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SAMARA DE MACÊDO MORAIS

POTENCIAIS MARCADORES DE TIPICIDADE AROMÁTICA DE VINHOS TROPICAIS DO VALE DO SÃO FRANCISCO EM PROCESSO DE INDICAÇÃO GEOGRÁFICA

JOÃO PESSOA - PB
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Tese apresentada ao Programa de Pós-Graduação em Ciência e Tecnologia de Alimentos, da Universidade Federal da Paraíba em cumprimento aos requisitos para obtenção do Grau de Doutor em Ciência e Tecnologia de Alimentos.

Orientador: Prof. Dr. Flávio Luiz Honorato da Silva

Coorientadora: Prof.ª Dr.ª Luciana Leite de Andrade Lima Arruda

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“Peçam, e lhes será dado. Procurem, e encontrarão. Batam, e lhes será aberto. Pois, todo aquele que pede recebe, quem procura encontra, e a quem bate se abrirá”

(Mateus 7, 7-8)

RESUMO

O Vale do São Francisco (VSF), segunda maior região produtora de vinhos do Brasil, apresenta uma vitivinicultura diferenciada, uma vez que se encontra localizada no bioma caatinga, com particularidades edafoclimáticas como: clima tropical semiárido, alto índice de insolação, baixo índice pluviométrico e água disponível para irrigação. Estas particularidades permitem a produção escalonada de uvas, com duas colheitas por ano, em um mesmo vinhedo, e consequente elaboração de vinhos tintos e espumantes com composição química que abrange uma diversidade de compostos, dos quais os voláteis conferem autenticidade e qualidade à bebida. Neste contexto, esta pesquisa teve como principal objetivo identificar potenciais marcadores químicos voláteis para tipificar o grupo seleto de vinhos tintos e espumantes que fazem parte do processo de obtenção da Indicação Geográfica (IG) VSF. Diante do exposto, o perfil de compostos voláteis destes vinhos, 4 espumantes e 9 tintos, foi determinado por microextração em fase sólida no modo *headspace* associado à técnica de cromatografia gasosa acoplada à espectrometria de massa (HS-SPME/GC/MS), cujos resultados foram avaliados por análises estatísticas multivariadas. Nos vinhos espumantes foram identificados 109 compostos voláteis classificados em 13 grupos químicos, dos quais os ésteres, terpenos e álcoois foram majoritários. Do total, 33 compostos foram identificados em todos os vinhos espumantes, alguns compostos com representação de área mais expressiva foram identificados exclusivamente nos diferentes tipos de vinho espumante, sendo um total de 23 no moscatel, 9 no brut, 5 no brut rosé e 4 no demi-sec, com destaque para os compostos 2-fenil-undecano, 3-metil-4-heptanol, 4-fenil-undecano e germacreno B, identificados pela primeira vez em vinhos espumantes elaborados no VSF. Os resultados dos vinhos espumantes indicaram forte associação das variedades de uvas e dos processos tecnológicos de vinificação. Nos vinhos tintos foram identificados 103 compostos voláteis, classificados em 13 grupos químicos dos quais os ésteres e álcoois foram os grupos majoritários. Do total de compostos, 27 foram identificados em todos os vinhos tintos, as cultivares influenciaram na distinção de voláteis expressos exclusivamente em apenas um tipo de vinho. Dos 103 compostos identificados nos vinhos tintos desta pesquisa, 22 se destacaram por sua primeira identificação em vinhos tintos elaborados no VSF, a exemplo dos aromáticos 3-fenil-undecano e 4-fenil-decano. Neste contexto, os perfis voláteis dos vinhos espumantes e tintos comerciais do VSF apresentaram possíveis marcadores de tipicidade que podem ser úteis para a rastreabilidade e indispensáveis para confirmação da autenticidade e tipicidade dos vinhos desta região, pré-requisitos necessários para auxiliar no processo de estruturação de IG.

Palavras-chave: Compostos voláteis. HS-SPME/GC/MS. Indicação Geográfica. Vinhos tintos. Vinhos espumantes. Vale do São Francisco.

ABSTRACT

The São Francisco Valley (VSF), the second largest wine producing region in Brazil, presents a differentiated viticulture, since it is located at the caatinga biome, with particularities such as: tropical semi-arid climate, high rate of solar radiation, low rainfall and water available for irrigation. These particularities allow the staggered production of grapes, with two harvests per year, in the same vineyard, and the consequent elaboration of fine still and sparkling wines with a chemical composition that includes a diversity of compounds, of which the volatile ones confer authenticity and quality to the drink. In this context, this research had as main objective to identify volatile chemical markers to typify the select group of red and sparkling wines that are part of the process of obtaining the Geographical Indication (GI) VSF. In view of the above, the profile of volatile compounds of these wines, 4 sparkling and 9 red, was determined by microextraction in solid phase in headspace mode associated with the technique of gas chromatography coupled to mass spectrometry (HS-SPME/GC/MS), whose results were evaluated by multivariate statistical analysis. In sparkling wines, 109 volatile compounds were identified, classified into 13 chemical groups, of which the esters, terpenes and alcohols were the majority. Of the total, 33 compounds were identified in all sparkling wines, some compounds with more expressive area representation were identified exclusively in the different types of sparkling wine, being a total of 23 in muscatel, 9 in brut, 5 in brut rosé and 4 in demi-sec, with emphasis on compounds 2-phenyl-undecane, 3-methyl-4-heptanol, 4-phenyl-undecane and germacrene B, identified for the first time in sparkling wines from VSF. The results of sparkling wines indicated a strong association of grape varieties and technological processes of winemaking. In red wines 103 volatile compounds were identified, classified into 13 chemical groups of which the esters and alcohols were the major groups. Of the total of compounds, 27 were identified in all red wines, the cultivars influenced the distinction of volatiles expressed exclusively in only one type of wine. Of the 103 compounds identified in red wines, 22 stood out for their first identification in wines from VSF, like the aromatic 3-phenyl-undecane and 4-phenyl-decane. In this context, the volatile profiles of the commercial sparkling and red wines of the VSF presented possible markers of typicity that can be useful for traceability and indispensable for confirming the authenticity and typicity of wines of this region, necessary prerequisites to assist in the GI structuring process.

Keywords: Volatile compounds. HS-SPME/GC/MS. Geographical Indication. Red wines. Sparkling wines. San Francisco Valley.

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LISTA DE ABREVIAÇÕES E SIGLAS

AB	Alicante Bouschet
ATT	Acidez Total Titulável
AV	Acidez Volátil
AG	Aragonês
CS	Cabernet Sauvignon
CS/SY	Mistura de Cabernet Sauvignon e Syrah
CS/SY/AB	Mistura de Cabernet Sauvignon, Syrah e Alicante Bouschet
CS/SY/AB/TN/AG	Mistura de Cabernet Sauvignon, Syrah, Alicante Bouschet, Touriga Nacional e Aragonês
GC	Cromatografia gasosa (do inglês, *Gas chromatography*)
HS	Espaço confinado (do inglês, *Headspace*)
IF	Índice de frio noturno
IG	Indicação Geográfica
IP	Indicação de Procedência
IH	Índice heliométrico
IS	Índice de seca
MÍN	Mínimo
MÁX	Máximo
MS	Espectro de massas (do inglês, *mass spectrum*)
RC	Ruby Cabernet
SPME	Microextração em fase sólida (do inglês, *solid phase micro extraction*)
SY	Syrah
TDN	1,1,6-trimetil-1,2-dihidronaftaleno (do inglês, *1,1,6-trimethyl-1,2-dihydronaphthalene*)
TN	Touriga Nacional
TP	Tempranillo
VSF	Vale do São Francisco

SUMÁRIO

1 INTRODUÇÃO

A viticultura brasileira é caracterizada por sua diversidade e particularidades regionais como cultivares, época de colheita, ciclo de produção e manejo viticultural. Em 2019, o Brasil elaborou 2 milhões de hectolitros de vinhos, destacando-se na produção de vinhos no hemisfério sul, ocupando a quinta posição com produtos de alta qualidade, entre vinhos tintos, espumantes e brancos (MELLO; MACHADO, 2020; IBRAVIN, 2020a; OIV, 2020). Um total de 30,74 milhões de litros de espumantes foram comercializados em 2019, sendo 24,581 milhões de litros de espumantes nacionais, o que mostra que estes apesentam grande representatividade no mercado brasileiro (MELLO; MACHADO, 2020).

O Brasil é o único país do mundo onde temos três tipos de vinhos. Nos estados do Sul e Sudeste, assim como nos países tradicionais do mundo, são produzidos os vinhos tradicionais, com uma poda e uma colheita por ano. No Vale do São Francisco (VSF), Nordeste do Brasil, são produzidos os vinhos tropicais, com duas podas da videira e duas colheitas por ano, em qualquer período. E mais recentemente, desde 2004, são produzidos os vinhos de inverno nos estados do Sudeste, Centro-Oeste e Nordeste do Brasil (Chapada Diamantina-BA), em regiões com altitude entre 600-1.300 m (PEREIRA et al., 2020; PEREIRA, 2020; TONIETTO et al., 2020).

A região Nordeste possui 10.485 hectares de videiras, representando 13,85% da área vitícola nacional e concentra sua viticultura no VSF (Pernambuco e Bahia). Nesta região se elabora cerca de 4 milhões de litros de vinhos finos (*Vitis vinífera L.*) por ano, dos quais aproximadamente 29% são tintos, 1% brancos e 70% espumantes. Dos espumantes, 50% são moscatéis (doces) e 50% são espumantes finos bruts (secos) ou demi-secs (meio doces) brancos ou rosados (MELLO; MACHADO, 2020; PEREIRA et al., 2018).

O VSF, localizado no bioma caatinga, tem por características clima tropical semiárido, alta insolação, baixo índice pluviométrico, solo, em geral, de baixa fertilidade, água disponível para irrigação do rio São Francisco, e produção escalonada de uvas ao longo do ano, com duas safras anuais em mesmo vinhedo (IBRAVIN, 2020b; TONIETTO; TEIXEIRA, 2004; TEIXEIRA et al., 2013).

As vinícolas brasileiras vêm investindo nas Indicações Geográficas (IG) nos últimos 20 anos. Hoje são sete regiões com IG, seis no estado do Rio Grande do Sul e uma em Santa Catarina (EMBRAPA, 2020). A IG, espécie de selo de qualidade que atesta a especificidade do *terroir* de cada região produtora, é capaz de impulsionar o desenvolvimento territorial em seus aspectos sociais, econômicos, políticos e culturais, agregando valor diferencial aos produtos e serviços, e dando notoriedade à região (SIEDENBERG; THAINES; BAGGIO, 2017).

A Região do VSF possui IG para uvas de mesa desde 2009, dadas as suas particularidades edafoclimáticas, mas, por falta de organização do processo, não está funcionando corretamente, e os produtores não utilizam esta IG, chamada de Vale do Submédio São Francisco. No ano de 2014, a partir de um grande projeto financiado pelo CNPq e Embrapa Uva e Vinho, após solicitação das empresas vinícolas associadas ao Instituto do Vinho Vale do São Francisco (Vinhovasf), pesquisadores deram início ao processo de levantamento dos dados e resultados necessários para a solicitação da IG VSF, para vinhos tintos, brancos e espumantes. Esta solicitação está sendo feita em dezembro de 2020, pelo Vinhovasf para o Instituto Nacional da Propriedade Industrial (INPI) (EMBRAPA, 2020). Espera-se que o Vinhovasf receba a autorização de uso do selo da Indicação de Procedência ainda em 2021, o que contribuirá com uma melhoria na qualidade, da notoriedade, valor agregado, estimulando o setor vitivinícola da região, com melhores condições mercadológicas e competitividade.

Indicações Geográficas identificam produtos ou serviços associados a sua origem geográfica com características próprias que traduzem a identidade do local de produção (PINTO; PAIXÃO, 2018). A obtenção deste título para os vinhos do VSF depende, dentre vários fatores, da delimitação da área geográfica, descrição do meio natural (clima, solo, relevo, etc), importância socioeconômica, descrição dos produtos (vinhos e espumantes, além de sua caracterização físico-química e aromática, indicação de marcador(es) de tipicidade que possam auxiliar na notoriedade destes vinhos.

Há uma diversidade de compostos aromáticos nos vinhos com intensidade e complexidade variadas, associados à expressão de uma única casta ou à mistura de várias castas, dos quais os voláteis contribuem de forma significativa nas propriedades sensoriais e sua determinação também pode ser utilizada para estabelecer autenticidade e qualidade da bebida, auxiliando no processo de IG do vinho (NICOLLI et al., 2015; PONS et al., 2017; FERNANDES et al., 2018).

Nos vinhos, os compostos voláteis são divididos em três classes: aromas primários, associados à uva, são produzidos durante o amadurecimento da fruta; os aromas secundários que são provenientes da fermentação alcoólica, revelados pela ação das leveduras; e os aromas terciários que são os aromas de envelhecimento (DRAPPIER et al., 2017). Fatores como variedade da uva, condições edafoclimáticas e processo de vinificação influenciam na composição aromática do vinho (CAMARA; ALVES; MARQUES, 2006). Vale citar que mais de 1000 compostos voláteis - álcoois, ésteres, aldeídos, éteres, cetonas e terpenos – em distintas concentrações já foram identificados em vinhos (MENDES; GONÇALVES; CÂMARA, 2012).

A extração dos compostos voláteis por microextração em fase sólida (SPME, do inglês *solid phase micro extraction*) associada à separação por cromatografia gasosa (GC, do inglês *gas chromatography*) e o detector de espectrometria de massa (MS, do inglês *mass spectrum*) representam uma ferramenta confiável para análise de voláteis e semivoláteis de vinhos (OLEGÁRIO et al., 2019; RUIZ et al., 2019) com a finalidade de diferenciar cultivares, determinar a qualidade e tipicidade dos vinhos (CINCOTTA et al.,2015; Sánchez-Palomo et al., 2017) e diferenciar a origem geográfica desta bebida (ZIÓŁKOWSKA; WĄSOWICZ; JELEŃ,2016).

Nesse contexto, o *terroir* específico do VSF pode conferir atributos únicos e distinção aromática aos vinhos desta região. A literatura científica, até o presente momento, contempla poucos estudos com o perfil volátil de vinhos tintos e espumantes desta região, a exemplo das publicações de Nascimento et al. (2018) com vinhos espumantes experimentais das cultivares Chenin Blanc e Syrah, Barbará et al. (2020) com vinhos experimentais da cultivar Syrah e Fernandes et al. (2018), que analisaram vinho tinto comercial do VSF (monovarietal Cabernet Sauvignon). Estes estudos indicam que fatores como a cultivar, o processo tecnológico de vinificação e a origem geográfica influenciam na composição volátil dos vinhos produzidos no VSF.

A escassez de pesquisas voltadas para a descrição e determinação do perfil aromático dos vinhos tintos e espumantes comerciais elaborados no VSF, associada ao interesse em atender à demanda de informações dos vitivinicultores e consumidores motivaram a realização desta pesquisa, que utilizou um grupo de vinhos selecionados por *experts* para compor a Indicação Geográfica VSF. Neste contexto, objetivou-se: i) identificar o perfil de voláteis de espumantes produzidos no VSF, cujos produtos farão parte da Indicação Geográfica VSF; ii) auxiliar produtores, consumidores e a comunidade científica no conhecimento detalhado dos principais aromas presentes nos vinhos espumantes do VSF; iii) caracterizar e identificar importantes marcadores químicos voláteis de um grupo seleto de vinhos tintos comerciais jovens e envelhecidos de distintas cultivares, safras e vinícolas, indicados no processo de estruturação de Indicação Geográfica VSF; iv) obter potenciais marcadores de qualidade e identidade de alguns vinhos tintos e espumantes do VSF.

2 REVISÃO DE LITERATURA

O vinho, bebida apreciada e reconhecida mundialmente, tem por definição estabelecida pela legislação brasileira “ bebida obtida da fermentação alcoólica do mosto simples de uvas sãs, frescas e maduras” (BRASIL, 1988) que, independente da cultivar, apresentam como principais componentes - água, álcoois, ácidos orgânicos, compostos fenólicos, proteínas e outras substâncias nitrogenadas, polissacarídeos, açúcares, compostos aromáticos, minerais e vitaminas (GUERRA; BARNABÉ, 2005; FERNANDES et al., 2017).

A síntese destes compostos nas uvas e consequentemente sua concentração nos vinhos está condicionada à variedade de uva, fatores que influenciam o desenvolvimento da baga (condições edafoclimáticas, localização geográfica e manejo agronômico) e processos de vinificação (BORGHEZAN, 2017).

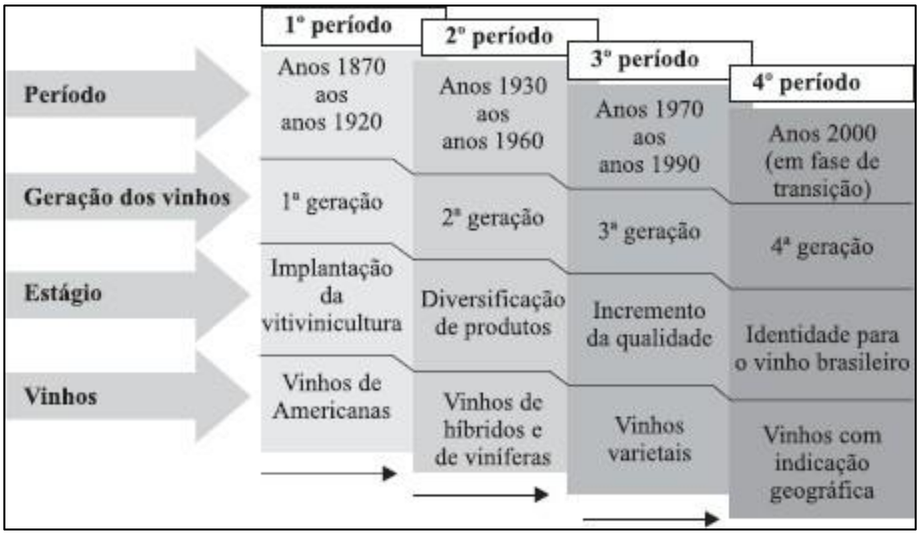
2.1 EVOLUÇÃO DA VITICULTURA NO BRASIL

A história da vitivinicultura brasileira teve início no século XVI, coincidindo com a sua colonização. Embora as primeiras videiras *Vitis vinifera L.* tenham sido trazidas em 1532 por Martin Afonso de Souza, condições desfavoráveis durante o cultivo postergaram a elaboração do primeiro vinho brasileiro por Brás Cubas, para 1551. Em 1626, os Jesuítas, entre os quais o padre Roque Gonzáles de Santa Cruz, introduziram o cultivo de videiras no Rio Grande do Sul (IBRAVIN, 2020c). Após um período de estagnação, a viticultura foi retomada entre 1870-1875 com a vinda dos italianos para a Serra Gaúcha (PACHECO, 2006).

No final de 1950, a viticultura estava restrita aos três estados do Sul e regiões leste de São Paulo e sul de Minas Gerais. No entanto, desse momento em diante, houve uma grande ampliação da fronteira vitícola, com a plantação de uvas na região do Vale do São Francisco, seguindo-se as regiões norte do Paraná, noroeste de São Paulo e norte de Minas Gerais (CAMARGO; TONIETTO; HOFFMANN, 2011). Todavia, até 1960, os vinhos brasileiros apresentaram uma limitada evolução, situação modificada a partir de 1970, no qual, o vinho brasileiro obteve um bom conceito junto ao consumidor local (TONIETTO, 2003), principalmente aqueles produzidos na Serra Gaúcha.

Tonietto (2003) listou as principais etapas da evolução da viticultura brasileira, sendo esta, dividida em quatro períodos (Figura 1): o primeiro, representa o início dos vinhedos com produção de vinhos elaborados com cultivares americanas; o segundo, marca a diversificação de produtos com a elaboração de vinhos de cultivares híbridas e *Vitis vinifera L.*; o terceiro, prioriza a qualidade na elaboração com destaque para vinhos varietais; e o quarto e atual período, busca identidade regional dos vinhos e certificação por meio de Indicações Geográficas.

Figura 1 - Representação pictórica dos períodos evolutivos da vitivinicultura brasileira



Fonte: Tonietto (2003)

Na elaboração dos vinhos brasileiros, dada a variação de altitude, incluem-se regiões de clima temperado, subtropical e tropical. Há uma diversidade de uvas utilizadas, pois são mais de 120 cultivares *Vitis vinifera* e mais de 40 cultivares de uvas americanas - *Vitis labrusca*, *Vitis bourquina* e híbridas interespecíficas (CAMARGO; TONIETTO; HOFFMANN, 2011).

Atualmente, o Brasil é o quinto maior produtor de vinhos do hemisfério Sul, com produção em 2019 de 2 milhões de hectolitros (mhL) e área de vinhedo de 81 mil hectares (kha) (Ibravin, 2020a; OIV, 2020). Possui videiras cultivadas em 18 estados, dos quais se destacam o Rio Grande do Sul, responsável por 90,00 % da produção nacional de vinhos e sucos de uva, e aproximadamente 85,00 % dos espumantes do Brasil, com 62,72% da área vitícola nacional ((MELLO; MACHADO, 2020).

Os espumantes nacionais ocupam lugar de maior representatividade no mercado brasileiro, já que de um total de 30,74 milhões de litros de espumantes comercializados em 2019, 24,58 milhões de litros de espumantes eram nacionais (MELLO; MACHADO, 2020). Em relação aos vinhos finos, estima-se que foram consumidos 132,16 milhões de litros, dos quais, 114,175 milhões de litros eram vinhos importados e 17,988 milhões de litros, vinhos nacionais (*Vitis Vinífera L.)* (MELLO; MACHADO, 2020).

A região Nordeste, cuja viticultura se concentra no VSF, possui 10.485 hectares de videiras, representando em 2019, 13,85% da área vitícola nacional (MELLO E MACHADO, 2020). Esta região está localizada nos estados de Pernambuco e Bahia, e é responsável pela elaboração de cerca de 4 milhões de litros de vinhos finos por ano e contemplando uma área de vinhedos de aproximadamente 400 hectares (PEREIRA et al., 2018). Além disso, é considerada uma região emergente na produção de vinhos, desde 1980, e se encontra em expansão, elaborando vinhos finos distintos dos vinhos originários das tradicionais regiões produtoras do mundo (ALMEIDA et al., 2016).

2.2 VINHOS TROPICAIS DO VALE DO SÃO FRANCISCO

Os vinhos denominados tropicais se referem aqueles elaborados entre os trópicos de Câncer e Capricórnio, cujas condições naturais não são suficientes para induzir a videira à dormência. Com o crescimento contínuo, faz se necessário o uso de tecnologias apropriadas que permitem duas ou mais colheitas por ano em mesmo vinhedo (CAMARGO; TONIETTO; HOFFMANN, 2011; BIROLO; ZANELLA, 2017).

A elaboração de vinhos tropicais se destaca na América do Sul: Brasil, Venezuela, Peru e Equador; na Ásia: Myanmar, Índia, Tailândia, Indonésia e Vietnã; na África: Etiópia, Gabão, Quênia, Namíbia e Tanzânia; e na Oceania: Polinésia Francesa (BIROLO; ZANELLA, 2017). O Brasil apresenta como principais polos de viticultura tropical o VSF, noroeste Paulista e norte de Minas Gerais, com expansão por vários outros estados como Espírito Santo, Mato Grosso do Sul, Mato Grosso, Goiás, Rondônia, Ceará e Piauí. (CAMARGO; TONIETTO; HOFFMANN, 2011).

O VSF é a única região vinícola do mundo localizada em clima semiárido e no bioma caatinga, considerada uma nova fronteira internacional na produção de vinhos, a região está situada no Nordeste do Brasil, entre os paralelos 8º e 9º Sul com altitude entre 200 a 800 m. Ademais, é caracterizada por topografia ondulada, com altitude média de 500m, variabilidade climática intra-anual que se enquadra em três grupos climáticos – IH+3(índice heliométrico: muito quente), IF-2 (índice de frio noturno: de noites quentes), IS+2 (índice de seca: forte)., IS+1(índice de seca: moderada) ou IS-1(índice de seca: subúmido) ao longo do ano (Tabela 1), baixo índice pluviométrico, elevada insolação (superior a 3.000 h/ano). Nestas condições, com altas temperaturas médias anuais (26,5 ºC), elevada radiação solar, disponibilidade de água para irrigação, é possível produzir uvas todos os dias do ano, mediante escalonamento das parcelas vitícolas. Os solos são classificados como argissolo amarelo eutrófico / plintossolo típico (taxonomia do solo alfisolo), geralmente com baixa fertilidade. As videiras são podadas uma vez por ano e as uvas colhidas duas vezes ao ano, processos definidos pelo produtor, em função das demandas de mercado, e busca pela tipicidade nos diferentes períodos de produção (TONIETTO; TEIXEIRA, 2004; BENEDETTI et al., 2011; TONIETTO et al., 2012; ANDRADE et al., 2013; TEIXEIRA et al., 2013; IBRAVIN, 2020b).

Tabela 1 - Clima vitícola e grupos climáticos da Região do Vale do São Francisco ao longo dos 12 meses de colheita potencial de uvas para vinificação

Período	**Clima vitícola**			**Classe do clima vitícola**		
	IH	**IF (°C)**	**IS**	**IH**	**IF**	**IS**
Agosto-Janeiro	3659	21,3	-136	IH+3	IF-2	IS+2
Setembro-Fevereiro	3650	21,6	-85	IH+3	IF-2	IS+1
Outubro-Março	3654	21,3	-1	IH+3	IF-2	IS+1
Novembro-Abril	3563	21,0	46	IH+3	IF-2	IS+1
Dezembro-Maio	3490	20,0	51	IH+3	IF-2	IS-1
Janeiro-Junho	3376	18,8	43	IH+3	IF-2	IS+1
Fevereiro-Julho	3289	18,1	8	IH+3	IF-2	IS+1
Março-Agosto	3298	18,7	-52	IH+3	IF-2	IS+1
Abril-Setembro	3294	19,9	-110	IH+3	IF-2	IS+2
Maio-Outubro	3385	21,3	-162	IH+3	IF-2	IS+2
Junho-Novembro	3458	22,2	-182	IH+3	IF-2	IS+2
Julho-Dezembro	3572	21,7	-169	IH+3	IF-2	IS+2

IH (Índice Heliométrico); IH+3 (Índice Heliométrico: muito quente); IF (Índice de frio noturno); IF-2 (Índice de frio noturno: de noites quentes); IS (Índice de seca); IS-1 (Índice de seca: subúmido); IS+1(Índice de seca: moderada); IS+2 (Índice de seca: forte). Fonte: Tonietto et al., 2012

No VSF a viticultura requer conhecimento profundo das necessidades das videiras e dos produtos a serem elaborados, a exemplo da aplicação de hormônios para a quebra de dormência (cianamida hidrogenada), uso racional da ferti-irrigação, controles de pragas e doenças, definição da data ideal de colheita, bem como diversificação dos processos enológicos (PEREIRA et al., 2018).

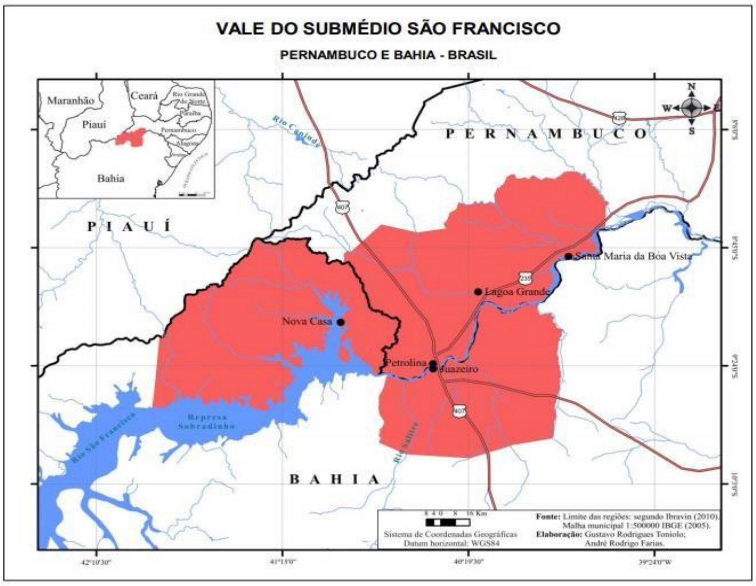
Na elaboração dos vinhos desta região predominam uvas de origem europeia (*Vitis vinifera L.)* como: Syrah, Tempranilo, Cabernet Sauvignon, Alicante Bouschet, Touriga Nacional, Grenache, Ruby Cabernet, como tintas, assim como Chenin Blanc, Sauvignon Blanc, Verdejo, Moscatos Itália e Canelli (LIMA et al., 2015; PADILHA et al., 2017; PEREIRA et al., 2018).

Dos 4 milhões de litros de vinhos finos (*Vitis vinifera*) elaborados por ano, cerca de 29% são tintos, 1% brancos e 70% espumantes, dos quais 50% são moscatéis (doces) e 50% são espumantes finos bruts (secos) ou démi-secs (meio doces) brancos ou rosados (PEREIRA et al., 2018).

Atualmente, o VSF (Figura 2) possui sete vinícolas, distribuídas entre os municípios pernambucanos de Petrolina, Lagoa Grande e Santa Maria da Boa Vista, além de Casa Nova e Curaçá na Bahia (PEREIRA et al., 2018). São aproximadamente 6.848 hectares de vinhedos em Pernambuco, e 2.119 hectares na Bahia, com produção de 237.367 e 56.940 toneladas de uvas, respectivamente.

Dentre as vinícolas que ganharam notoriedade e reconhecimento internacional, vale ressaltar a Terra Nova Miolo na Expovinis 2012, com o melhor vinho tinto do país (monovarietal Syrah); e a Vitivinícola Santa Maria/Global Wines, que no concurso mundial de Bruxelas 2014, recebeu medalha de ouro com vinhos tintos (monovarietais Touriga Nacional e Alicante Bouschet). Em outras premiações que recebidas posteriormente, destacam-se a Vitivinícola Santa Maria/Global Wines, no concurso mundial de Bruxelas edição 2018, com medalha grande ouro para o Espumante Rio Sol Extra Brut Gran Reserva (LIMA, 2019; COELHO-COSTA; CORIOLANO, 2017; MELLO, 2017).

Figura 2 – Mapa da região vitícola do Vale do São Francisco, em Pernambuco e na Bahia, Brasil.



Fonte: Tonietto et al., 2004

Os vinhos elaborados na região do VSF têm sido objeto de uma gama de pesquisas científicas com foco em alterações de manejo agronômico, época de colheita, processos de vinificação e caracterização cromática, fenólica e antioxidante, com destaque em vinhos tintos e brancos experimentais e comerciais (LIMA et al., 2015; PADILHA et al., 2017; MUCACA et al., 2017; PEREIRA et al., 2018; OLIVEIRA et al., 2019). Todavia, são escassas as pesquisas com descrição de perfil volátil de vinhos tintos (BARBARÁ et al., 2020; FERNANDES et al., 2018) e vinhos espumantes (NASCIMENTO et al., 2018).

2.3 INDICAÇÃO GEOGRÁFICA DOS VINHOS BRASILEIROS

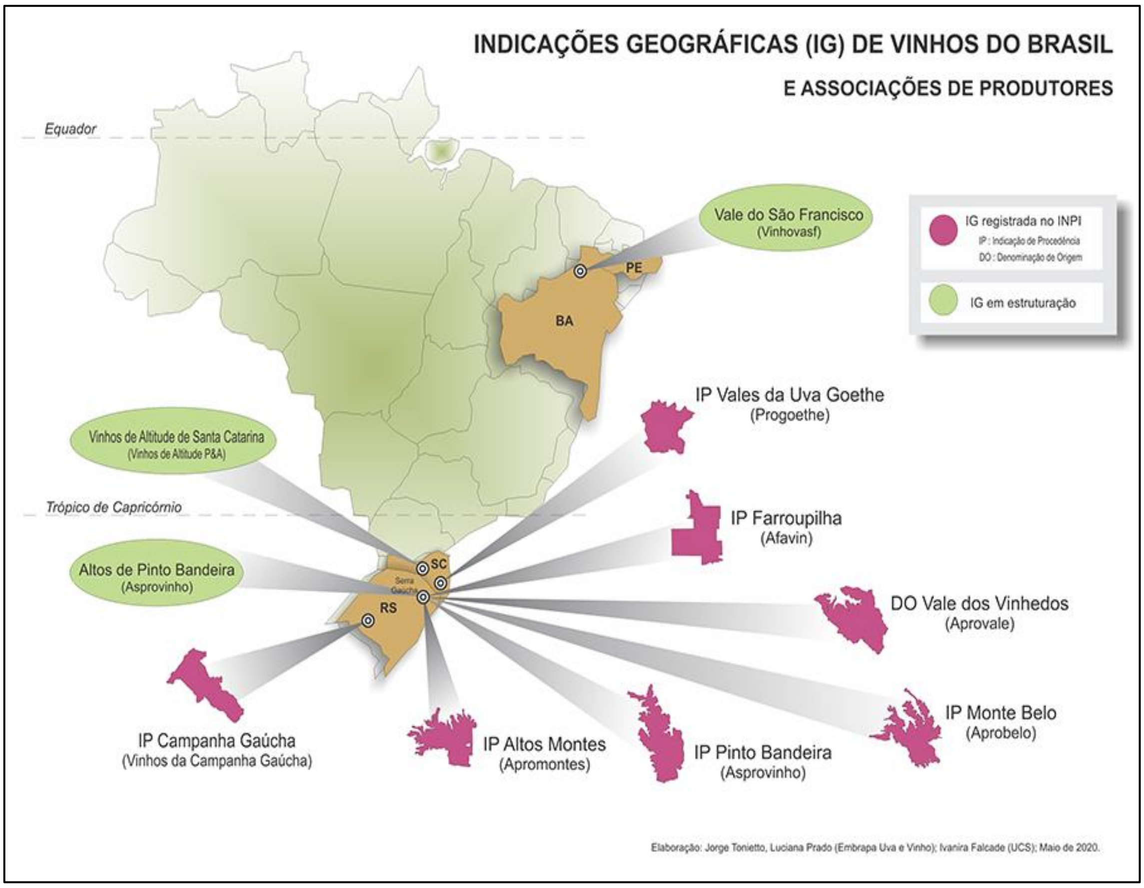
Historicamente, os vinhos de qualidade se referiam àqueles que suportavam longas viagens sem alterar suas características, como o sabor, fato que refletia no preço do produto. Dessa forma, o comércio e a qualidade do produto possuíam uma forte ligação, a qual gerou um vínculo da qualidade do produto com a região onde foi produzido: os *terroirs* (MELONI; SWINNEN, 2018).

No mundo, as primeiras Indicações Geográficas foram para vinhos e tiveram por base a delimitação dos *terroirs*, sendo o delineamento dos vinhos da Borgonha datado do século XV, o mais antigo. Outro fato importante ocorreu no século XVIII, onde os vinhos do Porto e vinhos Chianti, foram os primeiros a obter status de IG, junto com os vinhos Tokay da Hungria. Já no século XX, a delineação de Champagne foi a primeira introdução de "Denominação de Origem". Os famosos vinhos de Bordeaux na França foram delimitados e classificados em 1855. As delimitações de Indicações Geográficas atuais para Porto, Champagne, Chianti, e Borgonha, foram criadas em 1907, 1927, 1932 e 1935, respectivamente, e seguem em vigor até hoje com os limites dessas Indicações Geográficas praticamente inalterados (MELONI; SWINNEN, 2018).

No Brasil, a Propriedade Industrial é regida pela Lei 9.279 de 14 de maio de 1996, que dispõe sobre a Indicação Geográfica, existindo duas formas, a Indicação de Procedência (IP) e a Denominação de Origem (DO). A lei considera a IGP, conforme Artigo 177, como “o nome geográfico do país, da cidade, da região ou de localidade do seu território que tenha se tornado conhecido como centro de extração, produção ou fabricação de determinado produto ou de prestação de determinado serviço” (BRASIL, 1996).

A primeira Indicação Geográfica brasileira para vinhos ocorreu, em 2002, na Serra Gaúcha (IP Vale dos Vinhedos). Dando início a entrada do Brasil no círculo mundial das Indicações Geográficas para vinhos (Figura 3), certificações protegidas pelo Instituto Nacional da Propriedade Industrial (INPI), cujo estilo de produção, área delimitada, *terroir* específico, processos enológicos de vinificação, dentre outras especificidades são contempladas nas normas para Indicação Geográfica no setor de vinhos (PINTO; PAIXÃO, 2018; SIEDENBERG; THAINES; BOGGIO, 2017; NIERDELE; KELLY; VIEIRA, 2016).

Figura 3 - Mapa ilustrativo das Indicações Geográficas de Vinhos do Brasil



Fonte: Embrapa (2020)

Segundo o INPI (2020), estão reconhecidas na Legislação Brasileira sete (7) Indicações Geográficas (Figura 3 e Quadro 1) para vinhos e/ou espumantes, das quais seis (6) são Indicações de Procedência (IP), uma (1) Denominação de origem (DO), além de outras três (3) em processo de estruturação, incluindo a futura IP dos vinhos e espumantes do VSF (Figura 3).

Quadro 1 - As Indicações Geográficas de vinhos e espumantes registradas no Instituto Nacional da Propriedade Industrial - INPI

LOCAL	NÚMERO DE REGISTRO	DENOMINAÇÃO	VINHOS
Vale dos vinhedos	IG201008	DO	Tinto, branco e espumante
Alto dos Montes	BR4020120000020	IP	Espumantes finos (brancos e rosados), moscatel espumante e vinhos finos (tranquilos, brancos, rosados e tintos secos)
Farroupilha	BR4020140000069	IP	Espumante moscatel, vinho fino tranquilo branco moscatel, frisante e licoroso moscatel, mistela e brandy de moscatel
Monte Belo	BR4020120000063	IP	Espumante moscatel e vinhos finos tranquilos (brancos e tintos secos)
Pinto Bandeira	IG200803	IP	Espumante moscatel e os vinhos finos tranquilos (brancos, rosados e tintos secos)
Vale das Uvas Goethe	IG201009	IP	Vinho branco e leve branco - seco, suave ou demi-sec, o espumante - brut ou demi-sec e o vinho licoroso
Campanha Gaúcha	BR402017000009-1	IP	Espumantes naturais e os vinhos finos tranquilos (brancos, rosés e tintos)

DO: Denominação de Origem; IGP: Indicação Geográfica de Procedência.

Fonte: elaborado a partir de Embrapa (2020) e INPI (2020)

Das Indicações Geográficas em estruturação, vale ressaltar o VSF, cuja área a ser delimitada engloba 100% de todos os vinhedos do VSF, na Rede Integrada de Desenvolvimento (RIDE), do polo Petrolina-Juazeiro. A região está localizada em um clima tropical semiárido, cuja delimitação corresponde aos municípios de Petrolina, Lagoa Grande, Santa Maria da Boa Vista e Orocó, em Pernambuco, bem como Juazeiro, Casa Nova, Sobradinho e Curaçá, na Bahia (PEREIRA et al., 2018). A futura IP foi possível com apoio financeiro de um projeto financiado pelo MCT/Conselho Nacional de Desenvolvimento Científico e Tecnológico, e Embrapa Uva e Vinho, com vigência de 2014 a 2018 (PEREIRA et al., 2018; EMBRAPA, 2020; LIMA, 2020). A solicitação de registro da IP Vale do São Francisco será realizada ainda em 2020 pelo VINHOVASF, o Instituto do Vinho do VSF, que abriga todas as vinícolas da região. O registro deverá ser concedido pelo INPI até o final de 2021.

A concessão da IG não possui prazo de validade e pode ser utilizada por membros da área geográfica delimitada na qual, produz-se ou são prestados serviços, que devem seguir as normas contidas no regulamento de uso – Caderno de Especificações (INPI, 2020). Cada IG possui uma associação de produtores atuando na gestão, controle, proteção e promoção da sua certificação (EMBRAPA, 2020). Além de propiciar uma organização coletiva dos produtores, este reconhecimento tem por finalidade proteger o renome da região, preservar as características do produto e valorizá-lo junto ao consumidor, protegendo de falsificações e concorrências desleais. Adicionalmente, propicia o aumento do enoturismo e o desenvolvimento social, econômico, político e cultural da região (JACKSON, 2014; NETO et al., 2016; EMBRAPA, 2020).

Para auxiliar na obtenção das características reconhecidas como pertencentes a determinado produto, faz-se necessário a tipificação por meio da composição química e das propriedades sensoriais (DA COSTA; CASTRO; BARBOSA, 2016). A identificação de marcadores voláteis dos vinhos tintos e espumantes da região do VSF visa a tipificação da bebida, satisfazendo assim pré-requisitos necessários para auxiliar no processo de estruturação de IG do VSF.

2.4 COMPOSIÇÃO AROMÁTICA DOS VINHOS

O *bouquet* de um vinho é formado pela interação dos aromas primário, secundário e terciário, formado por vários compostos químicos voláteis e semivoláteis de distintas origens, polaridades e volatilidades, cuja estrutura química e concentração influenciam nas características do vinho e produzem um efeito nas percepções sensoriais dos consumidores

(RUIZ et al. 2019; PLUTOWSKA; WARDENCKI, 2008; PETRONILHO et al., 2020). A composição volátil dos vinhos exibe complexidade e diversidade molecular, em função de efeitos sinérgicos e antagônicos entre elas (BONINO et al., 2003). Conforme Drappier et al. (2017) e Visan et al., (2018), esta complexidade provém de distintas fontes: uva (compostos primários), levedura e fermentações (compostos secundários) e tratamentos pós-fermentativos como: estocagem em barrica de carvalho e armazenamento em garrafa (compostos terciários). Essa complexidade e diversidade dos *flavors* são valorizadas por especialistas e consumidores de vinhos. Importante observar que, até mesmo a diferença evidente entre vinhos brancos e tintos provém de nuances de aroma muito sutis (PARKER et al., 2017).

Os compostos que aparecem em baixas concentrações têm, frequentemente, maior influência nas propriedades sensoriais dos produtos alcoólicos (PLUTOWSKA; WARDENCKI, 2008). Além da concentração, o impacto dos aromas depende também da intensidade, geralmente expresso como o limite de detecção de odor, que é a menor concentração de um determinado composto detectado pelo olfato humano (ILC; WERCK-REICHHART; NAVROT, 2016).

Conforme Ilc; Werck-Reichhart; Navrot (2016), o aroma sofre grandes alterações no processo de vinificação como a desglicosilação dos compostos voláteis sintetizados nas uvas e a biossíntese de novos compostos. Estudo de Moreno et al. (2017) em vinhos Tempranillo da Espanha, reportou que a retirada precoce das folhas da videira induziu ao aumento da concentração de todas as famílias de compostos voláteis quantificados, exceto lactonas, com aumento significativo observado em 23 dos 34 compostos voláteis analisados. Enquanto, Barbará et al. (2020) estudaram o perfil volátil de vinhos elaborados com a uva Syrah e verificaram que uma maceração de 10 dias e 19° Brix foram as melhores condições experimentais para que se obtivesse um impacto mais agradável dos compostos voláteis. Ambos os estudos mostram a influência das práticas viticulturais e de vinificação na composição volátil de vinhos.

Outro fator de mudança na concentração de muitos compostos voláteis ocorre durante o armazenamento e envelhecimento do vinho em barricas de madeira como o carvalho. Como exemplo, cita-se a formação do composto β-metil-γ-octalactona (conhecido como carvalho ou uísque-lactona), extraído da madeira e que confere notas amadeiradas, de carvalho e de coco ao vinho (POLÁŠKOVÁ; HERSZAGE; EBELER, 2008). Em estudo de Garcia-Carpintero, Sánchez-Palomo e Viñas (2014), vinhos fermentados com pedaços (*chips*) de carvalho durante a etapa de fermentação alcoólica apresentaram, em geral, maiores concentrações de ésteres como o butanoato de etila, hexanoato de etila, octanoato de etila, decanoato de etila e acetatos de etila, hexila e isoamila do que o vinho de controle.

Além da extração de compostos voláteis do carvalho, reações oxidativas químicas e microbianas (por exemplo, acetobacter) podem contribuir para o *flavour* de vinhos envelhecidos como resultado da formação de compostos como o acetaldeído (aroma de nozes e “xerez”) e ácido acético (aroma de vinagre). Estes aromas são indesejáveis no vinho, quando estão em altas concentrações (POLÁŠKOVÁ; HERSZAGE; EBELER, 2008).

2.4.1 Principais classes químicas dos compostos voláteis de vinhos

A qualidade dos aromas dos vinhos está diretamente relacionada ao aroma global e, por conseguinte com a composição volátil responsável por estes aromas. Mais de 1000 compostos voláteis foram identificados em vinhos, dentre eles: ésteres, álcoois, aldeídos, éter, cetonas, C13-norisoprenóides e terpenos (VILANOVA et al., 2012; MENDES; GONÇALVES; CÂMARA, 2012).

- **Ésteres**

Os ésteres, classe mais abundante nos vinhos, da qual já foram identificados mais de 160 ésteres específicos, são formados pela condensação entre o grupo carboxila de um ácido orgânico e o grupo hidroxila de um álcool ou fenol. Em sua maioria, são formados durante a fermentação e o armazenamento, encontrados em baixas quantidades e volatilidades, entretanto os ésteres mais comuns ocorrem em concentrações acima de seus limiares sensoriais (JACKSON, 2020).

Em bebidas fermentadas, duas classes de ésteres se destacam, os ésteres de acetato com grupo acil derivado de acetato (na forma de acetil-CoA), e o grupo álcool com o etanol ou um álcool complexo derivado do metabolismo de aminoácidos. Os representantes significativos desta classe são acetato de etila, responsáveis pelos aromas frutados, semelhantes a solvente, acetato de isoamila, descritor aromático de banana, e acetato de 2-feniletil, que produzem os aromas florais, de mel, de rosas (CORDENTE, 2012).

A segunda classe é composta por ésteres etílicos de ácido graxo de cadeia média com o etanol no grupo do álcool e ácidos graxos de cadeia média no grupo acil, cujos representantes dessa classe são hexanoato de etila e octanoato de etila, ambos com aromas frutados como o aroma de maçã. Além dessas duas classes, os ésteres cíclicos com anéis de 5 membros (γ - lactonas) também podem contribuir para os aromas dos vinhos (Figura 4) (CORDENTE, 2012;

WATERHOUSE; SACKS; JEFFERY, 2016).

Figura 4 - Estrutura geral das principais classes dos ésteres que contribuem para o aroma dos vinhos

Fonte: Adaptado de Waterhouse; Sacks; Jeffery, 2016

Em vinhos envelhecidos, os ésteres resultam do equilíbrio de esterificação / hidrólise, onde altas concentrações de etanol favorecem o processo de esterificação de ésteres etílicos (BORDIGA et al., 2013).

No estudo de Karabagias et al. (2020), o composto acetato de isoamila foi identificado em maiores proporções em vinhos tintos secos da variedade Agiorgitiko. Este composto também apresentou a classe majoritária no estudo de Nicolli et al. (2018), na qual analisaram a influência de diferentes práticas viticulturais no perfil volátil de vinhos Merlot do Sul do Brasil. Os autores verificaram que os vinhos elaborados com uvas provenientes de uma videira com uma menor quantidade de gemas (20 por planta) obtiveram destaque no aroma do vinho com maiores níveis compostos como o hexanoato de etila e o octanoato de etila.

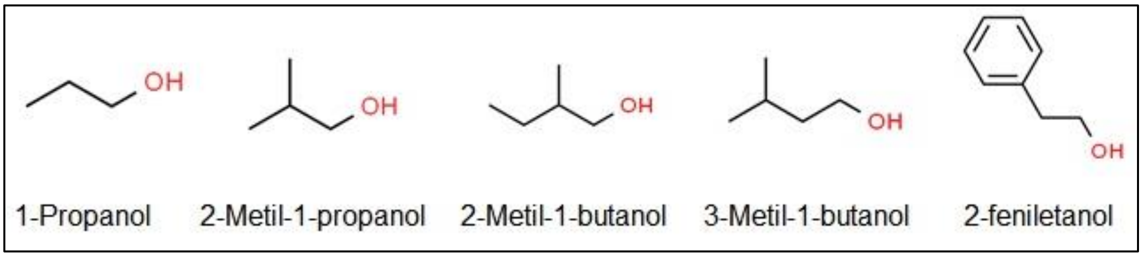
Os ésteres também foram destaque no estudo de Nicolli et al. (2015) realizado com 21 espumantes moscateis do Sul do Brasil e dois espumantes moscateis italianos, onde foram identificados 70 compostos voláteis dos quais a maior quantidade (27) pertenceram à classe dos ésteres, com maior percentagem de área total cromatográfica (57,96%). Neste estudo, os ésteres que exibiram maior área cromatográfica nas amostras dos espumantes moscateis brasileiros foram: octanoato de etila (7,30%), hexanoato de etila (4,37%), succinato de dietila (2,35%) e acetato de 2-feniletil (1.32%). Conforme Bordiga et al. (2013), os ésteres são componentes importantes do aroma dos vinhos, especialmente naqueles à base de moscatel, por suas notas frutadas e florais.

- **Álcoois**

A maioria dos álcoois dos vinhos são subprodutos da fermentação de levedura e podem ser provenientes de duas formas: do catabolismo de seu aminoácido correspondente, a exemplo da valina e leucina, e no anabolismo do aminoácido por meio do catabolismo do açúcar (ÉTIEVANT, 1991; JACKSON, 2020).

Os álcoois superiores mais importantes em vinhos (Figura 5), quantitativamente, são: 1-propanol, 2-metil-1-propanol, 2-metil-1-butanol, 3-metil-1-butanol e 2-feniletanol, responsável pelo aroma floral de rosas. A maioria dos álcoois podem atribuir aromas fortes aos vinhos (a exemplo do herbáceo), que em alta concentração podem mascarar a fragrância da bebida e em baixas concentrações (até 0,3 g/L) auxiliam na complexidade aromática (JACKSON, 2020).

Figura 5 - Estrutura química de alguns álcoois superiores importantes no vinho



Fonte:www.chemspider.com/Chemical-Structure

Bordiga et al. (2013) estudaram vinhos Asti espumante e Moscato d'Asti provenientes da Itália, armazenados por 6 meses em três diferentes temperaturas, e constataram na classe dos álcoois que em geral, os vinhos Asti espumante continham maiores quantidades de 3-metil-1-butanol e 2-metil-1-butanol comparado com as amostras de Moscato, e por sua vez os vinhos Moscato d'Asti continham mais 2-feniletanol, isobutanol, hexanol, propanol e butanol.

Estudos realizado por Somkuwar et al. (2020) com vinhos tintos elaborados na Índia, (cultivares Cinsault, Grenache, Cabernet Franc, Petit Verdot, Cabernet Sauvignon, Nielluccio, Tempranillo, Syrah, Merlot e Caladoc) reportaram ao obterem o perfil volátil destes vinhos, que a classe dos álcoois foi majoritária com destaque para o vinho Nielluccio (61,56 mg / L) no qual o principal composto dos álcoois, o 2, 3-butanodiol obteve maior concentração (28,08 mg/L).

- **Terpenos**

Os terpenos são constituintes secundários da planta, cuja biossíntese começa com acetil-CoA dos quais os compostos odoríferos são possivelmente monoterpenos e sesquiterpenos. Os monoterpenos, estrutura com 10 átomos de carbonos, formados a partir de duas unidades de isopreno, ocorrem na forma de hidrocarbonetos simples, aldeídos, álcoois, ácidos e ésteres (RIBÉREAU-GAYON et al., 2006; BORDIGA et al., 2013)

A variabilidade dos monoterpenos nas uvas tem possível origem nas enzimas que oxigenam o linalol em diferentes posições. A maioria destes compostos podem atribuir notas aromáticas florais e cítricas nos vinhos (ILC; WERCK-REICHHART; NAVROT, 2016).

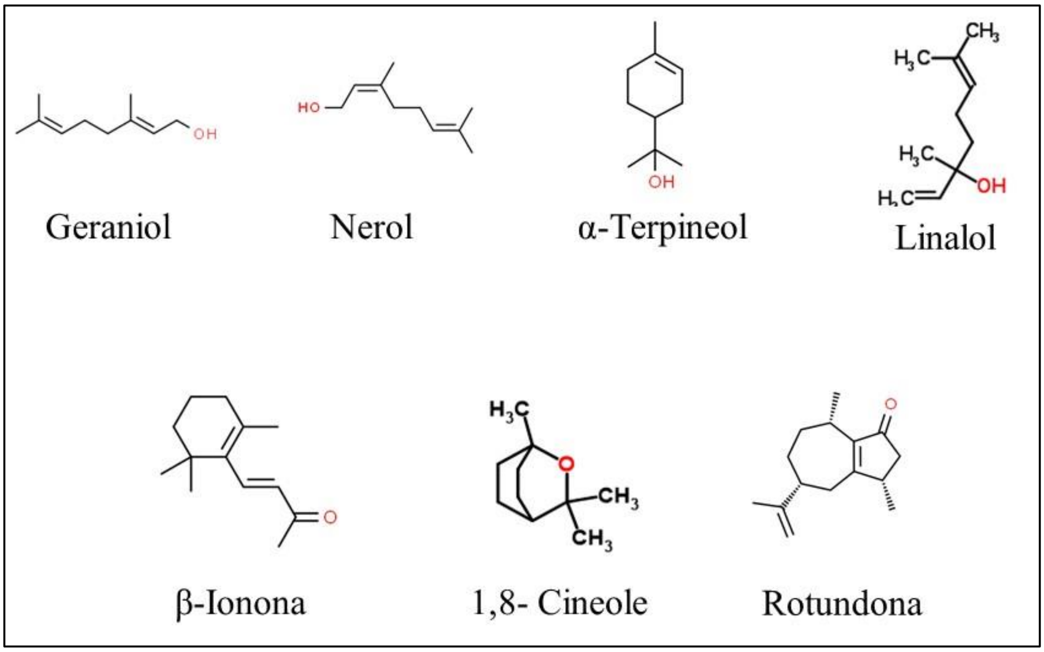
Os sesquiterpenos, estruturas com 15 átomos de carbonos, são formados a partir de três unidades de isopreno cujas concentrações nas uvas e vinhos provavelmente são muito baixas para serem detectados, porém também contribuem para o aroma de alguns vinhos (ILC; WERCK-REICHHART; NAVROT, 2016).

A casca da uva possui, em geral, maior concentração de monoterpenos livres e glicosilados em comparação com a polpa ou o suco. Variedade de uva Moscatel apresenta maiores concentrações de terpenos glicosídeos, compostos hidrolisados pela levedura durante a etapa de fermentação e pelas condições ácidas da fermentação (pH de 3,5, aproximadamente) com formação de terpenos voláteis (GONZALES-BARREIRO et al., 2014). Nestas condições os terpenos atribuem notas aromáticas florais para cultivares Moscatéis, aromas florais e cítricos para a Riesling (monoterpenos), aroma de frutas vermelhas em vinhos tintos (β-ionona), dentre outros aromas como eucalipto/menta (1,8- cineole) ou pimenta preta (rotundona) (BLACK et al., 2015).

Os álcoois monoterpênicos, geraniol, nerol, α-terpineol e linalol (Figura 6) são importantes para o aroma dos vinhos, em destaque nos vinhos brancos de uvas aromáticas, a exemplo da Moscatel e Malvasia (PEÑA, 2005; BORDIGA et al., 2013).

Mudanças naturais no conteúdo desses compostos podem ocorrer durante o armazenamento em garrafa resultando na conversão em seus respectivos óxidos (derivados das formas pirânicas e furânicas correspondentes) a exemplo do nerol oxide 3,6-dihidro-4-metil-2-(2- metil-1-propenil)-2H-piran) que é produto da oxidação do monoterpeno nerol (PEÑA, 2005; BORDIGA et al., 2013; KARABAGIAS et al., 2020).

Figura 6 - Estrutura química de alguns terpenos importantes para o vinho



Fonte: www.chemspider.com/Chemical-Structure

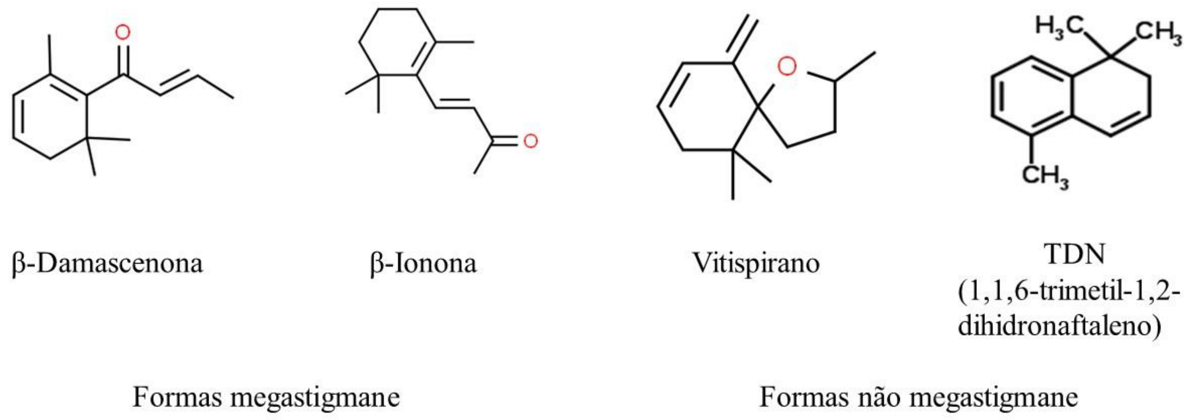
Estudo realizado por Condurso et al. (2016), em vinho Syrah de clima mediterrâneo (Itália) com e sem poda, relataram que dos aromas primários, os monoterpenos e hidrocarbonetos sesquiterpenos foram os principais contribuintes para o aroma dos vinhos de Syrah, principalmente nos vinhos cuja cultivar recebeu o tratamento da poda, onde a quantidade de (E)-nerolidol foi cinco vezes maior do que nos vinhos controle. Segundo o mesmo autor, o (E)-nerolidol, característico por suas notas florais, é um sesquiterpeno que provém do difosfato de farnesila.

O perfil dos terpenos é muito útil na diferenciação dos vinhos monovarietais daqueles elaborados com uma mistura de variedades. Dessa forma, a obtenção e disponibilidade dos perfis voláteis é imprescindível para detecção de fraude (PEÑA, 2005).

- **Norisoprenóides**

Os compostos norisoprenóides são provenientes da decomposição química ou enzimática (dioxigenases) dos carotenóides da uva, resultando em produtos de distintos tamanhos como o C13-norisoprenóide (13 átomos de carbono) e também ocorrem na forma de precursores glicosilados. Os C13-norisoprenóides são divididos em duas formas principais, megastigmane e não megastigmane, cujos principais compostos na uva encontram-se na Figura 7 (RIBÉREAU-GAYON et al., 2006; ILC; WERCK-REICHHART; NAVROT, 2016).

Figura 7 – Fórmulas estruturais dos principais compostos C13-norisoprenóides encontrados em uvas



Fonte: www.chemspider.com/Chemical-Structure

Estes compostos, em geral não estão associados a uma variedade de uva específica, dependem das condições de vinificação e apresentam um baixo limiar de odor, a exemplo do composto β-damascenona (200 ng/L) (GONZALEZ-BARREIRO et al., 2015; ILC; WERCK-REICHHART; NAVROT, 2016; VOCE et al., 2019). Esta classe de compostos contribui com notas frutadas, florais ou picantes, propiciando efeitos benéficos na qualidade sensorial dos vinhos (CAÑAS et al., 2008).

Destaque para o composto TDN (1,1,6-trimetil-1,2-dihidronaftaleno) classificado como um importante marcador de envelhecimento em vinhos, em geral está ausente em uvas e vinhos jovens, apresenta notas de queimado/cigarro/fumo/herbáceo, atingindo concentrações de 200 µg / L, enquanto seu limiar de percepção é da ordem de 20 µg/L (RIBÉREAU-GAYON et al., 2006; UBEDA et al., 2019).

Estudo com 35 vinhos espumantes comerciais, Cava, Champagne e vinho espumante Andalusia (Espanha) destacou dentre os compostos C13 norisoprenoides, evidenciando-se a importância do β-damascenona em modular a tipicidade dos vinhos elaborados com a uva Chardonnay (MUÑOZ-REDONDO et al., 2020). Conforme Voce et al. (2019), a presença de β-damascenona em vinhos espumantes comerciais italianos da cultivar Ribolla Gialla são importantes não apenas pelas altas concentrações, mas também pela possível modificação da percepção sensorial de alguns ésteres.

- **Outros compostos voláteis (ácidos, aldeídos e cetonas, hidrocarbonetos, fenóis, furanonas)**

No vinho, a maioria dos ácidos voláteis são saturados de cadeia linear que variam de 2 a 18 átomos de carbono, divididos em ácidos voláteis de cadeia curta (C2-C4), média (C6-C10) e longa (C12-C18). Os ácidos de cadeia ramificada incluem 3-ácido metil butanóico, ácido 2-metil butanóico e 2-metil ácido propanóico (RUIZ et al., 2019).

A produção de ácidos no vinho tem influência da composição do mosto e das condições de fermentação (SOMKUWAR et al., 2020). Conforme Étievant (1991) o impacto aromático dos ácidos é, em geral, insignificante, cujo aroma, em geral, é desagradável com odor rançoso e de queijo, por exemplo (ILC; WERCK-REICHHART; NAVROT, 2016).

Em relação à classe dos aldeídos e cetonas, os aldeídos possuem o grupo carbonila na posição terminal, enquanto as cetonas o grupo carbonila se posiciona no carbono interno. Poucos aldeídos são provenientes da uva, a maioria são produzidos durante a fermentação, processamento ou no armazenamento em carvalho (JACKSON, 2020).

O acetaldeído é o principal aldeído do vinho, do qual uma concentração de 100 a 125 mg/L, é indesejável para a maioria dos vinhos. Dos aldeídos o furfural e o 5-hidroximetil-2-furaldeído propiciam o aroma cozido/caramelado característico de alguns vinhos (JACKSON, 2020).

Na classe das cetonas, estas são produzidas durante a fermentação, mas poucas atribuem impacto sensorial aos vinhos (JACKSON, 2020). Ambas as classes possuem limiares sensoriais de 100 a 10000 vezes mais baixos ao comparar com seus álcoois correspondentes, dessa forma, uma mínima oxidação já pode modificar o aroma do vinho (WATERHOUSE; SACKS; JEFFERY, 2016).

Em relação aos hidrocarbonetos, estes, em geral, são associados a detritos celulares da uva que se perdem antes ou durante o processo de vinificação, não influenciando diretamente nas características sensoriais do vinho. Entretanto, os produtos da degradação de hidrocarbonetos podem produzir compostos voláteis importantes, a exemplo do β-damascenona, α e β-ionona e 1,1,6-trimetil-1,2-dihidronaftaleno (TDN) (JACKSON, 2008).

Na classe dos fenóis voláteis, presentes nos vinhos em concentrações de μg/L a mg/L, os compostos podem derivar de precursores originários das uvas, transformados por processos microbiológicos ou químicos, ou podem ser extraídos no armazenamento em madeira de carvalho torrada, transmitindo odores remanescentes de fumaça, medicamentos/produtos de limpeza, baunilha, especiarias e couro (WATERHOUSE; SACKS; JEFFERY, 2016). Alguns compostos desta classe, em baixas concentrações, podem contribuir para o aroma do vinho, a citar o 4-etilfenol, 4-etilguaiacol, 4-vinilfenol, 4-vinilguaiacol, guaiacol, eugenol e cresóis (ÉTIEVANT, 1991). Mas em concentrações mais elevadas, se transformam em defeitos, com odor de suor, cavalo, chiqueiro.

Também contribuem para o aroma do vinho, o grupo das furanonas provenientes da uva e do barril de carvalho e que demandam estudos quanto as origens químicas e bioquímicas para auxiliar na compreensão de fatores que influenciam as concentrações e a diversidade desses compostos no vinho (ROBINSON et al., 2014).

- **Pirazinas**

As pirazinas são formadas durante a desidratação da uva e possuem possíveis descritores aromáticos vegetativos e herbáceos, mais aparentes em uvas pouco maduras, e alguns aromas torrados derivados de reações de Maillard entre açúcares e aminoácidos (GONZALES-BARREIRO, et al., 2015; FERREIRA; LOPEZ, 2019).

As pirazinas possuem baixo limiar de odor e são correlacionadas com aromas herbáceos em uvas Cabernet Sauvignon e Sauvignon Blanc, apresentando compostos como 2-metoxi-3-isobutilpirazina (IBMP), 2-metoxi-3-isopropilpirazina e 2-metoxi-3-sec-butilpirazina (RIBÉREAU-GAYON et al., 2006; ROBINSON et al., 2014). As metoxipirazinas podem se sobressair no aroma do vinho, inibindo a percepção de outros compostos e, por consequência, a complexidade aromática (JACKSON, 2020).

Ademais, características não apreciadas em vinhos tintos de Bordeaux (França), local onde o solo é fator determinante nas concentrações de metoxipirazina em vinhos de Merlot, Cabernet Franc e Cabernet Sauvignon, dos quais as uvas provenientes de solos de cascalho bem drenados apresentam concentrações mais baixas de metoxipirazinas, enquanto que solos de calcário ou argila-silte propiciam teores mais altos deste composto volátil na cultivar Cabernet Sauvignon (RIBÉREAU-GAYON et al., 2006). E, conforme Jackson (2020), a concentração de metoxipirazina permanece consideravelmente mais alta em climas mais frios do que em climas mais quentes.

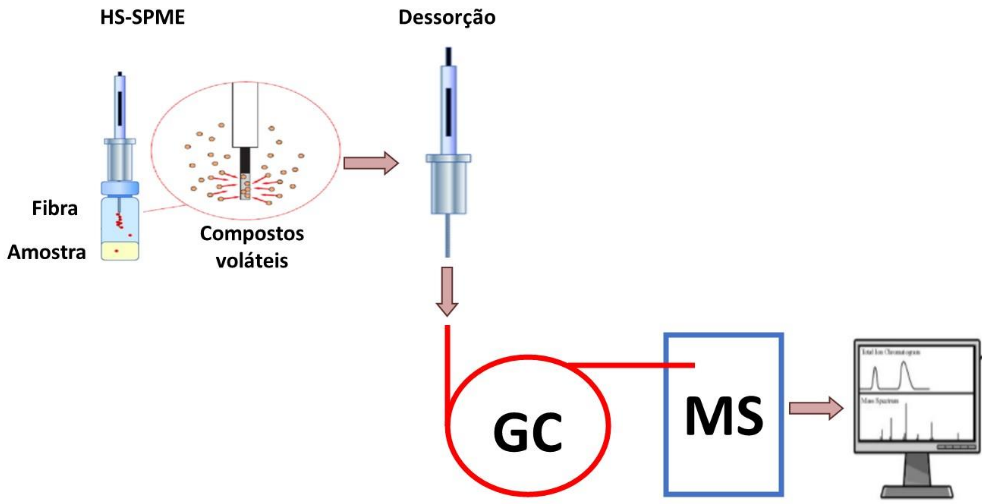
2.4.2 Perfil volátil por micro extração em fase sólida associada a cromatografia gasosa e espectro de massas

Os aromas são diretamente influenciados pela composição volátil dos vinhos. Para obtenção do perfil volátil, métodos analíticos usam técnicas de extração, separação e identificação de compostos aromáticos voláteis e uso da cromatografia gasosa. A exemplo da técnica de micro extração em fase sólida (SPME, do inglês *solid phase microextraction*) em espaço confinado (HS, do inglês *headspace*), associada ao cromatógrafo gasoso (GC, do inglês *gas chromatograph*) e ao detector de espectro de massas (MS, do inglês *mass spectrum*) que representam uma ferramenta confiável para análise e são muito utilizadas em artigos com vinhos (CINCOTTA et al. 2015; ARCANJO et al. 2018; FERNANDES et al. 2018; OLEGÁRIO et al., 2019; KARIMALI et al. 2020).

Etapas prévias para a preparação das amostras são essenciais para estabelecer um método cromatográfico sensível e seletivo para a análise de traços em matrizes complexas como o vinho (DIONISIO, 2010). Existem diversas alternativas de pré-preparo das amostras, como a *Stir Bar Sorptive Extraction* (SBSE) e a *Purge and Trap* (PT), entretanto, a extração em *headspace* é uma das técnicas mais comuns, com destaque para a microextração em fase sólida em *headspace* – HS-SPME (CUBERO-LEON, PEÑALVER E MAQUET, 2014).

A SPME (Figura 8) tem por base a sorção dos analitos de uma matriz (aquosa, por exemplo) para uma fina fibra de sílica fundida revestida por camada polimérica na qual, encontra-se em um suporte com forma de seringa, podendo ser inserida na matriz da amostra de forma direta ou em *headspace* (essencialmente utilizada em análise de voláteis que se desprendem fácil da matriz) como ilustrada na Figura 8. Trata-se de uma técnica rápida, simples e seletiva e que não requer solvente (ALMEIDA et al., 2004; POLÁŠKOVÁ, HERZAGER E EBELER, 2008). Variáveis são otimizadas afim de obter um método sensível, preciso e reprodutível para cada analito e tipo de amostra analisada (POLÁŠKOVÁ, HERZAGER E EBELER, 2008).

Figura 8 - Esquema ilustrativo do processo de micro extração em fase sólida associado à cromatografia gasosa com detector de espectrometria de massas (HS-SPME-GC-MS)



Fonte: autoria própria

Ressalta-se que a análise por GC – MS é uma das técnicas mais utilizadas em compostos voláteis por seu poder de separação e reprodutibilidade. Além da existência de bibliotecas de dados espectrais de massa que auxiliam na identificação dos compostos (CUBERO-LEON, PEÑALVER E MAQUET, 2014).

Por fim, nos vinhos, esta análise dos compostos voláteis vem sendo utilizada com o intuito de diferenciar cultivares, determinar a qualidade e tipicidade dos vinhos (SÁNCHEZ-PALOMO et al., 2017), e diferenciar a origem geográfica desta bebida (ZIÓŁKOWSKA et al., 2016).

3 MATERIAIS E MÉTODOS

3.1 PADRÕES

Padrões analíticos: mistura de hidrocarbonetos (*n*-C8-C20) com grau de pureza acima de 98%, foram adquiridos da Aldrich (Milwaukee, WI, EUA) onde o *n* em C*n* indica o número de carbonos na molécula de um dado alcano linear.

3.2 AMOSTRAS

Esta pesquisa contempla vinhos comerciais do bioma caatinga, indicados para compor a IG do VSF, em processo de estruturação desde 2014. Quatro vinhos espumantes, foram agrupados em quatro (4) categorias comerciais de vinhos espumantes do bioma Caatinga, elaborados a partir de uvas de 120 hectares de vinhedos (60% para espumantes) de uma mesma vinícola (9 ° 15 'S e 40 ° 50' W), feitos com: monovarietal moscatel (Moscato Itália) e brut rosé (Grenache) e mistura (*blend*) de castas demi-sec (*blend* de Chenin Blanc, Sauvignon Blanc e Verdejo, cerca de 33% de cada um) e brut (*blend* de Chenin Blanc, Sauvignon Blanc e Verdejo, também cerca de 33% de cada um) (Tabela 2). A diferença entre os vinhos espumantes brut e demi-sec é apenas a quantidade de açúcar (menos de 15 g L^{-1} para o brut e entre 20 a 60 g L^{-1} para o demi-sec). Estes quatro espumantes selecionados representam em termos de volume produzido/comercializado e em tipos, aproximadamente 50-60% do total da região, sendo desta forma, bastante representativos.

Tabela 2 - Vinhos espumantes em processo de Indicação Geográfica do Vale do São Francisco.

Vinhos (Código)	Cultivares	Vinícolas	Lote
DS	Demi-sec – Chenin Blanc/Sauvignon Blanc/ Verdejo	9° 15’ S; 40° 50’W	L17135
BT	Brut - Chenin Blanc/ Sauvignon Blanc/ Verdejo	9° 15’ S; 40° 50’W	L18006
BR	Brut Rosé – Grenache	9° 15’ S; 40° 50’W	L17139
MOSC	Moscatel – Moscato Itália	9° 15’ S; 40° 50’W	L18011

Nove amostras de vinhos tintos provenientes de duas vinícolas distintas também foram utilizadas e representam entre 55 a 65% de todos os tipos de vinhos produzidos/comercializados na região do VSF. As amostras de vinhos espumantes e tintos foram obtidas a partir de três garrafas (750 mL), de mesmo lote, para cada tipo de vinho. As análises foram realizadas em triplicata e todos os vinhos foram estocados a 16 º ± 1º C até as análises, por um período não superior a seis (6) meses. As características e especificidades de cada vinho tinto se encontram na Tabela 3.

Tabela 3 - Vinhos tintos em processo de Indicação Geográfica do Vale do São Francisco.

Vinhos (Código)	**Cultivares**	**Vinícolas (localização)**	**Safra**	**Lote**	**TM* (meses)**
AB	Alicante Bouschet	9° 24’ 'S; 40° 29’W	2014	Sem lote	9
CS	Cabernet Sauvignon	9° 24’ 'S; 40° 29’W	2015	L1806A15	0
CS/SY	Cabernet Sauvignon/Syrah	9° 24’ 'S; 40° 29’W	2017	L1832D16	0
PR	Premium– Cabernet Sauvignon/Syrah/ Alicante Bouschet/ Touriga Nacional/Aragonês	9° 24’ 'S; 40° 29’W	2013	L17112A08	12
RC	Ruby Cabernet	8°47’S;39° 49’W	2016	L20/072016	0
RS	Reserva – Cabernet Sauvignon/Syrah/ Alicante Bouschet	9° 24’ 'S; 40° 29’W	2014	L1833D11	6
SY	Syrah	9° 24’ 'S; 40° 29’W	2015	L1819D16	0
TN	Touriga Nacional	9° 24’ 'S; 40° 29’W	2014	L1837E03	9
TP	Tempranillo	9° 24’ 'S; 40° 29’W	2015	L1820B26	0

*TM: tempo de maturação em barrica de carvalho francês

3.3 ANÁLISES ENOLÓGICAS CLÁSSICAS

Os parâmetros enológicos clássicos avaliados foram: densidade (método com picnômetro), acidez total, acidez volátil, dióxido de enxofre total e teor alcoólico, que foram realizados por métodos oficiais para análise de vinhos (OIV, 2014).

3.4 MICRO EXTRAÇÃO EM FASE SÓLIDA (SPME)

Uma alíquota de 30 mL de vinho tinto ou de espumante foi transferida para um frasco de vidro de 100 mL, com uma tampa de rosca contendo um orifício central de 3 mm de raio e um septo revestido de Teflon (Supelco®, Bellafonte, PA, EUA). As extrações foram realizadas em quadruplicata com aparelho SPME (Supelco®, Bellafonte, PA, EUA) contendo fibra de sílica fundida revestida com camada de 65 µm de Polidimetilsiloxano/Divinilbenzeno (PDMS/DVB). Antes da extração, a fibra foi condicionada conforme instruções do fabricante (250ºC por 30 min). A agulha de aço inoxidável, que aloja a fibra, penetrou no septo do frasco de vidro e, após equilíbrio a 45ºC, por 15 min, a fibra foi exposta ao espaço superior acima do vinho (*headspace*) por 30 min, sob agitação contínua (250 rpm), segundo método adaptado de Barros et al. (2012). Após a extração, a fibra foi recolhida e o dispositivo SPME foi removido do frasco de amostra do vinho e inserido diretamente na porta de injeção do CG/MS. As análises em branco foram realizadas antes da análise de cada amostra, com os mesmos métodos de análise de amostras.

3.5 CONDIÇÕES EXPERIMENTAIS DA CROMATOGRAFIA GASOSA ACOPLADA A UM DETECTOR DE ESPECTROMETRIA DE MASSA (CG/MS)

Um cromatógrafo gasoso (CG) 7890B acoplado a um detector de espectrometria de massa (MS) Agilent® Technologies 5977B (Little Falls, ME, EUA) e uma coluna capilar de sílica fundida de baixo sangramento/Varian® VF-5 MS (5% fenil / 95 % PDMS, 60 m x 0,25 mm x 0,25 µm de espessura de filme) foram usados para separar e identificar os voláteis coletados por SPME. O gás de arraste foi o hélio (pureza analítica de 99,9999 %, White Martins, Jaboatão dos Guararapes, Pernambuco, Brasil) a uma taxa de fluxo de 1,2 ml minuto $^{-1}$. As amostras foram injetadas colocando-se a fibra de SPME na entrada do GC a 250 ºC e o modo de injeção foi sem divisão de fluxo (*splitless*) com tempo de dessorção de 5 minutos. A temperatura inicial do forno foi de 40 ºC, a qual foi mantida por 10 minutos, aumentada para

250 ºC a 7 ºC por minuto, e então mantida a 250 ºC por 5 minutos conforme método adaptado de Barros et al. (2012) e Arcanjo et al. (2015).

O detector de espectrometria de massa foi operado no modo de impacto de elétrons com uma temperatura de 250ºC na linha de transferência e na fonte, uma ionização de elétrons de 70 eV e uma faixa de varredura de razão massa/carga (m/z) de 35 a 350 a 3,33 varreduras/s. A linha de transferência foi mantida a 250 ° C. Os dados da SPME foram adquiridos e analisados com o software Mass Hunter (Agilent®).

O índice de retenção foi calculado para cada composto volátil usando os tempos de retenção de uma série homóloga de n-alcanos C8-C20. Foram considerados identificados, os compostos voláteis que apresentarem semelhança espectral com os da biblioteca NIST/EPA/NIH Mass Spectral Database (Versão 2.2 2014) exibindo os coeficientes Match > 600 e RMatch > 700 e índices de retenção linear confirmados pela literatura científica (KONDJOYANG; BERDAGUÉ, 1996). Foram considerados tentativamente identificados, os compostos voláteis cuja identificação se baseou somente nas informações da biblioteca NIST, exibindo os coeficientes Match > 600 e RMatch > 700. Os dados foram representados em termos a área total cromatográfica e porcentagem de área e discutidos de acordo com suas classes químicas. Uma busca de anterioridade foi realizada para rastrear os compostos voláteis identificados em vinhos tintos e espumantes do mundo publicados nos periódicos disponíveis no Periódicos Capes. Todos os resultados foram comparados e suas similaridades e diferenças discutidas.

3.6 ANÁLISE ESTATÍSTICA

O teste de Shapiro-Wilk foi realizado em todos os dados com o intuito de verificar se os resultados apresentavam uma distribuição normal. Como os dados dos compostos voláteis não seguiram uma distribuição normal ($p<0.05$), o teste não paramétrico de Kruskall-Wallis e o teste de comparação múltipla *post hoc* Dunn's ($p<0.05$) foram utilizados para verificar a diferença entre as médias de áreas totais dos grupos de compostos voláteis, exibidos na forma de gráficos. Em relação aos dados enológicos clássicos, estes seguiram distribuição normal e foram analisados por análise de variância (ANOVA) associada ao teste de médias de Tukey ($p<0,05$) para identificar possíveis diferenças entre as médias.

Os resultados dos compostos voláteis foram auto escalonados usando o MATLAB versão 7.10.0.499 (The Mathworks, Inc., Natick, MA, R2010a) para realizar a comparação da abundância de área obtida em cada amostra. Análises multivariadas (componentes principais (p<0.05), análise hierárquica de cluster e mapa de cor) foram realizadas com o software XLSTAT versão 5.03 (Addinsoft, New York, USA, 2014), com a finalidade de agrupar as amostras de vinhos tintos e espumantes comerciais de acordo com sua composição volátil.

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4 RESULTADOS E DISCUSSÃO

Os resultados obtidos no desenvolvimento da Tese estão apresentados na forma de artigos científicos submetidos em periódicos de impacto na área de Ciência e Tecnologia dos Alimentos, em atendimento a Norma Complementar nº 03/2011 do PPGCTA.

4.1 ARTIGO I: VOLATILE PROFILE OF COMMERCIAL SPARKLING WINES FROM THE CAATINGA BIOME BY HEADSPACE-SPME-GC/MS

O artigo foi submetido ao periódico *Food Chemistry* em 21 de outubro de 2020, sob o título *Volatile Profile of Commercial Sparkling Wines from the Caatinga Biome by Headspace-SPME-GC/MS* (ANEXO A).

Volatile profile of commercial sparkling wines from the Caatinga Biome by Headspace-SPME-GC/MS

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Abstract

The present research aimed to identify the volatile profile of sparkling wines from São Francisco Valley, which products will have soon the Geographical Indication requested by the producers. The extraction, separation and identification of the volatile compounds of moscatel, brut, brut rosé and demi-sec sparkling wines were performed. A total of 109 compounds were identified, classified in 13 chemical groups, which the major were esters, terpenes and alcohols. Some compounds with more expressive area representation were exclusively identified in each type of sparkling wine: a total of 23 in moscatel, 9 in brut, 5 in brut rosé and 4 in demi-sec. The results indicate a strong association between grape varieties and the technological winemaking processes. The volatile profiles of each commercial sparkling wine in the São Francisco Valley present possible chemical markers of typicity which can be used to distinguish the commercial wines from the region.

Keywords: Volatile compound; São Francisco Valley; Geographical Indication; Sparkling wine; Typicality marker; Gas chromatography.

1. Introduction

Global wine production in 2019 reached 260 million hectolitres (mhL), which 2.0 mhL were produced by Brazil, where it has been outstanding in wine production in the southern hemisphere, occupying the fifth position with high quality products, among red, sparkling and also white wines (Ibravin, 2020a; OIV, 2020). Brazilian wineries have been investing in Geographical Indications-GI in the last 20 years, a quality seal that attests the quality due to the specificity of the *terroir* of each producing region. Nowadays there are seven regions with GI, mainly in the South, in Rio Grande do Sul (Farroupilha, Monte Belo, Vale dos Vinhedos, Pinto Bandeira, Altos Montes and Campanha Gaúcha) and Santa Catarina States (Vale da Uva Goëthe) (Embrapa, 2020).

Geographical Indication is able to boost territorial development in its social, economic, political and cultural aspects, adding a differential value to products and services, and giving notoriety to the region (Siedenberg et al., 2017). In this regard, the São Francisco Valley (VSF) is a traditional winegrowing region, producing tropical wines since thirty years ago, actually with 4 million liters of wines (*Vitis vinifera*) per year, which sparkling wines represent about 70 % of the total production (Embrapa, 2020; Pereira et al., 2018). The VSF is exclusively located in the northeastern Brazil, in the caatinga biome, presenting a tropical semi-arid climate. In these conditions, with high annual average temperatures (26.5 ºC), high solar radiation, water availability for irrigation, it is possible to produce grapes every day of the year, by scheduling the plots. The soils are classified as yellow eutrophic argisol/typical plintustalf (soil taxonomy alfisol), usually with low natural fertility, and a vine is pruned once a year and the grapes are harvested twice (Benedetti et al., 2011; Ibravin, 2020b). In this region, the sparkling wines are mainly produced by the *asti* (single fermentation in pressure tanks) and *charmat* (second alcoholic fermentation in the pressure tanks or autoclaves) and methods (Brasil, 2004; Pereira et al., 2018; Soares et al., 2015).

In addition to winemaking protocols and grape variety, other factors such as soil and climatic conditions, as well as viticultural practices influence the chemical composition of wines, mainly volatile compounds (Fernandes et al., 2018). The aromas present varied intensity and complexity and are associated with the expression of a single grape variety or its mixture/blend, being considered decisive factors in the sensory quality, typicality and acceptability of wines (Sánchez-Palomo et al., 2017).

The aromas are directly influenced by the volatile composition of the wines. The extraction of the compounds by solid phase microextraction (SPME) associated with separation by high efficiency gas chromatography (GC) and the mass spectrophotometric detector represents a reliable tool for analysis (Olegário et al., 2019; Ruiz et al., 2019). These techniques have been used for wine analysis (Muñoz-Redondo et al., 2020; Tufariello et al., 2019; Ubeda et al., 2019) in order to differentiate cultivars, determine the quality and typicality of wines (Sánchez-Palomo et al., 2017), and differentiate the geographical origin of this beverage (Ziółkowska et al., 2016).

A study by Nascimento et al. (2018) with experimental sparkling wines from the Chenin Blanc and Syrah cultivars produced in the São Francisco Valley showed that the grape variety used can significantly influence the volatile profile. Barbará et al. (2020) studied the volatile profile of wines produced with Syrah grapes and it was shown that ten days of maceration and 19° Brix were significant for the volatile composition. Fernandes et al. (2018) analyzed wines from the VSF, Minas Gerais and Rio Grande do Sul in Brazil, and showed that the main volatile profile markers of red wines were esters and alcohols. The above-mentioned studies indicate that factors such as cultivar, technological winemaking process and geographical origin influence on the volatile composition of experimental wines produced in the VSF. However, in our knowledge, there is no studies to date characterizing the volatile composition of commercial sparkling wines from this region.

In this context, this study aimed to identify and quantify the volatile profile of the main sparkling wines produced in the region, which products will take part of the Geographical Indication São Francisco Valley, in the way of recognition by the Brazilian Government. The characterization of the products will help the scientific community, as well as the producers and consumers, to know in details which are the main aroma present in the sparkling wines.

2. Material and methods

2.1. Samples

Twelve sparkling wines indicated to compose the Vale do São Francisco Geographical Indication, were grouped into 4 commercial categories of sparkling wines from the Caatinga biome. All wines came from the same winery (9° 15' S and 40° 50' W), with 120 hectars of vineyards (60% for sparkling wines) and were separated in four groups: monovarietal moscatel (Itália Muscat) and brut rosé (Grenache) sparkling wines, and demi-sec (blend of Chenin Blanc, Sauvignon Blanc and Verdejo, around 33% of each one) and brut (blend of Chenin Blanc, Sauvignon Blanc and Verdejo, also around 33% of each one). The difference between brut and demi-sec sparkling wines is only the amount of sugar (less than 15 g L^{-1} for brut, and between 20 to 60 g L^{-1} for demi-sec). These four sparkling wines selected represent in terms of volume produced / marketed and in types, approximately 50-60% of the total of the region, being thus, quite representative. The samples were composed by three bottles (750mL) from the same batch and the experiments were carried out in triplicate. Sparkling wines were stored at 16º ± 1ºC until the analysis for a period not exceeding 6 months.

2.2. Solid-phase microextraction (SPME)

An aliquot of 30 mL of sparkling wine was transferred to a 100 mL glass vial with a screw cap containing one center hole of 3 mm radius and a Teflon-lined septum (Supelco®, Bellafonte, PA, EUA). Extractions were carried out with an SPME device (Supelco®, Bellafonte, PA, EUA) containing a fused-silica fiber coated with a 65 µm layer of Polidimetilsiloxano/Divinilbenzeno (PDMS/DVB) (Supelco®, Bellafonte, PA, EUA). The stainless steel needle housing the fiber penetrated the septum of the glass recipient, and after equilibration at 45ºC for 15 min, the fiber was then exposed to the headspace above the wine for 30 min, under continuous stirring (250 rpm) according to the method adapted from Barros et al. (2012). After extraction, the fiber was collected and the SPME device was removed from the wine sample vial and inserted directly into the GC-MS injection port. The fiber was conditioned before the extraction by heating it in the gas chromatograph injection port at 250ºC for 30 min. Blank analyses were carried out before the analysis of each sample, with the same methods of samples analyses.

2.3. Gas chromatography-mass spectrometry conditions

An Agilent® Technologies 5977B (Little Falls, ME, USA) mass spectrometer coupled to a 7890B gas chromatograph was used to separate and identify the volatiles collected by SPME. GC separation of the collected volatiles was performed on a Varian® VF-5 MS low bleed/MS fused-silica capillary column (5% phenyl/95% PDMS, 60 m x 0.25 mm x 0.25 µm film thickness). The temperature program employed was 10 min at 40ºC, a ramp of 7ºC/min to 250ºC, and held for 5 min. Helium (analytical purity of 99,9999 %, White Martins, Jaboatão dos Guararapes, Pernambuco, Brazil) was used as the carrier gas at a flow rate of 1.2 m ml min^{-1}. The injection port was in splitless mode at a temperature of 250ºC.

Mass spectrometry detector was operated in electron impact mode with a source temperature of 250ºC, an ionizing voltage of 70 eV, and a scan range from m/z 35 to 350 m/z at 3.33 scans/s. The transfer line was held at 250°C. The SPME data were acquired and analyzed using Mass Hunter software (Agilent®, Version 10.0, 2008).

The linear retention index was calculated for each volatile compound using the retention times of a homologous series of C8-C20 n-alkanes, of which the linear retention index below 800 were expressed as <800. Volatile compounds that have spectral similarity to those of the NIST/EPA/NIH Mass Spectral Database were considered identified (Version 2.2 2014) showing the Match> 600 and RMatch > 700 coefficients of linear retention confirmed by the scientific literature (KONDJOYAN & BERDAGUÉ, 1996). Volatile compounds whose identification was based only on information from the NIST library were tentatively identified, displaying the Match > 600 and RMatch > 700 coefficients. The data were represented in terms of total chromatographic area and percentage of area and discussed according to their chemical classes. A search for priority was carried out to track the volatile compounds identified in red and sparkling wines from the world published in the journals available at Periódicos Capes. All results were compared and their similarities and differences discussed.

2.4. Statistical analysis

The Shapiro-Wilk test was performed to check whether the results had a normal distribution. However, the data did not follow a normal distribution ($p<0.05$), so the Kruskal-Wallis non-parametric test and the Dunn's post hoc multiple comparison test ($p<0.05$) were used to verify the difference between the total area averages of the volatile compound groups, and subsequently displayed in the form of graphs.

The data were self-scaled and multivariate analyzes (principal component analysis and hierarchical cluster analysis with color map) were used to group the samples according to the sparkling wine categories according to their volatile composition.

The XLSTAT® version 5.03 (Addinsoft, New York, USA, 2014), MATLAB® version 7.10.0.499 (The Mathworks, Inc., Natick, MA, R2010a) and GraphPad Prism® version 6.01 (Graphpad Software Inc., San Diego, California, USA) software programs were used for these statistical analyzes.

3. Results and Discussion

3.1 Characterization and comparison of the volatile composition of sparkling wines from the São Francisco Valley

The identification of volatile compounds resulted in a total of 109 compounds classified into 13 groups according to their chemical characteristics: esters, terpenes, alcohols, aromatic compounds, acids, furans, aldehydes, ketones, hydrocarbons, phenols, C-13 norisoprenoid, pyrazines and pyranes. The average of chromatography area for each sparkling wine category are reported in the Table 1.

The total number of compounds identified for each category of sparkling wine was different: 83 for moscatel, 67 for brut rosé, 61 for brut and 52 for demi-sec. Some of these were the major in the four sparkling wines analyzed: ethyl octanoate, ethyl decanoate, ethyl hexanoate, ethyl 9-decenoate, 3-methyl-1-butanol. These five compounds together represented 72.69%, 82.2%, 79.07% and 71.13% of the total chromatography area of the identified compounds in moscatel, brut rosé, brut and demi-sec, respectively.

The main compounds among the chemical groups were: esters (37), followed by terpenes (16), alcohols (14), aromatics (8), acids (8) and furans (6). The comparative total area values of each volatile compound chemical group of the sparkling wines are shown in the Figure 1. It can be seen that significant differences were presented within a class between at least two categories of sparkling wines according to the Kruskal-Wallis test and the Dunn's *post hoc* multiple comparison test (p<0.05).

The esters class was the most abundant among the 13 groups of compounds, representing larger areas in the brut rosé category (85.43%), followed by brut (79.39%), moscatel (79.34%) and demi-sec (69.56%), and presenting significant differences (p<0.05) between them (as can be seen in the Figure 1**)**. Ethyl octanoate with 44%, 43%, 38% and 34% and ethyl decanoate with 18%, 25%, 24% and 21% of the total area of the moscatel, brut rosé, brut and demi-sec categories, respectively, are highlighted in this group. These compounds were also identified in other sparkling wine categories (Pérez-Magariño et al., 2015; Ubeda et al., 2019; Voce et al., 2019), however, in different proportions. It is also worth mentioning the Ethyl hexanoate as a fruity (pineapple and pear) and floral aromatic descriptor (Jiang et al., 2013), and ethyl decanoate with a sweet, fruity, fatty and pleasant aroma (Jiang et al., 2013).

Other esters detected with larger areas in the brut, brut rosé and demi-sec samples were Ethyl hexanoate, Diethyl succinate and Ethyl 9-decenoate (Table 1). When analyzing experimental sparkling wines from the Chenin Blanc cultivar, Nascimento et al. (2018) suggested that Diethyl succinate is one of the most relevant esters for the volatile profile of sparkling wines produced in the São Francisco Valley. These compounds were also identified in moscatel sparkling wines produced in southern Brazil (Nicolli et al., 2015). The presence of Diethyl succinate in sparkling wines from the Ribolla Gialla variety of Northeast Italy, suggests that the sparkling wine was produced with a more or less prolonged period of aging, and/or a refermentation inside the bottle, as Diethyl succinate is considered an aging ester (Voce et al., 2019).

When studying Italian sparkling wines of the Maresco cultivar, Tufariello et al. (2019) detected Ethyl octanoate, Isoamyl acetate, Ethyl hexanoate and Ethyl decanoate esters. All of these compounds were also identified in the four groups of sparkling wines in this study. Esters are mainly derived from alcoholic fermentation (Étievant, 1991), and contribute to the sensory attributes of wines, especially concerning their fruity aroma. Their production depends on factors such as the yeast used, temperature and aeration during fermentation and sugar content in the must (Jiang et al., 2013).

A total of 16 terpenes were identified, which fifteen of them were present in the moscatel sparkling wine and only one (α-Humulene) was present in the brut sparkling wine. Interestingly, the demi-sec sparkling wine contained only three terpenes (γ-Terpinene, p-Cymen-8-ol and α-

Terpineol) and represented the largest area (3% of the total area of compounds identified), significantly differing ($p<0.05$) from the brut sparkling wine (Figure 1). All of these number particularities and terpene area, mainly in moscatel and demi-sec sparkling wines, may be related to the different cultivars and winemaking processes used in each category of sparkling wine. The terpenes belong to the secondary constituents of the plant whose biosynthesis starts with acetylcoA (Jiang et al., 2013), consequently the concentration of sugars and the technological process used in the production of sparkling wines, one conducted by the *asti* method (moscatel - Italia Muscat) with only one fermentation, and the other by the *charmat* method (brut - Sauvignon Blanc, Chenin Blanc and Verdejo) with two fermentations, justify this variation between the terpenes. A study performed by Ubeda et al. (2019) verifying the evolution of different chemical families of volatile compounds during the production of sparkling wines from the País cultivar showed that the second fermentation slightly reduced the terpene concentration in sparkling wines of Chile, elaborated by the traditional method (champegnoise). Furthermore, according to a study by Nascimento et al. (2018), terpenes are not frequently identified in wines from the Chenin Blanc and Syrah cultivars, only finding the Carvone terpene in sparkling wines produced from Chenin Blanc. However, p-Cymen-8-ol, α-Terpineol and Nerol oxide showed the largest relative areas in this study.

A total of 14 compounds were identified in the alcohol class, representing a larger percentage area for the demi-sec sparkling wine category (15.40%), followed by brut (15.37%), brut rosé (5.77%), and moscatel (3.94%), and differing significantly (as shown in Figure 1**)**. Superior alcohols are composed of volatile molecules with more than two carbon atoms, considered to have a strong aromatic effect on wines, and whose final concentration in this beverage mainly depends on the yeast metabolism, among other factors such as the type of wine and chemical composition (Ruiz et al., 2019). Most alcohols can attribute strong aromas to wines (like the herbaceous), which in high concentration can mask the fragrance of the drink and in low concentrations (up to 0.3 g / L) help in aromatic complexity (Jackson, 2020). 3-Methyl-1-butanol alcohols and Phenylethyl alcohol were the major compounds in sparkling wines in this study. Their contributions to the wine aroma range from honey, roses and floral (Phenylethyl alcohol) to fruity, banana and alcohol (3-Methyl-1-butanol) (*The Good Scents Company*, 2020). Tyrosol was only identified in brut rosé and demi-sec sparkling wines, being associated with the honey aroma in wines (Lambrechts & Pretorius, 2000). Among the identified alcohols (14), five were detected in only one type of sparkling wine (2-Methyl-1-butanol, 3-Methyl-2-hexanol, 3-Methyl-4-heptanol, 1-Nonanol and 2-Heptadecanol), thus suggesting the influence of the varietal and the winemaking process on the aromatic quality of the final product.

Of the seven compounds identified in the aromatic class (aromatic hydrocarbons), all were detected for the first time in sparkling wines from VSF and do not have flavor descriptors in the literature (Jiang et al., 2013; *Pherobase,* 2020; *The Good Scents Company*, 2020). From these, only 5-Phenyl-undecane was identified in a survey of wine produced with the Cabernet Sauvignon grape and parts of the stalk of this grape (Nan et al., 2019). As shown in Figure 1, the total area of the aromatic class in demi-sec sparkling wine differed from moscatel and brut rosé sparkling wines, and the class of C13-norisoprenoid compounds in brut rosé sparkling wine differed from brut sparkling wine, with both classes representing <1% of the total area. The distinction of compounds is possibly associated with the different cultivars used for winemaking these sparkling wines, for which the brut rosé has a fermentative maceration protocol (contact with the Grenache grape skins). Moreover, 1,2-Dihydro-1,5,8-trimethyl-naphthalene showed the largest chromatographic areas among the class C13-norisoprenoid compounds identified, but it is worth noting the presence of TDN (1,1,6-Trimethyl-1,2-dihydronaphthalene) which was only detected in brut sparkling wine, and the presence of which has also been identified in sparkling wines from Chile (Ubeda et al., 2016, 2019) and Spain

(Muñoz-Redondo et al., 2020). TDN has been classified as an important aging marker with aromatic notes of burned/tabac/herb (Ubeda et al., 2019).

Many of the volatile acids in wines are generally saturated linear chain lengths ranging from 2 to 18 carbon atoms; another small group of branched-chain organic acids includes 3-Methyl butanoic acid, 2-Methyl butanoic acid, and 2-Methyl propanoic acid (Ruiz et al., 2019). The total acid area differed significantly between brut rosé and moscatel sparkling wine, which represented 4.74% and 1.02%, respectively. Decanoic acid and Hexadecanoic acid were identified in the four types of sparkling wines, and presented the largest areas among the eight acids found in this study. These two acids were also identified in commercial sparkling wines of the Ribolla Gialla variety produced in Northeastern Italy (Voce et al., 2019). Organic acids have been described with aromatic notes of fruit, cheese, fat and rancidity, while long-chain acids have a reduced effect on the aroma of wines, and C6-C10 chain acids have a positive impact on the quality of the overall aroma of wines (Fernandes et al., 2018).

The total area of the furan class in the moscatel (5.90%) and demi-sec (5.55%) sparkling wines differed significantly from brut rosé (0.51%) (Figure 1). The 5-Hydroxymethylfurfural compound is an intermediate product of the Maillard reaction and caramelization process (Gong et al., 2020), and was identified in all sparkling wines in this study, especially in demi-sec (representing 5.15% of the total area of the identified compounds), with caramel being one of its aromatic descriptors (Table 1). Since the winemaking process of these sparkling wines does not apply heating, the formation of this compound may have been influenced by the climatic conditions with high temperatures in the São Francisco Valley region. According to Lampír & Pavlousek (2013), each cultivated grape in a specific *terroir* reflects the location in its chemical composition. Storage time and temperature are also possible markers of the formation of this compound as described in a study by Serra-Cayuela et al. (2014) in commercial sparkling wines.

A total of 6 aldehydes were identified, most of which are produced during fermentation, processing or extracted from oak during the aging stage. When compared to ketones (which had four identified compounds in this study), the aldehydes are carbonyl compounds, which are differentiated by the terminal location of the functional carbonyl group (-C=O), while ketones are compounds related to the carbonyl group located in an internal carbon (Jackson, 2008). The total area of both classes (Figure 1) in the moscatel sparkling wine differed significantly from demi-sec. The following aldehydes may be highlighted: decanal, found in moscatel and brut rosé sparkling wines, with a grassy, orange skin-like aroma (Jiang et al., 2013); and Dodecanal, found in the four sparkling wines, which can confer a soapy, waxy, aldehydic, citrus, green and floral aroma (*The Good Scents Company*, 2020). Three of the identified ketones were only found in moscatel sparkling wine, with the 3-Dodecanone compound with the largest chromatographic area (representing 1% of the total area), and whose aromatic descriptors can be fatty, soapy, waxy, fruity (*The Good Scents Company*, 2020).

Only four high molecular weight hydrocarbons were identified in present study, observing variation among the sparkling wines studied, as shown in Table 1 and Figure 1. The hydrocarbons are generally associated to grape cell debris and lost before or during clarification or maceration. Thus, they do not directly influence the sensory characteristics of the wine; however, the hydrocarbon degradation products may produce important volatile compounds, such as β-Damascenone, α and β-ionone and 1,1,6-Trimethyl-1,2-dihydronaphthalene (TDN) (Jackson, 2008).

Other compound classes (phenol, pyran, pyrazine) were also identified in smaller numbers and with less representation in the total area. Phenol, 2,4-Di-tert-butylphenol was detected in brut rosé sparkling wine, compound also identified in other studies with sparkling wines (Nicolli et al., 2015; Soares et al., 2015) and p-Vinylguaiacol in moscatel and demi-sec sparkling wine. In addition, pyrazine 6-Methyl-2-pyrazinylmethanol was observed in all sparkling wines, except for moscatel. However, the compound pyrane 2,2,6-Trimethyl-6-

vinyltetrahydropyran was only found in this wine and in the study of Nicolli et al., 2015. This volatile variability among the analyzed samples was also observed by Arcanjo et al. (2018), which suggests the influence of factors such as the grape harvest time and the technological processes used in the final aromatic quality of the wine.

3.2 Principal Component Analysis (PCA) of volatile compounds in sparkling wines from the São Francisco Valley

The volatile profile of sparkling wines (Table 1) were analyzed by PCA (Figure 2). The first Principal Component (PC1) explained 40.46% of the total variation among the samples, which PC2 explained 37.66% of total variability. PC1 x PC2 explained 78.12% of the variability among the volatile profiles. Sparkling wines with similar volatile profiles were positioned in the quadrants in nearby regions. PC1 separated the brut rosé (in the positive side of PC1) from the brut and demi-sec (in the negative side of PC1) sparkling wines. The identified volatiles which best characterized each group of wines are represented by vectors, and those with significant factor loads and ≥0.8 are considered for discussion. The vectors which are very close are also indicative of highly correlated variables.

There are 40 associated volatile compounds in the positive side of PC1 that where associated to the brut rosé sparkling wine, and it was best characterized by the Hexadecanoic acid (Ac 108), (E)-2-Dodecenal (Ald 75), 1-Octanol (Al 27), 1,2-Dihydro-1,5,8-trimethyl-naphthalene (No 63), 2-Methyl-1-butyl acetate (Es 9), Ethyl hexanoate (Es 17), Ethyl hexanoate (Es 35), Ethyl octanoate (Es 41), Ethyl 2-phenylacetate (Es 46), Isobornyl acetate (Es 54), Propyl octanoate (Es 55), Ethyl nonanoate (Es 56), Isomenthol acetate (Es 57), Methyl decanoate (Es 60), Ethyl 9-decenoate (Es 67), 2-Methylbutyl octanoate (Es 73), Ethyl vanillate (Es 89), 2-Ethylhexyl octanoate (Es 97), 2-Furyl hydroxymethyl ketone (Fu 29), 1-Methoxy-2-ethylbutane (Hy 1), 3-Butyl-1,2,4-cyclopentanetrione (Hy 78), 2,4-Di-tert-butylphenol (Ph 80)

1,8-Cineole (Te 21), γ-Terpinene (Te 25), Nerol oxide (Te 33), Geranial (Te 50) and α-Humulene (Te 74).

Demi-sec and brut sparkling wines, both produced with the same cultivar, are located in the negative side of PC1, and they were associated to 33 vectors, characterized by the volatile 1-Dodecanol (Al 76), Undecanal (Ald 58), 6-Phenyl-undecane (Ar 92), 5-Phenyl-undecane (Ar 93), Geranyl iso-valerate (Es 91), 5-Hydroxymethylfurfural (Fu 45) and Pentadecane (Hy 79).

PC2 separated the moscatel sparkling wine (in the positive side) from the others, located in the negative side of PC2. The volatile compounds with the greatest contribution in the discrimination of the moscatel sparkling wine were Octanoic acid (Ac 37), Undecanoic acid (Ac 77), 3-Methyl-2-hexanol (Al 8), 2-Heptadecanol (Al 100), Decanal (Ald 42), Hexyl acetate (Es 18), Ethyl 2,4-Hexadienoate (Es 30), Bornyl acetate (Es 53), Propyl 2,4-hexadienecarboxylate (Es 64), Methoxy phenyl oxime (Fu 10), 2-Pentyl furan (Fu 15), Tetrahydro-2,2-dimethyl-5-(1-methyl-1-propenyl)-furan (Fu 22), 3-Dodecanone (Ke 65), 3-Tetradecanone (Ke 87) 2-Hexadecan-2-one (Ke 101), 2-Hydroxycyclopentadecanone (Ke 102), 2,2,6-Trimethyl-6-vinyltetrahydropyran (Pr 12), p-Cymene (Te 19), (*Z*)-β-Ocimene (Te 23), (*E*)-Linalool oxide (Te 26), (*E*)-Ocimenol (Te 34), Nerol (Te 44), Carvone (Te 48), (*Z*)-α-Bisabolene epoxide (Te 86) and Germacrene B (Te 88). All of these compounds are negatively correlated to the compounds associated with demi-sec and brut sparkling wines. Thus, PCA discriminated sparkling wines in 3 groups, and the cultivar used was a marker in the volatile composition of the beverage, influencing the quality and differentiating the wines produced in the same winery, from different technological processes.

3.3 Hierarchical cluster analysis and heatmap applied to the profile of volatile sparkling wines in the São Francisco Valley

A hierarchical cluster and heatmap analysis (Figure 3) were performed considering all the identified volatile compounds (Table 1) in order to analyze the expressive volatile composition of each sparkling wine. The hierarchical cluster analysis based on the volatile markers grouped the sparkling wines into two clusters with weak association between them. The first one is formed by the blends of sparkling wines: brut and demi-sec; and the second one is formed by the monovarietal sparkling wines: moscatel and brut rosé. These results suggest a strong association with the amount of sugars (brut and demi-sec), type and quantity of grape varieties/blend used during the technological winemaking practices.

The heatmap (Figure 3) shows that the most volatile compounds for brut sparkling wines were: Isoamyl decanoate, 2,6,10-Trimethyltetradecane, Hexanoic acid, 2-Phenyl-undecane, 3-Methyl-4-heptanol, 1-Nonanol, Benzaldehyde, 1,1,6-Trimethyl-1,2-dihydronaphthalene, Ethyl glutarate, Ethyl pentadecanoate, Isopropyl octanoate, Ethyl tetradecanoate, Ethyl hexadecanoate, Phenylethyl alcohol, Isoamyl acetate, 3-Methyl-1-butanol, Ethyl 3-hydroxytridecanoate and Ethyl dodecanoate, in which 50% belong to the ester class and 22.22% to the alcohols class. Of these, 2,6,10-Trimethyltetradecane, Ethyl tetradecanoate and Phenylethyl alcohol represented superior chromatographic areas in relation to the other sparkling wines (Table 1). It is worth mentioning that the compounds which were exclusively identified in the brut sparkling wine: Hexanoic acid, 1-Nonanol, Benzaldehyde, 1,1,6-Trimethyl-1,2-dihydronaphthalene, Ethyl glutarate, Ethyl pentadecanoate and Isopropyl octanoate, including 2-Phenyl-undecane and 3-Methyl-4-heptanol, which stand out for being identified for the first time in sparkling wines. The most relevant compounds identified in demi-sec sparkling wine were: Geranyl iso-valerate, 5-Phenyl-undecane, 4-Phenyl-decane, pentadecane, 6-Phenyl-undecane, Undecanal, 1-Dodecanol, Dodecanal, 1-Hexanol, 2,3-Butanediol, α-Terpineol, *p*-Vinylguaiacol, *p*-Cymen-8-ol, 4-Phenyl-undecane, 5-Phenyl-dodecane, 2-Methyl-1-butanol, Ethyl furoate, 5-Hydroxymethylfurfural, 3-Phenyl-decane, Hydroxydihydromaltol, Ethyl butanoate, Butanedioic acid ethyl 3-methylbutyl ester, Diethyl succinate and 2,4-Dihydroxy-2,5-dimethyl-3(2H)-furanone (Figure 3), which 25% belong to the aromatics class and 20.83% to the esters class. Among these, 2.3-Butanediol and 5-Hydroxymethylfurfural obtained superior chromatographic areas in relation to other sparkling wines (Table 1). The pentadecane, 6-Phenyl-undecane and Undecanal compounds showed greater area in relation to brut and p-Vinylguaiacol, p-Cymen-8-ol, in relation to Moscatel. In addition, the 4-Phenyl-undecane, 5-Phenyl-dodecane, 2-Methyl-1-butanol, and Ethyl furoate compounds were only identified in demi-sec sparkling wine, and 4-Phenyl-undecane was identified for the first time in sparkling wines. This composition is possibly associated to the *terroir* of the São Francisco Valley, considering that the synthesis and concentration of volatile compounds in the grape berry are influenced by factors such as temperatures during grape maturation, light intensity/solar radiation, rainfall index, thermal amplitude and soil conditions. These variables possibly participated in regulating the biosynthesis of volatile compounds of the grape berry, thus determining the geographical characteristics of the wines (Jiang et al., 2013).

The volatile compounds identified as most relevant in moscatel were: Isobutyl octanoate, limonene, Ethyl 2-phenylacetate, 1-Hexadecanol, Pentadecanoic acid, Carvone, (*Z*)-β-Ocimene, (*E*)-Linalool oxide, Bornyl acetate, 2-Hydroxycyclopentadecanone, (*Z*)-*α*-Bisabolene epoxide, Propyl 2,4-hexadienecarboxylate, 3-dodecanone, Germacrene B, Ethyl 2,4-hexadienoate, Tetrahydro-2,2-dimethyl-5-(1-methyl-1-propenyl) furan, Nerol, 3-Methyl-2-hexanol, 2,2,6-Trimethyl-6-vinyltetrahydropyran, Methoxy phenyl oxime, Octanoic acid, Hexyl acetate, 2-Heptadecanol, *p*-Cymene, 2-Pentyl furan, 2-Hexadecan-2-one, Undecanoic acid, (*E*)-Ocimenol, Decanal and 3-Tetradecanone (Figure 3), of which 30% are terpenes and 20% are esters. Decanal obtained the highest chromatographic area among these compounds in relation to the brut rosé (Table 1). Exclusive compounds were also identified in moscatel sparkling wine, which were: Carvone, (*Z*)-β-Ocimene, (*e)*-Linalool oxide, Bornyl acetate, 2-

Hydroxycyclopentadecanone, (*Z*)-*α*-Bisabolene epoxide, Propyl 2,4-hexadienecarboxylate, 3-Dodecanone, Germacrene B, Ethyl 2,4-hexadienoate, Tetrahydro-2,2-dimethyl-5-(1-methyl-1-propenyl) furan, Nerol, 3-Methyl-2-hexanol, 2,2,6-Trimethyl-6-vinyltetrahydropyran, Methoxy phenyl oxime, Octanoic acid, Hexyl acetate, 2-Heptadecanol, *p*-Cymene, 2-Pentyl furan, 2-Hexadecan-2-one, Undecanoic acid and (*E*)-Ocimenol, of which they account for 50% of the total terpenes in this study. Terpenes in muscat wines attribute floral aromas and the esters attribute fruity and floral notes, constituting important characteristics and possibly being responsible for the varietal aroma of , moscatel sparkling wine (Bordiga et al., 2013; Soares et al., 2015). Of the terpenes, Germacrene B has woody, earthy and spicy notes as its aromatic descriptors (*The Good Scents Company*, 2020), being identified in Baga grapes (Coelho et al., 2006) and in Nero d'Avola, Frappato, Nerello Mascalese and Cabernet Sauvignon grape stalk (Ruberto et al., 2008).

The most relevant volatile compounds to distinguish brut rosé were: Diethyl succinate, 10-Octadecenal, Isoamyl hexanoate, 1-Octanol, 1,2-Dihydro-1,5,8-trimethyl-naphthalene, γ-Terpinene, 2-Furyl hydroxymethyl ketone, Isobornyl acetate, Propyl octanoate, Nerol oxide, Ethyl octanoate, Geranial, Isomenthol acetate, 3-Butyl-1,2,4-cyclopentanetrione, Ethyl hexanoate, Methyl decanoate, Ethyl benzoate, α-Humulene, Decanoic acid, 3-Methyl octanoate, Tetradecanoic acid, 6-Methyl-2-pyrazinylmethanol, Tyrosol, Ethyl 9-decenoate, 1-Methoxy-2-ethylbutane, (*E*)-2-Dodecenal, 1,8-Cineole, Ethyl vanillate, 2,4-Di-tert-butylphenol, 2-Methyl-1-butyl acetate, 2-Ethylhexyl octanoate, Ethyl nonanoate, Hexadecanoic acid, 2-Methylbutyl octanoate, Ethyl decanoate, (*E*)-9-Hexadecenoic acid, β-Phenethyl acetate, 1-Decanol, Ethyl dodecanoate and Ethyl 2-phenylacetate (Figure 3), of which 53.5% belong to the ester class. Of the compounds mentioned above, γ-Terpinene, 3-Methyl octanoate, Tetradecanoic acid, 6-Methyl-2-pyrazinylmethanol, Ethyl 9-decenoate, 1-Methoxy-2-ethylbutane, Hexadecanoic acid, 2-Methylbutyl octanoate, Ethyl decanoate and β-

Phenethyl acetate obtained superior chromatographic areas in relation to other sparkling wines (Table 1). The following compounds also obtained superior areas: 3-Butyl-1,2,4-cyclopentanetrione in relation to moscatel and tyrosol in relation to demi-sec. The compounds: (E)-2-Dodecenal, 1,8-Cineole, Ethyl vanillate, 2,4-Di-tert-butylphenol and 2-Methyl-1-butyl acetate were only identified in brut rosé. In a study of wines made with the same varietal used in brut rosé (Grenache), Arias et al. (2019) obtained high concentration (280.11µg/L) of Ethyl vanillate compound associated to the origin of the cultivar. The 1,8-Cineole (eucalyptol) and 2,4-Di-tert-butylphenol compounds were also identified in moscatel (Moscato Bianco and Moscato R2) sparkling wines produced in Rio Grande do Sul, Brazil (Soares et al., 2015). According to Capone et al. (2012), the proximity of vines to Eucalyptus trees may influence the concentration of 1.8-Cineole in wines, which could attribute mint aromatic notes (*Pherobase*, 2020).

Furthermore, 51.78% of the most expressive compounds indicated by heatmap were also important markers in the principal component analysis, contributing with factor loads in each quadrant.

All the obtained results generally address the importance of knowing the volatile chemical composition of wine varieties. Measuring these characteristics can help winemakers in the technological adjustments of winemaking, making it possible to obtain wines with the typicality of the most pronounced cultivar and improving their quality. Moreover, the characterization and differentiation of the varietal wines obtained in this study may increase their commercialization value, as well as with helpful information for consumers (Lukic & Horvat, 2017).

4. Conclusions

The volatile profiles of brut, brut rosé, demi-sec and moscatel commercial sparkling wines were analyzed for the first time. A total of 109 compounds were identified and classified into 13 chemical groups. In comparison, significant compounds were exclusively identified in each type of sparkling wine, such as moscatel (23), brut (9), brut rosé (5) and demi-sec (4), with an emphasis on the compounds 2-Phenyl-undecane, 3-Methyl-4-heptanol, 4-Phenyl-undecane and Germacrene B, which were identified for the first time in sparkling wines from VSF to the best of our knowledge.

The PCA correlations and the hierarchical cluster analysis results indicated a strong association with the type and/or quantity of grape cultivars and the technological processes (*asti* and *charmat* methods) used in winemaking. This indicates a specific aromatic profile for each sparkling wine and therefore different overall aromas, which establish themselves as possible authenticity markers for commercial sparkling wines from the São Francisco Valley. In this context, future studies should be developed to identify the impact of these compounds on the overall aroma of wines, especially those reported for the first time in sparkling wines.

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Conflicts of interest

None.

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Figure Captions

Figure 1. Graph of the total area values of each chemical group according to the four commercial sparkling wine groups.

Footnote: Results with different letters for the same class of compounds differ significantly by the Kruskal-Wallis test and Dunn's *post hoc* multiple comparison test ($p<0.05$).

Figure 2. Principal components analysis (PCA) of the volatile compounds* of sparkling wines from the São Francisco Valley.

Footnote: * Legend of the compound codes is in **Table 1**.

Figure 3. Hierarchical cluster analysis and heatmap for each sparkling wine from the São Francisco Valley performed by Pearson’s correlation coefficient.

Figure 1

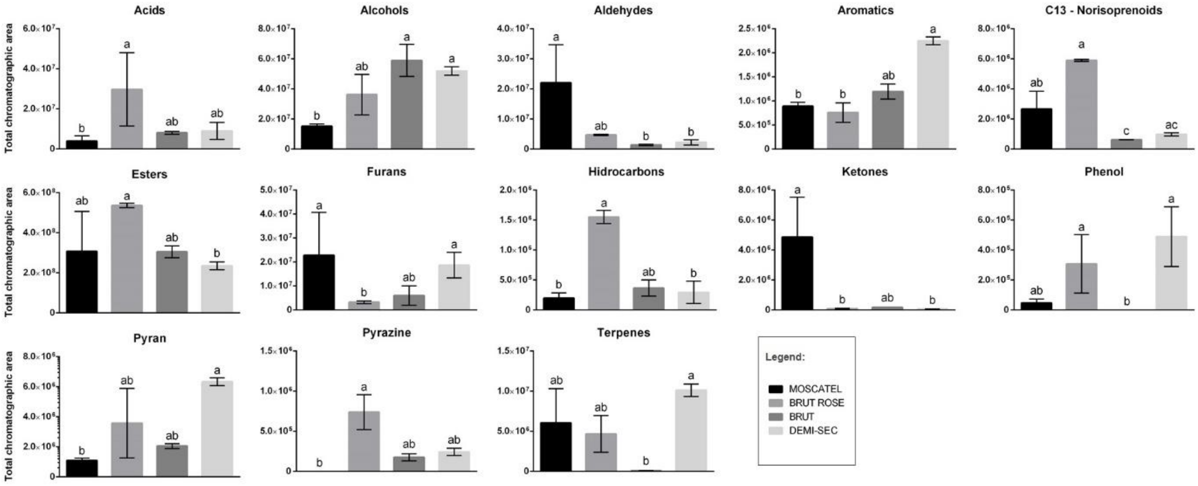
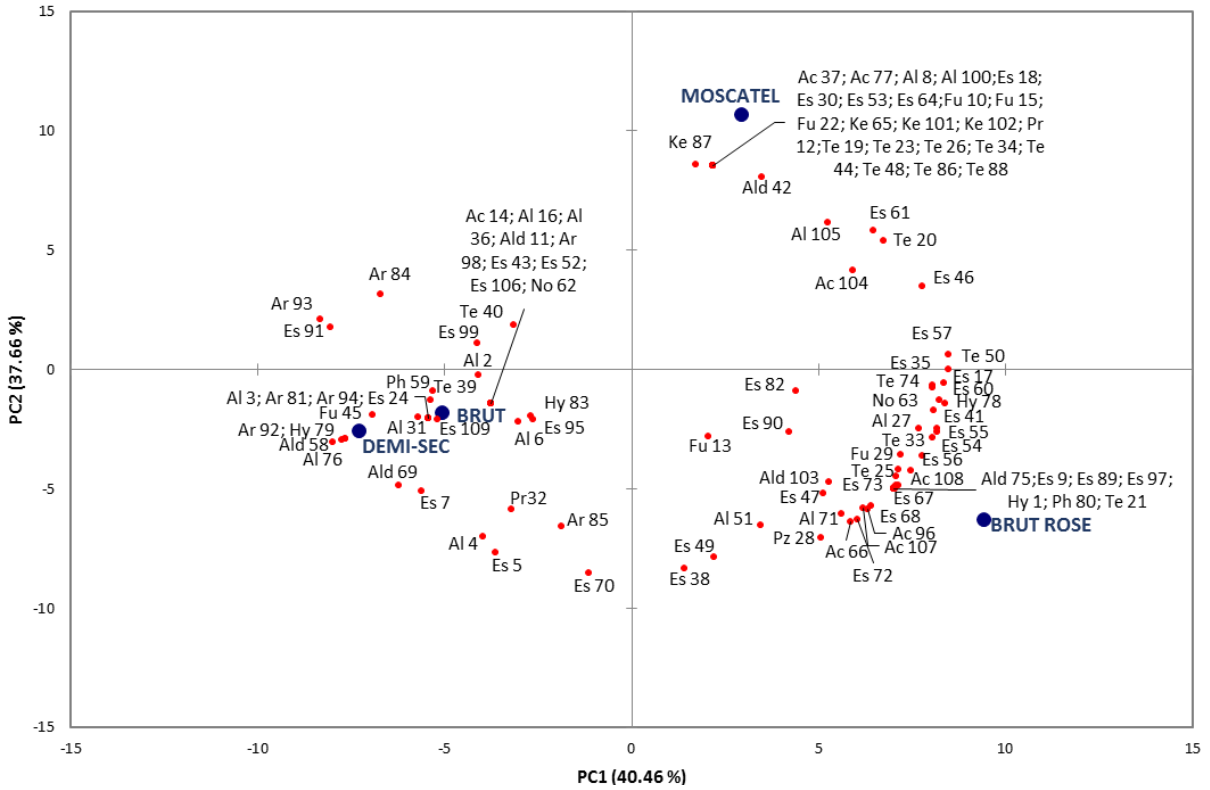

Acids
Alcohols
Aldehydes
Aromatics
C13 - Norisoprenoids
Esters
Furans
Hidrocarbons
Ketones
Phenol
Pyran
Pyrazine
Terpenes
Total chromatographic area
Legend:
MOSCATEL
BRUT ROSE
BRUT
DEMI-SEC

Figure 2



MOSCATEL
BRUT
DEMI-SEC
BRUT ROSE
Ac 37; Ac 77; Al 8; Al 100;Es 18; Es 30; Es 53; Es 64;Fu 10; Fu 15; Fu 22; Ke 65; Ke 101; Ke 102; Pr 12;Te 19; Te 23; Te 26; Te 34; Te 44; Te 48; Te 86; Te 88
Ac 14; Al 16; Al 36; Ald 11; Ar 98; Es 43; Es 52; Es 106; No 62
Al 3; Ar 81; Ar 94; Es 24
Ald 75;Es 9; Es 89; Es 97; Hy 1; Ph 80; Te 21
PC1 (40.46 %)
PC2 (37.66 %)

Figure 3

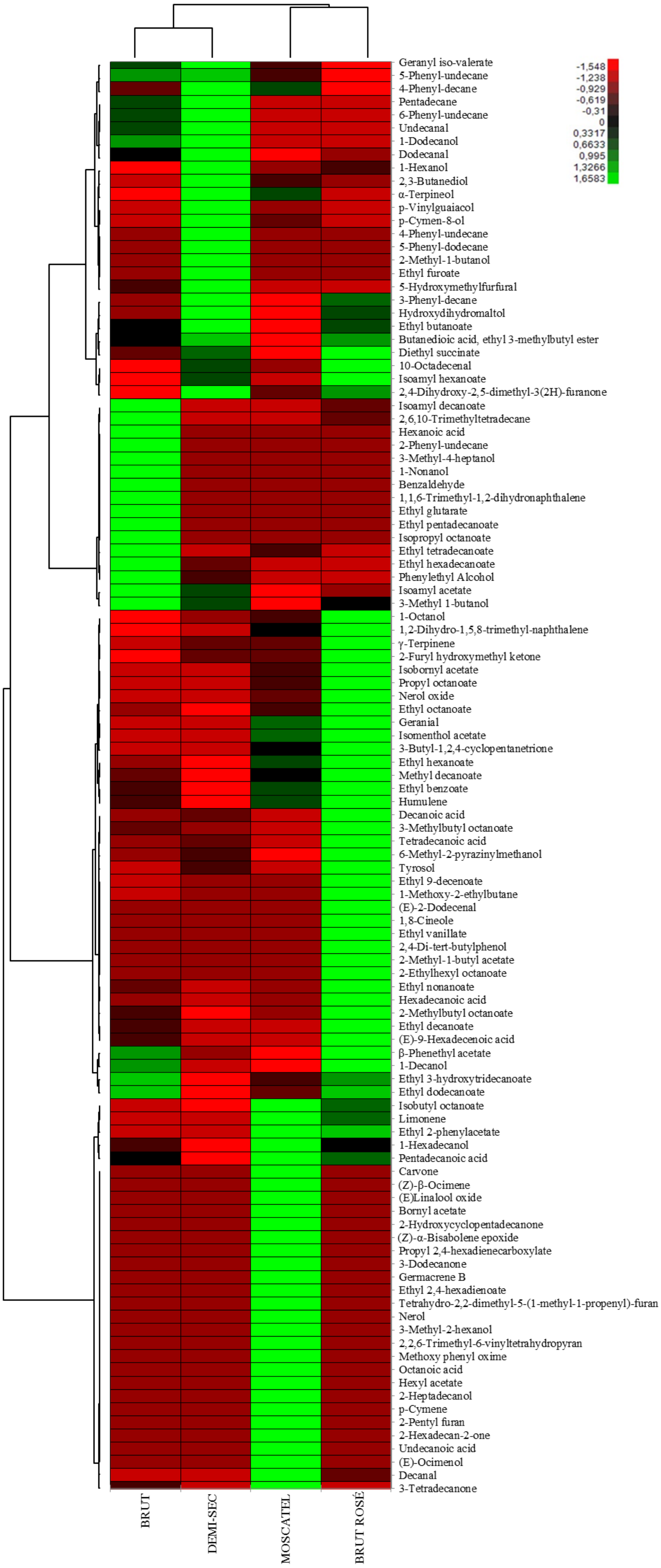

-1,548
-1,238
-0,929
-0,619
-0,31
0
0,3317
0,6633
0,995
1,3266
1,6583
Geranyl iso-valerate
5-Phenyl-undecane
4-Phenyl-decane
Pentadecane
6-Phenyl-undecane
Undecanal
1-Dodecanol
Dodecanal
1-Hexanol
2,3-Butanediol
α-Terpineol
p-Vinylguaiacol
p-Cymen-8-ol
4-Phenyl-undecane
5-Phenyl-dodecane
2-Methyl-1-butanol
Ethyl furoate
5-Hydroxymethylfurfural
3-Phenyl-decane
Hydroxydihydromaltol
Ethyl butanoate
Butanedioic acid, ethyl 3-methylbutyl ester
Diethyl succinate
10-Octadecenal
Isoamyl hexanoate
2,4-Dihydroxy-2,5-dimethyl-3(2H)-furanone
Isoamyl decanoate
2,6,10-Trimethyltetradecane
Hexanoic acid
2-Phenyl-undecane
3-Methyl-4-heptanol
1-Nonanol
Benzaldehyde
1,1,6-Trimethyl-1,2-dihydronaphthalene
Ethyl glutarate
Ethyl pentadecanoate
Isopropyl octanoate
Ethyl tetradecanoate
Ethyl hexadecanoate
Phenylethyl Alcohol
Isoamyl acetate
3-Methyl 1-butanol
1-Octanol
1,2-Dihydro-1,5,8-trimethyl-naphthalene
γ-Terpinene
2-Furyl hydroxymethyl ketone
Isobornyl acetate
Propyl octanoate
Nerol oxide
Ethyl octanoate
Geranial
Isomenthol acetate
3-Butyl-1,2,4-cyclopentanetrione
Ethyl hexanoate
Methyl decanoate
Ethyl benzoate
Humulene
Decanoic acid
3-Methylbutyl octanoate
Tetradecanoic acid
6-Methyl-2-pyrazinylmethanol
Tyrosol
Ethyl 9-decenoate
1-Methoxy-2-ethylbutane
(E)-2-Dodecenal
1,8-Cineole
Ethyl vanillate
2,4-Di-tert-butylphenol
2-Methyl-1-butyl acetate
2-Ethylhexyl octanoate
Ethyl nonanoate
Hexadecanoic acid
2-Methylbutyl octanoate
Ethyl decanoate
(E)-9-Hexadecenoic acid
β-Phenethyl acetate
1-Decanol
Ethyl 3-hydroxytridecanoate
Ethyl dodecanoate
Isobutyl octanoate
Limonene
Ethyl 2-phenylacetate
1-Hexadecanol
Pentadecanoic acid
Carvone
(Z)-β-Ocimene
(E)Linalool oxide
Bornyl acetate
2-Hydroxycyclopentadecanone
(Z)-α-Bisabolene epoxide
Propyl 2,4-hexadienecarboxylate
3-Dodecanone
Germacrene B
Ethyl 2,4-hexadienoate
Tetrahydro-2,2-dimethyl-5-(1-methyl-1-propenyl)-furan
Nerol
3-Methyl-2-hexanol
2,2,6-Trimethyl-6-vinyltetrahydropyran
Methoxy phenyl oxime
Octanoic acid
Hexyl acetate
2-Heptadecanol
p-Cymene
2-Pentyl furan
2-Hexadecan-2-one
Undecanoic acid
(E)-Ocimenol
Decanal
3-Tetradecanone
BRUT
DEMI-SEC
MOSCATEL
BRUT ROSÉ

Table 1 Volatile compounds identified in the sparkling wines of the São Francisco Valley by HS-SPME-GC-MS.

Code	Volatile Compound[1]	LRI (lit)	LRI (cal)	"Peak Area Count" ± SD (x10^6) MOSCATEL	BRUT ROSÉ	BRUT	DEMI-SEC	Odor Description[2]
	Acids (8)							
Ac 14	Hexanoic acid	990	995	nd	nd	0.09±0.08	nd	slightly, waxy, fatty
Ac 37	Octanoic acid	1180	1176	0.02±0.02	nd	nd	nd	fatty, rancid, soapy, cheesy, brandy
Ac 66	Decanoic acid	1383	1385	2.99±1.94	27.13±18.35	7.00±0.46	8.19±4.51	rancid, sour, fatty, citrus
Ac 77	Undecanoic acid	1475	1477	0.11±0.06	nd	nd	nd	waxy, creamy, cheese, fatty, coconut
Ac 96	Tetradecanoic acid	1763	1768	0.20±0.07	0.99±0.19	0.26±0.13	0.33±0.09	waxy, fatty, soapy, coconut
Ac 104	Pentadecanoic acid	1867	1866	0.07±0.06	0.05±0.00	0.05±0.02	nd	waxy
Ac 107	(*E*)-9-Hexadecenoic acid	1938	1940	nd	0.23±0.14	0.07±0.01	nd	waxy, creamy, fatty, soapy
Ac 108	Hexadecanoic acid	1968	1960	0.54±0.45	1.31±0.01	0.59±0.22	0.48±0.14	waxy, fatty
	Total Acids			3.94^{b}	29.71^{a}	8.05^{a,b}	9.00^{a,b}	
	Alcohols (14)							
Al 4	3-Methyl-1-butanol	736	< 800	6.85±3.88	26.08±11.95	39.28±12.81	29.13±2.42	fusel, oil, alcoholic, whiskey, fruity, banana
Al 3	2-Methyl-1-butanol	739	< 800	nd	nd	nd	6.43±2.05	roasted, winey, onion, fruity, fusel, alcoholic, whiskey
Al 2	2,3-Butanediol	788	< 800	1.41±1.27	0.85±0.00	0.24±0.01	3.93±0.34	fruity, creamy, buttery
Al 6	1-Hexanol	868	865	1.04±0.65	1.25±0.45	0.65±0.50	2.43±0.15	ethereal, fusel, oil, fruity, alcoholic, sweet, green
Al 8	3-Methyl-2-hexanol	906	898	0.06±0.05	nd	nd	nd	
Al 16	3-Methyl-4-heptanol	997	999	nd	nd	0.11±0.04	nd	
Al 27	1-Octanol	1075	1076	0.27±0.21	0.67±0.15	nd	0.17±0.01	waxy, green, orange, aldehydic, rose, mushroom
Al 31	Phenylethyl alcohol	1116	1114	5.03±4.92	4.75±1.11	16.48±1.78	8.26±1.98	floral, rose, dried, rose flower, rose water

Al 36	1-Nonanol	1173	1172	nd	nd	0.04±0.00	nd	fresh, clean, fatty, floral, rose, orange, dusty w et, oily
Al 51	1-Decanol	1273	1272	0.16±0.12	1.56±0.14	1.26±0.97	0.33±0.05	fatty, waxy, floral, orange, sweet, clean, watery
Al 71	Tyrosol	1444	1444	nd	0.66±0.01	nd	0.21±0.00	sweet, floral, fruity
Al 76	1-Dodecanol	1473	1474	0.25±0.21	0.25±0.03	0.81±0.13	1.03±0.26	earthy, soapy, waxy, fatty, honey, coconut
Al 100	2-Heptadecanol	1802	1799	0.01±0.01	nd	nd	nd	
Al 105	1-Hexadecanol	1884	1880	0.18±0.16	0.10±0.01	0.08±0.00	nd	waxy, clean, greasy, floral, oily
	Total Alcohols			15.23[b]	36.16 [a,b]	58.95[a]	51.91[a]	
	Aldehydes (6)							
Ald 11	Benzaldehyde	962	960	nd	nd	0.18±0.00	nd	sharp, sweet, bitter, almond, cherry
Ald 42	Decanal	1205	1206	21.69±12.41	3.62±0.13	nd	nd	sweet, waxy, orange peel, floral
Ald 58	Undecanal	1307	1307	nd	nd	0.42±0.15	0.77±0.51	waxy, soapy, floral, aldehydic, citrus, green fa tty, cloth, laundered cloth
Ald 69	Dodecanal	1409	1410	0.25±0.20	0.53±0.19	0.73±0.39	1.28±0.39	soapy, waxy, aldehydic, citrus, green, floral
Ald 75	(*E*)-2-Dodecenal	1468	1470	nd	0.25±0.08	nd	nd	citrus, metallic, mandarin, orange, waxy aldehydic
Ald 103	10-Octadecenal	1863	1857	0.11±0.07	0.30±0.05	0.04±0.01	0.19±0.05	
	Total Aldehydes			22.05[a]	4.70 [a,b]	1.37[b]	2.24[b]	
	Aromatics Compounds (7)							
Ar 84	4-Phenyl-decane	1546	1550	0.22±0.06	0.07±0.05	0.17±0.00	0.31±0.01	
Ar 85	3-Phenyl-decane	1568	1567	0.35±0.22	0.51±0.11	0.41±0.14	0.59±0.10	
Ar 92	6-Phenyl-undecane	1628	1635	nd	nd	0.13±0.05	0.26±0.06	
Ar 93	5-Phenyl-undecane	1632	1638	0.32±0.08	0.18±0.04	0.39±0.02	0.42±0.02	
Ar 94	4-Phenyl-undecane	1643	1649	nd	nd	nd	0.57±0.12	

Ar 98	2-Phenyl-undecane	1708	1711	nd	nd	0.09±0.06	nd	
Ar 81	5-Phenyl-dodecane	1730	1737	nd	nd	nd	0.10±0.02	
	Total Aromatics Compounds			0.89[b]	0.76[b]	1.20 [a,b]	2.25[a]	
	C13-Norisoprenoid (2)							
No 62	1,1,6-Trimethyl-1,2-dihydronaphthalene	1350	1351	nd	nd	0.62±0.01	nd	licorice
No 63	1,2-Dihydro-1,5,8-trimethyl-naphthalene	1354	1352	2.66±1.18	5.90±0.07	nd	0.98±0.10	
	Total C13-Norisoprenóide			2.66 [a,b]	5.90[a]	0.62[c]	0.98[b,c]	
	Esters (37)							
Es 5	Ethyl butanoate	802	801	0.02±0.00	0.39±0.11	0.36±0.12	0.56±0.06	fruity, juicy, fruit, pineapple, cognac
Es 7	Isoamyl acetate	876	875	0.57±0.38	1.20±0.05	2.53±2.52	1.75±0.16	sweet, fruity, banana, solvent
Es 9	2-Methyl-1-butyl acetate	880	881	nd	0.43±0.36	nd	nd	fruit, overripe fruit sweet banana juicy fruit fruity
Es 17	Ethyl hexanoate	1000	1003	21.79±15.54	26.66±4.72	18.70±0.82	14.87±1.14	sweet, fruity, pineapple, waxy, green banana
Es 18	Hexyl acetate	1011	1017	0.82±0.01	nd	nd	nd	fruity, green, apple, banana, sweet
Es 24	Ethyl furoate	1047	1055	nd	nd	nd	0.07±0.04	
Es 30	Ethyl 2,4-hexadienoate	1097	1100	20.89±15.51	nd	nd	nd	warm, fruity, anise, licorice, ether
Es 35	Ethyl benzoate	1171	1168	0.20±0.19	0.33±0.21	0.14±0.00	nd	fruity, dry, musty, sweet, wintergreen
Es 38	Diethyl succinate	1182	1182	1.77±1.17	20.96±0.74	10.18±0.20	16.38±5.02	mild, fruity, cooked, apple, ylang
Es 41	Ethyl octanoate	1196	1200	171.32±116.24	267.08±3.42	144.77±19.77	114.08±6.59	fruity, wine, waxy, sweet, apricot, banana brandy, pear
Es 43	Isopropyl octanoate	1218	1217	nd	nd	17.44±13.03	nd	fruity, banana, coconut, cognac
Es 46	Ethyl 2-phenylacetate	1246	1244	2.59±1.58	2.40±0.57	nd	nd	sweet, floral, honey, rose, balsamic, cocoa
Es 47	Isoamyl hexanoate	1252	1251	0.22±0.00	0.54±0.08	0.15±0.01	0.36±0.17	fruity, banana, apple, pineapple, green
Es 49	β-Phenethyl acetate	1258	1256	0.38±0.15	3.47±0.02	2.82±0.03	1.57±0.33	floral, rose, sweet, honey, fruity tropical
Es 52	Ethyl glutarate	1283	1283	nd	nd	0.06±0.00	nd	

Es 53	Bornyl acetate	1285	1286	0.02±0.00	nd	nd	nd	woody, pine, herbal, cedar, spice
Es 54	Isobornyl acetate	1286	1289	1.02±0.70	3.73±2.82	nd	nd	balsam, camphor, herbal, woody, sweet
Es 55	Propyl octanoate	1290	1291	0.30±0.24	0.92±0.53	0.07±0.02	nd	coconut, caco, gin
Es 56	Ethyl nonanoate	1296	1296	0.16±0.12	0.90±0.57	0.18±0.12	nd	fruity, rose, waxy, rum, wine natural tropical
Es 57	Isomenthol acetate	1305	1306	0.08±0.06	0.12±0.01	nd	nd	
Es 60	Methyl decanoate	1325	1325	0.11±0.08	0.21±0.00	0.07±0.02	nd	oily, wine, fruity, floral
Es 61	Isobutyl octanoate	1348	1349	0.78±0.69	0.47±0.01	0.11±0.01	nd	fruity, green, oily, floral
Es 64	Propyl 2,4-hexadienecarboxylate	1366	1363	0.63±0.44	nd	nd	nd	sweet, fruity
Es 67	Ethyl 9-decenoate	1387	1390	9.50±6.86	38.24±0.90	8.06±1.12	9.43±0.96	fruity, fatty
Es 68	Ethyl decanoate	1396	1401	71.51±42.64	157.40±6.39	92.50±0.32	72.32±8.47	sweet, waxy, fruity, apple, grape, oily brandy
Es 70	Butanedioic acid, ethyl 3-methylbutyl ester	1432	1431	nd	1.13±0.06	0.77±0.11	1.15±0.13	
Es 72	3-Methylbutyl octanoate	1446	1448	0.41±0.21	2.35±0.20	0.78±0.24	0.71±0.33	sweet, oily, fruity, green, soapy, pineapple coconut
Es 73	2-Methylbutyl octanoate	1449	1451	0.05±0.05	0.28±0.00	0.10±0.04	nd	
Es 82	Ethyl 3-hydroxytridecanoate	1539	1539	0.10±0.06	0.15±0.00	0.17±0.06	nd	
Es 89	Ethyl vanillate	1579	1590	nd	0.12±0.06	nd	nd	phenolic, burnt, guaiacol, smoky, powdery metallic
Es 90	Ethyl dodecanoate	1595	1596	0.52±0.27	0.80±0.09	0.81±0.03	0.28±0.02	mango, sweet, waxy, floral, soapy, clean
Es 91	Geranyl iso-valerate	1606	1600	0.16±0.14	nd	0.20±0.11	0.32±0.03	sweet, fruity, green, oily, herbal, fruity melon
Es 95	Isoamyl decanoate	1646	1651	0.06±0.05	0.29±0.08	1.67±1.33	nd	waxy, banana, fruity, sweet, cognac, green
Es 97	2-Ethylhexyl octanoate	1688	1694	0.09±0.07	4.58±4.15	0.07±0.04	0.05±0.00	
Es 99	Ethyl tetradecanoate	1794	1794	0.35±0.04	0.27±0.05	0.54±0.05	0.30±0.04	sweet, waxy, violet, orris
Es 106	Ethyl pentadecanoate	1894	1894	nd	nd	0.53±0.19	nd	honey, sweet
Es 109	Ethyl hexadecanoate	1993	1993	0.27±0.18	0.27±0.01	0.71±0.18	0.37±0.13	mild, waxy, fruity, creamy, milky, balsam
	Total Esters			306.70 [a,b]	535.66[a]	304.51 [a,b]	234.56[b]	
	Furans (6)							
Fu 10	Methoxy phenyl oxime	E	947	19.04±18.94	nd	nd	nd	
Fu 13	2,4-Dihydroxy-2,5-dimethyl-3(2H)-	989	992	0.44±0.38	0.75±0.33	0.11±0.01	0.82±0.23	fruity, green, earthy, beany, vegetable metallic

	furanone							
Fu 15	2-Pentyl furan	993	999	0.03±0.02	nd	nd	nd	sweet, citrus, herbal, green, celery, spicy minty, woody
Fu 22	Tetrahydro-2,2-dimethyl-5-(1-methyl-1-propenyl) furan	1047	1048	0.25±0.20	nd	nd	nd	
Fu 29	2-Furyl hydroxymethyl ketone	1087	1087	0.53±0.22	1.35±0.41	0.19±0.03	0.51±0.06	fatty, buttery, musty, waxy, caramellic
Fu 45	5-Hydroxymethylfurfural	1233	1235	2.51±1.82	1.11±0.47	5.71±4.03	17.38±5.57	
	Total Furans			22.81[a]	3.21[b]	6.01 [a,b]	18.71[a]	
	Hydrocarbons (4)							
Hy 1	1-Methoxy-2-ethylbutane	778	< 800	0.04±0.03	1.16±0.06	nd	0.05±0.02	
Hy 83	2,6,10-Trimethyltetradecane	1541	1543	0.01±0.01	0.04±0.01	0.24±0.02	nd	
Hy 78	3-Butyl-1,2,4-cyclopentanetrione	1486	1485	0.15±0.11	0.35±0.06	nd	nd	
Hy 79	Pentadecane	1500	1496	nd	nd	0.12±0.11	0.24±0.21	waxy
	Total Hydrocarbons			0.20[b]	1.55[a]	0.37 [a,b]	0.29[b]	
	Ketones (4)							
Ke 65	3-Dodecanone	1380	1384	3.75±2.65	nd	nd	nd	fatty, soapy waxy fruity
Ke 87	3-Tetradecanone	1573	1585	0.52±0.35	0.09±0.03	0.18±0.00	0.06±0.00	
Ke 101	2-Hexadecan-2-one	1806	1806	0.51±0.31	nd	nd	nd	fruity
Ke 102	2-Hydroxycyclo-pentadecanone	1846	1840	0.08±0.05	nd	nd	nd	
	Total Ketones			4.87[a]	0.09[b]	0.18 [a,b]	0.06[b]	
	Phenol (2)							
Ph 59	*p*-Vinylguaiacol	1307	1312	0.05±0.03	nd	nd	0.49±0.20	dry, woody, fresh, amber, cedar, roasted, peanut
Ph 80	2,4-Di-tert-butylphenol	1515	1515	nd	0.31±0.20	nd	nd	phenolic
	Total Phenol			0.05 [a,b]	0.31[a]	nd	0.49[a]	

	Pyran (2)							
Pr12	2,2,6-Trimethyl-6-vinyltetrahydropyran	972	972	0.44±0.42	nd	nd	nd	fresh, camphor, herbal, rosemary
Pr32	Hydroxydihydromaltol	1151	1149	0.66±0.28	3.58±2.32	2.05±0.16	6.33±0.26	
	Total Pyran			1.10[b]	3.58 [a,b]	2.05 [a,b]	6.33[a]	
	Pyrazine (1)							
Pz 28	6-Methyl-2-pyrazinylmethanol	1084	1084	nd	0.74±0.22	0.18±0.04	0.24±0.04	
	Total Pyrazine			nd	0.74[a]	0.18 [a,b]	0.24 [a,b]	
	Terpenes (16)							
Te 19	*p*-Cymene	1025	1022	0.07±0.02	nd	nd	nd	fresh, citrus, terpene, woody, spice
Te 20	Limonene	1030	1026	0.28±0.23	0.18±0.01	nd	nd	citrus, orange, fresh, sweet
Te 21	1,8-Cineole	1033	1030	nd	0.03±0.01	nd	nd	eucalyptus, herbal, camphor medicinal
Te 23	(*Z*)-β-Ocimene	1049	1050	0.14±0.00	nd	nd	nd	sweet, herbal
Te 25	γ-Terpinene	1060	1059	0.08±0.02	0.37±0.12	nd	0.08±0.02	oily, woody, terpene, lemon/lime tropical herbal
Te 26	(*E*)-2-(Tetrahydro-5-methyl-5-vinylfuran-2-yl)-propan-2-o((*E*)-Linalool oxide))	1074	1073	0.03±0.00	nd	nd	nd	floral, herbal, earthy, green
Te 33	Nerol oxide	1153	1154	0.43±0.33	2.33±1.81	nd	nd	green, weedy, cortex, herbal, diphenyl oxide, narcissus, celery
Te 34	(*E*)-Ocimenol	1169	1167	0.05±0.04	nd	nd	nd	fresh, citrus, lemon lime, cologne, sweet mace
Te 39	*p*-Cymen-8-ol	1186	1185	0.71±0.63	nd	nd	5.02±2.88	sweet, fruity, cherry, coumarin, floral camphor
Te 40	α-Terpineol	1192	1192	2.78±2.32	1.05±0.42	nd	5.02±2.14	pine, terpene, lilac, citrus, woody, floral
Te 44	Nerol	1228	1228	0.06±0.06	nd	nd	nd	sweet, natural neroli, citrus, magnolia
Te 48	Carvone	1255	1255	0.47±0.04	nd	nd	nd	minty, spearmint, herbal
Te 50	Geranial	1268	1267	0.32±0.25	0.55±0.05	nd	nd	citrus, lemon
Te 74	α-Humulene	1453	1454	0.10±0.06	0.17±0.01	0.07±0.01	nd	woody

Te 86	(*Z*)-*α*-Bisabolene epoxide	1586	1585	0.52±0.35	nd	nd	nd	
Te 88	Germacrene B	1591	1588	0.03±0.02	nd	nd	nd	woody, earthy, spicy
	Total Terpenes			6.07 [a,b]	4.68 [a,b]	0.07[b]	10.12[a]	

[1] The compounds are listed by chemical class; [2] Aroma description obtained from an online database available at *The good scents company* (2020) and Pherobase (2020); LRI lit.: linear retention index of literature; LRI cal.: linear retention index calculated; SD: standard deviation; nd: not identified. E: identification by the Mass Spectrum, the others were identified by the mass spectrum and the literature retention index. Results with different letters for the same class of compounds differ significantly by Kruskall-Wallis test and Dunn's post hoc multiple comparison test (p<0.05).

4.2 ARTIGO II: IDENTIFICATION OF CHEMICAL MARKERS IN COMMERCIAL RED WINES CANDIDATES FOR THE SÃO FRANCISCO VALLEY GEOGRAPHICAL INDICATION

O artigo foi submetido ao periódico *Food Research International* em 20 de novembro de 2020, sob o título I*dentification of Chemical Markers in Commercial Red Wines Candidates for the São Francisco Valley Geographical Indication* (ANEXO B).

Identification of chemical markers of commercial tropical red wine candidates for the São Francisco Valley Geographical Indication

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Abstract

The objective of this study was to identify chemical markers of commercial tropical red wines with potential to apply for the Geographical Indication-GI São Francisco Valley. Classical enological analyses were determined and volatile compounds of nine commercial red wines from the São Francisco Valley of different varieties was performed by HS-SPME/GC/MS, and the results were subsequently analyzed by multivariate statistical techniques. The analyzed wines comply with current Brazilian legislation regarding classic enological parameters. A total of 103 volatile compounds were identified and classified into 13 chemical groups, of which the esters and alcohols were the majority groups. Similarities were found in the composition of 27 compounds identified in all wines, however the cultivars influenced the distinction of volatiles expressed exclusively in only one type of wine. A total of 22 of all the identified compounds were highlighted for being identified for the first time in wines, such as 3-phenyl-undecane and 4-phenyl-decane. These compounds are possible markers which confirm the typicality of tropical red wines of this region, and can contribute to the qualitative description and enhancement of regional identity for wines from the São Francisco Valley.

Keywords: *Vitis vinifera L.*; grape; tropical wine; volatile compound; typicality.

1. Introduction

The aromatic quality of red wines is directly related to their volatile composition, with more than 1000 metabolite compounds among the alcohols, organic acid esters, aldehydes, ethers, ketones and terpenes. These compounds are present in different concentrations, having been identified in several red wines (Jiang et al., 2013; Mota et al., 2020; Sánchez-Palomo et al., 2017; Vilanova et al., 2012). The different concentrations among the volatiles present in wines contribute to their complexity and molecular diversity due to interactions between the metabolites, providing specific typicalities in function of synergetic and antagonistic effects among them (Bonino et al., 2003).

The complexity of aromas in red wines comes from different sources and are described and characterized by three types, namely: the first group originates from the specific grape variety (primary aromas); the second group is formed during winemaking, and may vary according to the types of yeast and elaboration/fermentation protocols (secondary aromas); and the third group is formed during the maturation/aging of wines in oak barrels, as well as during bottle storage (tertiary aromas) (Drappier et al., 2017; Ruiz et al., 2019). These three types of aromas together form what is called the "bouquet" of wines. Complexation/degradation/evolution reactions of volatile compounds may occur during the whole production and aging process of wines in barrels, and the formation of new aromas may also occur. These new volatiles are associated with five families of aromatic compounds: furanic, lactone, phenolic aldehydes, volatile phenols and phenyl ketones (Ruiz et al., 2019).

Knowing the identity (origin, formation and degradation) of the compounds responsible for the aroma and flavor of wines helps to understand the consequences of climate impacts, seasonal conditions, planting decisions, types of grapes, and processing, thus providing improvements in viticulture and winemaking practices (Parker et al., 2017), in addition to assisting in the geographical typification of wines.

It is estimated that 132.16 million liters of fine wines were consumed in Brazil in 2019, of which 114.175 million liters were imported wines and 17.988 million liters were domestic wines (*Vitis Vinífera L.)* (Mello & Machado, 2020). The Northeast region represented 13.85% of the national wine area, whose viticulture is concentrated in the São Francisco Valley, and has the exceptionality of producing two harvests per year (Mello & Machado, 2020).

The São Francisco Valley is the second largest producer of fine wines in the country, and is located in the Northeast of Brazil. The region belongs to the caatinga biome, with a tropical semi-arid climate with high annual average temperatures (26.5ºC), high solar radiation rates (over 3,000 MJ m^{-2} $year^{-1}$) and low rainfall (450-500 $mm.year^{-1}$) (Pereira, 2020). Seven wineries have about 700 hectares of vineyards, with an annual production of 7 million liters of fine wines per year, being responsible for 15% of the national production of fine wines, of which 29% are red wines, as well as young and aging wines. They can be marketed about 90 days after harvest or after a period of 4 to 12 months in oak barrels, respectively (Tonietto; Pereira, 2011; Pereira, 2020). An association of the region's producers/wineries (Vinhovasf) is seeking Geographical Indication (GI) for the stilland sparkling wines (*Vitis vinifera* L.) of the São Francisco Valley. This request should occur with the aim of obtaining a quality seal for the products of the region. Therefore, works that enable characterizing and describing the physical-chemical composition of commercial wines are fundamental.

Thus, this study aimed to perform a characterization of the volatile composition of commercial red wines of the VSF in order to contribute to the scientific community, as well as producers in seeking the GI of wines from the region. To our knowledge, this work is innovative and was the first carried out in this sense, even enabling the identification and quantification of volatile compounds, which had not been previously reported that are present in tropical red wines from the Brazilian Northeast.

2. Material and Methods

2.1 Samples and classical analyses

This research studied nine commercial red wines from the caatinga biome, whose products will be in the São Francisco Valley Geographical Indication and represent between 55-65% of all types of wines produced and marketed at VSF, being well representative of the region's potential. The wines were stored at a temperature of 16±1ºC until analysis for a period not exceeding 6 months. The characteristics and specificities of each wine are shown in Table 1. Some classic enological parameters were determined in order to confirm the quality of commercial wines according to Brazilian and international standards and are shown in Table 2 (OIV, 2014).

2.2 Extraction and chromatographic analyses to identify volatile compounds in red wines

The volatile compounds were extracted by headspace solid-phase microextraction (HS-SPME) adapted from Barros et al. (2012). The fiber used was Polidimetilsiloxano/Divinilbenzeno (PDMS/DVB) (Supelco, Bellafonte, PA, USA) and it was conditioned according to the manufacturer’s instructions prior to the extraction. First, 30 mL of red wine was transferred to a 100 ml glass vial with a screw cap containing one centre hole of 3 mm radius and a Teflon-lined septum. The volatile compounds were extracted by placing the flask in a 45ºC water bath with internal magnetic stirring. The sample reached equilibrium in 15 minutes and was then exposed to the fiber for 30 minutes. Blank analyses were carried out.

A 7890B gas chromatograph (GC) coupled to an Agilent® Technologies 5977B (Little Falls, DE, USA) mass spectrometer (MS) and a Varian® VF-5 MS low bleed/MS fused-silica capillary column (5% phenyl/95% PDMS, 60 m x 0.25 mm x 0.25 µm film thickness) were used to separate and identify the volatiles collected by SPME. The carrier gas was helium at a

1.2 ml minute $^{-1}$ flow rate. The samples were injected by placing the SPME fibre at the entrance of the GC at 250 ºC and splitless injection mode was used with a desorption time of 5 minutes. The initial oven temperature was 40ºC, which was maintained for 10 minutes, increased to 250ºC at 7ºC per minute, and then maintained at 250ºC for 5 minutes. The mass spectrometer was operated in electron impact mode with a source temperature of 250ºC, an ionising voltage of 70 eV, and a scanning range from m/z 35 to 350 m/z at 3.33 scans/s. The transfer line was held at 250°C. The SPME data were acquired and analysed using the Mass Hunter software program (Agilent).

The compound identification was based on the comparison of their mass spectra with spectra from NIST/EPA/NIH Mass Spectral Database (Version 2.2 2014 showing the Match> 600 and RMatch > 700 coefficients of linear retention confirmed by the scientific literature (KONDJOYAN & BERDAGUÉ, 1996). The linear retention index (LRI) was calculated for each volatile compound using the retention times of a homologous series of C8–C20 n-alkanes, of which the linear retention index below 800 were expressed as <800.

2.3 Statistical analysis

Analysis of variance (ANOVA) was used in the classic oenological data associated with the Tukey mean difference test ($p<0.05$) using the XLSTAT software version 5.03 (Addinsoft, New York, USA, 2014). The results of the volatile compounds were auto-scaled using MATLAB version 7.10.0.499 (The Mathworks, Inc., Natick, MA, R2010a) to perform the comparison of the abundance of area obtained in each sample, then these treated data were submitted to Pearson's correlation analysis (r), principal component analysis ($p<0.05$), and hierarchical cluster analysis using XLSTAT software version 5.03 (Addinsoft, New York, USA, 2014).

3. Results

3.1 Classical analyses

Table 2 presents the results for the classic enological parameters of the commercial tropical wine samples. Significant differences ($p<0.05$) were observed in these parameters, however, all results are consistent with Brazilian and international legislation (OIV, 2014; Lima et al., 2015; Padilha et al., 2017; Brasil, 2018; Oliveira et al., 2019). It is worth emphasizing that the pH presented very high values, which is justified by the high concentrations of potassium in the soils of the VSF, as well as the high temperatures during the grape ripening, which reduce the organic acids by degradation of malic acid (Lima et al., 2015; Oliveira et al., 2019; Pereira, 2020; Jackson, 2020).

3.2 Determination of volatile compounds in red wines from the São Francisco Valley

A total of 103 volatile compounds were identified by HS-SPME-CG-MS in the samples of commercial red wines in this study, and the percentage area for each wine is shown in Table 3. The total number of compounds identified in each wine was distinguished according to the varieties used in the elaboration, such as TP (71), SY (69), AB (68), PR (67), RS (60), and CS/SY (50), and similar in the CS, TN and RC samples (65 compounds). Among the total number of volatile compounds identified in this study, 13 were only identified in one type of red wine, being 1-pentanol and 2.4-dihydroxy-2.5-dimethyl-3(2H)-furanone (RS); hexanoic acid, 2-ethyl-1-hexanol, 4-ethylphenol, 4-ethyl guaiacol, 6-phenyl-dodecane, (Z)-9-tetradecenoic acid, ethyl 9-hexadecenoate and methyl 11-octadecenoate (RC); ethyl 2,4-hexadienoate (PR), ethyl benzoate and (E)-9-hexadecenoic acid (AB).

The volatile compounds were grouped into 13 chemical classes including esters (36 compounds), alcohols (16), terpenes (11), aromatics (10), acids (9), aldehydes (5), phenols (4), furans (4), hydrocarbons (3), C13-norisoprenoids (2), ketone (1), ether (1) and pyrane (1). A comparison of the sum for the total areas of each chemical group is shown in Figure 1. With the exception of esters and c13-norisoprenoids, all classes showed significant differences within a class between at least two red wines according to Conover-Iman's non-parametric comparison test ($p<0.05$).

The esters class was the majority in the number of identified compounds (a total of 36), with 14 being identified in all of the red wines analyzed. The esters class was also the majority in terms of percentage of chromatographic area, as it can be seen in the Table 3. The CS and SY wines obtained the largest number of compounds (30 and 29, respectively), representing 83.61% and 60.91% of the total chromatographic area, followed by the AB and PR wines (28 compounds each), representing 79.72% and 80.90% of the total area, respectively. The most abundant esters in terms of area percentage were ethyl octanoate (36.65% and 36.09% in AB and CS wines, respectively), diethyl succinate (22.02% in wine from PR) and ethyl decanoate (18.56% in wine from AB). Ethyl 2.4-hexadienoate (4.42% in PR wine), ethyl hexanoate (3.62% in CS wine), butanedioic acid ethyl 3-methylbutyl ester (2.74% in RS wine), ethyl 2-methylbutanoate (2. 26% in CS wine), ethyl butanoate (1.89% in AB wine), ethyl glutarate (1.34% in TP wine), ethyl 9-decenoate (1.05% in PR wine) and β-phenethyl acetate (1.01% in CS/SY wine) are also highlighted.

The alcohol class was the second majority in the number of compounds (Table 3) with 16 being identified, of which 6 are present in all nine types of wine, including: 3-methyl 1-butanol, 1-hexanol, 3-ethyl-4-methyl-1-pentanol, phenylethyl alcohol, 1-decanol, and hexadecanol. It was also the second major class regarding the area percentage, ranging from 10.72% to 65.97% for wines from the CS/SY and RC cultivars, respectively, which differed significantly among themselves (Figure 1). Some compounds in this class stood out for area percentage, such as phenylethyl alcohol (64.80% in RC wine), 2.3-butanediol (2.86% in CS wine), 3-methyl 1-butanol (2.66% in TN wine), and 1-hexanol (1.99% in SY wine).

A total of 11 compounds were identified in the terpenes class, with the majority in PR and TP wines with 8 compounds each. No terpenes showed chromatographic area >1%, and the sum of the total area varied between 0.18% and 1.28% (in CS and PR wines, respectively) (Table 3), differing significantly among themselves (Figure 1).

A total of 10 compounds were classified in the aromatic group, of which 9 compounds were identified in the RC and TN wines. The total chromatographic area of this class of compounds varied from 0.22% to 1.02% (in RS and NT wines, respectively), differing significantly (Figure 1).

There were 9 compounds identified for the acids class, with a variation in the total area from 0.62% to 3.52% (Table 3) in the RC and CS/SY wines, respectively, and decanoic acid (representing a chromatographic area of 2.79% in CS/SY wine) and undecanoic acid (1.09% in PR wine) compounds are highlighted.

The minority of compounds in terms of quantity, aldehydes obtained a maximum of 5 metabolites in CS wine, and the total area percentage varied from 0.07% to 0.90% in wines from AB and RS, respectively. There were 4 compounds identified within the phenols, 3 of which were detected in CR wine, with a total chromatographic area variation of 0.06% to 1.47% in wines from AB and CR, respectively. Furthermore, 4 compounds were identified among the furans, of which the majority of the wines detected 2 compounds, and presented a total area variation of 0.05% to 0.43% in the RC and TP wines, respectively.

Other identified minority compounds were classified as C13-norisoprenoid (2 compounds), and the others with one compound each, such as ketone, ether and pyrane groups, representing total chromatographic areas of 0.32%, 0.11% and 0.57%, respectively. Only the C13-norisoprenoid did not differ significantly from the classes of minority compounds mentioned above (Figure 1).

3.3 Clustering, Principal Component Analysis (PCA) and Pearson Correlation

A cluster hierarchical analysis was performed using the volatile compound data of the nine commercial red wines analyzed (Table 3). A graphical representation is presented in the form of a dendrogram, which the separation criterion was the Euclidean distance (%) (Figure 2). It is possible to clearly observe the formation of four groups, and cluster 4 is formed by a single wine (RC), having been isolated compared to the others. Cluster 1 is formed by the AB, SY and TP wines, while cluster 2 is formed by the PR, CS and RS wines, and cluster 3 is formed by the CS/SY and TN wines.

Principal Component Analysis (PCA) was performed with the area data of the auto-scaled volatile compounds of the nine red wines in this study, and differentiated by colors according to chemical class in Figure 3. The first Principal Component (PC1) explained 24.71% of the total variation between the samples, and together with the second component (PC2, which explained 18.84%), explained 43.55% of the variability between the volatiles. Figure 3 (PC1 x PC2) separates and groups the wines in a similar way as Figure 2 (dendrogram). Therefore, it is possible to more clearly observe the greater contribution of the ester, terpene and alcohol classes in the profile of wines from cluster 1; the alcohol, ether, and acid classes in the cluster 2; the aromatics class in the profile of wines from cluster 3; and some specific compounds in the cluster 4.

The red wines with similar volatile profiles were positioned in different regions in the PCA, with the compounds with significant factor loads and ≥ 0.7 being considered for discussion. Therefore, it was verified that only the RC wine was allocated in the positive axis of the PC1, separating this wine from the others. In addition, PC2 separated the TN and CS/SY wines (cluster 3) from the others, being located on the positive axis of PC2.

The volatile compounds which most contributed to the characterization of RC wine were ethyl isovalerate, 3-methyl-2-hexanol, hexanoic acid, 2-ethyl-1-hexanol, γ-terpinene, phenylethyl alcohol, 4-ethylphenol, β-phenethyl acetate, 4-ethyl guaiacol, damascenone, 6-phenyl-dodecane, (Z)-9-tetradecenoic acid, ethyl tetradecanoate, ethyl 9-hexadecenoate, ethyl hexadecanoate and methyl 11-octadecenoate. Moreover, the compounds associated with TP (cluster 1) and PR (cluster 2) wines were 1-nonanol, 1-decanol and methyl decanoate.

The CS/SY and TN wines (cluster 3) were characterized by the volatile compounds isoamyl hexanoate, dodecanal, humulene, 1-dodecanol, 5-phenyl-decane, 2,6,10-trimethyltetradecane, 4-phenyl-decane, dodecanoic acid, 6-phenyl-undecane, 5-phenyl-undecane, 3-phenyl-undecane, 4-isopropyl-1,6-dimethyl-naphthalene and 2-phenyl-undecane. Furthermore, the wines from AB and SY (cluster 1), RS and CS (cluster 2) obtained a greater contribution from the 1,2-dihydro-1,5,8-trimethyl-naphthalene compound.

A Pearson's correlation analysis (r) was subsequently performed on the 20 volatile compounds with percentage of area ≥ 1%, in order to identify the correlation between the volatile compounds detected in red wines (Table 4). Positive and significant correlations ($p<0.05$) were observed in the esters class, which ethyl octanoate correlated with three esters, namely ethyl hexanoate ($r = 0.82$), ethyl butanoate ($r = 0.70$) and ethyl decanoate ($r = 0.90$). Furthermore, ethyl decanoate correlated positively with ethyl butanoate ($r = 0.81$) and butanedioic acid, while ethyl 3-methylbutyl ester correlated with ethyl 2-methylbutanoate ($r = 0.69$).

Positive correlations were also observed between ethyl 2-methylbutanoate and 2,3-butanediol esters and alcohols ($r = 0.98$); between β-phenethyl acetate and phenylethyl alcohol ($r = 0.96$); and between ethyl 2,4-hexadienoate and undecanoic acid ($r = 0.70$). Other compounds also had positive correlations, such as 4-ethyl guaiacol with phenylethyl alcohol ($r = 0.94$), and β-phenethyl acetate ($r = 0.90$); 2-ethyl-1-butanol, methyl ether with 2,3-butanediol ($r = 0.85$), and ethyl 2-methylbutanoate ($r = 0.79$). A negative and significant correlation ($p<0.05$) was only obtained by ethyl glutarate and diethyl succinate ($r = -0.80$) in the other compounds.

4. Discussion

The volatile profile of nine commercial tropical red wines, which may in the future obtain the Geographical Indication São Francisco Valley, was analyzed here in for the first time. The objective was to identify the volatile compounds that could typify the red wines and be used as chemical markers. The study presented two important aspects. Firstly, commercial red wines, already validated in terms of quality and acceptability by consumers, were chosen to be studied. The second aspect is that the wines were indicated by the wineries' oenologists/owners based on the potential for obtaining the GI.

4.1 Classical analyses

All the results of the classical analyses performed (Table 2) are in accordance with the Brazilian and international wine laws (OIV, 2014; Brasil, 2018). The samples presented similarities and differences ($p<0.05$) regarding the different parameters. The alcohol content was similar to the values reported by Oliveira et al. (2019) and Garaguso & Nardini, (2015) in red wines from VSF and Italy, respectively. The registered variations are possibly due to the winemaking processes used and climate variations (Sánchez-Palomo et al., 2017).

The pH values obtained exceeded the ideal recommended range for red wines, between 3.4 and 3.8, due to high temperatures during maturation and high potassium concentration in the soils of the region (Rankine, 1989; Jackson, 2020). Agronomic management is among the alternatives for reducing pH to maintain balanced concentration of acids in ripe berries (increased productivity), as well as the use of correctives to reduce the concentration of potassium in the soil, and acidification during winemaking with tartaric or lactic acids (Ribéreau-Gayon et al., 2006; Lima et al., 2015; Jackson, 2020).

The density of the wines in this study shows that the samples were dry wines, being similar to those obtained in other studies (Ivanova-Petropulos et al.,2015; Lima et al., 2015; Oliveira, 2019). The results of total titratable acidity, volatile acidity and total sulfur dioxide were varied when compared to other studies, mainly depending on the oenological potential of the grapes at harvest (climate), as well as the elaboration protocols (Lombardi et al., 2017; Sánchez-Palomo et al., 2017; Oliveira et al., 2019; Valentin et al., 2020). However, all parameters are in accordance with Brazilian and international legislation (Brasil, 2018; OIV, 2014). Total acidity contributes to microbial/biological stabilization and the freshness taste of wines (Ribéreau-Gayon et al., 2006; Ivanova-Petropulos et al., 2015).

4.2 Volatile profile of wines and varietal effect

Red wines were characterized by a total of 103 volatile compounds belonging to different chemical classes. Some compounds were highlighted by their abundance of chromatographic area, such as ethyl octanoate, diethyl succinate, ethyl decanoate, ethyl 2,4-hexadienoate, ethyl hexanoate, butanedioic acid ethyl 3-methylbutyl ester, ethyl 2-methylbutanoate, ethyl butanoate, ethyl glutarate, ethyl 9-decenoate and β-phenethyl acetate; phenylethyl alcohol, 2,3-butanediol, 3-methyl 1-butanol,1-hexanol, and decanoic and undecanoic acids.

The esters are highlighted in quantity and number among the classes. These compounds are produced during the alcoholic fermentation and acil-CoA, and contribute with floral and fruity notes in wines (Ilc et al., 2016; Mota et al., 2020). The esters stood out in the CS wine profile, a French cultivar introduced in Brazil in 1921 (Orlando et al., 2008), with ethyl octanoate (36.09%), followed by diethyl succinate (20.88%), ethyl decanoate (14.85%) and ethyl hexanoate (3.62%). They were also the majority in the PR wine profile, but with lower area percentages, except in the diethyl succinate (22.02%) and ethyl decanoate (16.80%)

compounds. Diethyl succinate has been identified in previous studies as a marker for aged wines (Voce et al., 2019), including being identified after 30 and 42 months of bottling, being a marker linked to aging in the winter wines from Syrah (Mota et al., 2020). However, this compound was also reported in a study with young and experimental wines from different cultivars, such as Cabernet Sauvignon, Pinot Noir, Syrah and Merlot from Italy (Englezos et al., 2018), as well as in study with Malbec wines from different harvests (Sánchez-Palomo et al., 2017).

The class of alcohols, which the majority of the compounds are derived from the alcoholic fermentation by yeasts, is responsible for about 50% of the aromatic constituents of wines (excluding ethanol) (Jackson, 2020). The RC wine was highlighted in this class of compounds with a total area percentage of 65.96%, which 64.80% was represented by the phenylethyl alcohol compound. The second major wine in the alcohol class was the CS/SY blend, with 47.15% of total area percentage, which 44.23% were represented by the phenylethyl alcohol compound. This compound is considered the most important phenolic superior alcohol and it is responsible by the rose flavor (Jackson, 2020; *The Good Scents Company*, 2020). In a study of CS and Syrah wines from Greece, phenylethyl alcohol and 3-methyl 1-butanol compounds were prominent from CS, while 1-hexanol compound was the majority in wines from CS and SY (Karabagias et al., 2020). In the current study, 1-hexanol was also the majority in SY, considered the main red grape grown in the São Francisco Valley (Oliveira et al., 2019), contributing with fruity notes.

Terpenes were one of the minor classes of compounds, but no less important. This is because these compounds have a very low olfactory threshold, allowing the perception in low concentrations (Condurso et al., 2016). The 11 terpenes identified in the wines suggest a contribution to floral, sweet, fruity, citrus and woody aromas. Among the analyzed wines, AB presented 8 terpenes identified, more than TN wines (6 terpenes), which has been considered in previous studies as rich in terpenic compounds when compared with more than 75 different varietals (Pinho et al., 2007; Petronilho et al., 2020). In the sensorial profile of Touriga Nacional wines from VSF, they were described by floral aromas on the first harvest of the year (July), and fruity, spicy and empireumatic aromas on the second harvest (Oliveira et al., 2018). Thus, we suggest that the 6 terpenes identified in the TN wines, such as linalool oxide, nerol oxide, humulene, α-muurolene, (E)-calamenene and α-calacorene, were the potential compounds responsible for these aromatic descriptors.

4.3 Discrimination and similarities of wines

Several controlled or unknown factors can influence the similarities and differences of wines from different grape varieties. The results presented in the dendrogram (Figure 2), it can be observed that the combination of cultivar, viticultural management and winemaking techniques could influence the volatile composition of wines. All the red wines were made in the same winery, with the exception of the RC. It is worth mentioning that some of the young wines presented similar volatile characteristics to wines aged in oak barrels, and not differing in the formation of clusters 1, 2 and 3 (Figure 2). This result can be explained by possible blends between wines from the winery.

A large study conducted by Valentin et al. (2020), with 83 red wines from four South American countries, indicated that the chemical and volatile characteristics of two Brazilian red wines from Merlot were allocated to the same cluster of 18 wines of Carmenere from Chile, for unknown reasons. However, the wines in this study presented similar geographical location, which may have been influenced the similarity between wines of different varieties, blends, vintages and age. The RC wine was an exception, because it presented greater dissimilarity as compared to the the others. This differentiation can be attributed to the distinction of the vine management, as well as with possible specific enological protocols (Jackson, 2020).

One of the most common enological practices in the winemaking process is the blend of wines. This can be carried out by blending musts from different grape varieties, or even by blending monovarietal wines prepared differently in the cellar to obtain commercial wines (Alañón et al., 2015). The monovarietal CS and SY wines studied and the wine from the blending of their musts (CS/SY) were differentiated by clusters, and this can be attributed to enological practice.

The graphical representation by PCA (Figure 3) confirmed the results of the cluster hierarchical analysis. The wines located in the first two PCs were discriminated mainly by the main volatile markers, according to different vintages and cultivars. Chemometric studies carried out by Valentin et al. (2020) indicated that the wine discrimination, considering their volatile composition, may present low variance percentage. In the present study, PC1 x PC2 explained 43.55% of total variability, however they are important markers describing the typicality of the wines.

Some esters identified in the wine profiles presented positive and significant correlations ($p<0.05$) between them, and characterized wines from different clusters. The ethyl octanoate and ethyl hexanoate, ethyl butanoate and ethyl decanoate compounds; and the ethyl decanoate and ethyl butanoate volatile compounds characterized wines from cluster 1. The butanedioic acid and ethyl 3-methylbutyl ester compounds correlated with ethyl 2-methylbutanoate, characterized wines from cluster 2.

Other positive and significant correlations were presented by compounds of different classes, which characterized the wines of cluster 2, including the ethyl 2-methylbutanoate and 2,3-butanediol; ethyl 2,4-hexadienoate and undecanoic acid; 2-ethyl-1-butanol, methyl ether with 2,3-butanediol and ethyl 2-methylbutanoate. The positive correlation ($p<0.05$) between β-phenethyl acetate and phenylethyl alcohol, and 4-ethyl guaiacol, phenylethyl alcohol and β-phenethyl acetate, characterized the wines belonging to the cluster 4.

The only negative and significant correlation ($p<0.05$) was obtained between ethyl glutarate and diethyl succinate compounds, which characterized the wines of the clusters 2 and 3, respectively. This suggests that higher amounts of ethyl glutarate in wines from cluster 2, lower content of diethyl succinate in wines from cluster 3, and vice-versa. It is common that positive correlations are found between some compounds in wines and their precursors, as showed in previous study, between ethyl octanoate and octanoic acid compounds; and between ethyl hexanoate and hexanoic acid (Caliari et al.,2014).

4.4 Establishment of Potential Origin Markers

The wine composition is associated to several factors, such as their geographical origin (climate and soil), the grapevine management, as well as the winemaking process in enology. However, the description of its typicality, as well as its traceability is a great challenge from the legal and economic points of view to guarantee authenticity (Alañón et al., 2015). In this scenario, the description of the volatile composition of commercial products can provide the “fingerprint” of the wines and assist in their classification and traceability according to their terroir, geographical origin, variety and age/stability, with possible aging in barrels.

The volatile profile of the nine commercial wines analyzed in this study presented three particularities: i) compounds identified exclusively in only one kind of wine; ii) compounds identified in different area abundances in all wines; and iii) new volatile compounds, which were identified and reported for the first time in red wines from São Francisco Valley. Thus, the results obtained in this study allow us to identify and suggest potential volatile compound markers of the studied wines according to the different varieties, as well as according to the elaboration protocols.

The volatile compounds exclusively identified in the RC wine were (Z)-9-tetradecenoic and hexanoic acids, 2-ethyl-1-hexanol alcohol, 6-phenyl-dodecane aromatic compound, ethyl 9-hexadecenoate, methyl 11-octadecenoate esters, 4-ethyl guaiacol and 4-ethyl phenol as phenols. These two volatile phenol compounds can be markers of wine contamination by the *Brettanomyces*/*Dekkera* yeasts, with the increase of volatile acidity (Jackson, 2020). The distinction of this wine may not only have been due to the variety, but also to winemaking protocols. A previous study with Ruby Cabernet wines in Brazil showed the presence of vegetable, salt and oak aromatic descriptors (Miele & Rizzon, 2011). However, the volatile compounds identified in the RC wines of the present study suggest some descriptors, such as fatty, waxy, citrus, spicy, woody, sweet vanilla, smoky and phenols (Table 3).

It is interesting to highlight that the unique presence of (E)-9-hexadecenoic acid and ethyl benzoate compounds in AB wine, as well as 1-Pentanol and 2,4-dihydroxy-2,5-dimethyl-3(2H)-furanone compounds in RS wine. The furanone compound originates from aging in oak barrels (Jackson, 2020). Both wines were produced in the same winery and aged in French oak barrels for 9 and 6 months, respectively.

The compounds with the highest area representation that characterized all nine wine samples were 3-methylbutyl octanoate, butanedioic acid, ethyl 3-methylbutyl ester, diethyl succinate, ethyl 9-decenoate, ethyl decanoate, ethyl dodecanoate, ethyl hexadecanoate, ethyl hexanoate, ethyl nonanoate, ethyl octanoate, ethyl tetradecanoate, isoamyl hexanoate, and β-phenethyl acetate. Regardless of the vintage, cultivar, viticultural practices or winemaking, this set of compounds are possible markers of wines from the São Francisco Valley, belonging to the group of esters whose *terroir* is unique in the world, producing the tropical wines in Brazil (Pereira, 2020).

Some alcohols were also identified in all nine wines, such as 1-decanol, 1-hexanol, 3-ethyl-4-methyl-1-pentanol, 3-methyl 1-butanol, hexadecanol, and phenylethyl alcohol. In addition, other compounds of the acid, aromatic, and C13-norisoprenoid classes were identified. Decanoic acid and n-hexadecanoic acid were prominent in the acid class, while the 4-phenyl-dodecane, 5-phenyl-dodecane, 5-phenyl-undecane and 6-phenyl-undecane compounds from the aromatics class were common in all wines. These compounds need to be highlighted because they are new, being cited and reported for the first time in red wines. The two compounds identified in the C13-norisoprenoid class were present in all nine wines studied, which 1,2-dihydro-1,5,8-trimethyl-naphthalene was also identified for the first time in red wines.

Another 17 compounds were identified for the first time in red wines from VSF (totaling 22 compounds, with the compounds: (Z)-9-tetradecenoic acid, 2-heptadecanol, 10-octadecenal, 3-phenyl-undecane, 4-phenyl-decane, 4-phenyl-tridecane, 2-phenyl-undecane, 5-phenyl-decane, 6-phenyl-dodecane, 2-hexadecan-2-one, 2-ethylhexyl octanoate, geranyl iso-valerate, isomenthol acetate, 2,6,11-trimethyldodecane, 3-butyl-1,2,4-cyclopentanetrione, 2-ethyl-1-butanol methyl ether, and germacrene B. These compounds can contribute with olfactory descriptors as licorice, sweet, fruity, oily, herbal, woody, earth, and spicy notes (Table 2). From these, 45% belong to the aromatic class whose presence has already been identified in honey and fruit (El-hefny et al., 2018; Grygorieva et al., 2017; Tang et al., 2017).

5. Conclusion

The identification of volatile compounds enabled determining the volatile profile of nine commercial tropical red wines from the São Francisco Valley, all of them with identity and quality of required parameters recommended by Brazilian legislation. These wines will be indicated by the wineries to apply for the Geographical Indication of this region. In addition, exploring the data associated with multivariate statistical analysis allowed us to identify similarities and differences between the red wines, being influenced by characteristics such as vintage, variety and winery (enological practices). Some volatile compounds previously identified and described by the literature, and some exclusive compounds for the first time identified in these wines, were considered as potential markers. These compounds can be useful to describe the quality and typicality of the products, and also may contribute to the traceability and authenticity of wines from this region.

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Conflicts of interest

The authors declare no conflict of interest.

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Table 1. Description of the tropical red wine samples from the São Francisco Valley.

Wine (Code)	**Cultivars**	**Winery**	**Vintage**	**Lot**	**MT (months)**
AB	Alicante Bouschet	9° 24’ 'S; 40° 29’W	2014	n.d.	9
CS	Cabernet Sauvignon	9° 24’ 'S; 40° 29’W	2015	L1806A15	0
CS/SY	Cabernet Sauvignon/Syrah	9° 24’ 'S; 40° 29’W	2017	L1832D16	0
PR	Cabernet Sauvignon/Syrah/ Alicante Bouschet/ Touriga Nacional/Aragonês	9 24’ 'S; 40° 29’W	2013	L17112A08	12
RC	Ruby Cabernet	8°47’S;39° 49’W	2016	L20/072016	0
RS	Cabernet Sauvignon/Syrah/ Alicante Bouschet	9° 24’ 'S; 40° 29’W	2014	L1833D11	6
SY	Syrah	9° 24’ 'S; 40° 29’W	2015	L1819D16	0
TN	Touriga Nacional	9° 24’ 'S; 40° 29’W	2014	L1837E03	9
TP	Tempranillo	9° 24’ 'S; 40° 29’W	2015	L1820B26	0

MT: maturation time in French oak barrels; n.d.: not declared.

Table 2. Classic enological parameters of the commercial red wines studied from the São Francisco Valley.

Wine (Code)	Density	pH	Alcohol degree (% v/v at 20ºC)	Total acidity (meq L^{-1})	Volatile acidity (meq L^{-1})	Total SO_2 (mg L^{-1})
AB	0.9962 ^{e} ± 0.00	4.08^{c} ± 0.02	13.16 ^{b} ± 0.00	74.23 ^{d} ± 0.00	4.59 $^{b.c}$ ± 0.51	34.88 ^{b} ± 0.00
CS	0.9959 ^{f} ± 0.00	4.16 $^{a.b}$ ± 0.02	12.04 ^{e} ± 0.00	72.00 $^{d.e}$ ± 0.04	2.04 ^{e} ± 0.00	8.96 ^{e} ± 0.00
CS/SY	0.9968 ^{d} ± 0.00	4.16 $^{a.b}$ ± 0.02	12.12 ^{e} ± 0.00	66.74 $^{e.f}$ ± 0.00	3.26 ^{d} ± 0.35	17.78 ^{d} ± 0.00
PR	0.9995 ^{a} ± 0.00	4.08 ^{c} ± 0.00	13.16 ^{b} ± 0.00	86.61 ^{a} ± 0.07	4.65 $^{b.c}$ ± 0.41	15.36^{c} ± 0.00
RC	0.9991 ^{c} ± 0.00	4.13^{b} ± 0.00	13.51 ^{a} ± 0.00	84.91 $^{a.b}$ ± 0.02	4.01 $^{c.d}$ ± 0.41	nd
RS	0.9991 ^{b} ± 0.00	4.08 ^{c} ± 0.00	12.21 ^{d} ± 0.00	80.83 $^{b.c}$ ± 0.04	5.16 ^{b} ± 0.12	34.24 ^{b} ± 0.00
SY	0.9954 ^{h} ± 0.00	4.17^{a} ± 0.01	10.61 ^{f} ± 0.00	74.38$^{c.d}$± 0.00	4.18 $^{b.c.d}$ ±0.18	15.04$^{c.d}$ ± 0.03
TN	0.9991 $^{b.c}$ ± 0.00	4.08 ^{c} ± 0.00	13.16 ^{b} ± 0.00	81.85 $^{a.b}$ ± 0.02	6.89 ^{a} ± 0.12	39.04 ^{a} ± 0.01
TP	0.9958 ^{g} ± 0.00	4.17^{a} ± 0.01	12.81 ^{c} ± 0.00	66.36 ^{f} ± 0.00	6.52 ^{a} ± 0.54	16.64 ^{c} ± 0.01
Limits[1]			**8.6 to 14**	**40 to 130**	**Max 20**	**Max 300**

[1]Brasil, 2018; nd = not detected; Max: maximum; CS: Cabernet Sauvignon; CS/SY: Cabernet Sauvignon / Syrah; AB: Alicante Bouschet; SY: Syrah; TP: Tempranillo; PR: Cabernet Sauvignon / Syrah / Alicante Bouschet / Touriga Nacional / Aragonês; RS: Cabernet Sauvignon / Syrah / Alicante Bouschet; TN: Touriga Nacional; RC: Ruby Cabernet; SO_2: total sulfur dioxide. Means followed by the same letter do not differ by the Tukey test ($p < 0.05$).

Table 3. Volatile compounds identified in the red wines of the São Francisco Valley by HS-SPME-GC-MS.

Code	Volatile Compound	Chemical Family	LRI (lit)	LRI (cal)	(%) of Total Peak Area									Odor description [1]
					CS	CS/SY	RC	SY	TP	PR	RS	AB	TN	
99	(E)-9-Hexadecenoic acid	acid	1942	1939	nd	nd	nd	nd	nd	nd	nd	0.12±0.09	nd	waxy, creamy, fatty, soapy
91	(Z)-9-Tetradecenoic acid	acid	1783	1774	nd	nd	0.13±0.05	nd	nd	nd	nd	nd	nd	
54	Decanoic acid	acid	1373	1378	1.64±0.59	2.79±0.32	0.27±0.06	1.22±0.38	1.62±0.27	1.54±0.61	1.41±0.53	1.43±0.63	1.90±1.05	rancid, sour, fatty, citrus
75	Dodecanoic acid	acid	1568	1568	0.11±0.07	0.45±0.09	0.05±0.00	0.22±0.16	0.25±0.08	0.12±0.07	0.11±0.07	nd	0.22±0.11	coconut, Fatty, Waxy
13	Hexanoic acid	acid	990	998	nd	nd	0.06±0.01	nd	nd	nd	nd	nd	nd	slightly, waxy, fatty
100	n-Hexadecanoic acid	acid	1968	1960	0.05±0.01	0.28±0.20	0.05±0.03	0.15±0.09	0.04±0.01	0.14±0.17	0.11±0.08	0.12±0.03	0.10±0.13	waxy, fatty
97	Pentadecanoic acid	acid	1867	1866	0.02±0.01	nd	0.01±0.01	0.02±0.01	tr	nd	nd	0.06±0.04	nd	
90	Tetradecanoic acid	acid	1768	1762	0.05±0.03	nd	0.05±0.02	0.08±0.04	0.02±0.01	nd	0.08±0.03	0.20±0.16	0.12±0.11	waxy, fatty, soapy, coconut
65	Undecanoic acid	acid	1475	1478	0.42±0.25	nd	nd	nd	0.61±0.10	1.09±0.59	nd	nd	nd	waxy, creamy, cheese, fatty, coconut
	Total Acids				**2.29**	**3.52**	**0.62**	**1.68**	**2.54**	**2.89**	**1.71**	**1.94**	**2.33**	
40	1-Decanol	alcohol	1273	1272	0.13±0.04	0.10±0.05	0.04±0.01	0.09±0.00	0.12±0.06	0.13±0.02	0.07±0.02	0.13±0.05	0.14±0.05	fatty, waxy, floral, orange, sweet, clean, watery
64	1-Dodecanol	alcohol	1473	1474	0.21±0.15	0.45± 0.17	0.13±0.03	nd	0.24±0.15	0.38±0.39	0.19±0.08	0.24±0.17	0.37±0.27	earthy, soapy, waxy, fatty, honey, coconut
8	1-Hexanol	alcohol	868	865	0.83±0.26	0.70±0.02	0.27±0.09	1.99±3.00	0.73±0.21	0.46±0.25	0.44±0.16	0.42±0.16	0.71±0.25	ethereal, fusel, oil, fruity, alcoholic, sweet, green
28	1-Nonanol	alcohol	1173	1172	0.50±0.12	0.37±0.03	nd	0.22±0.06	0.44±0.10	0.54±0.12	0.34±0.18	0.26±0.12	0.37±0.15	fresh, clean, fatty, floral, rose, orange, dusty wet, oily
2	1-Pentanol	alcohol	765	<800	nd	nd	nd	nd	nd	nd	0.19±0.15	nd	nd	balsamic, sweet, fusel like
4	2,3-Butanediol	alcohol	788	<800	2.86±0.20	nd	nd	nd	nd	nd	2.40±0.27	0.04±0.01	nd	fruity, creamy, buttery
18	2-Ethyl-1-hexanol	alcohol	1030	1034	nd	nd	0.17±0.03	nd	nd	nd	nd	nd	nd	citrus
93	2-Heptadecanol	alcohol	1802	1799	0.01±0.01	nd	nd	0.01±0.00	0.01±0.00	0.06±0.06	nd	0.02±0.01	nd	
85	2-Hexadecanol	alcohol	1702	1698	nd	nd	tr	0.01±0.00	0.01±0.00	0.01±0.01	0.01±0.00	0.02±0.01	nd	
49	2-Undecanol	alcohol	1308	1304	0.08±0.04	nd	0.04±0.01	0.23±0.32	0.06±0.02	0.05±0.01	nd	0.04±0.01	nd	waxy, fatty, clean, oily, fresh, fishy, nut
17	3-Ethyl-4-methyl-1-pentanol	alcohol	1023	1023	0.06±0.03	0.04±0.01	0.07±0.01	0.08±0.11	0.02±0.01	0.04±0.04	0.01±0.01	0.04±0.01	0.02±0.01	
1	3-Methyl 1-butanol	alcohol	736	<800	1.74±1.49	1.00±0.27	0.27±0.04	1.79±0.75	2.24±0.55	2.17±0.57	2.60±2.01	0.31 ± 0.50	2.66±2.36	fusel, oil, alcoholic, whiskey, fruity, banana
11	3-Methyl 2-hexanol	alcohol	906	898	nd	0.06±0.01	0.15±0.06	0.04±0.02	nd	nd	nd	nd	nd	

98	Hexadecanol	alcohol	1884	1880	0.02±0.01	0.05±0.01	0.01±0.01	0.04±0.01	0.03±0.00	0.03±0.01	0.02±0.00	0.06±0.04	0.03±0.02	waxy, clean, greasy, floral,
21	Octanol	alcohol	1075	1075	0.24±0.15	0.16±0.03	nd	0.20±0.24	0.10±0.06	0.46±0.65	0.40±0.41	0.13±0.03	0.18±0.11	waxy, green, orange, aldehydic, rose, mushroom
23	Phenylethyl alcohol	alcohol	1116	1110	4.04±1.44	44.23±3.41	64.80±5.96	29.71±3.77	21.26±7.26	8.60±10.96	21.34±3.60	14.76±7.49	20.37±10.23	floral, rose, dried, rose flower, rose water
	Total alcohols				**10.72**	**47.15**	**65.96**	**34.41**	**25.27**	**12.94**	**28.00**	**16.47**	**24.84**	
63	(E)-2-Dodecenal	aldehyde	1468	1465	0.12±0.09	nd	nd	0.19±0.18	0.08±0.00	nd	nd	nd	nd	citrus, metallic, mandarin, orange, waxy aldehydic
96	10-Octadecenal	aldehyde	1863	1860	0.02±0.01	nd	nd	0.04±0.02	0.01±0.00	0.03±0.02	nd	nd	0.05±0.06	
31	Decanal	aldehyde	1205	1204	0.10±0.11	0.08±0.03	nd	0.14±0.12	nd	nd	0.85±1.39	0.03±0.01	0.04±0.01	sweet, waxy, orange peel, floral
58	Dodecanal	aldehyde	1409	1409	0.12±0.19	0.19±0.10	0.05±0.04	0.05±0.06	0.12±0.09	0.14±0.18	0.05±0.06	0.04±0.03	0.27±0.32	soapy, waxy, aldehydic, citrus, green, floral
38	Geranial	aldehyde	1268	1267	0.10±0.04	nd	0.07±0.04	nd	0.18±0.09	nd	nd	nd	nd	citrus, lemon
	Total aldehydes				**0.46**	**0.27**	**0.13**	**0.42**	**0.40**	**0.17**	**0.90**	**0.07**	**0.36**	
86	2-Phenyl-undecane	aromatic	1708	1703	nd	0.02±0.00	0.01±0.00	nd	0.01±0.00	tr	0.01±0.00	0.01±0.01	0.02±0.02	
82	3-Phenyl-undecane	aromatic	1667	1668	nd	0.17±0.03	0.06±0.02	nd	0.15±0.14	0.11±0.07	nd	0.07±0.02	0.34±0.24	
74	4-Phenyl-decane	aromatic	1546	1550	nd	0.06±0.01	0.01±0.00	nd	nd	0.03±0.02	0.02±0.01	0.03±0.00	0.11±0.04	
89	4-Phenyl-dodecane	aromatic	1742	1749	0.02±0.01	0.01±0.00	0.01±0.00	0.02±0.01	0.03±0.01	0.01±0.01	0.02±0.01	0.03±0.02	0.03±0.02	
95	4-Phenyl-tridecane	aromatic	1840	1839	0.02±0.01	nd	nd	nd	0.02±0.00	nd	nd	nd	0.07±0.09	
71	5-Phenyl-decane	aromatic	1535	1542	nd	0.08±0.00	0.02±0.02	0.04±0.06	0.09±0.09	0.04±0.03	0.01±0.01	0.04±0.03	0.14±0.12	
88	5-Phenyl-dodecane	aromatic	1730	1737	0.04±0.02	0.05±0.01	0.01±0.00	0.02±0.01	0.05±0.01	0.08±0.10	0.04±0.03	0.01±0.01	0.04±0.04	
80	5-Phenyl-undecane	aromatic	1632	1638	0.09±0.06	0.15±0.02	0.04±0.02	0.09±0.11	0.11±0.09	0.09±0.06	0.06±0.02	0.09±0.05	0.18±0.12	
87	6-Phenyl-dodecane	aromatic	1726	1731	nd	nd	0.03±0.01	nd	nd	nd	nd	nd	nd	
79	6-Phenyl-undecane	aromatic	1628	1634	0.04±0.04	0.06±0.02	0.01±0.01	0.02±0.00	0.05±0.03	0.05±0.04	0.02±0.01	0.03±0.03	0.08±0.08	
	Total aromatic				**0.21**	**0.61**	**0.22**	**0.19**	**0.51**	**0.43**	**0.17**	**0.31**	**1.02**	
52	1,2-Dihydro-1,5,8-trimethyl-naphthalene	C13-norisoprenoid	1354	1351	0.15±0.03	nd	0.07±0.02	0.17±0.07	0.19±0.05	0.20± 0.06	0.12±0.07	0.17±0.08	0.03±0.01	licorice
83	4-Isopropyl-1,6-dimethyl-naphthalene	C13-norisoprenoid	1674	1679	0.11±0.04	0.23±0.15	0.06±0.01	0.08±0.04	0.13±0.07	0.11±0.01	0.07±0.03	0.04±0.01	0.13±0.04	
	Total C13-norisoprenoids				**0.25**	**0.23**	**0.13**	**0.25**	**0.31**	**0.32**	**0.19**	**0.22**	**0.16**	
84	2-Ethylhexyl octanoate	ester	1688	1693	0.02±0.01	nd	nd	0.07±0.03	0.03±0.00	0.05±0.04	0.03±0.02	0.07±0.03	nd	
10	2-Methylbutyl acetate	ester	880	878	0.16±0.15	nd	nd	0.43±0.08	0.07±0.03	0.11±0.03	0.07±0.01	0.18±0.07	0.08±0.08	fruit, sweet banana, juicy fruit, fruity

61	2-Methylbutyl octanoate	ester	1449	1450	0.03±0.01	nd	0.02±0.02	0.04±0.03	0.10±0.07	0.01±0.01	0.05±0.04	nd	0.02±0.02	
60	3-Methylbutyl octanoate	ester	1446	1447	0.12±0.06	0.19±0.03	0.13±0.06	0.17±0.10	0.24±0.05	0.12±0.05	0.11±0.08	0.17±0.10	0.17±0.07	sweet, oily, fruity, green, soapy, pineapple coconut
44	Bornyl acetate	ester	1285	1286	nd	nd	nd	nd	nd	0.02±0.00	nd	nd	0.01±0.00	woody, pine, herbal, cedar, spice
59	Butanedioic acid, ethyl 3-methylbutyl ester	ester	1432	1431	0.74±0.20	0.83±0.22	0.69±0.03	0.63±0.46	0.55±0.13	0.83±0.25	2.74±3.77	0.54±0.17	0.73±0.25	
29	Diethyl succinate	ester	1182	1182	20.88±8.45	15.44±0.60	9.43±1.11	9.30±2.28	13.43±4.80	22.02±7.73	17.83±6.83	14.68±5.15	19.92±7.45	mild, fruity, cooked, apple
22	Ethyl 2,4-hexadienoate	ester	1097	1103	nd	nd	nd	nd	nd	4.42±3.06	nd	nd	nd	warm, fruity, anise, licorice, ether
6	Ethyl 2-methylbutanoate	ester	849	842	2.26±0.75	nd	0.27±0.39	nd	nd	nd	2.17±1.06	0.02±0.01	0.03±0.00	fruity, estry and berry
35	Ethyl 2-phenylacetate	ester	1246	1244	0.36±0.45	1.97±0.12	0.18±0.06	1.49±1.11	1.09±0.86	0.31±0.30	nd	0.15±0.06	0.36±0.22	sweet, floral, honey, rose, balsamic, cocoa
56	Ethyl 9-decenoate	ester	1387	1389	0.40±0.01	0.78±0.17	0.15±0.03	0.25±0.09	0.46±0.13	1.05±0.10	0.36±0.12	0.43±0.22	0.56±0.03	fruity, fatty
101	Ethyl 9-hexadecenoate	ester	1977	1974	nd	nd	0.19±0.11	nd	nd	nd	nd	nd	nd	
27	Ethyl benzoate	ester	1171	1168	nd	nd	nd	nd	nd	nd	nd	0.29±0.25	nd	fruity, dry, musty, sweet, wintergreen
5	Ethyl butanoate	ester	802	801	nd	nd	nd	1.14±0.73	nd	nd	nd	1.89±1.05	0.95±1.34	fruity, juicy, fruit, pineapple, cognac
57	Ethyl decanoate	ester	1396	1398	14.85±2.81	7.80±0.61	6.51±3.12	16.02±5.87	16.62±4.80	16.80±5.37	11.71±6.97	18.56±8.20	16.13±6.47	sweet, waxy, fruity, apple, grape, oily brandy
77	Ethyl dodecanoate	ester	1595	1596	0.46±0.14	0.29±0.04	0.40±0.19	0.53±0.14	0.53±0.19	0.56±0.16	0.42±0.22	0.58±0.29	0.55±0.21	mango, sweet, waxy, floral, soapy, clean
43	Ethyl glutarate	ester	1283	1280	1.20±0.12	nd	0.04±0.05	0.97±0.29	1.34±0.35	0.02±0.01	0.01±0.01	nd	0.01±0.01	
102	Ethyl hexadecanoate	ester	1993	1994	0.04±0.02	0.10±0.01	0.88±0.76	0.10±0.02	0.13±0.00	0.13±0.05	0.11±0.02	0.16±0.10	0.13±0.06	mild, waxy, fruity, creamy, milky, balsam
15	Ethyl hexanoate	ester	1000	1003	3.62±0.91	1.40±0.17	0.81±0.38	1.61±0.65	1.98±0.24	2.78±0.76	2.68±0.55	2.76±0.96	2.22±0.44	sweet, fruity, pineapple, waxy, green banana
7	Ethyl isovalerate	ester	854	847	0.10±0.03	nd	0.63±0.75	0.01±0.00	nd	nd	0.61±0.48	0.07±0.04	0.08±0.05	sweet, diffusive, estry, fruity, sharp, pineapple, apple, green
47	Ethyl nonanoate	ester	1296	1297	0.17±0.03	0.14±0.03	0.07±0.04	0.21±0.05	0.18±0.07	0.21±0.08	0.08±0.02	0.28±0.08	0.15±0.09	fruity, rose, waxy, rum, wine natural tropical
30	Ethyl octanoate	ester	1196	1198	36.09±6.14	14.95±0.24	7.72±4.17	26.61±7.47	30.12±9.10	29.07±11.13	25.98±9.54	36.65±7.63	25.27±10.31	fruity, wine, waxy, sweet, apricot, banana brandy, pear
39	Ethyl salicylate	ester	1270	1268	0.03±0.01	nd	tr	0.11±0.06	nd	0.03±0.01	nd	0.11±0.03	nd	
92	Ethyl tetradecanoate	ester	1794	1794	0.03±0.01	0.01±0.00	0.57±0.24	0.02±0.00	0.02±0.00	0.02±0.01	0.04±0.03	0.04±0.01	0.03±0.02	sweet, waxy, violet, orris
78	Geranyl iso-valerate	ester	1606	1599	0.06±0.04	0.09±0.00	nd	0.04±0.01	0.07±0.02	0.05±0.03	0.04±0.01	0.05±0.02	0.09±0.04	sweet, fruity, green, oily, herbal, fruity
16	Hexyl acetate	ester	1011	1018	0.02±0.00	0.02±0.00	nd	0.01±0.01	0.04±0.03	0.04±0.04	0.02±0.01	nd	nd	fruity, green, apple, banana, sweet
9	Isoamyl acetate	ester	876	875	0.85±0.17	0.68±0.14	0.46±0.06	nd	0.51±0.06	0.70±0.09	0.62±0.09	0.70±0.13	0.58±0.16	sweet, fruity, banana, solvent
81	Isoamyl decanoate	ester	1646	1650	0.10±0.03	0.50±0.16	0.24±0.17	0.16±0.06	0.31±0.17	0.44±0.37	nd	0.29±0.11	0.23±0.19	waxy, banana, fruity, sweet, cognac, green

36	Isoamyl hexanoate	ester	1252	1250	0.03±0.01	0.76±0.75	0.02±0.02	0.05±0.01	0.05±0.03	0.08±0.07	0.03±0.03	0.05±0.03	0.04±0.03	fruity, banana, apple, pineapple, green
45	Isobornyl acetate	ester	1286	1289	0.04±0.00	0.09±0.02	0.02±0.01	0.07±0.02	0.08±0.03	0.06±0.02	nd	0.07±0.02	0.07±0.03	balsam, camphor, herbal, woody, sweet
51	Isobutyl octanoate	ester	1348	1345	0.03±0.02	nd	0.01±0.00	0.03±0.02	0.05±0.02	nd	0.03±0.02	0.05±0.01	nd	fruity, green, oily, floral
48	Isomenthol acetate	ester	1305	1302	0.09±0.07	nd	nd	0.10±0.02	0.19±0.22	0.13±0.08	nd	0.06±0.02	nd	
103	Methyl 11-octadecenoate	ester	2115	2123	nd	nd	0.05±0.03	nd	nd	nd	nd	nd	nd	
50	Methyl decanoate	ester	1325	1326	0.03±0.01	nd	nd	0.03±0.01	0.05±0.01	0.06±0.03	0.04±0.02	0.03±0.02	0.06±0.02	oily, wine, fruity, floral
46	Propyl octanoate	ester	1290	1293	0.04±0.02	nd	0.02±0.01	0.04±0.01	0.06±0.01	nd	nd	nd	0.08±0.05	coconut, caco, gin
37	β-Phenethyl acetate	ester	1258	1256	0.75±0.18	1.01±0.08	0.90±0.01	0.66±0.26	0.73±0.22	0.80±0.19	0.56±0.16	0.81±0.39	0.78±0.25	floral, rose, sweet, honey, fruity tropical
	Total esters				**83.61**	**47.03**	**30.42**	**60.91**	**69.02**	**80.90**	**66.34**	**79.72**	**69.33**	
3	2-Ethyl-1-butanol, methyl ether	ether	778	<800	2.06±1.50	nd	nd	0.62±0.64	nd	nd	1.59±2.64	0.08 ± 0.03	nd	
	Total ether				**2.06**	**0.00**	**0.00**	**0.62**	**0.00**	**0.00**	**1.59**	**0.08**	**0.00**	
32	2,3-Dihydrobenzofuran	furan	1224	1220	nd	0.21±0.12	0.05±0.02	0.10±0.08	0.05±0.03	0.13±0.12	0.16±0.12	0.11±0.13	0.06±0.06	
12	2,4-Dihydroxy-2,5-dimethyl-3(2H)-furanone	furan	989	995	nd	nd	nd	nd	nd	nd	0.02±0.01	nd	nd	fruity, green, earthy, beany, vegetable metallic
14	2-Pentyl Furan	furan	993	999	nd	0.04±0.02	nd	0.02±0.01	nd	nd	nd	nd	nd	sweet, citrus, herbal, green, celery, spicy minty, woody
34	5-Hydroxymethylfurfural	furan	1233	1230	nd	nd	nd	nd	0.38±0.49	0.03±0.01	nd	nd	0.11±0.08	fatty, buttery, musty, waxy, caramellic
	Total furans				**0.00**	**0.25**	**0.05**	**0.11**	**0.43**	**0.16**	**0.18**	**0.11**	**0.16**	
72	2,6,10-Trimethyltetradecane	hydrocarbon	1541	1545	nd	0.04±0.00	nd	0.02±0.01	0.02±0.00	nd	nd	0.01±0.01	0.03±0.02	
41	2,6,11-Trimethyldodecane	hydrocarbon	1275	1275	nd	nd	nd	nd	nd	nd	nd	0.03±0.02	0.07±0.05	
66	3-Butyl-1,2,4-cyclopentanetrione	hydrocarbon	1486	1485	0.19±0.05	0.26±0.06	0.19±0.02	0.12±0.02	0.14±0.01	0.67±0.11	0.11±0.01	nd	nd	
	Total hydrocarbon				**0.19**	**0.30**	**0.19**	**0.14**	**0.17**	**0.67**	**0.11**	**0.05**	**0.09**	
94	2-Hexadecan-2-one	ketone	1806	1808	0.02±0.01	nd	nd	0.01±0.01	0.04±0.01	nd	nd	nd	0.11±0.06	fruity
	Total ketones				**0.02**	**0.00**	**0.00**	**0.01**	**0.04**	**0.00**	**0.00**	**0.00**	**0.11**	
69	2,4-Di-tert-butylphenol	phenol	1519	1514	nd	nd	nd	0.07±0.01	0.07±0.01	0.04±0.03	0.07±0.01	0.06±0.02	0.11±0.03	phenolic
42	4-Ethyl guaiacol	phenol	1282	1279	nd	nd	1.10±0.24	nd	nd	nd	nd	nd	nd	spicy and clove-like with medicinal, woody and sweet vanilla nuances

26	4-Ethylphenol	phenol	1169	1167	nd	nd	0.36±0.30	nd	nd	nd	nd	nd	nd	smoke, phenolic
53	Eugenol	phenol	1357	1357	nd	nd	0.01±0.00	nd	nd	0.07±0.01	nd	nd	nd	sweet, spicy, clove like, woody,
	Total phenols				**0.00**	**0.00**	**1.47**	**0.07**	**0.07**	**0.11**	**0.07**	**0.06**	**0.11**	
24	Hydroxydihydromaltol	pyran	1151	1147	nd	0.20±0.00	nd	0.05±0.04	0.57±0.45	0.13±0.07	0.29±0.14	0.08±0.01	0.26±0.16	creamy, sweet, fruity peach,
	Total pyran				**0.00**	**0.20**	**0.00**	**0.05**	**0.57**	**0.13**	**0.29**	**0.08**	**0.26**	
70	(E)-Calamenene	terpene	1529	1527	nd	nd	nd	0.03±0.01	0.04±0.00	0.13±0.12	0.03±0.00	0.03±0.01	0.05±0.01	clove-like, herbaceous
33	Citronellol	terpene	1228	1228	nd	0.09±0.06	0.01±0.00	nd	0.02±0.01	nd	0.03±0.02	0.03±0.01	nd	floral, rosy, sweet, citrus
55	Damascenone	terpene	1386	1385	0.02±0.01	nd	0.02±0.00	nd	0.01±0.01	nd	nd	nd	nd	woody, sweet, fruity, earthy with green floral nuances
76	Germacrene B	terpene	1591	1588	nd	nd	nd	0.02±0.00	nd	0.03±0.01	0.05±0.03	nd	nd	woody, earthy, spicy
62	Humulene	terpene	1453	1453	0.04±0.02	0.08± 0.01	nd	0.03±0.00	0.06±0.01	0.09±0.07	nd	0.04±0.01	0.09±0.05	woody
20	Linalool oxide	terpene	1074	1071	nd	0.24±0.02	nd	0.35±0.18	0.21±0.07	0.35±0.09	nd	0.49±0.30	0.42±0.15	woody, floral, cooling, terpy and slightly green
25	Nerol oxide	terpene	1153	1154	nd	nd	nd	nd	nd	0.33±0.55	nd	nd	0.12±0.09	green, vegetative and floral
73	α-Calacorene	terpene	1542	1548	0.07±0.01	nd	0.02±0.01	0.08±0.02	0.15±0.03	0.13±0.05	0.07±0.04	0.10±0.05	0.09±0.06	woody
68	α-Farnesene	terpene	1508	1513	nd	nd	0.01±0.00	0.04±0.01	0.04±0.01	0.11±0.06	nd	0.05±0.01	nd	citrus, herbal, lavender, bergamot
67	α-Muurolene	terpene	1499	1501	nd	nd	nd	0.57±0.31	0.16±0.09	0.12±0.09	0.12±0.07	0.17±0.05	0.32±0.30	
19	γ-Terpinene	terpene	1060	1063	0.05±0.02	0.03±0.02	0.71±0.15	nd	nd	nd	0.14±0.05	nd	0.13±0.02	oily, woody, terpene, lemon/lime tropical herbal
	Total terpenes				**0.18**	**0.44**	**0.77**	**1.12**	**0.69**	**1.28**	**0.45**	**0.91**	**1.23**	

[1] Aroma description obtained from an online database available at Thegoodscentscompany (2020) & Pherobase (2020); LRI lit.: linear retention index of literature; LRI cal.: linear retention index calculated; nd = not detected; tr = trace. CS: Cabernet Sauvignon; CS/SY: Cabernet Sauvignon / Syrah; AB: Alicante Bouschet; SY: Syrah; TP: Tempranillo; PR: Cabernet Sauvignon / Syrah / Alicante Bouschet / Touriga Nacional / Aragonês; RS: Cabernet Sauvignon / Syrah / Alicante Bouschet; TN: Touriga Nacional; RC: Ruby Cabernet.

Table 4. Results of Pearson's correlation analysis (r) between volatile compounds from São Francisco Valley red wines with a chromatographic area (≥1%).

Code*	**Volatile compounds**	**54**	**65**	**1**	**4**	**8**	**23**	**5**	**6**	**15**	**22**	**29**	**30**	**35**	**37**	**43**	**56**	**57**	**59**	**3**	**42**
54	Decanoic acid	**1**																			
65	Undecanoic acid	-0.1378	**1**																		
1	3-Methyl 1-Butanol	0.2106	0.2286	**1**																	
4	2,3-Butanediol	-0.2139	-0.1664	0.1485	**1**																
8	1-Hexanol	0.1718	-0.2411	0.3242	-0.2780	**1**															
23	Phenylethyl alcohol	-0.2994	-0.3790	-0.3718	-0.2727	0.0532	**1**														
5	Ethyl butanoate	0.1247	-0.4359	0.0044	-0.3522	0.3548	-0.1982	**1**													
6	Ethyl 2-methylbutanoate	-0.2896	-0.2199	0.1201	**0.9817**	-0.3021	-0.1016	-0.3923	**1**												
15	Ethyl hexanoate	-0.1298	-0.1000	0.1413	0.4155	-0.2605	-0.5490	0.5166	0.3665	**1**											
22	Ethyl 2,4-hexadienoate	-0.1873	**0.7019**	0.0580	-0.1874	-0.3167	-0.2731	-0.2450	-0.2073	-0.0135	**1**										
29	Diethyl succinate	-0.0021	-0.1909	0.1105	0.0046	-0.5903	0.2659	0.0381	0.1065	0.2170	0.1265	**1**									
30	Ethyl octanoate	0.0252	0.0005	0.2621	0.0349	0.2001	-0.5380	**0.7023**	-0.0349	**0.8180**	-0.1373	-0.1330	**1**								
35	Ethyl 2-phenylacetate	0.6564	-0.0199	0.0994	-0.4585	0.6456	0.1040	-0.0695	-0.4947	-0.6569	-0.2521	-0.5060	-0.2190	**1**							
37	β-Phenethyl acetate	-0.1962	-0.3464	-0.4692	-0.4565	-0.0461	**0.9575**	-0.0612	-0.2957	-0.4945	-0.2240	0.3526	-0.4622	0.1021	**1**						
43	Ethyl glutarate	-0.0696	0.3426	0.3032	-0.0772	0.6277	-0.1742	-0.0660	-0.1407	-0.2118	-0.2399	**-0.7991**	0.2426	0.4782	-0.2764	**1**					
56	Ethyl 9-decenoate	0.5961	0.3636	0.2237	-0.3492	-0.2678	-0.2980	-0.0896	-0.3864	-0.1146	0.6151	0.3864	-0.1751	0.1852	-0.1564	-0.4404	**1**				
57	Ethyl decanoate	-0.0660	-0.0662	0.2786	-0.2840	0.3367	-0.2203	**0.8071**	-0.2976	0.6206	-0.1316	0.0140	**0.8965**	-0.1512	-0.1259	0.2124	-0.1675	**1**			
59	Butanedioic acid, ethyl 3-methylbutyl ester	-0.1453	-0.3872	0.1576	0.5605	-0.2006	0.4060	-0.3092	**0.6887**	0.1488	-0.1770	0.5087	-0.1614	-0.3131	0.2619	-0.4105	-0.1309	-0.1611	**1**		
3	2-Ethyl-1-butanol, methyl ether	-0.2999	-0.1932	0.0494	**0.8543**	0.0758	-0.3276	-0.1873	**0.7917**	0.2746	-0.2441	-0.4172	0.0646	-0.2660	-0.5336	0.2326	-0.5613	-0.2322	0.1984	**1**	
42	4-Ethyl guaiacol	-0.5713	-0.2224	-0.4471	-0.1874	-0.1610	**0.9357**	-0.2450	-0.0194	-0.4234	-0.1250	0.3106	-0.5113	-0.1839	**0.8988**	-0.2088	-0.3767	-0.2195	0.3487	-0.2441	**1**

* See Table 2 for wine codes. Values in bold are different from 0 with significant correlations at 5% probability of error ($p < 0.05$). CS: Cabernet Sauvignon; CS/SY: Cabernet Sauvignon / Syrah; AB: Alicante Bouschet; SY: Syrah; TP: Tempranillo; PR: Cabernet Sauvignon / Syrah / Alicante Bouschet / Touriga Nacional / Aragonês; RS: Cabernet Sauvignon / Syrah / Alicante Bouschet; TN: Touriga Nacional; RC: Ruby Cabernet.

Figure captions

Figure 1. Total area values of the chemical group (A) acids; (B) alcohols; (C) aldehydes; (D) aromatics; (E) C13-norisiprenoids; (F) esters; (G) ethers; (H) furans; (I) hydrocarbon; (J) ketones; (K) phenols; (L) pyrans; (M) terpenes, identified in red wines.

Footnote: a,b,c Different letters in the same bar chart indicate significant difference by the Conover-Iman test ($p < 0.05$). CS: Cabernet Sauvignon; CS / SY: Cabernet Sauvignon / Syrah; AB: Alicante Bouschet; SY: Syrah; TP: Tempranillo; PR: Cabernet Sauvignon / Syrah / Alicante Bouschet / Touriga Nacional / Aragonês; RS: Cabernet Sauvignon / Syrah / Alicante Bouschet; TN: Touriga Nacional; RC: Ruby Cabernet;

Figure 2. Dendrogram formed from the volatile compounds of nine wines obtained by the Ward method and Euclidean distance.

Footnote: CS: Cabernet Sauvignon; CS/SY: Cabernet Sauvignon / Syrah; AB: Alicante Bouschet; SY: Syrah; TP: Tempranillo; PR: Cabernet Sauvignon / Syrah / Alicante Bouschet / Touriga Nacional / Aragonês; RS: Cabernet Sauvignon / Syrah / Alicante Bouschet; TN: Touriga Nacional; RC: Ruby Cabernet;

Figure 3. PCA projection of volatile compound data of red wines obtained using the HS-SPME-GC–MS method.

Footnote: See Table 2 for wine codes. CS: Cabernet Sauvignon; CS/SY: Cabernet Sauvignon / Syrah; AB: Alicante Bouschet; SY: Syrah; TP: Tempranillo; PR: Cabernet Sauvignon / Syrah / Alicante Bouschet / Touriga Nacional / Aragonês; RS: Cabernet Sauvignon / Syrah / Alicante Bouschet; TN: Touriga Nacional; RC: Ruby Cabernet;

Figure 1

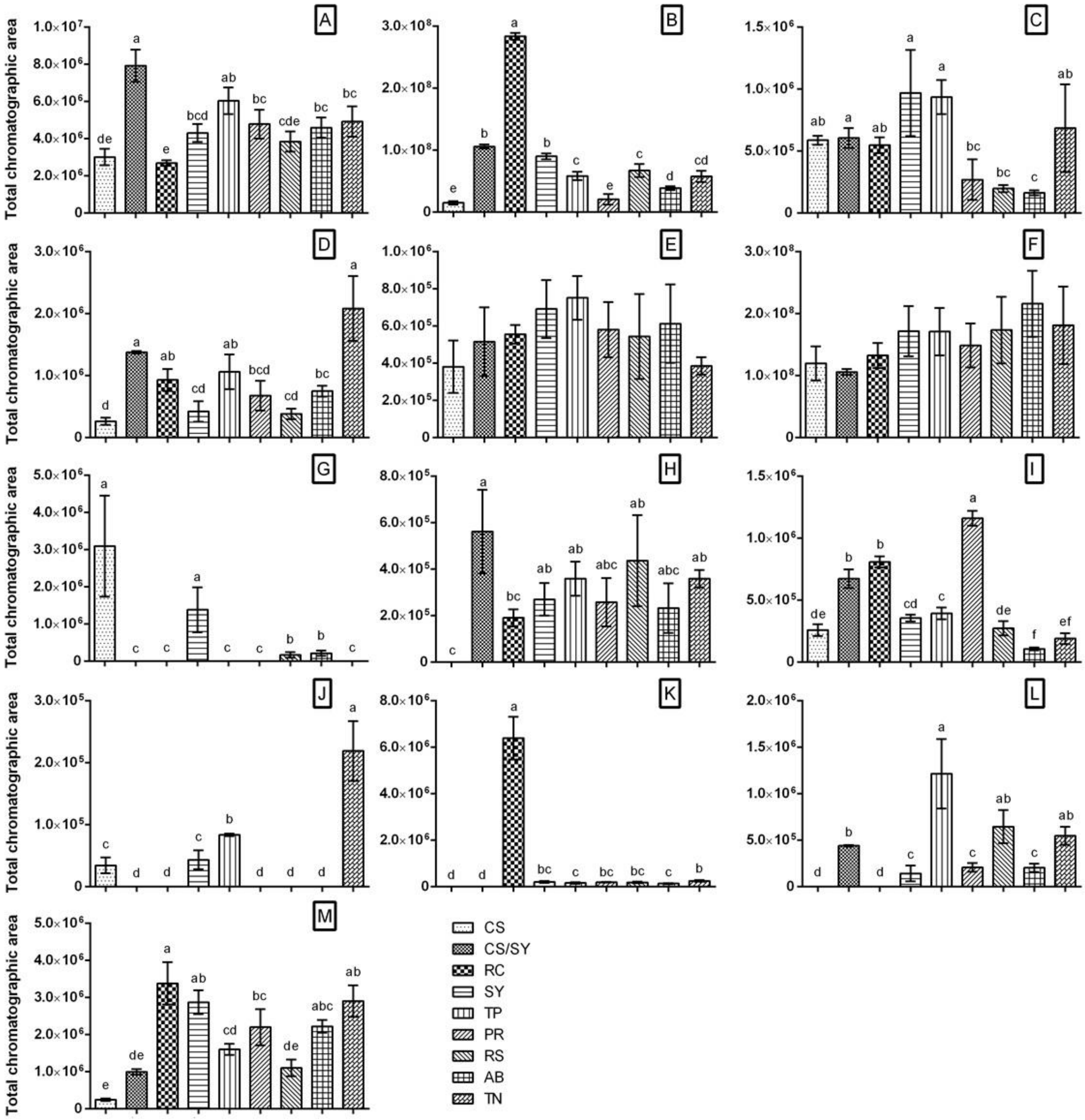

A
B
C
D
E
F
G
H
I
J
K
L
M
Total chromatographic area
CS
CS/SY
RC
SY
TP
PR
RS
AB
TN

Figure 2

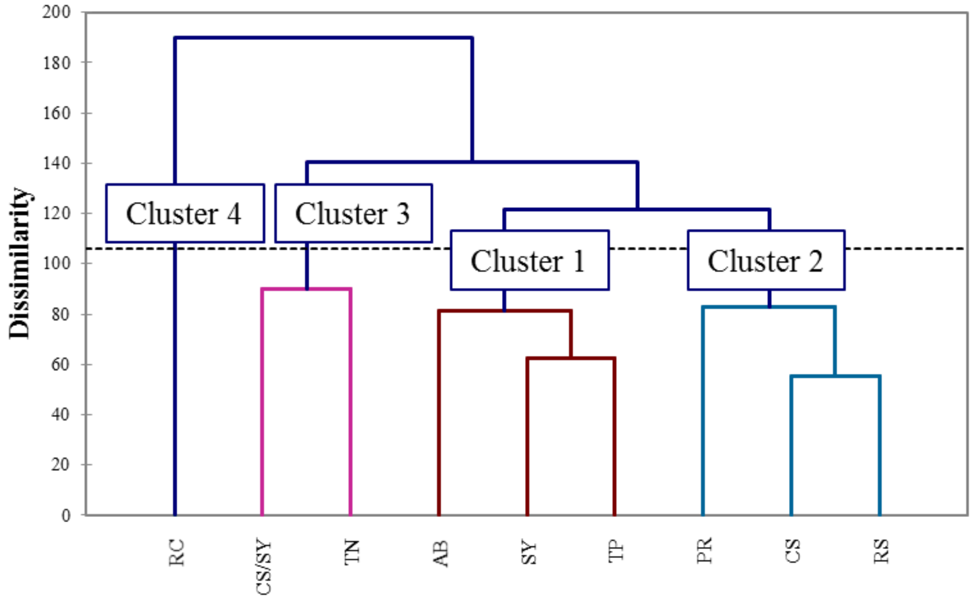
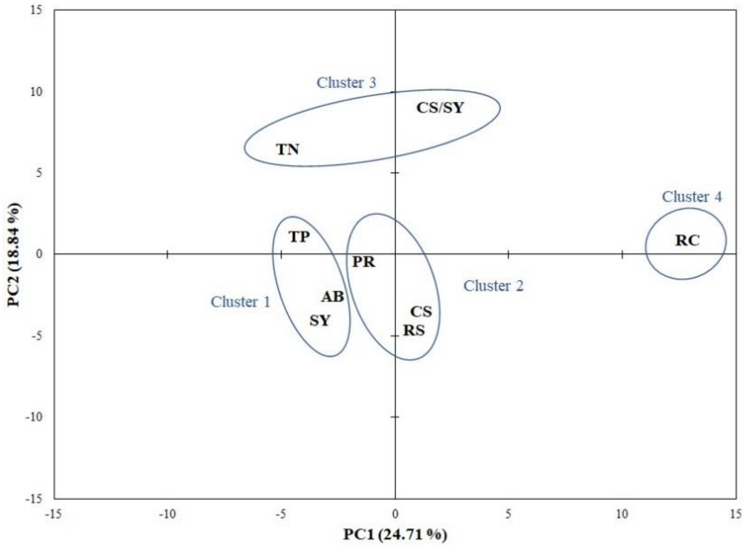
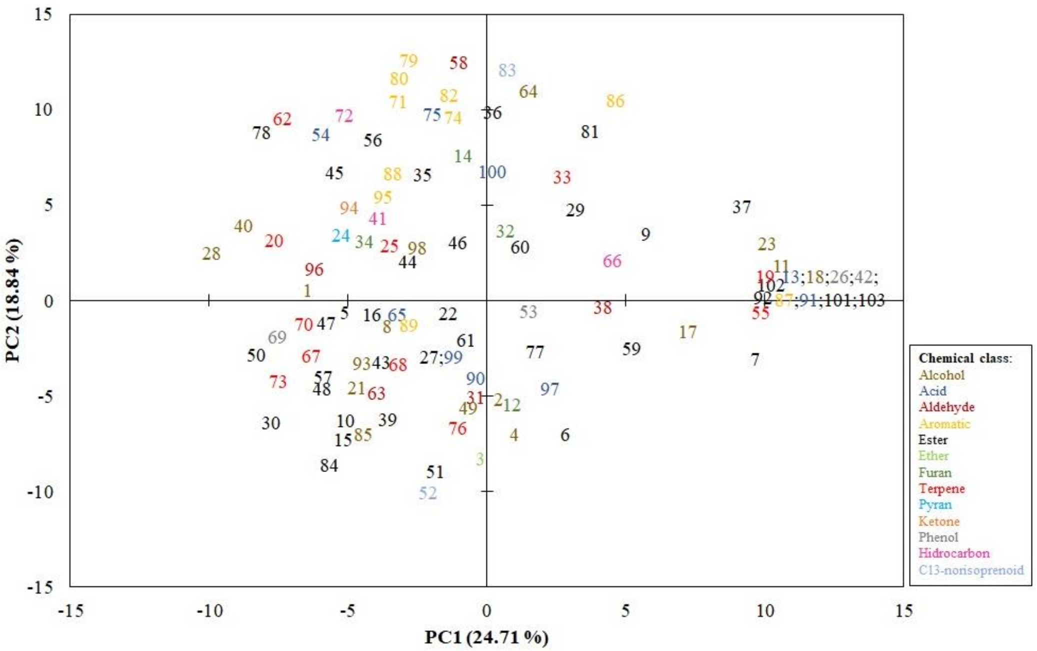

Dissimilarity
200
180
160
140
120
100
80
60
40
20
0
Cluster 4
Cluster 3
Cluster 1
Cluster 2
RC
CS/SY
TN
AB
SY
TP
PR
CS
RS

Figure 3


Cluster 3
CS/SY
TN
Cluster 4
RC
TP
PR
Cluster 1
AB
SY
Cluster 2
CS
RS
PC2 (18.84 %)
PC1 (24.71 %)


PC2 (18.84 %)
PC1 (24.71 %)
Chemical class:
Alcohol
Acid
Aldehyde
Aromatic
Ester
Ether
Furan
Terpene
Pyran
Ketone
Phenol
Hidrocarbon
C13-norisoprenoid

5 CONCLUSÕES GERAIS

Os resultados das análises clássicas dos vinhos tintos mostraram que estes estiveram em conformidade com o estabelecido pela legislação brasileira vigente.

Por sua vez, a aplicação da técnica cromatográfica (HS-MEFS/CG/EM) permitiu a determinação do perfil volátil de um grupo de vinhos tintos e espumantes comerciais do Vale do São Francisco indicados ao processo de Indicação Geográfica desta região. Um total de compostos voláteis de 103 e 109 compostos foram identificados para os vinhos tintos e os vinhos espumantes, respectivamente.

Em ambos os tipos de vinhos os compostos foram classificados em 13 grupos químicos, cujos resultados foram associados a análises estatísticas multivariadas (análise hierárquica de cluster, mapa de cor e análise de componentes principais) que permitiram a determinação de similaridades e distinções entre os vinhos influenciados por características como cultivar, safra e vinícola (práticas enológicas). Nestes vinhos foram considerados potenciais marcadores de tipicidade os compostos comuns, exclusivos e aqueles identificados pela primeira vez em vinhos elaborados na região do Vale do São Francisco.

Os perfis voláteis identificados no grupo seleto de vinhos tintos e espumantes de distintas cultivares, safras, vinícolas, métodos de vinificação e armazenamento sugerem uma qualidade aromática única que pode ser explorada em trabalhos futuros quanto a sensorialidade e a aceitabilidade com destaque para os compostos identificados pela primeira vez em vinhos e seus respectivos impactos no aroma global da bebida.

Os resultados obtidos no presente trabalho podem ser úteis para a rastreabilidade e indispensáveis para confirmação da autenticidade dos vinhos desta região, além de gerar informações para os consumidores, viticultores e banco de dados dos vinhos tintos e espumantes comerciais tropicais brasileiros. Desta forma, poderá contribuir para descrever os vinhos comerciais da futura Indicação Geográfica Vale do São Francisco, colaborando assim com o desenvolvimento científico e tecnológico da vitivinicultura da região.

Pesquisas futuras poderão se concentrar no estudo quantitativo dos voláteis nos vinhos tintos comerciais e espumantes da futura IG do VSF. Além disso, seria importante avaliar os efeitos da época do ano de colheita das uvas na composição volátil e tipicidade dos produtos. A comparação destes resultados com outros obtidos a partir de vinhos e espumantes de outras regiões do Brasil e do mundo, poderá enriquecer a discussão sobre a qualidade aromática e identidade regional de cada produto.

ANEXO

ANEXO A – Comprovante de submissão do artigo I

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Corresponding Author: Marta Madruga
Co-Authors: Samara M Morais; Mércia S Galvão; Leila M de Carvalho; Lary S Olegario; Giuliano E Pereira; Luciana Leite A Lima; Flávio Luiz H da Silva;

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ANEXO B – Comprovante de submissão do artigo II

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Corresponding Author: Dr. Marta Madruga
Co-Authors: Samara de Macêdo Morais; Mércia de Sousa Galvão; Lary Souza Olegario; Leila Moreira de Carvalho; Giuliano Elias Pereira; Luciana Leite de Andrade Lima Arruda; Flávio Luiz Honorato da Silva
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