Changes in Volatile Compounds and Overall Aroma Profile during Storage of Coffee Brews at 4 and 25º C

Mónica Pérez-Martínez, Patricia Sopelana, M. Paz de Peña, Concepción Cid*

Department of Nutrition, Food Science, Physiology and Toxicology, School of Pharmacy, University of Navarra, E-31080-Pamplona, Spain

**RUNNING TITLE:** Aroma Changes During Storage of Coffee Brews

**Published in**

**Journal of Agricultural and Food Chemistry 56 (9), 3145-3154 (2008)**

*Author to whom correspondence should be addressed. Phone: +34 948 425600 (Ext. 6404); Fax: +34 948 425649; E-mail: ccid@unav.es

Mónica Pérez-Martínez: mperezma@alumni.unav.es

Patricia Sopelana: psopelana@unav.es

M. Paz de Peña: mpdepena@unav.es

**ABSTRACT**

In this work, the chemical changes occurring in the volatile fraction of Arabica coffee brews during storage at 4 and 25ºC for 30 days have been characterized for the first time by means of HS-GC-MS. A total of 47 compounds were identified and quantified: 2 sulfur compounds, 7 aldehydes, 3 esters, 15 furans, 5 ketones, 1 alcohol, 2 thiophenes, 4 pyrroles, 1 pyridine, 5 pyrazines, 1 alkene and 1 acid. No new volatile compounds were detected at the end of the storage time. The changes observed are, in general, slower and less pronounced at refrigeration temperature. Storage also affects the sensory characteristics of the stored coffee brews, which lose part of their aroma intensity and freshness, acquiring some non desirable notes such as rancid aroma, mainly during storage at 25ºC. Furthermore, seven aroma indices have been proposed as indicators of coffee brew staling, which show a good correlation with some sensory attributes, not only for aroma but also overall sensory quality. Consequently, they could be considered useful to monitor both the "age" and the sensory quality of stored coffee brews.

**KEYWORDS:** coffee, coffee brew, aroma, headspace analysis, GC-MS, storage, temperature, aroma indices, sensory analysis

## INTRODUCTION

Sensory quality is the ultimate criterion for the acceptance of food products. Moreover, one of the most contributory factors for the high acceptability of coffee by population is its aroma that involves more than 800 volatile compounds. However, it is well known that the aroma of coffee brews changes very quickly after its preparation, resulting in a loss of quality. This matter becomes especially important when trying to obtain a ready-to-drink coffee brew, destined to be stored for a period of time before consumption, without losing its sensory characteristics. Although the causes of the changes that lead to the deterioration of coffee brews are not completely understood, Holscher and Steinhart (*1*) suggested two mechanisms for staling: loss of low-boiling potent-aroma components, particularly of sulfur-containing key odorants responsible for the fresh aroma, partly explained by interactions with non-volatile compounds, such as melanoidins (*2-5*); and oxidative reactions, the latter being responsible for off-flavor formation.

The changes in the volatile compounds of roasted coffee during storage, and the influence of the temperature and other conditions have been widely studied (*1, 6-11*), but the same is not true for coffee brews. Thus, to the best of our knowledge, only Steinhart et al. (*12*) have investigated the changes occurring in the volatile fraction of a coffee brew kept at a high temperature (80ºC) for a short period of time (4.5 hours). However, the results of this study cannot be extrapolated to coffee brews stored at lower temperatures for a longer period, since previous investigations have revealed that some changes occurring at high temperatures are not observed at lower ones (*13, submitted for publication*). Moreover, the work of Steinhart et al. (*12*) was focused on only 14 compounds, while there are other volatile compounds which contribute to the coffee aroma (*14-16*).

On the other hand, the study of the chemical changes of a stored coffee brew should be completed with the knowledge of how these changes affect the sensory properties of the

brews. In fact, in the coffee industry, sensory profiling is still the most widespread technique employed to evaluate the final quality of both raw material and finished products. Several research groups have tried to associate coffee staling with chemical changes in roasted coffee, obtaining the ratios between certain pairs of volatile compounds, namely aroma indices, have been used as indicators of coffee storage time (*6, 17-19*). Although most of the studies on coffee staling deal with whole coffee beans or ground coffee, Steinhart et al. (*12*) found that some indices which are valid for the roasted coffee could be transferable to monitor the ageing of the coffee brew at high temperature (80ºC).

For all these reasons, and taking into account the very limited knowledge about the behavior of the volatile compounds of coffee brews during storage at low temperatures, this study was conducted to monitor and characterize the changes in the composition of the volatile fraction of coffee brews stored at room and refrigeration temperatures for one month by means of HS-GC-MS. Moreover, the behavior of the volatile compounds was examined in order to find some aroma indices which could be good indicators of the sensory staling of Arabica coffee brews by the application of several multivariate statistical techniques. The results of this study would give us an idea about the viability of obtaining coffee brews with a long shelf-life, destined for being consumed as hot coffee brews at any time, and the possibility of control its quality by measuring only a few volatile compounds.

## MATERIALS AND METHODS

### Materials

Vacuum-packed Colombian Arabica ground roasted coffee (2.25% water content, L* 19.57±0.09) was provided by a local factory. L* value was analyzed by means of tristimulus colorimeter (Chromameter-2 CR-200, Minolta, Osaka, Japan) using the D65 illuminant and the CIELab scale. The instrument was standardized against a white tile before sample measurements. Ground roasted coffee was extended in a 1cm Petri plate and the L* value was measured in triplicate.

Pure reference standards of acetaldehyde, 2-methylpropanal, 2-methylbutanal, 3-methylbutanal, 2-methyl-2-butenal, 3-methylfuran, 2,5-dimethylfuran, 2-methyltetrahydrofuran-3-one, furfural (2-furancarboxaldehyde), 2-furfuryl methyl sulfide, 2-acetylfuran, 2-furfuryl acetate, 2-propanone, 2-butanone, 2,3-butanedione, 2,3-pentanedione, 2-ethyl-1-hexanol, 1-methylpyrrole, pyridine, pyrazine, 2,5-dimethylpyrazine and 2-ethylpyrazine were purchased from ACROS (Springfield, New Jersey, USA); dimethyl sulfide, dimethyl disulfide, propanal, hexanal, furan, 2-methylfuran, 5-methylfurfural, furfuryl alcohol, thiophene, 2-methylthiophene, 1*H*-pyrrole, 2-methylpyrazine, 2,6-dimethylpyrazine, 1,3-pentadiene and acetic acid were obtained from Sigma-Aldrich (Steinheim, Germany).

### Coffee brew preparation

The ground coffee packages were opened immediately before the preparation of the coffee brew to avoid aroma losses. Coffee brews were prepared from 90 g of ground roasted coffee for a water volume of 1 L, using a French press coffeemaker. Extraction time was 3 min and water temperature 90±2ºC (pH=7.0). The freshly prepared coffee brews were immediately poured into 330 mL sterilized glass flasks, up to a volume of 135 mL, and hermetically closed. The filling of the flasks was carried out aseptically in a laminar flow

cabin, to avoid the microbiological contamination of the samples. Afterwards, coffee brews were cooled with ice and stored at 4ºC and 25ºC for 30 days. This experiment was made in duplicate.

**Volatile compounds analysis**

The profiles of volatile compounds were obtained with the method described by Sanz et al. (*20*), adapted to coffee brew by Maeztu et al. (*21*), and using Static Headspace-Gas Chromatography-Mass Spectrometry (SH-GC-MS).

After opening the flask, six mL of a homogenized coffee brew were introduced into a 10 mL vial, which was immediately sealed with a silicone rubber Teflon cap. Each vial was equilibrated at 40ºC for 60 min in the static headspace sampler (model 7694, Agilent Technologies, Palo Alto, CA). Each vial was pressurized with carrier gas for 12 s, and 3 mL of the coffee headspace sample were injected into an HP-Wax glass capillary column (60 m x 0.25 mm x 0.5 μm film thickness) in an HP 6890 gas chromatograph (Agilent Technologies). Injector temperature was 180ºC, and carrier gas was Helium (1 mL/min linear speed). The oven temperature was maintained at 40ºC for 6 min and then raised at 3ºC/min up to 190ºC. Mass spectrometry analysis was performed with a Hewlett-Packard mass selective detector model 5973 (Agilent Technologies) operating in the electron impact ionization mode (70 eV), with a scan range of 33-300 amu. Ion source temperature was set at 230ºC. Each sample was analyzed in triplicate.

Identification and quantification of the volatile compounds. The volatile compounds were identified by comparing their mass spectra with those of the pure reference compounds and Wiley library, and also by comparison of their Kovats indices with those of standard compounds and with data from the literature. The Kovats indices were calculated according to the method of Tranchant (*22*) and compared with available literature data (*23*). Peak areas were measured by calculation of each volatile total area

based on integration of a single ion. The Quantification Ion of each volatile compound is given in the Table 1.

**Sensory descriptive analysis**

Twenty judges were recruited among members of the Nutrition, Food Science, Physiology, and Toxicology Department at the University of Navarra. Selection and training were carried out as described by Maeztu et al. (*21*, *24*) to have a 10-member panel. Although judges had experience on sensory evaluation of coffee brews, they were retrained during four sessions to adapt their evaluation to the detection and quantification of parameters related to staling. Attention was focused in rancidity and the distinction of acidity, typical from a Colombian coffee, and sourness, typical from an old coffee brew. Reference coffee brews were prepared with a Colombian Arabica ground roasted coffee stored for 1 year for rancidity, other stored for less than 1 month for acidity and the positive aromas and flavors, and a coffee brew prepared with the same coffee but stored for 2 months for sourness. A scorecard with the most frequently perceived sensory attributes was developed during training. Two lines for "other" aromas and flavors were added. All the descriptors were rated 11-point scales from "none" (0) to "very high" (10).

Each coffee brew sample was heated in a microwave oven at 90±2ºC immediately before tasting and served monadically in a white porcelain coffee cup. The order of presentation was randomized among sessions. A freshly prepared coffee brew was evaluated at first place, as a reference and in order to avoid first impression. All evaluations were conducted in isolated sensory booths illuminated with white light in the sensory laboratory under standardized conditions by UNE 87-004-79 (*25*). Rinse water was provided between samples. After the individual evaluation of each sample, results were discussed and established by panel consensus.

**Statistical analysis**

Analysis of Variance (ANOVA) was applied for each storage temperature. The source of variation was the time. T-Tukey was applied as the test *a posteriori* with a level of significance of 95%. t-Student analysis was applied to the results of the two storage temperatures in each analysis time.

Correlations among variables were assessed by means of the Pearson's correlation test. Principal Components Analysis (PCA), based on the Pearson correlation matrix, was applied to the obtained data of aroma attribute values, to the aroma indices and to the taste values (*13, submitted for publication*). All statistical analyses were performed using the SPSS v.13.0 software package for Windows.

## RESULTS AND DISCUSSION

### Volatile profile

A total of 47 volatile compounds were identified and quantified in the headspace of Arabica coffee brews throughout 30 days of storage at 4ºC and 25ºC. Table 1 shows the evolution during storage of 2 sulfur compounds, 7 aldehydes, 3 esters, 15 furans, 5 ketones, 1 alcohol, 2 thiophenes, 4 pyrroles, 1 pyridine, 5 pyrazines, 1 alkene and 1 acid. Most of the volatiles were present in the coffee brews stored at both temperatures (4ºC and 25ºC).

Sulfur compounds are of high importance for the freshness of roasted coffee (*1*). Methanethiol, one of the key odorants responsible for the aroma freshness in ground roasted coffee (*1*) and in espresso coffee (*21*), was not detected in our samples. However, its oxidation product, dimethyl sulfide, also used as a marker compound for the aroma freshness (*26, 27*) of coffee brews, was detected in little amounts at the beginning, to decrease up to undetectable levels during the first day in the brews stored at 25ºC, and during the first 3 days in those stored at 4ºC. Dimethyl disulfide did not show significant variations throughout storage in the brews stored at 4ºC, whereas in those stored at 25ºC, a progressive and significant decrease was observed. Other authors have also observed losses of these compounds during the storage of roasted coffee beans (*1, 28*) and ground roasted coffee (*6, 8*) in air conditions.

Among the aldehydes detected, Strecker aldehydes (2-methylpropanal, 2-methylbutanal and 3-methylbutanal), propanal and acetaldehyde were the most abundant. Acetaldehyde and propanal, compounds related to the fruity flavor of coffee brews (*14, 21*), increased significantly during storage in the headspace of the brews stored at 25ºC. In those stored at 4ºC, a significant increase was only observed for acetaldehyde.

Strecker aldehydes were proposed as responsible for the malty flavor in brewed coffee

(*14, 15*). In general, these key odorants decreased significantly until day 1 at 25ºC and day 7 at 4ºC, to increase up to days 10-15 at 25ºC and day 15 at 4ºC, and finally decrease again at 25ºC or remain practically constant at 4ºC. A decrease in Strecker aldehydes was observed by Czerny and Schieberle (*9*) in ground roasted coffee stored at 20ºC in the presence of oxygen; in contrast, other authors (*6*) reported an increase ranging from 13% to 36% in hermetically sealed ground coffee during 117 days at 37ºC.

The formation of hexanal, an odor impact compound related to rancid flavor, due to the oxidation of polyunsaturated fatty acids such as linoleic acid (*29, 30*), seems to have certain influence on the staling of ground coffee. However, in the headspace of the coffee brew, hexanal remained at low levels. This could be because of the low proportion of fat in coffee brews. Thus, although this volatile compound may contribute to staling, should not be considered as a good marker by itself in coffee brews, because rancid aroma and taste increased during storage.

Three volatile esters were identified and quantified during the storage of Arabica coffee brews. The most abundant was formic acid methyl ester, followed by acetic acid methyl ester. These esters were also the most abundant in roasted coffee (*31*). The ester most affected by the storage temperature was formic acid methyl ester, which exhibited a significant decrease, mainly at 25ºC. A loss of this compound was also observed by Steinhart et al. (*12*) in a coffee beverage after 4.5 hours of hot storage at 80ºC.

Fifteen volatile furan compounds were identified in the coffee brews throughout storage, being 2-methylfuran, furan, furfural (2-furancarboxaldehyde), 2,5-dimethylfuran and 3-methylfuran the most abundant. Numerous furans have been proposed as responsible for the burnt sugar, burnt and caramel aroma in roasted coffee (32), and also for the caramel flavor in coffee brews (*2*6). Furan did not exhibit significant changes throughout storage time, either at 25 or at 4ºC. With regard to 2-methyfuran, 3-methylfuran and 2,5-

dimethylfuran, non significant differences were observed throughout storage in the coffee brews stored at 4ºC, whereas in those stored at 25ºC, there was a significant decrease, mainly during the first day. Other furans, such as 2-vinylfuran, 2-vinyl-5-methylfuran, 2-furfuryl acetate and 2-furfurylfuran showed, in general, a significant decrease at both storage temperatures, faster and more intense at 25 than at 4ºC. In contrast, storage temperature hardly seemed to affect the amounts of 2-methyltetrahydrofuran-3-one, furfural, 2-acetylfuran and 5-methylfurfural. Therefore, it is clear that, even though the total amount of furan compounds tends to decrease during storage, not all the compounds are affected in the same way either by time or temperature.

Within the group of ketones, special mention deserves the significant decrease of 2,3-butanedione and 2,3-pentanedione, key odorants responsible for the buttery flavor in ground coffee (*14, 32, 33*) and in coffee brew (*15, 21*). This drop was faster and more intense in the headspace of the coffee brews stored at 25ºC, mainly from day 10. The degradation of these two diketones has also been observed during the storage of roasted coffee (*1, 6, 9*).

A significant decrease of thiophenes, volatile compounds present in heat-treated foods, was observed in the headspace of the coffee brews stored at 25ºC, mainly during the first day. A loss of thiophene in the presence of air in roasted coffee was also reported by Vitzthum and Werkhoff (*19*).

Pyrroles, responsible for coffee burnt flavors (*26*), were some of the volatile compounds most affected by storage in coffee brews, because their amounts decreased significantly, mainly at 25ºC, during the first week. Some of the minor volatiles, such as 1*H*-pyrrole and 1-ethyl-1*H*-pyrrole were undetectable after 1 day of storage at 25ºC or 3 days at 4ºC.

Pyridine, another volatile compound formed during coffee roasting which contributes to the smoky flavor in coffee brews (*26*), exhibited a significant decrease at both storage

temperatures, mainly during the first day, when was reduced by half.

Pyrazines are related to roasty and earthy/musty flavors in ground roasted coffee and coffee brews (*16, 21, 33, 34*). The most abundant pyrazine in our coffee brews was 2-methyl-pyrazine, which showed a similar behavior to pyridine. However, some of the most odorant pyrazines in coffee brews, such as 2-ethylpyrazine, 2-ethyl-6-methylpyrazine and 2-ethyl-3,5-dimethylpyrazine (*14, 21, 35*), were in very little or undetectable amounts.

Among the other volatiles detected, acetic acid showed an increase throughout the storage time, which was faster at 25ºC, reaching more than twice the initial amount at 15 days.

**Looking for aroma indices**

After characterizing the volatile profile of the coffee brews at each storage time, following the mathematical method proposed by Kallio et al. (*6*), it was tried to find some indices which could allow us to estimate the age and the quality of stored coffee brews. For this purpose, the area of each volatile compound was drawn against the storage time (data not shown). The objective was to know if the evolution of these compounds followed the linear regression model, considering appropriate for the calculation of indices only those compounds with excellent linear correlation coefficients ($R^2 > 0.75$). Only 12 volatiles complied with this criterion for at least one of the storage temperatures. As it can be observed in Table 2, only three compounds showed $R^2$ values higher than 0.75 for both storage temperatures: acetaldehyde, 2,3-butanedione and 2,3-pentanedione. Moreover, 1-methylpyrrole and N-furfurylpyrrole had $R^2$ values >0.75 in the coffee brews stored at 4ºC, and dimethyl disulfide, formic acid methyl ester, 2-methylfuran, 3-methylfuran, 2-vinylfuran, 2-furfurylfuran and 2-butanone in the brews stored at 25ºC.

According to Kallio et al. (*6*), the calculation of aroma indices requires that one compound decreases with time and the other increases at the same time. Thus, two indices

were calculated by combining acetaldehyde, the only volatile whose area rose linearly at both storage temperatures, with the other two compounds which exhibited a linear decrease, also at both temperatures (2,3-butanedione and 2,3-pentanedione). In Figure 1, it can be observed that these two indices (acetaldehyde/2,3-butanedione and acetaldehyde/2,3-pentanedione) follow the linear regression model with $R^2$ values higher than 0.75, being good indicators of coffee brew quality at 4ºC and 25ºC.

Additional indices were calculated by combination of acetaldehyde with the rest of the volatiles with $R^2>0.75$ for only one temperature (Table 2), with the exception of 2-butanone, whose area rised too. Among the six possible indices for the coffee brews stored at 25ºC, five (acetaldehyde/dimethyl disulfide, acetaldehyde/formic acid methyl ester, acetaldehyde/2-methylfuran, acetaldehyde/3-methylfuran and acetaldehyde/2-vinylfuran) were found to be useful ($R^2>0.75$) (Figure 2). In contrast, neither of the potential indices for the coffee brews stored at 4ºC (acetaldehyde/1-methylpyrrole and acetaldehyde/N-furfurylpyrrole) complied with the linearity criterion.

Some of the compounds in Table 2, such as 2,3-butanedione or 2-methylfuran, have been also used by other authors to calculate ageing indices for ground roasted coffee (*6*). However, acetaldehyde had not been previously used either for whole coffee beans or ground roasted coffee. Moreover, allthough the ratios methanol/2-methylfuran, methanol/2-butanone, dimethyl sulfide/2-butanone and dimethyl disulfide/2-butanone were found to be useful as ageing indices in coffee beverages maintained at 60/80ºC (*12*), they do not work at room and refrigeration temperatures.

**Relationship between instrumental and sensory analysis in coffee brew aroma**

Taking into account that sensory quality is the ultimate criterion for the acceptance of food products, sensory scores of the most relevant aromas of the stored coffee brews are shown in Figure 3. Aroma intensity and freshness, typical of a good fresh coffee brew, tend to go

down throughout storage at 25 and 4ºC. In contrast, rancid aroma started to be perceived at day 3 in the coffee brews stored at 25ºC and at day 7 in those stored at 4ºC, and the scores increased with storage time, higher and faster at 25ºC. Also, burnt aroma was first detected by the judges at days 3 and 7 in the coffee brews stored at 25 and 4ºC, respectively, reaching a maximum at day 10. The spicy aroma was only perceived only in the coffee brews stored at 25ºC, at days 7 and 15.

Multivariate statistical techniques were applied to combine instrumental and sensory analyses of coffee aroma. Thus, principal components analysis (PCA) was applied to examine the efficiency of the obtained aroma indices in relation to the sensory characteristics of the coffee brews. Together with the aroma attributes, data corresponding to some taste attributes were also added to have at a glance a global vision of the changes in the coffee brew sensory attributes. These latter were taken from a previous work (*13*, *submitted for publication*). Four principal components (PC), with eigenvalues greater than 1, explaining 88% of the total variance of the data, were obtained. Figure 4 shows the bidimensional representation of the scores corresponding to the two first principal components for all the variables and coffee samples.

PC1 explained 60.49% of the total variance. Typical and good quality attributes of Colombian Arabica coffee brews, such as aroma intensity, fresh aroma or acid taste, are on the left half graphic whereas low quality attributes, such as rancid aroma or sour taste, related to the staling of coffee brews, and aroma indices are on the right half. Burnt aroma and spicy aroma characterized the PC2 (15.5%). These attributes are more typical of the coffee samples at intermediate storage times, mainly of those stored at 25ºC. When storage time increases, these notes become less perceivable, maybe because aroma intensity decreases and other low quality sensory attributes, such as rancid aroma, increase.

During the first days, coffee brews are on the left-half graphic, but they move to the right with the storage time, acquiring at the end of the storage sensory notes such as rancid flavor, aftertaste, spicy flavor, astringency, sour taste and rancid aroma. It must be noticed that the changes in the coffee brews stored at 4ºC and at 25ºC follow the same behavior. However, there is a higher number of coffee samples stored at 25ºC on the right-half graphic, showing that good sensory characteristics were lost faster than at 4ºC. In addition, the coffee brews stored at 25ºC were closer to the top and right extremes of the PC axes in comparison with those stored at 4ºC, indicating that changes are more intense in the former.

The PCA also shows that the proposed aroma indices are very correlated with some sensory attributes. The correlations between all the sensory notes of the coffee brews and the seven aroma indices are shown in Table 3. Very highly significant ($p<0.001$) excellent ($r>0.75$) correlations between the seven aroma indices and rancid aroma were found. Furthermore, fresh aroma showed an excellent ($r>0.75$) very significant ($p<0.01$) negative correlation with the acetaldehyde/dimethyl disulfide (A/D) index but only good ($0.5<r<0.75$) with the others. Similarly, aroma intensity exhibited significant ($p<0.05$) or very significant ($p<0.01$) good ($0.5<r<0.75$) negative correlations with the seven aroma indices.

On the other hand, all the indices proposed in this work showed very significant ($p<0.01$) positive correlations with sour taste, being these correlations excellent ($r>0.75$) for A/B, A/2MF and A/3MF indices, and significant ($p<0.05$) or very significant ($p<0.01$) good ($0.5<r<0.75$) negative correlations with acid taste. In addition, significant ($p<0.05$) good ($0.5<r<0.75$) positive correlations were found between most of the aroma indices and aftertaste. Therefore, it could be said that the proposed aroma indices are very good indicators of the sensory staling of stored coffee brews.

In summary, in this work, the chemical changes occurring in the volatile fraction of Arabica coffee brews during storage at 4 and 25ºC for 30 days have been characterized for the first time, showing that no new volatile compounds by HS-GC-MS were detected at the end of the storage time. Furthermore, seven aroma indices are proposed as useful indicators of coffee brew staling, not only for aroma but also overall sensory quality.

**ACKNOWLEDGEMENT**

The authors thank the "Ministerio de Educación y Ciencia" for the financial support (AGL 2003-04045), for the grant given to M. Pérez-Martínez and for the "Juan de la Cierva" contract given to P. Sopelana. The authors also thank the Unión Tostadora, S.A. for providing the coffee, and the panel of judges because this study could not have been carried out without them.

**LITERATURE CITED**


1. Holscher, W.; Steinhart, H. Investigation of roasted coffee freshness with an improved headspace technique. *Z. Lebensm. Untersuch. Forsch.* **1992**, *195*, 33-38.

2. Hofmann, T.; Czerny, M.; Calligaris, S.; Schieberle, P. Model studies on the influence of coffee melanoidins on flavor volatiles of coffee beverages. *J. Agric. Food Chem.* **2001**, *49*, 2382-2386.

3. Hofmann, T.; Schieberle, P. Chemical interactions between odor-active thiols and melanoidins involved in the aroma staling of coffee beverages. *J. Agric. Food Chem.* **2002**, *50*, 319-326.

4. Charles-Bernard, M.; Rutz, A.; Roberts, D. B. Interactions between volatile and non-volatile coffees components. 2. Mechanistic study focused on volatile thiols. *J. Sci. Food Agric.* **2005**, *53*, 4426-4433.

5. Müller, C.; Hofmann, T. Quantitative studies on the formation of phenol/2-furfurylthiol conjugates in coffee beverages toward the understanding of the molecular mechanisms of coffee aroma staling. *J. Agric. Food Chem.* **2007**, *55*, 4095-4102.

6. Kallio, H.; Leino, M.; Koullias, K.; Kallio, S.; Kaitaranta, J. Headspace of roasted ground coffee as an indicator of storage time. *Food Chem.* **1990**, *36*, 135-148.

7. Nicoli, M. C.; Innocente, N.; Pittia, P.; Lerici, C. R. Staling of roasted coffee: volatile release and oxidation reactions during storage. In *Proceedings of the 15th Colloquium ASIC*; Montpellier, 1993; pp. 557-566.

8. Cappuccio, G.; Full, V.; Lonzarich, V.; Savonitti, O. Staling of roasted and ground coffee at different temperatures: combining sensory and GC analysis. In *Proceedings of the 19º Colloquium ASIC*; Trieste, 2001.

9. Czerny, M.; Schieberle**,** P. Changes in roasted coffee aroma during storage-influence of the packaging. In *Proceedings of the 19th Colloquium ASIC*; Trieste, 2001.

10. Sanz, C.; Pascual, L.; Zapelena, M. J.; Cid, M. C. A new “Aroma Index” to determine the aroma quality of a blend of roasted coffee beans. In *Proceedings of the 19º Colloquium ASIC*; Trieste, 2001.
11. Anese, M.; Manzocco, L.; Nicoli, M. C. Modelling the secondary shelf life of ground roasted coffee. *J. Agric. Food Chem.* **2006**, *54*, 5571-5576.
12. Steinhart, H.; Grötzbach, C.; Wilkens, J. Physical and chemical changes during hot storage of the coffee beverage. In *Proceedings of the 16th Colloquium ASIC*; Kyoto, 1995; pp. 380-388.
13. Pérez-Martínez, M.; Sopelana, P.; de Peña, M. P.; Cid, C. Effects of refrigeration and oxygen on the coffee brew composition. Submitted for publication.
14. Semmelroch, P.; Grosch, W. Analysis of roasted coffee powders and brews by gas chromatography-olfactometry of headspace samples. *Lebensm. Wiss. Technol.* **1995**, *28*, 310-313.
15. Semmelroch, P.; Grosch, W. Studies on character impact odorants of coffee brews. *J. Agric. Food Chem.* **1996**, *44*, 537-543.
16. Sanz, C.; Czerny, M.; Cid, C.; Schieberle, P. Comparison of potent odorants in a filtered coffee brew and in an instant coffee beverage by aroma extract dilution analysis (AEDA). *Eur. Food Res. Technol.* **2002**, *214*, 299-302.
17. Arackal, T.; Lehmann, G. Messung des Quotienten 2-Methylfuran/2-Butanon von ungemahlenem Röstkaffee wärhrend der Lagerung unter Luftausschluss. *Chem. Mikrobiol. Technol. Lebensm.* **1979**, *6*, 43-47.
18. Kwasny, H.; Werkhoff, P. Abhängigkeit der Aromaindex-Kennzahl M/B von verschiedenen Parametern. *Chem. Mikrobiol. Technol. Lebensm.* **1979**, *6*, 31-32.
19. Vitzthum, O. G.; Werkhoff, P. Messbare Aromaveränderungen bei Bohnenkaffee in sauerstoffdurchlässiger Verpackung. *Chem. Mikrobiol. Technol. Lebensm.* **1979**, *6*, 25-

30.

20. Sanz, C.; Ansorena, D.; Bello, J.; Cid, C. Optimizing headspace temperature and time sampling for identification of volatile compounds in ground roasted Arabica coffee. *J. Agric. Food Chem.* **2001**, *49*, 1364-1369.
21. Maeztu, L.; Sanz, C.; Andueza, S.; de Peña, M. P.; Bello, J.; Cid, C. Characterization of espresso coffee aroma by static headspace GC-MS and sensory flavor profile. *J. Agric. Food Chem.* **2001**, *49*, 5437-5444.
22. Tranchant, J. *Manuel Pratique de Chromatographie en Phase Gazeuse;* Masson: Paris, 1982; pp. 30-307.
23. Kondjoyan, N.; Berdagué, J. L. *A compilation of relative retention indices for the analysis of aromatic compounds*. Theix, France: Laboratoire Flaveur (INRA), 1996.
24. Maeztu, L.; Sanz, C.; Andueza, S.; de Peña, M. P.; Bello, J.; Cid, C. Multivariate Methods for Characterization and Classification of espresso coffees from different botanical varieties and types of roast by foam, taste and mouthfeel. *J. Agric. Food Chem.* **2001**, *49*, 4743-4747.
25. AENOR. *Análisis sensorial. Tomo 1. Alimentación. Recopilación de Normas UNE*. Madrid, Spain, 1997.
26. Flament, I. The individual constituents: structure, nomenclature, origin, chemical and organoleptic properties. In *Coffee Flavor Chemistry*; Wiley, J. and sons (Ltd.), Eds.; Baffins Lane, Chichester, West Sussex, England, 2002.
27. 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*, 6685-6691.
28. Steinhart, H.; Holscher, W. Storage-related changes of low-boiling volatiles in whole coffee beans. In *Proceedings of the 14$^{th}$ Colloquium ASIC*; San Francisco, 1991; pp.

156-164.

29 Czerny, M.; Grosch, W. Potent odorants in raw Arabica coffee. Their changes during roasting. *J. Agric. Food Chem.* **2000**, *48*, 868-872.

30. Vila, M.; de Peña, M. P.; Cid, C. Influence of packaging conditions in FFA and aroma evolutions during storage of ground roasted coffee. In *Proceedings of the Euro Food Chem XIII. Macromolecules and their degradation products in food-Physiological, analytical and technological aspects*; Hamburg, 2005; Vol. 2, pp. 680-683.

31. Sanz, C.; Maeztu, L.; Zapelena, M. J.; Bello, J.; Cid, C. Profiles of volatile compounds and sensory analysis of three blends of coffee: Influence of different percentages of Arabica and Robusta and Influence of roasting coffee with sugar. *J. Sci. Food Agric.* **2002**, *82*, 840-847.

32. Leino, M.; Lapveteläinen, A.; Menchero, P.; Malm, H.; Kaitaranta, J.; Kallio, H. Characterisation of stored Arabica and Robusta coffees by Headspace-GC and sensory analyses. *Food Qual. Pref.* **1991/2**, *3*, 115-125.

33. Blank, I.; Sen, A.; Grosch, W. Aroma impact compounds of Arabica and Robusta coffee. Qualitative and quantitative investigations. In *Proceedings of the 14th Colloquium ASIC*; San Francisco, 1991; pp. 117-129.

34. Holscher, W.; Vitzthum, O. G.; Steinhart, H. Identification and sensorial evaluation of aroma impact compounds in roasted Colombian coffee. *Cafe Cacao The* **1990**, *34*, 205-212.

35. López-Galilea, I.; Fournier, N.; Cid, C.; Guichard, E. Changes in headspace volatile concentrations of coffee brews caused by the roasting process and the brewing procedure**.** *J. Agric. Food Chem.* **2006**, *54*, 8560-8566.

**FIGURE CAPTIONS**

**Figure 1.** Aroma indices for coffee brews stored at 4 and 25ºC for 30 days.

**Figure 2.** Aroma indices for coffee brews stored at 25ºC for 30 days.

**Figure 3.** Changes in aroma sensory attributes of coffee brews throughout storage at 4 and 25ºC.

**Figure 4.** Principal Component Analysis (PCA) of the coffee brew stored at 4 and 25ºC for 30 days.

## TABLES

**Table 1.** Evolution of the area (x $10^{-3}$) of the volatile compounds identified in the headspace of coffee brews throughout storage at 4 and 25ºC.[a]

| | | | Storage time | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **QI[b]** | **KI[c]** | | **Day 0** | **Day 1** | **Day 3** | **Day 7** | **Day 10** | **Day 15** | **Day 20** | **Day 30** |
| SULFUR COMPOUNDS | | | | | | | | | | |
| 62 | 671 | Dimethyl sulfide [Ad] | | | | | | | | |
| | | 25ºC | 92±26[b] | nd [a] | nd [a] | nd [a] | nd [a] | nd [a] | nd [a] | nd [a] |
| | | 4ºC | 92±26[b] | 111±7[c] | nd [a] | nd [a] | nd [a] | nd [a] | nd [a] | nd [a] |
| | | SL | - | *** | - | - | - | - | - | - |
| 94 | 1077 | Dimethyl disulfide[A] | | | | | | | | |
| | | 25ºC | 333±35[d] | 281±6[c] | 279±6[c] | 261±4[c] | 267±6[bc] | 267±14[bc] | 240±6[b] | 149±2[a] |
| | | 4ºC | 333±35[ab] | 387±17[b] | 335±23[ab] | 299±12[a] | 292±4[a] | 328±14[a] | 285±4[a] | 328±41[a] |
| | | SL | - | *** | * | ** | ** | ** | *** | *** |
| ALDEHYDES | | | | | | | | | | |
| 43 | 645 | Acetaldehyde [A] | | | | | | | | |
| | | 25ºC | 670±41[a] | 694±11[a] | 646±32[a] | 823±53[b] | 855±42[b] | 763±10[ab] | 990±75[c] | 1015±81[c] |
| | | 4ºC | 670±41[a] | 703±75[a] | 785±55[ab] | 688±87[a] | 793±57[ab] | 779±117[a] | 952±121[b] | 1009±141[b] |
| | | SL | - | ns | * | * | ns | ns | ns | ns |
| 58 | 712 | Propanal [A] | | | | | | | | |
| | | 25ºC | 743±73[bc] | 686±4[ab] | 673±3[a] | 771±7[c] | 849±12[d] | 979±21[f] | 950±15[ef] | 889±7[de] |
| | | 4ºC | 743±73[ab] | 704±64[ab] | 675±42[ab] | 567±57[b] | 695±58[ab] | 889±168[b] | 877±80[b] | 881±89[b] |
| | | SL | - | ns | ns | * | * | ns | ns | ns |
| 41 | 747 | 2-Methylpropanal [A] | | | | | | | | |
| | | 25ºC | 2711±198[bcd] | 2273±8[a] | 2301±25[a] | 2562±3[b] | 2778±26[cde] | 2950±42[e] | 2867±37[de] | 2651±33[bc] |
| | | 4ºC | 2711±198[cd] | 2615±88[bc] | 2434±87[b] | 1967±59[a] | 2351±83[b] | 2831±141[cd] | 2885±77[cd] | 2907±75[d] |
| | | SL | - | * | ns | ** | ** | ns | ns | ** |
| 39 | 880 | 2-Methylbutanal [A] | | | | | | | | |
| | | 25ºC | 3339±253[c] | 2436±49[a] | 2784±35[b] | 2949±24[b] | 3282±18[c] | 3274±32[c] | 3225±13[c] | 2968±24[b] |
| | | 4ºC | 3339±253[d] | 3194±162[cd] | 3002±99[bc] | 2405±93[a] | 2849±80[b] | 3343±130[d] | 3316±67[d] | 3493±30[d] |
| | | SL | - | *** | * | ** | ** | ns | ns | *** |
| 44 | 884 | 3-Methylbutanal [A] | | | | | | | | |
| | | 25ºC | 4782±324[d] | 3741±0[a] | 3889±64[ab] | 4172±20[abc] | 4755±271[d] | 4318±288 [bc] | 4542±87[cd] | 4130±87[abc] |
| | | 4ºC | 4782±324[cd] | 4347±16[bc] | 4266±234[b] | 3419±87[a] | 4157±236[b] | 4814±233[cd] | 4767±23[cd] | 4988±191[d] |
| | | SL | - | *** | ns | *** | * | ns | * | ** |
| 56 | 1084 | Hexanal [A] | | | | | | | | |
| | | 25ºC | 50±4[ab] | 45±0[a] | 55±4[abc] | 55±4[abc] | 94±9[d] | 71±16[c] | 65±4[bc] | 55±9[abc] |
| | | 4ºC | 50±4[bc] | 48±5[bc] | 37±7[b] | 11±5[a] | 67±0[c] | 52±13[bc] | 67±15[c] | 65±4[c] |
| | | SL | - | ns | * | *** | * | ns | ns | ns |
| 84 | 1102 | 2-Methyl-2-butenal [A] | | | | | | | | |
| | | 25ºC | 22±3[c] | 14±0[b] | traces[a] | traces[a] | 25±3[cd] | 28±0[d] | 26±3[d] | traces[a] |
| | | 4ºC | 22±3[de] | 19±0[bc] | 14±0[ab] | nd[a] | 14±0[ab] | 23±5[e] | 28±5[e] | 25±3[e] |
| | | SL | - | ns | ns | - | * | ns | ns | ** |
| ESTERS | | | | | | | | | | |
| 60 | 682 | Formic acid, methyl ester [B] | | | | | | | | |
| | | 25ºC | 1172±97[e] | 894±29[cd] | 870±6[cd] | 922±16[d] | 953±20[d] | 806±22[bc] | 742±16[b] | 527±6[a] |
| | | 4ºC | 1172±97[d] | 1092±59[cd] | 1016±33 [bc] | 745±33[a] | 943±33[b] | 1102±85[cd] | 1137±42[cd] | 1082±45[bcd] |
| | | SL | - | ** | ** | ** | ns | ** | *** | *** |
| 43 | 782 | Acetic acid, methyl ester [B] | | | | | | | | |
| | | 25ºC | 596±47[b] | 528±38[ab] | 483±8[a] | 536±5[ab] | 533±6[ab] | 555±24[ab] | 564±34[ab] | 497±39[a] |
| | | 4ºC | 596±47[c] | 596±74[c] | 510±11[bc] | 417±19[a] | 500±25[b] | 586±51[c] | 591±22[c] | 603±20[c] |
| | | SL | - | ns | * | *** | ns | ns | ns | * |
| 43 | 1484 | 1-Hydroxy-2-propanone acetate [B] | | | | | | | | |
| | | 25ºC | nd[a] | nd[a] | nd[a] | nd[a] | 131±10[b] | 158±22[c] | nd[a] | nd[a] |
| | | 4ºC | nd[a] | nd[a] | nd[a] | nd[a] | nd[a] | nd[a] | 124±26[b] | nd[a] |
| | | SL | - | - | - | - | ** | *** | *** | - |

FURANS

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 68 | 716 | Furan [A] | | | | | | | | |
| | | 25ºC | 2127±244$^{a}$ | 1809±129$^{a}$ | 1763±226$^{a}$ | 1924±24$^{a}$ | 1922±258$^{a}$ | 1932±56$^{a}$ | 1902±121$^{a}$ | 1731±233$^{a}$ |
| | | 4ºC | 2127±244$^{ab}$ | 2250±330$^{ab}$ | 1958±305$^{ab}$ | 1645±208$^{a}$ | 1710±245$^{a}$ | 2092±419$^{ab}$ | 1866±223$^{ab}$ | 2459±109$^{b}$ |
| | | SL | - | * | ns | ns | ns | ns | ns | ** |
| 82 | 832 | 2-Methylfuran [A] | | | | | | | | |
| | | 25ºC | 9961±1208$^{d}$ | 7039±770$^{bc}$ | 7467±1231$^{c}$ | 6839±90$^{bc}$ | 6936±1010$^{bc}$ | 5543±194$^{bc}$ | 5182±432$^{b}$ | 3405±518$^{a}$ |
| | | 4ºC | 9961±1208$^{a}$ | 9946±1540$^{a}$ | 9040±1682$^{a}$ | 6907±1036$^{a}$ | 7202±1190$^{a}$ | 8063±1875$^{a}$ | 6576±969$^{a}$ | 8124±378$^{a}$ |
| | | SL | - | * | ns | ns | ns | ns | ns | *** |
| 82 | 858 | 3-Methylfuran [A] | | | | | | | | |
| | | 25ºC | 572±76$^{c}$ | 397±47$^{b}$ | 434±69$^{b}$ | 429±6$^{b}$ | 442±68$^{b}$ | 349±12$^{b}$ | 343±31$^{b}$ | 229±37$^{a}$ |
| | | 4ºC | 572±76$^{a}$ | 553±79$^{a}$ | 531±107$^{a}$ | 397±63$^{a}$ | 429±76$^{a}$ | 483±114$^{a}$ | 412±57$^{a}$ | 518±23$^{a}$ |
| | | SL | - | * | ns | ns | ns | ns | ns | *** |
| 96 | 930 | 2,5-Dimethylfuran [A] | | | | | | | | |
| | | 25ºC | 650±110$^{b}$ | 415±61$^{a}$ | 485±96$^{ab}$ | 505±16$^{ab}$ | 561±77$^{ab}$ | 461±25$^{a}$ | 514±0$^{ab}$ | 392±59$^{a}$ |
| | | 4ºC | 650±110$^{a}$ | 611±101$^{a}$ | 612±121$^{a}$ | 468±81$^{a}$ | 483±87$^{a}$ | 531±134$^{a}$ | 480±81$^{a}$ | 636±33$^{a}$ |
| | | SL | - | * | ns | ns | ns | ns | ns | *** |
| 94 | 1075 | 2-Vinylfuran [B] | | | | | | | | |
| | | 25ºC | 198±12$^{d}$ | 132±6$^{c}$ | 139±16$^{c}$ | 124±2$^{c}$ | 127±9$^{c}$ | 93±3$^{b}$ | 91±3$^{b}$ | 52±1$^{a}$ |
| | | 4ºC | 198±12$^{b}$ | 195±17$^{b}$ | 183±23$^{b}$ | 138±11$^{a}$ | 139±12$^{a}$ | 139±18$^{a}$ | 124±9$^{a}$ | 150±3$^{a}$ |
| | | SL | - | ** | ns | ns | ns | * | ** | *** |
| 108 | 1160 | 2-Vinyl-5-methylfuran [B] | | | | | | | | |
| | | 25ºC | 286±30$^{e}$ | 174±5$^{d}$ | 118±15$^{c}$ | 56±2$^{b}$ | 56±6$^{b}$ | 16±3$^{a}$ | nd $^{a}$ | nd $^{a}$ |
| | | 4ºC | 286±30$^{f}$ | 245±8$^{d}$ | 188±25$^{e}$ | 100±15$^{c}$ | 69±6$^{bc}$ | 37±9$^{ab}$ | 23±4$^{a}$ | 19±2$^{a}$ |
| | | SL | - | *** | * | ** | * | * | * | * |
| 81 | 1252 | 2-Furfuryl methylether [B] | | | | | | | | |
| | | 25ºC | 35±2$^{abc}$ | 31±7$^{ab}$ | 28±2$^{a}$ | 31±2$^{ab}$ | 36±0$^{abc}$ | 38±7$^{bc}$ | 41±7$^{c}$ | 37±4$^{abc}$ |
| | | 4ºC | 35±2$^{a}$ | 38±7$^{a}$ | 30±3$^{a}$ | 28±7$^{a}$ | 32±4$^{a}$ | 35±2$^{a}$ | 36±3$^{a}$ | 38±2$^{a}$ |
| | | SL | - | ns | ns | ns | ns | ns | ns | ns |
| 43 | 1284 | 2-Methyltetrahydrofuran-3-one [A] | | | | | | | | |
| | | 25ºC | 90±14$^{ab}$ | 78±2$^{a}$ | 80±5$^{a}$ | 90±1$^{ab}$ | 104±7$^{bc}$ | 111±10$^{c}$ | 108±5$^{c}$ | 98±4$^{bc}$ |
| | | 4ºC | 90±14$^{abc}$ | 79±7$^{ab}$ | 84±5$^{abc}$ | 63±6$^{a}$ | 95±10$^{bc}$ | 129±14$^{d}$ | 113±20$^{cd}$ | 101±11$^{bcd}$ |
| | | SL | - | ns | ns | ** | ns | ns | ns | ns |
| 96 | 1490 | Furfural (2-Furancarboxaldehyde) [A] | | | | | | | | |
| | | 25ºC | 1139±40$^{bc}$ | 976±0$^{a}$ | 948±45$^{a}$ | 1104±21$^{b}$ | 1158±66$^{bc}$ | 1163±26$^{bc}$ | 1217±48$^{c}$ | 1012±16$^{a}$ |
| | | 4ºC | 1139±40$^{b}$ | 978±96$^{b}$ | 973±65$^{b}$ | 794±58$^{a}$ | 1085±55$^{b}$ | 1141±52$^{b}$ | 1315±107$^{c}$ | 1087±88$^{b}$ |
| | | SL | - | ns | ns | ** | ns | ns | ns | ns |
| 81 | 1516 | 2-Furfuryl methyl sulfide [A] | | | | | | | | |
| | | 25ºC | 42±4$^{c}$ | 34±4$^{c}$ | 21±3$^{b}$ | nd$^{a}$ | nd$^{a}$ | nd$^{a}$ | nd$^{a}$ | nd$^{a}$ |
| | | 4ºC | 42±4$^{c}$ | 41±0$^{c}$ | 28±4$^{b}$ | nd$^{a}$ | nd$^{a}$ | nd$^{a}$ | nd$^{a}$ | nd$^{a}$ |
| | | SL | - | ns | * | - | - | - | - | - |
| 95 | 1536 | 2-Acetylfuran [A] | | | | | | | | |
| | | 25ºC | 95±13$^{ab}$ | 87±3$^{a}$ | 86±6$^{a}$ | 97±4$^{ab}$ | 104±8$^{abc}$ | 110±3$^{bc}$ | 116±7$^{c}$ | 95±4$^{ab}$ |
| | | 4ºC | 95±13$^{bc}$ | 87±10$^{abc}$ | 84±5$^{ab}$ | 71±7$^{a}$ | 101±7$^{bcd}$ | 107±9$^{cd}$ | 122±12$^{d}$ | 97±8$^{bc}$ |
| | | SL | - | ns | ns | ** | ns | ns | ns | ns |
| 81 | 1559 | 2-Furfuryl acetate [A] | | | | | | | | |
| | | 25ºC | 358±65$^{f}$ | 327±0$^{f}$ | 269±11$^{e}$ | 225±8$^{de}$ | 186±11$^{cd}$ | 136±8$^{bc}$ | 102±3$^{ab}$ | 49±0$^{a}$ |
| | | 4ºC | 358±65$^{c}$ | 352±42$^{bc}$ | 269±22$^{abc}$ | 247±42$^{ab}$ | 233±41$^{a}$ | 223±15$^{a}$ | 289±0$^{abc}$ | 242±65$^{a}$ |
| | | SL | - | ns | ns | ns | ns | *** | *** | * |
| 110 | 1605 | 5-Methylfurfural [A] | | | | | | | | |
| | | 25ºC | 456±24$^{abc}$ | 424±0$^{ab}$ | 408±21$^{a}$ | 461±12$^{abc}$ | 494±52$^{bcd}$ | 522±24$^{cd}$ | 550±41$^{d}$ | 442±21$^{ab}$ |
| | | 4ºC | 456±24$^{ab}$ | 419±67$^{ab}$ | 396±34$^{ab}$ | 346±35$^{a}$ | 486±45$^{bc}$ | 507±48$^{bc}$ | 588±81$^{c}$ | 432±43$^{ab}$ |
| | | SL | - | ns | ns | ** | ns | ns | ns | ns |
| 91 | 1636 | 2-Furfurylfuran [B] | | | | | | | | |
| | | 25ºC | 77±10$^{d}$ | 68±0$^{d}$ | 50±4$^{c}$ | 45±4$^{bc}$ | 45±4$^{bc}$ | 34±0$^{b}$ | 43±8$^{bc}$ | 7±0$^{a}$ |
| | | 4ºC | 77±10$^{c}$ | 58±5$^{b}$ | 47±0$^{b}$ | 47±0$^{b}$ | 50±4$^{b}$ | 50±4$^{b}$ | 52±4$^{b}$ | 34±0$^{a}$ |
| | | SL | - | ** | ns | ns | ns | * | ns | ** |
| 98 | 1686 | Furfuryl alcohol [A] | | | | | | | | |
| | | 25ºC | nd$^{a}$ | 709±27$^{bc}$ | nd$^{a}$ | 663±24$^{b}$ | 838±128$^{cd}$ | 878±11$^{de}$ | 988±69$^{e}$ | 758±72$^{bcd}$ |
| | | 4ºC | nd$^{a}$ | 686±154$^{bc}$ | 648±11$^{bc}$ | 498±95$^{b}$ | 934±48$^{d}$ | 798±169$^{cd}$ | nd$^{a}$ | 585±123$^{bc}$ |
| | | SL | - | ns | *** | * | ns | ns | ** | ns |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| KETONES | | | | | | | | | | |
| 58 | 753 | 2-Propanone [A] | | | | | | | | |
| | | 25ºC | 1169±95$^{b}$ | 1042±3$^{a}$ | 1032±25$^{a}$ | 1171±12$^{b}$ | 1290±7$^{c}$ | 1436±23$^{e}$ | 1400±19$^{d}$ | 1327±12$^{cd}$ |
| | | 4ºC | 1169±95$^{bcd}$ | 1129±81$^{bc}$ | 1020±42$^{b}$ | 817±45$^{a}$ | 1093±51$^{b}$ | 1368±141$^{d}$ | 1359±70$^{d}$ | 1301±67$^{cd}$ |
| | | SL | - | ns | ns | *** | * | ns | ns | ns |
| 43 | 866 | 2-Butanone [A] | | | | | | | | |
| | | 25ºC | 396±28$^{bc}$ | 369±1$^{ab}$ | 358±5$^{a}$ | 399±7$^{cd}$ | 426±3$^{d}$ | 463±14$^{e}$ | 484±6$^{e}$ | 480±11$^{e}$ |
| | | 4ºC | 396±28$^{bc}$ | 366±34$^{b}$ | 373±35$^{b}$ | 301±26$^{a}$ | 361±8$^{b}$ | 424±23$^{bc}$ | 441±13$^{c}$ | 421±17$^{bc}$ |
| | | SL | - | ns | ns | ** | *** | ns | ** | ** |
| 43 | 962 | 2,3-Butanedione [A] | | | | | | | | |
| | | 25ºC | 458±42$^{e}$ | 381±6$^{d}$ | 376±12$^{cd}$ | 337±8$^{c}$ | 356±11$^{cd}$ | 228±15$^{b}$ | 245±4$^{b}$ | 141±0$^{a}$ |
| | | 4ºC | 458±42$^{c}$ | 413±53$^{c}$ | 400±27$^{c}$ | 364±32$^{abc}$ | 404±41$^{c}$ | 364±25$^{abc}$ | 377±40$^{bc}$ | 274±48$^{a}$ |
| | | SL | - | ns | ns | ns | ns | ** | ** | ** |
| 43 | 1058 | 2,3-Pentanedione [A] | | | | | | | | |
| | | 25ºC | 740±63$^{e}$ | 588±23$^{d}$ | 603±40$^{d}$ | 453±7$^{c}$ | 454±11$^{c}$ | 271±2$^{b}$ | 235±24$^{b}$ | 113±0$^{a}$ |
| | | 4ºC | 740±63$^{f}$ | 714±61$^{ef}$ | 668±23$^{def}$ | 485±42$^{bc}$ | 599±11$^{cde}$ | 497±54$^{bc}$ | 558±70$^{bcd}$ | 363±38$^{a}$ |
| | | SL | - | ** | ns | ns | ns | ** | ** | *** |
| 43 | 1323 | 1-Hydroxy-2-propanone [B] | | | | | | | | |
| | | 25ºC | 145±21$^{c}$ | 107±7$^{ab}$ | 105±7$^{ab}$ | 95±10$^{a}$ | 137±10$^{ab}$ | 129±23$^{c}$ | 138±9$^{c}$ | 132±0$^{bc}$ |
| | | 4ºC | 145±21$^{c}$ | 110±8$^{abc}$ | 131±11$^{bc}$ | 77±13$^{a}$ | 140±17$^{bc}$ | 136±34$^{bc}$ | 139±17$^{bc}$ | 96±18$^{ab}$ |
| | | SL | - | ns | * | ns | ns | ns | ns | ns |
| ALCOHOLS | | | | | | | | | | |
| 57 | 1509 | 2-Ethyl-1-hexanol [A] | | | | | | | | |
| | | 25ºC | 153±36$^{c}$ | 87±8$^{b}$ | 66±3$^{b}$ | nd$^{a}$ | 72±3$^{b}$ | 125±29$^{c}$ | nd$^{a}$ | 74±7$^{b}$ |
| | | 4ºC | 153±36$^{c}$ | 90±12$^{b}$ | nd$^{a}$ | nd$^{a}$ | nd$^{a}$ | 132±7$^{c}$ | 73±4$^{b}$ | 73±4$^{b}$ |
| | | SL | - | ns | ** | - | ** | ns | *** | ns |
| THIOPHENES | | | | | | | | | | |
| 84 | 1021 | Thiophene [A] | | | | | | | | |
| | | 25ºC | 202±11$^{c}$ | 155±5$^{ab}$ | 174±10$^{b}$ | 163±0$^{ab}$ | 171±11$^{b}$ | 172±8$^{b}$ | 164±4$^{ab}$ | 149±12$^{a}$ |
| | | 4ºC | 202±11$^{cd}$ | 216±13$^{d}$ | 176±18$^{abc}$ | 154±9$^{a}$ | 150±9$^{a}$ | 187±21$^{bcd}$ | 160±11$^{ab}$ | 200±4$^{cd}$ |
| | | SL | - | *** | ns | ns | ns | ns | ns | ** |
| 97 | 1097 | 2-Methylthiophene [A] | | | | | | | | |
| | | 25ºC | 102±7$^{c}$ | 77±4$^{b}$ | 81±11$^{b}$ | 77±3$^{b}$ | 86±5$^{b}$ | 73±2$^{b}$ | 73±5$^{b}$ | 55±6$^{a}$ |
| | | 4ºC | 102±7$^{b}$ | 101±8$^{b}$ | 87±14$^{ab}$ | 75±9$^{a}$ | 73±7$^{a}$ | 81±11$^{ab}$ | 75±9$^{a}$ | 95±3$^{ab}$ |
| | | SL | - | ** | ns | ns | ns | ns | ns | ** |
| PYRROLES | | | | | | | | | | |
| 81 | 1149 | 1-Methylpyrrole [A] | | | | | | | | |
| | | 25ºC | 429±28$^{d}$ | 305±18$^{c}$ | 219±2$^{b}$ | 28±5$^{a}$ | traces$^{a}$ | nd$^{a}$ | nd$^{a}$ | nd$^{a}$ |
| | | 4ºC | 429±28$^{f}$ | 437±9$^{f}$ | 311±12$^{e}$ | 169±2$^{d}$ | 121±0$^{c}$ | 60±5$^{b}$ | traces$^{a}$ | nd$^{a}$ |
| | | SL | - | *** | *** | *** | ** | * | - | - |
| 80 | 1194 | 1-Ethyl-1*H*-pyrrole [B] | | | | | | | | |
| | | 25ºC | 34±4$^{c}$ | 28±3$^{b}$ | traces$^{a}$ | nd$^{a}$ | nd$^{a}$ | nd$^{a}$ | nd$^{a}$ | nd$^{a}$ |
| | | 4ºC | 34±4$^{c}$ | 40±3$^{d}$ | 21±4$^{b}$ | nd$^{a}$ | nd$^{a}$ | nd$^{a}$ | nd$^{a}$ | nd$^{a}$ |
| | | SL | - | ** | ** | - | - | - | - | - |
| 67 | 1542 | 1*H*-Pyrrole [A] | | | | | | | | |
| | | 25ºC | 57±12$^{b}$ | 49±6$^{b}$ | traces$^{a}$ | nd$^{a}$ | nd$^{a}$ | nd$^{a}$ | nd$^{a}$ | nd$^{a}$ |
| | | 4ºC | 57±12$^{c}$ | 75±9$^{d}$ | 28±4$^{b}$ | nd$^{a}$ | nd$^{a}$ | nd$^{a}$ | nd$^{a}$ | nd$^{a}$ |
| | | SL | - | ** | ** | - | - | - | - | - |
| 81 | 1833 | *N*-Furfurylpyrrole [B] | | | | | | | | |
| | | 25ºC | 43±0$^{e}$ | 36±2$^{d}$ | nd$^{a}$ | 14±3$^{c}$ | 7±2$^{b}$ | nd$^{a}$ | nd$^{a}$ | nd$^{a}$ |
| | | 4ºC | 43±0$^{e}$ | 37±8$^{e}$ | 27±3$^{d}$ | 25±3$^{d}$ | 23±3$^{cd}$ | 17±3$^{c}$ | 5±2$^{b}$ | nd$^{a}$ |
| | | SL | - | ns | ** | * | ** | ** | * | - |
| PYRIDINES | | | | | | | | | | |
| 79 | 1203 | Pyridine [A] | | | | | | | | |
| | | 25ºC | 462±136$^{c}$ | 237±18$^{ab}$ | 220±42$^{ab}$ | 172±7$^{a}$ | 224±68$^{ab}$ | 322±3$^{b}$ | 261±40$^{ab}$ | 178±32$^{a}$ |
| | | 4ºC | 462±136$^{c}$ | 233±78$^{ab}$ | 140±38$^{a}$ | 141±38$^{a}$ | 249±102$^{ab}$ | 210±0$^{ab}$ | 328±70$^{bc}$ | 103±10$^{a}$ |
| | | SL | - | ns | ns | ns | ns | *** | ns | ns |
| PYRAZINES | | | | | | | | | | |
| 80 | 1231 | Pyrazine [A] | | | | | | | | |
| | | 25ºC | nd$^{a}$ | 44±0$^{bc}$ | 36±7$^{b}$ | 36±3$^{b}$ | 43±12$^{bc}$ | 58±9$^{c}$ | 54±9$^{c}$ | 43±4$^{bc}$ |
| | | 4ºC | nd$^{a}$ | 51±9$^{c}$ | 23±4$^{b}$ | 21±0$^{b}$ | 47±7$^{c}$ | 61±9$^{c}$ | 57±16$^{c}$ | 22±2$^{a}$ |
| | | SL | - | ns | * | * | ns | ns | ns | ** |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 94 | 1288 | 2-Methylpyrazine [A] | | | | | | | | |
| | | 25ºC | 418±74$^{c}$ | 296±3$^{abc}$ | 269±22$^{a}$ | 272±15$^{a}$ | 316±65$^{abc}$ | 388±20$^{bc}$ | 380±52$^{abc}$ | 296±26$^{abc}$ |
| | | 4ºC | 418±74$^{b}$ | 292±76$^{ab}$ | 212±43$^{a}$ | 196±38$^{a}$ | 316±58$^{ab}$ | 358±68$^{ab}$ | 403±96$^{b}$ | 247±65$^{ab}$ |
| | | SL | - | ns | ns | * | ns | ns | ns | ns |
| 108 | 1347 | 2,5-Dimethylpyrazine [A] | | | | | | | | |
| | | 25ºC | 50±2$^{bc}$ | 45±1$^{abc}$ | 39±3$^{a}$ | 41±1$^{a}$ | 45±5$^{abc}$ | 51±4$^{c}$ | 52±5$^{c}$ | 42±2$^{ab}$ |
| | | 4ºC | 50±2$^{bc}$ | 46±7$^{abc}$ | 37±3$^{ab}$ | 31±4$^{a}$ | 45±5$^{abc}$ | 51±6$^{bc}$ | 55±9$^{c}$ | 38±6$^{ab}$ |
| | | SL | - | ns | ns | * | ns | ns | ns | ns |
| 108 | 1353 | 2,6-Dimethylpyrazine [A] | | | | | | | | |
| | | 25ºC | 69±19$^{c}$ | 32±6$^{ab}$ | 28±6$^{ab}$ | 24±0$^{a}$ | 36±11$^{ab}$ | 48±0$^{abc}$ | 52±11$^{bc}$ | 29±6$^{ab}$ |
| | | 4ºC | 69±19$^{d}$ | 26±3$^{ab}$ | 4±0$^{a}$ | traces$^{a}$ | 40±11$^{bc}$ | 40±11$^{bc}$ | 60±26$^{bc}$ | traces$^{a}$ |
| | | SL | - | ns | ** | * | ns | ns | ns | * |
| 107 | 1359 | 2-Ethylpyrazine [A] | | | | | | | | |
| | | 25ºC | 59±21$^{bc}$ | 43±0$^{abc}$ | 39±9$^{abc}$ | 32±3$^{a}$ | 41±0$^{ab}$ | 74±6$^{c}$ | 62±11$^{c}$ | 39±4$^{abc}$ |
| | | 4ºC | 59±21$^{cd}$ | 41±9$^{bc}$ | traces$^{a}$ | traces$^{a}$ | 52±6$^{cd}$ | 35±9$^{bc}$ | 61±26$^{d}$ | 18±0$^{ab}$ |
| | | SL | - | ns | ** | ** | ** | * | ns | ** |
| OTHERS | | | | | | | | | | |
| 67 | 624 | 1,3-Pentadiene [A] | | | | | | | | |
| | | 25ºC | 484±19$^{b}$ | 284±5$^{abc}$ | 217±14$^{ab}$ | 205±10$^{ab}$ | 287±0$^{c}$ | 194±19$^{a}$ | 367±9$^{bc}$ | 204±14$^{ab}$ |
| | | 4ºC | 484±19$^{c}$ | 367±0$^{b}$ | 284±5$^{a}$ | 270±4$^{a}$ | 280±3$^{a}$ | 364±24$^{b}$ | 317±24$^{ab}$ | 481±38$^{b}$ |
| | | SL | - | ** | *** | * | ns | *** | ** | *** |
| 45 | 1480 | Acetic acid [A] | | | | | | | | |
| | | 25ºC | 369±76$^{a}$ | 538±1$^{bc}$ | 647±129$^{abc}$ | 540±98$^{ab}$ | 653±148$^{abc}$ | 950±98$^{c}$ | 850±29$^{bc}$ | 727±142$^{bc}$ |
| | | 4ºC | 369±76$^{ab}$ | 385±104$^{ab}$ | 563±167$^{bc}$ | 572±110$^{bc}$ | 496±11$^{abc}$ | 327±55$^{a}$ | 690±138$^{c}$ | 630±59$^{c}$ |
| | | SL | - | * | ns | ns | ns | *** | ns | ns |

[a] All values are shown as means ± standard deviations. In each row, different letters indicate statistically significant differences ($p<0.05$) throughout the time. SL, significance level between the two storage temperatures in the same day: ns non-significant ($p>0.05$); * significant ($p<0.05$); ** very significant ($p<0.01$); *** highly significant ($p<0.001$). nd, not detected.

[b] QI: Ion used for the Quantification of the compound.

[c] KI: Kovats Index calculated for the HP-Wax capillary column.

[d] The reliability of the identification proposal is indicated by the following: A, mass spectrum, KI and retention time according to standards; B, tentative identification (no reference compound available).

**Table 2**. Compounds which follow the linear regression model with excellent linear correlation coefficients ($R^2$>0.75) for at least one of the storage temperatures, together with the values of these coefficients at both temperatures.

| | **$R^2$** | |
|---|---|---|
| **Compound** | **25ºC** | **4ºC** |
| Dimethyl disulfide | **0.8211** | 0.1596 |
| Acetaldehyde | **0.8097** | **0.8379** |
| Formic acid, methyl ester | **0.7672** | 0.0198 |
| 2-Methylfuran | **0.8306** | 0.3145 |
| 3-Methylfuran | **0.7537** | 0.1109 |
| 2-Vinylfuran | **0.8122** | 0.4629 |
| 2-Furfurylfuran | **0.8271** | 0.4904 |
| 2-Butanone | **0.8122** | 0.3239 |
| 2,3-Butanedione | **0.9124** | **0.7698** |
| 2,3-Pentanedione | **0.9254** | **0.7504** |
| 1-Methylpyrrole | 0.5654 | **0.8010** |
| *N*-Furfurylpyrrole | 0.4668 | **0.9224** |

**Table 3.** Correlations between the aroma indices proposed and the sensory notes of coffee brews throughout storage at 4 and 25ºC.

| Sensory notes | A/B | A/P | A/D | A/F | A/2MF | A/3MF | A/2VF |
|---|---|---|---|---|---|---|---|
| Aroma intensity | -0.663** | -0.617* | -0.632** | -0.686** | -0.674** | -0.684** | -0.656** |
| Fresh aroma | -0.744** | -0.665** | -0.785** | -0.662** | -0.702** | -0.693** | -0.659** |
| Rancid aroma | 0.889*** | 0.884*** | 0.901*** | 0.877*** | 0.911*** | 0.898*** | 0.918*** |
| Burnt aroma | -0.151 | -0.197 | -0.080 | -0.104 | -0.075 | -0.072 | -0.106 |
| Spicy aroma | 0.117 | 0.068 | 0.000 | 0.040 | 0.079 | 0.075 | 0.097 |
| Acid taste | -0.652** | -0.581* | -0.610* | -0.607* | -0.648** | -0.651** | -0.623** |
| Sour taste | 0.789** | 0.720** | 0.708** | 0.691** | 0.766** | 0.755** | 0.740** |
| Bitter taste | -0.473 | -0.419 | 0.030 | -0.421 | -0.386 | -0.373 | -0.352 |
| Astringency | 0.253 | 0.186 | 0.283 | 0.274 | 0.337 | 0.337 | 0.284 |
| Aftertaste | 0.511* | 0.444 | 0.526* | 0.510* | 0.564* | 0.558* | 0.539* |
| Spicy flavor | 0.491 | 0.459 | 0.450 | 0.427 | 0.506* | 0.499* | 0.514* |
| Rancid flavor | 0.540* | 0.471 | 0.424 | 0.403 | 0.480 | 0.461 | 0.495 |

**A/B**: acetaldehyde/2,3-butanedione; **A/P**: acetaldehyde/2,3-pentanedione; **A/D**: acetaldehyde/dimethyl disulfide; **A/F**: acetaldehyde/formic acid, methyl ester; **A/2MF**: acetaldehyde/2-methylfuran; **A/3MF**: acetaldehyde/3-methylfuran; **A/2VF**: acetaldehyde/2-vinylfuran.

The symbols *, **, *** indicate significance at the 0.05, 0.01 and 0.001 probability levels, respectively.

**FIGURES**

**Figure 1**

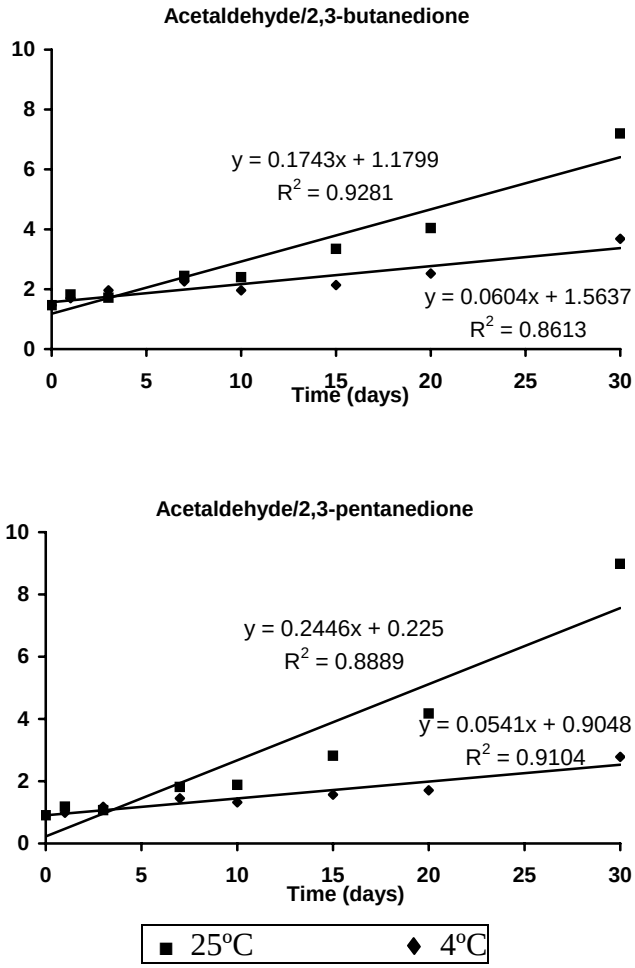


**Figure 2**

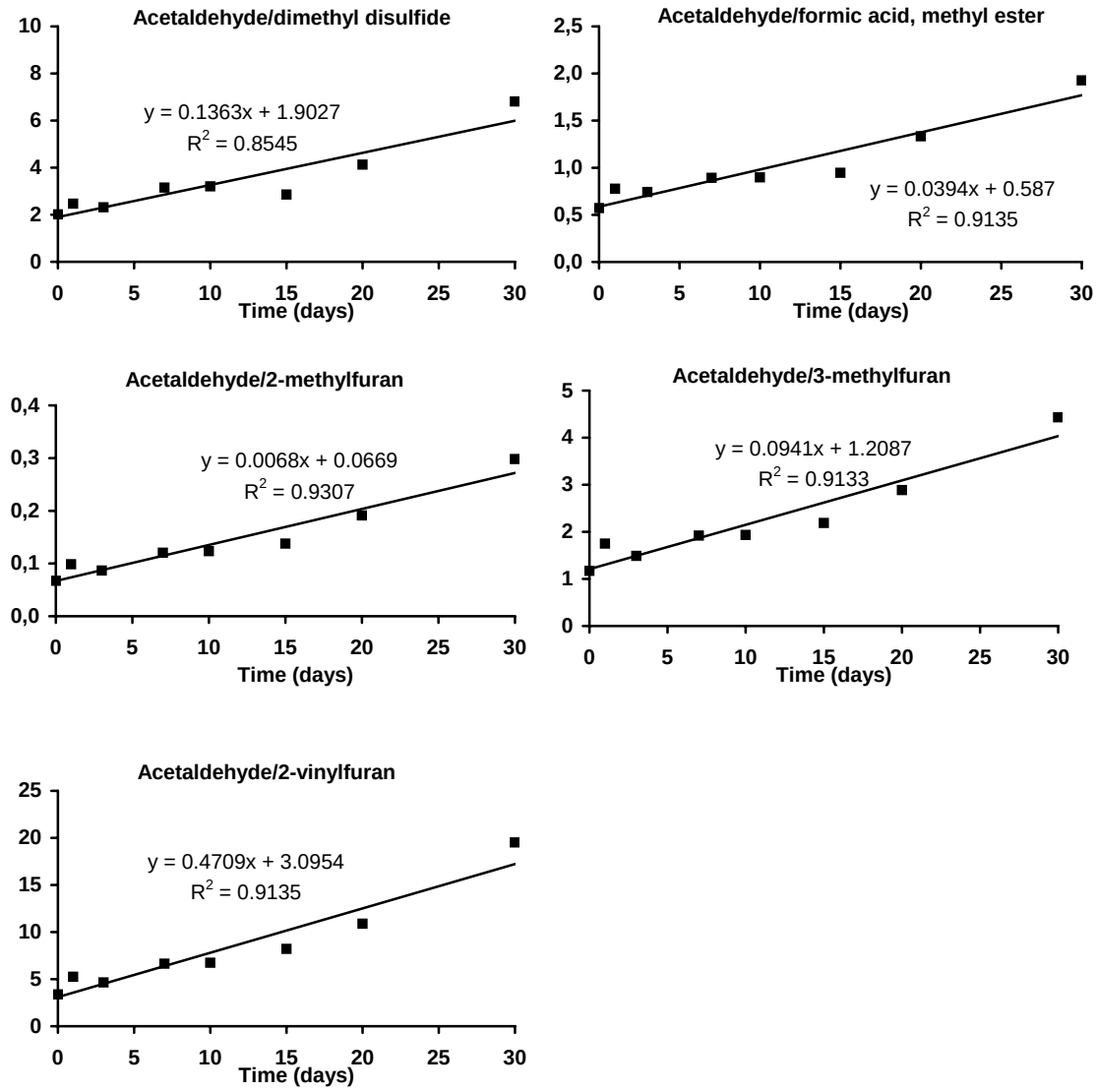

Acetaldehyde/dimethyl disulfide
y = 0.1363x + 1.9027
R2 = 0.8545
Time (days)
Acetaldehyde/formic acid, methyl ester
y = 0.0394x + 0.587
R2 = 0.9135
Time (days)
Acetaldehyde/2-methylfuran
y = 0.0068x + 0.0669
R2 = 0.9307
Time (days)
Acetaldehyde/3-methylfuran
y = 0.0941x + 1.2087
R2 = 0.9133
Time (days)
Acetaldehyde/2-vinylfuran
y = 0.4709x + 3.0954
R2 = 0.9135
Time (days)

**Figure 3**

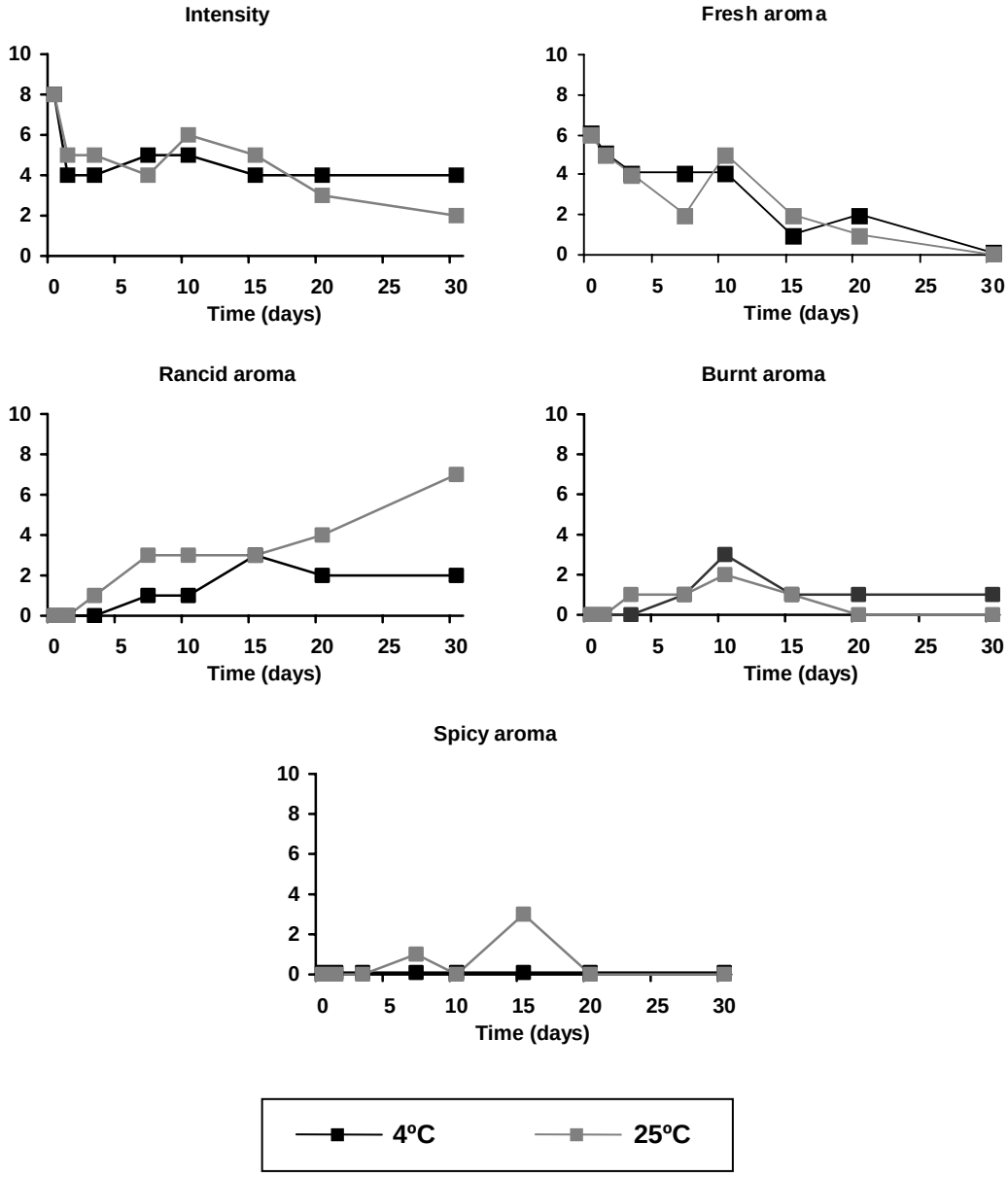
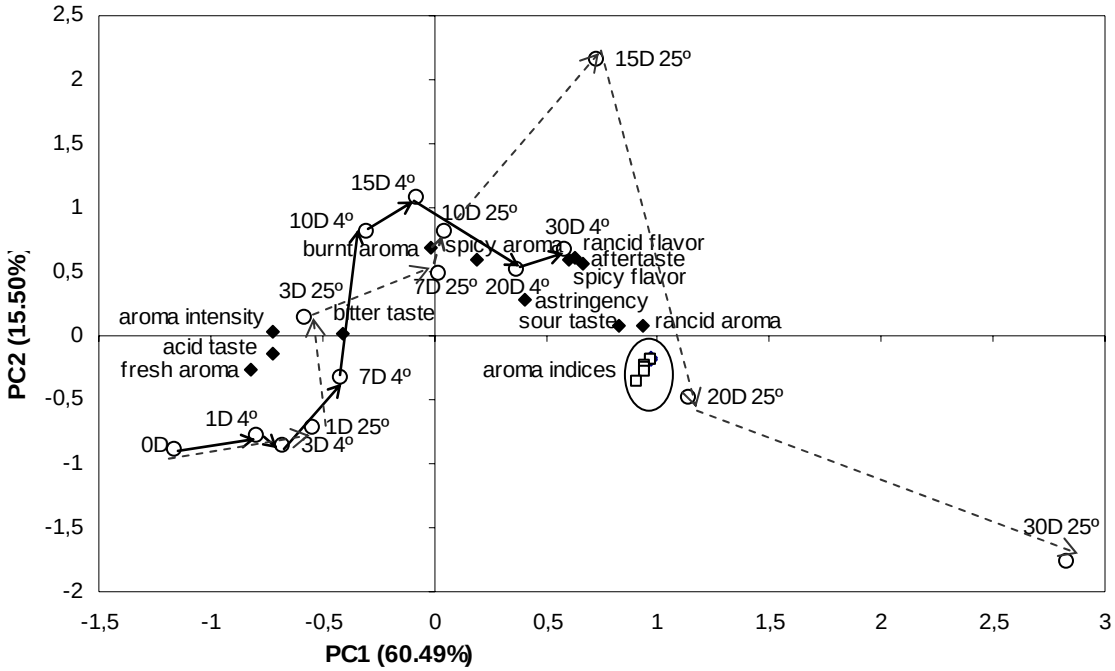

Intensity
Fresh aroma
Rancid aroma
Burnt aroma
Spicy aroma
Time (days)
4ºC
25ºC

**Figure 4**


2,5
2
1,5
1
0,5
0
-0,5
-1
-1,5
-2
-1,5
-1
-0,5
0
0,5
1
1,5
2
2,5
3
PC2 (15.50%)
PC1 (60.49%)
15D 25º
15D 4º
10D 4º
10D 25º
30D 4º
rancid flavor
aftertaste
spicy flavor
burnt aroma
spicy aroma
7D 25º
20D 4º
astringency
sour taste
rancid aroma
3D 25º
bitter taste
aroma intensity
acid taste
fresh aroma
7D 4º
aroma indices
20D 25º
1D 4º
1D 25º
0D
3D 4º
30D 25º