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CARLOS ARTUR NASCIMENTO ALVES

PHENOLIC TYPICALITY AND DETERIORATION STUDY OF RED WINES FROM THE SUB-MIDDLE SÃO FRANCISCO VALLEY

FORTALEZA
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Dissertation presented to the Graduate Program in Food Science and Technology at the Federal University of Ceará, as a partial requirement to obtain the title of Master in Food Science and Technology. Concentration area: Science and Technology of Products of Vegetable Origin.

Advisor: Prof. Dr. Lucicléia Barros de Vasconcelos Torres.
Co-Advisor: Prof. Dr. Aline Telles Biasoto Marques.

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ABSTRACT

This work evaluated the phenolic profile and chemical traits of red wines from Sub-middle São Francisco Valley (SSFV), Brazil, to propose the phenolic typicity and study deterioration mechanisms of this peculiar wine-producing frontier. Then, six varietal red wines were obtained from the grape cultivars (*Vitis vinifera* L.) Syrah, Tannat, Petit Verdot, Merlot, Malbec, and Tempranillo, harvested in 2019 second semester in SSFV. All the wines were elaborated following the traditional winemaking, without corrections, and applying 96 hours of maceration. Syrah is the better-adapted grape variety in SSFV, followed by Tempranillo; but the other ones are non-trade-grown or few commercially explored. Tannat is a grape variety that has a high content of phenolic compounds, showing intense coloration, well-bodied, and great aging potential, which becomes one great option to use in SSFV. Therefore, this work wasdivided into three chapters. The first one aimed to compile scientific knowledge on red wines from the SSFV, regarding sensory and chemical traits, and both the edaphoclimatic conditions and scientific perspectives currently approached in the SSFV. The second chapter aimed to characterize for the first time the phenolic typicity and antioxidant potential of Tannat wine from this region, comparing it with Syrah, the better-adapted variety in SSFV. Despite the short-applied maceration, the tropical Tannat had great phenolic contents and antioxidant activity, standing out the compounds *trans*-caftaric, malvidin-3-*O*-glucoside, and procyanidin B1.Tannat had the potential to be an important grape variety in tropical wine-producing regions inBrazil, presenting high bioactive contents and typical traits of these regions. The other varieties were used to study the deterioration mechanisms under primary conditions and manufacturing interventions. Then, the third chapter aimed to explain how the high pH and short maceration time influence the physical and chemical deterioration of red wines. Color, acetaldehyde, and free SO_2 were used as indicators of spoilage, and physicochemical analyses, higher alcohols, total phenolics, monomeric anthocyanins, antioxidant activity, and individual phenolic characterization were studied to make sure about the influence pathways of pH and macerationover the deterioration. Tempranillo wine was the sample with the highest deterioration rate, pHand lowest color, monomeric anthocyanins, and catechins. Petit Verdot wine was the lowest deteriorated sample, also having the highest total phenolic compounds, color, anthocyanins, catechins, and antioxidant activity. pH had a strong correlation with anthocyaninspolymerization and acetaldehyde. Caffeic and ρ-coumaric acids were related to major deterioration rates,

whereas catechins, procyanidins, and anthocyanins were related to antioxidant activity and more resistance to oxidation. Only high pH values may not be enoughto spoil the wine, as other parameters may provide chemical stability, such as phenolic compounds and their antioxidant activity. Then, red musts with high pH may require longer maceration time to improve the major shelf-life of these wines.

Keywords: tropical wines; Tannat; deterioration mechanisms; short maceration; high pH.

RESUMO

O presente trabalho avaliou o perfil fenólico e as características químicas de vinhos tintos do Submédio Vale do São Francisco (SSFV), Brasil, para propor a tipicidade fenólica e estudar osmecanismos de deterioração dessa peculiar fronteira vinícola. Desse modo, seis vinhos tintos varietais foram obtidos das cultivares de uvas (*Vitis vinifera* L.) Syrah, Tannat, Petit Verdot, Merlot, Malbec e Tempranillo, colhidos no segundo semestre de 2019 na região do SSFV. Todosos vinhos foram elaborados seguindo a vinificação tradicional, sem correções, e aplicando 96 horas de maceração. Syrah é a variedade de uva mais bem adaptada no SSFV, seguida pela Tempranillo; enquanto as outras são cultivadas não comercialmente ou poucos explorados comercialmente. A Tannat é uma variedade de uva que possui alto teor de compostos fenólicos, apresentando coloração intensa, bem encorpada e com grande potencial de envelhecimento, o que a torna uma ótima opção para utilização no SSFV. Este trabalho foi dividido em três capítulos. O primeiro teve como objetivo compilar o conhecimento científico sobre os vinhos tintos do SSFV, no que se refere aos traços sensoriais e químicos, bem como às condições edafoclimáticas e às perspectivas científicas atualmente abordadas no SSFV. O segundocapítulo teve como objetivo caracterizar pela primeira vez a tipicidade fenólica e o potencial antioxidante do vinho Tannat dessa região, comparando-o com o Syrah, a variedade mais adaptada no SSFV. Apesar da maceração de curta aplicação, o vinho Tannat tropical apresentouótimo conteúdo fenólico e atividade antioxidante, destacando-se os compostos *trans*-caftárico, malvidina-3-*O*-glicosídeo e procianidina B1. A Tannat tem potencial para ser uma importante variedade de uva nas regiões vitivinícolas tropicais do Brasil, apresentando altos teores de bioativos e características típicas dessas regiões. Os vinhos das outras variedades foram usados para estudar os mecanismos de deterioração em condições primárias e intervenções de fabricação. Em seguida, o terceiro capítulo teve como objetivo explicar como o alto pH e o curto tempo de maceração influenciam na deterioração física e química dos vinhos tintos. Cor, acetaldeído e SO_2 livre foram usados como indicadores de deterioração, e análises físico- químicas, álcoois superiores, fenólicos totais, antocianinas monoméricas, atividade antioxidante e caracterização fenólica individual foram estudados para ter certeza sobre as viasde influência do pH e maceração sobre a deterioração. O vinho Tempranillo foi a amostra commaior taxa de deterioração, pH e menor cor, antocianinas monoméricas e catequinas. O vinho Petit Verdot foi a amostra

com menor deterioração, tendo também os maiores compostos fenólicos totais, cor, antocianinas, catequinas e atividade antioxidante. O pH teve uma forte correlação com a polimerização de antocianinas e acetaldeído. Os ácidos cafeico e ρ-cumárico foram relacionados às maiores taxas de deterioração, enquanto as catequinas, procianidinas e antocianinas foram relacionadas à atividade antioxidante e maior resistência à oxidação. Apenasvalores elevados de pH podem não ser suficientes para estragar o vinho, pois existem outros parâmetros que podem fornecer estabilidade química, como os compostos fenólicos e sua atividade antioxidante. Assim, os mostos tintos com pH alto podem exigir um tempo de maceração mais longo para melhorar a vida útil desses vinhos.

Palavras-chave: vinhos tropicais; Tannat; mecanismos de deterioração; maceração curta; alto pH.

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1 GENERAL INTRODUCTION

According to Brazilian legislation, wine is a beverage produced from the alcoholic fermentation of sound, fresh, and ripe grape must (BRASIL, 1988). This beverage has cultural, social, and economic values intrinsic to different people, from its origin in the Caucasus to thedissemination of wine production culture to other regions. (AMORIM, 2005). The Sub-middleSão Francisco Valley (SSFV), a region of prominence due to its peculiar edaphoclimatic conditions such as Caatinga biome and semi-arid tropical climate, produces quality wines and allows the cultivation of wine grapes (*Vitis vinifera* L.) throughout the year. (EMBRAPA, 2017).This is the main Brazilian table grape-producing and the first tropical wine-producing region, being an important producer of sparkling and red wines. Its vitiviniculture is developed mainlyby medium and large companies, which settled in the region since 1980 (MELLO, 2018).

The national production of fine wines did not increase in the same way as national consumption, mainly due to high importation. The higher consumption growth of foreign winesin Brazil is due to the low price and great quality of fine wines from neighboring countries, such as Chile and Argentina (OIV, 2018). Also, wine consumption in Brazil was strongly affected by the Covid-19 pandemic, becoming from the 17th to 13th largest wine consumer in 2020, with a positive variation of 18 % in relation to 2019 (OIV, 2021). Then, this intense presence of international wines makes necessary response from the national market, requiring advances in research to obtain a constant evolution in the quality and diversification of productmix by Brazilian wineries (MELLO, 2015). Therefore, studies aiming to evaluate new grape varieties' potential and adaptation in Brazilian wine regions to obtain fine quality wines becomenecessary, even as approaches that establish, explain, and prove the linkage between intrinsic wine traits or techniques applied to deterioration mechanisms.

Syrah is the better-adapted red wine grape to the SSFV region, and one of the five mostcultivated red grapes on the planet (OIV, 2017). However, there are other red grapes of great relevance in the world wine market, such as Tannat, but which have less relevance in the SSFV.Tannat is one of the red grape varieties of *Vitis vinifera* with the highest anthocyanins and otherphenolic compounds concentration, as great antioxidant activity. On the other hand, thegeographical conditions of SSFV may be responsible for enhancing pH in grapes and wines (LEÃO; SOARES, 2009; OLIVEIRA *et al*., 2018), which may be a challenge to

produce wineswith high aging ability. This trait and maceration technique (Alencar *et al*., 2018) may influencethe success of the wine, since their interference on the stability and extraction of phenolic compounds with antioxidant potential. Its import understands how these factors may influencethe spoilage of wine, so granting knowledge to further better solutions to this problem. Then, itis necessary to evaluate the phenolic and antioxidant potential of these wines, to prove the productive versatility of the region, and to study the adaptation of Tannat variety to intensify the use by wineries in the next years, avoiding any problems related to pH.

Thus, this present study has been divided into three chapters. The first one consists of areview compiling scientific knowledge on red wines from the SSFV, regarding sensory and chemical traits, relating the geography, soil, climate, grapevine varieties, interventions, and techniques to the red wines' characteristics. The second chapter aimed to characterize the phenolic typicity and antioxidant activity of Tannat red wines from SSFV. Finally, the last one uses four wines (Petit Verdot, Merlot, Malbec, and Tempranillo) under the same maceration time, but with natural pH, without interference, to investigate their influence on the physical and chemical deterioration mechanisms of red wines.

2 RED WINES FROM THE BRAZILIAN SEMI-ARID REGION: *TERROIR*, CHEMISTRY, SENSORY, AND SCIENTIFIC PERSPECTIVES

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Abstract

Sub-middle São Francisco Valley (SSFV) is the pioneer wine-producing region amongst tropical countries, having requested and filed the first structured Geographical Indication regarding these conditions. Also, red wines have great potential in the SSFV seeing that they have a wide scope for market growth and that red grapes are the main grapes that are adapted to the Valley's geographical conditions. Therefore, this review aims to compile scientific knowledge on red wines from the SSFV, regarding sensory and chemical traits, and both the edaphoclimatic conditions and scientific perspectives currently approached in the SSFV. An extensive literature review has been performed relating the geography, soil, climate, grapevine varieties, interventions, and techniques to the red wines' characteristics. Furthermore, this is the first critical review to approach this content, ensuring knowledge about the quality and growth potential of this new wine frontier.

Keywords: Tropical vitiviniculture. New Geographical Indication. Phenolic compounds. São Francisco Valley.

1. Introduction

Sub-middle São Francisco Valley (SSFV) is a distinct wine region in the Brazilian Northeast, in the States of Pernambuco and Bahia and it has peculiar conditions such as tropicalsemi-arid climate and Caatinga biome. This region is the main Brazilian table grape-producingregion and an important producer of sparkling and red wines. Its grape and wine production arepossible due to the irrigation provided by the São Francisco River, which enabled this area to be the world's pioneer in wine production in a tropical climate. The main countries of the Old-World Wine, for example, Italy, France, Spain, and Portugal; and of the New World Wine, suchas the United States, Argentina, Australia, and Brazil (South region) have the distinguished fourseasons and their vineyards exhibit one vegetative cycle per year. Due to the edaphoclimatic conditions in the SSFV, each vineyard can produce more than one harvest per year, which increases the production capacity and warrants a production schedule (EMBRAPA, 2017). It ispossible to cultivate quality grapes in this region due to the advanced technologies and sciencethat allow high vineyard productivity. Thus, thanks to the SSFV, Brazil participates in a groupof tropical wine-producing countries (EMBRAPA, 2016).

Red wines are the second major SSFV product, only behind sparkling wines. These wines may present typicity such as great alcoholic and phenolic potential, besides intense colorand high astringency, due to the tropical semi-arid climate characteristics (PEREIRA *et al*., 2018). Commonly, red wines are known for “French Paradox”, bringing benefits to human health, because of their chemical composition, consisting mainly of phenolic compounds, such as tannins, resveratrol, and anthocyanins, which may provide high antioxidant activity and prevent diseases (CHEN *et al*., 2019). An approach with extracts of SSFV’ red wines has showna great concentration of phenolic compounds (mainly flavonols), providing hypotension and endothelium-dependent vasorelaxation in hypertensive rats, which confirm this bioactivity (Ribeiro et al., 2016). Furthermore, among the most cultivated grapes on the planet, the majorityare red, and the primary product of these grapes is red wine (OIV, 2017a). Therefore, the greatpotential of red wines in the SSFV is possible because of many factors, such as the increase inwine consumption in Brazil (MELLO, 2018; OIV, 2018), and an increase in the market share of the New World Wines (ANDERSON, 2004; CHEN; KINGSBURY, 2019).

Despite this new wine frontier with a great growth capacity, it is necessary to compile scientific information about all aspects concerning the red wines from the Sub-middle São

Francisco Valley. Furthermore, the scarcity of information about tropical wines explains the necessity of researches on the topic, showing to the population and scientific community about this new geography of wine production, and above all else, about the wines' sensorial andchemical features.

2. New Wine Geography

Wine geography can be divided into Old World and New World: the former consists ofEurope and a few Asian countries, and the latter of all the other wine-producing countries outside of Europe, as those located in America, Asia, Oceania, and Africa. Traditionally, wineis produced in temperate and subtropical regions, located between the 30th and 50th parallels, where the vineyards have one phenological cycle and harvest per year, due to the four well- defined seasons (JOHNSON; ROBINSON, 2008). However, in past decades, some wine regions have emerged, as is the case with the Sub-middle São Francisco Valley. In addition to Brazil, there are many other tropical wine-producing countries, for example, Ecuador, Peru, and Venezuela in South America; Thailand, India, Indonesia, Myanmar, Vietnam, and Bali in Asia; Ethiopia, Gabon, Kenya, Namibia, and Tanzania in Africa and French Polynesia, in Oceania. (EMBRAPA, 2016).

This new wine geography between the Tropics focuses on the possibility of two or moreharvests per year, even with a lot of different climate conditions. There are many climates, suchas the tropical monsoon in Thailand and India; tropical, arid, and warm-temperature regions innorth Peru; tropical altitudes in Bahia and Minas Gerais, and the tropical semi-arid in Pernambuco and Bahia, both in Brazil. (BIROLO; ZANELLA, 2017). Also, to promoteresearch, development, and innovation in the production of tropical wines, public and private institutions from the aforementioned countries come together at events such as the International Symposium on Tropical Wines (ISTW), stimulating interaction and cooperation between theseregions (EMBRAPA, 2016).

The tropical regions may be an important reference to traditional regions in the study ofviticulture in different climate conditions, in addition to investigating future climatic impacts. These changes in the wine industry may be a challenge to producers in the next years, mainly regarding parameters for wine quality, such as alcohol, acidity, pH, and aroma. Furthermore, some solutions already applied by the industry in tropical regions may be used, like drip irrigation, deficit hydric strategies (MOZELL; THACHN, 2014), choice of plant material as varieties, clones (VAN LEEUWEN; DARRIET, 2016), and rootstocks (MARÍN

et al., 2021).

3. Historical Backgroud

Wine has been a part of human culture for a long time, being important to the economy,religion, social status, medicine, and art. Wine history began around 8000 B.C. in the Caucasus,Georgia, between the Black Sea and the Caspian Sea (AMORIM, 2005; JOHNSON, 2009). The Portuguese introduced vineyards in the Brazilian southeast in 1532, and in the northeast in 1549,where they could harvest two times per year, due to the northeastern climate (LEÃO; SOARES,2009). These viticulture practices were actuated by the Dutch invasion in the XVII century, mainly in the Itamaracá Island in Pernambuco (BARLÉU, 2005) and in other parts of the country, because of the Portuguese royal family escape to Brazil and the Italian immigration inthe 19th century (MELLO, 2007; RUGGIERO, 2018).

SSFV wine production began developing around the 1960s when Cinzano Emprise introduced a large-scale grape production in Floresta (Pernambuco State). After that, fine winemanufacturing started in Santa Maria da Boa Vista (Pernambuco State), and Embrapa's Agricultural Research Center of the Semi-Arid Tropics was installed in the region, in 1975 (LEÃO; SOARES, 2009; VITAL, 2009). Partnered with the private initiative, the Center develops research work on the vines, boosting the scientific knowledge on wine.

In the 1990s, some companies settled in Lagoa Grande (Pernambuco), and the producersin this region have invested in grape varieties and technology, with appropriate spaces for grapes, ensuring advancement in the quality of production (LEÃO; SOARES, 2009; PACHECO; SILVA, 2005). In Casa Nova (Bahia), production started in the 1980s, but with major investments in the 2000s. Afterward, plantations of grapevines began in Curaçá (Bahia)and production of wine in Petrolina (Pernambuco). Nowadays, there are five wineries in Pernambuco and two in Bahia, and they correspond to the Sub-middle São Francisco Valley area (PEREIRA *et al*., 2018).

The wine culture expansion in the SSFV took place with the installation, modernization,and expansion of other wineries in this area, in addition to the structuring of the wine industry,with the presence of research and dissemination of scientific knowledge about wine. Therefore,some factors such as land availability, many laborers, and injection of national and internationalcapital have played an important role in the consolidation of wine production in the SSFV. Also, a Geographic Indication, requested in December 2020 (section 4.2), may provide wine quality recognition, elevating the products, and strengthening the

wine culture in this tropical semi-arid region. Thus, the world scientific community and market acceptance may confirm this potential, generating income and developing wine tourism in the SSFV cities (EMBRAPA,2020; PEREIRA *et al*., 2018; VITAL, 2009).

4. Geographic Features and Viticulture Practices

The SSFV is located between the 8th and 9th parallel of the south equatorial plane, including the grape-producing cities Petrolina, Lagoa Grande, Santa Maria da Boa Vista (Pernambuco), and Casa Nova, Juazeiro, and Curaçá (Bahia). This region is flat, having a 350 m altitude, and receives strong influence from the São Francisco River. Furthermore, the tropical semi-arid climate and the proximity to the Equator provide an increase in insolation (average of 3,000 sunny hours year^{-1}) and temperature (average of 26 ºC), a decrease in the thermal amplitude, and prevent the well-defined occurrence of four seasons (EMBRAPA, 2017;PEREIRA *et al*., 2018).

A comparative study between Bebedouro and Mandacaru experimental fields (located in Petrolina, Pernambuco, and Juazeiro, Bahia, respectively) spanning a long period (1965-2009) presented October and November as the driest and warmer months, with averages of 8.6-and 8.8-hours day^{-1} of insolation to Bebedouro and Mandacaru, respectively. Regarding temperatures, monthly averages range from 24.1 to 28 ºC in Bebedouro, with a minimum of 18to 22.1 ºC and a maximum of 29.6 to 34 ºC, whereas the averages to Mandacaru are 24.4 to
28.5 ºC, with a minimum of 18.4 to 22.2 ºC and a maximum of 29.6 to 33.9 ºC. The coldest months, on the other hand, are June and July (TEIXEIRA, 2010).

The annual average of about 60% relative moisture is related to the high vapor-pressuredeficit. This characteristic shall be observed as a quality mark to the SSFV, as it increases the evaporative rates and decreases the possibility of fungal diseases in vineyards. Due to the rainfall, the wettest months are March and April, presenting moisture below 55 % and in agreement with the higher insolation period. The rainy season, between January and April, concentrates 70 % of the annual precipitation, whereas from June to October is the period withalmost no rain. The annual rainfall is 500 mm, the minimum being about 4.3 mm and the maximum approximately 128.4 mm (CAMARGO, GUERRA; PEREIRA, 2011; EMBRAPA, 2017; TEIXEIRA, 2010).

The soil coverage in the SSFV is mostly Latosols, Argisols, and the acid and deep

Quartzarenic Neosols, which are the major soil incorporated into the vineyard productive systems (CUNHA *et al*., 2008). In general, the SSFV soils have high potassium concentrations,which may enhance grape potassium and pH, besides decreasing acidity, due to the reduction of free tartaric acid. When in excess, this essential mineral may present problems to aging ability, due to the potassium bitartrate precipitation and its role in wine instability. Furthermore, the removal of the Caatinga natural coverage may increase the pH in cultivation fields. On theother hand, agronomic strategies have been tested to avoid potassium excess accumulation on berries, like rootstock selection, canopy management, and elements inputting as sulfur and calcium sulfate (BIASOTO *et al*., 2014; PRESTON *et al.*, 2017).

Grape and wine production in the SSFV is possible due to the efficient drip irrigation system from the São Francisco River, making up for the low rainfall and ensuring water availability throughout the year, accelerating the continuous physiological processes (HORA, 2016; TEIXEIRA; BASTIAANSSEN; BASSOI, 2007). Therefore, the geographic features andthis irrigation system are responsible for the possibility to produce grapevines all the year, withshort phenological cycles and resting induced by a hydric deficit. The time interval between thepruning and the harvest lasts between 100 and 130 days and the vineyard rests for about 30 days (TONIETTO *et al.*, 2012). This stage occurs with a water availability reduction between 5% and 10%, because this induces a decrease in the photosynthetic rates, so that vines accumulate reserves, simulating typical winter characteristics. Then, pruning and input application are carried out to stimulate the sprouting of new branches, irrigation is resumed at 100% and a new productive cycle begins (EMBRAPA, 2017).

From May to July and from October to December are the two major harvesting periodsin the SSFV, as they are the driest months in each semester, according to Tonietto *et al*. (2012).These authors use some parameters to assess intra-annual climatic variation, such as the Heliothermic Index (HI), Night Cold Index (CI), and Drought Index (DI). For the values of HIand CI, there is no such significant difference; however, the DI ranges from Moderate Droughtto Strong Drought, in the first and second semesters, respectively.

Oliveira *et al*. (2018) carried out research using Touriga Nacional to evaluate the influence of the harvest season on the chemical and sensorial traits. They used two harvests from the first semester and two from the second semester in different years. In the harvests fromthe first semesters, varietal wines presented higher calcium contents (probably due to the higheruse of agricultural inputs against fungal diseases influenced by the rain), malvidins, and monomeric anthocyanins, floral aromas, besides there is the possibility of a relation

between terpenes synthesis and first-semester climatic conditions. On the other hand, wines from the second semester presented more non-flavonoid compounds and fruity, spicy, herbaceous, and empyreumatic aromas.

As per these conditions, there may be vineyards in all phenological stages in the same area, so the producer can choose the pruning date to avoid harvesting in the rainy season. Furthermore, the winemaker can program harvests in straight weeks due to the usage of the winery structure all year, ensuring to always have young wines on market, avoid seasonal staffin favor of a permanent and specialized team, which ensures lower costs (BIROLO; ZANELLA, 2017).

4.1 Principal red grape varieties

According to Camargo *et al*. (2011), studying cultivars' adaptation is the first step to understandgeographical conditions and to recognize a new wine region. So, these authors carried out a study with 28 varieties found in the Brazilian semi-arid, concluding the best results to be Syrah,Tempranillo, Alicante Bouschet, and Ruby Cabernet, among the red ones. Pereira (2013) presents other important varieties, like Touriga Nacional and Cabernet Sauvignon. Tonietto *et al*. (2012) state Syrah, Tempranillo, Touriga Nacional, and Cabernet Sauvignon as the main cultivars used to still red wines. Therefore, Table 1 shows the traits of the principal red grapevines produced in SSFV.

4.2 Looking for a Geographic Indication

There are two types of Geographic indication in Brazil: the Indicação de Procedência (IP) and the Denominação de Origem (DO), granted by the Instituto Nacional de Propriedade Industrial (INPI). The IP refers to the name of a location that became a reference in certain product fabrication, whereas the DO is more rigorous and corresponds to a location relating thecharacteristics and quality of the product to the producing region (INPI, 2019). Referring to Brazil, there are six IPs and one DO of wine production region registered, but all in the South region (BRASIL, 2019).

The Sub-middle São Francisco Valley currently seeks recognition of the Indicação de Procedência (IP), with a request deposited in December 2020 (EMBRAPA, 2020). The Valleyis the pioneer Geographic Indication structured regarding tropical wines, based on rules of theEuropean Union (EU) and those deposited in the INPI. However, white, rosé, and

red wines, besides *brut*, *demi-sec*, and moscatéis sparkling wines will be permitted to be elaborated from 23 selected grapes *Vitis vinifera* L. from the delimited area. Thus, the cities delimited for the IPrequest are Juazeiro, Casa Nova, Sobradinho and Curaçá, in Bahia, and Petrolina, Lagoa Grande, Santa Maria da Boa Vista and Orocó, in Pernambuco.

Table 1: Principal grape varieties of *Vitis vinifera* L. cultivated in Sub-middle São Francisco Valley.

Grape variety	Origin	Usually cultivated	SSFV relation	Major traits	Other names	References
Syrah	France	France, Australia, Argentina, Chile, USA, and Brazil	The most important and the greater adapted grape, corresponding to 65% of the production of red wines. Also important to the elaboration of wite and rosé sparkling wines	Red intense color, high phenolic compounds concentration, red and black fruit notes	Shiraz	ALENCAR *et al*., 2019; ANDRADE *et al*., 2013; CARVALHO *et al*., 2020; OIV, 2017; WURZ *et al*., 2017.
Tempranillo	Spain	Spain and Portugal	Well adapted	Potent tannins, high alcohol, aromas of cherry, dill, and tobacco	Tinta Roriz and Aragonez	PADILHA *et al*., 2017; PUCKETT; HAMMACK, 2016; TONIETTO *et al*., 2012
Touriga Nacional	Portugal	Portugal, Spain, Australia, USA, and Brazil	Well adapted due to hot climate and good adaptation to large soil variability	High phenolic concentration, intense color, good astringency, and blackfruit aromas	-	OLIVEIRA *et al*., 2018; PRATA-SENA *et al*., 2018; PUCKETT; HAMMACK, 2016; ROBINSON; HARDING; VOUILLAMOZ, 2013
Alicante Bouschet	France	Spain, Portugal, Morocco, Algeria, and Turkey	Well adapted, has the potential to produce young varietal, blended, and aging wines	Intense color and high astringency, alcohol, and phenolic compounds	Garnacha Tintorera	OLIVEIRA *et al*., 2020; PUCKETTE; HAMMACK, 2018; VASCONCELOS *et al*., 2012
Cabernet Sauvignon	France	France, Chile, USA, Australia, Spain, Argentina, Italy, and South Africa	Commercially explored, but not very well adapted	Intense color, typical aromas of black fruit jam, great tannins.	-	OIV, 2017; TONIETTO *et al*.,2012; VINHOVASF, 2007; WURZ *et al*., 2017

Source: Elaborated by the author (2021).

5. Production Data

Brazil produced approximately 2.2 million hectoliters in 2020, according to the estimates from the International Organization of Vine and Wine (OIV, 2020b), not having an absolute production increase in the last 25 years, only a few fluctuations (OIV, 2018). Compared to the largest producer, Italy, Brazilian production is approximately 21 times lower (OIV, 2020b). However, there may be a surprising increase of more than 70% in the production of 2021, due to a record harvest in the Brazilian temperate region (OIV, 2021), perhaps due to the great harvest and increase in consumption. Regarding consumption, Brazil was the 17th largest wine consumer in the world, having a value of approximately 3.3 million hectoliters in 2019 (OIV, 2020a). However, wine consumption in Brazil was strongly affected by the Covid-19 pandemic, becoming the 13th largest wine consumer, with a positive variation of 18 % in relation to 2019 (OIV, 2021). This happened due to social isolation measures and the great growth of wine e-commerce, becoming easier to purchase wine. Furthermore, consumption in Brazil grew 28,7% from 1998 to 2018, probably because of a significant increase of 357% in wine imports in this period (OIV, 2018). According to Mello (2018), imported wines represented around 88% of the Brazil fine wine market in 2017.

The SSFV produces approximately 40,000 hectoliters of wines per year (BIROLO; ZANELLA, 2017). Therefore, according to OIV data (2020b), this production volume may represent between 1.5 % and 2 % of the total Brazilian wine production. Moreover, sparkling wines correspond to about 64 % of the fine wines produced in the SSFV, whereas red wines represent 34 %, the majority being varietal and young, also having blended wines and others with aging potential and oak barrels stage (EMBRAPA, 2016).

6. Chemical and Sensorial Traits

The wine quality is strongly related to the chemical composition, grapes, geographic conditions, and technical details applied in the production. The chemical components are responsible for differences in the sensory perception, besides being indicators of some edaphoclimatic conditions and players of typicity. Concerning the sensorial parameters, sensations received and perceived should be balanced, coherent, and never be disturbed by any artificial sensation presence. Also, the harmony depends on the equilibrium of the principal wine components (FERREIRA *et al.*, 2007; Jackson, 2020).

6.1 Alcohols

Alcohols are organic molecules that have hydroxyls (-OH) at the end of their structures. Ethanol is the major alcohol present in wines and the main compound resulting from alcoholic fermentation. Also, there are other alcohols as the higher alcohols (also known as fusel alcohols), that contribute to a fruity aroma and complexity in low concentrations, and pungent notes in higher contents (DE-LA-FUENTE-BLANCO; SÁENZ-NAVAJAS; FERREIRA, 2016). However, ethanol is especially important to the visual perception of viscosity and tears (NIKOLOV; WASAN; LEE, 2018), equilibrium, microbiological stability, and aging ability (JACKSON, 2020). Moreover, concerning alcohol in-mouth behavior, this component is important to shape body sensation, hotness, and flavor intensity (MORENO-ARRIBAS; POLO, 2009).

The OIV establishes guidelines for member countries aiming to ease international standards and information about the wine. Concerning alcohol, the OIV considers that wines should not have less than 8.5 % of volume, except in particular circumstances, such as geographical conditions, grapevine varieties, or other qualitative factors (OIV, 2015). In these cases, special legislation of the region may allow a minimum alcoholic content of 7 %. In Brazil, the alcoholic graduation of fine dry wines should be between 8.6% and 14% of the total volume, and between 14 % and 16 % to noble wines, expressed in the Gay Lussac degrees at 20º C (BRASIL, 2019).

Red wines from the SSFV have great alcoholic potential due to the high temperatures that may influence sugar contents. Therefore, the alcohol intensity is the main discrepant sensory descriptor between the two harvests, being more intense at the end of the year (TONIETTO *et al*., 2012). The higher moisture in the first semester of the harvest contributes to the dilution of fermentable sugars and reduces the alcoholic strength of the wine. Nevertheless, it is important to mention that alcohol amounts depend on other factors such as winemaker practices, temperature fermentation, and the yeast utilized, whereas the sugar contents in grapes can vary according to the maturation stage of the berries (OLIVEIRA *et al.*, 2019a).

6.2 Sugars

Sugars are organic macromolecules that are essential to the metabolism of living cells, serving as a substrate for energy production and vital functions. Glucose and fructose are the

main sugars present in the ripe grape, being fermented by the yeasts present in the must. However, residual sugars are mostly non-fermentable sugars by yeasts, such as arabinose, rhamnose, and xylose, besides small fractions of unfermented fructose and glucose (MORENO-ARRIBAS; POLO, 2009). Furthermore, sugars are the main substances responsible for the presence of sweetness in wines, also being accentuated by alcohol and glycerol (JACKSON, 2017).

Coelho *et al.* (2018) characterized the sugars of wines from the Brazilian semi-arid. They suggested that wines originated from a semi-arid tropical climate, such as the SSFV climate, may present higher sugar amounts than other wine-producing regions. The authors also reported higher fructose contents than glucose, probably due to the yeast preference. According to Tronchoni *et al.* (2009), *Saccharomyces cerevisiae*, the main yeast used in wine production, primarily metabolizes glucose, resulting in a higher fructose content in the fermented grape.

In addition, as a guideline to OIV members, dry wines, in general, contain a maximum of 4 g L^{-1} of sugars (glucose plus fructose); and medium dry more than 4 and up to 12 g L^{-1}; with both classifications possibly being influenced by the total acidity. Thus, mellow or semi-sweet wines contain between 12 and 45 g L^{-1}; and sweet wines more than 45 g L^{-1} of glucose plus fructose (OIV, 2015). In Brazil, fine wines can be classified into three classes according to the total sugar content: dry 4 g L^{-1}; semi-dry, with values above 4 up to 25 g L^{-1}; and sweet, with amounts greater than 25 and up to 80 g L^{-1}, both express in g L^{-1} of glucose per liter (BRASIL, 2019).

6.3 Organic acids

Organic acids are chemical components capable of transferring H^+ ions into chemical reactions. Such compounds may influence the chemical acidity and the pH, besides the sourness sensation and the microbiological stability of wines (COELHO *et al.*, 2018; LIMA *et al*., 2014; SILVA *et al.*, 2015). Among the main organic acids, the tartaric and the malic acids correspond to 80% of acids in grapes, whereas the succinic and the acetic acids are produced in alcoholic fermentation, and the lactic results from the malic degradation in malolactic fermentation (OLIVEIRA *et al*., 2019a). Acetic acid is the main volatile acid found in wines and is produced by alcohol-fermenting bacterias, indicating the absence of good practices when it is found in high concentrations during manufacturing (JACKSON, 2020).

High temperatures may damage organic acids accumulation due to the ripeness degradation process. As also heat, luminosity, and water availability may support the higher

plant respiratory activity and accelerate the maturation reactions, as organic acids degrade to result in sugars and aromatic compounds (COELHO *et al*., 2018; RIBEIRO; LIMA; ALVES, 2012). Furthermore, some steps in red wine production obligatorily increase the pH, such as maceration and malolactic fermentation (RIBÉREAU-GAYON *et al*., 2006). Therefore, low acidity is understandable in wines from the SSFV, and high pH values are common in red wines (LEÃO; SOARES, 2009; OLIVEIRA *et al*., 2018), demanding, in some cases, agronomic interventions, as described in section 4, and oenological ones, as pH correction with tartaric acid addition.

6.4 Phenolic compounds

Phenolic compounds are substances with a benzene ring bound to hydroxyls as a basic structural principle. These substances act as defense mechanisms against microorganisms or other adverse conditions in plants (PEIXOTO *et al.*, 2018). Also, phenolic compounds are responsible for all the differences between red and white wines due to the visual, olfactory, and gustatory influence (RIBÉREAU-GAYON *et al.*, 2006), such as color and tonality (GABRIELYAN; KAZUMYAN, 2018), aromatic intensity, and complexity (PEREZ-JIMÉNEZ; CHAYA; POZO-BAYÓN, 2019), and astringency and bitterness (LESSCHAEVE; NOBLE, 2005).

Red wines have more phenolic compounds than white or rosé wines, due to the maceration phenolic extraction (RIBÉREAU-GAYON *et al.*, 2006; WOJDYLO; SAMOTICHA; CHMIELEWSKA, 2021). Also, these compounds are related to the red wines aging ability (AGAZZI, 2018; MONAGAS; GÓMEZ-CORDOVÉS; BARTOLOMÉ, 2006) and human cardiovascular diseases reduction (CHASSOT *et al.*, 2018; FABJANOWICZ; PLOTKA-WASYLKA; NAMIÉSNIK, 2018), because of their antioxidant activity. The most interesting phenolic compounds in red wines are flavonoids, such as flavonols, anthocyanins, and flavan-3-ols, and non-flavonoids phenolic acids and stilbenes.

6.4.1 Flavonoids

Flavanols (flavan-3-ols) are the main flavonoids found in wines. The major flavanols are the monomers catechins, epicatechins, and the polymers proanthocyanidins, which are also called condensed tannins (WATERHOUSE *et al*., 2016). Widely known as tannins, these components are responsible for the astringency perception as a result of their reaction with

glycoproteins in saliva, resulting in lubrication loss in the mouth (RIBÉREAU-GAYON *et al.*, 2006; VIDAL *et al*., 2004). Bitterness is also related to tannins, being easily confused with their astringent capacity. During wine aging, there is a decline in the bitterness and astringency of the tannins because of their polymerization capacity (JACKSON, 2020). Furthermore, they also act in the red wine aging ability because of their structure and enzymatic inhibition capacity (MA *et al.*, 2014; RIZZON, 2010).

Catechin and procyanidins B1 and B2 (PADILHA *et al*., 2017), and epicatechins and procyanidin B2 (OLIVEIRA *et al*., 2019d) have been reported as the main flavanols present in commercial red wines and Syrah grapes (seeds and skins) from the SSFV as well. Even in low concentrations, monomeric flavanols can be used as markers of phenolic extraction (WATERHOUSE *et al*., 2016), as well as used to study possible influences of the geographic conditions, grapevines, and rootstocks in the chemical organization of the wine.

Flavonols are present in grape skins and they require sunlight exposure for their synthesis (WATERHOUSE *et al.*, 2016). Quercetin 3-rutinoside (rutin), quercetin, and kaempferol 3-O-glucoside (astragalin) are reported as important flavonols present in red wines from the SSFV (PADILHA *et al*., 2017). In this sense, a comparative study regarding phenolic contents of the South American wines was conducted (BELMIRO; PEREIRA; PAIM, 2017). Syrah wines from the SSFV presented higher individual contents of catechin and quercetin-3-glucoside than Argentinian samples of Syrah wine. Also, the myricetin and quercetin concentrations of Cabernet Sauvignon from the SSFV were higher than the Southern Brazil and Argentina samples. Furthermore, phenolic compounds can distinguish red wines from different geographical origins due to the influence of the *terroir* conditions and due to the biosynthetic pathways followed by grape cells.

Anthocyanins are the principal pigments in wines, are mainly produced in grape skins. All the red wines from *Vitis vinifera* cultivars have malvidins as the most frequent anthocyanin, as they predominantly have the monomer malvidin 3-glucoside in young wines. These components are chemical markers of traceability of grape varieties and *terroirs* due to the biosynthesis pathways influenced by genetic materials and edaphoclimatic conditions, respectively (RIBÉREAU-GAYON *et al*., 2006). Also, anthocyanins' composition may change during winemaking and storage, as they are determinant as a chemical marker to the oxidation process. Furthermore, the change in red wine hue – from red to tawny – over aging occurs through the polymerization and the copigmentation reactions of monomeric anthocyanins (MARQUEZ; SERRATOSA; MERIDA, 2014; SOUZA *et al*., 2018).

An approach comparing anthocyanins in Brazilian and Chilean red wines was conducted

(ANDRADE *et al*., 2013). The Cabernet Sauvignon wines from the SSFV (69.4–179 mg L^{-1}) presented a lower total of anthocyanins contents than the Southern Brazil (94.6–310 mg L^{-1}) and Chilean samples (246 mg L^{-1}), whereas that the SSFV's Tannat (64.3–162 mg L^{-1}) presented lower values than the Southern Brazillian ones (75.2–184 mg L^{-1}), probably due to the warmth, the accumulation of harming pigments in the berries from a less-adapted grape cultivar. On the other hand, these authors showed that the SSFV's Syrah wines (92.1–386 mg L^{-1}) have a higher total of contents than the Chilean wines (74.5–199 mg L^{-1}), which demonstrate a satisfactory adaptation in this *terroir*. Also, wine anthocyanins from the Brazilian semi-arid may follow a different biosynthetic pathway from other regions, which explains why cyanidin-3-glucoside and peonidin-3-glucoside were more representatives to Cabernet Sauvignon and Tannat wines when they are compared to the respective cultivars from other regions. The edaphoclimatic conditions, such as high temperature and soils, can be responsible for these disparities. Therefore, the authors affirm that acetylated and coumarylated anthocyanin forms were higher in the wines from the SSFV.

6.4.2 Non-flavonoids

The main non-flavonoids present in wines is the phenolic acids and the stilbenes. Caftaric, coumaric, caffeic, ferulic, (hydroxycinnamic), and gallic (benzoic) are relevant phenolic acids found in wines, being the first one (caftaric) the major non-flavonoid found in grapes and wines (JACKSON, 2020) and it is reported as the main phenolic acid in wines from the SSFV (DUTRA *et al*., 2018; PADILHA *et al.*, 2019). Regarding the astringent role, these acids - mainly caftaric and caffeic - are susceptible to enzymatic oxidation and browning reactions, as well as to the lactic acid bacterias (LABs) metabolism, being converted into volatile phenols of off-flavors (GIL-SÁNCHEZ; SUÁLDEA; MORENO-ARRIBAS, 2019). Although they are important to color spoilage, these compounds can act as anthocyanin copigments, having positive effects on the stabilization of the wine color (CONSTANTINI; GARCÍA-MORUNO; MORENO-ARRIBAS, 2009).

Regarding stilbenes, some compounds, such as resveratrol and its isomers, piceatannol, and pterostilbene have great marketing appeal to red wines, thanks to their relation with antioxidant activity and potential health benefits. The most important stilbene to red wines is the resveratrol; It is exhaustively studied because of its relation to the reduction of cardiovascular diseases, cancer (CHASSOT *et al*., 2018; FABJANOWICZ *et al*., 2018), and it has antiobesity, antidiabetic, and neuroprotective properties (Reinisalo *et al.*, 2015). The *cis* and

trans forms of resveratrol have different syntheses, being the *trans* form produced by grapes, whereas the *cis* one is obtained from a light-inducing method (WATERHOUSE *et al*., 2016). Moreover, the high amounts of the *cis* form in the red wines from the SSFV can be related to higher sunlight exposure, seeing that the light induces the isomerization of *trans* form produced by the grapes (KATALINIĆ *et al.*, 2010; PADILHA *et al*., 2017).

6.5 Minerals

Minerals are natural elements present in grapes and wines and their contents depend mainly on geographical origin, winemaking techniques (SHIMIZU *et al*., 2020), grape variety, and phytosanitary products (JACKSON, 2020). The main minerals present in red wines are potassium (K), iron (Fe), sodium (Na), copper (Cu), calcium (Ca), magnesium (Mg), aluminum (Al), manganese (Mn), and zinc (Zc). On the other hand, identifiable concentrations of heavy metals such as lead (Pb), cadmium (Cd), and nickel (Ni) must be regulated internationally (WATERHOUSE *et al.*, 2016). These metals can be analyzed in wines through an ash characterization process and also play an important role in wine cleanliness due to the presence of particles, which reflect light in all directions and become visible. According to Rizzon (2010), deposits resulting from pigments and crystals of potassium bitartrate precipitations can be tolerated in aged wines. On the other hand, Jackson (2020) argues that turbidity is considered a defect and names potassium bitartrate, calcium tartrate crystals, and yeasts and bacteria lees as the main particles present in wines.

According to Rizzon (2010), potassium is the most important cation in wines due to its association with wine stabilization. The mineral may behave in wine through the potassium bitartrate precipitation along with tartaric acid, which occurs more commonly in pH values higher than 3.7 (BIASOTO *et al.*, 2014; BOULTON, 1980). As described in section 4, SSFV soils have high potassium concentrations, which are reflected in the wines and cause a stability problem. Then, solutions to adjust pH and potassium can be used in association, as pH correction with tartaric acid during vinification, cold stabilization, and tartaric stabilizer addition, providing better stability to wines in potassium-rich soil and warm regions (KODUR, 2011; MPELASOKA *et al.*, 2003; RIBÉREAU-GAYON *et al*., 2006). Furthermore, Dutra *et al.* (2018) states copper (Cu), iron (Fe), and manganese (Mn) values to organic and conventional Tempranillo and Barbera red wines from SSFV. The Mn mineral was higher to organic samples (1.15 mg L^{-1}) than the conventional ones (0.56 mg L^{-1}).

6.6 Aromatic composition

The wine aroma is produced by various volatile chemical groups, such as esters, aldehydes, terpenes, alcohols, ketones, volatile phenols, and acids. The number of different volatile aromatic compounds present in the wine is related to its chemical complexity (SPENCE; WANG, 2018). This component concentration and type are influenced by biochemical and technological conditions involved in winemaking processes, such as grape variety, edaphoclimatic conditions, metabolism, microorganisms involved, and chemical and enzymatic reactions during grape ripening and wine aging (AYESTARÁN *et al.*, 2019). Regarding olfactory perception, wine aromas can be classified as primary, when are preexisting in the grape; secondary, when they are formed in the fermentation process by microorganisms' action; and tertiary, when they develop throughout aging, resulting from the evolution of primary and secondary aromas (PEYNAUD; BLOUIN, 2010).

Although there are few complex wines in the SSFV, in general, most red wines are young and varietal, presenting typical primary aromas as fruity, which makes them easy to smell (PEREIRA *et al*., 2018). However, the Syrah variety has been reported presenting other primary and secondary aromas, such as fruity, spicy, floral, herbaceous, and empyreumatic aroma (OLIVEIRA *et al*, 2019a; OLIVEIRA *et al*. 2019b; TONIETTO *et al*., 2012). Fruity and floral odors can be related to esters, alcohols, and terpenes, synthesized by yeasts, or to be present in the grape as precursors (MORENO-ARRIBAS; POLO, 2009). Fruity aromas of the SSFV's red wines from esters and alcohols have been reported, enhancing compounds as β-ionone, 2-phenyl ethanol, and 2-methyl-1-butanol to explain aromatic sensations of Syrah wines (PEREIRA; ARAÚJO; SANTOS, 2011). Furthermore, blackberry jam (a black fruit) was disclosed as an important descriptor of Syrah from warm regions (PUCKETTE; HAMMACK, 2016); while in Australia, Syrah presents fruity and spicy descriptors to warm and cold climates, respectively (Geue *et al.*, 2011).

According to Oliveira *et al.* (2018), Touriga Nacional from the SSFV has presented floral aroma mainly in the first semester, whereas it has presented fruity, spicy, and empyreumatic in the second semester (warmer). Black fruit notes are more related to warm climate than red fruit, as described in the 4.1 section. Thus, fruity and other primary aromas can be defined as the main olfactive trait related to red wines from SSFV, regardless of aging or young wines (BIROLO; ZANELLA, 2017), which may establish a typicity of red wines from SSFV.

7. SSFV Scientific Perspectives

As a New World region, SSFV's success depends on the technology employed in vitiviniculture techniques. Therefore, the Semiárido and Uva e Vinho Units of Embrapa and the Federal Institute of Sertão Pernambucano play an important role in enology research, studying manners to make advances and constant evolution in the wine quality, aggregating value and diversifying the product. Concerning red wine quality, the main research developed is maceration types (to enhance phenolic extraction), oak chips, new varieties adaptation (BIROLO; ZANELA, 2017), as well as rootstock influences, fertigation techniques, and harvest seasons effects described in section 4.

Some studies have shown the influence of maceration time in chemical traits of red wines, as the higher phenolic extraction increasing maceration time, however, lengthy maceration may decrease color intensity due to the reduction of monomeric anthocyanins (ALENCAR *et al*., 2018; BARBARÁ *et al.*, 2017; BARBARÁ *et al*., 2019; BARBARÁ *et al.*, 2020; MARQUES *et al.*, 2016). Thermovinification has been reported as a good method of extracting phenolic compounds in red wines (SILVA *et al*., 2019), and the best non-traditional method to phenolic extraction using Touriga Nacional from SSFV, among carbonic maceration and cryomaceration. Furthermore, some studies have shown good results using cryomaceration in white and rosé wines (BARROS *et al*., 2019a; BARROS *et al*., 2019b; BARROS *et al*., 2019c), and may further be used in future studies with red wines.

Oak barrels are commonly used to age wines (mostly red ones) and ensure certain features, like mature tannins, woody aroma, desirable oxidation, complexity, and tertiary aromas. However, their high-cost production is their principal disadvantage, mainly in oak barrel importing countries, like Brazil. Therefore, some alternatives may be employed to replace oak barrels with low-cost barrels, which can be achieved by making barrels with oak chips (MORENO-ARRIBAS; POLO, 2009). In SSFV, studies have been carried out with American and European oak chips under different times and toast stages (ALENCAR *et al*., 2019; ALENCAR *et al*., 2020; Silva *et al.*, 2020).

Some studies have been using Syrah to evaluate variables like rootstocks, harvest season, and or training systems influence (Alves Filho et al., 2019; Carvalho et al., 2020; Nassur, Pereira, Glória, & Lima, 2017; Oliveira et al., 2019b; Oliveira et al., 2019c). Harvest season has been reported as the major SSFV's edaphoclimatic player in wine quality, concerning higher primary metabolites such as tartaric and succinic acids and glycerol (ALVES FILHO *et al*., 2019), and as the lower total acidity and higher total phenolic contents (CARVALHO *et al.*, 2020), both in the second semester.

Furthermore, non-trade-grown or few commercially explored varieties, such as Merlot, Petit Verdot, Malbec, and Tannat have been chosen to be tested regarding their potential to adapt to SSFV edaphoclimatic conditions (NOGUEIRA *et al.*, 2017). These studies are essential to new wine-producing regions, mainly with a tropical climate, because of the continuous adaptation and search for new products.

8. Conclusions

The new wine geography of tropical wines has emerged in the past few years, with exotic edaphoclimatic conditions of different regions and countries. The Sub-middle São Francisco Valley, in Brazil, has shown good potential for producing quality wines due to the scientific and technological development of wineries and research institutions. Therefore, considering current literature, it is possible to comprehend why this region is peculiar under different perspectives, like historic, geographic, chemical, and regarding sensory points of view. On the other hand, production data and excellent adaptation of varieties such as Syrah, Tempranillo, Touriga Nacional, and Alicante Bouschet have shown that red wines are products with important market share and potential to grow, due to their unique traits that may promote good benefits to human health. Furthermore, scientific advances in research and knowledge-producing in enology play an important role in the development of tropical regions and ensure a large enhancement in the quality of products. Thus, good market strategies may turn SSFV more popular, breaking up bias and reaching the Indicação de Procedência.

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3 CHEMICAL TYPICITY OF TROPICAL TANNAT RED WINES FROM SUB-MIDDLE SÃO FRANCISCO VALLEY, BRAZIL

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Abstract

Tannat is a *Vitis vinifera* cultivar with typically high phenolic compound contents, showing intense coloration, well-bodied, and great aging potential. However, even with this great potential, this variety is still commercially underexplored in the Sub-middle São Francisco Valley (SSFV). This work aimed to characterize the typicity of Tannat red wines from Sub-middle São Francisco Valley (SSFV), Brazil. In addition, the present work represents the first study featuring phenolic compounds quantification and antioxidant activity of Tannat in tropical climate wine-producing regions. Considering the condition of a short-applied maceration time during the winemaking, the tropical Tannat wine showed significant antioxidant activity and high phenolic contents. *Trans*-caftaric, malvidin-3-*O*-glucoside, and procyanidin B1 stood out among the phenolic compounds quantified, presenting Tannat with the potential to be an important grape variety to tropical wine-producing regions in Brazil, containing high contents of bioactive compounds. Previously results to compounds (-)-epigallocatechin gallate, procyanidin B2, quercetin-3-β-D-glucoside, pelargonidin-3-*O*-glucoside, chlorogenic acid, and piceatannol were not found in Tannat wines. Further studies are necessary to make the Tannat grape's adaptation better in tropical climate conditions, including investigating the phenolic profile and antioxidant activity of Tannat red wines with longer maceration times during the winemaking.

Keywords: tropical viticulture, phenolic compounds, bioactive compounds, HPLC-DAD-FD, *in vitro* antioxidant activity.

1. Introduction

Sub-middle São Francisco Valley (SSFV) is a recent wine-producing region in Northeast Brazil, with a tropical semi-arid climate and Caatinga biome, without the traditional well-defined occurrence of four seasons. Then, the terroir is composed of geographic characteristics such as high insolation (3,000 sunny hours $year^{-1}$), low annual rainfall (500 mm), high average temperature (26 ºC), relative moisture of 60 %, and altitude of 350 m (EMBRAPA, 2017). These features associated with the irrigation system and applied intervention technologies in the vineyard, permit more than two harvests per year and the production of full-bodied red wines, with a high concentration of phenolic compounds and values of antioxidant activity (ALVES FILHO *et al.*, 2019). Syrah is the most commercially important wine grape to SSFV, however, few commercially explored grape varieties may present adaptation and growth potential, such as Tannat. This cultivar is one of the red grape varieties of *Vitis vinifera* with the highest anthocyanins and other phenolic compounds concentration, traits great to blend with other wines, enhancing the phenolic profile and antioxidant activity, as well as, sensory complexity, providing mainly more color intensity, structure, body, and aging potential to the beverage (VARELA; GÁMBARO, 2006). This French variety is the principal grape of Uruguayan viticulture, which makes it known as the emblematic wine of Uruguay.

Extraordinary values of phenolics have been reported to Tannat, as total phenolic contents of 4,410 mg GAE L^{-1} (PAZZINI *et al.*, 2015), while in general the mean of total phenolics in red wines around 2,000 mg GAE L^{-1} (WATERHOUSE *et al.*, 2016). Also, the name of Tannat is derived from the word “tannin”, due to its richness in phenolic compounds, which provide health benefits for the consumers and outstanding sensorial traits, such as color, structure, body, and stability (VARELA; GÁMBARO, 2006; VIDAL *et al.*, 2018; WATERHOUSE *et al.*, 2016). The phenolic compounds in red wines, both flavonoids (flavonols, monomeric flavanols and tannins, and anthocyanins), and non-flavonoids (phenolic acids and stilbenes), may be related to high antioxidant capacity and cardiovascular disease reduction. Therefore, the phenolic composition is an important parameter of red wines, especially in new regions. Then, this helps in understanding the geographic contribution of the region and provides the necessary knowledge to those producers to make decisions concerning new products potential and possible agronomic and oenological interventions.

Considering the possible projection that Tannat may assume, this research aimed to analyze, for the first time, the phenolic typicity and antioxidant potential of Tannat to produce tropical red wines in Sub-middle São Francisco Valley, Brazil, by comparing it with Syrah, the better-adapted variety in this region.

2. Material and methods

2.1 Raw material

Tannat and Syrah grapes were collected from vineyards diagrammed in Vertical Shoot Position (VSP) training system, rootstock Paulsen 1103, and irrigated per drip scheme. Tannat vineyards were planted in 2000, in the Mandacaru experimental vineyard at Juazeiro, Bahia, Brazil (latitude: 9º 24' S, longitude 40º 26' W, height 375.5m). Pruning was performed on July 29th, 2019, and grapes were harvested on December 9th, 2019, about 133 days after pruning (DAP). Syrah vineyards were planted in 2013, in Bebedouro, an experimental field at Petrolina, Pernambuco, Brazil (latitude: 9º 9' S, longitude 40º 22' W, height 365.5m). Pruning was carried out on August 9th, 2019, and the grapes were harvested on December 10th, 2019, with about 123 days DAP. Tannat (51 kg) and Syrah (49 kg) were received and processed on the same day in the Laboratory of Enology of Embrapa Semiárido, Petrolina, Pernambuco, Brazil.

2.2 Winemaking

Potassium metabisulfite (0.1 g L^{-1}, Synth, São Paulo, Brazil), pectinolytic enzyme (0.03 g L^{-1} Endozym rouge, AEB – Brescia, Italy), dry yeasts (0.2 g L^{-1}, Saccharomyces cerevisiae bayannus – Mauvirim PDM, Amazon Group, Monte Belo do Sul, RS, Brazil), and fermentation activator (0.2 g L^{-1}, Gesferm plus, Amazon Group) were applied as enological inputs.

Initially, the grapes were weighed, destemmed, and treated with potassium metabisulfite and enzyme. Then, the musts were placed in 20 L glass bottles, capped with glass valves of Müller airlock-type. Subsequently, the yeasts were inoculated to start the alcoholic fermentation (AF) under a controlled temperature of 24 ± 2ºC. AF and maceration evolution were monitored daily with density using an electronic hydrostatic balance (Super Alcomat, Gibertini, Milano, Italy). The wine pressing was performed after 96 hours and AF completion (approximately 10 days) was determined with constant density lower than 0.999, confirmation of the alcoholic grade (≥ 11.6 % v/v), and total reducing sugars content (≤ 2.7 g L-1). The spontaneous malolactic fermentation was conducted at 18 ± 2 ºC until all malic acid was converted to lactic acid. Its completion was determined through chromatography of malic acid paper. The stabilization was performed with cold storage (0 ºC) for 20 days and with the addition of 400 mg L^{-1} of a mixture of the arabic gum with the metatartaric acid stabilizer Stabigum® (AEB Group, Viseu, Portugal). The free sulfur dioxide content of the wines was adjusted to 50 mg L^{-1}. The wines were bottled (750 mL), corked, and stored in the cellar at 18 ºC for six months until the analysis was accomplished.

2.3 Oenological classic parameters – physicochemical and color analyses

Classic oenological parameters of wines were determined by pH, using pHmeter (Hanna PAT. CPNQ Edge, Romênia); titratable acidity (TA) using NaOH 0.1 N as titrator, pH 8.2 as the turning point and expressing the result in tartaric acid (g L^{-1}); volatile acidity determined for steam distillation, using oenological distiller (Super Dee – Gibertini, Milano, Italy) and results expressed in acetic acid (g L^{-1}); density and dry extract using an electronic hydrostatic balance (Super Alcomat, Gibertini, Milano, Italy), expressed in g mL^{-1} and g L^{-1}, respectively; alcohol content percentage using the same oenological distiller and electronic hydrostatic balance (OIV, 2021). Total reducing sugars were determined using the Eynon Lane titratable method and the results were expressed in g L^{-1} (RIBÉREAU-GAYON *et al.*, 1980). Total phenolic index (TPI) was also performed (HARBERTSON; SPAYD, 2006), using a UV-Vis spectrophotometer (Thermo Fisher Scientific Oy Ratastie 2, FI-01620 Vantaa, Finland), at 280 nm wavelengths.

The wine's color intensity (CI) was determined by the sum of the readings in the wavelengths 420, 520, and 620 nm using a spectrophotometer (Thermo Fisher Scientific Oy Ratastie 2, FI-01620 Vantaa, Finland) and the tonality by the reason among the readings in the 420 and 520nm (GLORIES, 1984). The color was performed in the colorimeter (HunterLab ColorQuest-XE, Virginia, USA) coupled with EasyMatch QC 4.81 software, in the transmittance mode, excluded specular, illuminant D65 and 10º observer angle (CIE, 2004), using the CIELab and CIEL*C*h systems, to determine L* (luminosity), a* (red-green coordinate), b* (yellow-blue coordinate), C* (Chroma), and h (hue angle).

2.4 Bioactive contents – total phenolic and total monomeric anthocyanins

The content of total phenolic compounds was determined following Rufino *et al.* (2010). The content of phenolic compounds was quantified by reading the absorbance at 700 nm wavelengths in a spectrophotometer (Shimadzu Corporation, UV-1800, Japan), expressing results in mg L^{-1} of the gallic acid equivalent of wine (mg GAE L^{-1}). Monomeric anthocyanins were determined according to buffer solutions (pH 1.0; 4.5) method (LEE; DURST; WROLSTAD, 2005), and the readings were performed at 520 nm and 700 nm in a spectrophotometer (Shimadzu Corporation, UV 1800, Japan).

2.5 Quantification of individual phenolic compounds by HPLC-DAD-FD

The phenolic compounds were quantified by High-Performance Liquid Chromatography (HPLC-DAD-FD), according to methods validated under the same analytical conditions (DA COSTA *et al.*, 2020; NATIVIDADE *et al.*, 2013), using a chromatograph (Waters model Alliance e2695, USA) coupled simultaneously to the Diodes Array Detectors - DAD (280, 320, 360, and 520 nm) and Fluorescence – FD (280 nm excitation and 320 nm emission), Gemini-NX C18 analytical column (150mm x 4.60mm x 3µm) and the Gemini-NX C18 security guard cartridge (4.0mm x 3.0mm), both from Phenomenex (Torrance, USA). 28 phenolic compounds were quantified in wines: malvidin-3-O-glucoside, cyanidin-3-O-glucoside, petunidin-3-O-glucoside, delphinidin-3-O-glucoside, peonidin-3-O-glucoside, and pelargonidin-3-O-glucoside (anthocyanins), gallic, caffeic, trans-caftaric, chlorogenic, ρ-cumaric and ferulic acids (phenolic acids), quercetin 3-β-D-glucoside, rutin, myricetin, kaempferol-3-O-glucoside and isorhamnetin-3-O-glucoside (flavonols), trans-resveratrol, cis-resveratrol, and piceatannol (stilbenes), (+) - catechin, (-) - epicatechin, (-) – epigallocatechin gallate, (-) - epicatechin gallate, procyanidins A2, B1 and B2 (flavanols and condensed tannins). Employing gradient elution, the mobile phase consisted of a 0.85% solution of orthophosphoric acid (Fluka, Switzerland) in ultra-pure water (Purelab Option Q Elga System, USA) as phase A, and acetonitrile HPLC grade (J. T. Baker, USA) as phase B, totaling 60 minutes of running. The oven temperature was maintained at 40°C and the flow at 0.5 mL min-1. The wine was injected without dilution in the equipment, after filtration in a 13 mm diameter nylon membrane and 0.45 µm pore size (Phenomenex®, USA), using 10 µL per sample as the injection volume.

The ferulic acid standard was obtained from ChemService (West Chester, USA). The caffeic, trans-caftaric, ρ-coumaric, chlorogenic and gallic acids, and piceatannol were acquired from Sigma-Aldrich (USA). The (-)-epicatechin gallate, (-)-epigallocatechin gallate, (+)-catechin, (-)-epicatechin, procyanidins A2, B1, B2, kaempferol-3-O-glucoside, quercetin 3-β-D-glucoside, isorhamnetin-3-O-glucoside, rutin, malvidin-3-O-glucoside, petunidin-3-O-glucoside, peonidin-3-O-glucoside, pelargonidin-3-O-glucoside, delphinidin-3-O-glucoside, and trans-resveratrol standards were obtained from Extrasynthese (France); and the cis-resveratrol was acquired from Cayman Chemical (Michigan, USA).

2.6 Antioxidant capacity

The *in vitro* antioxidant capacity was determined using the FRAP and ABTS methods, following Rufino *et al*. (2010). FRAP (ferric reduction method) readings were performed with 595 nm and results were expressed in mmol ferrous sulfate L^{-1} of the sample. ABTS (2,2-azino-bis (3-eth- ylbenzthiazoline-6-sulphonic acid)) results were expressed in mmol Trolox

Equivalent Antioxidant Capacity (TEAC) L^{-1} of the sample, with readings at 743 nm. Both analyses used a spectrophotometer (Shimadzu Corporation, UV-1800, Japan).

2.7 Statistical analysis

Each replicate of vinification of the Tannat and Syrah red wines was analyzed using three different bottles in triplicate. All data were evaluated by the analyses of variance (one-way ANOVA) using the R Studio Desktop program (1.4.1106 version, Boston, USA) to statistically certify the equality or differences among the results ($p \leq 0.05$). Shapiro-Wilk, Levene, and Student's t-Test ($p \leq 0.05$) were applied to test the means' normality, variance homogeneity, and the comparison, respectively.

3 Results and discussion

3.1 Wine musts parameters

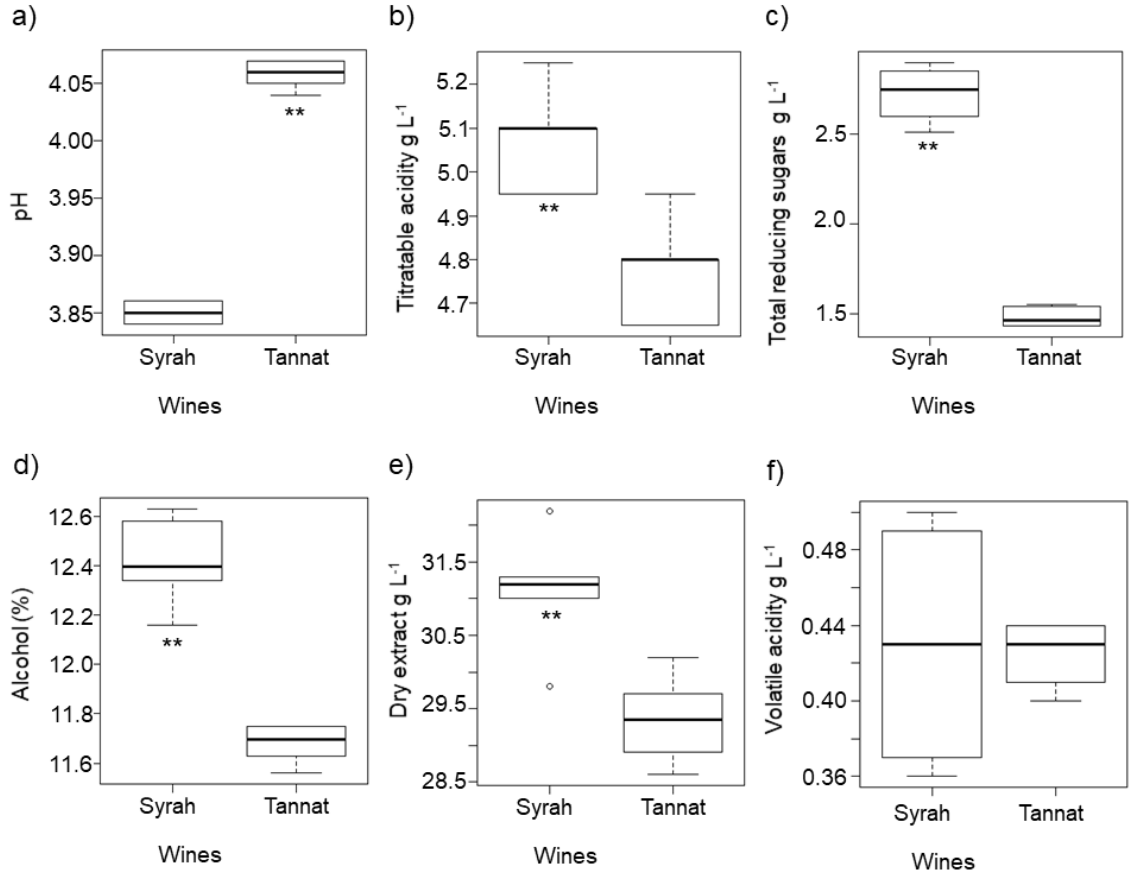
Tannat and Syrah musts presented 3.71 and 3.70 of pH; titrable acidity (TA) of 5.80 and 6.90 g L^{-1}; 1.0890 and 1.0965 g cm^{-3} of density; soluble solids of 21.34 and 23.03 ºBrix; 212.94 and 225.76 g L^{-1} of reducing sugars.

3.2 Classic parameters

The results of the classic parameters are presented in Figure 1. All quality parameters (total acidity, total reducing sugars, alcohol, and volatile acidity) are following Brazilian current legislation to table dry wines (BRASIL, 2004; BRASIL, 2010). The pH and titratable acidity (TA) presented consistent and inversely proportional results, that is, 4.06 and 3.85 for pH; 4.77 and 5.07 g L^{-1} for TA, concerning Tannat and Syrah, respectively. According to the literature, typical values of pH and TA in red wines ranged 3.3-3.7 and 5-8 g L^{-1}, respectively (JACKSON, 2014; WATERHOUSE *et al*., 2016). Uruguayan commercial Tannat wines were reported with a pH of 3.39 (VALENTIN *et al*., 2020). Also, these authors presented similar pH results for Uruguayan Tannat (3.39), Argentinian Malbec (3.37), Chilean Carménère (3.38), and Brazilian (Southern) Merlot (3.37) wines, which may indicate few influences of the grape variety in the pH values. Thus, this parameter is possibly more influenced by the similarities of climatic conditions of these regions and distinct from tropical climate regions, as the Sub-middle São Francisco Valley (SSFV).

Figure 1: Physicochemical analyses of tropical Tannat and Syrah red wines from Sub-middle São Francisco

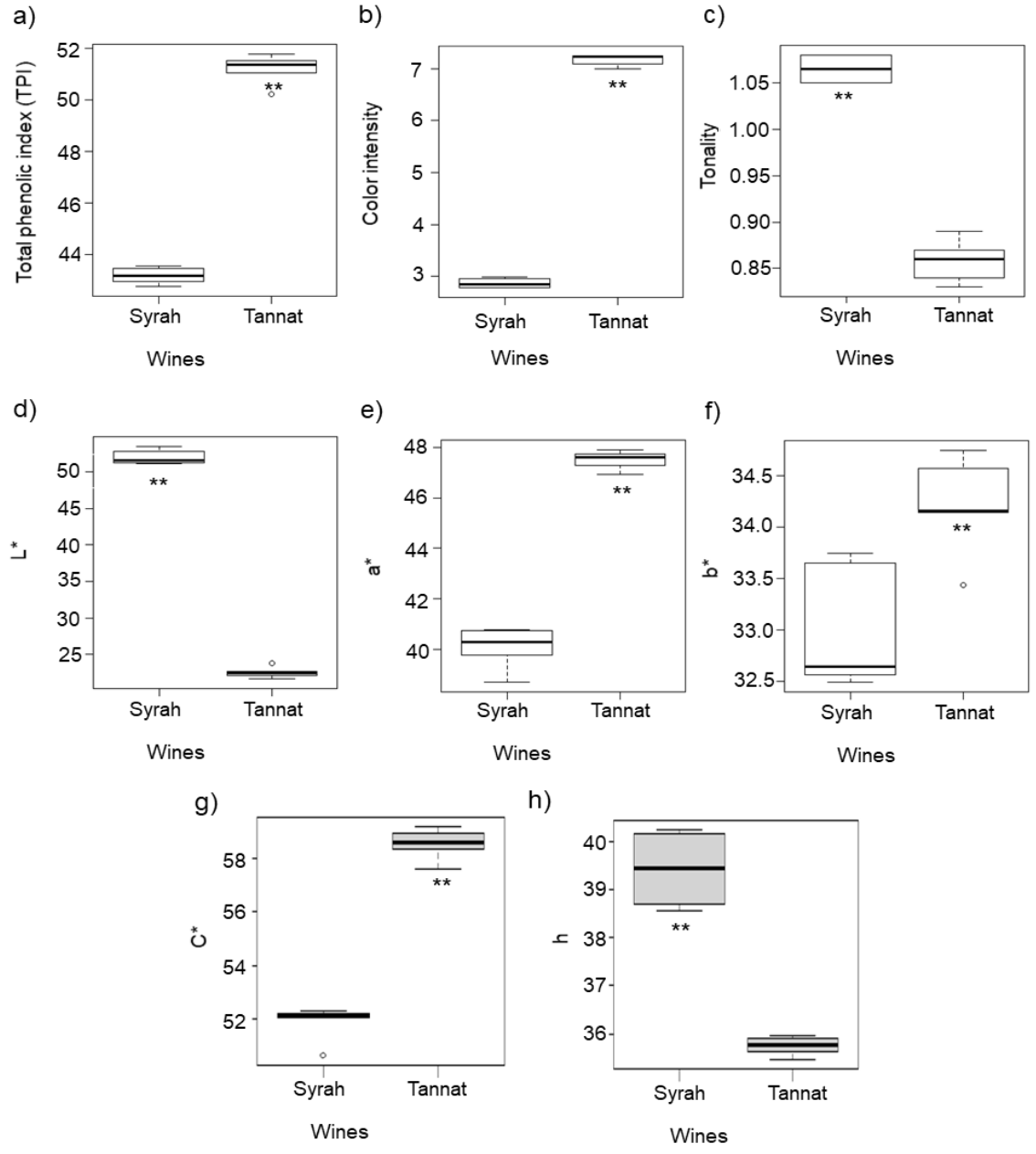
Valley, Brazil.



Means with asterisks differ by Student's T-Test '*' ($p \leq 0.05$) '**' ($p \leq 0.01$).

Thus, in SSFV the intense temperature and sunlight exposure, and the high levels of potassium in the soil (ALBUQUERQUE *et al*., 2009, OLIVEIRA *et al*., 2018) may be responsible for the high pH and low acidity obtained in the Tannat and Syrah red wines (Figure 1). The heat may increase plant respiratory activity and maturation reactions, harming the organic acid accumulation. Furthermore, in this present research, these climatic conditions are related to the phenological shorter cycle of grapes (133 DAP to Tannat), compared with temperate wine-producing regions, which have the four seasons well-defined and grapes' harvest once per year. Additionally, the high potassium in soil enhances the potassium in the wine, decreasing free tartaric acid by the precipitation with potassium forming potassium bitartrate, and consequently decreasing acidity and increasing the pH of the beverage (OLIVEIRA *et al*., 2018).

Figure 2: Total phenolic index and color measurements of tropical Tannat and Syrah red wines from Sub-middle São Francisco Valley, Brazil.



Means with asterisks differ by Student's T-Test '*' ($p \leq 0.05$) '**' ($p \leq 0.01$).

Color intensity (CI) and TPI results were consistent with each other (Figure 2). As expected, Tannat presented considerably higher levels of CI and TPI than Syrah, due to the varieties' traits. Also, lower luminosity and higher chromaticity (Figure 2d and 2g, respectively) confirm Tannat's stronger color depth, while a* and b* showed the lower feature of redness and yellowness of Syrah. In complement, the hue angle (h) shows Tannat closer to redness than Syrah. However, lower values of L* (16.67) in commercial Tannat wines (VALENTIN *et al.*, 2020) and higher levels of CI (around 9.5 – 20.5) (GONZÁLEZ-NEVES *et al*., 2014) in experimental Tannat wines with 8 days of maceration (192h), were reported. These results indicate that higher maceration time during the winemaking possibly will be induced to the major extraction of pigments and intensity of color in the Tannat wine from the SSFV.

3.3 Phenolic compounds

Table 2: Phenolic compounds in Tannat and Syrah tropical red wines from Sub-middle São Francisco Valley, Brazil.

Phenolic Compounds (mg L^{-1})[1,2]	**Tannat wine**	**Syrah wine**
Flavanols		
(+)-Catequin	11.94 ± 0.69 **	9.79 ± 0.56
(-)-Epicatechin	8.04 ± 0.82	6.95 ± 1.41
(-)-Epicatechin gallate	2.44 ± 0.47	2.25 ± 0.16
(-)-Epigallocatechin gallate	3.07 ± 0.52	4.77 ± 0.18 **
Procyanidin A2	2.23 ± 0.62 **	1.09 ± 0.28
Procyanidin B1	28.95 ± 1.15 **	12.14 ± 0.21
Procyanidin B2	9.17 ± 0.49 **	6.04 ± 0.17
Total flavanols	65.84 ± 3.71 **	43.03 ± 1.94
Flavonols		
Kaempferol-3-*O*-glucoside	0.97 ± 0.09	3.25 ± 0.44 **
Quercetin 3-β-D-glucoside	4.66 ± 0.17	25.74 ± 1.29 **
Isorhamnetin-3-*O*-glucoside	2.44 ± 0.18	15.35 ± 0.92 **
Myricetin	0.56 ± 0.04	0.52 ± 0.05
Rutin	1.11 ± 0.03	1.1 ± 0.16
Total flavonols	9.74 ± 0.3	45.96 ± 2.71 **
Anthocyanins		
Malvidin-3-*O*-glucoside	72.49 ± 1.22 **	18.07 ± 0.6
Pelargonidin-3-*O*-glucoside	7.37 ± 0.17 **	0.56 ± 0.02
Cyanidin-3-*O*-glucoside chloride	0.3 ± 0.04	0.21 ± 0.01
Delphinidin-3-*O*-glucoside	2.13 ± 0.06	ND
Petunidin-3-*O*-glucoside	0.84 ± 0.03 **	0.49 ± 0.02
Peonidin-3-*O*-glucoside	0.94 ± 0.0377	1.47 ± 0.03 **
Total anthocyanins	84.07 ± 1.43 **	20.8 ± 0.65
Phenolic acids		
Gallic acid	11.77 ± 0.42 **	6.15 ± 0.29
Ferulic acid	0.33 ± 0.01	0.59 ± 0.01 **
ρ-Coumaric acid	4.38 ± 0.17	21.11 ± 0.8 **
Caffeic acid	8.31 ± 0.21	25.77 ± 0.45 **
Trans-caftaric acid	298.78 ± 1.42	523.69 ± 4.24 **
Chlorogenic acid	0.83 ± 0.04	0.94 ± 0.07 **
Total phenolic acids	324.40 ± 4.7 **	578.25 ± 4.83 **
Stilbenes		
Trans-resveratrol	0.27 ± 0.01	0.29 ± 0.01 **
Cis-resveratrol	0.46 ± 0.01	0.63 ± 0.01 **
Piceatannol	0.37 ± 0.01 **	0.29 ± 0.01
Total stilbenes	1.10 ± 0.01	1.21 ± 0.01 **
Total phenolic compounds[3]	1,212.87 ± 57.98 **	596.85 ± 33.85 **

Total monomeric anthocyanins[4]	151.54 ± 5.3 **	69.08 ± 5.43 **

[1]Means followed by asterisks differ by Student's T-Test '*' ($p \leq 0.05$) '**' ($p \leq 0.01$). [2]ND = not detected. [3]Total phenolic compounds result expressed in mg GAE L^{-1}, using the spectrophotometric method and Folin Ciocateau reagent (Rufino et al., 2010). [4]Total monomeric anthocyanins result expressed in malvidin-3-*O*-glucoside mg L^{-1}, as in Lee, Durst, & Wrolstad (2005).

3.3.1 Flavanols

The monomeric flavanols and proanthocyanidins (condensed tannins) contents of the red wines analyzed are shown in Table 1, where the total quantified varied from 43.02 to 65.83 mg L^{-1} for Syrah and Tannat wines, respectively. Significant differences were observed in most compounds. The monomeric flavanols and proanthocyanidins quantified in the greatest composition were procyanidin B1, followed by (+)-catechin, and procyanidin B2. Tannat presented higher values to (+)-catechin (11.94 mg L^{-1}), procyanidin A2 (2.23 mg L^{-1}), procyanidin B1 (28.95 mg L^{-1}), and procyanidin B2 (9.17 mg L^{-1}), except for (-)-epigallocatechin gallate, that Syrah presented higher content (4.77 mg L^{-1}).

Valentin *et al.* (2020) characterized phenolics of 14 commercials Uruguayan Tannat wines, obtaining (+)-catechin (20.19 mg L^{-1}), and (-)-epicatechin (19.1 mg L^{-1}) as the flavanols quantified (Table 2). These contents were higher than presented in this research, probably due to the low maceration time applied (96 hours), which justifies lower values herein presented. Young red wines are commonly pressed after five days (120h) of maceration during alcoholic fermentation (JACKSON, 2014). In this sense, surprising contents of (+)-catechin (43 mg L^{-1}) and (-)-epicatechin (65 mg L^{-1}), in Tannat wines from Southern Uruguay, with 15 days of maceration were reported (BOIDO *et al*., 2011). Phenolic data from Syrah musts from SSFV evaluated every 5 days during 30 days of maceration have been reported (ALENCAR *et al*. 2018). With 5 days of vinification, only (-)-epigallocatechin gallate (5.6 mg L^{-1}) presented higher values than Syrah and Tannat wines from the present research, whereas (+)-catechin (4.5 mg L^{-1}), (-)-epicatechin (1.0 mg L^{-1}), (-)-epicatechin gallate (6.2 mg L^{-1}), procyanidin A2 (0.3 mg L^{-1}), procyanidin B1 (3.4 mg L^{-1}), and procyanidin B2 (4.6 mg L^{-1}) presented lower values.

(-)-Epicatechin and procyanidin B2 were reported as the principal flavanols presented in skins and seeds of Syrah grapes in SSFV (OLIVEIRA *et al.*, 2019). Also, procyanidin B2 and, procyanidin B1 as (+)-catechin were reported as the major flavanols present in commercial *Vitis vinifera* red wines from this region (PADILHA *et al*., 2017). The finding procyanidin B1 content presented surprising results in the Tannat tropical wine. A Uruguayan Tannat approach has shown a strongly lower value (0.61 mg L^{-1}) to procyanidin B1 (FAVRE *et al*., 2014), in comparison with the Tannat from SSFV (28.95 mg L^{-1}). Procyanidins, such as B1 and B2, are strongly related to astringency perception (Waterhouse et al., 2016) and antioxidant activity in

SSFV red wines (ALENCAR *et al*., 2018).

3.3.2 Anthocyanins

Table 2 provides the monomeric anthocyanins amounts. Total anthocyanins by HPLC-DAD-FD presented a huge difference between the varieties, being 84.07 mg L^{-1} to Tannat and 20.80 mg L^{-1} to Syrah wines. In agreement, Tannat presented quite higher total monomeric anthocyanins quantified by spectrophotometry method than Syrah, about 151.54 and 69.08 mg L^{-1}, respectively. These results presented the same behavior as CI, TPI, and colorimetry, with Tannat having a deeper color, shown in Figure 2. Also, anthocyanins have been reported with inversely proportional behavior relating to L, and direct relation with a*, the reddish coordinate (CASTRO *et al.*, 2021). In an approach with Uruguayan red wines, Tannat also presented higher total monomeric anthocyanins than Syrah (GONZÁLEZ-NEVES *et al*, 2016).

Regarding individual anthocyanins, Tannat showed greatly higher results than Syrah to malvidin-3-*O*-glucoside (72.49 mg L^{-1}), pelargonidin-3-*O*-glucoside (7.37 mg L^{-1}), cyanidin-3-*O*-glucoside (0.3 mg L^{-1}), and petunidin-3-*O*-glucoside (0.84 mg L^{-1}); and delphinidin-3-*O*-glucoside (2.13 mg L^{-1}), while only peonidin-3-*O*-glucoside were higher to Syrah red wines (1.47 mg L^{-1}). The behavior of these results agrees with data reported to Uruguayan Tannat and Syrah wines (GONZÁLEZ-NEVES *et al*., 2016), showing delphinidin-3-*O*-glucoside (11.8 and 3.3 mg L^{-1}), cyanidin-3-*O*-glucoside (0.9 and 0.8 mg L^{-1}), malvidin-3-*O*-glucoside (143.0 and 137.3 mg L^{-1}), petunidin-3-*O*-glucoside (23.4 and 8.2 mg L^{-1}), and peonidin-3-*O*-glucoside (6.7 and 8.5 mg L^{-1}). In both samples, only the peonidin-3-*O*-glucoside was higher in Syrah wines, and malvidin-3-*O*-glucoside was the most abundant anthocyanin.

Table 3: Comparative results of the quantification of phenolic compounds in tropical Tannat red wine from Sub-middle São Francisco Valley, Brazil, and Tannat red wines from other wine-producing regions.

Phenolic Compounds[1]	**Brazilian Tannat wines**		**Uruguayan Tannat wines**			
	SSFV[2]	DE ANDRADE *et al* (2013)[3]	VALENTIN *et al* (2020)	VIDAL *et al* (2018b)	BOIDO *et al* (2011)	FAVRE *et al*, 2014)
Flavanols						
(+)-Catequin	11.94 ± 0.69	-	20.19 ± 1.94	48.8 ± 13.7	43 ± 6	0.80 ± 0.16
(-)-Epicatechin	8.04 ± 0.82	-	19.10 ± 1.20	36.3 ± 14.9	65 ± 7	-
(-)-Epicatechin gallate	2.44 ± 0.47	-	-	4.7 ± 2.4	-	-
(-)-Epigallocatechin gallate	3.07 ± 0.52	-	-	-	-	-
Procyanidin A2	2.23 ± 0.62	-	-	-	-	-
Procyanidin B1	28.95 ± 1.15	-	-	-	-	0.61 ± 0.02

Procyanidin B2	9.17 ± 0.49	-	-	-	-	-
Procyanidin-dimmer-B3	-	-	-	-	-	1.48 ± 0.42
Procyanidin-dimmer-C1	-	-	-	-	-	1.49 ± 0.05
Flavonols						
Kaempferol-3-*O*-glucoside	0.97 ± 0.09	-	3.86 ± 0.40	-	-	-
Quercetin 3-β-D-glucoside	4.66 ± 0.17	-	-	-	-	-
Isorhamnetin-3-*O*-glucoside	2.44 ± 0.18	-	-	2.7 ± 1.9	-	-
Myricetin	0.56 ± 0.04	-	16.18 ± 1.49	5.0 ± 3.3	-	-
Rutin	1.11 ± 0.03	-	6.70 ± 0.58	-	-	-
Quercetin	-	-	7.21 ± 0.69	3.0 ± 2.1	-	1.60 ± 0.13
Anthocyanins						
Malvidin-3-*O*-glucoside	72.49 ± 1.22	8.34–86.5	56.31 ± 6.94	70.7 ± 48.5	470 ± 36	-
Pelargonidin-3-*O*-glucoside	7.37 ± 0.17	-	-	-	-	-
Cyanidin-3-*O*-glucoside	0.3 ± 0.04	7.14–7.99	1.80 ± 0.26	0.9 ± 0.8	14 ± 1	-
Delphinidin-3-*O*-glucoside	2.13 ± 0.06	6.32–16.4	6.03 ± 0.65	5.3 ± 4.4	98 ± 8	-
Petunidin-3-*O*-glucoside	0.84 ± 0.01	14.8–18.2	6.73 ± 0.89	13.7 ± 10.9	106 ± 13	-
Peonidin-3-*O*-glucoside	0.94 ± 0.04	6.49–14.6	8.48 ± 1.27	5.4 ± 4.4	27 ± 3	-
Phenolic acids						
Gallic acid	11.77 ± 0.42	-	15.20 ± 1.65	84.1 ± 38.9	86 ± 11	5.13 ± 0.48
Ferulic acid	0.33 ± 0.01	-	2.93 ± 0.29	-	-	-
ρ-Coumaric acid	4.38 ± 0.17	-	-	92.0 ± 32.2	30 ± 22	-
Caffeic acid	8.31 ± 0.21	-	6.46 ± 0.56	-	-	-
Cis-caftaric acid	-	-	-	110.0 ± 45.0	-	-
Trans-caftaric acid	298.78 ± 1.42	-	-	49.2 ± 70.4	41 ± 25	10.85 ± 1.57
Chlorogenic acid	0.83 ± 0.04	-	-	-	-	-
Stilbenes						
Trans-resveratrol	0.27 ± 0.01	-	-	-	-	0.26 ± 0.01
Cis-resveratrol	0.46 ± 0.01	-	-	-	-	0.38 ± 0.03
Piceatannol	0.37 ± 0.01	-	-	-	-	-

[1]Phenolic compounds expressed in mg L^{-1}. [2]Wines from Sub-middle São Francisco Valley are analyzed in the present study. [3]Wines from Vale dos Vinhedos localized in the Brazilian South region with temperate climate conditions.

Southern Brazilian Tannat wines (Campanha Gaúcha and the Serra Gaúcha) presented higher concentrations than the Northeastern Tannat ones of delphinidin-3-*O*-glucoside (6.23-16.4 mg L^{-1}), malvidin-3-*O*-glucoside (8.34-86.5 mg L^{-1}), and petunidin-3-*O*-glucoside (14.8-18.2 mg L^{-1}) (ANDRADE *et al*, 2013), as shown in Table 3. On the other hand, Tannat from the Northeast showed higher results to cyanidin-3-*O*-glucoside (4.69-11.5 mg L^{-1}) and peonidin-3-*O*-glucoside (5.68-19.1 mg L^{-1}) than the Southern ones. These authors suggest a

different biosynthetic pathway of anthocyanins in wines from SSFV, explaining the most more representative proportion of cyanidin-3-*O*-glucoside (11 %) and peonidin-3-*O*-glucoside (16 %), decreasing the proportion of malvidin-3-*O*-glucoside (43 %) in tropical red wines from this region. However, the anthocyanins in this present study did not present the same behavior, as malvidin-3-*O*-glucoside showed strongly greater representativity (86.22 %), while cyanidin-3-*O*-glucoside (0.36 %) and peonidin-3-*O*-glucoside (1.12 %) presented the least percentages. In addition, complement, lower values of malvidin-3-*O*-glucoside (56.31 mg L^{-1}) have been reported to commercial Uruguayan Tannat wines (VALENTIN *et al.,* 2020), in comparison to the wine Tannat herein presented.

3.3.3 Phenolic acids

Results obtained from phenolic acids are shown in Table 2. Total phenolic acids were the highest phenolic quantified in these wines, presenting 324.40 and 578.24 mg L^{-1}, to Tannat and Syrah wines, respectively. Syrah showed higher contents to ferulic acid (0.59 mg L^{-1}), ρ–coumaric acid (21.11 mg L^{-1}), caffeic acid (25.77 mg L^{-1}), *trans*-caftaric acid (523.69 mg L^{-1}), and chlorogenic (0.94 mg L^{-1}) acids whereas only gallic acid (11.77 mg L^{-1}) presented higher values to Tannat. Similar results were reported to gallic (15.2 mg L^{-1}) and caffeic (6.46 mg L^{-1}), concerning commercial Tannat wines (VALENTIN *et al*., 2020), as shown in Table 3, while previously chlorogenic acid values were not found to Tannat wines.

Isomers of caftaric acid were reported to Uruguayan Tannat wines (Table 3), *cis*-caftaric (48 mg L^{-1}), and *trans*-caftaric (41 mg L^{-1}), being strongly below in comparison with data herein presented (BOIDO *et al*., 2011). Also, even lower results of 10.85 mg L^{-1} were presented to *trans*-caftaric in another approach (FAVRE *et al*., 2014). These data confirm the greater value of *trans*-caftaric (298.78 mg L^{-1}) to Tannat wine from SSFV. Likewise, *trans*-caftaric acid has been reported as the principal phenolic acid obtained in grapes and wines from the SSFV region (DUTRA *et al*., 2018; PADILHA *et al*, 2019) and as the major non-flavonoid in grapes (Jackson, 2014).

3.3.4 Flavonols and Stilbenes

Quantifications of the classes of flavonols and stilbenes are also shown in Table 2. Tannat presented lower contents to flavonols: kaempferol-3-*O*-glucoside (0.97 mg L^{-1}), quercetin 3-β-D-glucoside (4.66 mg L^{-1}), and isorhamnetin-3-*O*-glucoside (2.44 mg L^{-1}), while myricetin and rutin did not present significant difference among the wines. Similar results of isorhamnetin-3-*O*-glucoside (2.7 mg L^{-1}) and higher values of myricetin (5.0 mg L^{-1}) were

reported in Uruguayan Tannat wines (Vidal et al., 2018b). Also, rutin (6.7 mg L^{-1}) and kaempferol-3-*O*-glucoside (3.86 mg L^{-1}) from commercial Tannat wines were quantified in higher amounts than this present study (VALENTIN *et al*., 2020).

Flavonols are presented in grape skins and their extraction in red wines depends on maceration. Besides, sunlight exposure may enhance this flavonols synthesis (WATERHOUSE *et al.*, 2016), which can relate these compounds with great contents found in SSFV red wines. This can explain the great values obtained for quercetin 3-β-D-glucoside and isorhamnetin-3-*O*-glucoside from Syrah wines, due to cultivar good adaptation in this region.

According to Table 2, piceatannol presented higher contents to Tannat (0.34 mg L^{-1}), whereas the isomers *trans*-resveratrol and *cis*-resveratrol were more abundant in Syrah wines (0.29 and 0.63 mg L^{-1}, respectively). Piceatannol is related to the protection of grape skin, antioxidant and anti-inflammatory activities (BANIK *et al*., 2020). Moreover, there is a scarce of studies with piceatannol quantification in Tannat and tropical red wines, which reinforces the importance of characterization of this compound.

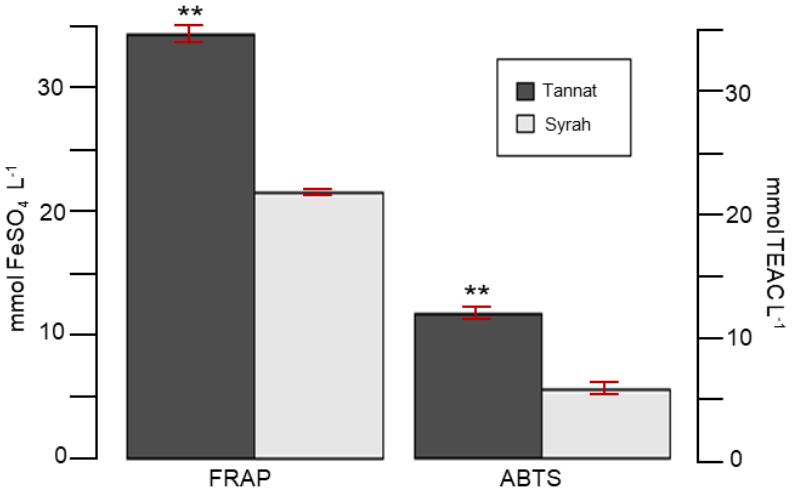
The contents of resveratrol isomers are consistent with those found in Uruguayan Tannat wines, with 0.26 and 0.38 mg L^{-1} for *trans* and *cis* forms, respectively (FAVRE *et al*., 2014). Generally, grapes produce the *trans* form, while the *cis* is obtained with light-inducing (WATERHOUSE *et al*., 2016). Also, some authors have suggested that regions with high temperature and luminosity presented major amounts to *cis* form, following that light-inducing isomerization (KATALINIĆ *et al.*, 2010; PADILHA *et al*., 2017), which may confirm herein results to higher *cis* form to both studied varieties. Furthermore, resveratrol is the major stilbene present in wines and its synthesis is related to a response against fungal attacks. This compound is related to heart diseases and cancer reduction, but the concentrations in red wines would require more than 10 times the doses of a glass of wine (FABJANOWICZ; PLOTKA-WASYLKA; NAMIÉSNIK, 2018; WATERHOUSE *et al*., 2016).

3.4 Total bioactive compounds and antioxidant activity

Total phenolic compounds (TPC) presented significant differences between the varieties studied (Table 2), being Tannat (1,212.38 mg GAE L^{-1}) with higher results than Syrah ones (596.85 mg GAE L^{-1}), as expected. According to Waterhouse et al. (2016), TPC in red wines varies around 2,000 mg GAE L^{-1}, and a value of 4,410 mg GAE L^{-1} has been reported for a commercial Tannat wine from the Rio Grande do Sul, Brazil (PAZZINI *et al*., 2015). Therefore, as already described, this low concentration presented is due to the short maceration applied, only 96 hours. Nevertheless, Tannat is a grape with high phenolic potential (FARIÑA *et al*.,

2015; VIDAL *et al*., 2017), which explains the quantification of total phenolic compounds to Tannat wine be twice over to Syrah wine. Similar data to this research were reported by Favre et al. (2014) to Uruguayan Tannat wine vinified with eight days (192h) of maceration. This comparison may indicate that the cultivar Tannat from the SSFV stood out in the potential to synthesize of bioactive compounds, favored by the geographic conditions of this region.

Figure 3: *In vitro* antioxidant activity (ABTS and FRAP assays) of Tannat and Syrah tropical red wines from São Sub-middle Francisco Valley.



Means with asterisks differ by Student's T-Test '*' ($p \leq 0.05$) '**' ($p \leq 0.01$). $FeSO_4$ = Ferrous sulfate; TEAC = Trolox Equivalent Antioxidant Capacity.

The *in vitro* Antioxidant Activity (AOX), obtained using FRAP and ABTS assays, is shown in Figure 3. Tannat and Syrah wines presented 11.55 and 5.46 mmol TEAC L^{-1} to ABTS, and 34.14 and 21.34 mmol $FeSO_4$ L^{-1} to FRAP, respectively. The AOX presented the same behavior as TPC and TPI, exposing quite higher results to Tannat than Syrah wine, relating both methods. AOX using ABTS scavenging method ranging from 11.2 to 23.17 mmol TEAC L^{-1} has been reported for various Southern Brazilian red wines (GRIS *et al.*, 2011). Similar results from these red wines and the Tannat wine from SSFV may confirm its greatly phenolic and antioxidant potential. Also, an approach with Merlot wines from Serbia, France, Italy, Macedonia, Slovenia, and Spain (MAJKIĆ *et al*, 2019) has reported to ABTS results with great variability (5.22-17.9 mmol TEAC L^{-1}) and lower AOX results to FRAP (8.08-19.2 $FeSO_4$

mmol L^{-1}), in comparison with Tannat wines from SSFV. Furthermore, SSFV environmental conditions may influence the synthesis of phenolic compounds with great AOX, highlighting the potential of these compounds (PADILHA *et al*., 2017). AOX by DPPH (2,2-diphenyl-1-picrylhydrazyl) scavenging capacity of 71 % has been reported to Tannat wines from Southern Brazil (PAZZINI *et al*., 2015). This value is higher than those found in Turkish wines, such as 32.3 %, 37.7 %, 40.4 %, and 65 % of DPPH inhibition to wines from native grapes, which may confirm the great antioxidant capacity that Tannat wines may assume (PORGALI; BÜYÜKTUNCEL, 2012).

Some individual phenolic compounds may be important in increasing AOX. The flavonoid AOX approach has been reported, showing (-)-epicatechin gallate, (-)-epigallocatechin gallate, (+)-catechin, and (-)-epicatechin as having high ABTS scavenging capacity and ferric reducing power in FRAP. Furthermore, the authors presented caffeic and chlorogenic acids showing higher FRAP reactivity, while ρ-coumaric acid had high ABTS scavenging capacity (GRZESIK *et al*, 2018). Similar to this, an approach with grape juices from SSFV presented (-)-epicatechin gallate, rutin, myricetin, gallic and caffeic acids, and delphinidin-3-*O*-glucoside as a strong correlation with AOX (LIMA *et al*., 2014). Moreover, peonidin-3-*O*-glucoside, ρ-coumaric acid, (+)-catechin, cyanidin-3-*O*-glucoside, procyanidin A2, and (-)-epicatechin have been reported to be highly correlated with the ABTS scavenging method (PADILHA *et al*., 2017). Thus, among these compounds, (+)-catechin, gallic acid, delphinidin-3-*O*-glucoside, and procyanidin A2 may have positively influenced the great AOX of Tannat wines.

4. Conclusion

This was the first research featuring phenolic compounds and antioxidant activity of tropical red wine Tannat from the SSFV region, Brazil. These wines showed interesting values of bioactive compound contents, even with the short maceration time applied in the winemaking. Additionally, as expected, Tannat wine had higher total phenolic compounds and antioxidant activity (by ABTS and FRAP assays) than Syrah wine, as well as, had higher total phenolic index (TPI), color intensity (CI), total monomeric anthocyanins, and flavanols, including monomeric flavanols, and proanthocyanidins. Regarding individual phenolic compounds quantified by HPLC-DAD-FD, Tannat wine had important contents of procyanidin B1, (+)-catechin, procyanidin B2, gallic acid, malvidin-3-*O*-glucoside, cyanidin-3-*O*-glucoside, delphinidin-3-*O*-glucoside, and pelargonidin-3-*O*-glucoside. Previously results to compounds (-)-epigallocatechin gallate, procyanidin B2, quercetin-3-β-D-glucoside, pelargonidin-3-O-

glucoside, chlorogenic acid, and piceatannol were not found in Tannat wines. Therefore, the excellent results of *trans*-caftaric acid and procyanidin B1 in tropical Tannat wines compared to Tannat from temperate climate wine-producing regions may suggest the influence of the distinct environmental conditions in the Brazilian semi-arid region of SSFV in increasing concentrations of these compounds in the grapevines. The Tannat cultivar has a great phenolic and antioxidant potential to be explored in wine-producing regions with tropical climate conditions. These geographical conditions may enhance nutraceutical the variety's potential and use it for the production of blends and full-bodied wines. Therefore, future studies are necessary to expand the knowledge about the behavior of this variety in the SSFV region, mainly applying typical commercial maceration time during winemaking.

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4 INFLUENCE OF THE HIGH PH AND SHORT MACERATION TIME ON THE PHYSICAL AND CHEMICAL DETERIORATION OF TROPICAL RED WINES

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Abstract

Wine deterioration may occur due to many factors, including intrinsic traits or techniques applied to vinification, such as high pH, related to color stability, and maceration, responsible for phenolics extraction. Varietal Petit Verdot, Merlot, Malbec, and Tempranillo wines were elaborated with natural high pH (without any interference) and short maceration time (96 hours), to explain how these drivers may influence the physic and chemical deterioration, using approaches such as color, physicochemical analyses, acetaldehyde, higher alcohols, individual phenolics, and antioxidant activity. Color (L, a*, and b*), free SO_2, and acetaldehyde stood out Tempranillo as the sample with the highest deterioration rate. This wine also had the highest pH, and the lowest color, monomeric anthocyanins, and catechins. Petit Verdot was the lowest deteriorated sample, also having the highest total phenolic compounds, color, anthocyanins, catechins, and antioxidant activity. pH had a strong correlation with anthocyanins polymerization and acetaldehyde. Caffeic and ρ-coumaric acids were related to major deterioration rates, whereas catechins, procyanidins, and anthocyanins were related to antioxidant activity and more resistance to oxidation. This is the first acetaldehyde, 1-propanol, and 3-methyl-1-butanol quantification in wines using GC-BID.

Keywords: spoilage indicators, phenolic compounds extraction, anthocyanins, acetaldehyde, *in vitro* antioxidant activity.

1. Introduction

Wine deterioration may be explained as a set of undesirable changes occurring from the grape harvest to the wine bottle storage, making the product sensory unpalatable. (ZEA *et al.*, 2015). Concerning the deterioration mechanisms, chemical and physical changes are related to each other, while microbiological spoilage occurs in different ways. Therefore, all physical changes have chemical agents as causers (WATERHOUSE; ELIAS, 2010).

Loss of color is the main player in physical deterioration and occurs due to decreasing of monomeric anthocyanins, which polymerize and copigment with other anthocyanins and acetaldehyde, to form stable polymeric pigments (FIGUEIREDO-GONZÁLEZ; CANCHO-GRANDE; SIMAL-GÁNDARA, 2013; WATERHOUSE; SACKS; JEFFERY, 2016). On the other hand, the accumulation of acetaldehyde is the major indicator of chemical deterioration (HAN; WEBB; WATERHOUSE, 2019). This compound is produced from ethanol oxidation and reacts with phenolics, which intensify the color losses and interfere in aroma profile, adding

an often-undesirable odor descriptor of ripe/rotten apple (BUENO *et al.*, 2018; ZEA *et al.*, 2015). Furthermore, the loss of sulfur dioxide may also be an important method to monitoring chemical deterioration, as its consumption can be related to polyphenols oxidation (WATERHOUSE; ELIAS, 2010). Sulfur dioxide is the main preservative and antioxidant agent added in wines (GABRIELE *et al.*, 2018).

In general, oxygen dissolved concentration, and time and temperature over storage are the main studied drivers related to wine deterioration. However, as low oxygen levels are common during bottle storage (ALEIXANDRE-TUDO; DU TOIT, 2020), the deterioration may be of other factors as intrinsic traits, such as pH (FORINO *et al.*, 2020), total acidity and alcoholic content, or techniques applied in the winemaking, such as maceration (ALENCAR *et al.*, 2018). These drivers may influence the success of the wine, since their interference on the stability and extraction of phenolic compounds with antioxidant potential (FORINO *et al.*, 2020; WOJDYLO; SAMOTICHA; CHMIELEWSKA, 2021). Therefore, these conditions may play important roles in chemical and physical deteriorations, making it necessary to explain this linkage.

The control of pH is essential to red wines, as this parameter plays an important role in the beverage's chemical stability and sensory equilibrium. In general, typical pH values ranged from 3.3 to 3.7 in red wines (JACKSON, 2020). So, higher pH values (> 3.7) favor oxidative reactions in monomeric anthocyanins, which induce self-association and affect the color stability, making the red wine lose color and reaching hue close to brick red or tawny, with orange reflections. Also, pH may be related to the sulfur dioxide effectiveness, since the greater is pH, the lower is the percentage of reactive SO_2 and capable of binding acetaldehyde and protecting wines from chemical oxidation and deterioration by the microorganisms (COMUZZO; BATTISTUTTA, 2018), making necessary higher dosages of potassium metabisulfite. However, great free sulfur contents may cause irritation and burning sensation in the nose due to chemical aroma (RIBÉREAU-GAYON *et al.*, 2006a), besides intolerance and allergenic adverse reaction (OIV, 2021a).

The recent climatic changes have provided different chemical traits in wine quality such as pH rise and reduction of the acidity levels in the grapes, which bring up challenges to wine producers (VAN LEEUWEN; DARRIET, 2016). Nowadays, studies relating chemical traits and harvest seasons are common in tropical wines-producing regions (OLIVEIRA *et al.*, 2018), to propose the best harvest months to produce wines with lower pH and high acidity, as these conditions reduce chemical instability. In tropical wine-producing regions, the common high pH and low acidity provide red wines with low aging ability, recommending immediate

consumption (2 to 3 years) (GUERRA; PEREIRA, 2018). Therefore, these studies may play an important role as a reference to temperate wine-producing regions to adapt to these changes, using some solutions already applied in warm regions (MARÍN *et al.*, 2021; MOZELL; THACHN, 2014).

Maceration is a necessary technique that must is put in contact with grape skins and seeds, being always applied to red wines winemaking (RIBÉREAU-GAYON *et al.*, 2006b). This process aims to extract, minerals, polysaccharides, volatile compounds (and precursors), pigments (anthocyanins), tannins, and other interesting phenolic compounds, important to the chemical and sensory quality of wines (JACKSON, 2020). The maceration time influence this extraction, as below five days (120 hours) does not provide the maximum obtention of anthocyanins (DAUDT; FOGAÇA, 2013; JACKSON, 2020). Then, short maceration time may not be enough to extract sufficient other phenolic compounds to red wines, such as procyanidins, catechins, and flavonols, also providing low antioxidant activity to the beverage (ALENCAR *et al*., 2018), which is related to wines shelf-life (WATERHOUSE *et al*., 2016) and human cardiovascular diseases reduction (CHEN *et al.*, 2019). Therefore, the low antioxidant activity would make necessary major applications of sulfites, which also explains why white and rosé wines receive higher amounts of preservatives (GABRIELE *et al*., 2018).

In this present approach, indicators of physical and chemical deterioration of red wines were investigated, aiming to explain how these processes may be influenced by the high pH and short maceration time applied during the winemaking. So, without interference, four red grape cultivars with different phenolic potential were tested to winemaking with a short maceration time (<120 hours). Individual phenolic compounds, antioxidant activity, and higher alcohols were studied to ensure other influence pathways of these drivers over the red wine deterioration.

2. Material and methods

2.1 Red wine trial

For this experiment, four red grape cultivars from the same vineyard and with different phenolic potential were selected: Petit Verdot, Merlot, Malbec, and Tempranillo. Pruning of vines was carried out in August 2020, and grapes were harvested in December 2020 (cycle about 120 days) from Bebedouro experimental vineyard in Petrolina, Pernambuco, Brazil (latitude: 9º 9’ S, longitude 40º 22’ W, altitude 365.5m).

Total grapes Petit Verdot (58.3 kg), Merlot (40.05 kg), Malbec (61.45 kg), and Tempranillo (66.25 kg) were destemmed and received potassium metabisulfite (0.1 g L^{-1}, Synth, São Paulo, Brazil), and the enzyme (0.03 g L^{-1} Endozym rouge, AEB – Brescia, Italy). It is important to mention that metabisulfite applications were carried out with coherent dosages to red wines, as per the manufacturer's indications. Initial musts were characterized and quality parameters analyzed in triplicate are available in Table 5. Must's pH and total acidity did not suffer any enological intervention during the winemaking. Then, each grape cultivar must (Malbec, Merlot, Petit Verdot, and Tempranillo) was divided into 20 L glass bottles capped with cylindrical glass airlock valves, for a total of 8 experimental samples (two for each grape cultivar). Dry yeasts (0.2 g L^{-1}, *Saccharomyces cerevisiae* bayannus – Mauvirim PDM, Amazon Group, Monte Belo do Sul, RS, Brazil) were inoculated. Then the fermentation activator (0.2 g L^{-1}, Gesferm plus, Amazon Group) were applied to start the alcoholic fermentation (AF).

The winemaking followed the traditional method of red wines suggested by Blouin & Peynaud (2012). The AF was carried out under a controlled temperature (24 ± 2 ºC) for approximately 10 days. During the AF, a short maceration time of four days (96 hours) concomitant with AF was performed to all samples, before pressing. The end of AF was determined with the constant density (≤ 0.997), using an electronic hydrostatic balance (Super Alcomat, Gibertini, Milano, Italy); confirmed by the alcoholic content (≥ 10.1 % v/v) and total reducing sugars (≤ 2.23 g L^{-1}). The spontaneous malolactic fermentation under controlled temperature (18 ± 2 ºC) was performed until all malic acid content was transformed into lactic acid. This transformation was confirmed by paper chromatography analysis (RIBÉREAU-GAYON, 2006b). The stabilization was performed with cold storage (0 ºC) for 20 days, followed-up by the addition of 400 mg L^{-1} of Stabigum® (AEB Group, Viseu, Portugal). Wine's free SO_2 content was adjusted to 65 mg L^{-1} and total SO_2 was around 100 mg L^{-1}. Wines were bottled (750 mL) and stored in the cellar at 18 ºC for six months until the assays were accomplished.

2.2 Physicochemical and instrumental color evaluations

The pH level was measured using pHmeter (Hanna PAT. CPNQ Edge, Romênia), titrable acidity (TA) was expressed in g L^{-1} of tartaric acid, volatile acidity (VA) using titrimetry after wine distillation in an oenological distiller (Super Dee – Gibertini, Milano, Italy) was expressed in g L^{-1} of acetic acid, density (g cm^{-3}) using an electronic hydrostatic balance (Super Alcomat, Gibertini, Milano, Italy), alcohol content using oenological distiller and electronic

hydrostatic balance, sulfur dioxide by Ripper titrimetric method expressing results in mg L^{-1} of free SO_2 (OIV, 2021b). Total reducing sugars were analyzed according to Lane-Eynon titratable method and expressed in g L^{-1} (Ribéreau-Gayon et al., 1980). Soluble solids (º Brix) were determined using an electronic hydrostatic balance (Super Alcomat, Gibertini, Milano, Italy).

The instrumental color was performed by the CIELab system, being the parameters L* (luminosity), a* (red-green coordinate), b* (yellow-blue coordinate), using a colorimeter (ColorQuest-XE, HunterLab, Virginia, USA).

2.3 Spectrophotometry measurements of phenolic compounds and color

Total phenolic compounds (TPC) were determined using the Folin Ciocateau reagent as per Singleton and Rossi (1965). Readings were carried out at 700 wavelengths and the results were expressed in mg L^{-1} of gallic acid. Monomeric anthocyanins were performed using the pH buffers pH 1.0 and 4.5 methods (Lee, Durst, & Wrolstad, 2005), with readings performed at 520 nm and 700 nm, and expressing the results in malvidin-3-*O*-glucoside equivalents in mg L^{-1}. Monomeric, polymeric, and copigmented anthocyanins and their respective percent of distribution in the wine samples were determined as per Cliff, King, and Schlosser (2007), using acetaldehyde 20% and SO_2 5% (w/v) solutions, and performing readings at 520 nm wavelength. Both measurements were carried out using a spectrophotometer (Shimadzu Corporation, UV 1800, Japan). Color intensity (CI) and tonality were determined by the wine sample reading in the 420, 520, and 620 nm wavelengths (Ribéreau-Gayon et al., 2006b), using a UV-Vis spectrophotometer (Thermo Fisher Scientific Oy Ratastie 2, FI-01620 Vantaa, Finland).

2.4 Antioxidant activity

In vitro total antioxidant activity was determined using ABST (MILLER *et al*., 1993) and FRAP (BENZIE; STRAIN, 1996) methods, following modifications described by Rufino *et al.* (2010). ABTS (2,2-azino-bis (3-eth- ylbenzthiazoline-6-sulphonic acid)) evaluation was performed at 743 nm wavelength, expressing results in mmol Trolox Equivalent Antioxidant Capacity (TEAC) L^{-1} of the sample. FRAP (ferric reduction method) results were expressed in mmol ferrous sulfate L^{-1} of the sample, with readings realized in 595 nm. Both measurements were determined using a spectrophotometer UV-1800 (Shimadzu Corporation, Japan).

2.5 Acetaldehyde and higher alcohols determinations

Acetaldehyde, 3-methyl-1-butanol, and 1-propanol were determined using gas chromatography with barrier discharge ionization detection (GC-BID) by injection of 1 µL of wine sample spiked with 1-pentanol as internal standard (RIBANI *et al.*, 2004). A GC-2010 Plus (Shimadzu Corporation, Kyoto, Japan) with a Carbowax (30 m x 0.25 mm ID x 25µm) capillary column (Shimadzu, USA) was used. Helium 5.0 (99.999 %) was used as the carrier gas at a constant flow of 1.8 mL min^{-1} in column and 50 mL min^{-1} in the detector, using purifiers (VICI Valco Instruments Co. Inc). The injector was kept at 200 ºC with a split ratio of 35. BID temperature was maintained at 300 ºC. The column temperature program was 40 ºC for 3 min, raised to 65 ºC, and then to 200 ºC for 10 min (total 20.70 minutes). Calibration curves ranging from 15 to 250 mg L^{-1} to acetaldehyde and 100 to 800 mg L^{-1} to alcohols (3-methyl-1-butanol, and 1-propanol) were used. Acetaldehyde, 3-methyl-1-butanol, 1-propanol, and 1-pentanol standards were obtained from Sigma-Aldrich (USA).

2.6 Quantification of individual phenolic compounds by High-performance liquid chromatography (HPLC-DAD-FD)

The phenolic compounds were quantified by High-Performance Liquid Chromatography (HPLC-DAD-FD), according to methods validated under the same analytical conditions (DA COSTA *et al.*, 2020; NATIVIDADE *et al.*, 2013). The chromatograph (Waters model Alliance e2695, USA) was coupled simultaneously to the detectors Diodes Array Detectors - DAD (280, 320, 360, and 520 nm) and Fluorescence – FD (280 nm excitation and 320 nm emission). Gemini-NX C18 column (150mm x 4.60mm x 3µm) and the Gemini-NX C18 pré-column (4.0mm x 3.0mm) (Phenomenex®, USA) was used to separate the 28 phenolic compounds that were quantified in the wines: malvidin-3-*O*-glucoside, cyanidin-3-*O*-glucoside, petunidin-3-*O*-glucoside, delphinidin-3-*O*-glucoside, peonidin-3-*O*-glucoside, and pelargonidin-3-*O*-glucoside (anthocyanins), gallic, caffeic, *trans*-caftaric, chlorogenic, ρ-cumaric and ferulic acids (phenolic acids), quercetin 3-β-D-glucoside, rutin, myricetin, kaempferol-3-*O*-glucoside, and isorhamnetin-3-*O*-glucoside (flavonols), *trans*-resveratrol, *cis*-resveratrol, and piceatannol (stilbenes), (+) - catechin, (-) - epicatechin, (-) – epigallocatechin gallate, (-) - epicatechin gallate, procyanidins A2, B1 and B2 (flavonols and tannins). Employing gradient elution, the mobile phase consisted of a 0.85% solution of orthophosphoric acid (Fluka, Switzerland) in ultra-pure water (Purelab Option Q Elga System, USA) as phase A and acetonitrile HPLC grade (J. T. Baker, USA) as phase B, totaling 60 minutes of running. The oven temperature was maintained at 40 ° C and the flow at 0.5 mL min^{-1}. The wine was

injected without dilution in the equipment, after filtration in a 13 mm diameter nylon membrane and 0.45 µm pore size (Phenomenex®, USA), using 10 µL / sample as the injection volume.

The ferulic acid standard was obtained from ChemService (West Chester, USA). The caffeic, *trans*-caftaric, ρ-coumaric, chlorogenic and gallic acids plus the standards of piceatannol, viniferin were acquired from Sigma-Aldrich (USA); the (-)-epicatechin gallate, (-)-epigallocatechin gallate, (+)-catechin, (-)-epicatechin, procyanidin A2, procyanidin B1, procyanidin B2, kaempferol-3-*O*-glucoside, quercetin 3-β-D-glucoside, isorhamnetin-3-*O*-glucoside, rutin, malvidin-3-*O*-glucoside, petunidin-3-*O*-glucoside, peonidin-3-*O*-glucoside, pelargonidin-3-*O*-glucoside, delphinidin-3-*O*-glucoside, and *trans*-resveratrol standards were obtained from Extrasynthese (France); and the *cis*-resveratrol was acquired from Cayman Chemical (Michigan, USA).

2.7 Statistical analysis

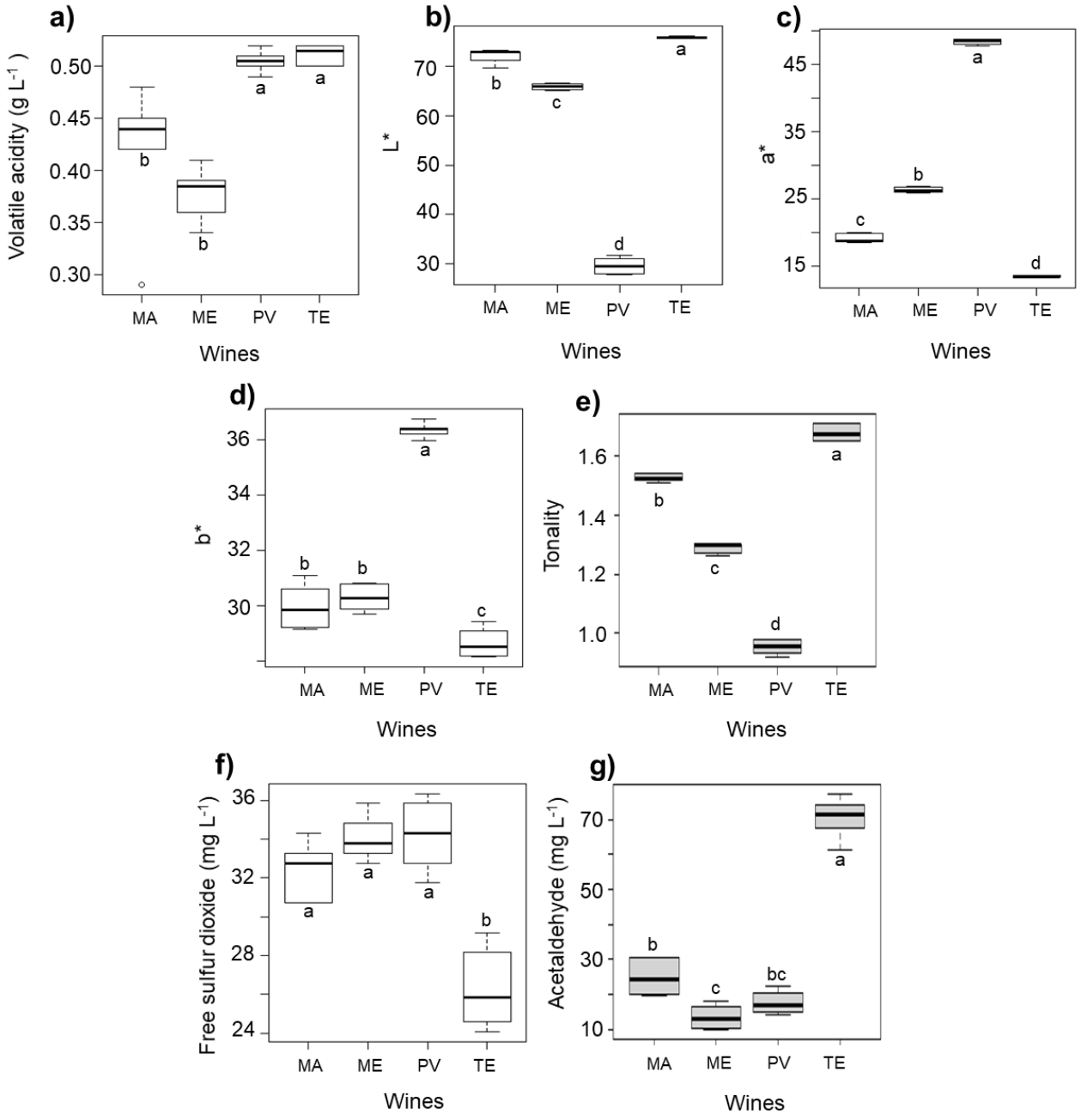
Each replicate of vinification was analyzed using three different bottles. All data were evaluated by the analyses of variance (one-way ANOVA) and Tukey test ($p \leq 0.05$), applying Shapiro-Wilk and Levene tests to normality and homogeneity, respectively; both using the R Studio Desktop program (1.4.1106 version, Boston, USA). Correlation among the deterioration indicators was carried out using Spearman coefficient and Principal Component Analysis (PCA), using Pearson's correlation matrix, was performed to confirm the relations among analysis and the wines, both using XLStat (Addinsoft Inc., Anglesey, UK, 2015).

3. Results and discussion

3.1 Deterioration mechanisms in red wines and spoilage indicators

Figure 4 shows the spoilage indicators investigated in this work, to prove the existing deterioration mechanisms (WATERHOUSE; ELIAS, 2010). Volatile acidity (VA) is the first measure of wine quality, acting as an indicator of microbiological deterioration, as bacterias may produce acetic acid from ethanol oxidation (JACKSON, 2020). All samples presented sound values to VA (Figure 4a), as per the maximum acceptable limits (1.2 g L^{-1}) of the International Organization of Vine and Wine (OIV, 2021b), suggesting the absence of microbiological contamination and forwent this mechanism of deterioration.

Figure 4: Spoilage indicators to Petit Verdot, Merlot, Malbec, and Tempranillo red wines produced with high pH grape values and short maceration time (96h) during winemaking.



MA = Malbec; ME = Merlot; PV = Petit Verdot; TE = Tempranillo.

Tempranillo and Malbec were the samples with major lightness (L) (75.89 and 72.16, respectively) and lower a* (13.4 and 19.08, respectively), as per Figure 4 (b and c). These data suggest that these samples may be the ones with a major deterioration rate, as the trend of red wines being oranges can mean signs of spoilage (WATERHOUSE *et al.*, 2016). On the other hand, Petit Verdot presented the opposite behavior, being more reddish and with the deepest

color. Coordinate b* (yellowness) did not present large variations such as L and a*, but these high values in all samples may suggest changes in wine tones, toward orangeness. Spanish sound red wines of Tempranillo grape have presented greatly lower values of L (58.3) and b* (6.0) and higher values of a* (37.2) (GARCÍA-MARINO *et al.*, 2013). Herein Malbec wine took only six months to reach similar L* values (72.16) of Argentinean Malbecs with 24 months of storage at 25 ºC (Esteban et al., 2019). Furthermore, tonality is another important indicator, calculated from the ratio of abs 420 nm/520 nm. As per Figure 4e, Tempranillo and then Malbec presented the major results, which suggest lower values of the wavelength 520 nm, showing consistent data with the L* and a* coordinates.

According to Figure 4f, all samples presented a reduction in the SO_2 contents compared to the last SO_2 adjustment (to reach 65 mg L^{-1}), as described in section 2.1 on Material and Methods. Sulfur dioxide is the antioxidant agent in wines, deriving from the potassium metabisulfite addition, and its consumption increase with the oxidation rate increase. Tempranillo presented lower values than the other samples, with a reduction of 60%, suggesting less chemical stability than Petit Verdot, Malbec, and Merlot. The acetaldehyde quantification confirms this behavior, with Tempranillo presenting the higher levels (70.52 mg L^{-1}), followed up by Malbec (24.88 mg L^{-1}), Petit Verdot (17.59 mg L^{-1}), and then Merlot (13.48 mg L^{-1}). This compound is derived from ethanol oxidation, which makes it the major chemical spoilage product in wines (WATERHOUSE *et al*., 2016). Acetaldehyde is a highly reactive compound, bondering with phenolics and inducing polymerization reactions with tannins and anthocyanins, which may spoil the wine color and reduce astringency (HAN; WEBB; WATERHOUSE, 2019). Bueno *et al*. (2018) quantified acetaldehyde in red wines (vintages from 2009 to 2014) with oxygen exposure to force oxidation, showing values ranging from 11.3 to 31.8 mg L^{-1}. Picariello *et al.* (2017) found less than 30 mg L^{-1} of this compound in experimental red wines treated with hydrogen peroxide and oxygen to simulate two years of aging, and analyzed after 30 days; while Han *et al*. (2019) quantified at most 17.69 mg L^{-1} in wines with 12 months of storage with forced oxidation using oxygen ingress. These data reinforce a large amount of acetaldehyde found in the Tempranillo wine, suggesting the high oxidation degree probably caused by the deterioration drivers analyzed.

Table 4 corroborates the results of the indicators and provides more consistency to the discussion, proving the direct relationship between the chemical and physical spoilage mechanisms. Chemical deterioration indicators (acetaldehyde and free SO_2) presented a strong negative correlation (r = -0.8), while the physical ones (L*, a*, b*, and tonality) had perfect correlations among each other, as expected. The lightness (L*) and tonality showed a strong

positive correlation (r = 0.8) with acetaldehyde and a perfect negative correlation (r = -1.0) with free sulfur dioxide. In exactly opposite behavior, the other colorimetric coordinates (a* and b*) had a strong negative correlation (r = -0.8) with acetaldehyde and a positive perfect one (r = 1.0) to free sulfur dioxide. Volatile acidity did not present expressive correlations with other indicators (except acetaldehyde).

Table 4: Spearman correlation among deterioration indicators in red wines.

Variables	L*	a*	b*	Acetaldehyde	Volatile acidity	Free SO2	Tonality
L*	**1**						
a*	-1.000	**1**					
b*	-1.000	1.000	**1**				
Acetaldehyde	0.800	-0.800	-0.800	**1**			
Volatile acidity	0.400	-0.400	-0.400	0.800	**1**		
Free SO2	-1.000	1.000	1.000	-0.800	-0.400	**1**	
Tonality	1.000	-1.000	-1.000	0.800	0.400	-1.000	**1**

Correlation: weak ($r \geq 0.5$), moderate ($0.5 \leq r \leq 0.8$), strong ($0.8 \leq r < 1.0$), perfect ($r = 1.0$). (Granato et al., 2014).

3.2 Influence of the pH value in red wines deterioration

Results of pH are shown in Table 5. The major pH value was to the wine Tempranillo (4.08), followed up by Petit Verdot (3.98), Malbec (3.83), and Merlot (3.78). Therefore, all pH samples may be considered high, due to typical red wines values ranging from 3.3 to 3.7 (JACKSON, 2020; WATERHOUSE *et al.*, 2016). The main influence of the pH in the physical deterioration of red wines occurs due to instability of the pigmentation (anthocyanins) with high pH, reducing the intensity and changing the color of the red wines (FORINO *et al.*, 2019). The color is the first aspect perceived by consumers in this beverage, playing an imperative role in the purchase decision, being able to influence the olfactive and gustative perceptions of the wine (WANG; SPENCE, 2019). Then, according to Tables 5 and 6, Tempranillo wine was the sample with lower color intensity (1.52), total monomeric anthocyanins (22.34 mg L^{-1}), and high pH value (4.08), confirming this behavior. However, the phenolic profile of the grape cultivar seems to interfere with this relation. Petit Verdot promotes to the wine greatly higher color intensity (5.85), total monomeric anthocyanins (132.23 mg L^{-1}), and total phenolic compounds (828.89 mg L^{-1}), although this product also showed a high pH value (3.98). In fact, the lower value of Petit Verdot pH must (Table 5) may contribute to these results,
due to the anthocyanins contents are greatly lower with must pH increasing, as explained by

Forino *et al*. (2020).

Table 5: Physicochemical parameters of Petit Verdot, Merlot, Malbec, and Tempranillo red wines produced with high pH and short maceration time (96 hours) during winemaking.

Must wines				
Parameters	Petit Verdot	Merlot	Malbec	Tempranillo
pH	3.56 ± 0.01 d	3.82 ± 0.01 b	3.72 ± 0.01 c	3.89 ± 0.01 a
Total soluble solids (ºBrix)	21.87 ± 0.07 b	22.29 ± 0.10 a	20.38 ± 0.06 c	19.62 ± 0.11 d
Titratable acidity (g L^{-1})	6.65 ± 0.09 a	4.55 ± 0.09 c	5.3 ± 0.31 b	4.9 ± 0.09 bc
Volatile acidity (g L^{-1})	0.01 ± 0.01 a	0.01 ± 0.01 a	0.01 ± 0.01 a	0 ± 0.01 a
Density (g cm^{-3})	1.091 ± 0.01 b	1.093 ± 0.01 a	1.085 ± 0.01 c	1.081 ± 0.01 d
Total reducing sugars (g L^{-1})	180 ± 0.01 c	214.98 ± 1.19 a	190.18 ± 3.37 b	189.09 ± 1.59 b
Wines				
Parameters[1]	Petit Verdot	Merlot	Malbec	Tempranillo
pH	3.98 ± 0.01 b	3.78 ± 0.01 d	3.83 ± 0.04 c	4.08 ± 0.01 a
Titratable acidity (g L^{-1})	4.98 ± 0.06 a	4.23 ± 0.11 c	4.53 ± 0.11 b	4.15 ± 0.08 c
Total reducing sugars (g L^{-1})	1.54 ± 0.01 b	2.23 ± 0.15 a	2.15 ± 0.06 a	1.5 ± 0.02 b
Alcohol (%)	11.13 ± 0.21 b	12.24 ± 0.13 a	10.1 ± 0.11 d	10.35 ± 0.07 c
Color intensity	5.85 ± 0.32 a	1.99 ± 0.08 c	2.28 ± 0.1 b	1.52 ± 0.06 d

[1]Means followed by different letters in the same lines differ significantly according to the Tukey means test ($p \leq 0.05$).

Color intensity is another important physic parameter, standing out Petit Verdot and Tempranillo with the highest and lowest values, respectively. According to Jackson (2020), musts macerated for a few days may show color losses over the fermentation, despite the anthocyanins contents remaining constant, which may explain the low results of color intensity showed in Table 5. This data is consistent with the physic indicators colorimetry and tonality (Figure 4), even as total monomeric anthocyanins, present in Table 3. In accordance, Petit Verdot had a quite different anthocyanins profile from the other samples, as shown in Figure 5 from Appendix B, with a significantly higher monomeric anthocyanins percentage (53 %). Forino et al. (2020) reported that pH increasing induce more orange nuances in red wines due to lower values of 520 nm absorbance, which occurs in wines less rich in monomeric anthocyanins, as per the relation of these compounds with color coordinates (CASTRO *et al*., 2021), which may explain why Tempranillo had less color intensity. Cliff *et al.* (2007) reported higher concentrations of monomeric anthocyanins in younger wines, analyzing 173 commercial red wines from 7 vintages (1995-2001). This author's data showed that possibly getting the polymerics represented 69.3% of anthocyanins in the oldest vintage, facing 39.5% in the youngest. Following these approaches, Tempranillo and Malbec wines had higher polymeric anthocyanins index, 60%, and 55%, respectively (Figure 2, Appendix B), showing that polymerization is most present in wines towards deterioration. However, the other samples also presented significant percentages of polymeric anthocyanins, concluding that the instability

provided by high pH induces anthocyanins to polymerize and bound up with other molecules, including acetaldehyde.

High pH may also affect the chemical quality of red wines, mainly decreasing the effectiveness of free sulfur dioxide, besides requiring higher potassium metabisulfite dosages. Butzke (2018) states that wines at pH 4.0 requires 10 times higher free sulfur dioxide concentrations than wines at pH 3.0. Figure 4 shows Tempranillo wine as the sample with the lowest free sulfur dioxide concentrations (26.28 g L^{-1}), confirming the higher consumption of free SO_2 at high pH. Petit Verdot wine had the second higher pH (3.98). However, its free SO_2 concentration (34.22 g L^{-1}) did not track this behavior, probably due to its high phenolic compound concentration (Table 6). It is having reported that correct dosages of SO_2 delay phenolic oxidation (ĆURKO *et al.*, 2021) and provide a higher concentration of bioactive compounds and antioxidant activity in wines during the storage of the product (GABRIELE *et al.*, 2018).

Table 6: Phenolics compounds, total phenolic compounds, total monomeric anthocyanins, and antioxidant activity in Petit Verdot, Merlot, Malbec, and Tempranillo red wines produced with high pH grape values and short maceration time (96 hours) during the winemaking.

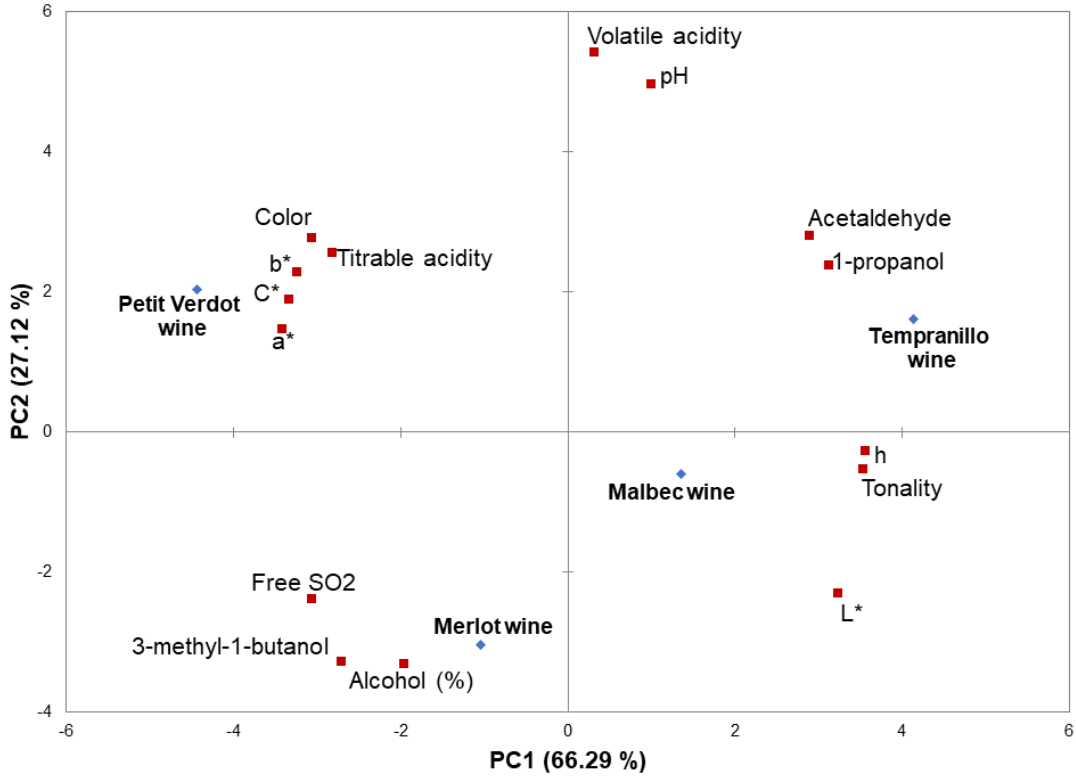
Phenolic compounds[1,2]	Petit Verdot	Merlot	Malbec	Tempranillo
Flavanols and condensed tannins				
(+)-Catechin	11.52 ± 1.19 a	6.54 ± 0.46 b	1.44 ± 0.07 d	3.67 ± 0.55 c
(-)-Epicatechin	4.06 ± 0.38 a	2.6 ± 0.21 b	0.88 ± 0.07 c	1.07 ± 0.18 c
(-)-Epicatechin gallate	0.57 ± 0.15 b	0.6 ± 0.02 b	0.93 ± 0.09 a	0.90 ± 0.04 a
(-)-Epigallocatechin gallate	2.37 ± 0.1 b	3.18 ± 0.07 b	4.37 ± 0.11 a	3.65 ± 0.2 a
Procyanidin A2	1.26 ± 0.12 a	1.02 ± 0.05 b	0.8 ± 0.01 c	0.73 ± 0.02 c
Procyanidin B1	12.18 ± 0.49 a	7.06 ± 0.53 b	5.94 ± 0.16 c	1.68 ± 0.08 d
Procyanidin B2	3.28 ± 0.45 a	1.84 ± 0.08 c	2.29 ± 0.17 b	ND
Total flavanols	35.233 ± 2.53 a	22.85 ± 1.09 b	16.58 ± 0.22 c	11.70 ± 0.96 d
Flavonols				
Kaempferol-3-*O*-glucoside	1.56 ± 0.18 b	2.12 ± 0.03 a	0.54 ± 0.04 c	1.61 ± 0.25 b
Quercetin 3-β-D-glucoside	8.92 ± 0.63 b	15.82 ± 0.93 a	1.87 ± 0.11 d	5.69 ± 0.88 c
Isorhamnetin-3-*O*-glucoside	8.65 ± 0.72 a	6.25 ± 0.11 a	2.34 ± 0.13 c	1.42 ± 0.12 d
Myricetin	0.55 ± 0.06 a	0.47 ± 0.01 b	0.45 ± 0.01 b	0.45 ± 0.01 b
Rutin	2.39 ± 0.18 a	0.62 ± 0.09 b	0.63 ± 0.03 b	0.58 ± 0.02 b
Total flavonols	22.07 ± 1.71 b	25.27 ± 1.02 a	5.85 ± 0.23 d	9.75 ± 1.22 c
Monomeric anthocyanins				
Malvidin-3-*O*-glucoside	55.45 ± 2.54 a	14.85 ± 1.55 b	12.2 ± 0.25 c	4.76 ± 0.82 d
Pelargonidin-3-*O*-glucoside	1.74 ± 0.11 a	0.47 ± 0.05 c	0.66 ± 0.02 b	0.33 ± 0.02 d
Delphinidin-3-*O*-glucoside	0.44 ± 0.04 a	ND	ND	ND

Petunidin-3-*O*-glucoside	0.95 ± 0.04 a	0.38 ± 0.02 b	0.31 ± 0.01 c	0.23 ± 0.01 d
Peonidin-3-*O*-glucoside	0.38 ± 0.03 a	0.40 ± 0.05 a	0.03 ± 0.01 b	ND
Total anthocyanins	58.96 ± 2.74 a	16.11 ± 1.64 b	13.21 ± 0.24 c	5.32 ± 0.83 d
Phenolic acids				
Gallic acid	7.47 ± 0.9 a	1.31 ± 0.06 b	1.23 ± 0.02 b	1.73 ± 0.06 b
Ferulic acid	0.7 ± 0.02 a	0.46 ± 0.06 c	0.52 ± 0.03 b	0.49 ± 0.03 bc
ρ-Coumaric acid	4.81 ± 0.37 b	5.15 ± 0.2 b	9.05 ± 0.24 a	8.97 ± 0.35 a
Caffeic acid	14.3 ± 0.75 b	8.45 ± 0.1 d	10.99 ± 0.22 c	33.04 ± 0.19 a
Trans-caftaric acid	495.03 ± 32.6 a	96.74 ± 3.94 c	71.36 ± 1.1 c	297.51 ± 1.99 b
Chlorogenic acid	0.73 ± 0.08 b	0.91 ± 0.04 a	0.75 ± 0.03 b	0.90 ± 0.1 a
Total phenolic acids	523.05 ± 34.65 a	113.02 ± 3.86 c	93.89 ± 1.53 c	342.64 ± 2.08 b
Stilbenes				
Trans-resveratrol	0.26 ± 0.01 b	0.26 ± 0.01 b	0.27 ± 0.01 ab	0.27 ± 0.01 a
Cis-resveratrol	0.89 ± 0.02 b	0.57 ± 0.01 d	1.04 ± 0.05 a	0.7 ± 0.08 c
Piceatannol	0.7 ± 0.01 a	0.46 ± 0.01 c	0.52 ± 0.01 b	0.49 ± 0.01 bc
Total stilbenes	1.44 ± 0.03 b	1.11 ± 0.02 d	1.59 ± 0.05 a	1.25 ± 0.07 c
Total phenolic compounds	828.89 ± 45.88 a	368.68 ± 16.53 b	358.91 ± 25.62 b	399.48 ± 26.76 b
Total monomeric anthocyanins	132.23 ± 7.73 a	41.37 ± 1.96 b	34.19 ± 2.54 c	22.34 ± 1.05 d
ABTS[3]	5.99 ± 0.35 a	3.42 ± 0.19 b	2.61 ± 0.55 c	2.29 ± 0.20 c
FRAP[4]	23.22 ± 1.60 a	11.64 ± 0.99 b	12.15 ± 1.07 b	11.44 ± 0.75 b

[1]Means followed by different letters in the same line differ significantly according to the Tukey means test ($p \leq 0.05$). [2]ND= Not detected, below the method's quantification limit. [3]Results expressed in mmol TEAC L^{-1}. [4]Results expressed in mmol $FeSO_4$ L^{-1}.

The pH values also had a direct positive relation with the acetaldehyde and 1-propanol contents in the red wines, as shown in Figure 5, due to the closeness of their vectors. Merlot wine had the lower values of pH (3.78), acetaldehyde (13.48 mg L^{-1}), and 1-propanol (49.46 mg L^{-1}), while Tempranillo wine showed the exact opposite behavior (highest values of pH, acetaldehyde, and 1-propanol). This result confirming a direct relation between acetaldehyde and 1-propanol concentrations previously reported by Muñoz *et al.* (2006). Thus, this behavior may be related to free SO_2 losses, as the sulfur dioxide antioxidant activity may limit the reactivity of acetaldehyde (Waterhouse et al., 2016). On the other hand, the 3-methyl-1-butanol vector was localized on the opposite side of the PC1 concerning pH vector. The Merlot wine stood out in 3-methyl-1-butanol and presented 746.40 mg L^{-1}, followed by Petit Verdot, Malbec, and Tempranillo wines, with 630.21, 483.17, and 395.52 mg L^{-1}, respectively (Figure 2, Appendix B). In high amounts in the wines, the higher alcohols may provide an undesirable pungent aroma, besides being substrates to oxidation and forming aldehydes, which intensify the “oxidized aromas” (WATERHOUSE *et al*., 2016).

Figure 5: Principal Component Analysis obtained by the physicochemical analysis, including spoilage indicators and higher alcohols quantified in the red wines Petit Verdot, Merlot, Malbec, and Tempranillo produced with high pH grape values and short traditional maceration time (96h) during the winemaking.



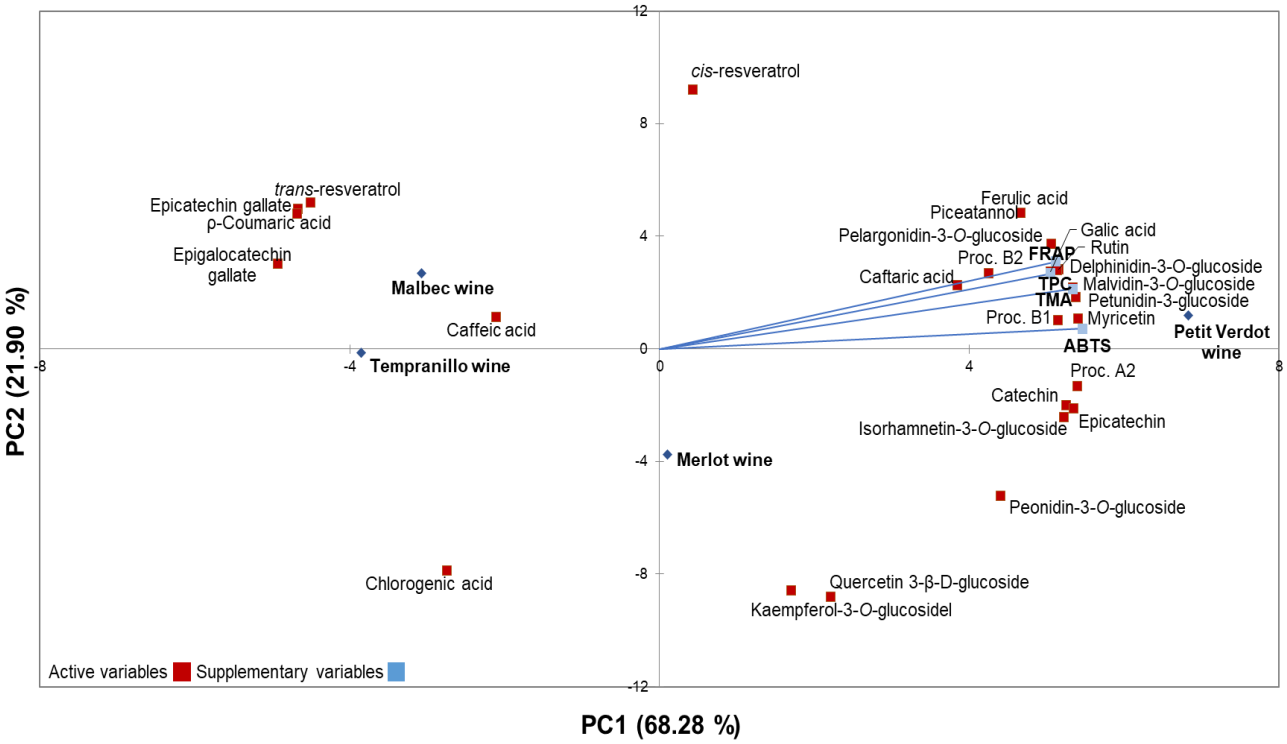
Ethanol is the main alcohol present in wines, and it was clustered with the 3-methyl-1-butanol and free SO_2 (Figure 5). This alcohol may play an important role to prevent chemical spoilage or chemical reactions provided by microorganisms, due to its properties of dehydration, hydrophobicity, hydrophilicity, and disinfectant (RIBÉREAU-GAYON *et al.*, 2006). Merlot wine was the sample with the highest alcohol content (12.24 %) and it must also present the highest total reducing sugars (214.98 g L^{-1}), according to Table 5. Interestingly, this sample had the lowest pH. On the other hand, Tempranillo wine did not fit this behavior, as it had lower alcohol (10.35 %) than Petit Verdot wine (11.13 %) even with must richer in sugar (189.09 g L^{-1} facing 180 g L^{-1}, respectively). These samples had the highest pH. Then, pH may have provided an influence on alcohol production, which implies that high pH may have decreased the yeast fermentation performance, and ethanol is the main result of this process. High pH levels reducing the activity of the yeasts Saccharomyces ssp. have been reported by Forino *et al.*, (2020). The authors observed the concentration of yeast's secondary metabolites behavior in pH 3.2, 3.5, and 3.7.

3.3 Total phenolic compounds, antioxidant activity, and short maceration time during red wine

winemaking

The results of total phenolic compounds (TPC) and antioxidant activity (AOX) are presented in Table 6. Tempranillo and Malbec wines were similar in TPC (399.48 and 358.91 mg L^{-1} GAE), ABTS (2.29 and 2.62 mmol L^{-1} TEAC, respectively), and FRAP (11.44 and 12.15 mmol L^{-1} $FeSO_4$ equivalent, respectively), having the lowest contents. This fact supports the thesis of these samples had a major spoilage rate, in agreement with all data previously presented. The phenolic compounds extraction occurs with the liquid in contact with skins and seeds, which explains the fewer contents in all herein wines, which possess only 4 days of maceration (96h). Barbará et al. (2019) worked with tropical Syrah wines, with three maceration times (10, 20 and 30 days), stating the longer time (30 days) as the one producing wines with higher amounts of total phenolic compounds (1,861 mg L^{-1}), flavanols (73.49 mg L^{-1}), flavonols (15.32 mg L^{-1}), and phenolic acids (40 mg L^{-1}). In general, red wines present phenolic compounds contents around 2,000 mg L^{-1} expressed in GAE (WATERHOUSE *et al*., 2016). Nevertheless, the phenolic extraction coefficient may suffer interference of reactive losses such as phenolic reactions with acetaldehyde (WATERHOUSE *et al.*, 2016).

Figure 6: Principal Component Analysis obtained by the quantification of the phenolic compounds using spectrophotometric and HPLC-DAD-FD methods, and evaluation of the antioxidant activity in the red wines Petit Verdot, Merlot, Malbec, and Tempranillo produced with high pH grape values and short maceration time during the winemaking (96h).



TMA = Total monomeric anthocyanins; TCP = Total phenolic compounds.

As expected, ABTS and FRAP presented a similar behavior to TPC, being Petit Verdot the wine with the highest amounts of these compounds and AOX (Table 6). Phenolic compounds are known as components with high antioxidant activity, which explains why wines rich in phenolics may have major aging potential (ALEIXANDRE-TUDO; DU TOIT, 2020), and why red wines are usually more long-lived than white wines. This happens because this molecule's bioactivity work as a wine's natural protection, stabilizing free radicals and preventing oxidation. Furthermore, the presence of bioactive compounds is related to less free sulfur dioxide consumption, as both have the same mechanism of action. The opposite cause-and-effect relationship also occurs as per Gabriele et al. (2018), as they found higher contents of gallic acid, tyrosol, resveratrol, caffeic acid, and malvidin when the SO_2 dosage was higher. According to Figure 4 and Table, 6, Petit Verdot wine had great free SO_2 (34.22 g L^{-1}) and the highest values of ABTS and FRAP assays (6.0 mmol L^{-1} TEAC and 23.22 mmol L^{-1} of $FeSO_4$, respectively). It is important to mention that all samples had the same free SO_2 at the bottling, as per section 2.1 in Material and methods.

Clustered with TPC (Figure 6), (+)-catechins, (-)-epicatechins, and procyanidins A1, B1, and B2 were presented in great values in the Petit Verdot wine. On the other hand, (-)-epicatechin gallate and (-)-epigallocatechin gallate were higher in the Tempranillo and Malbec

wines. Nevertheless, the total of flavanols followed the expected behavior, being higher to Petit Verdot, then Merlot, Malbec, and Tempranillo wines, and the majority flavanols being procyanidin B1 and (+)-catechin. ABTS and FRAP also were plotted as the same side of these compounds and Petit Verdot wine (Figure 6), confirming the important contribution of these compounds to the antioxidant activity of the red wine. Thus, these compounds probably increased the oxidation resistance of this sample. An approach has reported (+)-catechin as an important compound with high antioxidant property (GRZESIK *et al.*, 2018), showing high ABTS scavenging capacity and potential of Fe^{3+} reduction (FRAP), in comparison with hydroxycinnamic acids, stilbenes, and other bioactive compounds.

The flavonols presented expected values, with Petit Verdot having the greatest contents of isorhamnetin-3-*O*-glucoside (8.65 mg L^{-1}), myricetin (0.55 mg L^{-1}), and rutin (2.39 mg L^{-1}). However, Merlot had the highest contents of total flavonols, due to its great contents of quercetin 3-β-D-glucoside (15.82 mg L^{-1}), the most important flavonol in red wines, and the kaempferol-3-*O*-glucoside (2.12 mg L^{-1}). Despite these compounds are easy to oxidate (Ivanova-Petropulos et al., 2015), a weak relation between these contents and wine storage time (close to deterioration) has been reported (AGAZZI *et al.*, 2018). Flavonols concentration is also strongly dependent on grape skins time extraction during the maceration process (WATERHOUSE *et al.*, 2016).

Anthocyanins amounts are shown in Table 6. As expected, malvidin-3-*O*-glucoside was the major anthocyanin present in all the samples. Petit Verdot wine had the highest contents of malvidin-3-*O*-glucoside, pelargonidin-3-*O*-glucoside, and petunidin-3-glucoside and was the only sample in which it was detected contents of delphinidin-3-*O*-glucoside. Merlot wine also had great contents, being higher in peonidin-3-*O*-glucoside. On the other hand, Tempranillo wine stood out as the sample with the smallest amounts of monomeric anthocyanins quantified by HPLC-DAD-FD, and it was not possible to detect the presence of delphinidin-3-*O*-glucoside and peonidin-3-*O*-glucoside. The increasing of pH values changes the chemical structure of the grouping linked of aromatic rings of the monomeric anthocyanins, changing the color hue and promote featuring violet tones in the red wines at pH values above 4. The Tempranillo wine did not present this color due to the deterioration rate in this sample, which resulted in the polymerization of the anthocyanins (Figure 1, Appendix B).

Phenolic acids presented a quite different behavior than other phenolics. Petit Verdot wine presented the greatest contents to gallic (7.47 mg L^{-1}), ferulic (0.70 mg L^{-1}), and *trans*-caftaric (495.03 mg L^{-1}) acids. Tempranillo wine had the second-highest total phenolic acids, standing out in the contents of caffeic, ρ-coumaric, and chlorogenic acids, and showed relevant

amounts of *trans*-caftaric acid, the main non-flavonoid compound present in red wines (JACKSON, 2020) This phenolic acid class is strongly associated with wine sensory changes and play an important role in wine deterioration, such as anthocyanins acylation (with ρ-coumaric and caffeic acids) and color stabilization (CHEYNIER *et al.*, 2010; CONSTANTINI; GARCÍA-MORUNO; MORENO-ARRIBAS, 2009), being the primary substrate (caftaric acid) for the polyphenol oxidase enzyme (JACKSON, 2020). Also, phenolic acids have been reported with an inversely proportional behavior to the aging potential of the red wines, indicating the ability of these compounds to compose more complex phenolic structures (ALEIXANDRE-TUDO; DU TOIT, 2020), commonly present in aged and deteriorated red wines. Furthermore, the higher amounts of ρ-coumaric in the Malbec and Tempranillo wines may be related to the major deterioration rate of these samples, since the ρ-coumaric has been reported with a great increase in older wines, indicating the hydrolysis of coutaric acid, its corresponding tartaric acid ester (AGAZZI *et al*., 2018). Similar behavior has been observed in other phenolic acids, as Tempranillo wine having more caffeic acid than Petit Verdot wine seems to be related to the fact of Petit Verdot had more caftaric acid than Tempranillo. The fact of caftaric acid is the corresponding tartaric acid ester of the caffeic (WATERHOUSE *et al*., 2016) may be related to this behavior, suggesting a relation between more deteriorated samples and hydrolysis of tartaric acid ester phenolic acids. Figure 6 may confirm that relation, as ρ-coumaric and caffeic acids are clustered with Malbec and Tempranillo wines, while the caftaric, ferulic, and galic acids are plotted on the opposite side, together with Petit Verdot wine. Chlorogenic acid is the only phenolic acid explained by PC2, closer to Tempranillo and Merlot wines.

On the other hand, stilbenes class had heterogeneous results and did not fit with a single sample (Figure 6), with the greatest contents of *trans*-resveratrol in the Tempranillo (0.27 mg L^{-1}) and Malbec (0.27 mg L^{-1}) wines, *cis*-resveratrol (1.04 mg L^{-1}) in the Malbec wine, and piceatannol (0.70 mg L^{-1}) in the Petit Verdot wine. Concerning the total stilbenes, results are quite low, due to the total level usually close around 7 mg L^{-1} (WATERHOUSE *et al*., 2016).

4. Conclusions

The influence of high pH grape value and short maceration time during the winemaking over red wine deterioration has been investigated, using Petit Verdot, Merlot, Malbec, and Tempranillo cultivars. The effect of high wine pH over several compounds and chemical parameters had great implications, however, it was affected by the natural grape variety phenolic profile, which may delay the spoilage reactions and protect the wines. The short

maceration time (until 96 hours) was harmful to red wines, as decreased the extraction of the phenolic compounds, shortening the antioxidant activity of the product and toward the acceleration of their deterioration. Colorimetric parameters, tonality, acetaldehyde, and free SO_2 greatly work as physical and chemical spoilage indicators, respectively. Acetaldehyde content had a strong correlation with free SO_2 losses, color changes in the wine, and high pH values. The phenolic profile point to a spoilage resistance increasing of red wines riches in (+)-catechin, procyanidins, and anthocyanins, while some esters-hydrolyzed hydroxycinnamic acids may relate with deterioration (ρ-coumaric and caffeic acids). Reduce maceration may not be the best alternative to musts with high pH, as the phenolic extraction is necessary to increase the wine spoilage resistance. In addition, other acetaldehyde, 1-propanol, and 3-methyl-1-butanol quantification in wines using GC-BID were not found. Red wines elaboration with high pH grapes may require maceration time increasing or great SO_2 dosages, to improve major shelf-life to these wines.

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FINAL CONSIDERATIONS

An extended chemical study about Tannat, Syrah, Petit Verdot, Merlot, Malbec, and Tempranillo varietal red wines from Sub-middle São Francisco Valley, Brazil, with different approaches has been carried out. This region composes the new wine geography of tropical wines, which has proved the possibility to produce wines in non-traditional and warm regions. These regions may be important references to traditional wine-producing countries to face the global heating and future climatic impacts in viticulture. The pH raising may be a consequence of this heating, despite being common in tropical countries. Then, the wines produced in this present work had different behaviors facing these pH values, being the phenolic contents the determinant factor to the quality of wines. Concerning Syrah and Tannat wines, the high pH value and short maceration time did not avoid great results of some phenolic compounds such as *trans*-caftaric acid and procyanidin B1, as well as antioxidant activity by ABTS and FRAP methods. Therefore, Tannat stood out as a grape cultivar with great phenolic and antioxidant potential to be explored in wine-producing regions with tropical climate conditions, as these edaphoclimatical features may enhance these potentials. In agreement, the approach with the Petit Verdot, Merlot, Malbec, and Tempranillo wines deepened the investigation, using indicators of deterioration to prove the presence of physical and chemical spoilage in these wines. Also, the other evaluations confirmed and explained the influence of high pH value over the color losses, acetaldehyde, 1-propanol, alcohol content, anthocyanins, free SO_2, antioxidant activity; and the influence of short maceration in phenolics extraction, antioxidant activity, and spoilage resistance of the wines. Only high pH values may not be enough to spoil the wine, as other parameters may provide chemical stability, such as phenolic compounds and their

antioxidant activity. Therefore, longer macerations or cryomaceration with traditional maceration combined may be an alternative to increase the high-pH wine's stability, through greater extraction of phenolic compounds, besides acidity correction or field interventions to reduce pH.

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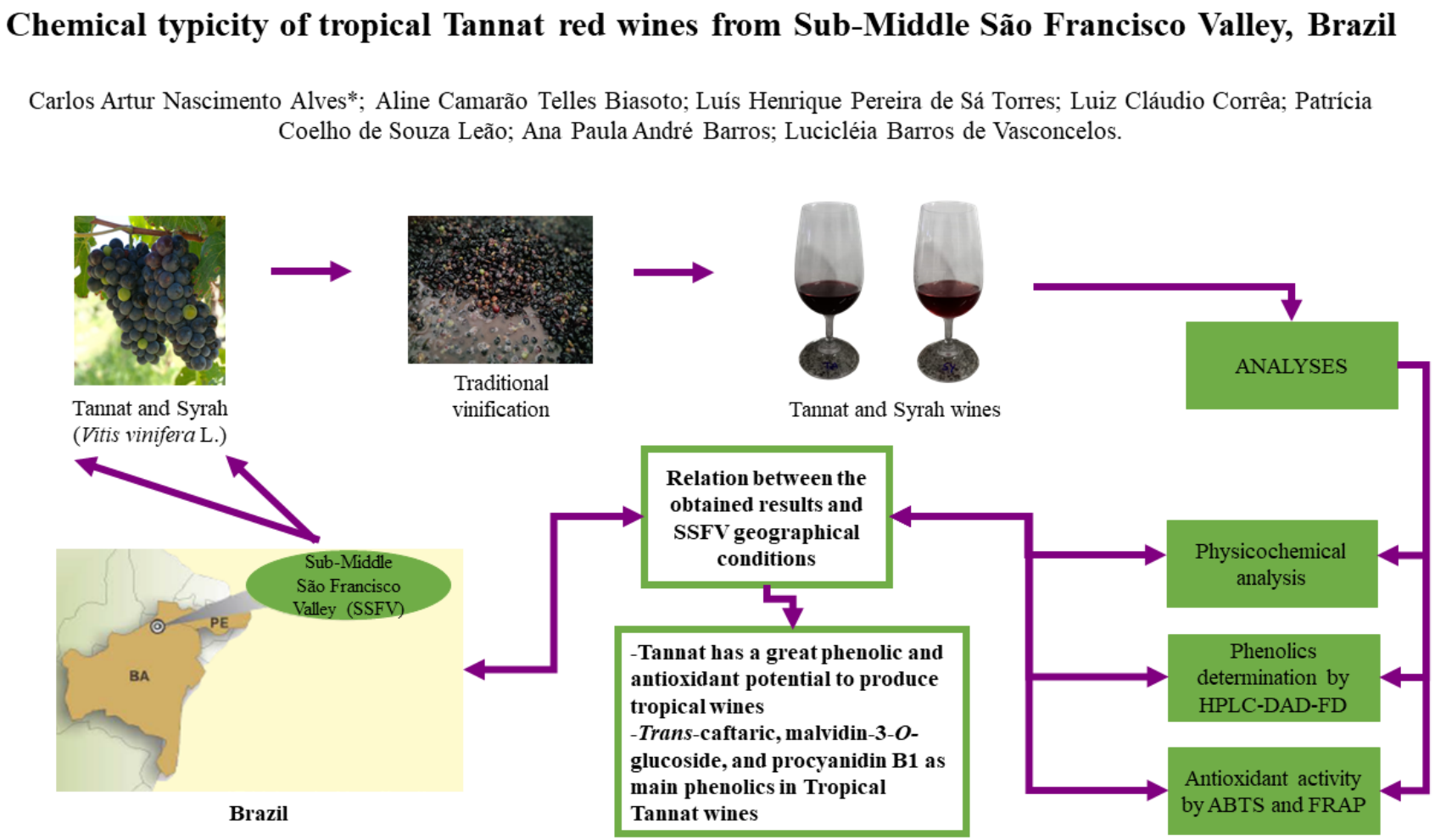
APPENDIX A – GRAPHICAL ABSTRACT OF CHAPTER 2



APPENDIX B – SUPPLEMENTARY MATERIAL OF CHAPTER 4

Figure 1: Anthocyanin's profile of the red wines Petit Verdot, Merlot, Malbec, and Tempranillo produced with high pH grape values and short maceration time (96h) during the winemaking.

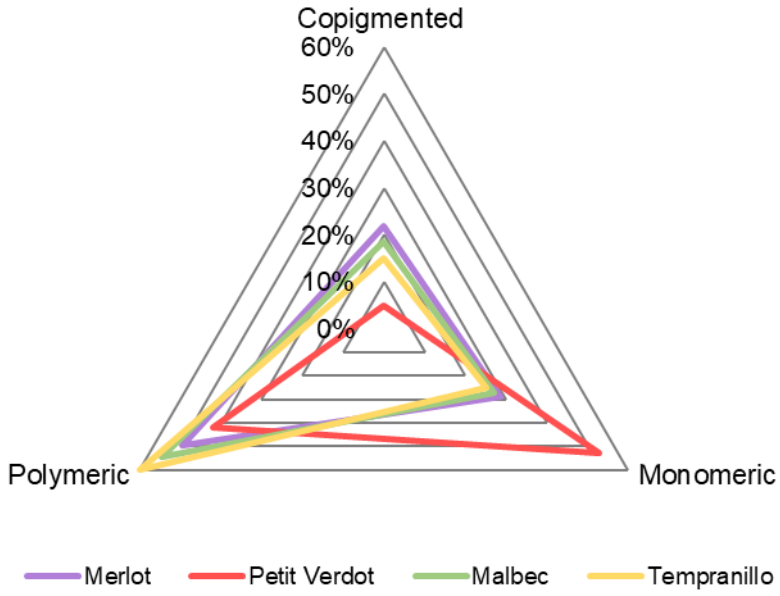
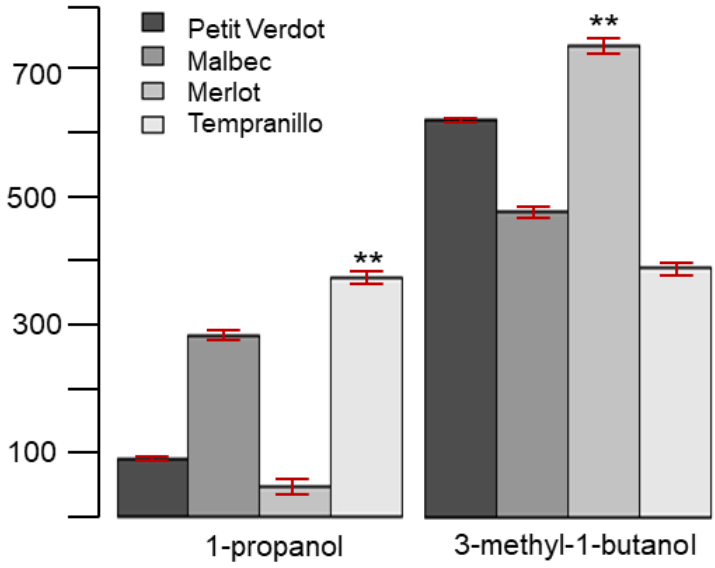


Figure 2: higher alcohols of the red wines Petit Verdot, Merlot, Malbec, and Tempranillo produced with high pH and short maceration time.



Means with asterisks differ by Student's T-Test '*' ($p \leq 0.05$) '**' ($p \leq 0.01$).

APPENDIX C – GRAPHICAL ABSTRACT OF CHAPTER 4

How the short maceration time and high pH may influence physical and chemical deterioration of red wines

Carlos Artur Nascimento Alves; Aline Camarão Telles Biasoto*; Grace da Silva Nunes; Hélio Oliveira do Nascimento; Ronaldo Ferreira do Nascimento; Luiz Cláudio Corrêa; Patrícia Coelho de Souza Leão; Lucicléia Barros de Vasconcelos.

Petit Verdot, Merlot, Malbec, and Tempranillo grapes (*Vitis vinifera* L.)

Grapes and musts with high pH

Wines in deterioration stage

short maceration (96 hours) applied during traditional winemaking

Are there which mechanisms of deterioration in these wines?

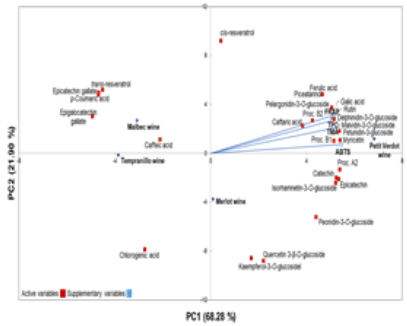
Chemical
Indicators: free SO_2 and acetaldehyde

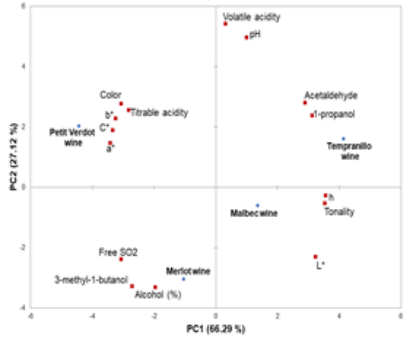
Physical
Indicators: color and tonality

Microbiological
Indicator: volatile acidity

YES

How the high pH value and short maceration influence these mechanisms





The effect of high pH value had great implications over several compounds and chemical parameters

The short maceration time decreased the phenolic compounds extraction, antioxidant activity, and accelerated wine deterioration