based Meals—Qualitative, Nutritional and Technological Aspects*; Porretta, S., Ed.; AITA-ASTER: Parma, Italy, 1994; pp 57–81.
- Lin, J.; 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. Vinyl ketones. *J. Agric. Food Chem.* **1999**, *47*, 2822–2829.
- Schnabel, H. W.; Grimm, D.; Jensen, H. Simple synthesis of cepham derivatives. *Liebigs Ann. Chem.* **1974**, *3*, 477–495.
- Kadam, A. J.; Desai, U. V.; Mane, R. B. Synthesis of deuterium labelled acids. *J. Labelled Compd. Radiopharm.* **1999**, *42*, 835–842.
- Ayyar, K. S.; Cookson, R. C.; Kagi, D. A. Synthesis of  $\delta$ -damascone [*trans*-1-(2,6,6-trimethylcyclohex-3-enyl)but-2-en-1-one] and  $\beta$ -damascenone [*trans*-1-(2,6,6-trimethylcyclohexa-1,3-dienyl)but-2-en-1-one]. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1727–1736.
- Engel, W.; Bahr, W.; Schieberle, P. Solvent assisted evaporation—a new and versatile technique for the careful and direct isolation of aroma compounds from complex food matrices. *Eur. Food Res. Technol.* **1999**, *209*, 237–241.
- Kerscher, R.; Grosch, W. Comparative evaluation of potent odorants of boiled beef by aroma extract and concentration analysis. *Z. Lebensm. Unters. Forsch.* **1997**, *204*, 3–6.
- Schieberle, P. New developments in methods for analysis of volatile flavor compounds and their precursors. In *Characterization of Food: Emerging Methods*; Gaonkar, A. G., Ed.; Elsevier Science: Amsterdam, The Netherlands, 1995; pp 403–431.
- Kolb, B.; Ettre, L. S. *Static Headspace-Gas Chromatography: Theory and Practice*; Wiley-VCH: New York, 1997; Vol. 13, pp 163–173.
- Sen, A.; Laskawy, G.; Schieberle, P.; Grosch, W. Quantitative determination of  $\beta$ -damascenone in foods using a stable isotope dilution assay. *J. Agric. Food Chem.* **1991**, *39*, 757–759.
- Jong, S. de. SIMPLS: An Alternative Approach to Partial Least Squares Regression. *Chemom. Intell. Lab. Syst.* **1993**, *18*, 251–263.
- Eckerle, J. R.; Harvey, C. D.; Chen, T. S. Life cycle of canned tomato paste: correlation between sensory and instrumental testing methods. *J. Food Sci.* **1984**, *49*, 1188–1193.
- Cole, M. E. Review: prediction and measurement of pasta quality. *Int. J. Food Sci. Technol.* **1991**, *26*, 133–151.
- Krumbein, A.; Auerswald, H. Characterization of aroma volatiles in tomatoes by sensory analyses. *Nahrung* **1998**, *42*, 395–399.
- Langlois, D.; Etiévant, P. X.; Pierron, P.; Jorrot, A. Sensory and instrumental characterisation of commercial tomato varieties. *Z. Lebensm. Unters. Forsch.* **1996**, *203*, 534–540.
- Buttery, R. G.; Ling, L. C. Volatile components of tomato fruit and plant parts. In *Bioactive Volatile Compounds from Plants*; Teranishi, R., Buttery, R. G., Sugisawa, H., Eds.; ACS Symposium Series 525; American Chemical Society: Washington, DC, 1993; pp 23–34.
- Askar, A. Flavour changes during production and storage of fruit juices. *Fluessiges Obst.* **1984**, *51*, 610–612.
- Wong, F.; Carson, J. F. Isolation of *S*-methyl methionine sulfonium salt from fresh tomatoes. *J. Agric. Food Chem.* **1966**, *14*, 247.
- Lindsay, R. C.; Rippe, J. K. Enzymatic generation of methanethiol to assist in the flavor development of cheddar cheese and other foods. In *Biogenesis of Aromas*; Parliament, T. H., Croteau, R., Eds.; ACS Symposium Series 317; American Chemical Society: Washington, DC, 1986; pp 286–308.
- Yu, T. H.; Ho, C. T. Volatile compounds generated from thermal reaction of methionine and methionine sulfoxide with or without glucose. *J. Agric. Food Chem.* **1995**, *43*, 1641–1646.
- Ames, J. M.; Mandin, O.; Dunckham, S. C. Effect of linoleic acid and phosphatidylcholine on the volatile compounds of a heated glucose-methionine model potato system. In *Frontiers of Flavour Science*; Schieberle, P., Engel, K. H., Eds.; Deutsche Forschungsanstalt für Lebensmittelchemie: Garching, Germany, 2000; pp 503–508.
- Schieberle, P. Formation of Furanol in heat-processed foods. In *Flavor Precursors Thermal and Enzymatic Conversions*; Teranishi, R., Takeoka, G. R., Guntert, M., Eds.; ACS Symposium Series 490; American Chemical Society: Washington, DC, 1992; pp 164–175.
- Haleva-Toledo, E.; Naim, M.; Zehavi, U.; Rouseff, R. L. 4-Hydroxy-2,5-dimethyl-3(2H)-furanone formation in buffers and

- model solutions of citrus juice. *J. Agric. Food Chem.* **1997**, *45*, 1314–1319.
- (35) Grosch, W. Lipid degradation products and flavour. In *Food Flavor. Part A. Introduction*; Morton, I. D., MacLeod, A. J., Eds.; Elsevier Science Publishing: Amsterdam, The Netherlands, 1982; pp 325–398.
- (36) Gassenmeier, K.; Schieberle, P. Formation of the intense flavor compound *trans*-4,5-epoxy-(*E*)-2-decenal in thermally treated fats. *J. Am. Oil Chem. Soc.* **1994**, *71*, 1315–1319.
- (37) Braell, P. A.; Acree, T. E.; Butts, R. M.; Zhou, P. G. Isolation of nonvolatile precursors of  $\beta$ -damascenone from grapes using Charm analysis. In *Biogeneration of Aromas*; Parliament, T. H., Croteau, R., Eds.; ACS Symposium Series 317; American Chemical Society: Washington, DC, 1986; pp 75–84.
- (38) Hofmann, T.; Munch, P.; Schieberle, P. Quantitative model studies on the formation of aroma-active aldehydes and acids by Strecker-type reactions. *J. Agric. Food Chem.* **2000**, *48*, 434–440.

---

Received for review September 26, 2001. Revised manuscript received February 22, 2002. Accepted February 22, 2002.

JF011249I