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Corresponding Author: Dr. andrea salvo,

Corresponding Author's Institution: university of messina

First Author: Giuseppe Avellone

Order of Authors: Giuseppe Avellone; andrea salvo; Rosaria Costa; Emanuele Saija; David Bongiorno; Vita Di Stefano; Giorgio Calabrese; Giacomo Dugo

Abstract: The purpose of the present work was to find a correlation between microencapsulation technology applied to wines and resulting quality of the wine itself in terms of volatile composition and phenolic profile. To this aim, samples of Nero d'Avola wines produced in Sicily (Italy) were investigated in order to: i) elucidate the aromatic composition by means of HS-SPME coupled with GC-MS; ii) assess the polyphenolic content by UHPLC mass spectrometry; iii) compare the results obtained from both the screenings with those relative to the same wines that had previously been subjected to spray-drying. The results showed a marked reductionThe results here obtained evidenced a marked reduction of odour active compounds in microencapsulated wines, after resolubilization in water/ethanol; when considering the total amount of volatiles, a twofold reduction was observed. Conversely, the qualitative analysis of phenolic compounds and anthocyanin-derived pigments showed no influence of the spray-drying process on these functional constituents.

Dr. Andrea Salvo

Dip. Biomorf
(Scienze Biomediche,
Odontoiatriche, e delle Immagini
Morfologiche e Funzionali)
University of Messina
Viale Annunziata
98168 Messina
Tel. +39-090-3503996
e-mail: costar@unime.it

Editorial Office

FOOD CHEMISTRY

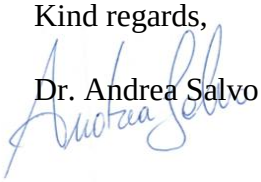
Messina, July 14, 2017

Dear Editor,

Please find attached the revised manuscript titled "**Investigation on the influence of spray-drying technology on the quality of Sicilian Nero d'Avola wines"** after second revision.

All the changes advised by editor have been completed. I hope that the manuscript is now suitable for publication in Food Chemistry.

Kind regards,



Dr. Andrea Salvo

***Response to Reviewers**

FINAL EDITORIAL COMMENTS

Line 31: ….to the same wines that had previously been subjected to spray-drying. The results showed a marked reduction….

Line 53: Spray-drying has been applied in the food industry for many decades,….

Line 61: ….the advantages derived from spray-drying are numerous:…

Line 73: ….destined for food consumption.

Line 87: On the other hand, the wine aroma cannot be neglected as a fundamental parameter….

Line 220: ….the volatile composition was in good agreement….

Line 223: …..esters, were found to be odour active.

Line 253: ….fiber, which was more selective towards alcohols…..

Line 262: …terpenoids, sulfur-containing, and others…..

Line 263: The content of volatiles was lower….

Line 276: …wines are presented in Figures….

Line 284: The results led to the conclusion that…..did not affect….

Line 321: The results showed a marked reduction….

Table 1: Round values to at most 3 significant figures (e.g. 59.6 rather than 59.592; 1.89 rather than 1.885 etc.

AUTHORS:

All the modifications have been carried out and highlighted in red.

***Highlights (for review)**

1. The aromatic and phenolic fractions of spray dried wines were investigated
2. Wines under investigation were from red grapes “Nero d’Avola”, produced in Sicily.
3. The microencapsulation process affected the volatile composition of wines.

Investigation on the influence of spray-drying technology on the quality of Sicilian Nero d'Avola wines

Giuseppe Avellone[a], Andrea Salvo[b,c]*, Rosaria Costa[b,c]*, Emanuele Saija[b,c], David Bongiorno[a], Vita Di Stefano[a], Giorgio Calabrese[d], Giacomo Dugo[a,b].

[a]Dipartimento di Scienze e Tecnologie Biologiche Chimiche e Farmaceutiche (STEBICEF), Università di Palermo, Viale delle Scienze, Parco d'Orleans II, 90128 Palermo, Italy

[b]Dipartimento di Scienze Biomediche, Odontoiatriche, e delle Immagini Morfologiche e Funzionali (Biomorf), University of Messina, Viale Annunziata, 98168 Messina, Italy

[c]Science4Life s.r.l., a spin-off of the University of Messina, Messina, Italy

[d]Dipartimento di Scienze Agrarie e Forestali, Universita' degli Studi di Torino, Via Verdi 8, 10124 Torino, Italy

*Corresponding author: Dipartimento Biomorf c/o Scienze Veterinarie, University of Messina, Viale Annunziata, 98168 Messina (Italy); e-mail address (dr. Andrea Salvo): asalvo@unime.it;

Abstract:

The purpose of the present work was to find a correlation between microencapsulation technology applied to wines and the resulting quality of the wine itself in terms of volatile composition and phenolic profile. To this aim, samples of Nero d'Avola wines produced in Sicily (Italy) were investigated in order to: i) elucidate the aromatic composition by means of HS-SPME coupled with GC-MS; ii) assess the polyphenolic content by UHPLC mass spectrometry; iii) compare the results obtained from both the screenings with those relative to the same wines that had previously been subjected to spray-drying. The results showed a marked reductionThe results here obtained evidenced a marked reduction of odour active compounds in microencapsulated wines, after resolubilization in water/ethanol; when considering the total amount of volatiles, a twofold reduction was observed. Conversely, the qualitative analysis of phenolic compounds and anthocyanin-derived pigments showed no influence of the spray-drying process on these functional constituents.

Keywords: Spray-drying; wine; Nero d'Avola; phenolic compounds; aroma; SPME; anthocyanins.

1. Introduction

Spray-drying falls within the group of microencapsulation technologies, including spray-chilling, fluidized-bed coating, extruding, lyophilisation, coacervation, among others (Desai and Park, 2005; Nedovic et al., 2011). Spray-drying has been applied in the food industry for many decades, basically due to its cheapness, flexibility, robustness, efficiency. Based on a simple definition, "encapsulation" is a technique which entraps particles (usually bioactive compounds) within a wall material, working as a "shell" or "matrix". The products of such a technological process are microcapsules with diameters comprised in the range of μm – mm, generally containing active ingredients. More specifically, spray-drying is a technological process where a liquid is atomized through a hot gas (air or nitrogen) current, becoming consequently a powder (Gharsallaoui et al., 2007). Mainly because of the water removal from food commodities, the advantages derived from spray-drying are numerous: i) reduction of microbiological decay events; ii) instantaneous solubilisation of spray-dried products (improved product's handling); iii) decrease of transport costs due to consistent volume reduction of powdered products ("green" feature of the technology); iv) protection of the core material against environmental factors (i.e. moisture, light, oxygen); v) improvement of organoleptic properties of a food (e.g. masking bitterness of an ingredient by coating it with a wall material having a pleasant taste); vi) elimination of cross reactions between more ingredients. A key role in a successful spray-drying procedure is played by the wall material chosen as encapsulating agent; the latter must be able to protect the capsule content, to be

70 stable over time and to avoid interaction with the outer environment. Encapsulation
71 technologies are utilized not only in food industry, but also in other fields (e.g. dried
72 detergents reconstituted upon use). A variety of synthetic polymers is available as wall
73 material; however, this list is definitely restricted when the spray-dried product is destined for
74 food consumption. Commonly, carbohydrates (starches, syrup solids, maltodextrins, pectins),
75 gums (gum Arabic, mesquite gum) or milk proteins are employed as wall material
76 (Gharsallaoui et al., 2007).
77 Red wines are suitable matrices for spray-drying, since they are mainly constituted of water,
78 ethanol and bioactive molecules, such as polyphenols. The beneficial effects exerted by
79 moderate consumption of red wine are today well recognized (Di Majo et al., 2008; Dugo et
80 al., 2009). "Nero d'Avola" is one of the most valuable grape varieties of the Italian
81 production. The name refers to the municipality of Avola, in Sicily, where this specific variety
82 was originally selected by vine growers. Nero d'Avola grapes grow easily in a dry and hot
83 environment; grapes strongly recall blackberries, both for the look and the taste. In general,
84 the taste of Nero d'Avola wine ranges from a full-bodied and black-fruit note to an elegant and
85 red cherry-like note, with very little or no aging at all (Nesto and Di Savino, 2013). The
86 phenolic composition of Nero d'Avola wines has been extensively investigated over the past
87 decade (Agozzino et al., 2015; La Torre et al., 2005; La Torre et al., 2014; Dugo et al., 2006).
88 On the other hand, the wine aroma cannot be neglected as a fundamental parameter for its
89 identification, evaluation and traceability, fact testified by a long list of scientific reports on
90 this topic (Gonzalez-Barreiro et al., 2015). Numerous reports on the aromatic fraction of wines
91 are based on the use of headspace techniques, in particular of solid-phase microextraction
92 (SPME), mainly because of its simplicity, low cost, effectiveness, sensitivity and selectivity

(Costa, 2014; Dugo et al., 2014; Panighel and Flamini, 2014). From an overview of literature data, it is evident that the aroma of Nero d'Avola wines has been scarcely investigated (Cincotta et al., 2015; Verzera et al., 2016; Esti and Tamborra, 2006; Papucci et al., 1999). Against this background, in the present work samples of Nero d'Avola wines produced in Sicily (Italy) were investigated in order to: i) elucidate the aromatic composition by means of HS-SPME coupled with GC-MS; ii) assess the polyphenolic content by UHPLC-HESI-Orbitrap mass spectrometry; iii) compare the results obtained from both the screenings with those relative to the same wines, but preliminarily subjected to spray-drying processing. The purpose was basically to determine if and how microencapsulation affects the quality of Nero d'Avola wine as concerns its volatile composition and phenolic profile.

2. Materials and methods

2.1. Samples and chemicals

Commercial Nero d'Avola wines (geographical indication) were from the brand "Conte di Matarocco, Terre Siciliane" and produced by Cantine Paolini (Sicily, Italy). Wines were purchased at local retailers.

Maltodextrin (dextrose equivalent 13.0-17.0) and 1-Hexan-d_{13}-ol were supplied by Sigma-Aldrich (Milan, Italy). All solvents, unless specified, were from Merck (Darmstadt, Germany). Acetonitrile, acetone and methanol (LC-MS grade) were purchased from Biosolve B.V. (Valkenswaard, The Netherlands). Acetic acid (100% purity) and formic acid (98-100% purity) were from VWR International B.V. (Roden, The Netherlands). PTFE syringe filters (0.45 μm pore size) were supplied by Sigma-Aldrich. Gallic acid, caffeic acid, quercetin, (+)-

catechin, epicatechin, cyaniding-3-O-glucoside and myricetin were all purchased from Sigma-Aldrich.

2.2. Spray-drying

For spray-drying procedures, a Mini Spray Dryer B-290 (Büchi, Cornaredo, Italy), was exploited. A 200 mL aliquot of wine (12% v/v ethanol) was added with 40 g of maltodextrin in a screw capped conical flask, and homogenized for 15 min ca, at room temperature (19-20°C) until complete dissolution. Inlet and outlet temperatures (nitrogen) were 105 and 65°C, respectively; feed flow rate was set at 18% of the maximum tolerated by the instrument. Drying rate was approximately of 5 mL of wine per 1 min. The yield was estimated as 82% w/v ca.

2.3. Solid-Phase Microextraction

For SPME extraction, four different fiber coatings were used: divinylbenzene/carboxen/polydimethylsiloxane (DVB/Car/PDMS, 50/30 μm), carbowax/divinylbenzene (CW/DVB, 70 μm), carboxen/polydimethylsiloxane (Car/PDMS, 85 μm), polydimethylsiloxane (PDMS, 100 μm). All SPME fibers were provided by Sigma-Aldrich/Supelco (PA, USA).

In order to assess the best extraction time for each fiber several preliminary tests at increasing times (5, 10, 15 and 20 min) were evaluated (data not showed), it was determined that 15 min was suitable to obtain equilibrium and to reproduce the extraction procedure.

Spray-dried wines were resolubilized by dissolving 2 g of powdered wine in 10 mL of an ethanol/water (12:88, v/v) solution.

4 mL of wine, whether untreated or resolubilized, were added with 0.6 g of NaCl and 10 μL of a 200 ppm solution of internal standard (1-hexan-d_{13}-ol) and placed in a 8 mL amber glass headspace vial, with pierceable silicone rubber septum coated with PTFE film. Wine samples were pre-conditioned at 35 °C for 30 min and under agitation (250 rpm); successively extraction took place by fiber exposure at the same temperature and for a 15 min period. Once the extraction was complete, the fiber was withdrawn from the vial and inserted in the hot (250°C) GC injector. A sample of powdered wine was analyzed apart for a rough qualitative screening, by applying the same SPME conditions above reported, with the exception of fiber exposure time, which was prolonged until 72 hours. In order to avoid carry over effects or artifact formation, blank runs were carried out every three analyses, whereas fibers were suitably cleaned up into a GC injector between consecutive analyses.

2.4. GC-MS

A Focus GC- DSQ II gas chromatograph/mass spectrometer (Thermo, CA, USA) equipped with a 30 m × 0.25 mm i.d. × 0.25 μm film thickness ZB-WAX column (Phenomenex, CA, USA) was used. The oven temperature program was from 40°C (3 min) at 10°C/min to 250°C, hold 2 min. Gas flow rate (He) was 0.8 mL/min. Injection took place in splitless mode (3 min) and at a temperature of 250°C. Data were acquired in the electron impact (EI) mode with an ionisation energy of 70 eV, using full scan ion monitoring for a mass range 35-400 m/z.

159 Component assignment was based on computer matching with the WILEY 7 and NIST 02
160 mass spectral libraries; and on comparison with data retrieved from literature (Cincotta et al.,
161 2015; Verzera et al., 2016; Esti and Tamborra, 2006; Papucci et al., 1999).
162 The relative amounts of volatiles (semiquantitative analysis) were obtained by multiplying the
163 area ratio of target compound/internal standard by the concentration (μg/L) of the internal
164 standard.
165 *2.5. UHPLC-HESI-MS*
166 For identification of polyphenols (phenolic acids and anthocyanin-derived pigments) in wines,
167 UHPLC-HESI-MS methodology was exploited.
168 The UHPLC-HESI-MS system was a UHPLC (Dionex UltiMate®3000 Rapid Separation LC)
169 system by Thermo Fischer Scientific equipped with an autosampler, a diode array detector,
170 and controlled by *Chromeleon 7.2* software, by Thermo Fisher (Bremen, DE) and Dionex
171 Softron GmbH (Germering, DE). The UHPLC system was coupled to a Orbitrap mass
172 spectrometer instrument (Q Exactive) (Thermo Scientific, Germany), equipped with heated
173 electrospray (HESI) ion source. Different conditions for identification of phenolic compounds
174 and anthocyanins were applied. Electrospray conditions for analysis in negative ion mode of
175 gallic acid, caffeic acid, quercetin, myricetin, catechin, epicatechin included: sheath gas flow
176 rate 35 (arbitrary units); auxiliary gas unit flow rate 4 (arbitrary units); sweep gas flow rate 7
177 (arbitrary units); spray voltage 3.5 kV; S lens RF level 30; capillary temperature 250 ˚C;
178 auxiliary gas heater temperature 250 ˚C. UV detection was performed at 254 and 278 nm.
179 Positive electrospray conditions for the determination of anthocyanins were optimized by
180 infusion of a solution of cyanidin-3-O-glucoside, and were the same as above reported for

phenolic compounds, with the exception of: sheath gas flow rate 30 (arbitrary units); sweep gas flow rate 0 (arbitrary units); spray voltage 3.2 kV. UV detection was set at 520 nm.

In both cases, the UHPLC column was a Phenomenex Luna C18 (2) 50×1mm, 2.5µm. The column temperature was set at 25 ˚C and the injection volume at 1.0 µL. Mobile phase composition: formic acid/water 2% v/v (eluent A), formic acid/acetonitrile 2% v/v (eluent B), at a flow rate of 50 $\mu L \cdot min^{-1}$. The gradient was: 0 – 1 min, 3% B; 1 - 10 min, linear increase to 15% B; 10 - 22 min, linear increase to 25% B; 22 - 28 min, linear increase to 50% B; 28 – 30 min, hold 50% B; 30 – 31 min, linear decrease 3% B; 31 – 33 min, hold 3% B.

The MS was operated in electrospray negative and positive mode and the analyses were conducted in two acquisition modes: Full-Scan (positive and negative mode) and SIM. The resolution power in full scan was 70,000 FWHM (at m/z 200) and the scan range was 100-800 m/z. Scan rate was 2 $scan \cdot s^{-1}$ and the automatic gain control (AGC) target was set at 1e 5 ions for a maximum injection time of 200 ms. For targeted SIM analyses, with a 15 s time window, a mass inclusion list containing expected retention times of target phenolic analytes was built and applied. The resolution power was 70,000 FWHM (at m/z 200) and the isolation window was 1.2 m/z.

Data were analyzed with Qual Browser Xcalibur 3.0 (Thermo Fisher Scientific) and identification of individual phenolic compounds and anthocyanins was greatly supported by compound's accurate mass and retention time (if a reference standard was available), as reported in **tables S1** and **S2**.

Prior to injection, samples of untreated wines were filtered through PTFE 0.45 µm syringe filters. Aliquots of 2 g of spray dried wines were dissolved in 10 mL of a 88:12 (v/v) H_2O/EtOH solution, and filtered as well.

3. Results and Discussion

3.1. Aromatic fraction

Figures S1 and **S2** show the HS-SPME-GC-MS chromatograms of untreated and spray-dried Nero d'Avola wine samples, each extracted with four different fibers. Almost 100 different volatile compounds were determined in total, distributed among the different types of samples investigated. In order to have a comprehensive view of the whole volatile fraction, all the SPME fibers tested were taken in consideration in data handling. **Table 1** reports quantitative results for samples of Nero d'Avola wines, either untreated or resolubilized after spray-drying treatment. As expected, in several cases a specific fiber showed higher selectivity toward an analyte compared to another one. For instance, all the fibers were successful in the extraction of compound nr. 8 (2,3-butanedione), whereas no traces of compound nr. 43 (1-octen-3-ol) could be determined, unless using a CW/DVB fiber. However, more than a half volatiles were likewise isolated by the all four fibers. One of the experiments carried out consisted of the SPME fiber exposure directly to the headspace of spray-dried and powdered wine. Headspace preconditioning (no fiber exposure) lasted 72 hours, at 35°C, followed by 15 min of fiber exposure: around 75 volatiles could be detected in total, at consistently lower amounts compared to spray-dried and resolubilized wines (data not shown). In general, the volatile composition was in good agreement with previous reports on the same type of wine (Verzera et al., 2016). Aroma, both in terms of intensity and complexity, is the most important factor in the evaluation of wine quality. In the last years, numerous studies have unequivocally demonstrated that the aromatic label of a wine derives from a combination of different aromatic notes, more than from a dominant component (San-Juan et al., 2011). In the process of flavour formation, chemical complexity is a key element, being directly correlated to the

228 variety of odorants, namely different olfactory characters and thresholds. Following an already
229 established procedure, in order to identify among all volatiles those possessing a real olfactory
230 impact, odour activity values were measured for each compound. The odour activity value
231 (OAV) is obtained by dividing the amount of an analyte by its odour threshold. Compounds
232 were considered "olfactorily active" when their OAVs were higher than 0.5. As can be seen
233 from **table 1**, where odour thresholds retrieved from literature have been reported, eight
234 components, mainly belonging to the group of esters, were found to be odour active. When
235 considering these specific compounds, the observation of their amount in neat and in spray-
236 dried wines evidenced a dramatic reduction, attributable to the microencapsulation process, in
237 the range of 48.8 – 99.1% (median = 92.8%). In some cases, the reduction reached 100% (i.e.
238 compound nr. 7). For some compounds (e.g. compounds nrs. 28, 55 and 70), detection
239 occurred only, or at higher levels, in spray-dried wines, presumably due to either phenomena
240 of co-elution or displacement effects exerted by multicoated SPME fibers. However, the
241 amounts of volatiles in such cases were quite negligible.
242 In general, when the total volatile composition was taken into account, PDMS and CW/DVB
243 fibers showed the highest extraction capability (see **figure 1**). Almost superimposable were
244 the extraction performances registered for DVB/Car/PDMS and Car/PDMS fibers. Regardless
245 of the fiber used, the total amount (ppb) of volatiles resulted to be lower for spray-dried (and
246 resolubilized) wine samples; this finding denotes once again a partial loss of components
247 consequent to the spray-drying process. However, this loss of volatiles didn't compromise to a
248 great extent the volatile composition of spray-dried wines, which reported, on average, an
249 amount of compounds lower by a 1.8 factor.

Figures 2 and **3** show quantitative results organized by group-type. In order to better understand the different selectivities reported by the SPME fibers, the predominant component, namely ethanol, was subtracted from quantitative plots. In neat wines, alcohols and esters constituted the predominant fractions extracted by all the fibers, with the exception of the CW/DVB fiber, which was more selective towards alcohols (57.6 vs. 31.4%, respectively). DVB/Car/PDMS, Car/PDMS and PDMS fibers led to the isolation of 46% ca. of alcohols and 47-50% ca. of esters. The PDMS fiber was the most selective toward an important group of aroma compounds, i.e. ethyl esters of fatty acids, such as ethyl octanoate, ethyl-9-decenoate and ethyl decanoate, produced enzymatically during yeast fermentation and from ethanolysis of acyl-CoA. These esters usually give mature fruit flavour nuances and are responsible for the fruity and floral sensory properties of wine. Among less represented classes of volatiles, acids were selectively extracted at higher percentages by CW/DVB fiber (8.2%) followed by PDMS (4.8%), Car/PDMS (2.1%) and DVB/Car/PDMS (1.6%). Minor classes of compounds, namely aldehydes, ketones, terpenoids, sulphur-containing, and others, were evenly distributed among the various fibers. The content of volatiles was lower in spray-dried wines, fibers' selectivities described so far showed a similar trend in resolubilized samples. Therefore, even in the extraction of this type of samples, the CW/DVB fiber extracted the highest amount of acids, whereas the other three fiber coatings showed similar selectivity. Precision of SPME-GC-MS method was evaluated by measurement of RSD% relative to three replicates for each sample and preliminary tests to be analyzed: values obtained were in the range 0.5-7.6%, with an average RSD% of 3.4%.

3.2. Phenolic content

A targeted qualitative screening of the polyphenolic fraction was carried out by means of UHPLC-HESI-MS analysis. Measured masses of target analytes have been reported in **tables S1** and **S2**.

Comparison of the phenolic profiles of untreated and spray-dried wines are presented in **figures 4** and **5**. The elution profiles of anthocyanins are shown in **figures S3** and **S4**. Selected ion monitoring allowed to achieve the identification of different anthocyanins and phenolic derived products in both the types of samples investigated. As can be seen from figures, delphinidin-3-O-glucoside, cyanidin-3-O-glucoside, petunidin-3-O-glucoside, peonidin-3-O-glucoside, malvidin-3-O-glucoside, delphinidin-(6-acetyl)-3-glucoside, malvidin-(6-acetyl)-3-glucoside and malvidin-(6-coumaroyl)-3-glucoside, caffeic acid, gallic acid, catechin, epicatechin, myricetin and quercetin, were detected in the two types of samples and compared. The results led to the conclusion that the microencapsulation process did not affect the qualitative composition of the polyphenolic fraction. Although only a rough screening was carried out in this study, by comparing the signal intensities of target analytes, it might be supposed that the amounts of phenolics are quite similar in both neat and spray-dried samples. All the polyphenols determined in this study were previously reported for Nero d'Avola wines (La Torre et al., 2005; La Torre et al., 2014; Dugo et al., 2006).

For LC-MS method development, all the parameters were optimized based on repetitive injections of reference standards. Solutions of standards were prepared by taking into account possible matrix effects, therefore by dissolving standards of phenolic compounds into aqueous formic acid (pH 3)/methanol (90:10). Each standard was injected 5 times consecutively, at one concentration level (namely 1 ppm) and repeatability assessed through RSD% (on average ≤2.5%). Also, the mobile phase composition for LC gradient elution was suitably varied both

296 in terms of type of solvents and their concentration. The mobile phase composition was indeed
297 a crucial parameter affecting not only the chromatographic resolution (retention, selectivity
298 and efficiency), but also the quantitative transfer of target analytes to the mass spectrometer
299 through the ESI interface. In general, all the parameters were tuned in order to get the best
300 signal from the MS detector. For instance, the use of 2% formic acid at the specific gradient
301 program above reported resulted to be fundamental for improving the parameters of efficiency
302 (peak shape) and sensitivity.
303 As shown in **figures 4** and **5**, the elution time of the polyphenols investigated was about 30
304 min. As above mentioned, **table S1** lists nominal and measured masses of target phenolic
305 compounds. The acquisition of mass spectra further confirmed the identification process
306 carried out by standard co-injection. The choice of the ESI interface in negative ionization
307 mode (for phenolic compounds) and in positive ionization mode (for anthocyanin-derived
308 pigments) was dictated by the proven higher ionization efficiency and enhanced signals
309 (Kruve et al., 2014; Di Stefano et al., 2017). All the polyphenols shown in **figures 4** and **5**
310 were determined at levels well above their S/N ratios.
311
312
313 **4. Conclusions**
314 Microencapsulation techniques are becoming widespread in food and beverage industry, in
315 consideration of their numerous advantages, some of them being preservation from microbial
316 and environmental contamination, elimination of interferences, concentration of bioactive
317 ingredients. In this study, red wines from the cultivar Nero d'Avola were subjected to spray-
318 drying technology and successively analyzed by GC/MS and UHPLC-HESI-MS, for the

assessment of the volatile and phenolic composition. The purpose of the study was basically to evaluate if the spray-drying process somehow affects the important components of aroma and phenolic and anthocyanin-derived compounds. The results showed a marked reduction of odour active compounds in microencapsulated wines, after resolubilization in water/ethanol; when considering the total amount of volatiles a twofold reduction was observed. Conversely, the qualitative analysis of polyphenols showed no influence of the spray-drying process on these functional constituents, thus confirming the efficiency of microencapsulation in the isolation and concentration of bioactive molecules. The results here presented give a hint for the development of a sustainable wine product, namely a "wine powder", which could be exported worldwide with a considerable cost reduction due to the elimination of the liquid volume. Prior to selling/consumption, the wine powder can be safely reconstituted as normal wine through the addition of a hydroalcoholic solution. The final product, as shown in this report, might have a slightly poorer aroma, but would certainly remain a wine of acceptable quality.

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Figure 1 – Extraction performance of the four SPME fiber coatings expressed as total amount of volatiles (μg/L).

Figure 2 – Groups of volatile compounds (ethanol excluded) extracted from untreated wine samples by means of four different SPME fiber coatings.

Figure 3 – Groups of volatiles (ethanol excluded) extracted from spray-dried wine by using four different fiber coatings.

Figure 4 – UHPLC-HESI-MS(-) SIM chromatogram profiles of phenolic compounds determined in samples of untreated wines.

Figure 5 - UHPLC-HESI-MS(-) SIM profiles of phenolic compounds present in resolubilized spray-dried wine samples.

Figure S1 – HS-SPME-GC-MS (TIC) fingerprints of untreated wine samples extracted by means of four different fiber coatings.

Figure S2 - HS-SPME-GC-MS (TIC) chromatograms of spray-dried wines after resolubilization, extracted by different fibers.

Figure S3 – UHPLC-HESI-MS (+) SIM chromatograms of anthocyanins identified in samples of untreated wines.

Figure S4 - UHPLC-HESI-MS (+) SIM profiles of anthocyanins identified in resolubilized spray-dried wine samples.

Table(s)

Table 1 – HS-SPME-GC-MS composition of wine samples. Compounds in bold are "odour active" (see text). Values are means of triplicate analyses. n.f. = not found. N/A = not available.

			DVB/Car/PDMS		CW/DVB		Car/PDMS		PDMS	
Nr.	**Compound**	**Odour threshold* (µg/L)**	**Neat wine (µg/L)**	**Spray-dried wine (µg/L)**	**Neat wine (µg/L)**	**Spray-dried wine (µg/L)**	**Neat wine (µg/L)**	**Spray-dried wine (µg/L)**	**Neat wine (µg/L)**	**Spray-dried wine (µg/L)**
1	Acetaldehyde	120	0.08	0.03	0.11	0.40	0.21	0.16	0.05	0.07
2	Dimethyl sulfide	1	0.02	n.f.	n.f.	n.f.	0.01	n.f.	n.f.	n.f.
3	Ethyl formate	N/A	0.02	0.02	n.f.	n.f.	0.01	0.07	0.15	0.08
4	Ethyl acetate	7,500	12.2	0.50	4.23	0.23	19.8	1.29	37.7	1.65
5	Ethanol	100,000	59.6	47.6	336.0	219.0	59.3	66.7	210.0	316.0
6	Ethyl propanoate	10	0.32	n.f.	n.f.	n.f.	0.21	n.f.	0.68	n.f.
7	**Ethyl isobutyrate**	0.1	1.01	n.f.	0.38	n.f.	0.45	n.f.	2.45	n.f.
8	2,3-Butanedione	0.86	0.04	0.04	0.29	0.25	0.12	0.11	0.08	0.17
9	Ethyl butyrate	1,600	0.88	n.f.	0.31	n.f.	0.49	n.f.	2.13	n.f.
10	1-Propanol	50,000	0.25	0.17	0.17	0.13	0.35	0.13	0.31	0.16
11	Succinic acid, butyl propyl ester	N/A	0.04	n.f.	n.f.	n.f.	0.04	n.f.	n.f.	n.f.
12	Ethyl 2-methylbutyrate	18	0.39	n.f.	0.13	n.f.	0.23	n.f.	0.88	n.f.
13	**Ethyl isovalerate**	3	0.60	0.02	0.15	n.f.	0.28	<0.01	1.36	n.f.
14	2-Methylbutyl acetate	5	n.f.	0.02	n.f.	n.f.	n.f.	0.02	n.f.	n.f.
15	Isobutanol	40,000	1.31	0.04	1.88	0.07	0.79	0.06	4.42	0.22
16	2,2,6-Trimethyl-6-vinyltetrahydropyran	N/A	0.09	n.f.	n.f.	n.f.	0.041	n.f.	n.f.	n.f.
17	Isoamyl acetate	30	3.03	0.08	0.73	0.06	1.60	0.06	5.54	0.34
18	Ethyl valerate	5	0.02	0.11	n.f.	0.17	n.f.	0.02	0.04	0.15
19	1-Butanol	150,000	0.06	n.f.	n.f.	n.f.	0.07	n.f.	0.17	n.f.
20	Sulfur dioxide	N/A	n.f.	n.f.	0.61	2.23	n.f.	n.f.	n.f.	n.f.
21	Limonene	200	n.f.	0.07	n.d.	0.09	n.f.	n.f.	0.13	0.16
22	Isoamyl alcohol	30,000	37.3	2.44	63.5	3.64	26.9	2.24	93.9	5.50
23	**Ethyl hexanoate**	14	7.36	0.13	2.57	0.15	3.51	0.03	12.2	0.39
24	2,4-Hexadienoic acid, ethyl ester (2E,4E)-	N/A	n.f.	0.01	n.f.	0.06	n.f.	n.f.	n.f.	n.f.

25	(1E,2E)-Dipropenylcyclobutane	N/A	n.f.	n.f.	n.f.	n.f.	0.20	n.f.	n.f.	n.f.
26	Isoamyl butyrate	N/A	n.f.	n.f.	n.f.	n.f.	n.f.	n.f.	0.06	n.f.
27	Hexyl acetate	1,500	0.05	n.f.	0.01	n.f.	n.f.	n.f.	0.07	n.f.
28	**Octanal**	0.7	n.f.	0.06	0.13	0.05	n.f.	0.07	0.49	0.12
29	Acetoin	800	0.51	n.f.	0.39	0.26	0.48	n.f.	n.f.	n.f.
30	3-Hexenoic acid, ethyl ester	N/A	0.03	n.f.	0.01	n.f.	n.f.	n.f.	0.05	n.f.
31	4-Methyl-1-pentanol	5,000	0.01	n.f.	0.05	n.f.	0.02	n.f.	0.03	n.f.
32	2-Heptanol	300	n.f.	n.f.	0.01	n.f.	0.02	n.f.	n.f.	n.f.
33	3-Methyl-1-pentanol	2.2	0.06	n.f.	0.07	n.f.	0.04	n.f.	0.09	n.f.
34	Ethyl heptanoate	2.2	0.05	n.f.	0.02	n.f.	0.01	n.f.	0.15	n.f.
35	Ethyl lactate	14,000	1.85	0.59	6.17	2.44	1.96	0.91	2.84	0.71
36	1-Hexanol	8,000	1.35	0.15	1.16	0.09	1.52	0.20	1.42	0.11
37	(3E)-Hexen-1-ol	400	n.f.	n.f.	0.04	n.f.	n.f.	0.06	0.02	n.f.
38	(3Z)-Hexen-1-ol	400	n.f.	n.f.	0.15	n.f.	n.f.	n.f.	0.01	n.f.
39	Methyl octanoate	200	0.11	0.02	0.07	n.f.	0.03	n.f.	0.13	n.f.
40	Nonanal	1	0.08	0.20	0.05	0.35	0.02	n.f.	0.35	0.95
41	Carbon disulfide	N/A	0.02	n.f.	n.f.	n.f.	0.02	n.f.	n.f.	n.f.
42	**Ethyl octanoate**	5	11.06	0.52	10.5	1.29	1.99	0.17	23.4	2.57
43	1-Octen-3-ol	1	n.f.	n.f.	0.02	n.f.	n.f.	n.f.	n.f.	n.f.
44	1-Heptanol	300	0.22	0.03	0.15	0.04	0.12	n.f.	0.20	0.06
45	Isoamyl hexanoate	N/A	n.f.	n.f.	0.02	n.f.	n.f.	n.f.	n.f.	n.f.
46	Furfural	14,100	0.35	0.18	0.10	0.14	0.24	0.15	0.08	n.f.
47	Acetic acid	N/A	n.f.	n.f.	8.31	9.62	1.04	0.31	n.f.	n.f.
48	2-Propyl-1-pentanol	N/A	0.93	0.85	1.51	4.29	0.46	0.71	1.12	0.99
49	3-Ethyl-4-methylpentanol	N/A	0.11	n.f.	0.12	n.f.	0.08	n.f.	0.18	n.f.
50	Ethyl nonanoate	N/A	n.f.	0.09	n.f.	n.f.	n.f.	n.f.	0.26	n.f.
51	2,3-Butanediol	120,000	0.09	n.f.	0.89	1.86	0.07	0.04	0.20	n.f.
52	Linalool	25	0.26	0.07	0.24	0.21	0.15	0.05	0.29	n.f.
53	n-Octyl formate	N/A	0.21	0.02	0.23	0.09	0.08	n.f.	0.29	n.f.

54	Isoamyl lactate	200	0.28	0.02	0.44	n.f.	0.18	0.02	0.42	n.f.
55	**β-Ionone**	0.09	n.f.	n.f.	0.24	0.60	0.02	0.02	0.03	n.f.
56	Hexadecane	N/A	n.f.	0.03	n.f.	n.f.	0.06	0.02	n.f.	0.47
57	Propylene Glycol	N/A	0.06	n.f.	0.46	0.32	n.f.	n.f.	n.f.	n.f.
58	n-Nonylcyclohexane	N/A	n.f.	0.03	n.f.	0.10	n.f.	n.f.	n.f.	0.29
59	Terpinen-4-ol	110	n.f.	n.f.	n.f.	n.f.	n.f.	0.01	n.f.	n.f.
60	Diethylene Glycol ethyl ether	N/A	n.f.	n.f.	0.13	0.19	n.f.	n.f.	n.f.	n.f.
61	2-Furancarboxylic acid, ethyl ester	N/A	0.10	<0.01	0.11	0.01	0.02	n.f.	0.09	n.f.
62	Ethyl decanoate	200	1.01	0.03	1.52	1.49	0.22	0.04	2.61	2.09
63	Dihydro-2(3H)-furanone	50,000	0.05	0.02	0.29	0.42	0.04	0.05	0.04	0.06
64	Butanoic acid	240	0.29	0.05	0.48	0.25	0.10	0.04	0.42	0.17
65	Furfuryl alcohol	2,000	n.f.	n.f.	n.f.	n.f.	0.05	0.065	n.f.	n.f.
66	Diethyl succinate	200,000	11.2	2.08	17.7	11.2	2.35	0.59	20.2	6.45
67	Ethyl dec-(9E)-enoate	100	n.f.	n.f.	n.f.	n.f.	n.f.	n.f.	0.05	n.f.
68	2-Methylhexanoic acid	N/A	n.f.	0.03	0.69	0.41	0.09	0.04	0.14	n.f.
69	α-Terpineol	330	0.36	0.10	0.33	n.f.	0.09	0.03	0.34	0.07
70	**Ethyl decanoate**	200	n.f.	0.01	n.f.	0.05	n.f.	n.f.	n.f.	n.f.
71	3-(Methylthio)-1-propanol	1,000	0.06	0.01	0.49	0.25	0.04	0.01	0.15	n.f.
72	Diethyl glutarate	N/A	0.04	n.f.	0.13	0.04	0.01	n.f.	0.05	n.f.
73	Methyl salicylate	100	n.f.	n.f.	0.13	n.f.	n.f.	n.f.	n.f.	n.f.
74	Phenylethyl acetate	250	0.41	0.11	0.49	0.07	0.08	n.f.	0.46	0.27
75	**β-Damascenone**	0.05	0.22	0.05	0.56	0.29	0.05	0.01	0.53	0.13
76	Ethyl dodecanoate	1,500	n.f.	0.21	n.f.	1.25	n.f.	0.01	n.f.	1.64
77	Hexanoic acid	200,000	0.19	0.04	0.56	0.61	0.11	0.03	0.51	0.17
78	Benzyl alcohol	200,000	0.28	0.09	0.85	1.20	0.09	0.04	0.36	0.20
79	Butanedioic acid, ethyl-3-methylbutyl ester	N/A	0.25	0.02	0.46	0.14	0.04	0.01	0.51	0.11
80	Phenethyl alcohol	14,000	4.37	1.31	10.1	18.1	1.26	0.59	7.76	3.59
81	1-Dodecanol	1,000	0.07	0.66	0.09	6.43	0.05	0.05	0.12	3.79
82	Diethylene glycol	N/A	0.15	0.05	0.07	0.07	0.05	0.02	n.f.	0.04

83	Ethyl tetradecanoate	2,000	n.f.	n.f.	n.f.	0.78	n.f.	n.f.	n.f.	0.61
84	Octanoic acid	500	0.57	0.06	1.19	0.86	0.10	0.02	1.70	0.41
85	4-Hexyl-2,5-dihydro-2,5-dioxo-3-furanacetic acid	N/A	0.08	0.03	0.24	0.34	n.f.	n.f.	0.20	0.33
86	Hexadecanal	4,500	n.f.	n.f.	0.20	n.f.	n.f.	n.f.	n.f.	n.f.
87	1-hexadecanol	N/A	n.f.	n.f.	n.f.	0.44	n.f.	n.f.	n.f.	n.f.
88	4-Ethylphenol	440	n.f.	n.f.	n.f.	n.f.	<0.01	n.f.	n.f.	n.f.
89	Nonanoic acid	3,000	n.f.	n.f.	n.f.	n.f.	0.01	<0.01	0.29	0.14
90	Ethyl palmitate	1,500	0.04	0.06	0.10	1.61	n.f.	n.f.	0.28	1.09
91	Decanoic acid	1,000	0.08	n.f.	0.09	n.f.	0.01	n.f.	0.27	n.f.
92	2,4-di-t-Butylphenol	200	1.58	0.55	3.19	4.31	0.51	0.25	3.55	2.86
93	Dodecanoic acid	10,000	n.f.	n.f.	n.f.	n.f.	n.f.	n.f.	0.24	0.16
94	Tetradecanoic acid	10,000	0.14	0.03	n.f.	n.f.	n.f.	n.f.	n.f.	n.f.
95	Octadecanoic acid	20,000	n.f.	n.f.	n.f.	n.f.	n.f.	n.f.	2.60	0.32
96	9-Octadecenoic acid	N/A	0.29	n.f.	0.71	0.05	n.f.	0.02	5.27	0.95
TOTAL			**164.0**	**59.8**	**485.0**	**299.0**	**129.0**	**75.6**	**453.0**	**357.0**

*Values retrieved from references Tao & Zhang, 2010; Verzera et al., 2016; L.J. van Gemert, 2011.

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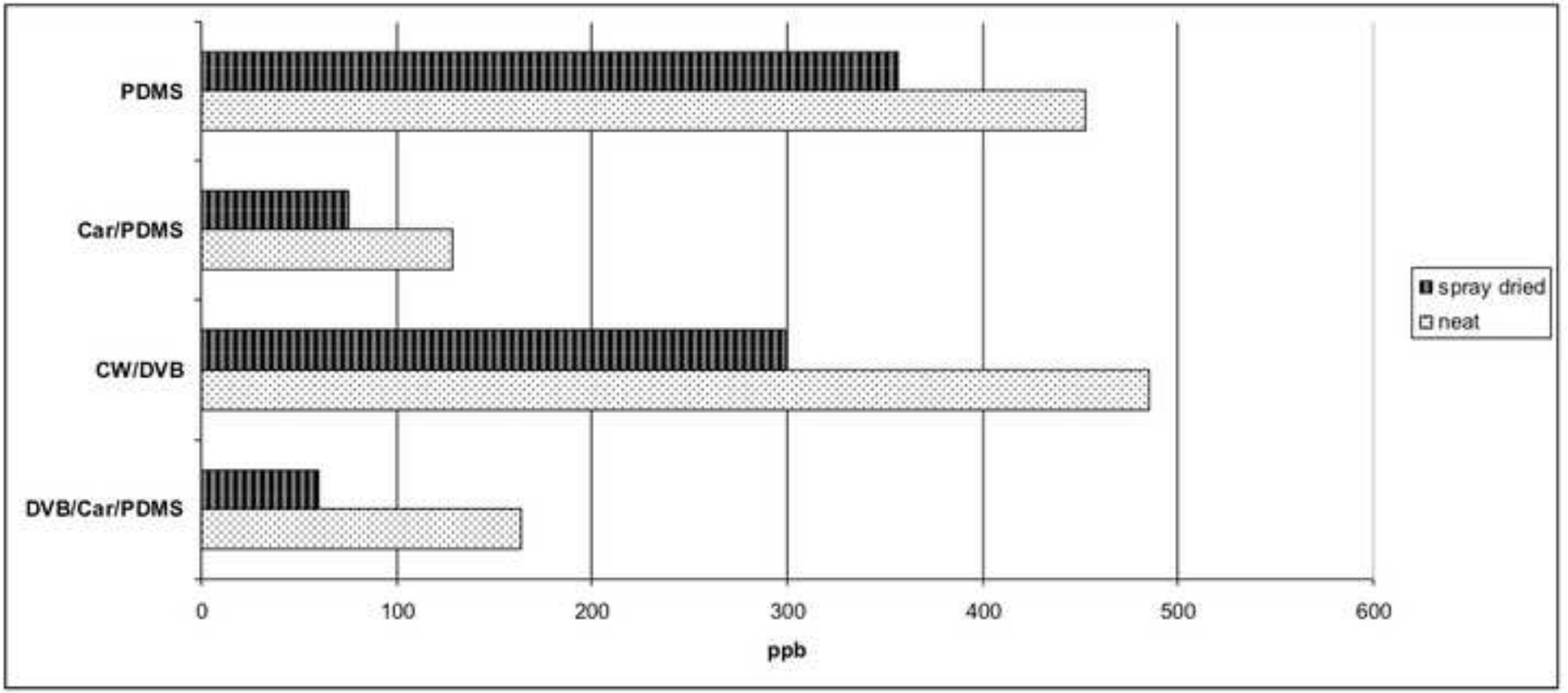

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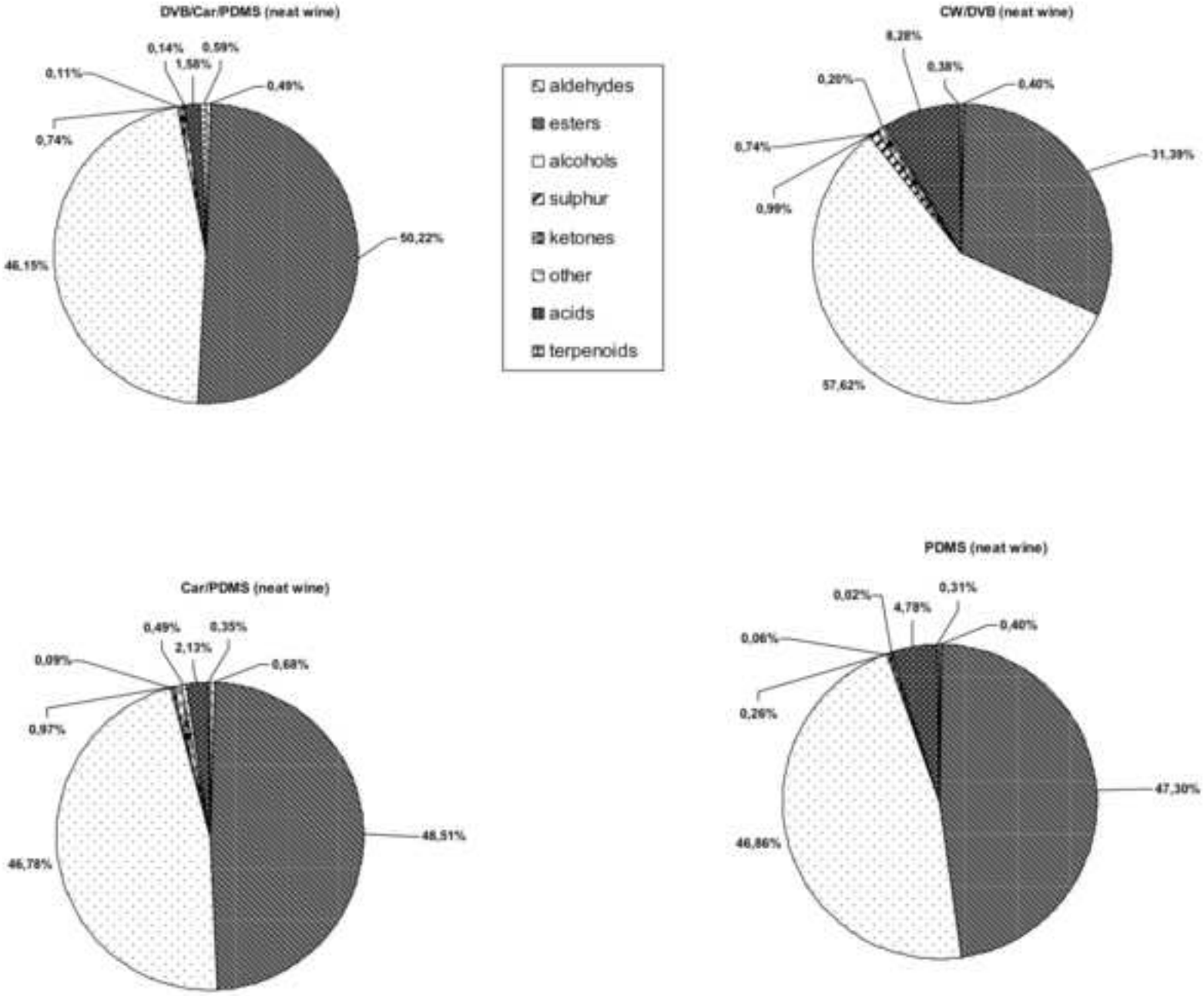

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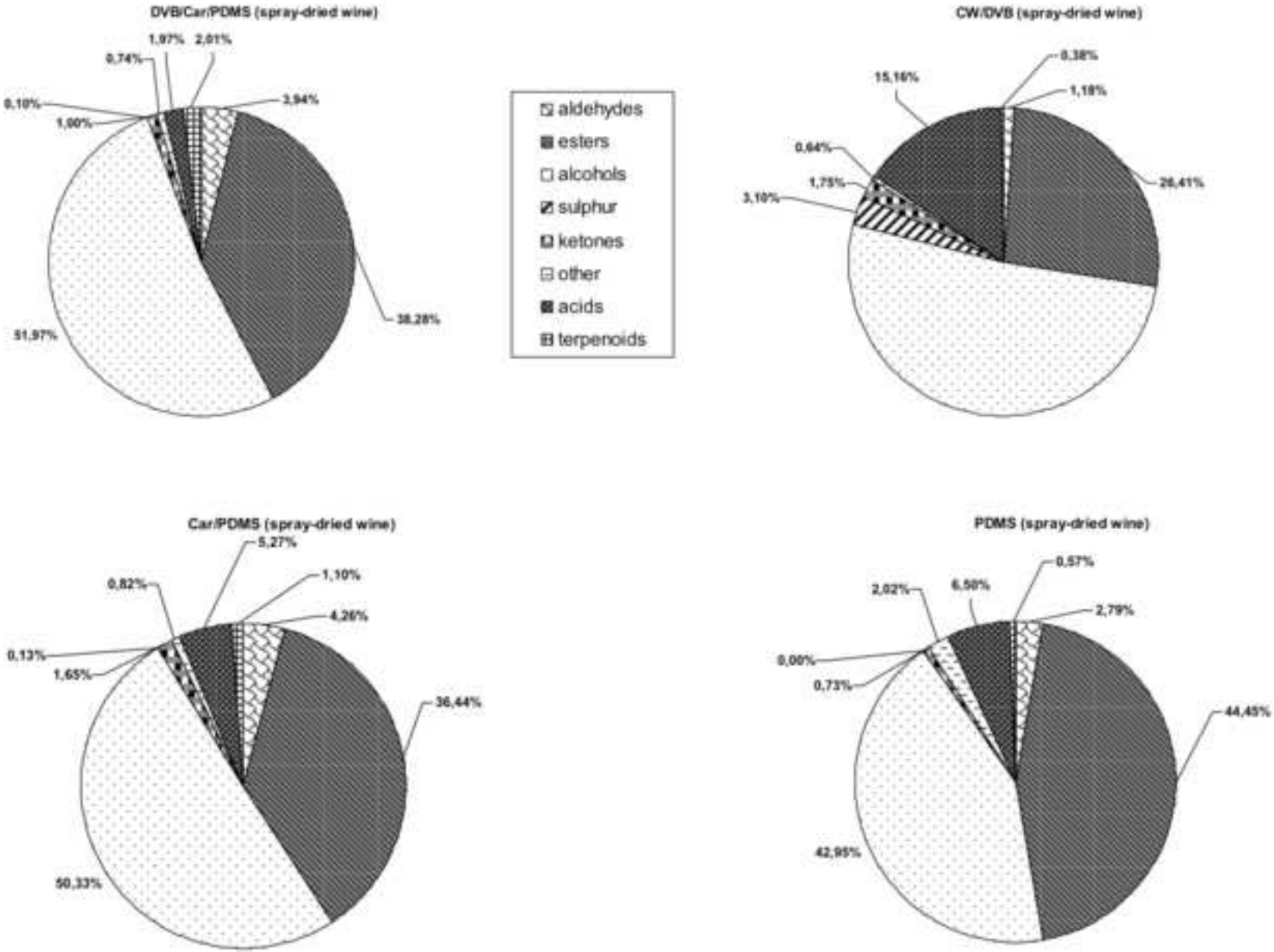

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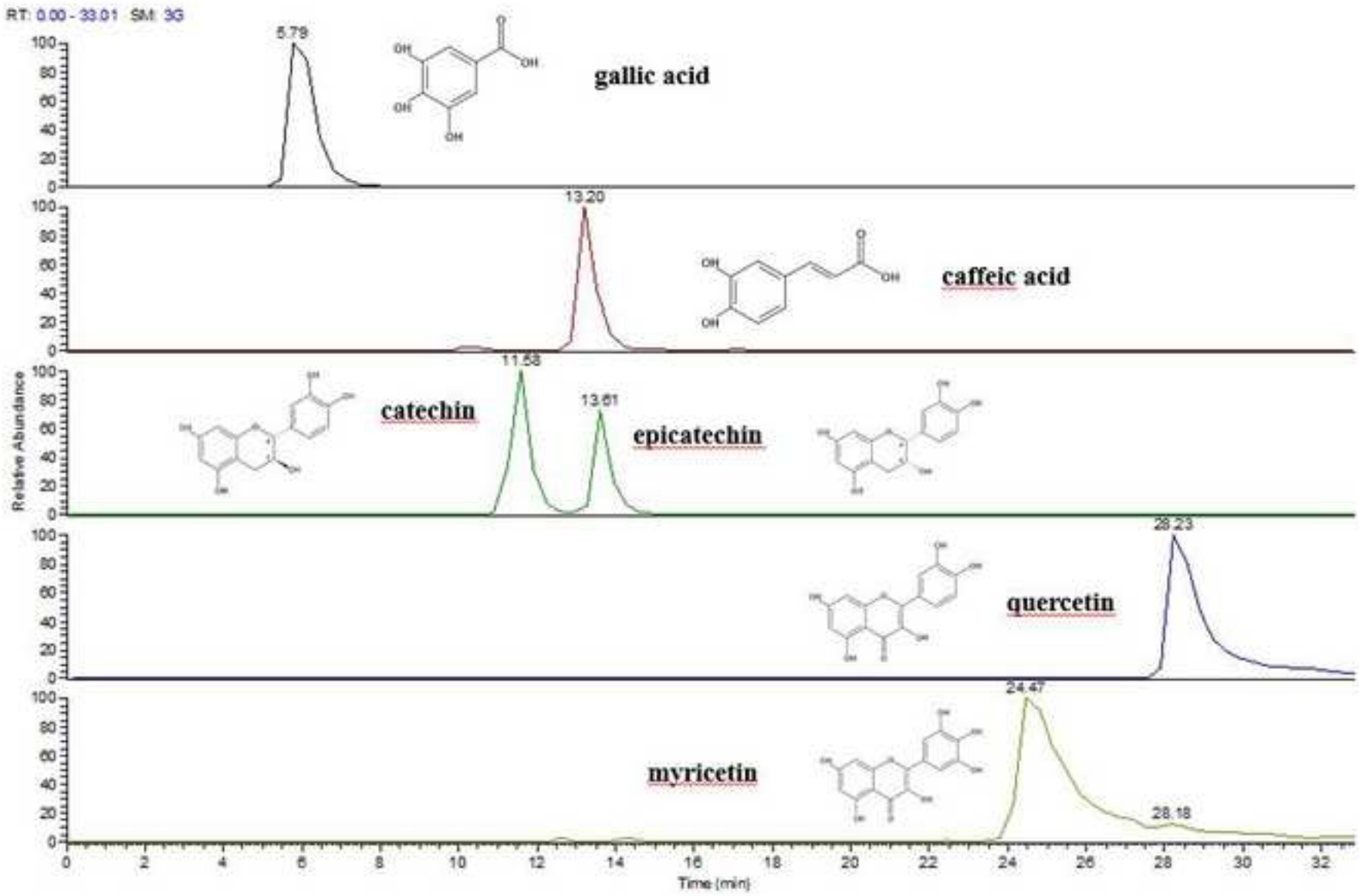

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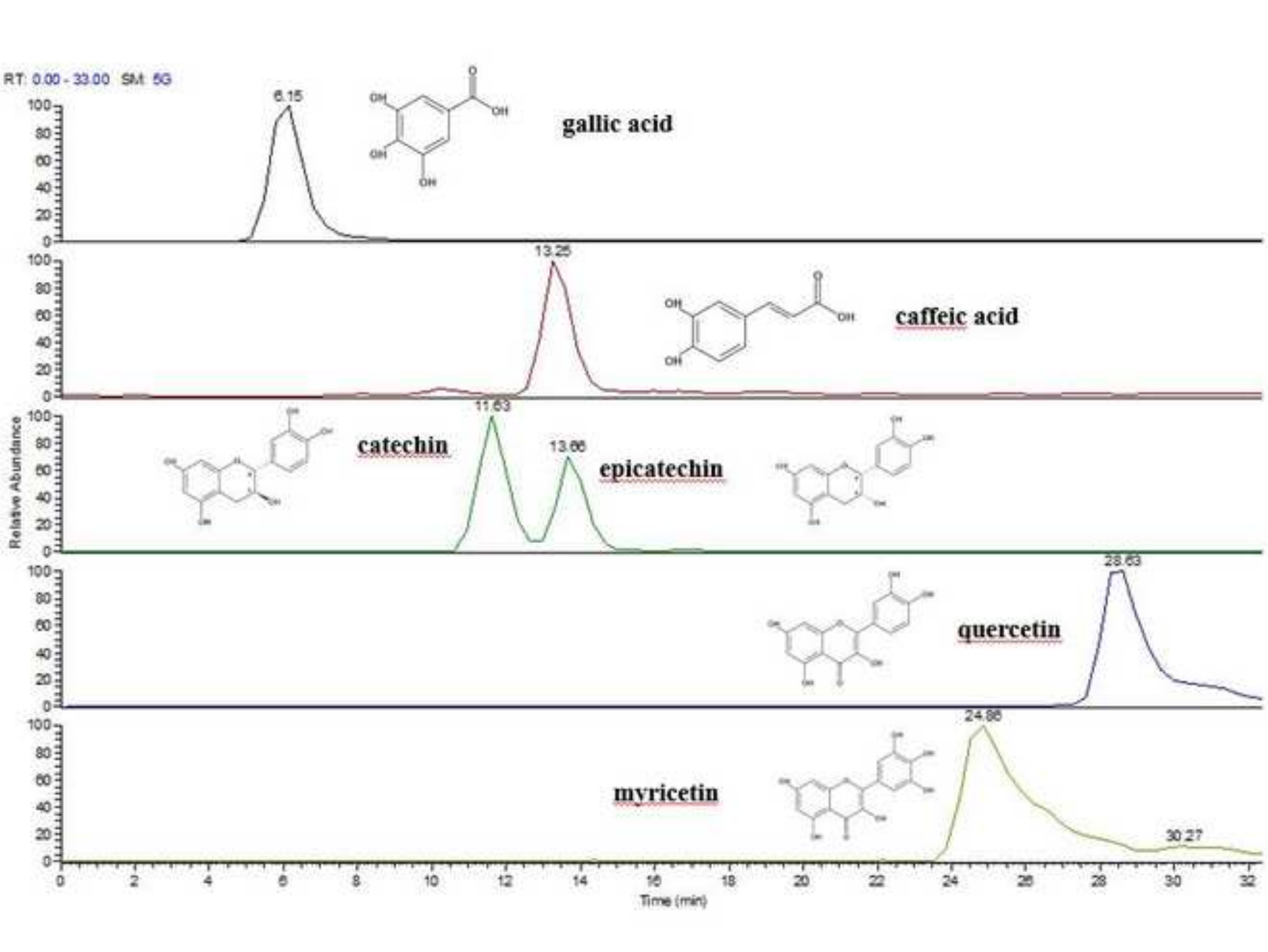

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