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Evaluation of the behaviour of phenols and alkaloids in samples of roasted and ground coffee stored in different types of packaging: Implications for quality and shelf life

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ABSTRACT

The most important factor in determining coffee quality and consumer choice is the flavour. During roasting, hundreds of simultaneous chemical reactions take place that contribute to the formation of the basic flavour of the coffee drink, imparting bitterness, astringency and acidity. The main chemical compounds responsible for these qualitative sensory properties are chlorogenic acids (CQAs), hydroxycinnamic acids and alkaloids. However, during storage, roasted and ground coffee can undergo several chemical and physical reactions that alter its flavour. This study focuses on LC-DAD analysis to investigate the effects of storing commercial coffee blends in different packaging, namely standard (multilayer film with aluminium barrier) and Eco-capsules. The results show relative stability of the phenolic and alkaloid fractions, although the CQA isomers behave differently and a decrease in caffeine and caffeic acid is observed during prolonged storage under 75% relative humidity compared to 65%, especially in Eco-friendly packaging.

1. Introduction

Coffee is one of the most popular drinks in the world, thanks to its psychoactive effects and pleasant taste (Panusa, Zuorro, Lavecchia, Marrosu, & Petrucci, 2013). Taste and aroma are the most important properties to assess the quality of coffee and consumer preferences. Roasting is the fundamental process that contributes to the development of flavour, which is essential for obtaining high-quality coffee. Hundreds of chemical reactions take place simultaneously during roasting, favourin the degradation of proteins, sugars, trigonelline and chlorogenic acids, and the formation of substances originating from Maillard reactions and Strecker degradation, which influence both the taste and the aroma of the coffee beverage. Many of these compounds, including volatiles, lipids, phenolics and alkaloids, contribute to the basic taste sensation of coffee drinks, imparting bitterness, astringency, strength and body to the coffee brew (Bressanello et al., 2021; Buffo & Cardelli-freire, 2004; Clarke & Vitzthum, 2014; Dos Santos Scholz, Kitzberger, Durand, & Rakocevic, 2018; Folmer, 2017; Farah, Monteiro, Calado, Franca, & Trugo, 2006; Sunarharum, Williams, & Smyth, 2014). Although roasted and ground coffee (R&G) is considered a stable product, many physical and chemical changes occur in coffee during storage. The rate at which they take place depends on environmental variables that could be limited by the use of proper materials, correct packaging methodologies and storage conditions (Manzocco, Calligaris, Anese, & Nicoli, 2016; Nicoli, 2012). Despite the numerous studies that have dealt with the loss of flavour freshness during storage of roasted coffee, only recently systematic investigations have been carried out, taking into account different species, packaging and materials (Cincotta, Tripodi, Merlino, Verzera, & Condurso, 2020; Czerny & Schieberle, 2001; Glöss, Schönbächler, Rast, Deuber, & Yeretzian, 2014; Marin, Požrl, Zlatić, & Plestenjak, 2008; Strocchi et al., 2022; Toci, Neto, Torres, & Farah, 2013; Toledo, Pezza, Pezza, & Toci, 2016). The changes in sensory features are generally due to the loss of key aroma compounds and the appearance of oxidation products derived from lipids degradation with the formation of peroxides that cause unpleasant flavours (Czerny & Schieberle, 2001; Goodman & Yeretzian, 2015; Strocchi et al., 2022; Telo & Vieira, 1997; Toci et al., 2013). Studies on the change of phenolics and alkaloids of R&G commercial coffees during storage

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however lack. Coffee beans have a different amount of chlorogenic acids, depending not only on the species (*Coffea canephora* Pierre (Robusta) contains the highest amount), but also on the variety, agricultural practises, environmental conditions and the processing (Clifford, Jaganath, Ludwig, & Crozier, 2017; Król, Gantner, Tatarak, & Hallmann, 2020; Narita & Inouye, 2015). Chlorogenic acids predominate as a group of esters of one or more of the three analogues of *trans*-hydroxycinnamic acids (caffeic, ferulic and p-coumaric, also in free form) with quinic acid. Depending on the type and number of conjugated hydroxycinnamic acids, different groups of CQAs are present in coffee: 1) caffeoylquinic acids (CQA) (caffeic acid esterified with quinic acid), among which, 3-CQA, 5-CQA and 4-CQA stand in for chlorogenic acid, neo-chlorogenic acid and crypto-chlorogenic acid, respectively; 2) di-caffeoylquinic acids (di-CQA) (two caffeic acids esterified with quinic acid), 3) feruloylquinic acids (FQA) (ferulic acid esterified with quinic acid) and 4) coumaric acids (p-CoQA)(p-coumaric acid esterified with quinic acid). In addition, depending on the position of the ester bond(s), different isomers can be formed (Clifford et al., 2017; Farah & Donangelo, 2006; Panusa et al., 2013; Perrone, Farah, Donangelo, de Paulis, & Martin, 2008). Fig. 1 shows the different CQAs structures present in coffee, with their precursors (Farah & Donangelo, 2006; Perrone et al., 2008). Chlorogenic acids have a significant influence on coffee quality and play an important role in the formation of coffee flavour. However, during the roasting process chlorogenic acids decreases as they degrades to form volatile phenols such as guaiacols and chlorogenic lactones contributing to increase bitterness (Correia et al., 2016; Perrone et al., 2008). Trigonelline, a pyridine derivative, and caffeine, a xanthine derivative, belonging to the class of alkaloids (Fig. 1), are responsible for the main stimulant effects and contribute to the bitter taste of the drink (Liang et al., 2023; Preedy, 2015). The two alkaloids and the phenolic acids have been studied mainly in terms of their physiological effects, and few studies have addressed the effects that storage conditions have on these chemical components over time. Since these compounds have antioxidant activity, the driving hypothesis of this study was to investigate their variation over time as a function of packaging and blends.

Król and co-workers showed how, after 12 months of storage, the caffeine content did not change in the roasted coffee samples, while the content of phenolic components decreased, due to both the enzymatic and non-enzymatic oxidative effect, that lead to an increase of caffeic, salicylic and gallic acids (Król et al., 2020). On the contrary,

This study investigates the capability of different coffee capsules to maintain flavour quality during storage in stressful conditions of temperature and humidity. Innovative environmentally friendly capsules (Eco capsules) were compared with conventional capsules commercialized by the brand, referred from now as "standard capsules", which are based on a copolymer with aluminium. The behaviour over time of phenols and alkaloids in these packages was studied as representatives of the astringency and bitter notes of coffee flavour together with their relationship to peroxide values, pH, moisture content and acidity.

2. Materials and methods

2.1. Samples

Single-served coffee capsules suitable for Espresso preparation, of three different roasting grounded coffee blends ("I", "P" and "B") were kindly supplied by Lavazza Group s.p.a (Turin, Italy). Samples P and B were 100% *Coffea arabica*, while I consisted of 50/50 *Coffea arabica*/*Coffea robusta*. The three blends were available in two different types of capsules: i) Eco capsules are 100% compostable caps made of an innovative biopolymer capable of degrading to compost in 180 days and becoming compost, and ii) Standard capsules made of a copolymer based on polypropylene and aluminium. The coffees in Eco capsules are named: IC, PC and BC, and the coffees in standard capsules: IS, PS and BS. The samples were stored in accelerated storage conditions in a climatic chamber for the control of temperature and humidity (FDM Environment Makers model CB-CS Serie, Rome – Italy). Coffee capsules were subjected to stress conditions at 45 °C and a relative humidity (RH) corresponding to 65% from T0 to T90 and then stored in the freezer before analysis. P blend in Eco capsules was also investigated at different relative humidity (RH 75%)) to evaluate how an increase in humidity affects coffee characteristics. The stressed samples were analysed on the T0, T30, T60, T90 days for both packaging (Eco and standard). The storage conditions were chosen taking into consideration the industrial partner know how regarding the preservation of the quality of the coffee. The information were from previous studies and the knowledge of the raw material under testing and an external organisation specialised in sensory analysis and shelf life, as well as the advice of a research group working with coffee for many years (Manzocco, Calligaris, Anese, & Nicoli, 2016). Extreme environment and conditions were applied. In

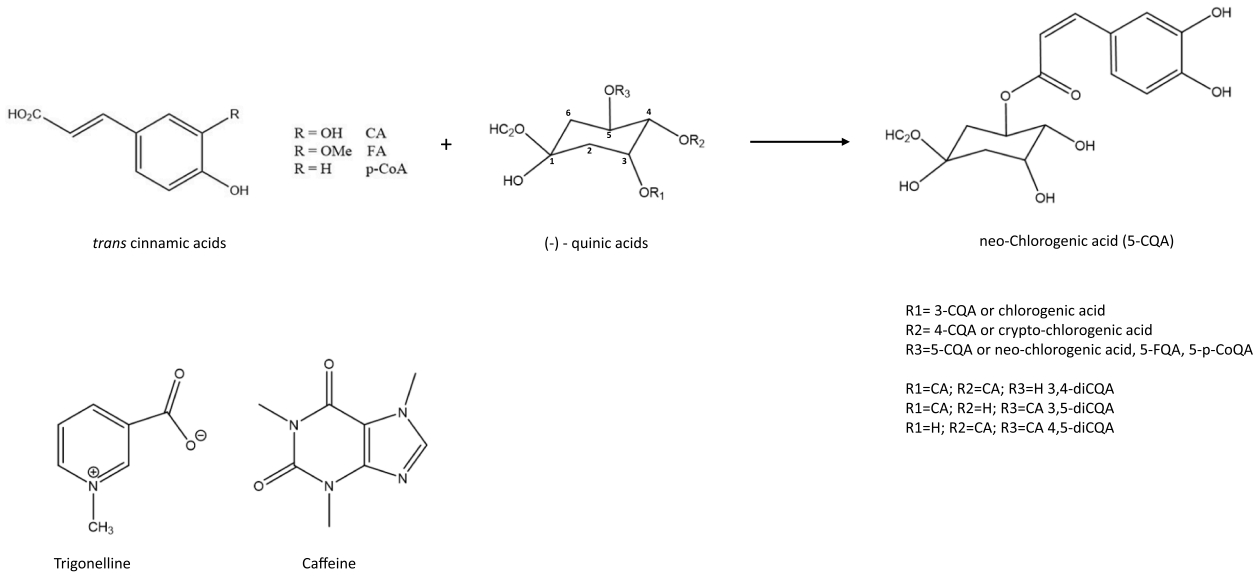

Fig. 1. Structures of chlorogenic acids (CGAs) precursors *trans*-cinnamic acids (quinic acid, caffeic acid (CA), ferulic acid (FA), p-coumaric acid (p-CoA)) and quinic acid. CGAs' main subclasses: caffeoylquinic acids (CQA), feruloylquinic acids (FQA), p-coumaroylquinic acids (p-CoQA), dicaffeoylquinic acids (di-CQA) together those of the two alkaloids investigated.

particular, higher temperature and RH can be useful to have a to predict the results of the shelf life study in a shorter time, by accelerating the ageing processes. Furthermore, the conditions were chosen to be realistic and verifiable, considering that these products may also be subject to long shipments and storage in conditions that are not always controlled. Sensory acceptability was monitored through a qualitative descriptive test by a trained industrial sensory panel composed of 7 people (4 females and 3 males). The sensory quality of the Eco capsules was no longer acceptable between 60 and 90 days of storage, while the standard capsules could still be accepted. Sensory acceptability was monitored through a qualitative descriptive test by a trained sensory panel.

2.2. Chemicals and standards

3-CQA, 5-CQA, 3,4- di-CQA, trigonelline, caffeine and caffeic, p-coumaric, ferulic, isoferulic and quinic acids were obtained from Sigma-Aldrich (Bellefonte), while 4-CQA, 3,5- di-CQA and 4,5- di-CQA were from Phytolab (Vestenbergsgreuth, Germany).

2.3. CQAs and di-CQA, hydroxycinnamic acids, quinic acid and alkaloids extraction

The beverage was obtained by modified method of Bressanello et al. from the percolation of 100 mL of distilled water at 90 °C on 1 g of coffee powder and then filtered through filter paper and then a 13 mm syringe filter (nylon 0.20 μm) to obtain 16 mL of extract containing the compounds of interest (Bressanello et al., 2021). The extraction was carried out in two replicates for each sample.

2.4. LC-UV/DAD

20 μL of each extract was analysed in duplicate with an Agilent 1200 system (Little Falls, DE equipped with an Agilent 1100 series spectra system UV diode array detector (Little Falls, DE). Samples were separated using a reversed-phase C18 column (Eclipse XDB-C18) (250 × 4.6 mm, 80 Å, 5 μm) (Alltech, Deerfield), under controlled temperature condition at 25 °C and a flow rate of 1 mL/min. The mobile phases were: solvent A: water with formic acid (999: 1, v/v), solvent B: acetonitrile with formic acid (999: 1, v/v). The gradient program was as follows: 15% B for 7 min, 15–55% B in 20 min, 55–100% B in 25 min and 100% B for 2 min, for a total running of 30 min. UV spectra were registered at 276 nm and 325 nm (Bressanello et al., 2021). The components were identified by comparing their retention times and UV spectra to those of authentic standards. The other components were tentatively identified. The stock standard solutions were prepared at 0.1 mg/mL in ACN/water.

The chromatograms resulting from the analysis were processed through the Enhanced ChemStation software (MSD ChemStation F.01.03.2357-copyright 1989–2015 Agilent Technologies).

2.5. Lipid extraction, peroxides and acidity values

Total lipids were extracted in duplicate from 1 g of coffee powder with 30 mL of organic solvents (n-heptane) using an ultrasonic bath (Branson 3200 model) followed by centrifuge (R-8D Remi Motors LTD, Vasai, India) (Cialiè Rosso et al., 2021). The surnatant containing coffee lipids was collected, concentrated and stored at −20 °C until analysis. Titratable acidity (expressed as the percentage of oleic acid), peroxide value (PV, determined by iodometric titration and expressed as millimoles of active O2 per kg of oil) of the extracted coffee oil samples were performed following CDR FoodLab® rapid testing procedures. CDR FOODLAB apparatus (Model SLB222, Florence, Italy) and the related analytical kits provide accelerated conditions for precise quality control of fat and oils. The accuracy of CDR methods has been already validated by obtaining a high correlation between individual curves from CDR method and the results from respective American Oil Chemists' Society (AOCS) official methods Cd 8–53 and Ca 5a-40 respectively with $R^2 = 0.9681$ and $R^2 = 0.9834$.

2.6. Moisture % and pH determination

Moisture content was determined according to the method of Benković et al. (Benković & Tušek, 2018). Samples were dried at 100 °C for 2.5 h in an oven dryer and weighed on an analytical balance. The difference in weight before and after drying was recorded as the mass of the water contained in the sample. Measurements were done in duplicate. The pH was measured, in duplicate, using the pH 70 portable pH-Mettler, Toledo© (Columbus, Ohio, USA) on coffee beverages.

2.7. Statistical analysis

The data were processed with the statistical and data analysis package XLSTAT software version 2021.2.1 (Addinsoft, New York, NY USA) in particular principal component analysis (PCA), correlation tests and one-way ANOVA, to assess the statistical differences between the samples along time were applied.

3. Results and discussion

In this study, the content of chlorogenic acids (5-CQA, 4-CQA, 3-CQA), di-chlorogenic acids (3,4 diCQA, 3,5 diCQA, 4,5-diCQA), hydroxycinnamic acids (caffeic acid, p-coumaric acid, ferulic acid, isoferulic acid), quinic acid and alkaloids (caffeine, trigonelline) of 24 samples of roasted coffee in various packaging was investigated. Acidity, peroxide value, moisture and pH were also measured in order to explore potential reactions involved over time.

3.1. Exploratory analysis of the untargeted signals

The principal component analysis (PCA) on the first 3 principal components of the untargeted LC-DAD signals (31 chemical variables) are visualised in Fig. 2a-c. In particular, it is evident two clusterings characterizing the different blends (100% Arabica (P and B) and blend (50% Arabica and 50% Robusta - I)) on the first principal component (Fig. 2a and Fig. 2b) accounting for 70.51% of the total variance. Within the first three PCs it is also displayed an effect of the packaging in the distribution of samples on PC2 (F2) for IS - IC and BS - BC, and on PC3 (F3) for PC - PS. Similar results are obtained with targeted profiles (13 chemical target variables), which can be seen in Fig. 2 d-e on the first 3 PCs with a similar total variance explained as for untargeted fingerprinting, which means that the thirteen variables contain useful information to describe the distribution of the samples. The observation of how the samples are distributed along the second component (F2) (Fig. 2d and 2e) can provide further relevant information mostly related to the time of ageing, although with a not linear trend.

3.2. Data exploration by chemical classes and the relationships with peroxides, acidity, pH and moisture

Chlorogenic acids significantly contribute to the flavour of coffee, supporting the bitterness, together with caffeine and trigonelline, and the astringent properties of the drink (Córdoba et al., 2021; Del Campo, Berregi, Caracena, & Zuriarrain, 2010; Heo, Adhikari, Choi, & Lee, 2020; Ribeiro, Ferreira, & Salva, 2011). The panel indicated at time between T60 and T90 days of storage a change of the flavour in Eco capsules for all blends investigated with an increased acidity, bitterness and oxidized notes. At T90 the sensory quality was no longer acceptable in these packages while resulted still satisfactory.

Analytical results were grouped by chemical classes to investigate the differences over time and the influence of packaging:

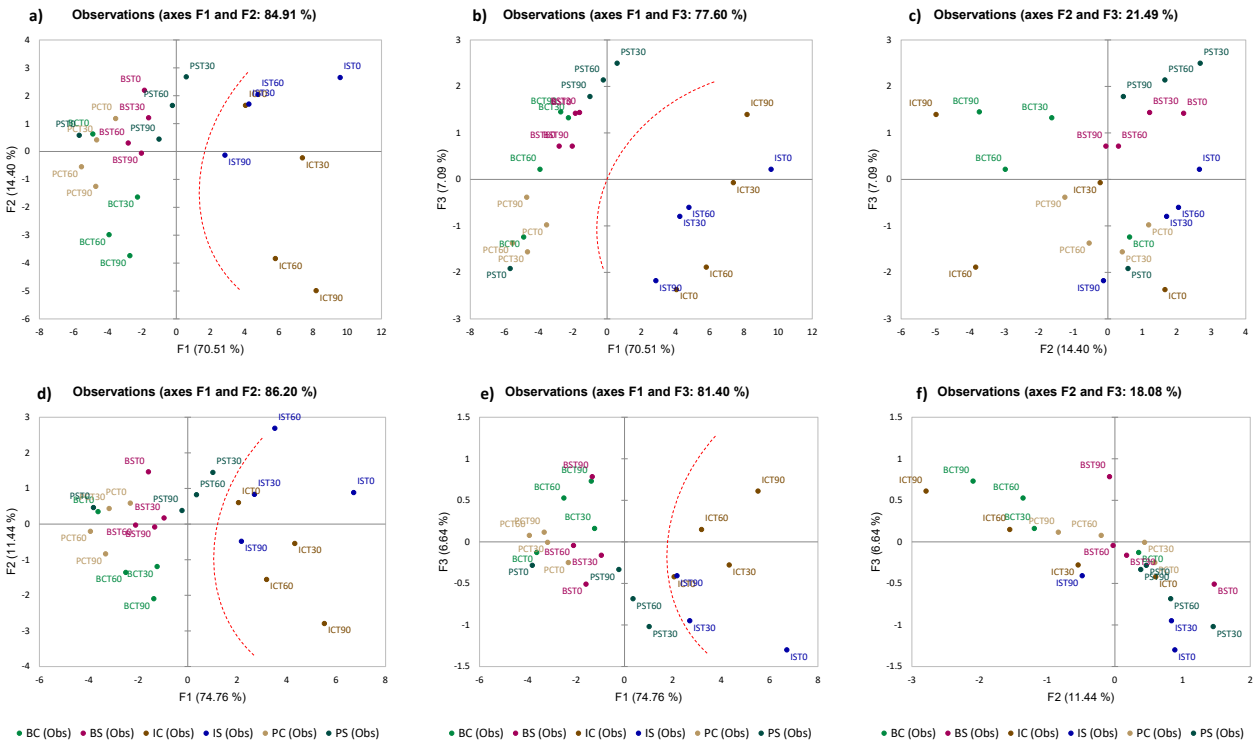

Fig. 2. A-c pca scores plot of untargeted LC-DAD signals of the different samples over time in Eco (IC, BC and PC) and Standard caps (IS, BS and PS). d-e PCA scores plot of target signals.

– CQAs includes all esterified chlorogenic acids (3-CQA; 4-CQA and 5-CQA) and di-chlorogenic acids (3,4-di-CQA; 3,5-di-CQA; 4,5-di-CQA);
– CINN encloses all non-esterified hydroxycinnamic acids (i.e.ferulic, isoferulic, caffeic and p-coumaric acids) and quinic acid;
– ALK comprises trigonelline and caffeine.

The variation over time of the CQAs, CINN and ALK in the different samples is reported in Figs. 3 and 4 (Fig. 3 for Eco caps and Fig. 4 for Standard caps). First of all, Figs. 3 and 4 show that the abundance of CQA and CINN in blend I is higher than that of other samples B and P, confirming literature data indicating that *Coffea canephora* is characterized by a higher proportion of phenolic compounds (Farah & Donangelo, 2006; Jeszka-Skowron, Sentkowska, Pyrzyńska, & De Peña,

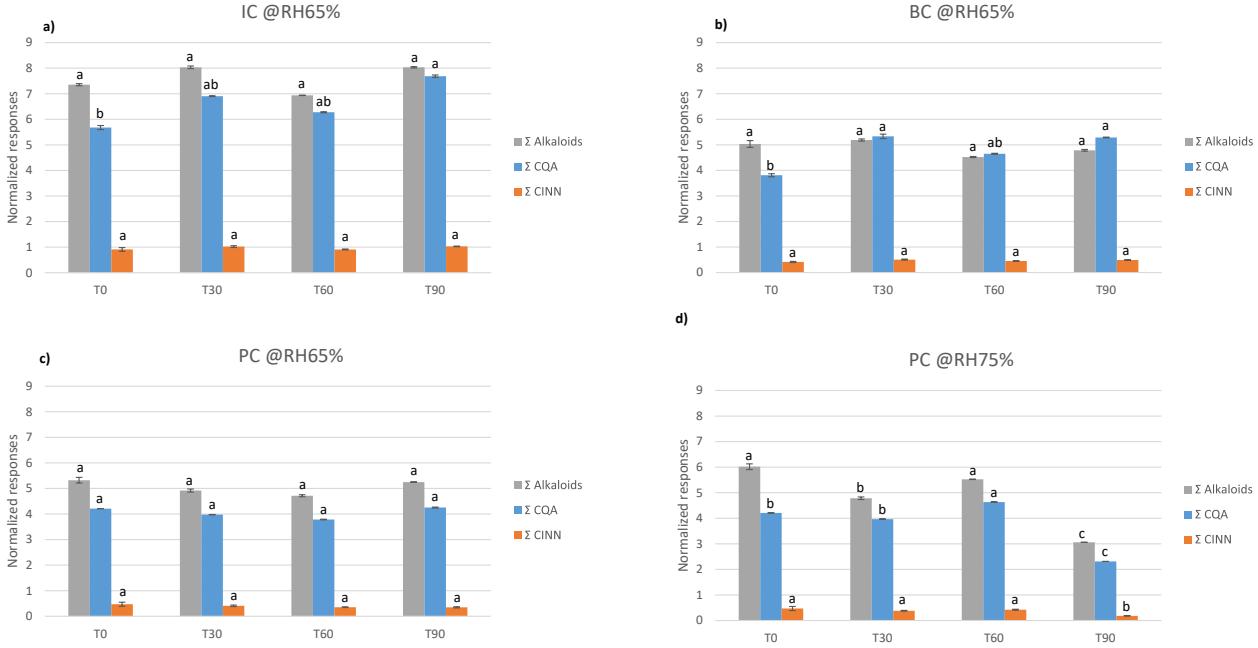

Fig. 3. Variation in time from T0 to T90 of the sum of CQAs that include the esterified chlorogenic acids and di-chlorogenic acids; the sum of the CINN acids and that of ALKs in the Eco capsules. Mean of two extractions and two analytical replicates for each extract. 5a) IC; 5b) BC; 5c) PC (at 65% RH); 5d) PC75% (at 75% RH). The same letters correspond to no variation (p-value $>$ 0.05).

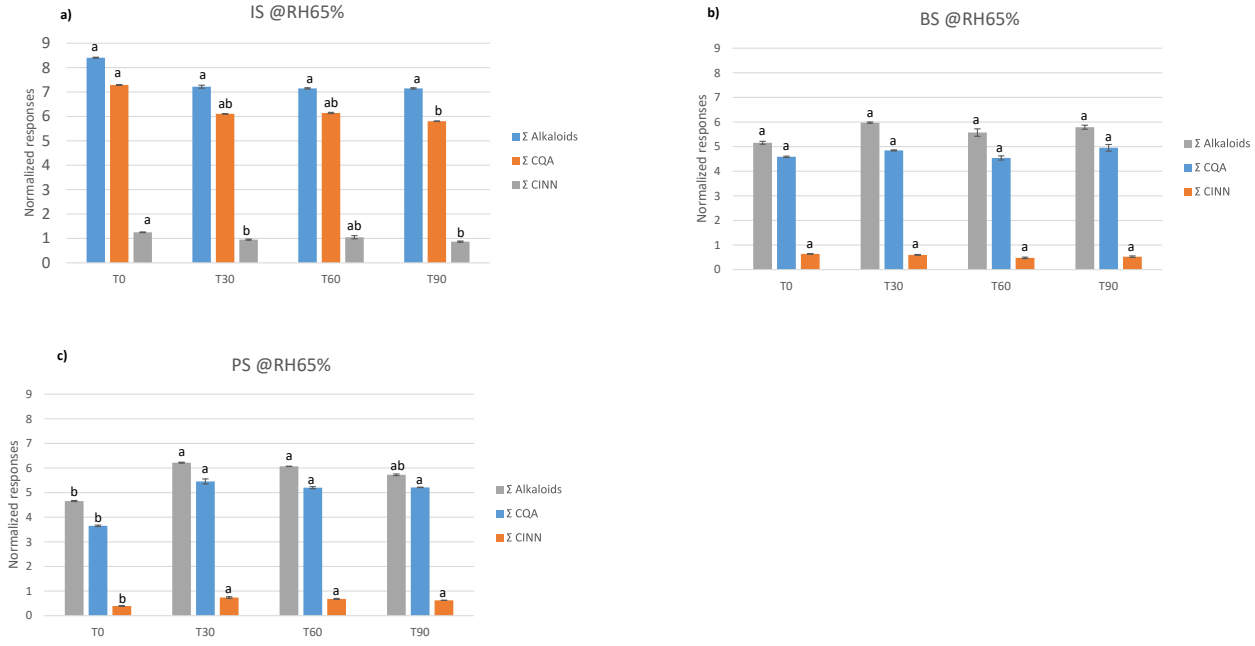

Fig. 4. Variation in time from T0 to T90 of the sum of CQAs that include the esterified chlorogenic acids and di-chlorogenic acids; the sum of the CINN acids and that of ALKs in the Standard capsules. Mean of two extractions and two analytical replicates for each extract. 5a) IS; 5b) BS; 5c) PS (at 65% RH). The same letters correspond to no variation (p-value > 0.05).

2016; Narita & Inouye, 2015). More in detail, as illustrated in Fig. 3, the levels of CQAs, CINN, and ALK do not significantly vary over time in the Eco caps at 65% relative humidity. As validated by the ANOVA test, they were not significant at alpha = 0.05, indicating that their abundance during storage is highly stable. However, only CQAs in IC show a small increase from T0 to T90 (Fig. 3a). Similarly, CQAs increased in BC, but only from T0 to T30,in the following they are stable over time (Fig. 3b). On the other hand, all the fractions in PC are stable over time and under the same relative humidity (RH 65%) (Fig. 3c), but when the storage humidity rises to 75%, the samples seem to be affected by moisture promoting degradation processes. Indeed, at T90 all fractions collapse (Fig. 3d). More specifically, in PC75%RH the Anova test (data not reported) shows that the CQAs (as sum) vary the most compared to the dimers of the CQAs (as sum). The chlorogenic acids class is sensitive to moisture and it decreases more when coffee is stored at higher ambient humidity. As reported by Dawidowicz ank Typek this behaviour could be explained by the fact that an increase in water content leads to an increase in hydrolytic reactions, that cleave the ester bond of the chlorogenic acids and form caffeic acid and quinic acid (Dawidowicz & Typek, 2017). However, this hypothesis cannot be supported by our data in Fig. 5, which shows the temporal evolution of the various phenolic components at the molecular level, because no increase in cinnamic acids is observed. It is also true that all these components have antioxidant properties as radical scavengers, which may partly explain the different decreases of some cinnamic acids (caffeic, ferulic and isoferulic) under the two humidity conditions. Furthermore, the measured peroxide levels show correlations with time, although not always in linear trends within the different samples (Fig. 6). This may be due to the different blends and packaging and the non-linear behaviour of the peroxides due to their high reactivity. For P samples, for example, under the same storage conditions, Fig. 6 shows an inverse correlation of peroxides with time in PScompared to PC, together with an inverse correlation between peroxide and acidity (measured as oleic acid equivalent), indicating slower oxidative reactions in the standard packaging.

In detail, it is clear that the same sample exposed to 75% humidity conditions (PC75%) is degraded more than those at PC65%, especially because of the rapid degradation of the three mono-CQA isomers at time T90 (Fig. 5a and 5b). All di-CQAs are degraded, with a much higher degradation rate for the 3,4-diCQA isomer (Fig. 5b). Contrary to expectations, the direct hydrolytic degradation products of the CQA acids, such as caffeic acid and quinic acid, do not seem to be related to the decrease in mono- and di-chlorogenic acids. One possible explanation is that the degradation reaction of CQAs is not related to a cleavage reaction, which would lead to the formation of hydrolysis by-products, but to an oxidation-like reaction since these acids have a strong antioxidant effect (Kamiyama, Moon, Jang, & Shibamoto, 2015; Vignoli, Bassoli, & Benassi, 2011). The other hydroxycinnamic compounds similarly behave with humidity at 65% and 75% (PC65% and PC75% RH), with caffeic acid being unstable at any moisture value (Fig. 5c and d). Finally, among the alkaloids, the compound most affected by moisture over time is caffeine, while trigonelline appears to be almost stable (Fig. 6e and f). Although few studies on caffeine reactions during the storage of coffee samples are reported in the literature our results suggest a degradative effect of caffeine influenced by time and humidity (Dalmázio, Santos, Lopes, Eberlin, & Augusti, 2005; Goodman & Yeretzian, 2015; Telo & Vieira, 1997). Telo and Vieira reported an oxidative effect related to the degradation of this alkaloid to 1,3,7-trimethyluric acid (8-hydroxycaffeine) (Telo & Vieira, 1997), and very recently Vandeponseele and co-workers (Vandeponseele, Draye, Piot, & Chatel, 2021) showed a decrease in caffeine levels in a humid environment due to an enzymatic effect that would lead to xanthine formation. These data, however, appear to be in contrast to Król's results (Król et al., 2020) that show an increase in caffeine levels after 12 months.

The standard packaged capsules remained more stable over time than the Eco capsules. They changed slightly over time in I and P (Fig. 4a and 4c) or not at all in B (Fig. 4b). This behaviour underlines the fact that this packaging has better stability under stress conditions compared to Eco and that the phenolic fraction is more stable over time.

In general, the relationships between blends, packaging and storage conditions can be seen in Fig. 6 from the correlations of the various parameters, which demonstrate a time-dependent increase in moisture in the samples with a simultaneous increase in acidity and a decrease in pH, which is less linear with time in eco-packaging due to the different permeability of the packaging.

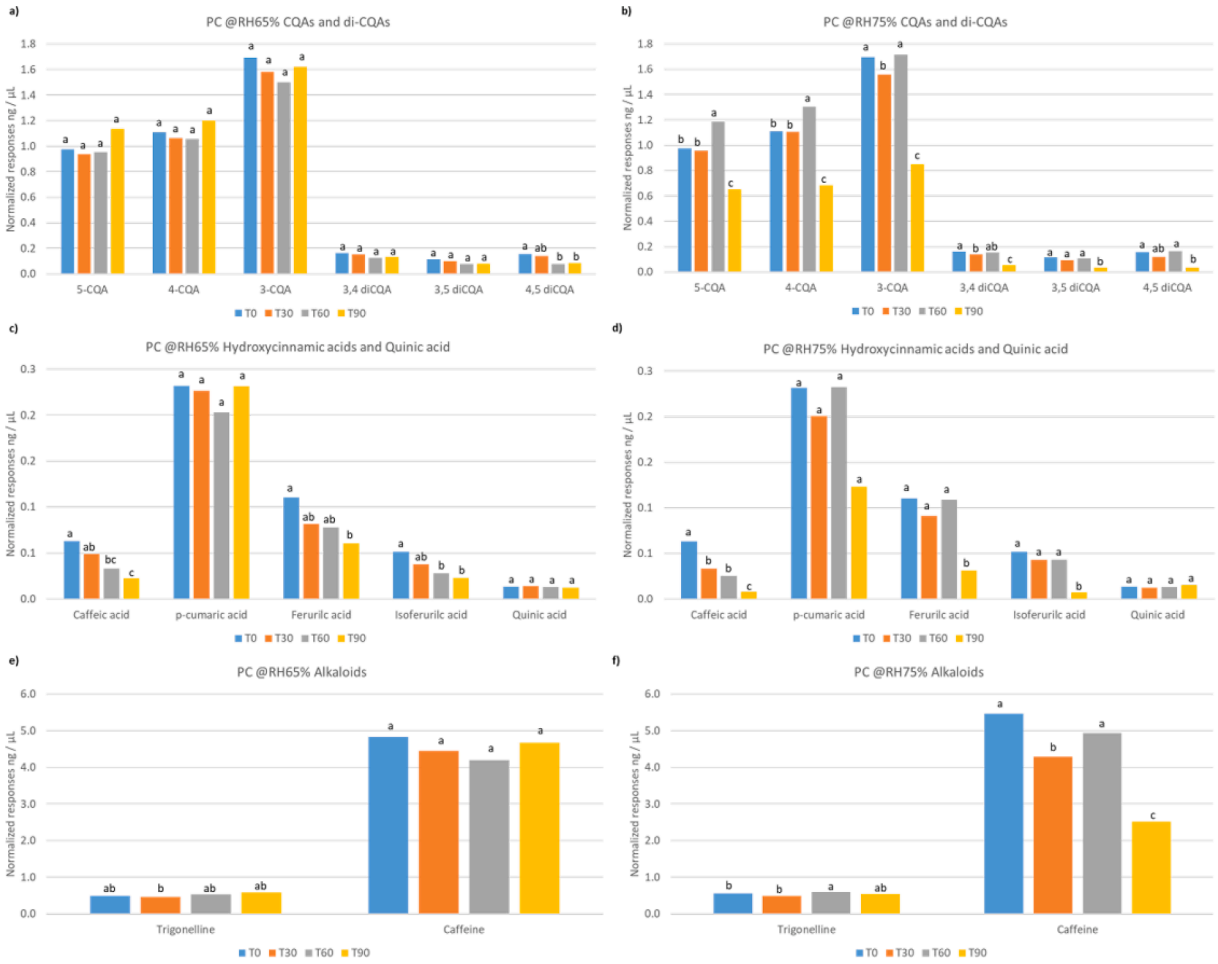

Fig. 5. Variation in time from T0 to T90 of the single phenolic components: a and b) CQAs and the di-CQAs; c and d) include all the non-esterified hydroxycinnamic acids and quinic acid, e and f) alkaloids. 6a), 6c) and 6e) PC (65%RH; 45 °C); 6b), 6d) and 6f) PC (75%RH; 45 °C). The same letters correspond to no variation (p-value > 0.05).

PC @RH65%

Variables	Time	Perox	Acidity	Moist%	pH
Time	**1**	0.694	0.468	**0.967**	**-0.984**
Perox	0.694	**1**	0.931	0.488	-0.722
Acidity	0.468	0.931	**1**	0.246	-0.462
Moist%	**0.967**	0.488	0.246	**1**	-0.934
pH	**-0.984**	-0.722	-0.462	-0.934	**1**

Values in bold are different from 0 with a significance level alpha=0.05

IC @RH65%

Variables	Time	Perox	Acidity	Moist%	pH
Time	**1**	0.804	0.796	0.938	**-0.965**
Perox	0.804	**1**	0.948	0.746	-0.700
Acidity	0.796	0.948	**1**	0.631	-0.631
Moist%	0.938	0.746	0.631	**1**	**-0.986**
pH	**-0.965**	-0.700	-0.631	**-0.986**	**1**

BC @RH65%

Variables	Time	Perox	Acidity	Moist%	pH
Time	**1**	0.261	**0.989**	0.927	**-0.951**
Perox	0.261	**1**	0.318	0.295	-0.421
Acidity	**0.989**	0.318	**1**	0.870	-0.917
Moist%	0.927	0.295	0.870	**1**	**-0.985**
pH	**-0.951**	-0.421	-0.917	**-0.985**	**1**

PC @RH75%

Variables	Time	Perox	Acidity	Moist%	pH
Time	**1**	0.487	0.382	**0.989**	**-0.988**
Perox	0.487	**1**	**0.965**	0.598	-0.600
Acidity	0.382	**0.965**	**1**	0.514	-0.517
Moist%	**0.989**	0.598	0.514	**1**	**-1.000**
pH	**-0.988**	-0.600	-0.517	**-1.000**	**1**

PS @RH65%

Variables	Time	Perox	Acidity	Moist%	pH
Time	**1**	-0.467	0.815	**0.989**	**-0.958**
Perox	-0.467	**1**	-0.266	-0.551	0.591
Acidity	0.815	-0.266	**1**	0.735	-0.666
RH%	**0.989**	-0.551	0.735	**1**	**-0.980**
pH	**-0.958**	0.591	-0.666	**-0.980**	**1**

Values in bold are different from 0 with a significance level alpha=0.05

IS @RH65%

Variables	Time	Perox	Acidity	Moist%	pH
Time	**1**	0.425	0.561	**1.000**	**-0.931**
Perox	0.425	**1**	0.657	0.407	-0.262
Acidity	0.561	0.657	**1**	0.563	-0.255
RH%	**1.000**	0.407	0.563	**1**	**-0.929**
pH	**-0.931**	-0.262	-0.255	**-0.929**	**1**

BS @RH65%

Variables	Time	Perox	Acidity	Moist%	pH
Time	**1**	0.864	**0.881**	**0.996**	-0.876
Perox	0.864	**1**	**0.901**	0.823	-0.748
Acidity	**0.881**	**0.901**	**1**	0.843	**-0.904**
RH%	**0.996**	0.823	0.843	**1**	-0.866
pH	-0.876	-0.748	**-0.904**	-0.866	**1**

Fig. 6. Pearson correlations (α = 0.05) between peroxide value, acidity, Moist% and pH on the different samples and storage conditions.

4. Conclusions

From this study, it appears that the fractions that determine the taste of coffee strongly depend on the composition of the blend. In particular, PCAs showed clear discrimination between 100% Arabica and 50% Arabica + 50% Robusta blends along the first principal component. Beside this, an effect of the packaging is observed within each blend. The phenolic fraction in general remains nearly stable over time, although under different moisture conditions, CQAs degrade to a different extent depending on the isomers (i.e. mono CQAs more than dimers). Another important factor influencing the variation in flavour quality is the storage conditions of the samples. In particular, a decrease in caffeine and caffeic acid has been observed in P blend with prolonged storage under 75% relative humidity compared to 65% confirming for this blend literature data on a decrease of caffeine in higher humidity environment. The above compounds were found to be more variable over time when stored in Eco caps compared to Standard caps, and an increase in the degradation of compounds related to bitterness is observed with an

increase in the relative humidity of the storage environment. The results observed in P blend at higher humidity storage need further investigation extended to other blends.

CRediT authorship contribution statement

Strocchi Giulia: Methodology, Formal analysis, Investigation, Data curation, Visualization. **Bagnulo Eloisa:** Methodology, Formal analysis, Investigation, Data curation, Visualization. **Ravaioli Giulia:** Methodology, Writing – review & editing, Project administration. **Pellegrino Gloria:** Conceptualization, Resources, Investigation, Writing – review & editing, Supervision, Funding acquisition. **Bicchi Carlo:** Writing – review & editing. **Liberto Erica:** Conceptualization, Methodology, Investigation, Data curation, Writing – review & editing, Visualization, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Dr.ssa Gloria Pellegrino and Giulia Ravaioli are employees of Lavazza S.p.a.

Data availability

The authors do not have permission to share data.

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