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Chemical Characterization and Antioxidant Evaluation of Young and Aged Wines from Aguascalientes and Queretaro

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This contribution is dedicated to professors Elsa, Joan, Ignacio, Jorge, Yunny, and Omar, who pioneered the electrochemical field in Mexico guiding its development in the academy and industry. Thanks for inspiring us all and being the light of many curious minds.

Abstract. Red wine is distinguished by a high economic and cultural value and therefore, its reliable characterization is important to assess its quality and authentication. Currently, Mexican wine consumption is growing due to wine tourism initiatives, then the determination of the chemical profile of commercial selected samples of young and aged red wines produced at wineries from Queretaro and Aguascalientes was performed. Seventy-eight nonvolatile compounds were identified by ultra performance liquid chromatography coupled to mass spectrometry. Three main families of secondary metabolites (Flavonols, ellagitannins and anthocyanins) were quantified by differential pulse voltammetry using carbon screen printed electrodes (SPEs). Tempranillo aged wine from Vinos del Marqués, Queretaro, showed the highest content of total polyphenols and anthocyanins from the evaluated wine samples. This research contributes to the knowledge of the chemical profile of commercial selected samples from wineries that belong to Mexican wine routes in a consolidated and experimental stage.
Keywords: Mexican red wine; electrochemical characterization; total polyphenols; differential pulse voltammetry; antioxidant activity.

Resumen. El vino tinto se distingue por un alto valor económico y cultural y, por lo tanto, su caracterización confiable es importante para evaluar su calidad y autenticación. Actualmente, el consumo de vinos mexicanos se encuentra en crecimiento debido a las iniciativas de enoturismo, por ello, se llevó a cabo la determinación del perfil químico de muestras comerciales seleccionadas de vinos tintos jóvenes y de conserva producidos en bodegas de Querétaro y Aguascalientes. Se identificaron setenta y ocho compuestos no volátiles mediante cromatografía líquida de alta resolución acoplada a espectrometría de masas. Tres familias principales de metabolitos secundarios (flavonoles, elagitaninos y antocianinas) fueron cuantificadas mediante voltamperometría de pulso diferencial utilizando electrodos serigrafiados (SPEs) de carbón. El vino

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Tempranillo conserva de Vinos del Marqués, Querétaro, mostró el mayor contenido de polifenoles totales y antocianinas de las muestras de vino evaluadas. Esta investigación contribuye al conocimiento del perfil químico de muestras comerciales seleccionadas de bodegas pertenecientes a las rutas del vino mexicano en etapa consolidada y experimental.
Palabras clave: Vino tinto mexicano; caracterización electroquímica; polifenoles totales; voltamperometría de pulso diferencial; actividad antioxidante.

Introduction

Currently, wine consumers demand information regarding its composition, nutritional properties and health benefits; characteristics that are usually related to the region where the grapefruit is grown. Therefore, the economic relevance in wine production lies in the consumer demand for higher quality products [1].

Many chemical compounds are involved in the sensory characterization of wine, and phenolic compounds are related to its identity and quality as they contribute to organoleptic characteristics such as aroma, color, astringency and flavor (bitterness). In addition, total phenolic content contributes to the red wine antioxidant activity [2, 3]. The abundance of these compounds in wine depends on various factors such as the cultivar, the age of the vineyard, the state of maturity and health of the grape, environmental factors, and technological processes used during winemaking [4], among others. Furthermore, wine ageing in wooden barrels, common practice to improve wine´s aroma, color, and mouthfeel, produces extraction of hydrolysable tannins and volatile phenols from the oak barrel to the wine. Under wine acid conditions, the extracted ellagitannins and gallotannins release ellagic acid and flavano-ellagitanins are produced by the condensation, hydrolysis, and oxidation reactions [5, 6], modifying the secondary metabolite profile of wine. During a few months of ageing, the monomeric anthocyanins are transformed into polymeric anthocyanins, which leads to an increase in the color stability [7].

Although the chemical composition of wine could change according to the factors cited above, there are compounds that are always present in wine and are known as compound markers of grape variety and geographic origin [5, 8]. Then, the analysis of the composition of phenolic compounds has been of interest not only to follow the maturation stage of grapes and to determine the evolution of the wine during its fermentation and conservation, but also to differentiate wines by grape variety and geographic origin [9].

Generally, the quality of wine is evaluated through sensory analyzes that depend on the perception of the expert or the consumer and therefore, it is subjective. In this regard, chromatographic methods capable of relating qualitatively as well as quantitatively the sensory description of the wine, assessing its stability, origin and authenticity, have been implemented [5]. These methods however are expensive, with long analysis periods and are not very ecological.

Since phenolic compounds are electrochemically active species some voltammetric techniques have been used for its characterization in food and beverages, with classic disk electrodes and disposable screen-printed electrodes (SPE's) [10, 11]. Lanzelloto et al., [12] for example, developed a sensor based on the functionalization of a conventional carbon working electrode with multilayers of gold nanoparticles (AuNPTs), fullerene and Laccase enzyme to determine the total polyphenol content in white and red wine using cyclic voltammetry coupled to a flow injection system (FIA). Newair et al., [13], also evaluated the total phenolic content on five French wines by square wave voltammetry (SWV) in a conventional cell equipped with a glassy carbon electrode and screen-printed carbon electrodes unmodified and modified with single and multi-walled carbon nanotubes.

In the last decade, wine production in Mexico has increased, in 2018 it was reported that the Mexican wine industry utilized 6,474 hectares, rendering more than 20 million bottles of wine that were distributed by the wineries in 14 states among them Aguascalientes and Querétaro. Querétaro is within the five most important wine producer areas of the country, and the development of wine tourism in Querétaro also promotes the consumption of wine from this region [14, 15]. La Redonda is one of the largest producers of wine in Queretaro, with an annual production of 450,000 bottles of which 95 % are placed in the national market and it has been producing quality wine for more than 40 years. Vinos del Marques was established in 2013 and is currently one

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of the exponents of Queretaro's extreme wine. Both wineries are part of the first wine cluster in Mexico. Meanwhile Valle Redondo from Aguascalientes has more than 50 years producing beverages among which Cu4tro Soles wines stand out [14, 16-18]. In Mexico, the more produced red grapes are Cabernet Sauvignon, Carignan, Merlot, Tempranillo and Syrah, and from these, red, white and rose wines are produced [14].

Despite the increase in wine production, studies regarding Mexican wine chemical characterization are scarce; then the aim of this study it's to contribute to the knowledge of the chemical profile of commercial selected samples of young and aged wines produced at wineries from Queretaro and Aguascalientes, which wine routes are in a consolidated and experimental stage, respectively.

Experimental

Materials

Commercial standards of protocatechuic, caffeic, rosmarinic, *p*-coumaric, chlorogenic, vanillic, ferulic, ellagic, gallic and syringic acids; rutin, quercetin, catechin, epicatechin, myricetin, naringenin, hesperetin, apigenin and formic acid, were purchased from Sigma-Aldrich (St. Louis Mo, USA). Water and acetonitrile (CH_3CN) were liquid/mass spectrometry (LC/MS) grade from Optima line, Fisher Chemical (New Jersey, USA).

Five young and two aged Mexican red wines produced from vine fruits (*Vitis vinifera* L.) were purchased, wine from Cabernet Sauvignon cultivar (2020) from La Redonda vineyards, (Ezequiel Montes, Queretaro, 20°38' N 99° 54' O, 1950 m.a.s.l), and Valle Redondo (cu4tro soles line, Aguascalientes, 21º 52' N, 102º 21' O, 1860 m.a.s.l), Merlot wine (2020) from Valle Redondo, cu4tro soles line, and Vinos del Marqués (ranch the Abadía, the Marqués, Queretaro, 20° 58' N, 100° 09' O, 1850 m.a.s.l), and Tempranillo wine (2020) from Vinos del Marqués. Two samples of Tempranillo and Merlot with 6 months aged from Vinos del Marqués were also acquired.

Determination of total polyphenols

Total phenolic content was determined according to the Folin–Ciocalteu method [19]. Briefly, appropriate dilutions of the wine samples were oxidized with the Folin–Ciocalteu reagent, then neutralized with Na_2CO_3 solution. After 2 h under darkness, the absorbance was measured against a prepared blank at 760 nm with a Spectra Max Tunable Microplate Reader (Molecular Devices Co., Sunnyvale, CA, USA). The results were expressed as mg of gallic acid equivalents per liter of wine (mg GAE/L). All samples were analyzed in triplicate.

Determination of total monomeric anthocyanins

Monomeric anthocyanin content was determined spectrophotometrically using the pH differential method [20]. Briefly, the wine samples were diluted with potassium chloride (0.025 M, pH 1.0) and sodium acetate buffer solution (pH 4.5, 0.4 M) and absorbance was measured at 510 nm and 700 nm against distilled water as blank. All samples were analyzed in triplicate. The monomeric anthocyanin contents were expressed as cyanidin-3-O-glucoside equivalents/L (C3G/L).

Determination of phenolic profile by UPLC/PDA/ESI-QTOF/MSe

A Waters Acquity UPLC™ system (Waters Co., Massachusetts, USA) fitted with a Vion IMS QToF mass spectrometer (Waters Co, Wilmslow, UK) was used. The analysis was carried out at 10 °C, using a reverse phase column BEH-C18 2.1 x 100 mm, 1.7 µm (Waters Co, Massachusetts, USA). The phenolic acids and flavonoids were detected at 280 nm and anthocyanins at 520 nm, in addition, a scan was performed in the 210-700 nm range. Solvent A (0.1 % formic acid in H_2O) and solvent B (0.1 % formic acid in acetonitrile) were used. An adaptation of the conditions reported by Tohge [21] was followed. Gradient elution from 0 to 2.5 min starting with 0 % B and ending with 15 % B, and from 2.5 to 10 min ending with 21 % B, from 10 to 12.0 min ending with 90.0 % B, then from 12.0 to 13.0 min ending with 95 % B and from 13.0 to 15.0 min ending with 0 % B, finally from 15.0 to 18.0 min an isocratic elution was carried out. The injection volume was 3 µL and the flow 0.3 mL/min. The assays were performed in positive and negative ionization mode and the parameters

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of the mass spectrometer were adequate for the implementation of the method. All samples were analyzed in triplicate in a randomized order.

Polyphenols were quantified by comparison of the area under the curve from standards of known concentration, and the area of the wines with and without the addition of standard solutions [22]. The quantification of quercetin, mirycetin, kaempferol and their derivatives was carried out with the specific aglycone, ishorhamnetin and its derivative with quercetin. The flavan-3-ols were quantified with (+)-catechin (epicatechin was quantified with the standard). The hydroxylbenzoic and hydroxycinnamic acids were quantified with the specific standard, only caftaric acid was quantified with caffeic acid. Stilbenes were quantified with trans-resveratrol, the flavanones with naringenin, the ellagitannins and galloyl esters with ellagic acid. Also (±)-malic acid and L-(+)-tartaric acid were quantified with the specific standard while fertaric and coutaric acids, with L-(+)-tartaric acid.

Phenolic compounds were identified by comparing the retention time, absorption spectra and mass spectrometry from each standard, with those obtained for each peak for the wines and by comparison with bibliographic references. Progenesis QI and UNIFI programs (Waters Co, Massachusetts, U.S.A) were used for data processing.

DPPH and ABTS radical scavenging activity

The antiradical activity (ARA) was determined using the stable DPPH and ABTS radical [23, 24]. For DPPH assay, a wine dilution (20 µL) was mixed with 200 µL of DPPH solution and the absorbance was recorded after 30 min at 520 nm in a Spectra Max Micro plate Reader (Molecular Devices Co., Sunnyvale, U.S.A). For the ABTS test 20 µL of sample was mixed with 230 µL of ABTS+• solution and the absorbance was recorded after 6 min at 734 nm. The ARA was calculated by interpolating with a Trolox calibration curve and expressed as mM Trolox equivalents per liter of wine (mM TE/L). All assays were performed in triplicate.

Electrochemical detection by DPV

Before the electrochemical determinations, each sample was concentrated from 10 to 1 mL in a rotary evaporator R-205 (BÜCHI Laborthechnik AG, Flawil, Switzerland) coupled to a high vacuum bomb FELISA-1400 (Fabricantes Feligneo, S. A. de C.V., Jalisco, Mexico) and a bath of water. The temperature was set to 35 ± 2 °C. The sample was analyzed immediately.

Differential pulse voltammetry (DPV) tests were carried out using a potentiostat-galvanostat (Epsilon BASi-E2, Bioanalytical Systems Inc., Lafayette IN). Commercial screen-printed electrodes (SPE´s) were used (DRP-110, DropSens, Oviedo, Spain). The SPE´s contained a reference electrode (Ag), an auxiliary electrode and working electrode of carbon. The SPE´s were connected using a connector (DRP-CAC70238; DropSens, Oviedo, Spain). The viability of the SPE´s electrodes was determined with Cyclic Voltammetry (CV), by testing the electroactivity of a 5 mM Ferro/Ferricyanide [Fe $(CN)_6]^{3-/4-}$] in KCl (0.01 M) solution. In this way, 50 µl of KCl were first placed to measure the baseline, then the measurement of the Ferro/Ferricyanide solution was carried out (scan rate of 0.2 V/s, start potential of -0.2 V, and switch potentials of +0.8 V and -0.6 V). Once the electrode was ready, 17 cleaning cycles of 15 segments were carried out with the supporting electrolyte. Subsequently, 50 µL of the buffer solution (MES 25 mM, pH 5.0) were placed to obtain the baseline for DPV (scan rate of 0.015 V/s, a starting potential of 0.0 V, end potential of +0.8 V, potential step of 3 mV, pulse width 50 ms, pulse period 200 ms and pulse amplitude 50 mV). A model solution at pH 5 (25 mM MES and 10 mM phosphates) containing ellagic acid, quercetin and pelargonidin (MSTD4) at 20, 70 and 100 µM concentration values, respectively, was assayed. The results were expressed as milligrams of standard/L of red wine ± the standard deviation for three repetitions.

Due to the complexity of the samples, the correction of the oxidation potentials was carried out by applying a Gaussian deconvolution model (Eq. 1).

$$y = y_0 + \frac{Ae^{\frac{-4\ln(2)(x-x_c)^2}{w^2}}}{w\sqrt{\frac{\pi}{4\ln(2)}}} \quad (1)$$

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Where, y_0 is the y value at the base of peak n, x_c corresponds to the x value at the center of peak n, w is the width of peak n at mid-height and A is the amplitude of peak n.

The oxidation potentials for each component in the MSTD4 and samples were obtained by means of average measurements (n=10 and 14, respectively). The variation coefficients in all cases were lower than 10 %.

Statistical analyses

The analysis of the relevant data was carried out by a one-way ANOVA and Tukey tests using OriginPro 9.0 (OriginLab Corporation, Northampton, MA). Multivariate Analysis (Pearson correlation) was carried out employing the JMP version 11.0.0.0 (SAS institute inc., Cary, North Carolina). A multivariate calibration was carried out by a Gaussian deconvolution model using OriginPro 9.0.

Results and discussion

Non-volatile compounds: Total anthocyanin, polyphenol content, identification and quantification by UPLC-MSe

The secondary metabolite contents in wines depend on factors like grape variety, geographic origin, climate conditions, and viticultural and ecological practices, among others [25, 26]. Wine anthocyanin profile is useful for the differentiation of wine types since the attributes of wine color are affected by reactions of anthocyanins with flavan-3-ols, tannins and procyanidins, as well as the formation of pyranoanthocyanins through wine aging [27]. The most reported anthocyanidins of red wines from *Vitis vinifera* varieties are malvidin, petunidin, peonidin, delphinidin and cyanidin; also, their anthocyanins are linked to one or more sugar molecules or acyl substituents [25,28]. Anthocyanin content ranging from 90 to 400 mg of malvidin-3-glucoside/L and more than 700 mg malvidin-3-glucoside /L have been reported for young and aged red wines, respectively [25,27,28]. The total anthocyanin content for the evaluated wines (Table 1) agrees with reported values. Cruz de Aquino et al., [29] reported that Merlot wines from Ezequiel Montes and Del Marques, localities of Queretaro, showed higher contents of anthocyanin than Cabernet samples. In agreement, the sample of C. Sauvignon from Ezequiel Montes (La Redonda) showed lower anthocyanin content that the Merlot wine from Del Marques. This trend is not observed for Aguascalientes wine. High anthocyanin content in wine is related to high sugar content in the grape must.

Generally, the anthocyanin content decreases through winemaking and conservation [30], due to the reaction of malvidin-3-O-glucoside with components such as pyruvic acid, acetaldehyde, hydroxycinnamic acids, and their corresponding vinylphenols, vinylflavanols or acetoacetic acid to form pyroanthocyanins (Vitisin A, B, among others). For the studied samples, the six-month conservation of wine increases the anthocyanin content, this effect has been ascribed to the slow reaction of malvidin-3-O-glucoside and ellagitannins in absence of pyruvic acid [7,31,32].

Red wine is an important polyphenol source, and its chemical composition is relevant for desirable biological functions such as cardiovascular protection effects, and for wine sensory attributes and stability. Polyphenols interact with volatile compounds promoting the loss of aroma and could be used as a quality criterion [25,33]. The total phenolic (TP) content for the studied red wines ranged from 2170 to 2511 mg GAE/L (Table 1).

Seventy-eight individual compounds were identified by UPLC-MSe and of these, forty-four were quantified and classified by chemical families (Table 1). Some representative structures are shown in Fig. 1. Flavonols constitute one of the most abundant type of compounds present in the *Vitis vinifera* red wine. These compounds show a yellow coloration and are color masked by the anthocyanins in wine. Flavanols affect the astringency, bitterness as well as the color by producing co-pigments through the winemaking process [25,26]. At present work, wines from Del Marqués showed the highest values of flavonols content which can be related to the soil agronomical characteristics. The evaluated aged wines showed a moderate decrease in the flavonols content due to the formation of more stable pigments by the reaction with anthocyanins, and oxidation and condensation reactions [30,34].

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Table 1. Total content and individual content of polyphenols identified by UPLC-DAD-MSe and antioxidant capacity (ABTS/DPPH).

T_r	Winery / Variety / Compound	La Redonda	Cu4tro soles		Vinos del Marqués			
		C. Sauvignon	C. Sauvignon	Merlot	Tempranillo	Merlot	Tempranillo‡	Merlot‡
	Total content of anthocyanins (mgC3G/L)							
		31.81 ± 0.82 ^{a}	168.91 ± 2.01 ^{b}	110.21 ± 1.89 ^{c}	231.00 ± 0.86 ^{d}	181.09 ± 2.48 ^{e}	243.69 ± 2.44 ^{f}	136.82 ± 4.04 ^{g}
	Total phenolic content by Folin-Ciocalteu method (mg GAE/L)							
		2221.7 ± 105.0^{ab}	2170.0 ± 188.7 ^{b}	2330.3 ± 191.7 ^{ab}	2251.0 ± 21.5 ^{ab}	2192.4 ± 58.3 ^{ab}	2511.3 ± 101.1 ^{a}	2173.5 ± 56.7 ^{b}
Antioxidant capacity (mM TE/L)								
ABTS Method		13.33 ± 0.02^{c}	13.34 ± 0.01 ^{bc}	13.34 ± 0.02 ^{bc}	13.35 ± 0.01 ^{bc}	13.39 ± 0.01 ^{b}	13.47 ± 0.02 ^{a}	13.35 ± 0.01 ^{bc}
DPPH Method		24.26 ± 0.05 ^{ab}	24.91 ± 0.17 ^{ab}	24.45 ± 0.26 ^{ab}	24.72 ± 0.11 ^{ab}	24.83 ± 0.01 ^{ab}	24.15 ± 0.44 ^{b}	25.11 ± 0.22 ^{a}
Content of polyphenols identified by UPLC-DAD-MSe (mgESTD/L)								
Flavonols								
2.39	Quercetin-3-glucoside Isoquercetin	ND	ND	ND	0.81 ± 0.18 ^{a}	0.40 ± 0.03 ^{b}	0.95 ± 0.07 ^{a}	0.40 ± 0.02 ^{b}
3.37	Myricetin-3-O-glucuronide	0.51 ± 0.10 ^{a}	0.45 ± 0.01 ^{ab}	0.29 ± 0.01 ^{b}	1.14 ± 0.03 ^{c}	0.40 ± 0.01 ^{ab}	1.94 ± 0.10 ^{d}	0.45 ± 0.02 ^{ab}
3.41	Myricetin-3-O-glucoside	1.93 ± 0.09 ^{a}	1.01 ± 0.06 ^{b}	ND	12.38 ± 0.33 ^{c}	14.99 ± 0.49 ^{d}	15.65 ± 0.47 ^{d}	15.03 ± 0.32 ^{d}
3.91	Myricetin-3-O-rhamnoside 1 (Myricitrin)	ND	0.41 ± 0.02 ^{a}	0.07 ± 0.01 ^{b}	ND	ND	ND	ND
4.06	Quercetin-3-O-glucuronide (Miquelianin)	8.8 ± 0.94 ^{a}	2.68 ± 0.12 ^{c}	1.08 ± 0.01 ^{d}	3.68 ± 0.22 ^{bc}	3.93 ± 0.14 ^{bc}	2.91 ± 0.12 ^{b}	3.74 ± 0.08 ^{bc}
4.12	Myricetin-3-O-rhamnoside 2 (Myricitrin)	ND	ND	ND	ND	1.46 ± 0.04 ^{a}	0.40 ± 0.05 ^{b}	1.04 ± 0.02 ^{c}

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5.34	Isorhamnetin-3-glucoside	ND	ND	ND	0.74 ± 0.02 ^{a}	1.04 ± 0.02 ^{b}	0.14 ± 0.02 ^{c}	0.87 ± 0.02 ^{d}
5.53	Myricetin*	10.82 ± 0.11 ^{e}	10.09 ± 0.13 ^{f}	10.47 ± 0.02 ^{d}	16.83 ± 0.19 ^{b}	12.37 ± 0.07 ^{c}	17.41 ± 0.27 ^{a}	1.92 ± 0.07 ^{d}
8.54	Quercetin*	8.89 ± 0.3^{a}	8.03 ± 0.11 ^{b}	10.61 ± 0.57 ^{c}	13.45 ± 0. 04 ^{d}	16.99 ± 0.05 ^{e}	9.28 ± 0.16 ^{a}	15.50 ± 0.09 ^{f}
11.09	Kaempferol*	0.03 ± 0.01^{f}	0.04 ± 0.00 ^{ef}	0.06 ± 0.00 ^{e}	0.45 ± 0.01^{d}	0.77 ± 0.01 ^{a}	0.54 ± 0.02 ^{b}	0.51 ± 0.01^{d}
11.20	Isorhamnetin	1.07 ± 0.09 ^{a}	2.79 ± 0.02 ^{b}	2.80 ± 0.21 ^{b}	5.00 ± 0.07 ^{c}	3.51 ± 0.04 ^{d}	1.89 ± 0.04 ^{e}	3.14 ± 0.03 ^{f}
	TOTAL	31.53 ± 0.99 ^{c}	25.51 ± 0.38 ^{d}	25.38 ± 0.77 ^{d}	54.48 ± 0.29 ^{a}	55.87 ± 0.51 ^{a}	51.11 ± 1.29 ^{b}	52.60 ± 0.52 ^{b}
	Flavan-3-ols							
1.85	Gallocatechin 1	0.57 ± 0.08 ^{d}	0.18 ± 0.02 ^{f}	0.40 ± 0.00 ^{e}	1.03 ± 0.03 ^{b}	0.91 ± 0.02 ^{bc}	1.58 ± 0.08 ^{a}	0.84 ± 0.02 ^{c}
2.34	Procyanidin B2 1	10.44 ± 0.26 ^{d}	12.52 ± 0.37 ^{c}	17.34 ± 1.82 ^{a}	11.51 ± 0.26 ^{cd}	14.68 ± 1.32 ^{b}	9.93 ± 0.42 ^{d}	15.47 ± 0.07 ^{ab}
2.34	Epigallocatechin-3-glucuronide	ND	0.06 ± 0.02 ^{a}	ND	2.86 ± 0.72 ^{b}	2.01 ± 0.10 ^{c}	2.53 ± 0.07 ^{bc}	2.02 ± 0.06 ^{c}
2.37	Gallocatechin 2	0.08 ± 0.02 ^{a}	0.16 ± 0.01 ^{b}	0.04 ± 0.00 ^{a}	0.48 ± 0.02 ^{c}	0.33 ± 0.02 ^{d}	0.68 ± 0.03 ^{e}	0.29 ± 0.02 ^{d}
2.55	(+)-Catechin*	1.68 ± 0.07 ^{a}	2.64 ± 0.05 ^{b}	2.05 ± 0.01 ^{c}	0.81 ± 0.02 ^{d}	1.35 ± 0.05 ^{e}	0.68 ± 0.05 ^{f}	1.33 ± 0.02 ^{e}
2.80	Procyanidin B2 2	5.85 ± 0.20 ^{a}	10.03 ± 0.28 ^{b}	9.97 ± 1.28 ^{b}	5.01 ± 0.06 ^{a}	10.38 ± 0.03 ^{b}	3.30 ± 0.18 ^{c}	10.44 ± 0.05 ^{b}
3.01	(-)-Epicatechin*	3.66 ± 0.06 ^{a}	4.72 ± 0.05 ^{b}	4.69 ± 0.06 ^{b}	4.70 ± 0.02 ^{b}	6.69 ± 0.07 ^{c}	2.11 ± 0.06 ^{d}	6.61 ± 0.04 ^{c}
3.15	Cinnamtannin A1 (procyanidin C1)	0.24 ± 0.08 ^{a}	1.92 ± 0.06 ^{b}	1.75 ± 0.21 ^{b}	0.98 ± 0.03 ^{c}	1.76 ± 0.06 ^{b}	0.65 ± 0.08 ^{d}	1.69 ± 0.09 ^{b}
	TOTAL	22.53 ± 0.44 ^{d}	32.23 ± 0.14^{b}	36.24 ± 2.06 ^{a}	27.37 ± 0.96 ^{c}	38.11 ± 1.45 ^{a}	21.47 ± 0.66 ^{d}	38.70 ± 0.32 ^{a}
	Hydroxybenzoic acid							
1.32	Gallic acid*	22.07 ± 0.17 ^{a}	32.61 ± 0.74 ^{b}	28.08 ± 0.33 ^{c}	1.17 ± 0.05 ^{d}	16.23 ± 0.05 ^{e}	1.25 ± 0.15 ^{d}	16.00 ± 0.11 ^{e}
1.91	Protocatechuic acid*	0.23 ± 0.00 ^{a}	0.09 ± 0.00 ^{b}	0.1 ± 0.01 ^{b}	ND	0.14 ± 0.01 ^{c}	ND	0.11 ± 0.01 ^{d}
	TOTAL	22.30 ± 0.12 ^{a}	32.70 ± 0.74 ^{b}	28.18 ± 0.23 ^{b}	1.17 ± 0.05 ^{c}	16.37 ± 0.03 ^{d}	1.25 ± 0.15 ^{c}	16.11 ± 0.12 ^{d}
	Hydroxycinnamic acid							
2.13	Caftaric acid	2.52 ± 0.08 ^{a}	1.03 ± 0.02 ^{b}	0.74 ± 0.06 ^{c}	0.16 ± 0.03 ^{d}	1.37 ± 0.02 ^{e}	0.02 ± 0.00 ^{f}	1.31 ± 0.03 ^{e}
2.14	Caffeic acid 1	1.17 ± 0.16 ^{a}	0.75 ± 0.01 ^{bc}	0.55 ± 0.01 ^{c}	0.21 ± 0.01 ^{d}	0.73 ± 0.29 ^{bc}	0.03 ± 0.01 ^{d}	0.85 ± 0.03 ^{b}
2.81	Caffeic acid* 2	0.71 ± 0.16 ^{a}	0.57 ± 0.01 ^{a}	0.57 ± 0.06 ^{a}	1.64 ± 0.02 ^{b}	0.52 ± 0.02 ^{a}	1.69 ± 0.04 ^{b}	0.54 ± 0.01 ^{a}
2.82	Ferulic acid	2.87 ± 0.17 ^{a}	4.04 ± 0.09 ^{b}	3.31 ± 0.29 ^{c}	0.20 ± 0.01 ^{d}	1.06 ± 0.05 ^{e}	0.25 ± 0.04 ^{d}	1.21 ± 0.06 ^{e}
3.45	*p*-Coumaric acid*	0.45 ± 0.02 ^{a}	0.42 ± 0.00 ^{a}	0.58 ± 0.03 ^{b}	1.92 ± 0.02 ^{c}	0.17 ± 0.00 ^{d}	2.04 ± 0.04 ^{e}	0.19 ± 0.00 ^{d}

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	TOTAL	7.72 ± 0.21 ^{a}	6.85 ± 0.05 ^{b}	5.79 ± 0.32 ^{c}	4.14 ± 0.08 ^{d}	3.89 ± 0.24 ^{d}	4.03 ± 0.14 ^{d}	4.10 ± 0.12 ^{d}
	Organic acids							
0.48	L-(+)-Tartaric acid*	850.94 ± 0.34 ^{bc}	776.99 ± 31.02 ^{c}	856.05 ± 42.64 ^{b}	800.81 ± 22.88 ^{bc}	1123.22 ± 18.24 ^{a}	541.04 ± 8.07 ^{d}	156.82 ± 4.99 ^{a}
0.56	(±)-Malic Acid*	11.1 ± 0.02 ^{b}	11.37 ± 0.02 ^{a}	11.03 ± 0.01 ^{c}	10.93 ± 0.04 ^{d}	11.08 ± 0.02 ^{bc}	10.93 ± 0.02 ^{d}	11.05 ± 0.02^{bc}
0.65	L-(+)-Tartaric acid 2	354.56 ± 6.79 ^{a}	266.50 ± 5.41 ^{b}	196.93 ± 1.34 ^{c}	110.41 ± 1.96 ^{d}	290.75 ± 0.94 ^{e}	13.00 ± 1.26 ^{f}	275.50 ± 6.88 ^{b}
2.15	L-(+)-Tartaric acid 3	29.22 ± 2.02 ^{a}	59.38 ± 1.63 ^{b}	59.74 ± 0.06 ^{b}	13.61 ± 0.68 ^{c}	17.94 ± 0.70 ^{d}	ND	17.42 ± 1.15 ^{d}
2.54	Coutaric acid	171.78 ± 12.35 ^{a}	70.48 ± 3.58 ^{b}	69.45 ± 1.34 ^{b}	17.80 ± 1.83 ^{cd}	28.79 ± 1.34 ^{c}	6.99 ± 1.07 ^{d}	27.17 ± 1.20 ^{c}
2.56	Fertaric acid	58.06 ± 1.56 ^{a}	85.38 ± 0.69 ^{b}	61.30 ± 0.62 ^{c}	ND	21.59 ± 1.14 ^{d}	ND	24.30 ± 1.16 ^{e}
	TOTAL	1475.65± 23.02^{a}	1270.10 ± 26.41 ^{b}	1279.11 ± 4.86 ^{b}	954.35 ± 24.65 ^{c}	1493.37 ± 14.51 ^{a}	571.97 ± 10.22 ^{d}	1512.27 ± 13.82 ^{a}
	Stilbenes							
3.87	*Trans*-piceid	3.50 ± 0.32 ^{a}	0.05 ± 0.00 ^{b}	ND	ND	4.71 ± 0.06 ^{c}	ND	4.25 ± 0.08 ^{d}
4.42	Trans-piceatannol	ND	0.10 ± 0.00 ^{a}	ND	1.57 ± 0.06 ^{b}	1.06 ± 0.01 ^{c}	0.69 ± 0.05 ^{d}	0.95 ± 0.04 ^{e}
6.07	*Trans*-resveratrol1	0.56 ± 0.06 ^{a}	0.04 ± 0.01 ^{b}	ND	0.13 ± 0.01 ^{c}	5.34 ± 0.17 ^{d}	ND	4.77 ± 0.11 ^{e}
6.22	*Trans* -resveratrol* 2	0.85 ± 0.03 ^{a}	0.06 ± 0.01 ^{b}	ND	3.47 ± 0.09 ^{c}	3.75 ± 0.16 ^{d}	2.04 ± 0.10 ^{e}	3.81 ± 0.07 ^{d}
9.47	Cis-resveratrol	0.06 ± 0.02 ^{a}	0.09 ± 0.01 ^{a}	ND	10.39 ± 0.17 ^{b}	10.34 ± 0.10 ^{b}	4.92 ± 0.14 ^{c}	9.70 ± 0.04 ^{d}
	TOTAL	4.97 ± 0.34 ^{a}	0.33 ± 0.05 ^{b}	ND	15.55 ± 0.31 ^{c}	25.20 ± 0.24 ^{d}	7.65 ± 0.28 ^{e}	23.47 ± 0.25 ^{f}
	Flavanones							
4.34	Astilbin	0.83 ± 0.05 ^{a}	0.87 ± 0.02 ^{a}	0.40 ± 0.11 ^{b}	0.17 ± 0.01 ^{c}	0.67 ± 0.01 ^{d}	0.04 ± 0.01 ^{c}	0.63 ± 0.01 ^{d}
4.55	Naringenin-7-rutinoside (Narirutin)	0.52 ± 0.09 ^{a}	0.16 ± 0.01 ^{b}	0.34 ± 0.01 ^{c}	0.72 ± 0.01 ^{d}	0.26 ± 0.01 ^{bc}	0.88 ± 0.04 ^{e}	0.28 ± 0.01 ^{bc}
5.42	Naringenin-7-O-glucoside (Prunin)	0.02 ± 0.0 ^{a}	0.10 ± 0.01 ^{b}	0.02 ± 0.01 ^{a}	ND	0.05 ± 0.01 ^{c}	ND	0.04 ± 0.0 ^{c}

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10.84	Naringenin	DNC	DNC	DNC	DNC	DNC	DNC	DNC
	TOTAL	1.30 ± 0.26 [a]	1.13 ± 0.02 [b]	0.73 ± 0.06 [e]	0.88 ± 0.02 [d]	0.98 ± 0.01 [c]	0.93 ± 0.04 [cd]	0.95 ± 0.02[cd]
	Others							
3.72	Ellagic acid*	52.95 ± 0.99 [a]	14.88 ± 0.14 [b]	38.43 ± 0.54 [c]	12.34 ± 0.36 [d]	2.41 ± 0.06 [e]	21.44 ± 0.84 [f]	17.46 ± 0.52 [g]
3.59	Ethyl gallate	53.56 ± 5.38 [a]	74.79 ± 0.78 [b]	57.29 ± 1.15 [a]	27.95 ± 0.17 [c]	44.37 ± 0.28 [d]	29.41 ± 0.47 [c]	45.43 ± 0.18 [d]
	TOTAL	106.52 ± 6.33 [a]	89.67 ± 0.91 [b]	95.72 ± 1.24 [b]	40.29 ± 0.46 [e]	46.79 ± 0.33 [de]	50.85 ± 1.31 [d]	62.89 ± 0.46 [c]
	Total content of phenolic compounds by UPLC-DAD-MSe (mg/L)							
		196.94 ± 10.10 [a]	189.41 ±4.14 [a]	190.88 ± 8.73 [a]	143.9 ± 3.27 [b]	187.19 ± 3.89 [a]	137.28 ± 4.22 [b]	198.82 ± 2.33 [a]

Data are expressed as mean ± standard deviation, ‡ Aged red wines at 6 months in barrel, * Reference standard was tested, T_r retention time (min), *ND* not detected, *DNC* detected but no quantifiable, *ESTD* equivalents of standard, *GAE* gallic acid equivalents, *C3G* cyanidin-3-glucoside, *TE* trolox equivalents, Different lower case letters on the same line indicate statistically significant differences between samples ($p < 0.05$).

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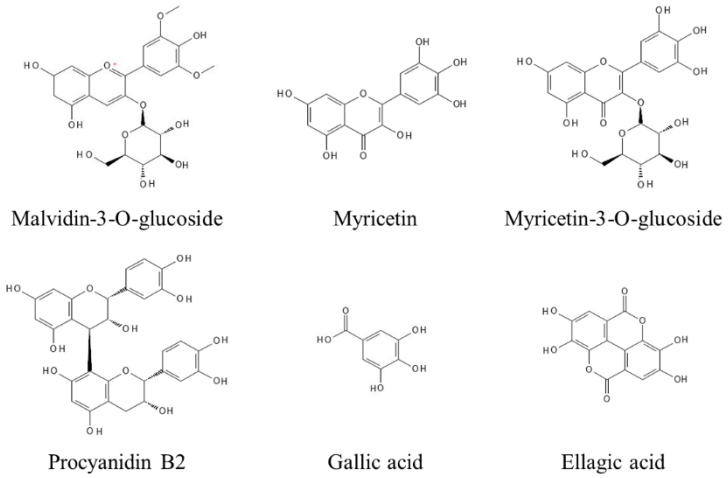

Fig. 1. Representative structures of phenolic compounds identified in red wines.

The principal flavan-3-ols reported in red wine are the monomeric forms (+)-catechin, (-)-epicatechin, epigallocatechin, and epicatechin-3-O-gallate, and for polymeric form proanthocyanidins [4,26,28,35]. For the evaluated wines, the main compounds were procyanidins B2, and contrary to the previously reported, (+)-Catechin and (-)-Epicatechin were present in low contents [36,37].

In the evaluated samples, hydroxybenzoic acids (HBA's) showed higher contents than the hydroxycinnamic acids (HCA's). Rentzsch et al., [38] reported that the amount of HCA's decrease by the formation of vinylphenols through the enzymatic decarboxylation of coumaric and ferulic acid, and the production of pyranoanthocyanins where caffeic and sinapic acids are involved. The representative HBA is gallic acid, the precursor of the hydrolysable tannins and the base moiety for the formation of the condensed tannins in red wine [28]. In this work, Tempranillo wine samples showed very low content of gallic acid, which could be used for its differentiation.

The presence of stilbenes helps to the preservation of the wine attributes such as color, flavor and hence is clearly related to wine quality [26,28,39]. Wines from regions with warmer and drier climates such as California, South America and South Africa, produce wines with low content of stilbene. In this study, the stilbene content for Aguascalientes wine samples was lower than the Queretaro wine samples, suggesting that the climate of Aguascalientes winery in 2020 was warmer and drier than the Queretaro wineries.

The organic acids were the non-phenolic compounds more abundant for all wines evaluated. It´s presence is important because they can lead a reduction in the pH, which increases the color stability. The tartaric acid is the main acid present in the evaluated wines in agreement with reports for other wine samples [40-42].

For the studied samples, there are compounds that are present either in specific grape varieties, wineries, and aged wines. For example, Myricetin-3-O-glucoside is absent in Aguascalientes Merlot wine, myricitrin and isorhamnetin-3-O-glucoside are present in most of Del Marques wine, fertaric acid is absent in Tempranillo wine and stilbenes were not identified in Aguascalientes Merlot wine. Further studies are required to identify these compounds as wine markers for the grape variety or winery.

Antioxidant activity: relationship with phenolic profile

The antioxidant capacity of the wine samples was determined by the ABTS and DPPH assays (Table 1). No significant differences were observed between the wine's antioxidant activities which agree with previous reports [43, 44]. Multiple regression analysis (Pearson correlation) was used to determine correlations between the secondary metabolite content and the antioxidant capacity. High correlations of phenolic total content and DPPH assay values (r = 0.9155, p = 0.05) as well as monomeric anthocyanins and ABTS assay (r

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= 0.8038, p = 0.05) revealed that both secondary metabolite families are responsible for wine antioxidant activity [43, 45]. Quercetin, myricetin, gallic acid, catechin, isoquercetin, coutaric acid, (-) epicatechin, and kaempferol have been associated with the antioxidant activity [4,43,46]. For all the samples evaluated, myricetin, quercetin and gallic acid were the more abundant compounds, and coutaric acid and (-)-epicatechin were also present (Table 1). Although wine is a complex mixture of compounds in which synergism, antagonism and addition reactions may occur, our analysis suggests that these compounds are probably related to the wine samples antioxidant activity [43,45].

Differential pulse voltammetry (DPV)

For the electrochemical study of the wine samples, three standards were used, quercetin as a representative compound for the phenolic and flavonoids family, ellagic acid for the ellagic derivatives and pelargonidin for the anthocyanin group. In a preliminary test to decide which electrochemical technique was to be used for the detection and quantification of target compounds in the samples under study, differential pulse voltammetry (DPV) and square wave voltammetry (SWV) experiments were carried out on a SD150 SPE using the mixture of standards that were previously described. As can be seen in the resulting voltammetric response curves in Fig. 2, better peak resolution was obtained when DPV was employed and therefore this electrochemical technique was selected for all the electroanalytic experiments discussed in the following sections of this work [13,47]. Two buffer solutions (Phosphates 10 mM and MES 25 mM) at different pH values (5, 8 and 9) were tested (data not shown) and considering the best peak separation, MES 25 mM at pH 5.0 solution was chosen for further studies. Fig. 3 shows the DPV electrochemical response of the standards, as can be seen, quercetin exhibits a prominent oxidation peak at 210 mV associated with the oxidation of the hydroxyl functional group of the resorcinol moiety (Fig. 3**(A)**). Pelargonidin on the other hand, displays two oxidation peaks positioned at 237 mV and 627 mV, which have been related to the oxidation of the hydroxyl groups of the aromatic rings B and A, respectively (Fig. 3**(C)**). The voltammetric response of ellagic acid (Fig. 3**(B)**) is characterized by and oxidation peak at 336 mV which is associated to the oxidizable hydroxyl moieties of the molecule [48-50]. The voltammetric response of the compound mixture (Fig. 3**(D)**) shows some slight potential displacements, specifically for the oxidation peak at 186 mV. This potential shift is expected when considering not only intermolecular interactions but also the addition of the electrochemical responses.

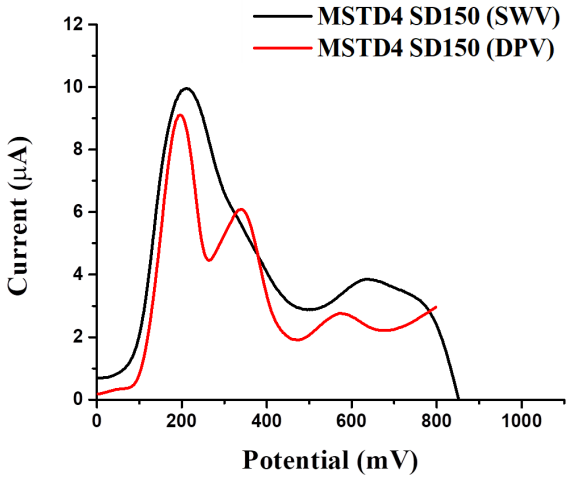

Fig. 2. Electrochemical response for the model wine solution (MSTD4) by square wave voltammetry (SWV) and differential pulse voltammetry (DPV).
Square Wave Voltammetry parameters: S.W. Amplitude 25 mV, S.W. Frequency 15 Hz; DPV parameters: pulse width 50 ms, pulse period 200 ms, pulse amplitude 50 mV. Both assays were carried out in MES 25 mM, pH 5.0, with Step E 3 mV.

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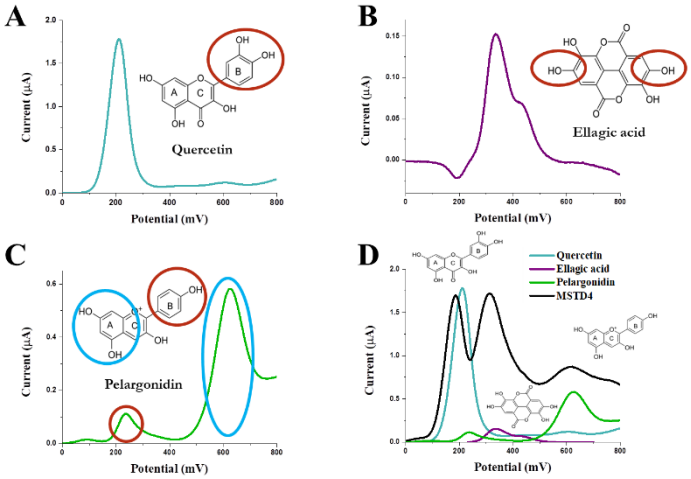

Fig. 3. DPV voltammograms of the individual standards: **(A)** quercetin, **(B)** ellagic acid, **(C)** pelargonidin, and of the mixture of these compounds **(D)** (MES 25 mM, pH 5.0).

It is important to note that quercetin and pelargonidine oxidation potential values agree with the results reported by Newair et al., [13] in which a mixture of gallic and caffeic acids, cathechin and malvidin-3-O-glucoside were employed as a wine model solution (at pH 3.6) and the SWV response of the mixture using SWCNT-SPE *vs* Ag/AgCl showed two predominant oxidation peaks (400-420 and 600 mV).

Fig. 4 shows the electrochemical response for the MSTD4 and wine samples. For wine samples four oxidation peaks are observed. The first oxidation peak, below 150 mV, can be ascribed to the response of the more oxidable components of wine such as phenolic acids. To corroborate that the second oxidation wave in wine samples corresponds to the oxidation of flavonol-like compounds, a co-elusion experiment was carried out. In this way, a 1 mg/mL quercetin solution (5 µL) was added to the wine sample (Fig. 5), and as expected, the current of the oxidation peak at 174 mV was substantially increased. Therefore, the oxidation peak around 174 mV in wine samples was assigned to flavonol-like compounds.

On the other hand, the oxidation peaks at 396 and 660 mV were associated to the electrochemical oxidation of ellagitannin derivatives and anthocyanins, respectively. Wine samples show slight potential shifts of these two signals towards higher oxidation potentials when compared with the standards. This has been expected, since wine is a complex mixture of secondary metabolites which contribute to the overall redox process. It contains other chemical species that interact with the tested electroactive compounds through intermolecular association that results in slight peak potential displacements [43,45].

In this context, the aged Tempranillo wine shows the highest oxidation potential when compared with young wines. This can be the result of wine ageing chemical reactions in which phenolic compounds react with the metabolites from the oak barrel to form ellagitannins, gallotannins and flavano-ellagitannins, among others [6,13].

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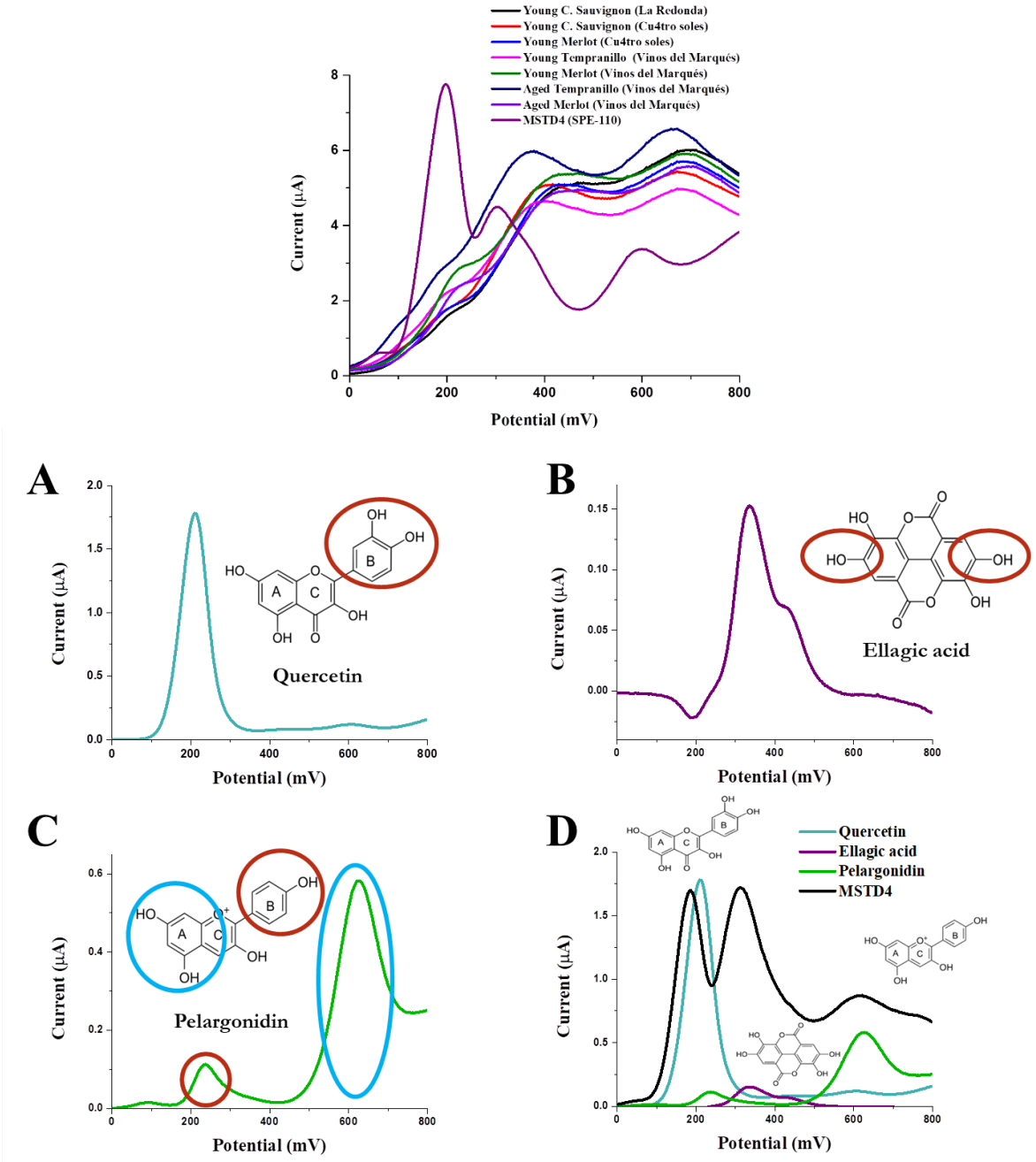

Fig. 4. Electrochemical response for the model wine solution (MSTD4) and wine samples (MES 25 mM, pH 5.0).

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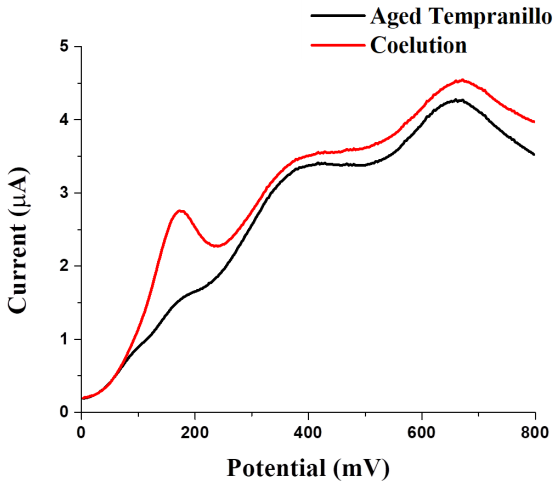

Fig. 5. Voltammogram of aged Tempranillo sample Vs. the enrichment of sample with 5 µL of quercetin (1 mg/mL).

Fig. 6 shows the voltammograms deconvolution (A, B, C) and the calibration curve of pelargonidin (D). The adjusted oxidation potentials for quercetin, ellagic acid, and pelargonidin of the MSTD4 correspond to 203.5 ± 6.3, 317.3 ± 6.7 and 607.0 ± 12.5 mV, respectively, while the oxidation potentials of the wine samples were observed at 195.3 ± 32.5, 397.0 ± 28.6, and 660.4 ± 16.6, respectively.

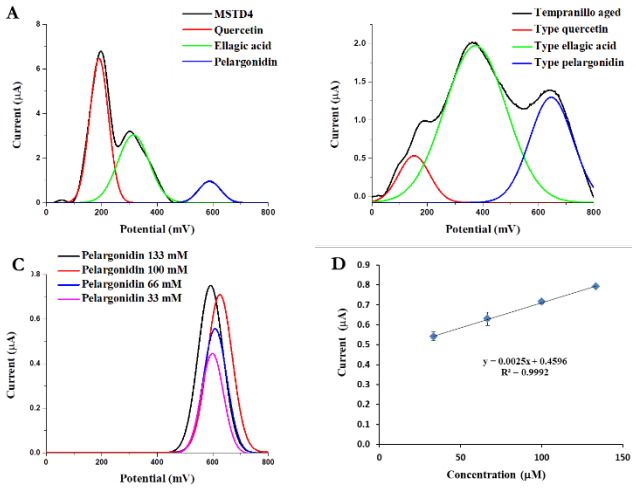

Fig. 6. Voltammograms deconvolution (A, B, C) and the calibration curve of pelargonidin (D) (MES 25 mM, pH 5.0).

The method sensibility was evaluated by the current measurement of the MSTD4 with 20 µM of quercetin, 70 µM of ellagic acid and 100 µM of pelargonidin (n=3). Relative standard deviation (RSD) of 1.1 % for quercetin and ellagic acid and 3.3 % for pelargonidine was obtained. Reported values of RSD for DPV evaluation of samples from polyphenol standard mixtures [51-53], honey [54], fresh fruits and juices from apple/pear, Spanish wine and green beans [52, 55] ranged between 0.85 and 7 %. The RSD values of this

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research agree with reported values. Table 2 summarizes the analytical parameters of the individual standard calibration plots evaluated by DPV, the value of the slope indicates the method sensitivity; values closer to 0 are related to low sensitivity [53,55]. Lower sensitivity for anthocyanins detection was observed compared to the other evaluated phenolic families. This is confirmed with the value of LOQ (S/N = 10) and LOD (S/N = 3). The response in the measurement is influenced by the structure of the compound and their interactions [53, 55-56]. In this respect, the sensitivity of the electrochemical method shows the following trend: quercetin > ellagic acid > pelargonidin.

Table 2. Analytical performance of electrochemical method for phenolic compounds determination in wines.

Phenolic family	**Regression equation**	**R^2**	**LOD** mg/L	**LOQ** mg/L
Quercetin (Flavanols)	y = 0.2111x + 0.1943	0.9956	0.04	0.14
Ellagic acid (Ellagitannins)	y = 0.0243x - 0.3885	0.9962	0.48	1.59
Pelargonidin (Anthocyanins)	y = 0.0025x + 0.4596	0.9992	4.05	13.51

At the equation y = current and x = concentration. LOD: Limit of detection; LOQ: Limit of quantification.

Table 3 shows the contents of the three selected families (flavonols, ellagitannins, and anthocyanins) calculated from the corresponding calibration curves. From inspection of the corresponding data, the Tempranillo variety wine (Vinos del Marqués) that was aged six months in barrels, according to the standard practices of the commercial winery, showed the highest polyphenolic content, while the aged Merlot (Vinos del Marqués) and young C. Sauvignon (La Redonda) showed the lowest values. The electrochemical results show the same trend as that obtained from the Folin-Ciocalteu assay (Table 1), and the Pearson's correlation test shows a positive relationship between them (r = 0.8976, p = 0.05) as well as with the DPPH antioxidant capacity assay (r = 0.8432, p = 0.05).

Regarding quantification of quercetin-type compounds (flavonols), the DPV results shows the same trend as the UPLC/PDA/ESI-QTOF/MSe determination, where the flavonols content for wine samples from Vinos del Marqués showed the highest content, and the aged wines showed less content than the young wines due to favano-ellagitanins formation [6, 26]. A Pearson's correlation test also shows a positive relationship between the electrochemical and UPLC/PDA/ESI-QTOF/MSe results (r = 0.7156, p = 0.05).

As in the case of flavanols, anthocyanin content (pelargonidin type) determined by the electrochemical method showed the same trend as the chromatographic results, aged Tempranillo wine (Vinos del Marqués) and C. Sauvignon (La Redonda) displayed the highest and the lowest values. However, a low Pearson's correlation value between these assays was obtained (r = 0.6339, p = 0.05), this may be due that quantification of total anthocyanin content by spectrophotometric technique relays on pH dependence absorption while the electrochemical assays is based on the compound electron donated capacity.

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Table 3. Total polyphenol contents by electrochemical method (mg STD/L).

Winery / Variety / **Type of compound**	La Redonda	Cu4tro soles		Vinos del Marques			
	C. Sauvignon	C. Sauvignon	Merlot	Tempranillo	Merlot	Tempranillo‡	Merlot‡
Quercetin (Flavanols)	25.4 ± 3.7 ^{c}	34.1 ± 0.8 ^{b}	16.0 ± 1.7 ^{d}	34.1 ± 2.2 ^{b}	60.1 ± 0.3 ^{a}	60.6 ± 2.1 ^{a}	41.0 ± 1.0 ^{b}
Ellagic acid (Ellagitannins)	2134.3 ± 51.1 ^{c}	2349.6 ± 183.6 ^{bc}	2326.1 ± 14.9 ^{bc}	2458.6 ± 142.0 ^{bc}	2506.3 ± 2.8 ^{b}	3890.9 ± 29.5 ^{a}	2252.8 ± 28.9 ^{bc}
Pelargonidin (Anthocyanins)	4707.4 ± 181.4 ^{d}	7648.1 ± 502.5 ^{b}	7205.3 ± 300.4 ^{b}	6002.4 ± 75.25 ^{c}	5902.6 ± 0.5 ^{cd}	21676.7 ± 257.1^{a}	5162.5 ± 442.6 ^{cd}
TOTAL	6867.1 ± 228.8 ^{d}	10031.8 ± 686.9 ^{b}	9547.4 ± 283.9 ^{b}	8495.2 ± 215.06^{c}	8469.0 ± 2.6 ^{c}	25628.3 ± 288.6^{a}	7451.4 ± 479.3 ^{d}

‡ Aged red wines at 6 months in barrel. Different lower case letters on the same line indicate statistically significant differences between samples ($p < 0.05$)

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Conclusions

Chemical characterization of the studied commercial wine samples determined by UPLC/PDA/ESI-QTOF/MSe allowed the identification of gallic acid, myricetin-3-O-glucoside, isorhamnetin-3-O-glucoside, fertaric acid, trans and cis- resveratrol as potential wine compound markers. Tempranillo aged wine was characterized by a high content of total polyphenols and anthocyanins determined by both, spectrophotometric and electrochemical methods.

Although no statistical difference in the antioxidant activity of the samples evaluated by ABTS and DPPH assays was found, the electrochemical approach allowed to find differences and three families of polyphenols (flavonols, ellagitannins and anthocyanins) were quantified by DPV on carbon SPE´s. The conventional technique of UPLC coupled to mass spectrometry undoubtably is a tool to determine the metabolomic profile of wine samples. However, electrochemical approaches can give reliable fast information about the content of the most representative antioxidant secondary metabolite families. The analysis of Mexican commercially available wine samples is valuable as it represents what is available to consumers.

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