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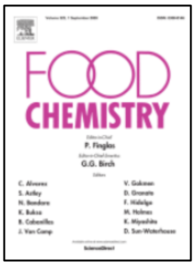

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Characterization of rums sold in Spain through their absorption spectra, furans, phenolic compounds and total antioxidant capacity

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ABSTRACT

A total of 42 different rums currently marketed in Spain were analyzed to study the effect of aging time and manufacturing steps (filtration, addition of additives or spices, solera aging method, use of different types of aging barrels) on several parameters: color, non-enzymatic browning, antioxidant capacity and phenolic profile. Different analytical techniques to obtain a broader descriptions of the samples were employed: absorption and UV-vis spectrophotometry, antioxidant capacity (DPPH, FRAP, ABTS methods), total phenols and HPLC to detect individual phenolic and furanic compounds. Results showed that spectrophotometric techniques could potentially be used to detect adulteration and frauds, as well as to differentiate rums by aging time. Those rums aged longer, especially those aged in oak barrels that had previously contained Bourbon or wine, showed higher phenolic content, antioxidant capacity and concentration of furanic compounds. Filtration results in the loss of antioxidant compounds while adding spices increases their concentration in rums.

KEYWORDS: rum; aging; antioxidant capacity; polyphenols; absorbance spectra; furanic compounds.

1. Introduction

Rum is an alcoholic beverage obtained from sugarcane juice or molasses (Pino, Tolle, Gök, & Winterhalter, 2012). Its high global consumption rate (more than 1 billion liters per year) shows that rum is one of the most popular alcoholic beverages (Belmonte-Sánchez et al., 2018). The main producers of rum are found in Caribbean countries: Cuba, Jamaica, Martinique, Dominican Republic and Venezuela. However, several other countries such as the Czech Republic, the Philippines, Spain or the United States are emerging as producers.

Regardless of the production country, one of the most important properties to define rum quality is its aroma (Osorio-Monsalve, López, & Zapata, 2016), which is a complex mixture of over a hundred different compounds that appear during rum production and aging (Franitza, Granvogl, & Schieberle, 2016a). Furanic compounds, fatty acids or polyphenols are some of the compounds that have been described. (González, Vázquez, & Redondo, 2006). Polyphenols come mostly from the barrel, from where they are released into the rum during the aging process (Sampaio, Reche, & Franco, 2008). They represent a large group of chemical structures (Brglez Mojzer, Knez Hrnčič, Škerget, Knez, & Bren, 2016) to which antioxidant and anti-inflammatory effects, among other health benefits, have been attributed (Arranz et al., 2012). On the other hand, furanic compounds such as 2-furaldehyde (furfural) or 5-hydroxymethylfurfural (HMF) are generated during non-enzymatic browning (Goldberg, Hoffman, Yang, & Soleas, 1999; Rufián-Henares, Delgado-Andrade & Morales, 2006), appearing at different stages of rum manufacturing, for example during distillation, or as result of adding caramel to unify the color (Alcázar, Jurado, Pablos, González, & Martín, 2006).

The presence and the concentration of those compounds in rum are highly dependent on the manufacturing process (**Figure S1**), finding as key factors: the quality of the raw material used (Osorio-Monsalve et al., 2016), the type of fermentation, type of distillation carried out (Sampaio et al., 2008), the addition of additives such as caramel or herbs (Persad-Doodnath, 2008), aging time and barrel proprieties (Belmonte-Sánchez et al., 2018), transfer methods during aging as the solera process (Blanco-Carvajal, Giménez-Martínez, González, & Vázquez, 2000), activated carbon filtration or water demineralization (Pino et al., 2012), the type of mixture before bottling and the alcoholic grade (Franitza, Granvogl, & Schieberle, 2016b).

Therefore, taking all this information into account, the objective of this project was to study the influence of several manufacturing steps, specifically aging time and type of barrel (oak barrel, oak barrel that used to contain wine, and oak barrel that used to contain bourbon), filtering, solera process, and spices-additives adding, in those characteristics that will determine the quality of rums sold in Spain: spectrophotometric profile, content of non-enzymatic browning indicators, antioxidant capacity, and phenolic profile. This study is one of the most comprehensive in terms of rum analysis. It not only involves a wide and diverse amount of samples, but also employs a large number of different analytical techniques, allowing to obtain detailed information on the samples.

2. Materials and Methods

2.1. Reagents, standards and solvents

2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt (ABTS), 2,2-diphenyl-l-picrylhydrazyl (DPPH), 2,4,6-tri(2-pyridyl)-s-triazine (TPTZ), 2-furaldehyde, 5-carboxyresorcinol, 5-hydroxymethylfurfural, 6-hydroxy-2,5,7,8-tetramethylchromane-2-carboxylic acid (Trolox), acetonitrile, anhydrous sodium sulfate, caffeic acid, chlorogenic acid, daidzein, diethyl ether, ellagic acid, (−)-Epicatechin, (−)-Epigallocatechin gallate, ethanol, ferulic acid, Folin-Ciocalteu phenol reagent, formic acid, formononetin, gallic acid, genistein, homoprotocatechuic acid, hydrochloric acid, iron (III) chloride hexahydrate, m-coumaric acid, methanol, methylvanillin, o-coumaric acid, p-coumaric acid, potassium persulphate, protocatechualdehyde, protocatechuic acid, sinapinic acid, sodium acetate, sodium carbonate, syringic acid, tyrosol, vanillic acid and vanillin were obtained from Merck (Darmstadt, Germany). All standards were of analytical grade and the solvents were HPLC quality. Double distilled deionized water was obtained from a Milli-Q system (Millipore, USA).

2.2. Samples

A total of 42 commercial rums, from 12 different countries, in addition to a sample of cachaça and a sample of homemade rum were used in this study, making a total of 44 samples. Samples were collected through different stores in Granada (Spain). Prior to the analysis, they were stored in sealed containers at -80ºC. Information about rum characteristics was extracted from the official website of the manufacturers and from the label of the bottles. Alcohol percentage was between 37.5 % - 40 % v⁄v. A code was assigned to each sample and the information extracted is summarized in **Table S1**. Samples were classified into groups by aging according to the information on the label and current Spanish legislation (Real Decreto 164/2014). The groups were as follows: 1 White; 2 Golden; 3 Añejos and three to five years barrel aging; 4 Extra Añejo rums and up to eight years barrel aging; 5 more than ten years barrel aging; 6 those with other denominations (**Table S2**). Other information obtained from the rums was also used to describe them. i. The countries of origin were obtained for all the samples except for two of them. Accordingly, samples (R20) and (R32) were classified as "Caribbean" origin, since the information provided by the producers only indicates such origin, but not a specific country. ii. The type of barrel (oak barrel, oak barrel that previously contained wine, and oak barrel that previously contained Bourbon) used during aging. iii. The manufacturing process as distillate by stainless steel columns or copper pot stills. iv. Information about other specific characteristics of the samples, such as activated carbon filtering, solera process and addition of additives (caramel) or spices. Variables whose information could not be recorded or accessed were classified as N/A.

2.3. Absorbance and UV-vis spectrophotometry

Absorbance and UV-vis spectrophotometry was performed according to Lehtonen, Keller, & Ali-Mattila (1999). This analysis was used to identify differences between rums of the same brand but with different aging time. Therefore, UV-vis absorbance was recorded at 420 nm and 280 nm for all samples with a LS 55 spectrophotometer (Perkin-Elmer, USA) using one-centimeter quartz glass cuvettes (QS-1,000 Suprasil, Hellma GmbH & Co, Germany). Data were expressed as arbitrary units (AU) × 10^3.

2.4. Antioxidant assays

A Fluostar Omega microplate reader (BMG Labtech, Ortenberg, Germany) was used for all antioxidant capacity assays. ABTS method (Trolox equivalent antioxidant capacity against $ABTS^{\cdot+}$ radicals) was carried out as described in Jiménez-Zamora, Delgado-Andrade, & Rufián-Henares (2016), DPPH method (Trolox equivalent antioxidant capacity against DPPH radicals) was carried out as described by Patrignani, Rinaldi, Rufián-Henares, & Lupano (2019) and FRAP method (Trolox equivalent reducing capacity against ferric ions) was carried out as described in Benzie & Strain (1996). The calibration curve for each method was performed with Trolox ranging from 0.01 mg/mL to 0.1 mg/mL, and the results were expressed as µmol of Trolox equivalent per mL.

2.5. Total phenolic content

Total phenolic content was estimated by Folin-Ciocalteu method as described in Moreno-Montoro, Olalla-Herrera, Giménez-Martínez, Navarro-Alarcon, & Rufián-Henares (2015). A calibration curve was prepared with gallic acid in distilled water, with concentrations between 0.1 and 0.01 mg/mL. Results were expressed as mg gallic acid equivalents per L.

2.6. Individual phenolic compounds

The identification and quantification of individual phenolic compounds was performed in triplicate by high performance liquid chromatography (HPLC) according to the methodology described in Moreno-Montoro et al. (2015). The HPLC system used was a Thermo Fisher-Scientific Accela 600 equipped with a quaternary pump, an automatic injector and a variable wavelength UV-vis (PDA) detector set at 280 nm. A calibration curve was performed with concentrations ranging from 0.001 to

40 mg/L for each phenolic compound selected. Identification was performed by retention times of the corresponding standards. Standards were analyzed under the same working conditions as the samples.

2.7. Furfural and HMF determination

Furfural and HMF were analyzed according to the procedure described in Rufián-Henares, García-Villanova, & Guerra-Hernández (2001) slightly modified (Rufián-Henares, García-Villanova, & Guerra-Hernández, 2008). The HPLC system (Thermo Fisher Accela 600) was equipped with a variable wavelength UV–vis detector (PDA) set at 284 nm. Furfural and HMF was quantified using retention time and calibration curves within the range 0.01–10.00 mg/L and 0.01–5.00 mg/L respectively. The analysis was performed in triplicate and the data are the mean values expressed as mg/L.

2.8. Statistical methods

All statistical analyses were conducted using SPSS 22.0 software package (SPSS Inc., USA). The mean and standard deviation of values for each group were determined, as were the differences between groups by means of a t-Student analysis and an analysis of variance (ANOVA). The Bonferroni post-hoc test was performed to detect significant differences. The differences were considered statistically significant for $p < 0.05$. In addition, the relationship between different assays was evaluated by computing the relevant correlation coefficient (Person linear correlation) at the $p < 0.05$ confidence level. Principal component analysis (PCA) was applied as a multivariate exploratory analysis to look for clustering variables. Also, linear discriminant analysis (LDA) was performed as a supervised technique. LDA is another dimension-reduction method, which uses the Mahalanobis distance method on the within-groups covariance matrix. LDA analysis was performed using a stepwise inclusion method and classification success was evaluated using leave-one-out cross-validation.

3. Results and discussion

3.1. UV-vis spectrophotometry and absorbance analysis

Some studies propose using spectrophotometric analytical techniques to distinguish certain alcoholic beverages (Lehtonen et al., 1999). Obviously, spectrophotometric techniques allow the differentiation between white and aged rums, but its use to differentiate among aged rums or to detect addition of additives is not so common. Since some products derived from non-enzymatic browning can confer a brownish color (Rufián-Henares, Guerra-Hernández & García-Villanova, 2006) with an increased absorbance near to 420 nm (Rufián-Henares, García-Villanova and Guerra-Hernández, 2002), spectrophotometric analytical techniques could be useful.

Figure 1A shows how the spectra changed depending on how long a rum from the same brand was aged (5-12 years), increasing the absorbance in the range of 340-450 nm, where some polyphenols and polymeric compounds derived from polyphenols had a maximum absorbance (Villalón-Mir, Montilla-Gómez, & Garcia-Villanova, 1987). On the other hand, **Figure 1B** clearly shows how white rums have a completely different spectrum than aged rums of the same brand due to the absence of polyphenols and other compounds added (i.e. caramel) who have a high absorption in the range of 340-450 nm. Since white rum had a different profile in **Figure 1B**, the analysis was extended to white rums from different brands (**Figure 1C**). A clear difference is observed at higher wavelengths between white rums and the rum aged for 3 years (sample R23) or cachaça (sample RX). Sample R23 had no color, so it was added to the comparison, although it was classified in another group due to its aging process. The results show the influence of aging and elaboration method (sample RX) also in these samples, despite the absence of color. These results are in line with those reported by other authors (Cardoso et al., 2004; De Souza, Vásquez, del Mastro, Acree, & Lavin, 2006). Finally, in **Figure 1D**, three samples from the same brand but different aging time (white, añejo and extra añejo) were compared with sample R28 (samples added with caramel). Both aged samples (añejo and extra añejo) had a fairly different spectrum. Aside from the obvious differences between white and aged rums, this spectroscopic method could not only be useful to classify rums according to their aging time but also to check whether additives were added. Therefore, this methodology could be used as a fast and cheap complementary analytical method to identify possible adulteration and fraud in rums as well as in other aged alcoholic beverages.

After analyzing the spectrum, rum color was analyzed at two different wavelengths, 280 nm and 420 nm. At 420 nm, absorbance values ranged from 2.656 for a spices-added rum (R29) to 0.008 for a white rum (R3). At 280 nm, absorbance values ranged from 2.887 for a 12-years aged rum (R11) to 0.0299 for a golden rum (R38). No significant differences were found at 280 nm. Although some authors (Picque et al., 2006) reported differences at this wavelength, they also stated that some products, such as the color of burnt sugar, can cause interferences in the determination of absorbance at 280 nm. At 420 nm differences between samples were clearly observed when they were grouped according to the type of oak barrel (**Table S3**) and aging time (**Figure 2**). For example, those rums that were aged in barrels that used to contain bourbon or wine had significantly higher ($p < 0.05$) absorbance than rums that had been kept in regular oak barrels (**Table S3**). In fact, this was expected since those rums with longer aging time are usually stored in oak barrels that previously contained bourbon or wine, which in turn increases the extraction of colored compounds from the wood, providing rums with differentiated organoleptic properties (Zhang, Cai, Duan, Reeves & He, 2015).

When rums were grouped according to aging time, an increase in absorbance at 420 nm was observed (**Figure 2**), probably related with a higher yield of extraction of colored compounds from the barrel (Villalón-Mir et al., 1987). Statistically significant differences ($p < 0.05$) were found between white and aged rums, as well as between rums aged up to 5 years from those aged more than ten years (0.838 *Vs.* 1.677 absorbance units for groups 3 and 5, respectively). No significant differences were found between groups 2 and 3 with group 4. Group 6, however, had great variability since any of the samples that did not fall under the previous groups (due to special manufacturing steps) were included here. In order to reinforce the idea of the usefulness of the analysis of absorbance at 420 nm to distinguish between the types of rums, the mean absorbance for each group (with its confidence intervals at 95%) was calculated: four group one 0.01 (0.01 - 0.02); for group two 0.59 (0.19 – 0.99);

for group three 0.84 (0.60 - 1.07); for group four 1.15 (0.86 – 1.43); for group five 1.77 (0.81 – 2.54). Therefore, absorbance measurements at 420 nm could also be used as a fast analytical technique to identify rums by aging time.

3.2. Antioxidant capacity

Since most of the antioxidant capacity in rums is provided by their phenolic content, which has been linked to some health benefits antioxidant capacity could be an important measurement to take into account regarding distilled beverages. Therefore, antioxidant capacity was evaluated through three different methods (ABTS, DPPH, and FRAP) which are widely used to evaluate antioxidant capacity in alcoholic beverages (Queirós, Tafulo, Paula, & Sales, 2013). Using three different methodologies allowed a wider picture of their antioxidant capacity since FRAP measures reducing capacity, while ABTS and DPPH measures anti-radical activity.

For all three methods, two samples of white rum showed the lowest antioxidant capacity values: R40 (which underwent a filtering process) and R32. On the other hand, the individual samples with the highest antioxidant capacity were R20 and R5, both belonging to rums over 10 years old and made with the solera method (group 5). Both of them were aged in barrels which used to contain wines or Bourbons.

When rums were classified by aging time, group 5 (rums aged longer than 10 years) showed significantly ($p < 0.05$) higher antioxidant capacity than the rest of the groups for all three antioxidant methodologies tested (**Figure 3A**). Additionally, in the case of FRAP method, some other statistically significant differences were observed: while añejo and extra añejo rums (groups 3 and 4, respectively) were more antioxidant than white rums, only extra añejo rums (group 4) were more antioxidant than golden rums (group 2). Although no other significant differences were found, antioxidant capacity showed a clear tendency to increase along aging time (**Figure 3A**). The absence of further significant differences could be explained by broad standard deviations found within groups.

On the other hand, **Figure 3B** depicts differences according to the elaboration process of rums. Those liquors added with spices or submitted to the solera aging process showed the highest antioxidant capacity. Conversely, the filtration process resulted in a loss of antioxidant compounds, as reported by other authors (Pino, Tolle, Gök, & Winterhalter, 2012).

Finally, when samples were grouped according to the type of barrel selected for aging (**Table S3**), those rums that were kept in wine or bourbon oak barrels showed significantly ($p < 0.05$) higher antioxidant capacity (for the three methods assessed). This type of barrels (specially those which had been in contact with wine) are known to have incorporated phenolic substances into their wood matrix (Zhang et al., 2015), releasing them into rums during aging. Moreover, these types of barrels are used for those rums with longer aging time, which could increase the extraction yield of phenolic compounds (responsible of the antioxidant capacity of rums).

3.3. Polyphenol content evaluation

Total polyphenol content of rum samples was analyzed by the Folin-Ciocalteu method. Total phenolic content ranged from 1.04 ± 0.57 mg of gallic acid equivalents/L for a white rum sample (R40) to 66.98 ± 6.25 mg of gallic acid equivalents/L for a 10 years aged rum (R20). The average content, considering all samples, was 24.38 ± 13.4 mg of gallic acid equivalents/L, which is a similar value than that reported in other studies using the same analytical technique (Regalado et al., 2011).

Regarding aging time, total phenolic content, as expected, followed the same behavior as antioxidant capacity values: a longer aging resulted in a higher phenolic content (**Figure 4**). As it can be seen, rums aged for longer than 10 years showed a significantly ($p < 0.05$) higher phenolic content than white and golden rums. This could be related to a higher extraction yield due to a longer contact with the barrel wood (González et al., 2006; Regalado et al., 2011). In relation to the type of barrel, total phenolic content was significantly ($p < 0.05$) higher when barrels used to contain bourbon or wine (**Table S3**), probably due to wine polyphenols incorporated into the wood matrix during its storage and their release into the rum during its aging (Zhang et al., 2015).

Although Folin-Ciocalteu method is widely used to estimate total polyphenol content in many foods as well as in alcoholic beverages, the tendency is to identify and to quantify individual polyphenols, which would make possible to find more specific differences between different types of rum. **Figure 5** depicts a heatmap plot with the phenolic species found in the studied samples. The main phenolic compounds found (with concentrations up to 18 mg/L) were vanillin, vanillic acid, syringic acid and epigallocatechin gallate, which have been previously found in rum by other authors (Barnaba et al., 2015; Goldberg et al., 1999; Osorio-Monsalve et al., 2016; Pino et al., 2012). Those rums aged longer had a much larger concentration of polyphenols, which is in agreement with the previous Folin-Ciocalteu results and other studies (Belmonte-Sánchez et al., 2018; González et al., 2006). This behavior has been also reported for other spirits aged in barrels (Zhang et al., 2015). Rums aged in wine or bourbon barrels (**Table S3**) showed higher concentrations of vanillin, caffeic acid, epicatechin and epigallocatechin, which are known to be present in wine or bourbon (Barnaba et al., 2015; Collins, Zweigenbaum, & Ebeler, 2014). Samples that underwent a filtration process showed significantly ($p < 0.05$) lower content of individual phenolics than the others (data not shown); during this process rums are purified, but at the cost of losing most of the phenolic compounds. On the other hand, sample R29 showed significantly higher phenolic content, highlighting the levels of 5-carboxyresorcinol, which could be due to the addition of spices during its elaboration.

3.4. HMF and furfural determination

HMF and furfural are common compounds found in heat treated foods (Rufián-Henares & de la Cueva, 2008) though they can also be present in alcoholic beverages (Monakhova & Lachenmeier, 2012). Regarding rums, these compounds usually come from either the production process and treatment of raw materials or from the barrel where they were aged. Barrels are thermally processed during their production, generating many of these compounds that could, afterwards, be passed in to the rum (Goldberg et al., 1999).

As stated in **table 1**, most white rums (group 1) did not showed relevant amounts of either HMF or furfural, which is consistent with previous studies (Villalón-Mir, Montilla-Gómez, & Garcia-Villanova, 1987). These findings could be due to the filtering process or to a lack of contact with the barrel, since these rums are not aged. However, an increase in the levels of both HMF and furfural along aging time was found (**Table 1**) which is in line with other studies (Alcázar et al., 2006; Belmonte-Sánchez et al., 2018). Statistically significant differences ($p < 0.05$) were found between not aged rums (group 1) and rums aged longer than 10 years (group 5) for HMF (**Table 1**). These differences were also significant for group 4 (rums aged more than 5 years) in the case of furfural. Average values for HMF and furfural were 22.1 and 0.66 mg/L, respectively. These results are in line with other studies (Alcázar et al., 2006; González et al., 2006; Sampaio et al., 2008). While HMF values ranged from below LOD (limit of detection) for white rums to 150 mg/L for a 10 years aged rum (R20), furfural values were much lower, ranging again from below LOD for white rums to 2.89 mg/L for a 10 years aged rum (R20). It should be noted that the RY sample, the homemade sample, showed values of 237 mg/L and 3.1 m/L for HMF and furfural, respectively. This could be related to a poor manufacturing process, probably in terms of temperature control, that could result in a significant increase of their content. Furthermore, R29 sample also showed values above the average (38.8 mg of HMF/L and 2.1 mg of furfural/L), which could be related to the addition of spices. Finally, sample R28 (with added additives) also showed HMF values above the average (24.4 mg/L), though that was not the case for furfural (0.3 mg/L), situation which has also been described in brandy (Granados, Mir, Serrana, & Martinez, 1996).

3.5. Statistical relationships among analytical parameters

In the previous sections it has been described the content of different chemical species (furanic and phenolic compounds), antioxidant capacity as well as physicochemical properties (absorbance at 280 and 420 nm). Similar grouping was observed for aging time and storage in different types of barrels, which could indicate some kind of relationship among them. Therefore, we first investigated the possible existence of linear correlations between the studied parameters (**Table S4**). Overall, for most of the correlations computed (50 out of 56), a high signification ($p < 0.01$) was found with Pearson correlation coefficients (R_s) ranging from 0.994 to 0.999. Slightly less significant correlations ($p < 0.05$) were obtained for other five associations. All this information would lead to hypothesize that those compounds extracted from the barrel during aging (polyphenols or furanic compounds, among others) could influence physicochemical characteristics of rums (i.e. colour) as well as nutritional properties (i.e. antioxidant capacity).

Finally, multivariate exploratory analysis was also performed by means of Principal Component Analysis (PCA) in order to check the relationship among groups of samples. No specific grouping of samples was observed according to country, distillation, raw material or brand, possibly because of the lack of information. However, rum samples tended to cluster together according to the type of barrel and aging time (**Figure S2**). According to PCA, both variables had a significant ($p < 0.05$) influence on samples distribution. The proportion of cumulative explained variance of PC1 (73.3%) and PC2 (16.1%) was of 89.4%. Nevertheless, clustering still showed how large the variability is, even between rums aged during the same time. In order to improve the analysis, a linear discriminant analysis (LDA) was performed. LDA is an alternative method, more stable for small sample sizes, that allows for a better separation between groups in a data set. As it can be seen in **Figure S3**, LDA achieved a much clearer discrimination between the six types of rum, in comparison with PCA. The first two discriminant functions explained an accumulated variance of 94.8%. Patterns in **Figure S3** evidenced that samples are well-established clusters. Only groups 3 and 4 are slightly superimposed in this LDA representation. Taking into account the results obtained in the analyses, rum samples are well defined and aging time is a good classification criterion.

4. Conclusions

In conclusion, aging time and some specific manufacturing processes affect rum composition. First, a longer aging time leads to a larger phenolic concentration and, therefore, to a greater antioxidant capacity. Moreover, longer aging times also translate into higher concentrations of furanic compounds. Specific manufacturing processes change the profile of the samples: filtration reduces the values of antioxidant compounds, as opposed to spices addition.

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Conflict of interest

The authors declare that there is no conflict of interest regarding the publication of this paper

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Figure captions

Figure 1. Absorbance spectra of rum samples of different ages and characteristics. Panel A: evolution of absorbance spectra of rum samples from the same commercial brand along aging. **Panel B:** differences on absorbance spectra of different samples from the same brand. **Panel C:** absorbance spectra of white rums compared to 3 years sample without color (R23) and cachaça (RX). **Panel D:** differences on absorbance spectra of different samples from the same brand and a sample added with additives in this case caramel, sample (R28).

Figure 2. Absorbance at 420 nm of rums according to their aging time. *The groups by aging were: 1 White; 2 Golden; 3 Añejos and three to five years; 4 Extra Añejo rums and up to eight years; 5 more than ten years; 6 those with other denominations.* **Significant differences between groups $p<0.05$

Figure 3. Antioxidant capacity of rums. Panel A: differences of samples grouped according to their aging time. *The groups by aging were: 1 White; 2 Golden; 3 Añejos and three to five years; 4 Extra Añejo rums and up to eight years; 5 more than ten years; 6 those with other denominations.* **Panel B:** differences of samples grouped according to special elaboration characteristics such as solera process, filtering or spice addition. **Significant differences between groups $p<0.05$.

Figure 4. Total phenolic content according to aging time. *The groups by aging were: 1 White; 2 Golden; 3 Añejos and three to five years; 4 Extra Añejo rums and up to eight years; 5 more than ten years; 6 those with other denominations.* **Significant differences between groups $p<0.05$.

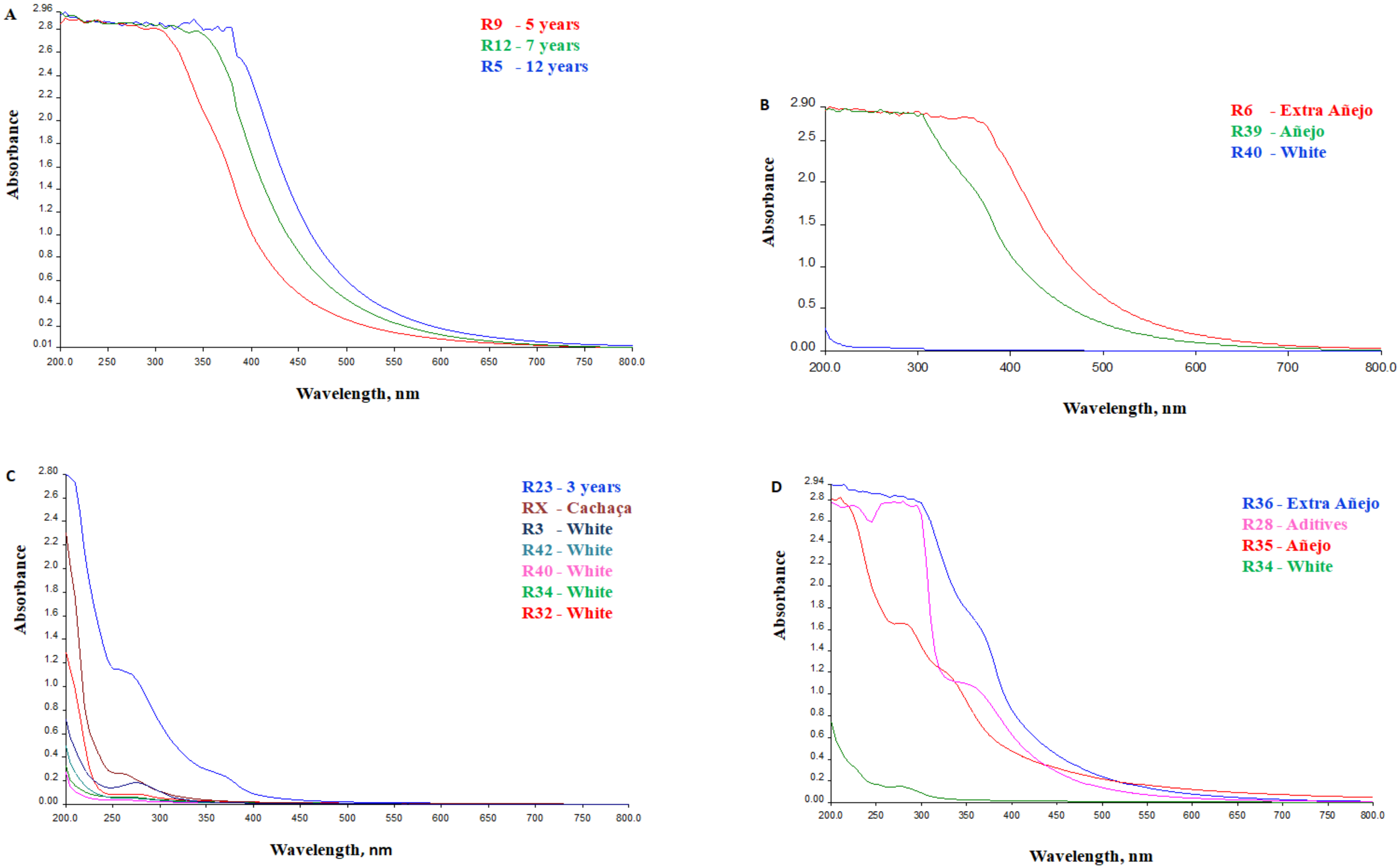
Figure 5. Concentrations of the individual polyphenols in the different samples displayed as a heatmap. The individual polyphenols are: gallic acid, vanillic acid, tyrosol, syringic acid, ellagic acid, protocatechuic acid, 5-carboxyresorcinol, homoprotocatechuic acid, protocatechualdehyde, caffeic acid, chlorogenic acid, vanillin, sinapinic acid, p-Coumaric acid, epicatechin, epigallocatechin gallate, ferulic acid, m-coumaric acid, methylvanillin, o-oumaricacid, daidzein, genistein, formononetin.

Table 1.HMF and furfural (mg/L) of samples classified by aging time.

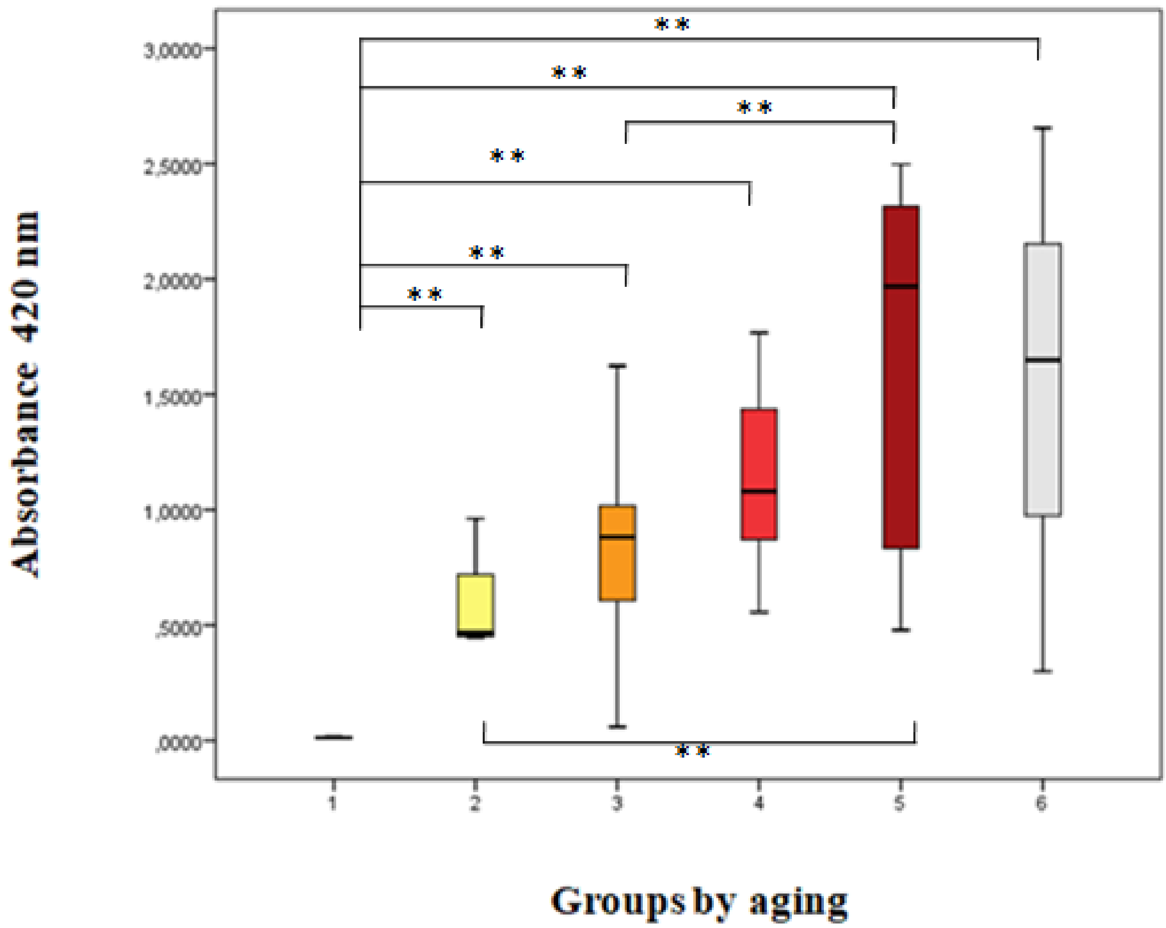
Groups by aging	HMF	Furfural
1	0.03 ± 0.05[a]	0.04 ± 0.04[a]
2	6.3 ± 5.3[ab]	0.21 ± 0.06[ab]
3	10.0 ± 8.4[ab]	0.53 ± 0.30[ab]
4	19.8 ± 24.5[ab]	0.74 ± 0.44[b]
5	44.2 ± 53.6[b]	1.04 ± 0.92[b]

[a]Different letters indicate statistically significant differences $p < 0.05$

Figure 1

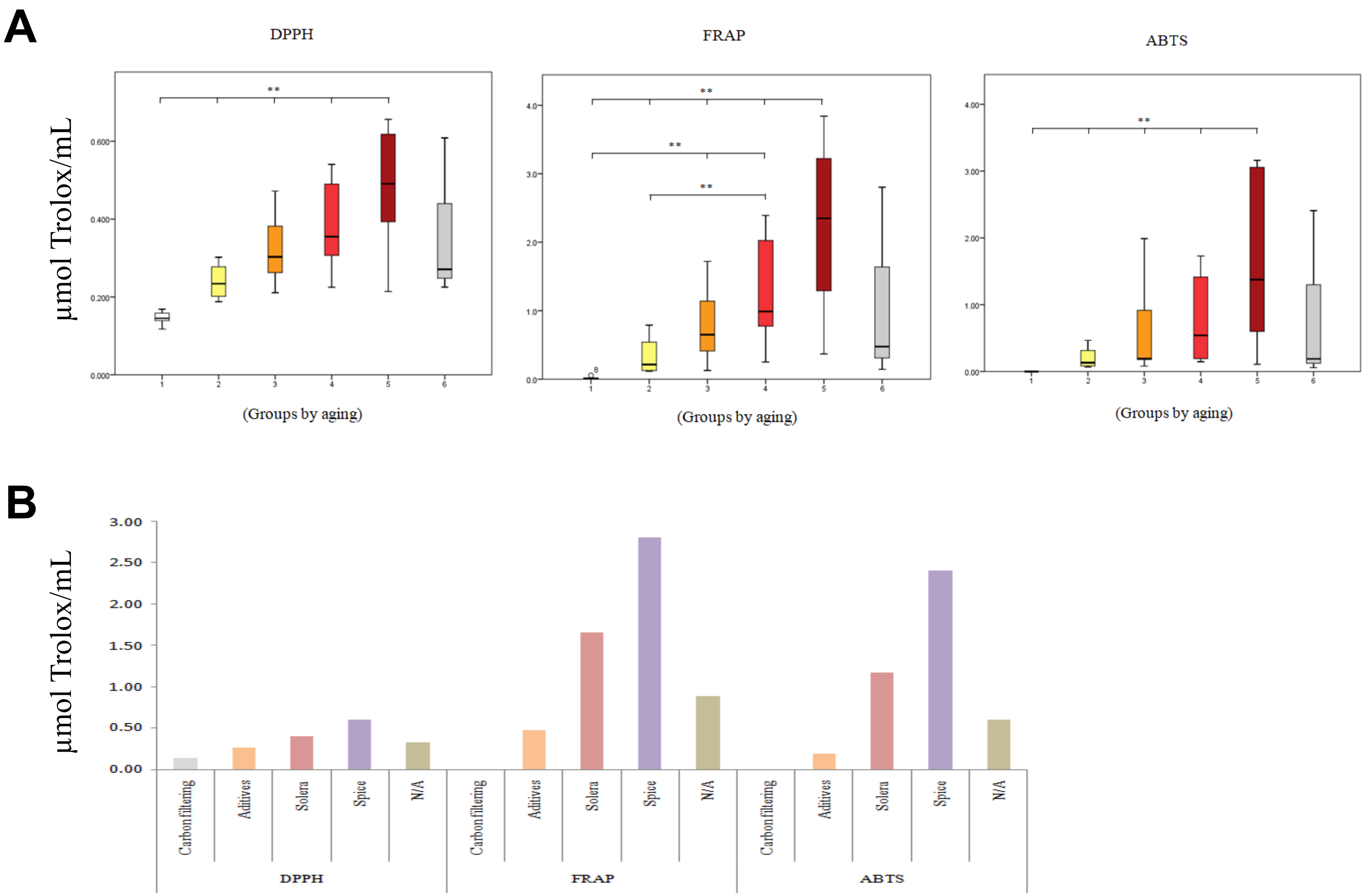

A
R9 - 5 years
R12 - 7 years
R5 - 12 years
Absorbance
Wavelength, nm
B
R6 - Extra Añejo
R39 - Añejo
R40 - White
Absorbance
Wavelength, nm
C
R23 - 3 years
RX - Cachaça
R3 - White
R42 - White
R40 - White
R34 - White
R32 - White
Absorbance
Wavelength, nm
D
R36 - Extra Añejo
R28 - Aditives
R35 - Añejo
R34 - White
Absorbance
Wavelength, nm

489 **Figure 2**



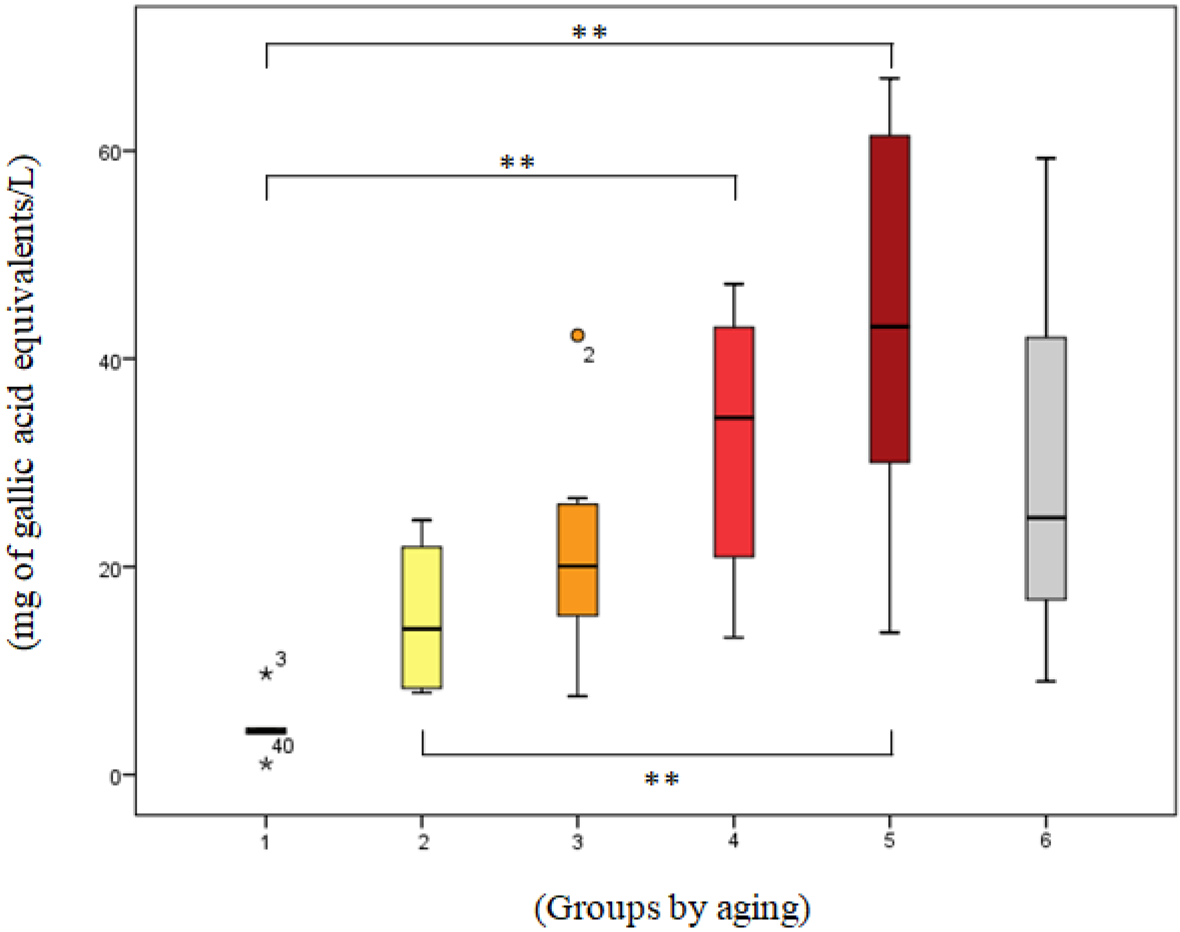
490

Figure 3



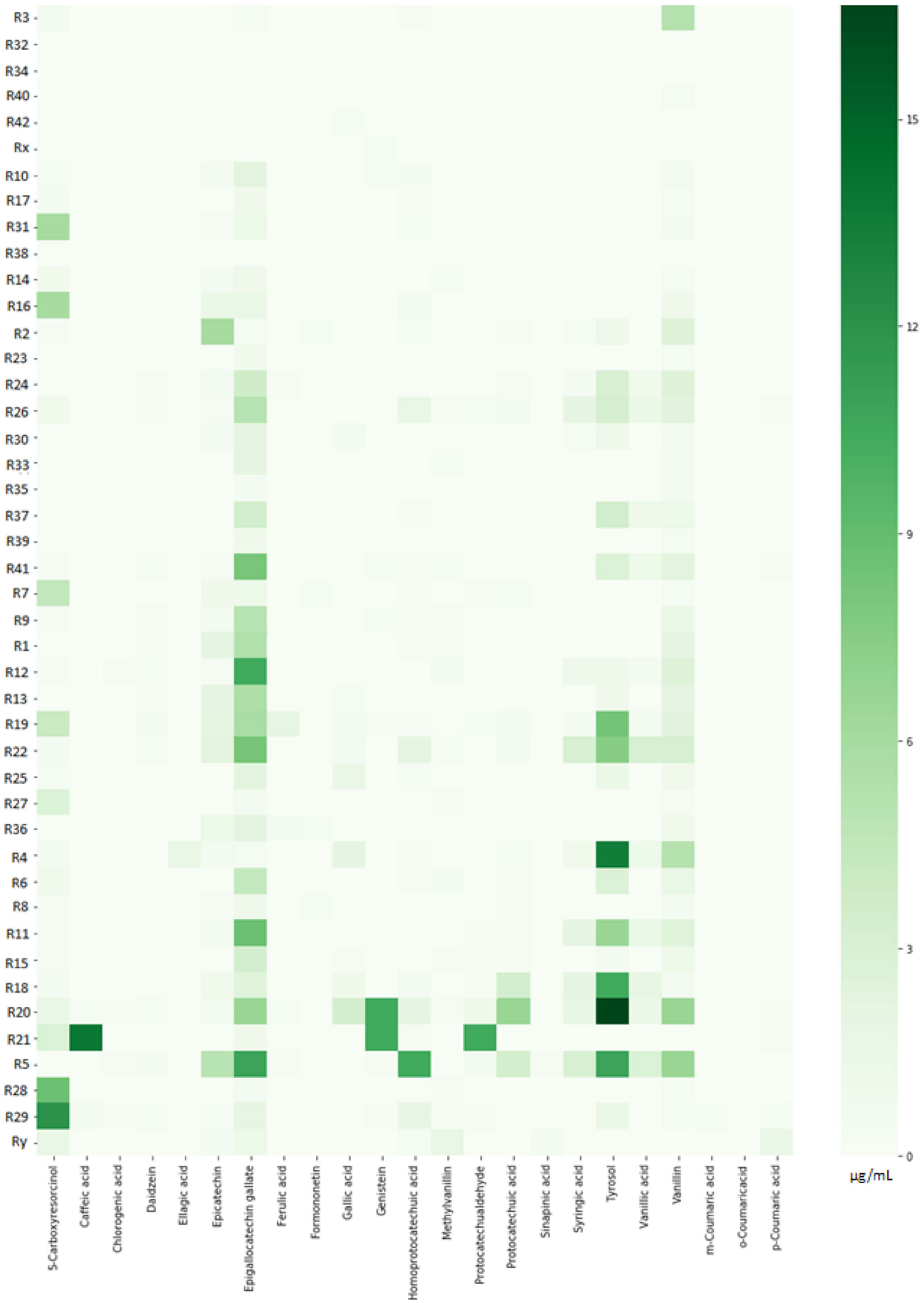
A
DPPH
FRAP
ABTS
µmol Trolox/mL
**
(Groups by aging)
B
µmol Trolox/mL
3.00
2.50
2.00
1.50
1.00
0.50
0.00
Carbon filtering
Aditives
Solera
Spice
N/A
DPPH
FRAP
ABTS

492 **Figure 4**



(mg of gallic acid equivalents/L)
0
20
40
60
1
2
3
4
5
6
(Groups by aging)
**
**
**
3
40
2

Figure 5


R3
R32
R34
R40
R42
Rx
R10
R17
R31
R38
R14
R16
R2
R23
R24
R26
R30
R33
R35
R37
R39
R41
R7
R9
R1
R12
R13
R19
R22
R25
R27
R36
R4
R6
R8
R11
R15
R18
R20
R21
R5
R28
R29
Ry
5-Carboxyresorcinol
Caffeic acid
Chlorogenic acid
Daidzein
Ellagic acid
Epicatechin
Epigallocatechin gallate
Ferulic acid
Formononetin
Gallic acid
Genistein
Homoprotocatechuic acid
Methylvanillin
Protocatechualdehyde
Protocatechuic acid
Sinapinic acid
Syringic acid
Tyrosol
Vanillic acid
Vanillin
m-Coumaric acid
o-Coumaricacid
p-Coumaric acid
15
12
9
6
3
0
μg/mL