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The impact of cold plasma on the phenolic composition and biogenic amine content of red wine

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Abstract

The effect of cold plasma (CP) on phenolic compound (PC) and biogenic amine (BA) contents of red wine was investigated for the first time. The influence of CP was compared with the effects of a wine preservation using potassium metabisulfite and a combined method. The PC profile was determined by UPLC-PDA-MS/MS while BAs using DLLME-GC–MS. Chemometric analysis also was used. The content of PCs was 3.1% higher in the sample preserved by CP treatment (5 min, helium/nitrogen) compared to a sample preserved by the addition of potassium metabisulfite (100 mg/L). On a positive note, CP treatment reduced the concentration of BAs in the wine samples. The lowest BA contents were recorded after 10 min of cold plasma (helium/oxygen) treatment with the addition of potassium metabisulfite (1120.85 μg/L). The results may promote interest in CP as a potential alternative method for the preservation of wine and other alcoholic beverages.

Keywords: cold plasma; phenolic compounds; biogenic amines; chemometric analysis; wine preservation; red wine

1. Introduction

Wine is an alcoholic beverage, the tradition of production and consumption of which has been known around the world for centuries (Gajek et al. 2021). The recent climatic changes have brought about alterations in the geographical distribution of areas used for viticulture. As a consequence of global warming, a significant increase in the area of vineyards and wine production has been observed across Central and Eastern Europe, including Poland (Koźmiński et al. 2020). Wine is produced by fermentation of sugars contained in fruit using naturally occurring microorganisms or starter cultures. This product is a complex matrix consisting of water, alcohol, carbohydrates, organic acids, polyphenols, minerals and aromatic substances (Robles et al. 2019).

One of the most abundant and important groups of compounds found in wines are polyphenols. They are responsible for the color (anthocyanins), taste (tannins), and aroma of wines. Additionally, they show antioxidant activity, which makes them beneficial in the prevention of cardiovascular diseases and other chronic medical conditions (Snopek et al. 2018). The polyphenol content of wine depends on the grapevine strain and the grape variety, the winemaking technology, the aging processes and the wine preservation methods used. Red wines are characterized by a higher content of polyphenolic compounds (PCs) compared to white wines, and thus show a higher antioxidant activity (Robles et al. 2019). Due to the growing consumer awareness of the health benefits associated with the consumption of polyphenol-rich products as well as the knowledge of the impact of these compounds on the final quality of a product, wine producers are looking for solutions that would minimize the loss of polyphenols during the entire winemaking process.

Besides health-promoting phenolic compounds, wines also contain biogenic amines (BAs), which may have a negative impact on human health. They are nitrogenous compounds that are mainly formed by the decarboxylation of amino acids, which in wine is the result of the activity of microbes such as yeast or lactic acid bacteria (LAB) (Smit and Maret du Toit, 2012). The content of biogenic amines depends mainly on the concentration of amino acid precursors in a product's matrix, but also on pH as well as alcohol and sulfur dioxide contents, which directly affect the growth of microorganisms (Papageorgiou et al. 2018). In addition, the presence of amino acid precursors is influenced by the grape variety, the geographical region, vinification methods, and the aging process (Płotka-Wasylka et al.

2018a). The biogenic amines most commonly found in wines include histamine (HIS), cadaverine (CAD), tyramine (TYR), 2-phenylethylamine (2-PE), putrescine (PUT), and tryptemine (TRP) (Esposito et al. 2019). High concentrations of biogenic amines in the final product may cause undesirable physiological effects in the consumer, such as headaches, nausea or tachycardia (Naila et al. 2010).

In order to prevent the negative effects of microorganisms on the quality of wine, methods of eliminating the undesirable microbes have been developed. Although classic thermal methods of food preservation still play a very important role in food technology, they are not suitable for vinification processes as they can negatively affect the unique taste, color and flavor of wine (Niu et al. 2019). Instead, sulfur dioxide, which has decontaminating and antioxidant properties, is commonly added to wine to remove unwanted microorganisms. However, despite its positive effects, it can cause allergic reactions in some consumers, which is why the World Health Organization (WHO) has introduced restrictions on its use. This has contributed to an increased search for new strategies to minimize or even replace SO_2 (Cordero-Bueso et al. 2019), but the problem of biogenic amines still remains unsolved. Therefore, scientists are looking for effective non-thermal preservation methods which allow to remove undesirable microorganisms without significantly affecting the final stability of the product (Puligundla et al. 2018).

Cold plasma is one of the most recent non-thermal methods used in sterilization processes. Numerous scientific publications confirm its effective antimicrobial activity, which is connected with the influence of reactive compounds, atoms in the excited and basic state, and UV photons on microbial cells (Bourke et al. 2017). Reactive compounds are produced by subjecting a working gas to various electrical discharges such as barrier discharge and corona discharge. Importantly, in the context of cold plasma applications in the food industry, the temperature of the free electrons in the working gas is lower than that of the other particles, which directly results in a slight increase in process temperature (Niedźwiedź et al. 2019). However, there is limited information in the literature regarding the impact of cold plasma on the final quality of alcoholic beverages, which means this problem is worth delving into.

The objective of the present study was to investigate the effect of a new wine preservation method using cold plasma on the phenolic composition and biogenic amine content of red wine. An additional objective was to compare the effect of preserving wine samples using the traditional method (addition of potassium metabisulfite at 30 mg/L or

100mg/L) and a combined method (cold plasma and the addition of potassium metabisulfite at 30 mg/L) with the effect of cold plasma alone. Wine sample storage was also considered in the study. In addition, chemometric analysis was conducted to discover specific relationships between the different wine preservation methods and the content of bioamines and selected phenolic compounds.

2. Materials and methods

2.1 Chemicals and materials

All reference materials used in the determination of the biogenic amines such as tryptamine hydrochloride, putrescine dihydrochloride, histamine dihydrochloride, tyramine hydrochloride, cadaverine hydrochloride and 2-phenylethylamine hydrochloride, as well as hexylamine (internal standard, IS), were purchased from Sigma-Aldrich (St. Louis, MO, USA). The derivatization reagent (isobutyl chloroformate) was purchased from Sigma-Aldrich. Ultrapure water was obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA). Stock solutions of BAs and IS (both at 1 mg/mL) were prepared daily in ultrapure water and stored at +4°C in silanized screw-capped vials with solid PTFE-lined caps (Supelco, Bellefonte, PA). Methanol, used as a dispersive solvent, was a high purity grade solvent purchased from Fluka. High purity grade chloroform, applied as an extractive solvent, was obtained from Sigma. 0.1 M HCl was supplied by Fluka. Other chemicals were of an analytical grade.

Analytical standards for phenolic profile determination such as cyanidin-3-O-glucoside, delphicin-3-O-glucoside, isorhamnetin-3-O-glucoside, kaempferol-3-O-glucoside, malvidin-3-O-glucoside, myricetin-3-O-glucoside, peonidin-3-O-glucoside, petunidin-3-O-glucoside, quercetin-3-O-glucoside, quercetin-4′-O-glucoside, quercetin-3-O-rutinoside, (+)-catechin, (-)-epicatechin, (-)-epicatechin-3-gallate, procyanidin A1 and A2, trans-resveratrol, and trans-piceid were purchased from Extrasynthese (Lyon, France). Caftaric acid, caffeic acid, coutaric acid, gallic acid, caftaric acid, ferulic acid, protocatechuic acid, and p-coumaric acid were purchased from PhytoLab (Vestenbergsgreuth, Germany). Formic acid (LC-MS grade) was purchased from Fischer Scientific (Schwerte, Germany). Acetonitrile was purchased from POCH (Gliwice, Poland).

2.2 Wine samples

The red wine used in this study was produced at Dom Bliskowice Winery (Poland, Lublin Province) from grapes of Regent and Rondo (1:1) varieties harvested in October 2019. The wine was subjected to different preservation processes (control sample – not preserved; cold plasma treatment; addition of 30 mg/L potassium metabisulfite; addition of 30 mg/L potassium metabisulfite combined with cold plasma treatment; and addition of 100 mg/L potassium metabisulfite). The samples were then analyzed immediately after preservation and also after three months of storage (15°C, limited light) (Table 1).

Table 1. Characterization of samples and sample coding

Sample	**Preservation method**	**Cold plasma exposure time**	**Gas used for preservation**	**Storage**
1	no preservation	0	No	No
2	cold plasma	2	He /O_2	No
3	cold plasma	5	He /O2	No
4	cold plasma	10	He /O2	No
5	cold plasma	2	He / N_2	No
6	cold plasma	5	He / N_2	No
7	cold plasma	10	He / N_2	No
8	30mg/L potassium metabisulfite	0	No	No
9	cold plasma and 30mg/L potassium metabisulfite	2	He / O_2	No
10	cold plasma and 30mg/L potassium metabisulfite	5	He / O_2	No
11	cold plasma and 30mg/L potassium metabisulfite	10	He / O_2	No
12	cold plasma and 30mg/L potassium metabisulfite	2	He / N_2	No
13	cold plasma and 30mg/L potassium metabisulfite	5	He / N_2	No
14	cold plasma and 30mg/L potassium metabisulfite	10	He / N_2	No
15	100 mg/L potassium metabisulfate	0	No	No

16	no preservation	0	No	Yes
17	cold plasma	2	He / O_2	Yes
18	cold plasma	5	He / O_2	Yes
19	cold plasma	10	He / O_2	Yes
20	cold plasma	2	He / N_2	Yes
21	cold plasma	5	He / N_2	Yes
22	cold plasma	10	He / N_2	Yes
23	30 mg/L potassium metabisulfite	0	No	Yes
24	cold plasma and 30 mg/L potassium metabisulfite	2	He / O_2	Yes
25	cold plasma and 30 mg/L potassium metabisulfite	5	He / O_2	Yes
26	cold plasma and 30 mg/L potassium metabisulfite	10	He / O_2	Yes
27	cold plasma and 30 mg/L potassium metabisulfite	2	He / N_2	Yes
28	cold plasma and 30 mg/L potassium metabisulfite	5	He / N_2	Yes
29	cold plasma and 30 mg/L potassium metabisulfite	10	He / N_2	Yes
30	100 mg/L potassium metabisulfate	0	No	Yes

2.3 Cold plasma treatment of wine

Wine samples were exposed to cold plasma for 2, 5 and 10 min. Mixtures of helium and nitrogen or helium and oxygen were used as the working gas. The samples were treated using a DBD (Dielectric Barrier Discharge) plasma jet reactor. The volume of 50 ml of wine was poured to a sterilized glass container and placed on a magnetic stirrer. To ensure homogenous exposure to plasma treatment, samples were stirred with a PTFE stir bar placed inside the sample. The DBD reactor consisted of a 1.4 mm internal diameter ceramic gas tube. Two metal electrodes were located as follows: a ring-shaped high voltage electrode was positioned 10 mm from the end of the jet and A flat, copper PCB laminated electrode was used as the ground. The latter electrode was placed on the magnetic stirrer, just beneath the sample container. The distance between the end of the reactor’s tube and the surface of the liquid was

2 mm. The flow rates of the substrate gas mixtures were 96 L/h of helium with 1.8 L/h of oxygen or nitrogen admixtures. The flow rates were adjusted by gas flow controllers (Automatic Works “ROTAMETR”, Gliwice, Poland). A schematic view of the experimental set-up is presented in Fig. 1. The mean power of the power supply was 6 W. For both gas mixtures, the sine-like voltage signals were quite similar, with a subtle difference in the maximum voltage, which was slightly higher in the case of the helium and oxygen mixture and ranged 8.3 kV.

A K-type thermocouple connected to a DT-847U meter was used to measure the temperature of the sample after plasma treatment. In the course of the experiment, the maximum registered temperature of the sample did not exceed 32°C, so the treatment can be considered a cold one.

2.4. Determination of polyphenolic compounds

The protocole reported by Kapusta et al. (2018) was used to determine polyphenolic compounds in the wine samples. The qualitative and quantitative determination of the phenolic compound profile was performer using ultra-performance reverse-phase liquid chromatography (UPLC-PDA-MS/MS). The UPLC-PDA-MS/MS Waters ACQUITY system (Walters, Milford, MA, USA) used consisted of a sample manager, a binary pump manager, a column manager, a photodiode array (PDA) detector, and a tandem quadrupole mass spectrometer (TQD) with electrospray ionization (ESI). A BEH C18 column (100 mm × 2.1 mm i.d., 1.7 µm, Waters) was used to separate the compounds. Wine samples were filtered before the analysis through a 0.45-µm Millipore filter and then injected onto the chromatographic column. The injected sample volume was 5 µL. The experiment was conducted in duplicate. Waters MassLynx software v.4.1 was used to collect and analyze the results. The results obtained are expressed in mg/L.

2.5 GC-MS dermination of biogenic amine content

The protocole reported by Płotka-Wasylka et al. (2018b) was used to determine biogenic amines (BAs) in the wine samples. Isolation of analytes was carried out simultaneously with their derivatization. The selected analytes were determined qualitatively and quantitatively using gas chromatography combined with mass spectrometry (GC–MS). A gas chromatography (GC) 7890A (Agilent Technologies, Santa Clara, CA, USA) system was interfaced with an inert mass selective detector (5975C, Agilent Technologies) with an electron impact ionization chamber (EI). A ZB-5MS capillary column (30 m × 0.25 mm I.D., 0.25 µm) supplied by Zebron Phenomenex was used for chromatographic separation. The injection was performed in the splitless mode at 230°C. The interface was set at 250°C. The injected sample volume was 2 μl. Helium was the carrier gas with a constant pressure of 30 psi. The oven temperature program was as follows: 50°C held for 1 min, ramped to 280°C at 15°C /min and held for 9 min (total run time was 25.3 min). The analysis was carried out in the selected ion monitoring (SIM) mode. The MS parameters were set as follows: EI ionization with 70 eV energy; ion source temperature, 250 °C. All the ion fragments with their relative intensities at the specific retention times were considered as a valid confirmation criterion and were used to identify the selected BAs. An Agilent ChemStation was used for data collection and GC-MS control.

The optimized method was evaluated using the following validation parameters: linearity, precision, sensitivity and accuracy in accordance to quality assurance protocol. Linearity was examined by application of 10 different concentrations. Hexylamine was used as internal standard. Limits of detection (LODs) and limits of quantification (LOQs) were calculated to estimate the sensitivity of the methodology. Both LODs and LOQs were calculated from spiked samples (*n*=3) and the minimum detectable analyte amount with a signal-to-noise ratio of 3 and 10, respectively, was established. The intra-day (RSD_r) and inter-day (RSD_R) precision were determined by the application of five replicates of wine samples spiked at two levels (0.10 and 0.25 mg/L). In addition to validation parameters, recovery rates were estimated using the ratio of the peak areas of the spiked samples of known concentration of biogenic amines to those of spiked water solution (*n*=3). The matrix effect (ME) of the optimized method was also evaluated by application the procedure described by Matuszewski et al. (Matuszewski, Constanzer, & Chavez-Eng, 2003). The ME was examined at a concentration level of 0.25 mg/L, and calculated by comparing the mean peak area of the analyte standards in the water solution (a, *n=3*) with the mean peak area of an analyte spiked postextraction (b, *n=3*). The following Equation was used:

$$ME\ [\%] = \frac{b}{a} \times 100\% \qquad \textit{(Equation 1)}$$

The MEs, were ranged from 79% and 99%. In general, ME has no impact on the qualitative and quantitative results of this method and can be omitted. Additionally, it was proven that it is justified to use an internal standard (IS) for calibration. Information on determined validation parameters and average recoveries (%) obtained with the optimized method in spiked wine samples are given in Table 1SI (Supporting Information).

2.6. Chemometric analysis

In the present study, multivariate statistical data mining was used to discover the specific correlations between the different wine preservation methods and determine the content of bioamines and selected phenolic compounds. The following chemometric methods were used for intelligent data analysis: cluster analysis (hierarchical and non-hierarchical or K-means clustering), two-way joining analysis, principal component analysis, and factor analysis. The analysis were performed using STATISTICA 8.0 software.

3. Results and Disscusion

3.1. Polyphenolic content

Red wine is a rich source of phenolic compounds that exert beneficial effects on the human health due to their antioxidant properties. Many studies have been conducted which indicate that the profile of phenolic compounds in a wine depends on the geographical location of the vineyard, the type of grapes, the method of production and preservation, and storage time (Manns et al. 2013; Stój et al. 2020). To evaluate the effect of the preservation method and storage time on the phenolic compound content of red wine samples, UPLC-PDA-MS/MS was used. A total of 54 compounds were determined in the studied samples by UPLC: 24 anthocyanins, 7 flavonols, 12 flavon-3-ols, 7 phenolic acids, and 4 stilbenes (Supplementary Material – Table S.1). The Retention times, molecular ion masses and the basic MS2 fragments of the individual phenolic compounds are presented in Supplementary Material - Table S.2. The contents of selected phenolic compounds detected in our red wine samples are shown in Table 2.

The most abundant group were anthocyanins, especially malvidin 3-O-glucoside-5-O-glucoside, malvidin 3-O-glucoside and delphinidin 3-O-glucoside, a profile that is characteristic of Rondo variety wines (Stój et al. 2020; Kapusta et al. 2018). Anthocyanins are responsible for the hue and color stability of wine and are indicative of its final quality. The basic structure of anthocyanins is their aglycone part (Khoo et al. 2017). In the examined wine, derivatives of five aglycones were determined: delphicin, malvidin, petunidin, peonidin and cyanidin. Anthocyanins are unstable compounds that can undergo reversible transformations in aqueous environments due to pH changes, thus affecting the color of the product. In addition, these compounds may degrade during processing when exposed to various factors, such as temperature, oxygen, or light (He et al. 2012; Yue et al. 2021). This is consistent with our results, which indicated that the storage process as well as the preservation method used affected the final anthocyanin concentration. Analyzing the influence of the storage proces, we noted a 8.23 to 47.51 % reduction in the subtotal levels of these compounds in each of the tested samples compared to samples which had not been stored. Additionally, a lower decrease in the content of diglycoside anthocyanins was observed, which indicates that they exhibit a higher stability than monoglycoside anthocyanins (Table S.1). This observation is confirmed by numerous scientific reports (He et al. 2012; Kim et al. 2010). The most stable molecule with the lowest level of reduction in all samples was cyanidin-3-O-glucoside-5-O-glucoside. By contrast, cyanidin-3-O-glucoside was the most susceptible to degradation, which was directly related to its structure. Malvidin-3-O-glucoside and peonidin-3-O-glucoside do not have hydroxyl groups in the ortho position, which makes them relatively more resistant to oxidation than cyanidin-3-O-glucoside (He et al.2012). Our results indicate that the content of each anthocyanin in both non-stored and stored samples was also dependent on the preservation method applied. In the present study, three preservation methods were used: cold plasma (variable process conditions), addition of potassium metabisulfite (30 mg/L or 100mg/L) and a method combining the use of cold plasma with the addition of potassium metabisulfite at 30 mg/L. In wine production, the standard method of wine preservation is sulfurization (Christofi et al. 2020). In the wine samples analyzed immediately after the addition of potassium metabisulfite (Table S.1 – samples no. 8 and 15), we observed a slight increase in the total content of anthocyanins compared to the control sample (no. 1). Moreover, the sample with the addition of 100 mg/L potassium metabisulfite had the highest content of anthocyanins (836.32 mg/L) compared to the other samples (580.36–811.73 mg/L). Sulfur compounds are used in vinification as antimicrobial and antioxidant agents. Furthermore, the addition of sulfur dioxide is thought to prevent enzymatic and non-enzymatic oxidation of wines (Esparza 2020). In our study, however, the total content of anthocyanins after the three-month storage period in samples subjected to sulfurization (Table S.1– samples 23 and 30) was similar to the control sample (sample 16); only the addition of 100 mg/L potassium metabisulfite caused a decrease in the content of these compounds by 5.77%. These results indicate that the application of potassium metabisulfite has a minimal effect on the reduction of the anthocyanin content. Despite their good preservative properties, sulfur compounds can have negative effects on consumer health causing allergic reactions in some consumers. Therefore, alternative wine preservation methods or combined methods are being sought to reduce the sulfate doses used (Christofi et al.2020). One of the new methods of food preservation, which we tested in this study, is cold plasma. To the best of our knowledge, there is no research so far regarding the effect of cold plasma treatment on the content of phenolic compounds in red wine samples in comparison with the effect of this method combined with potassium metabisulfite. In our experiment, we evaluated the impact of cold plasma treatment time (2, 5, 10 min) and the type of working gas used (helium/oxygen and helium/nitrogen) on the profile of phenolic compounds in red wine samples. Additionally, we tested the effect of cold plasma treatment combined with potassium metabisulfite (30 mg/L) treatment. Our results showed that both the duration of the process and the type of gas used contributed to a change in the content of individual compounds. The analysis of the level of anthocyanins in unstored samples indicated that the application of cold plasma for 10 min with the mixture of helium/oxygen as the working gas resulted in the highest reduction in the total anthocyanin content compared to the control (Table S.1). To date, there are few reports in the literature explaining the mechanism of action of cold plasma on food products (Alves Filho et al. 2020; Gavahian et al. 2018). However, cold plasma generation is accompanied by light emission, cavitation processes, shock wave generation and free radical generation, which directly contributes to the degradation of many organic compounds including phenolic compounds (He et al. 2012). On the other hand, in wine samples exposed to cold plasma with helium/nitrogen as the working gas, an increase in anthocyanin concentration was observed, which was the larger the longer the samples were exposed to treatment. The total anthocyanin content after 2, 5, and 10 min was, respectively, 707.23, 747.74, and 755.25 mg/L. Also, higher anthocyanin concentrations were recorded in the samples exposed to cold plasma with the addition of potassium metabisulfate compared to the same samples exposed to cold plasma alone (Table S.1). This was probably related to the protective effect of sulfate on anthocyanins discussed earlier in this section. We also observed a similar relationship related to the working gas used. Again, wine samples exposed to cold plasma generated using a mixture of helium and oxygen showed a higher reduction in the anthocyanin content compared to samples using a mixture of helium and nitrogen as the working gas. The disparities in the effect of the individual gases on anthocyanin stability were probably due to the fact that the different gases produced different reactive compounds during plasma generation. When oxygen is used in the working gas mixture, the plasma stream may contain hydrogen peroxide, hydroxyl radical, peroxyl anion or singlet oxygen, all of which can cause significant degradation of anthocyanins (Arjunan et al. 2015). Since red wine is a complex matrix and undergoes various chemical processes, the effects of different preservation methods on phenolic compounds after three months of storage were also analyzed. Interesting results were observed in most of the samples exposed to 5 min of cold plasma. A higher content of some anthocyanins was noted compared to samples that were plasma-treated for only 2 min (Table 2). In addition, the decrease in the anthocyanin content compared to the sample preserved by the same method but not stored was also lower than after a 2-min exposure to cold plasma. For example, for a 5-min cold plasma treatment with helium/nitrogen as the working gas, the total anthocyanin content before storage was 747.74 mg/L and dropped after storage by 11.57 % to 661.23 mg/L. By contrast, a 2-min cold plasma treatment resulted in a 30.27 % reduction in anthocyanins compared to the non-stored sample (Table S.1). Moreover, higher anthocyanin contents were observed in the samples subjected to 5 min of cold plasma treatment without potassium metabisulfite, which was an inverse relationship to that observed in the samples before storage. This may indicate that cold plasma, despite the initial degradation of anthocyanins, produces a better overall preservation effect than the mixed method. In addition, when samples with the same exposition time were compared, the anthocyanin content in samples exposed to cold plasma generated using the helium/nitrogen gas mixture was similar to that of the control sample and the sample with 30mg/L potassium metabisulfite, and 4.34 % higher than that of the sample with 100 mg/L potassium metabisulfite.

The contents of phenolic acids such as gallic acid, protocatechuic acid, caftaric acid, cutaric acid, caffeic acid, coumaric acid and ferulic acid were also determined in the studied wine. Gallic acid was the most abundant of those compounds at concentrations from 9.52 mg/L to 11.86 mg/L. In the samples before storage, the highest total content of phenolic acids was noted after a 2-min exposure to cold plasma – 24.68 mg/L (helium/nitrogen), a value that was 8.25% higher compared to the control sample (Table S.1). A study conducted on white wine by Lukić et al. (2019) also reported a slight increase in the content of some phenolic acids as a result of cold plasma exposure. Cold plasma also had a beneficial effect on the content of hydroxycinnamic acids in pomegranate juice (Herceg et al. 2016). Acids belonging to this group are characterized by a higher stability, which probably translates into their lower reactivity with the radicals formed during cold plasma generation.

In contrast to anthocyanins, the content of phenolic acids increased after storage in most samples (Table S.1). Interesting results were observed for the content of protocatechuic acid. In each sample after storage, the content of this acid increased compared to the non-stored samples. However, cold plasma treatment (10 min, helium/nitrogen) resulted in a substantial, up-to-4-fold increase in the content of this compound compared to non-stored samples (0.84 mg/L). The lowest content of this compound was observed in samples with 100mg/L potassium metabisulfite (0.19 mg/L) (Table 2). The contents of other acids showed a similar trend. Based on the literature data and our own results on the anthocyanin content, we can assume that such a large increase in protocatechuic acid in samples exposed to cold plasma was related to a decrease in the anthocyanin content. Under cold plasma treatment, anthocyanins degrade to phenolic acids, and the main products of their decomposition are protocatechuic, vanillic, syringic, and p-coumaric acids (Yang et al. 2018). Garofulić et al (2015), who evaluated the effect of cold plasma treatment on the contents of anthocyanins and phenolic acids in cherry juice, suggested that plasma acting on the food matrix for a short time caused the dissociation of agglomerates or particles, leading to an increase in the content of phenolic compounds.

In another experiment, we used ultraperformance chromatography to determine flavanols, flavan-3-ols, and stilbenes in the examined red wine samples. The content of flavanols in the wine was low and their total content ranged from 3.74 mg/L to 2.52 mg/L. The highest concentration was recorded in the non-stored control sample, while the lowest concentration was recorded after storage in the sample preserved by cold plasma (10 min, helium/nitrogen working gas) with the addition of potassium metabisulfite. The most abundant flavan-3-olswere (+)-catechin at 25.67 mg/L (sample no. 5) and procyanidin B1 at 10.46 mg/L (sample no. 12). *Cis* - and *trans*-resveratrol were also determined in the studied wine samples. The content of *cis*-resveratrol in the samples before and after storage was practically the same. A slight increase in its content was observed after storage in the sample exposed to cold plasma (10 min, helium/oxygen). An inverse correlation was noted for *trans*-resveratrol (Table S.1).

Table 2. Contents of selected phenolic compounds in red wine samples determined by UPLC-PDA-MS/MS (n=2)

Sample no.*	**3gM (mg/L)**	**3gD (mg/L)**	**3gC (mg/L)**	**3kGM (mg/L)**	**3kGPet (mg/L)**	**3kGPeo (mg/L)**	**PCA (mg/L)**
1	191.76 ± 3.02	82.38 ± 5.62	2.96 ± 0.01	45.67 ± 1.13	18.99 ± 1.84	4.94 ± 0.26	0.16 ± 0.00
2	142.6 ± 3.02	49.26 ± 5.60	1.91 ± 0.01	27.87 ± 1.07	13.35 ± 1.75	2.92 ± 0.26	0.2 ± 0.00
3	153.32 ± 3.24	50.93 ± 5.79	2.11 ± 0.01	31.25 ± 1.19	15.38 ± 2.02	3.22 ± 0.28	0.22 ± 0.00
4	126.35 ± 2.67	39.49 ± 4.49	1.67 ± 0.01	23.74 ± 0.91	11.36 ± 1.49	2.48 ± 0.22	0.2 ± 0.00

5	157.68 ± 3.34	55.64 ± 6.33	2.03 ± 0.01	33.75 ± 1.29	16.33 ± 2.15	3.32 ± 0.29	0.2 ± 0.00
6	166.42 ± 3.52	57.24 ± 6.51	2.07 ± 0.01	34.97 ± 1.34	16.4 ± 2.15	3.61 ± 0.32	0.21 ± 0.00
7	170.08 ± 3.60	58.03 ± 6.60	2.07 ± 0.01	35.98 ± 1.38	17.17 ± 2.26	3.63 ± 0.32	0.21 ± 0.00
8	182.88 ± 3.87	64.70 ± 7.36	2.44 ± 0.01	39.71 ± 1.52	19.23 ± 2.53	4.03 ± 0.35	0.17 ± 0.00
9	177.2 ± 3.75	64.19 ± 7.30	2.25 ± 0.01	37.73 ± 1.44	18.94 ± 2.49	3.89 ± 0.34	0.2 ± 0.00
10	170.57 ± 3.61	58.29 ± 6.63	2.2 ± 0.01	37.34 ± 1.43	17.98 ± 2.36	3.70 ± 0.33	0.22 ± 0.00
11	150.23 ± 9.16	57.69 ± 9.27	1.91 ± 0.05	30.75 ± 3.14	11.63 ± 0.89	2.99 ± 0.24	0.17 ± 0.01
12	178.48 ± 10.88	75.63 ± 12.16	2.41 ± 0.06	39.46 ± 4.03	15.64 ± 1.19	3.80 ± 0.31	0.18 ± 0.01
13	166.59 ± 10.16	72.04 ± 11.58	2.23 ± 0.05	38.68 ± 3.95	15.28 ± 1.16	3.63 ± 0.30	0.18 ± 0.01
14	171.68 ± 10.47	69.42 ± 11.16	2.08 ± 0.05	38.43 ± 3.93	14.93 ± 1.14	3.66 ± 0.30	0.19 ± 0.01
15	190.82 ± 11.63	64.7 ± 13.17	2.43 ± 0.06	43.86 ± 4.48	17.36 ± 1.32	3.96 ± 0.32	0.13 ± 0.01
16	149.42 ± 9.11	61.47 ± 9.88	2.12 ± 0.05	30.64 ± 3.13	12.09 ± 0.92	2.94 ± 0.24	0.32 ± 0.02
17	106.81 ± 6.51	15.13 ± 2.43	0.41 ± 0.01	18.55 ± 1.90	7.43 ± 0.57	2.03 ± 0.17	0.79 ± 0.06
18	121.59 ± 7.41	40.16 ± 6.46	1.45 ± 0.04	22.42 ± 2.29	8.69 ± 0.66	2.27 ± 0.19	0.7 ± 0.05
19	54.59 ± 3.33	14.78 ± 2.38	0.52 ± 0.01	6.96 ± 0.71	3.05 ± 0.23	1.07 ± 0.09	0.8 ± 0.06
20	101.6 ± 6.19	11.50 ± 1.85	0.34 ± 0.01	17.1 ± 1.75	6.32 ± 0.48	1.88 ± 0.15	0.78 ± 0.06
21	138.68 ±	53.03 ±	1.67 ± 0.10	26.58 ±	13.18 ±	2.59 ± 0.01	0.73 ±

	2.00	6.97		0.43	2.12		0.02
22	79.88 ± 1.15	12.89 ± 1.69	0.39 ± 0.04	11.36 ± 0.18	5.78 ± 0.93	1.44 ± 0.01	0.84 ± 0.02
23	143.55 ± 2.07	61.70 ± 8.11	2.28 ± 0.14	28.27 ± 0.46	14.36 ± 2.31	2.83 ± 0.01	0.25 ± 0.01
24	92.75 ± 1.34	7.81 ± 1.03	0.25 ± 0.02	14.19 ± 0.23	7.29 ± 1.17	1.63 ± 0.01	0.81 ± 0.02
25	97.01 ± 1.40	11.90 ± 1.56	0.33 ± 0.02	15.12 ± 0.25	7.74 ± 1.24	1.71 ± 0.01	0.79 ± 0.02
26	76.38 ± 1.10	19.42 ± 2.55	0.67 ± 0.04	11.26 ± 0.18	5.9 ± 0.95	1.4 ± 0.01	0.80 ± 0.02
27	84.70 ± 1.22	9.37 ± 1.23	0.28 ± 0.02	12.73 ± 0.21	6.49 ± 1.04	1.52 ± 0.01	0.84 ± 0.02
28	100.49 ± 1.45	23.42 ± 3.08	0.67 ± 0.04	16.68 ± 0.27	8.91 ± 1.43	1.83 ± 0.01	0.83 ± 0.02
29	97.29 ± 1.40	34.25 ± 4.50	1.18 ± 0.07	17.31 ± 0.28	8.86 ± 1.42	1.92 ± 0.01	0.74 ± 0.02
30	132.67 ± 1.91	57.73 ± 7.58	2.07 ± 0.13	26.45 ± 0.43	13.35 ± 2.15	2.7 ± 0.01	0.19 ± 0.00

3gM – malvidin 3-O-glucoside; 3gD – delphinidin 3-O-glucoside; 3gC – cyanidin 3-O-glucoside; 3kGM – malvidin 3-O-(600-O-coumaryl)-glucoside; 3kGPet – petunidin 3-O-(600-O-coumaryl)-glucoside; 3kGPeo – peonidin 3-O-(60 0-O-coumaryl)-glucoside; PCA – protocatechuic acid

* the coding of the samples is shown in Table 1

3.2 Biogenic amine content

DLLME-GC-MS was applied to determine the concentrations of biogenic amines in the red wine samples analyzed. The results are presented in Table 3. Six biogenic amines were identified: TRP, PUT, HIS, TYR, CAD and 2-PE, with histamine having the highest concentrations in all samples. This finding corresponds with the results reported by other researchers who indicate that histamine is the most abundant biogenic amine in wines(Plotka et al. 2018). High concentrations of histamine in a product can cause negative health effects in the consumer, so it is important to use methods that will reduce the content of this compound in the food matrix (Esposito et al. 2019). In our experiment, the highest HIS content was found in the unpreserved control sample (before storage: 818 ± 34 µg/L; after storage: 821 ±

30 µg/L). A significantly lower content of this compound was observed in the sample that had been exposed to cold plasma for 10 min using a helium/oxygen mixture as the working gas (584 ± 34 µg/L) in combination with the addition of 30 mg/L potassium metabisulfite. Also after three months of storage, the HIS content of this sample did not change significantly (586 ± 33 µg/L). When the effect of the wine preservation method on the content of other biogenic amines was analyzed, in all cases the 10-min application of cold plasma (helium/oxygen as working gas) with 30 mg/L potassium metabisulfite resulted in the highest reduction in the level of these compounds. Moreover, this effect persisted after storage. To date, the literature provides no information on or explanation of the effect of cold plasma on the content of biogenic amines in wine. However, because the formation of these compounds depends mainly on the microorganisms present in the food matrix (Restuccia et al. 2018), it can be assumed that cold plasma, which has a well-proven biocidal activity against unwanted microorganisms, indirectly contributes to the reduction of biogenic amines in food products (Bourke et al. 2017; Lu et al. 2014). Our results also showed that the efficiency of cold plasma in reducing biogenic amines in wine samples was affected by the duration of treatment and the type of working gas used. Increasing the duration of the process to 10 min and the use of a mixture of helium and oxygen as the working gas favourably affected the elimination of these compounds from the product matrix. The influence of the duration of the process as well as the type of gases used on the sterilizing efficiency of cold plasma has also been demonstrated by other authors. Hou et al. (2019), who sterilized blueberry juice using cold plasma for 2, 4 and 6 min, recorded the highest reduction in *Bacillus* spp. populations after the time of 6 min. Also our previous study on the effects of cold plasma on *Lentilactobacillus hilgardii* cells showed that increasing the duration of the process as well as using a mixture of helium and oxygen as the working gas resulted in higher cell reduction than using a mixture of helium and nitrogen (Niedźwiedź et al. 2020).

Table 3. Concentrations of selected biogenic amines determined in wine samples by DLLME-GC-MS; *n*=3

Sample no.*	**TRP (µg/L)**	**PUT (µg/L)**	**HIS (µg/L)**	**TYR (µg/L)**	**CAD (µg/L)**	**2-PE (µg/L)**
1	4.089 ± 0.012	489 ± 25	818 ± 34	27.74 ± 0.16	58.73 ± 0.15	18.70 ± 0.054
2	3.670 ± 0.011	475 ± 24	799 ± 31	27.58 ± 0.17	54.15 ± 0.12	18.68 ± 0.049
3	3.578 ± 0.008	455 ± 25	734 ± 37	27.34 ± 0.17	52.21 ± 0.12	18.73 ± 0.047

4	3.551 ± 0.009	449 ± 23	732 ± 36	26.43 ± 0.13	52.01 ± 0.14	18.63 ± 0.050
5	3.662 ± 0.010	471 ± 22	784 ± 29	27.51 ± 0.18	53.94 ± 0.13	18.71 ± 0.048
6	3.589 ± 0.008	466 ± 27	741 ± 33	27.44 ± 0.16	52.27 ± 0.11	18.75 ± 0.044
7	3.540 ± 0.010	457 ± 22	742 ± 34	26.78 ± 0.17	52.22 ± 0.13	18.66 ± 0.051
8	2.918 ± 0.008	344 ± 25	654 ± 34	<LOD	48.29 ± 0.16	23.74± 0.044
9	2.705 ± 0.011	324 ± 23	627 ± 38	<LOD	44.54 ± 0.14	23.77± 0.047
10	2.678 ± 0.013	299 ± 20	622 ± 33	<LOD	39.79 ± 0.12	23.68± 0.050
11	1.972 ± 0.006	278 ± 19	584 ± 34	<LOD	38.09 ± 0.14	23.76± 0.048
12	2.802 ± 0.014	348 ± 24	654 ± 38	<LOD	43.87 ± 0.16	23.72± 0.051
13	2.732 ± 0.016	320 ± 21	641 ± 32	<LOD	40.17 ± 0.13	23.63± 0.047
14	2.052 ± 0.008	291 ± 19	601 ± 36	<LOD	37.89 ± 0.11	23.69± 0.052
15	3.878 ± 0.013	466 ± 23	773 ± 30	<LOD	52.42 ± 0.17	25.88± 0.054
16	4.086 ± 0.011	490 ± 24	821 ± 30	27.71 ± 0.15	58.66 ± 0.18	18.78 ± 0.044
17	3.674 ± 0.010	479 ± 22	794 ± 29	27.66 ± 0.16	54.05 ± 0.14	18.75 ± 0.043
18	3.581 ± 0.012	457 ± 24	739 ± 35	27.91 ± 0.14	52.18 ± 0.13	18.79 ± 0.051
19	3.560 ± 0.010	449 ± 21	732 ± 33	26.38 ± 0.12	52.09 ± 0.18	18.60 ± 0.044
20	3.669 ± 0.010	476 ± 26	789 ± 31	27.79 ± 0.21	53.99 ± 0.15	18.77 ± 0.044
21	3.593 ± 0.013	471 ± 23	748 ± 27	27.49 ± 0.18	52.30 ± 0.17	18.70 ± 0.038
22	3.547 ± 0.011	457 ± 20	739 ± 31	26.85 ± 0.15	52.28 ± 0.10	18.71 ± 0.047
23	2.915 ± 0.009	349 ± 24	658 ± 33	<LOD	48.33 ± 0.16	23.81± 0.056
24	2.711 ± 0.013	332 ± 21	629 ± 38	<LOD	44.50 ± 0.19	23.84± 0.031
25	2.684 ± 0.012	309 ± 24	617 ± 31	<LOD	39.83 ± 0.10	23.77± 0.062
26	1.979 ± 0.011	279 ± 19	586 ± 33	<LOD	38.04 ± 0.14	23.85± 0.045
27	2.811 ± 0.017	353 ± 22	659 ± 36	<LOD	43.95 ± 0.11	23.77± 0.044
28	2.729 ± 0.014	320 ± 19	646 ± 31	<LOD	40.20 ± 0.17	23.56± 0.039

29	2.058 ± 0.009	289 ± 21	613 ± 35	<LOD	37.84 ± 0.15	23.71± 0.057
30	3.874 ± 0.012	469 ± 25	773 ± 34	<LOD	52.47 ± 0.20	25.93± 0.061

TRP – tryptamine, PUT – putrescine, HIS – histamine, TYR – tyramine, CAD – cadaverine, 2-PE – 2-phenylethylamine

* the coding of the samples is shown in Table 1.

3.3 Chemometric analysis

The major goal of multivariate statistical data mining was to reveal hidden specific relations between differently treated (different preservation conditions) wine samples (a total of 30 cases) characterized by 13 chemical variables (bioamines and phenolic compounds). Another important task was to find similarity patterns depending on the storage conditions and, beyond that, to identify specific chemical descriptors responsible for the classification of the different wine samples.

The following chemometric methods were used in the intelligent data analysis:

- Cluster analysis (hierarchical and non-hierarchical or K-means clustering);
- Two-way joining;
- Principal components analysis and factor analysis.

Hierarchical clustering was performed on standardized input data (z-normalization), with squared Euclidean distance as a similarity measure, using Ward’s method of linkage and Sneath’s significance test. Fig. 2 A1 shows a hierarchical clustering dendrogram of the 13 chemical variables. Three major clusters were identified at Sneath’s significance level of 1/3Dmax:

C1: 3gM, 3kGM, 3kGPeo, 3kGPet, 3gD, 3gC – phenolic cluster;

C2: HIS, PUT, TRP, CAD, TYR – amine cluster;

C3: 2PE, PCA – mixed cluster.

The hierarchical clustering of the chemical variables identified three patterns of similarity which could be conditionally determined as phenolic, amine and mixed clusters. There was a good separation between the phenolic and the amine variables, which indicated that both groups of variables had a separate impact on the quality of the different wine samples which was unrelated to the preservation or storage conditions. Fig. 2 A2 shows a hierarchical dendrogram linking 30 wine samples (with different preservation and storage conditions). Three major clusters of cases were formed (under the same clustering conditions):

C1: 17, 19, 20, 22, 24, 25, 26, 27, 28, 29 – samples after storage and preservation by plasma and by plasma in combination with potassium metabisulfite;

C2: 8, 9, 10, 11, 12, 13, 14, 23 – samples before storage with preservation by plasma and potassium metabisulfite;

C3: 1, 2, 3, 4, 5, 6, 7, 15, 16, 18, 21, 30 – samples before storage with plasma preservation.

Cluster 1 mainly included samples after storage preserved by plasma and plasma plus potassium metabisulfite. Cluster 2 chiefly consisted of samples before storage but preserved by plasma or by potassium metabisulfite. Cluster 3 aggregated 12 plasma-preserved samples before storage. The clustering of the wine samples showed separation into patterns which differed in the treatment and storage conditions.

K-means clustering is a non-supervised clustering method in whichclusters are not formed spontaneously but according to a preliminary hypothesis regarding the possible number of clusters. This a priori segmentation is based on an algorithm which selects centroids in the dataset under a predefined distance measure. The results of K-means clustering for the formation of 3 clusters of variables and 3 clusters of cases were identical to those obtained by hierarchical clustering. The members of the non-hierarchical clusters were the same. This is illustrated in Table 3 in Supplementary Materials (S.3) which shows cluster membership data for cases and variables along with the respective distances between the members in each identified cluster. It was important to reveal the role of the chemical variables as specific descriptors for each of the identified clusters. Fig. 3A presents the average values of each chemical variable for each cluster. The cluster which included plasma-preserved samples before storage (C1 in the plot below) was characterized by the highest levels of amines, moderate (rather high) levels of phenolic compounds and low levels of 2-PE and PCA. The cluster with samples before storage, preserved by plasma and potassium metabisulfite (C2 in the plot below) was characterized by the lowest levels of amines, the highest levels of phenolic compounds, the highest level of 2-PE, and the lowest level of PCA. The cluster with samples stored after preservation by plasma and by plasma in combination with potassium metabisulfite (C3 in the plot below) was characterized by moderate levels of amines, the lowest levels of phenolic compounds, moderate levels of 2-PE and the highest levels of PCA. It is readily seen that the storage conditions led to changes in the levels of all the chemical variables, which additionally depended on the preservation treatment used. In general, the levels of phenolic compounds fell after storage, whereas levels of amines were high before storage and plasma preservation but decreased substantially following preservation with potassium metabisulfite or after storage.

The relationship between the chemical variables and the wine samples is shown additionally in the plot of the results of two-way joining cluster analysis, in which variables and cases are in respective correspondence (Fig. 3B).

The plot confirms the conclusions above about the determination of specific chemical descriptors for the wine sample clusters.

Both chemometric methods are very similar and their basic task is to find hidden factors (principal components or factors) responsible for the structure of the data matrix. Additionally, they are typical projection methods and, as such, lead to a dimensionality reduction of the system under consideration. In the working algorithm, the data matrix is decomposed into a factor loading matrix and a factor score matrix, the former presenting the newly defined special directions in the variables space, and the latter – the new coordinates of the objects. Both of these matrices need to be correctly interpreted in order to find specific relationships between objects and variables. In our dataset, two latent factors were responsible for the data structure. The first of them, which explained 51.3 % of the total variance of the system, could be tentatively named the “phenolic factor”, and the second factor, with 40.5 % of explained variance could be called the “amine factor”. This is largely consistent with the results of cluster analysis. Table 4 (Supplemantary Materials S.4), in which statistically significant loadings are given in bold, shows that the variables 2-PE and PCA are reversely correlated to the rest of the significant factor loadings with regard to factor 1 and factor 2, and this specificity corresponds to the formation of the mixed cluster in cluster analysis. An interpretation of the data in the loadings table leads to the conclusion that the data structure is dependent on two latent relationships between the variables – a relationship between phenolic compounds as a similarity group and a relationship between biogenic amines as another similarity pattern. The graphical plot of the factor loadings in Fig. 2B clearly illustrates these relationships. Both clusters of variables are well-defined, and the more specific role of 2-PE as opposite to the amine group and PCA as opposite to the phenolic group is indicated. The factor scores plot illustrates the formation of three patterns of similarity between the wine samples. It matches the hierarchical and K-means clusters of wine samples almost perfectly.

4. Conclusion

In this study, for the first time, the effect of cold plasma on the content of phenolic compounds and biogenic amines in red wine was evaluated with respect to storage time. In addition, the effect of cold plasma was compared with the traditional method of preservation (addition of 30 mg/L and 100 mg/L of potassium metabisulfite) and a combined method (cold plasma with 30 mg/L of potassium metabisulfite). In general, cold plasma treatment caused a decrease in the total content of phenolic compounds in the wine samples subjected to three months of storage. However, the application of cold plasma for 5 min with helium/nitrogen as the working gas reduced the content of these compounds by only 2.85 % compared to the control. Moreover, the content of phenolic compounds was 3.1% higher in the sample preserved by this method compared to the sample preserved by the addition of potassium metabisulfite at a dose of 100 mg/L. Additionally, cold plasma increased the content of phenolic acids in the studied samples. Importantly, the use of cold plasma resulted in a reduction of biogenic amines, which can cause adverse health reactions in the consumer. The highest degree of reduction was observed in the samples exposed to 10 min of cold plasma (helium/oxygen). Our results indicate that the influence of the storage process as well as the preservation method on the phenolic profile and the content of biogenic amines is not unambiguous and depends mainly on the chemical properties of the individual compounds. However, the reported effects of cold plasma and cold plasma combined with the addition of potassium metabisulfite on the analyzed compounds allow us to assume that in the future these methods can be successfully used to reduce the use of SO_2 in winemaking.

To conclude, cold plasma may become an alternative method for the preservation of wine or other alcoholic beverages in the future, ensuring adequate product safety and preserving the pro-health values of these products. However, further research is needed to optimize the process conditions of cold plasma treatment.

CRediT authorship contribution statement

Iwona Niedźwiedź: Conceptualization, Project administration, Investigation, Methodology, Validation, Writing – original draft, Visualization. **Justyna Płotka-Wasylka:** Methodology, Software, Validation, Resources, Writing – original draft, Writing – review & editing. **Ireneusz Kapusta:** Methodology, Software. **Vasil Simeonov:** Methodology, Software,

Writing – original draft, Writing – review & editing. **Anna Stój:** Resources, Validation. **Adam Waśko:** Conceptualization, Writing – review & editing. **Joanna Pawłat:** Resources, Writing – original draft, Visualization **Magdalena Polak-Berecka:** Supervision, Conceptualization, Project administration, Writing – review & editing

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Figure Captions

Figure 1. A. Experimental set-up for plasma treatment of wine: 1– plasma jet reactor; 2 – sample in a glass container; 3 – magnetic stirrer; 4 – high voltage power supply; 5 – gas flow controller. B. Voltage signal between electrodes for the selected gas mixtures.

Figure 2. A. Hierarchical dendrogram. 1) clustering of 13 chemical variables 2) – clustering of wine samples. B. 1) Plot of factor loadings. 2) Plot of factor scores. 3gM – malvidin 3-O-glucoside; 3gD – delphinidin 3-O-glucoside; 3gC – cyanidin 3-O-glucoside; 3kGM – malvidin 3-O-(600-O-coumaryl)-glucoside; 3kGPet – petunidin 3-O-(600-O-coumaryl)-glucoside; 3kGPeo – peonidin 3-O-(60 0-O-coumaryl)-glucoside; PCA – protocatechuic acid; TRP – tryptamine, PUT – putrescine, HIS – histamine, TYR – tyramine, CAD – cadaverine, 2-PE – 2-phenylethylamine.

Figure 3. A. Plot of means for each variable for each identified cluster B. Correspondence between wine samples and chemical variables. . 3gM – malvidin 3-O-glucoside; 3gD – delphinidin 3-O-glucoside; 3gC – cyanidin 3-O-glucoside; 3kGM – malvidin 3-O-(600-O-coumaryl)-glucoside; 3kGPet – petunidin 3-O-(600-O-coumaryl)-glucoside; 3kGPeo – peonidin 3-O-(60 0-O-coumaryl)-glucoside; PCA – protocatechuic acid; TRP – tryptamine, PUT – putrescine, HIS – histamine, TYR – tyramine, CAD – cadaverine, 2-PE – 2-phenylethylamine.