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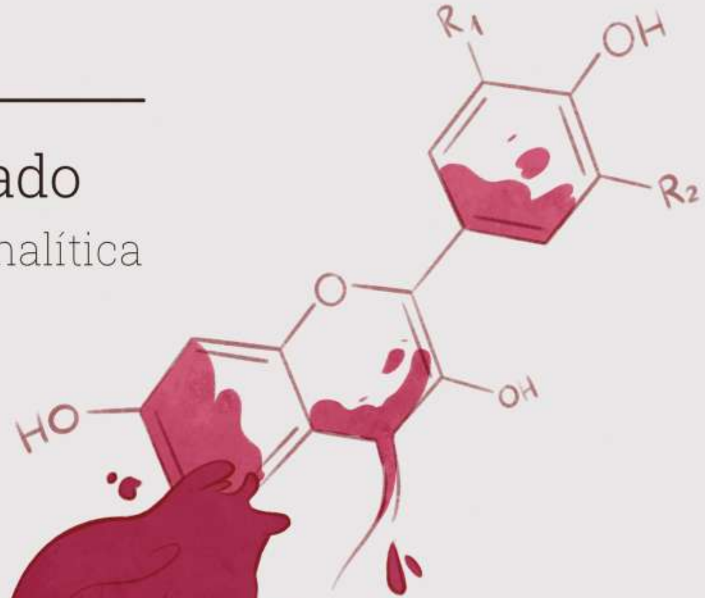
Doctoral Thesis



Carlos Asensio Regalado

Departamento de Química Analítica

Leioa, 2022

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Universidad del País Vasco

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FACULTY OF SCIENCE AND TECHNOLOGY

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PhD Thesis

Carlos Asensio Regalado

Supervisors:
Luis Ángel Berrueta Simal
Rosa María Alonso Salces

Leioa, Julio 2022

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Scientific contribution

Some of the results presented in this thesis have been published as scientific articles in peer-reviewed journals and reported at international conferences.

Publications:

[1] C. Asensio-Regalado, R. M. Alonso-Salces, B. Gallo, L. A. Berrueta, B. Era, F. Pintus, and C. Caddeo, "*Tempranillo* grape extract in transfersomes: A nanoproduct with antioxidant activity," *Nanomaterials*, vol. 12, no. 5, p. 746, 2022. DOI: 10.3390/nano12050746.

[2] C. Asensio-Regalado, R. M. Alonso-Salces, B. Gallo, L. A. Berrueta, C. Porcedda, F. Pintus, A. Vassallo, and C. Caddeo, "A liposomal formulation to exploit the bioactive potential of an extract from *Graciano* grape pomace," *Antioxidants*, vol. 11, no. 7, p. 1270, 2022. DOI: 10.3390/antiox11071270.

[3] L. A. Berrueta, Z. Rasines-Perea, N. Prieto-Perea, C. Asensio-Regalado, R. M. Alonso-Salces, M. B. Sánchez-Ilárduya, and B. Gallo, "Formation and evolution profiles of anthocyanin derivatives and tannins during fermentations and aging of red wines," *European Food Research and Technology*, vol. 246, no. 1, pp. 149–165, 2019. DOI: 10.1007/s00217-019-03405-x.

Congress Communications:

[1] C. Asensio-Regalado, A. Sasía-Arriba, A. A. Poliero, R. M. Alonso-Salces, B. Gallo Hermosa, and L. A. Berrueta Simal, "Effect of climate change on the polyphenolic composition of the main varieties of grape from La Rioja (Spain) and new oenological strategies to correct these effects on the quality of red wine," in *Polyphenols Communications*, vol. 1, Turku, Finalnd, 2021, pp. 269–270.

Table of Contents

List of Abbreviations

(epi)cat	(+)-catechin or (-)-epicatechin, unknown isomer
(epi)gallocat	(+)-Gallocatechin or (-)-Epigallocatechin, unknown isomer
A^+	flavylium cation
AA	antioxidant activity
Abs	absorbance
ac	acetyl
AF	alcoholic fermentation
ANOVA	analysis of variance
AO	quinone base
AOH	hemiacetal
APCI	atmospheric pressure chemical ionization
API	atmospheric pressure ionization
C*	chroma
caff	caffeoyl
cat	catechin
CE	collision energy
CI	color intensity
CID	collision induced dissociation
CIE	Commission Internationale de l'Èclairage
coum	coumaroyl
cryo-TEM	cryogenic-transmission electron microscopy
CV	cone voltage
Cy	cyanidin
DAD	diode array detector
DC	direct current
DCF	20,70-dichlorofuorescein
DCFH-DA	20,70-dichlorofuorescein diacetate
DMEM	Dulbecco's Modified Eagle's Medium
DMSO	dimethyl sulfoxide
Dp	delphinidin
DPPH	2,2-diphenyl-1-picrylhydrazyl
EE	entrapment efficiency
epicat	epicatechin
epigallocat	epigallocatechin
ESI	electrospray ionization
EtOH	ethanol
FBS	fetal bovine serum
FE	Fe^{2+} equivalents
FRAP	ferric reducing antioxidant power
GAE	gallic acid equivalents
gal	galactoside
gallocat	gallocatechin
GE	*Graciano* extract
glc	glucoside
glu	glucuronide
H*	hue
HAc	acetic acid
HaCaT	human skin keratinocytes
HCl	hydrochloric acid
HPLC	high-performance liquid chromatography
IT	ion trap
IV	intravenous
k_d	degradation constant
k_e	extraction constant
k_f	formation constant
L*	lightness
m/z	mass to charge ratio
MD	mean diameter
MeCN	acetonitrile
MeOH	methanol
MLF	malolactic fermentation
MRM	multiple reaction monitoring
MS	mass spectrometry
MS/MS	tandem mass spectrometry
MTT	3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide
Mv	malvidin
Mv-3-*O*-glc	malvidin-3-*O*-glucoside
MWCO	molecular weight cut-off
N_2	nitrogen gas
NMR	Nuclear Magnetic Resonance
O_2	gas oxygen
P90G	phospholipon 90G
PCB1	procyanidin B 1
PCB2	procyanidin B 2
PCC1	procyanidin C 1
PDO	Protected Designation of Origin

PI	polydispersity index
Pn	peonidin
Pt	petunidin
PTFE	polytetrafluoroethylene
QqQ	triple quadrupole
QToF	quadrupole time-of-flight
QToF/MS	quadrupole time-of-flight mass spectrometer/spectrometry
quer	quercetin
RF	radio frequency
ROS	reactive oxygen species
S75	phospholipid lipoid S 75
SD	standard deviation
SIM	single ion monitoring
SO_2	sulphur dioxide
SPE	solid phase extraction
t_R	retention time
TE	*Tempranillo* extract
TFA	trifluoroacetic acid
Ton	tonality
TPC	total phenolic contents
TPTZ	2,4,6-tris(pyridin-2-yl)-1,3,5-triazine
TrEq	Trolox equivalents
Trolox	6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid
Tween 80	polyoxyethylene (20) sorbitan monooleate
UHPLC	ultra high-performance liquid chromatography
UV-Vis	ultraviolet-visible spectrophotometry
Vitisin B	Mv-3-*O*-glc-acetaldehyde
Vitisin A	Mv-3-*O*-glc-pyruvic
ZP	zeta potential

Chapter 1

Introduction

1.1 Wine

Wine is defined as the alcoholic fermented juice from grapes which is used as a beverage. One of the earliest evidences of grape wine and viniculure was found in pottery fabrics found in an excavation in Georgia (South Caucasus) dating to the early Neolithic period (*ca.* 6000-5000 BC) [1].

Throughout the centuries, wine has been part of history, continuously evolving and arriving to our days in many different forms. Wine making has incorporated more technological elements as humans developed increasing knowledge of the different processes that occur during elaboration. The techniques employed play an important role in the extraction of natural components, such as phenolic compounds, from the grape and their subsequent stabilization in wine: maceration time and fermentation in contact with the grape seeds and skins, pressing, aging in barrel and in bottle,...

Grapevine (*Vitis vinifera* L.) is a perennial woody fruit crop used for wine, juice, fresh consumption (table grapes), dried fruit, and distilled liquor [2]. It is a highly plastic crop that exhibits large differences in fruit composition from a given variety depending upon the environmental conditions of the vineyard of origin [3]. Fruit traits that affect wine quality are thought to be largely driven by the interaction of a grapevine's genetic characteristics with environmental factors (*i.e.*, climate, soil, and topography) and vineyard management [4]. Temperature and water availability are also known to influence sugar concentration, acidity, pH, color, and other characteristics in the fruit [5, 6]. Moreover, climate change predictions of elevated CO_2 and rising temperature are also likely to have an effect on the grapevine reproductive cycle and on fruit composition [7].

1.1.1 Wine-making process

Wine color is greatly influenced by the grape cultivar and the different oenological techniques employed, the elaboration process, time and temperature of storage and oxygen exposure [8].

Grape source is the main factor affecting the quality of wine, followed by the elaboration methodology employed. The vintage and transportation of the grape to the winery is also an important step, since breaking of the grape berries at this point would suppose an undesirable early start of alcoholic fermentation (AF) and loss of must.

Once in the winery, the initial step is destemming. It consists on the separation of the plant material and the stems from the grape berries. During this process it is important that the seeds and stems are not pressed, damaged or cut, because this could produce liberation of vegetable juices that would give a herbaceous taste to the wine [9]. When the grape berries break, two processes start immediately and simultaneously: (i) maceration, consisting in the exchange of substances between the must and the solid part of the grape berries (grape pomace), and (ii) biochemical transformations induced by grape enzymes.

The AF is the main step of the whole process of wine-making. Nowadays, it is performed in stainless steel tanks. In this step, sugars in the grape must are transformed into ethyl alcohol and carbonic gas by the yeasts of the genus *Saccharomyces*. During red wine AF the gas produced pushes the grape pomace to the top of the tank, forming a natural barrier known as cap. Pumping-over operations can be performed in order to wet the cap material with the must, with the purpose of activating the maceration processes. In addition, this practice can provide sufficient air contact with the must, providing the required oxygen. Aeration of the yeasts during the process is a very effective way of helping complicated fermentation. Other than during pumping-over, the aeration can take place by means of microoxygenation [10, 11]. In the case of white wines, maceration with the skins is not performed.

The malolactic fermentation (MLF) is the step in which malic acid is biodegraded into lactic acid. The main lactic bacteria responsible for this process is *Oenococcus oeni*, and in the wine industry stains of this species are frequently employed as malolactic starter cultures [12]. Frequently, MLF occurs after the complete depletion of sugars. This technique was recognized since the end of the 20th century, however it has been only in the last few decades considered a consistent component of red wine-making. Before, red wine must acidification was a common practice [11]. The effects of MLF on red wines might be desirable or undesirable, depending on the purpose of the wine. In case of wines destined for aging, this step is essential to obtain biological stabilization that ensures conservation overtime. Malolactic bacteria produce hydrolyzation of the anthocyanins yielding unstable anthocyanidins. This results in a lower concentration of anthocyanins and also in a decrease in color intensity (CI). Wines produced without MLF show a slightly more purple hue, caused by the lower pH and higher amounts of flavylium form [13].

Wine aging originated as a consequence of the need of wine transportation. In the past, tanks were made of different materials, such as clay or treated leather. In northern countries, wooden tanks were employed for the production of wine, and they created smaller tanks for wine storage. By the time it was consumed, wine had been in the wooden barrels for some time, acquiring some characteristics from the wood. The aging process is like a slow oxidation of wine. Nowadays, the most common types of wood employed are French and American oak trees; the former contributes the most to provide solid extracts and phenolic compounds, and longer shelf-life. During this process, different substances in wine precipitate from the solution and decant to the bottom of the tank. In order to remove these sediments, the wine is racked from one barrel to another, producing also the elimination of excessive carbon dioxide and homogenization of the aged wine. Sulfur dioxide is added as stabilizing agent at different stages of wine-making. In order to have a successful wine aging, the relative concentrations of anthocyanins and flavanols prior to this stage should be around 1/4. This ensures that all the available anthocyanins can participate in polymerization reactions. The excess of flavanols are eliminated after aging to avoid condensations, which produce astringency in wine. Wines which are rich in anthocyanins and with low flavanol concentration are less suitable for aging, since the excess of anthocyanins would react by oxidation yielding colorless phenolic acids, and thus, causing a significant decrease in CI. Aging in wooden barrels is a procedure employed to stabilize the color and enrich the sensory characteristics of wine, due to the beneficial effects of the compounds extracted from the wood, such as ellagitannins or wood aldehydes [14, 15].

1.1.2 Protected Designation of Origin "Rioja" wine

Ideal growing conditions for *Vitis vinifera* consist of temperate climate regions with warm, dry summers with moderate precipitation, and mild winters [16]. In Spain the area located around the Ebro valley has been historically popular for vitiviniculture. Within this area the Rioja region is located south of the river Ebro and north of the Sierra de la Demanda. It has influences from both Atlantic and Mediterranean climates, and in addition to this geographical conditions, the climatic and soil constitution makes it a prime region for growing grapes.

Wines are permitted to be marketed under specific EU agricultural product quality schemes, named Protected Designation of Origin (PDO). PDO products must be produced, processed and prepared in a specific region using traditional production methods. The raw materials must also be from the defined area whose name the product bears. The quality or characteristics of the product must be due essentially or exclusively to its place of origin, *i.e.*, climate, the nature of the soil and local know-how [17]. In the case of wines, it refers to physicochemical and sensory properties that are particular to a specific wine and allow us to differentiate it from others [18]. In Spain there are at least 70 different PDOs for wine. PDO "Rioja" wine was the first region to receive this recognition (PDO-ES-A0117, 13/06/1986) and it was also the pioneer for achieving the higher "Calificada" status in 1991 [19].

Wines under the PDO "Rioja" must be elaborated from grapes of specific authorized varieties, namely *Tempranillo*, *Garnacha*, *Mazuelo* and *Graciano*. The *Tempranillo* grape cultivar is the most famous and highest quality grape for red wine production, being native from the region between La Rioja and Navarra, in the northern area of Ebro. Its name originates for having an early maturation, producing wines with a significant phenolic content and a characteristic aroma of black fruits and liquorice, being highly suitable for aging [20]. *Graciano* grape cultivar is generally used to complement *Tempranillo* cultivar during aging, and it is highly aromatic, and *Mazuelo* cultivar produces wines rich in tannins, with high CI and acidic, with low aroma [21].

Considering the diversity of terrain and climate in the area under the PDO "Rioja", three different subregions can be distinguished: Rioja Alta, Rioja Baja and Rioja Alavesa.

- **Rioja Alta** is the most western region of the three, and it is the most extended territory under the Qualified PDO accounting for a 40% of the total production. Their iron clay terrains and moderate rainfall allow quality wines with moderate alcohol content and colored, suitable for aging. The main grape varieties are *Tempranillo* (red wine) and *Viura* (white wine).

- **Rioja Baja** is located in the south of Logroño, and is characterized by rich alluvial soils and moderate rainfall. This subregion accounts for a 38% of the production of Rioja wines, and in the recent years there has been an increase on the use of *Tempranillo* grapes for red wine production. However, the varieties *Garnacha* (red wine) and *Viura* (white wine) are still predominant.

- **Rioja Alavesa** is the smallest of the three regions, but despite this, it still accounts for a 22% of the Rioja wine produced. Geographically is located in the southernmost part of Álava (Basque Country) near the border with La Rioja. The drier climate and calcareous soils produce wines with a moderate alcohol content, moderate acidity and suitable for both consumption and aging. The main varieties are *Tempranillo* (red wine) and *Viura* (white wine).

1.1.3 Phenolic compounds in wine

The consumption of wine has been associated for years to various health benefits. In 1974 the publication of a study that associated alcohol consumption with a lower risk of coronary heart disease set the basis for research in this area [22]. A few years later, around 1980, the concept "French Paradox" was first established by three authors. This concept was created after the observation that French population showed lower rates of coronary heart disease despite their high animal fat intake. They attributed this to the high consumption of alcohol and antioxidants in France, both supplied by wine [23, 24]. Nowadays, we know that these properties are due to phenolic compounds, among others, which are known to possess antioxidant, cardioprotective, anticancer, anti-aging, anti-inflammation and antimicrobial properties [25], and are present in wine as well as widely distributed in the plant kingdom.

Although many different components have been identified in wine along the years, it is difficult to know its exact composition. Wine is a very complex mixture of several hundred compounds, many of them present in very low concentrations [26]. Many of these components are formed during elaboration process and wine aging. However, most of them come from the grapes. There are many factors influencing grape composition, such as the type of soil, climatic conditions, grape maturity, agrotechnical works, etc. In grape plants, the berries constitute around a 95-97% of the grape mass. The grape berry consists of 73-95% of pulp, 2-20% of skin and 2-7% of seeds. The skin is rich in phenolics; anthocyanins, tannins, flavonols and phenolic acids being the main components [27].

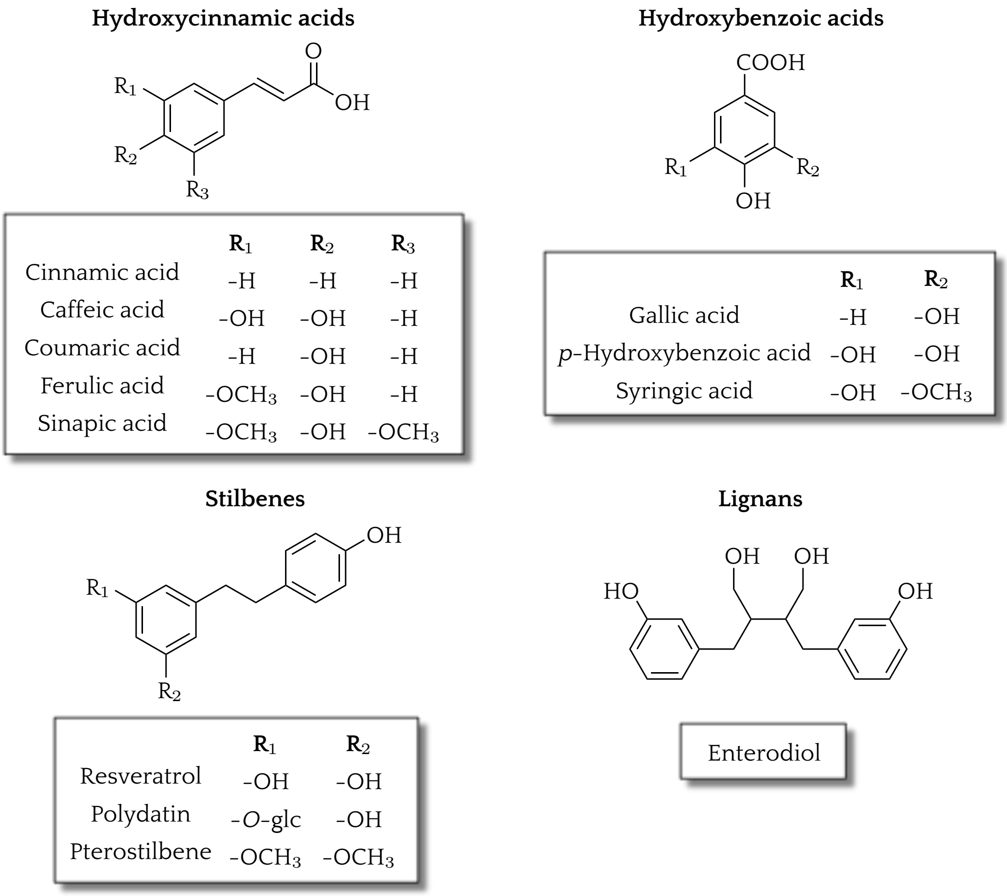
Grape must is made primarily of water and sugars, as well as malic and tartaric acids and other minor components. During AF of the pressed grape juice, most of the sugars are transformed into alcohol, but other interesting products remain, including phenolics. Phenolic compounds are responsible for most of its attributes and contribute to its organoleptic properties, such as color, astringency, bitterness and aroma of wine [28]. For this reason, it is very important to study in detail the evolution of these compounds during wine production. The concentration of phenolic compounds depends on the variety of *Vitis vinifera* employed for wine production and the climate under which it has grown.

Phenolic compounds constitute a wide and diverse group of natural products universally distributed in plants. They are an important class of secondary metabolites, derived from the biosynthetic pathway of shikimic acid and from the phenylpropanoic metabolism [29].

Phenolics are classified according to their skeleton backbone into flavonoids and non-flavonoids. Grapes contain flavonoids in the skins, seeds and woods, whereas non-flavonoid compounds are found in the flesh mainly. The most important non-flavonoid compounds in grapes and wine are phenolic acids (hydroxybenzoic and hydroxycinnamic acids), stilbenes and lignans (Figure 1.1).

Wine phenolics can be sorted into the following groups: (i) phenolic acids, namely hydroxybenzoic and hydroxycinnamic acids, which contribute to the color of red and rose wines as copigments of anthocyanins [30]; (ii) stilbenes, resveratrol and its glycosides being the most important; and (iii) flavonoids, which have different subfamilies: (a) anthocyanins, which are responsible for the color of red and rose wines [31]; (b) flavan-3-ols containing monomeric catechins and proanthocyanidins that are the main phenolic compounds involved in the astringency, bitterness and structure of wines, and are also an important factor in stabilizing the color of aging wines as anthocyanin copigments [32]; and (c) flavonols which play an important role in bitterness, and also act as copigments of anthocyanins [33, 34].

Flavonoid structure comprises two aromatic rings linked by a three-membered carbon chain, which leads to a C_6-C_3-C_6 diphenylpropane structure. The aromatic rings are named A and B, and the central heterocycle present in some flavonoid families is named C (Figure 1.2). Their reactivity is due to the acid character of the phenol functions and to the nucleophilic character of the benzene ring.



	R_1	R_2	R_3
Cinnamic acid	-H	-H	-H
Caffeic acid	-OH	-OH	-H
Coumaric acid	-H	-OH	-H
Ferulic acid	$-OCH_3$	-OH	-H
Sinapic acid	$-OCH_3$	-OH	$-OCH_3$

	R_1	R_2
Gallic acid	-H	-OH
p-Hydroxybenzoic acid	-OH	-OH
Syringic acid	-OH	$-OCH_3$

	R_1	R_2
Resveratrol	-OH	-OH
Polydatin	-*O*-glc	-OH
Pterostilbene	$-OCH_3$	$-OCH_3$

Figure 1.1. Summary of the main non-flavonoid compounds found in grapes and wine.

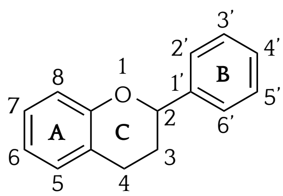


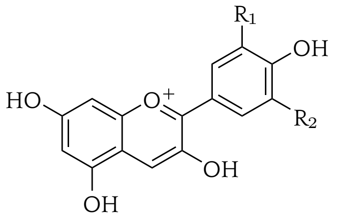
Figure 1.2. Molecular structure of flavonoids.

The main flavonoid families present in the grapes of the different cultivars of *Vitis vinifera* and in the wines made from them, are flavan-3-ols and anthocyanins, and derivatives of them. However, other flavonoids can also be found in lower concentrations, such as flavanones and flavanonols, which differ from one another on the hydroxy and methoxy groups on ring B. These compounds can appear glycosylated on carbon C3 in the case of flavonols and flavanones, and sometimes the glycosides can be found acylated (Figure 1.3) [35].

1.1.3.1 Flavan-3-ols

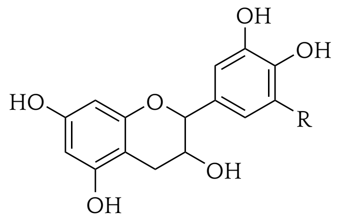
Flavanols are flavonoids that contain a saturated three-carbon chain (ring C). They are the only family found in their aglycone form, not liked to a sugar. They can be found in the solid part of the grape (seeds and skins) and can appear as monomers, oligomers or polymers; the last two

Anthocyanidins



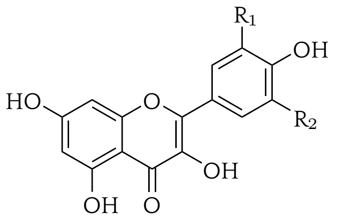
	R1	R2
Cyanidin (Cy)	-OH	-H
Delphinidin (Dp)	-OH	-OH
Peonidin (Pn)	$-OCH_3$	-H
Petunidin (Pt)	$-OCH_3$	-OH
Malvidin (Mv)	$-OCH_3$	$-OCH_3$

Flavan-3-ols



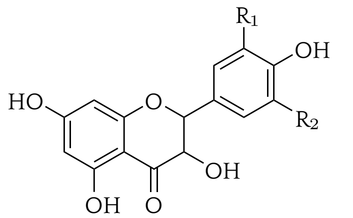
		R
(2*R*,3*S*)	Catechin	-H
	Gallocatechin	-OH
(2*R*,3*R*)	Epicatechin	-H
	Epigallocatechin	-OH

Flavonols



	R1	R2
Kaempferol	-H	-H
Quercetin	-OH	-H
Myricetin	-OH	-OH
Isorhamnetin	$-OCH_3$	-H

Flavanonols



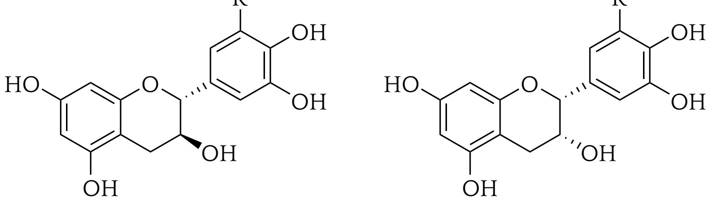
	R1	R2
2,3-dihydrokaempferol	-H	-H
2,3-dihydroquercetin	-OH	-H

Figure 1.3. Main flavonoid families present in *Vitis vinifera* grapes.

are also known as proanthocyanidins or condensed tannins. These compounds are antioxidants, anti-tumorgenics and anti-mutagenics, and thus, have beneficial health effects [36].

Flavan-3-ol monomers found in the grapes from *Vitis vinifera* variety are (+)-cat, (-)-epicat, (+)-gallocatechin (gallocat) and (-)-epigallocatechin (epigallocat). The former two are *ortho*-diphenols hydroxylated in positions 3′ and 4′ of ring B, and the other two are trihydroxylated in positions 3′, 4′ and 5′ (Figure 1.4) [37].

Flavanols



	R	
(+)-catechin	-H	(-)-epicatechin
(+)-gallocatechin	-OH	(-)-epigallocatechin

Figure 1.4. Chemical structure of the main flavanols.

These molecules have two asymmetric carbons, C2 and C3, leading to four monomers which can be grouped into two families of diastereoisomers, the first one including (+)-cat and

(+)-gallocat (2*R*, 3*S*), and the second one with (-)-epicat and (-)-epigallocat (2*R*, 3*R*) [38].

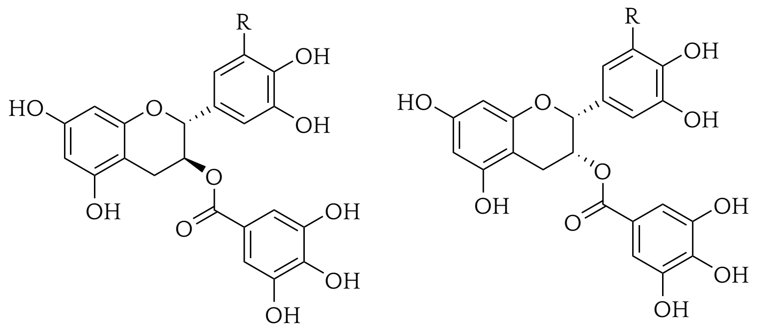
On these molecules the hydroxyl group on carbon C3 can undergo esterification with gallic acid to yield galloylated flavanols (Figure 1.5). These compounds have been found in grape seeds and skins in different concentrations; the former containing a greater diversity of these compounds [39].

Furthermore, flavan-3-ols can be found glycosylated, and in nature, have been detected as 3-, 5- and 7-*O*-glycosylated, as well as, 6- and 8-C-glycosylated [40]. These glycosylated compounds have been identified in grapes, the wood of some trees, some plants and in cocoa liquor [41].

1.1.3.2 Anthocyanins

Anthocyanins are the pigments responsible for the color of red grapes found mainly in the skin, except in some varieties, such as *Tintorera*, where they can also be found in the flesh. They are extracted to the pressed grape juice during wine-making, being responsible for the red color of young red wines, and the precursors for the derivative pigments formed during wine aging [42, 8].

Anthocyanins are hydroxylated or methoxylated derivatives of the 3,5,7,4'-tetrahydroxyflavylium cation (Figure 1.6). The electron deficiency of the flavylium cation (A^+) makes the free aglycones (anthocyanidins) highly reactive and thus, they are not found free in nature, but glycosylated [43].



	R	
(+)-catechin-3-*O*-gallate	-H	(-)-epicatechin-3-*O*-gallate
(+)-gallocatechin-3-*O*-gallate	-OH	(-)-epigallocatechin-3-*O*-gallate

Figure 1.5. Chemical structure of galloylated flavanols.

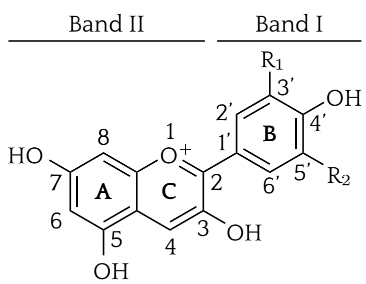


Figure 1.6. Structure of flavylium form of anthocyanins.

The anthocyanins identified in the *Vitis vinifera* grape cultivars and in wines produced from these grapes are 3-monoglucoside (glc)s of five anthocyanidins: delphinidin (Dp), cyanidin (Cy), petunidin (Pt), peonidin (Pn) and malvidin (Mv), which differ in the number and the position of the hydroxyl and methoxy groups on ring B of the aglycones. Acylated derivatives of the monoglucosides have also been reported, formed by esterification on carbon 6 of the glucose unit with acetic, *p*-coumaric or caffeic acids.

The monoglucosides of the five anthocyanidins, acetylglucosides, *p*-coumaroylglucosides and caffeoylglucosides have been identified in grapes and wines. In addition, the *cis* isomer of Mv-3-(6-*p*-coumaroyl (coum))-glc has been recently identified in different cultivars of grapes of *Vitis vinifera* and their wines [44].

Anthocyanins have a characteristic ultraviolet-visible spectrophotometry (UV-Vis) absorption spectrum with two differentiated bands: Band I in the visible region, between 330 and 535 nm, due to ring B (Figure 1.6), and Band II in the UV region, between 253 and 285 nm, due to ring A. The absorption maximum in the visible range is related to the substitution pattern in ring B, a greater number of oxygenated substituents leading to an increase on the relative intensity of band I/band II (hyperchromic effect).

For the anthocyanins trisubstituted in ring B (Dp-3-glc, Pt-3-glc and Mv-3-*O*-glc, the absorption maximum experiments a bathochromic shift of 10 nm with respect to the disubstituted counterparts (Cy-3-glc and Pn-3-glc) [45]. Methylation of the hydroxy group does not seem to produce a shift in the wavelength of absorption; the hypsochromic shift typical of methoxylated flavonoids not being measurable. This is probably due to the methoxylation occurring on positions 3′ and 5′, which are less effectively conjugated and affect the chromophore to a lesser extent.

Anthocyanins have various reactive positions. Nucleophilic attacks can occur at positions C2 and C4 of ring C, the hydration of C2 leading to the colorless hemiacetal (AOH) species. Electrophilic attack can occur *via* the hydroxyl groups and carbons C6 and C8 from ring A. The presence of the hydroxyl group in position C5 is very important for the reactivity.

The electronic deficiency is distributed through the whole molecule and not just concentrated on the oxygen of ring C. The cation is stabilized by resonance, the ring B being coplanar and also involved in charge delocalization. The bond distances in rings A and C are very similar; ring C having a similar stability as the aromatic system. This makes anthocyanins the flavonoid family with the most stable and difficult to break ring C. The absence of a keto group in position C4, present in other flavonoid families, hinders fragmentation.

In grapes of species other than *Vitis vinifera*, a second glc group linked to the hydroxy group in position C5. However, some studies show that small levels of the diglycosylated anthocyanins can also be found in the *Vitis vinifera* grapes [46].

The color of anthocyanins is also dependent of the pH of the medium. Anthocyanins are characterized by the coexistence of several acid-base species in equilibrium in solution. The different chemical forms of anthocyanins depending on the pH are shown in Figure 1.7.

At the pH of wine, *c.a.* 3.5, anthocyanins coexist in equilibrium in different forms: the A^+, which is red in color; the quinone base (AO) form, with a violet color; and the AOH form, which is colorless, and the most abundant [47]. Only about a 20-30% of the anthocyanins are present in the form of the colored A^+ and contribute to the color of wine.

When registering the UV-Vis spectrum of a solution of anthocyanins varying the pH in the range of 1-7, two different phenomena are observed: (i) in the range 1-3, a decrease of the intensity of the visible band (band I) as a result of the hydration of the A^+ group to yield the colorless AOH form, and (ii) at pH 4, a new band in the visible region 550-700 nm appears as a consequence of the formation of the AO by proton transfer. These types of acid-base equilibria can be shifted depending on the interactions between the anthocyanins and other molecules in the medium, in a process known as copigmentation.

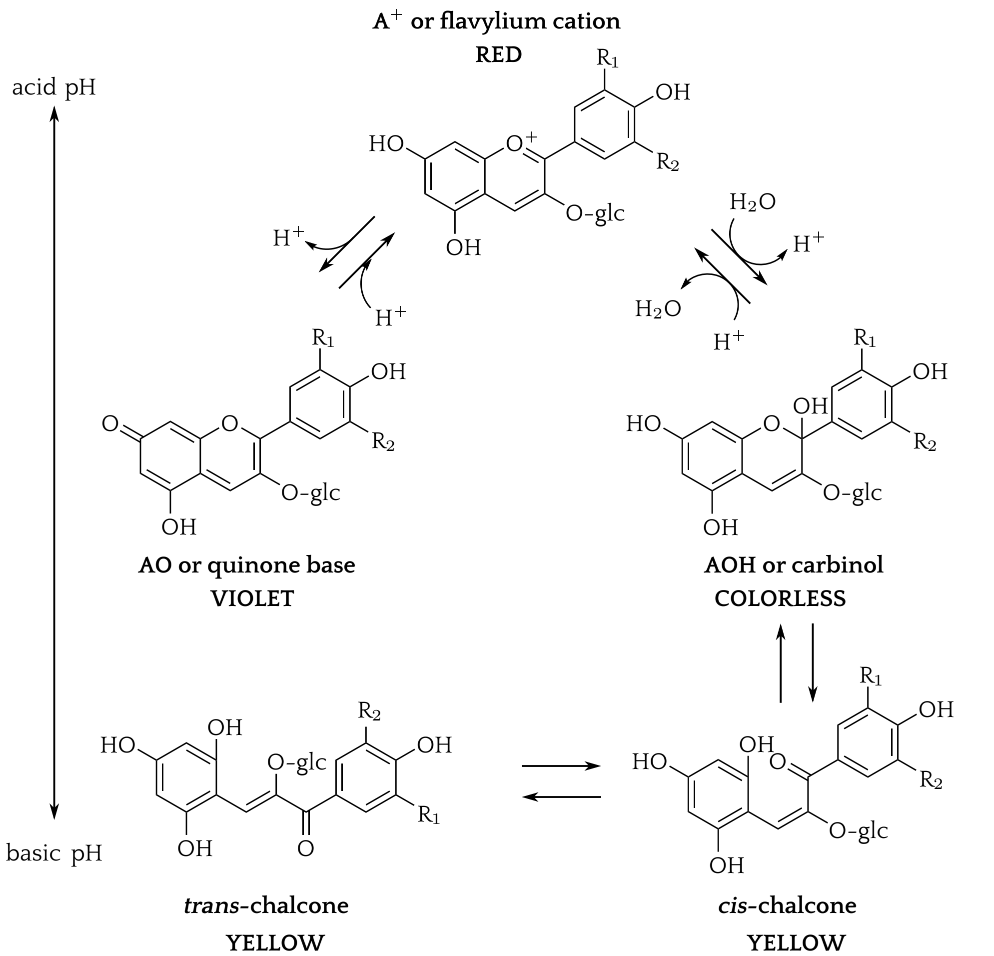


Figure 1.7. pH-dependent structures of anthocyanins.

Copigmentation. Copigmentation is based on a shift in the hydration equilibrium of anthocyanins as a result of the π-π interaction between the planar structure of the anthocyanin with other molecules in the medium that act as copigments. The molecules that can act as copigments need to have a planar arrangement, in order to stack with the anthocyanin [48].

Colored anthocyanins, in the A^+ and AO forms, can lead to this type of non-covalent interaction with other molecules in the medium. These interactions lead to shifts in the equilibrium towards colored forms, limiting the decolorization effect of weak acidity [49].

These kind of compounds adopt a sandwich-type arrangement that protects the chromophore A^+ group from nucleophilic attack, reducing the relative proportion of the AOH and chalcone forms. The final result is an increase on the intensity of the color compared to the one that is expected at a certain pH of the medium.

There are different types of compounds that can act as copigments, including aminoacids, nucleotides, hydrocarbons and phenolic compounds, and even anthocyanin chromophores can act as copigments themselves, as well as the aromatic residues of the molecule (intramolecular copigmentation). Intramolecular copigmentation protects the molecule from the nucleophilic attack of water more efficiently than the intermolecular [50].

Among phenolic compounds, flavonols and hydroxycinnamic acids are the most common copigments. Although the concentration of flavanols in wine is higher than that of these phenolics, they are less prone to act as copigments, due to their non-planar structure that hinders the interaction with the anthocyanin [51, 52]. Moreover, the presence of ethanol (EtOH) in the medium limits this interaction, since the presence of organic solvents weakens the hydrophobic intermolecular interactions, causing destabilization of the formed complexes [53].

It has been observed that an increase in the degree of methoxylation in ring B of the anthocyanin produces an increase in the magnitude of these interactions. This type of interaction increases the CI of red wines [54].

The study of the copigmentation processes is of great importance in order to find out the relationship between the composition of the grape and the color of the wine. Besides, this type of interactions are thought to be the first step in the formation of new pigments, which determines the color of aged wines [55].

Anthocyanin-derived pigments. At the end of fermentation, the concentration of anthocyanins starts decreasing, first due to the effect of yeasts, and after, *via* condensation, polymerization, oxidation and precipitation reactions.

Some of these reactions imply the degradation of anthocyanin molecules, but others lead to the formation of pigments that give the wine different hues. The wine color changes occurring during aging are attributed to the reaction between anthocyanins and other molecules in the medium, which lead to the formation of new and more stable pigments [56].

These pigments can be classified in two groups: (i) pigments formed by condensation of the anthocyanins with flavanols, which can occur directly or indirectly, mediated by acetaldehyde, and (ii) pyranoanthocyanins, which are products of cycloaddition reactions of anthocyanins with other molecules in the medium, such as pyruvic acid, acetaldehyde, hydroxycinnamic acids, vinylflavanols, etc.

According to their behavior towards pH changes, two different kinds of pigments can be differentiated: (i) Compounds with a similar behavior to that of anthocyanins, which are those formed by direct anthocyanin-flavanol condensation; and (ii) compounds characterized by a high resistance to hydration and decolorization by bisulphite, such as pyranoanthocyanins and pigments formed by acetaldehyde-mediated anthocyanin-flavanol condensation, which are more resistant than the precursor anthocyanins, thus increasing the color stability of aged wines [57, 58].

a) Anthocyanin-flavanol condensation. Pigments can be directly formed [59] or acetaldehyde-mediated [60], generating an ethyl bridge in the structure, by anthocyanin-flavanol condensation. The UV-Vis absorption spectra of these pigments are similar to those of free anthocyanins, which indicates the presence of the chromophore group in the structure, but show an additional shoulder at 450 nm, presents a higher intensity. The acetaldehyde-mediated pigments produce a bathochromic shift at the wavelength of maximum absorption, which give a violet hue to the wine [61].

a1) Direct anthocyanin-flavanol condensation. Two different mechanisms leading to the formation of pigments formed by direct anthocyanin-flavanol condensation have been described depending on the relative position of the flavanol and the anthocyanin in the structure: F-A^+ or A^+-F type pigments.

During the formation of the F-A^+ type pigments, an acid catalysis of the proanthocyanidin interflavanic bond occurs, leading to the formation of an intermediate carbocation F^+ that acts as electrophile as it reacts with the hydrated AOH form of the anthocyanin, which acts as nucleophile. This reaction yields a colorless F-AOH type compound, which undergoes a dehydration to form the red flavylium F-A^+ type pigment. Figure 1.8 shows the forming scheme of such compounds [61].

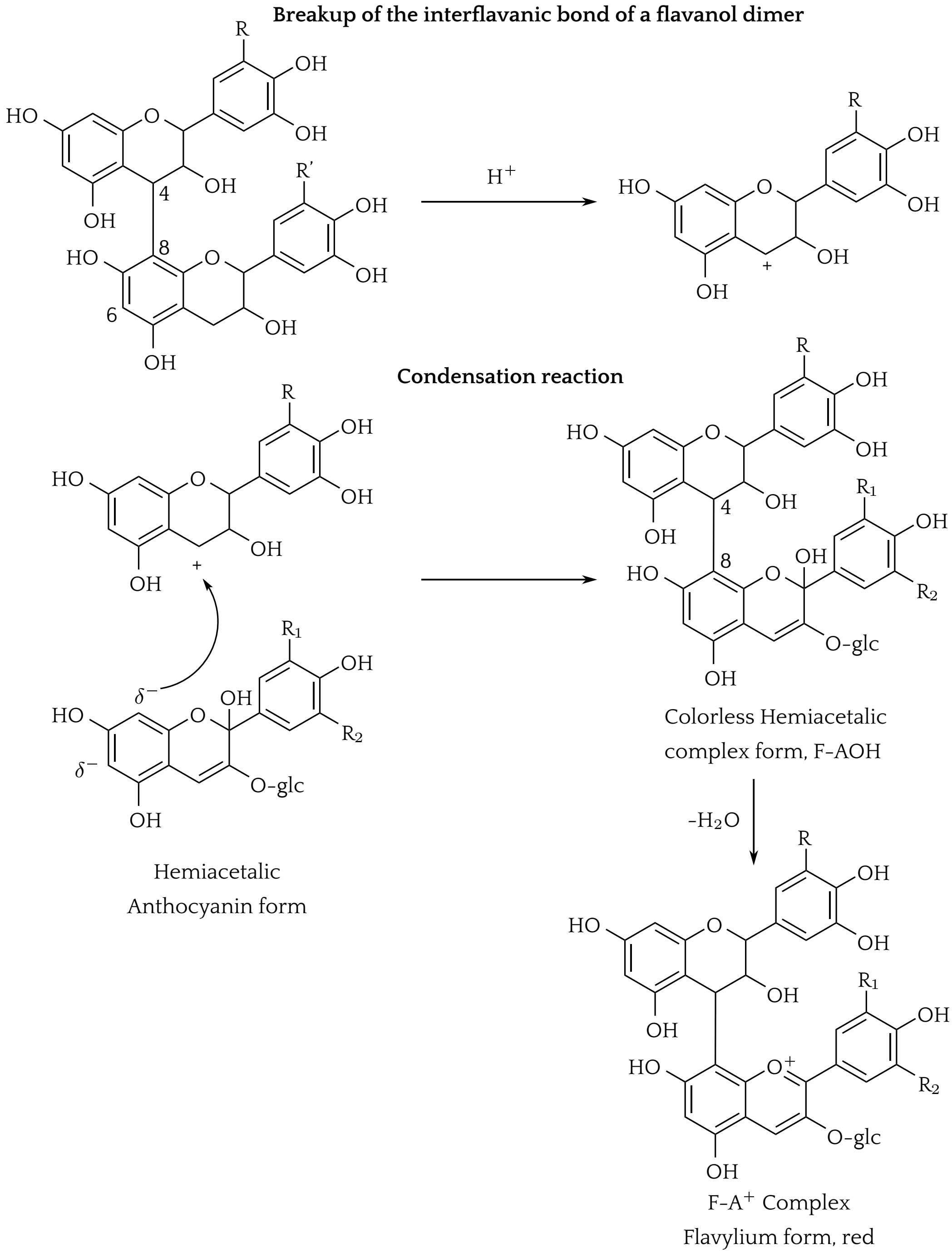


Figure 1.8. Formation scheme of F-A^+ type compounds from a flavanol dimer.

The acid rupture of the interflavanic bond of the proanthocyanidin is favored at acid pH, but it has also been demonstrated to occur at pH 3.2, proving that this kind of compounds can be formed in wine [62].

The flavanol-anthocyanin bond in F-A^+ type compounds can be formed between positions C4 of the flavanol and positions C6 or C8 of the anthocyanin; the F-A^+ compounds with C4-C8 bond being more stable. Mass spectrometry (MS) does not allow the differentiation of the nature of the condensation C4-C8 or C4-C6 [63].

For the formation of A^+-F type pigments, the anthocyanin is in the A^+ form and acts as electrophile. Besides, the hydroxyl groups in positions C5 and C7 of the flavanol have mesomeric effect, confering a nucleophilic character to the flavanol on carbons C6 and C8. A nucleophilic addition of the flavanol to the A^+ yields a complex in which the anthocyanin is present in the colorless flavene form. This compound can be oxidized to the colored A^+ form, and afterwards, to the yellow xanthylium salt or evolve to a colorless product of cyclic condensation with an A-type bond C4-C8 and C2-O-C7 of the anthocyanin and the flavanol, respectively. Figure 1.9 shows a scheme of this route of formation [64].

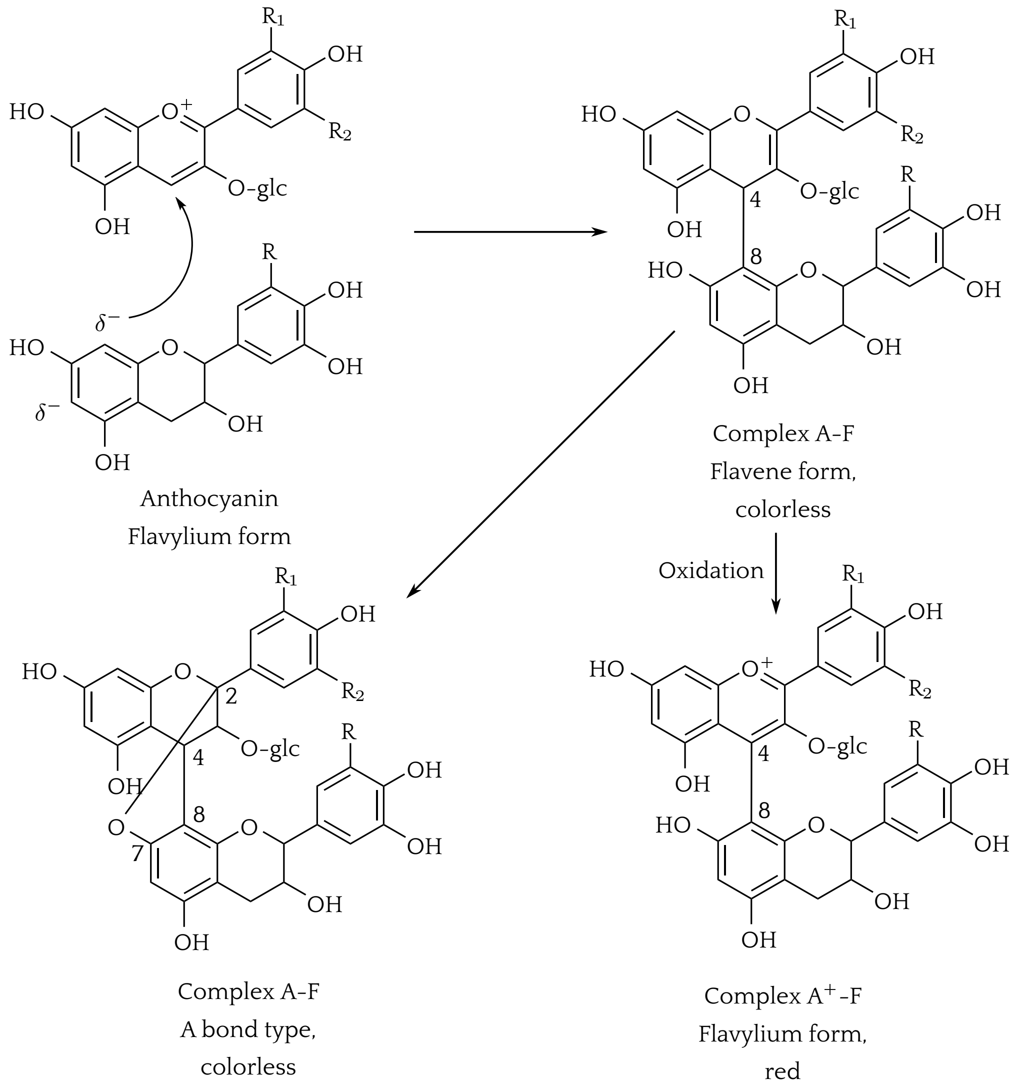


Figure 1.9. Formation scheme of A-F type compounds.

The A^+-F type compounds containing a bicyclic A-type bond are resistant to thiolysis, in contrast with those pigments in which the anthocyanin is present in the flavene form [65]. These colorless compounds have been detected in wine extracts [66].

The fragmentation pattern of A^+-F type compounds in MS is characterized by the loss of glucose (-162 *u*, or the acylated glucose, being in this case a loss of 204 *u*, 308 *u* or 324 *u* depending on the acylation being with acetic, *p*-coumaric or caffeic acid, respectively), the loss of water from the glycosylated compound and the loss of water from the aglycone. Other losses can also occur, such as that of 126 *u*, corresponding to the loss of a phloroglucinol ring (ring A), which indicates that the upper unit of the pigment is the flavanol moiety and the lower is the anthocyanin, since the loss of 126 *u* cannot occur in the ring A of the anthocyanin, and it is specific for the upper moiety of the dimers [67]. The loss caused by a retro Diels-Alder fragmentation of the flavanol does not yield structural information about the compound, since it can take place in both the upper and lower units. The loss corresponding to the elimination of the flavanol or part of the flavanol can also be observed.

At wine pH, anthocyanins react simultaneously as nucleophiles and electrophiles. Both types of reactions are dependent on the pH since the amount of cationic forms, A^+ or F^+, increases with the acidity.

Ellagitannins from wood can enhance the formation of direct condensation products between anthocyanins and flavanols. In addition, gas oxygen (O_2) favors the breakage of proanthocyanidins, reaching the highest concentration levels during the first months of aging in cask.

a2) Acetaldehyde-mediated anthocyanin-flavanol condensation. Acetaldehyde is generated by the oxidation of EtOH or by the metabolism of yeasts, and is naturally present in wine. It is formed at higher concentration in oxidizing conditions, thus the mechanisms in which it plays a role are favored in these conditions.

The formation of pigments as a result of the acetaldehyde-mediated anthocyanin-flavanol condensation requires acidic pH for the acetaldehyde to be in the cationic form. Once protonation of the acetaldehyde occurs, the resulting cation undergoes an addition to a nucleophilic position of ring A of the flavanol. This addition can take place in positions C6 or C8 of the phloroglucinol ring, leading to an unstable product that protonates to yield the ethyl-flavanol cation. This cation undergoes nucleophilic addition of the anthocyanin to yield the derivative anthocyanin-ethyl-flavanol pigment [68]. The nucleophilic attack between the two phloroglucinol A rings (flavanol and anthocyanin) can go *via* positions C6 or C8, but it is more likely to occur on position C8 as the negative charge is better stabilized [69]. As well, the ethyl-flavanol cation can undergo a dehydration process to yield the vinylflavanol, which can also react with anthocyanins to produce a different pyranoanthocyanin derivative. The scheme of formation of these derivatives is shown in Figure 1.10.

Different isomers can be found among the acetaldehyde-mediated condensation products. On the one hand, diastereoisomers (*R*, *S*) are formed due to the asymmetric carbon of the ethyl bridge. On the other hand, regioisomers (position isomers) (C8-C8 or C8-C6) result due to the different possible linking positions between the anthocyanin and the flavanol [70, 71]. Their formation and loss is faster than for the direct condensation reaction products [72]. These compounds are more stable regarding pH changes and decolorization by sulphur dioxide (SO_2). In contrast, they are less stable in aqueous solutions due to the breakage of the ethyl bridge between anthocyanin and flavanol [73].

In tandem mass spectrometry (MS/MS) spectra of these pigments, the ion fragment resulting from the breaking of the ethyl bridge is the most intense ion. The intensity of this fragment ion is higher than that corresponding to the loss of glycoside moiety, showing a different behavior compared to the other anthocyanin derivative pigment families.

The color of these pigments is bluish red, giving the wine a violet hue, especially straight after fermentation is finished. In general, the alkyl-interflavonoid bond leads to a bathochromic shift of about 15 nm, but the nature of the alkyl group does not seem to influence.

b) Pyranoanthocyanins. The other main group of anthocyanin-derived pigments is formed through a nucleophilic cycloaddition reaction of compounds present in wine to the anthocyanin in the A^+ form, leading to the formation of a new pyran ring between positions C4 and the hydroxyl group in position C5 of the anthocyanin. Due to the formation of this new ring these compounds are known as pyranoanthocyanins (Figure 1.11).

The formation mechanism shows that the presence of a polarizable double bond is required for the cycloaddition C4/C5 to occur [74]. Some of the molecules which can undergo this reaction are pyruvic acid, acetaldehyde, acetoacetic acid, hydroxycinnamic acids and vinylflavanols. These

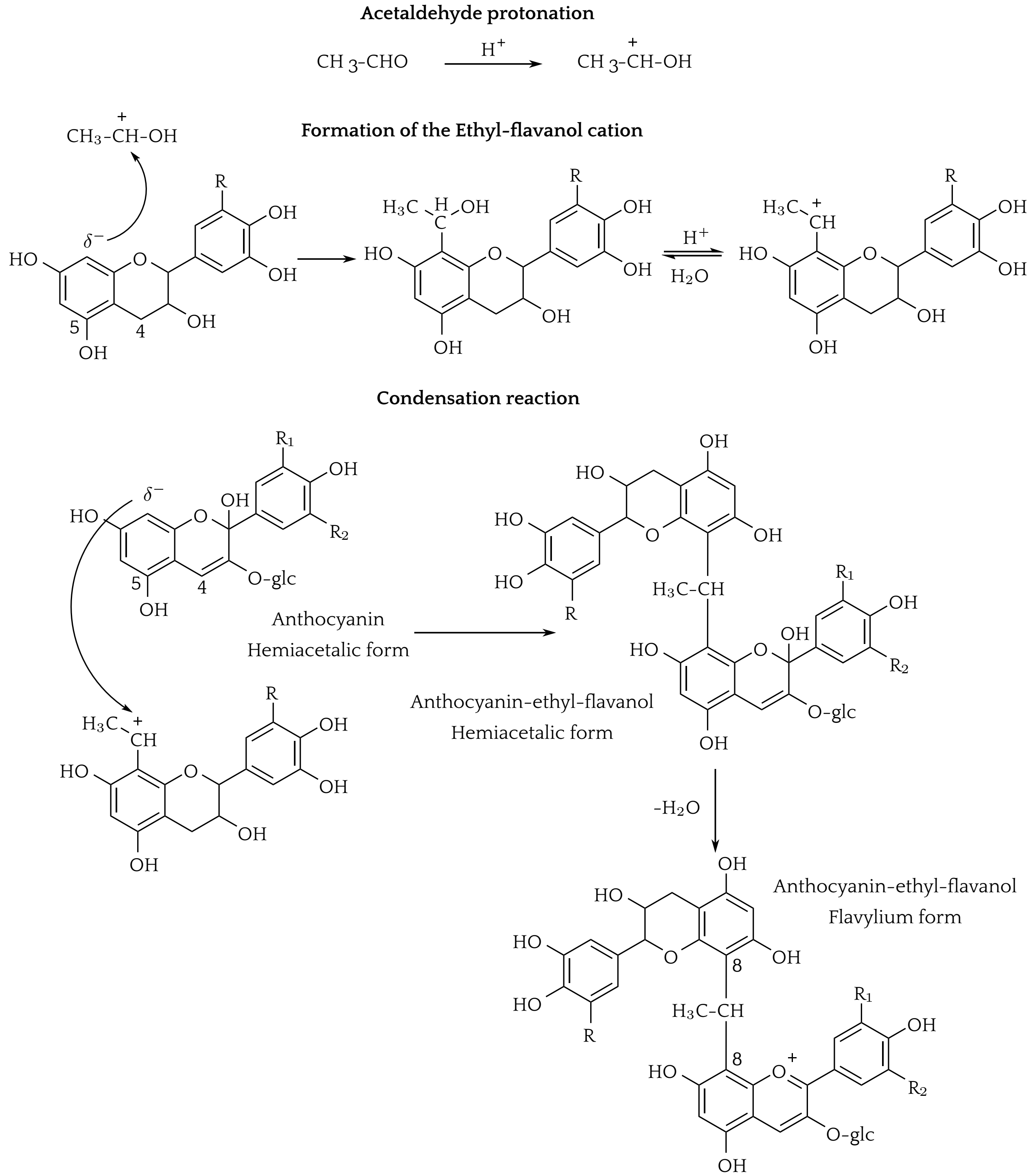


Figure 1.10. Formation scheme of A-ethylidene-F compounds.

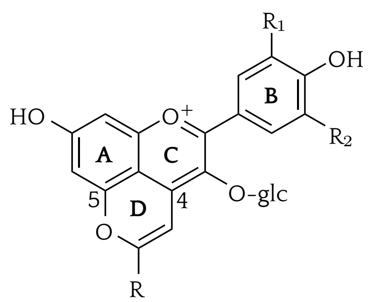


Figure 1.11. Basic chemical structure of pyranoanthocyanins.

compounds show keto-enol tautomerization and can react with anthocyanins in their enol form [75, 76, 77, 78, 79].

Portisins are more complex molecules which are also formed by this mechanism. When anthocyanin derivatives react with pyruvic acid, vinylflavanols and hydroxycinnamic acids. The name of "Portisin" comes from the fact that they were detected for the first time in Porto wines [80].

Due to the high stability of the new pyran ring, the mass spectra of pyranoanthocyanins only show the loss of the glucose or acylated glucose moieties. In the case of anthocyanin derivatives with vinylflavanols the fragment ion product of the retro Diels-Alder reaction of the flavanol is also detected since the new pyran ring does not break either in MS or in MS/MS. These derived pigments exhibit the same fragmentation pattern as the corresponding precursor anthocyanin [65].

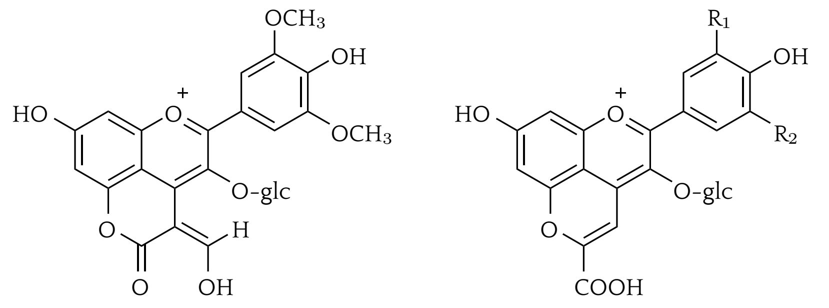
Pyranoanthocyanins, with the exception of the portisins, produce a hypsochromic shift of the wavelength of maximum absorbance in the UV-Vis spectrum (Band I), giving the wine a reddish hue. A possible explanation for the observed hypsochromic shift is that the charge in ring C might be stabilized by resonance, being partially delocalized in the oxygen atom of ring D. A small absorption band in the region of 370 nm is also observed, which is characteristic of C4 substituted anthocyanins [81].

The C4/C5 cycloaddition reaction gives a high chemical stability to the compound as it protects the position C4 from the nucleophilic attack of water, avoiding the formation of the colorless carbinol base; shields it from decolorization by SO_2; and provides it resistance to oxidation. While anthocyanins lose around 80% of color intensity when the pH is increased from 1 to 5 as a result of the formation of the colorless carbinol base, the color of pyranoanthocyanins does not change due to the protective effect of the new pyran ring.

b1) Derivatives with pyruvic acid, acetaldehyde and acetoacetic acid. Pyruvic acid is the most important metabolic intermediate, generated during the metabolism of the yeasts during AF and due to the activity of the lactic acid bacteria during MLF [82].

In 1997 Bakker and Timberlake [83] proposed a structure based on Nuclear Magnetic Resonance (NMR) experiments for a novel compound derived from Mv-3-*O*-glc, known as Vitisin A, which was not present in fresh grapes but only in stored grapes or aged wines. This structure consisted on a Mv-3-*O*-glc nucleus with an additional pyran ring with a keto and a hydroxyethylene group (Figure 1.12a). In 1998, Fulcrand *et al.* [81] proposed a different structure and mechanism of formation for the same compound. The proposed structure in this case consisted on a Mv-3-*O*-glc nucleus with a pyran ring containing a carboxylic substituent. This last structure (Figure 1.12b) has been confirmed by different authors based on NMR and MS experiments [54, 84].

The formation of this kind of pyranoanthocyanins result from the cycloaddition reaction between positions C4 and the hydroxyl group on position C5 of the anthocyanin with an ethylene bond of the molecules, pyruvic acid, acetaldehyde or acetoacetic acid. The initial bond formed between the position C4 of the anthocyanin and one of the carbons of the double bond of these molecules is due to the strongly electrophilic nature of the A^+ and the nucleophilic nature of the double bond of the enolizable molecule. The resulting intermediate reacts with the hydroxyl group in position C5 of the anthocyanin to yield a new pyran ring in the structure. Then, a dehydration process followed by an oxidation occurs, leading to the formation of the pyranoanthocyanin derivative, in which the conjugation of the π electrons enables aromatization of the new ring formed and charge delocalization (Figure 1.13). In an acidic medium, such as wine, the enolic form of pyruvic acid reacts with the anthocyanin. As mentioned previously, this reaction increases



(a) (b)

Figure 1.12. Anthocyanin-pyruvic derivative structure as proposed by (a) Bakker and Timberlake [83] and (b) Fulcrand *et al.* [81].

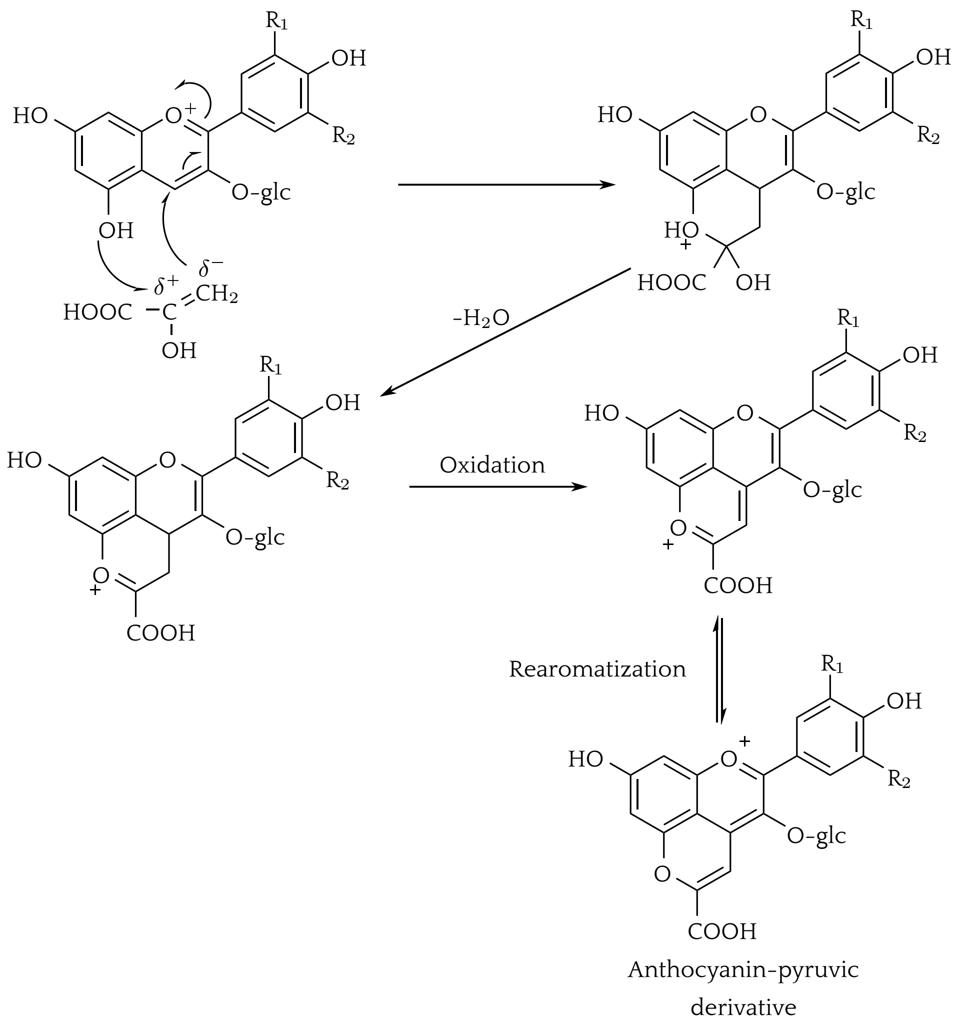


Figure 1.13. Formation scheme for anthocyanin-pyruvic derivatives type.

the stability of the product obtained, especially at high pH values, from SO_2 and temperature rise.

Aging of the wine in casks seems to favor the formation of the derivatives with these molecules, since their formation requires oxidizing conditions [85], not O_2 itself but species containing it.

These cycloaddition reactions can also occur with other secondary metabolites, such as acetaldehyde and acetoacetic acid. The corresponding derivative of anthocyanin Mv-3-*O*-glc and acetaldehyde is also known as Vitisin B.

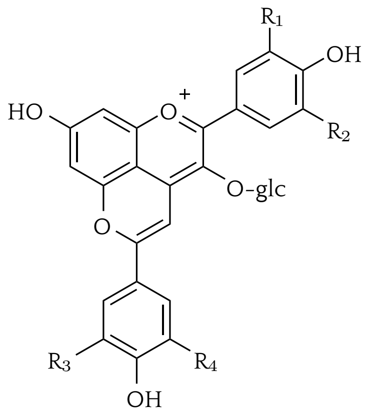
Acetaldehyde in wine comes from two sources, *i.e.* the metabolism of yeasts during AF and the oxidation of EtOH in the presence of phenolics during aging [51]. The highest concentrations of

Vitisin B are found in Porto wines since acetaldehyde is added during the wine-making process. The pyranoanthocyanin derivatives with acetaldehyde are also known as vinyl adducts [82].

Acetoacetic acid is formed during the second fermentation and the post-fermentation aging under reductive conditions. The pyranoanthocyanin derivatives with acetoacetic acid have been detected in wines produced from *Tempranillo* grapes [86]. The cycloaddition reactions of anthocyanins with acetaldehyde and acetoacetic follow the same formation route as the derivatives with pyruvic acid, with an additional decarboxylation step in the case of the acetoacetic acid. This reaction can also occur with acetone, but it is not observed in nature.

These pyranoanthocyanin derivatives produce a hypsochromic shift on the wavelength of maximum absorption in the UV-Vis spectrum (Band I). Vitisin A produces a hypsochromic shift from 503 to 510 nm, and Vitisin B from 490 to 494 nm [87]. The corresponding derivative of Mv-3-*O*-glc with acetoacetic acid has a similar UV-Vis spectrum to that to Vitisin B, but with a maximum wavelength of absorption at 478 nm (Band I).

b2) Derivatives with hidroxycinnamic acids. Vinylphenol, vinylcatechol, vinylguaiacol and vinylsyringol are the decarboxylated derivative compounds of hydroxycinnamic acids, *p*-coumaric, caffeic, ferulic and sinapic, respectively. These volatile compounds are associated with unpleasant aromas in wine. Hydroxycinnamic acids and some of their derivatives can react with anthocyanins to produce anthocyanin-vinylphenol, anthocyanin-vinylcatechol, anthocyanin-vinylsyringol and anthocyanin-vinylguaiacol derivatives (Figure 1.14).



	R_3	R_4
Vinylphenol	-H	-H
Vinylcatechol	-H	-OH
Vinylguaiacol	-H	$-OCH_3$
Vinylsyringol	$-OCH_3$	$-OCH_3$

Figure 1.14. Chemical structure of anthocyanin derivatives with hidroxycinnamic acids.

The formation of these derivatives has been described by two different mechanisms. On the one hand, anthocyanins can react with the product of decarboxylation of hidroxycinnamic acids [57], which occurs due to the activity of cinnamate decarboxylase present in the yeast *Saccharomyces cerevisae*, to give the corresponding anthocyanin-4-vinylphenol and anthocyanin-4-vinylguaiacol. This enzyme is specific for *p*-coumaric and ferulic acids and does not perform the decarboxylation of caffeic and sinapic acids [88]. This formation mechanism is fast and important in the early stages of wine aging (Figure 1.15) [89].

On the other hand, a cycloaddition reaction between anthocyanin and hydroxycinnamic acid [90], followed by a subsequent decarboxylation can give of the four different derivatives (Figure 1.16), including anthocyanin-4-vinylcatechol and anthocyanin-4-vinylsyringol derivatives. This formation mechanism is slow and important during maturation and aging [70], and requires the aromatic ring of the hydroxycinnamic acid to have donor substituents in order to stabilize the formed carbenium ion intermediate [91].

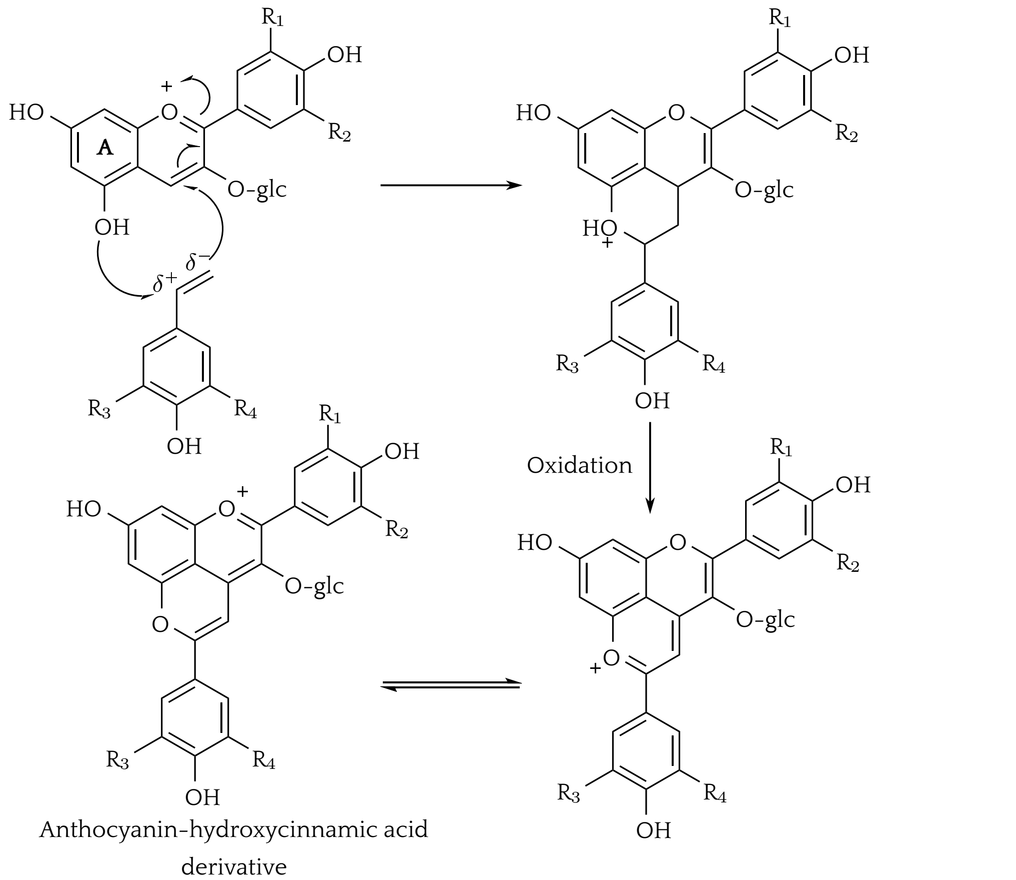


Figure 1.15. Formation scheme of the anthocyanin-decarboxylated hydroxycinnamic acid derivatives.

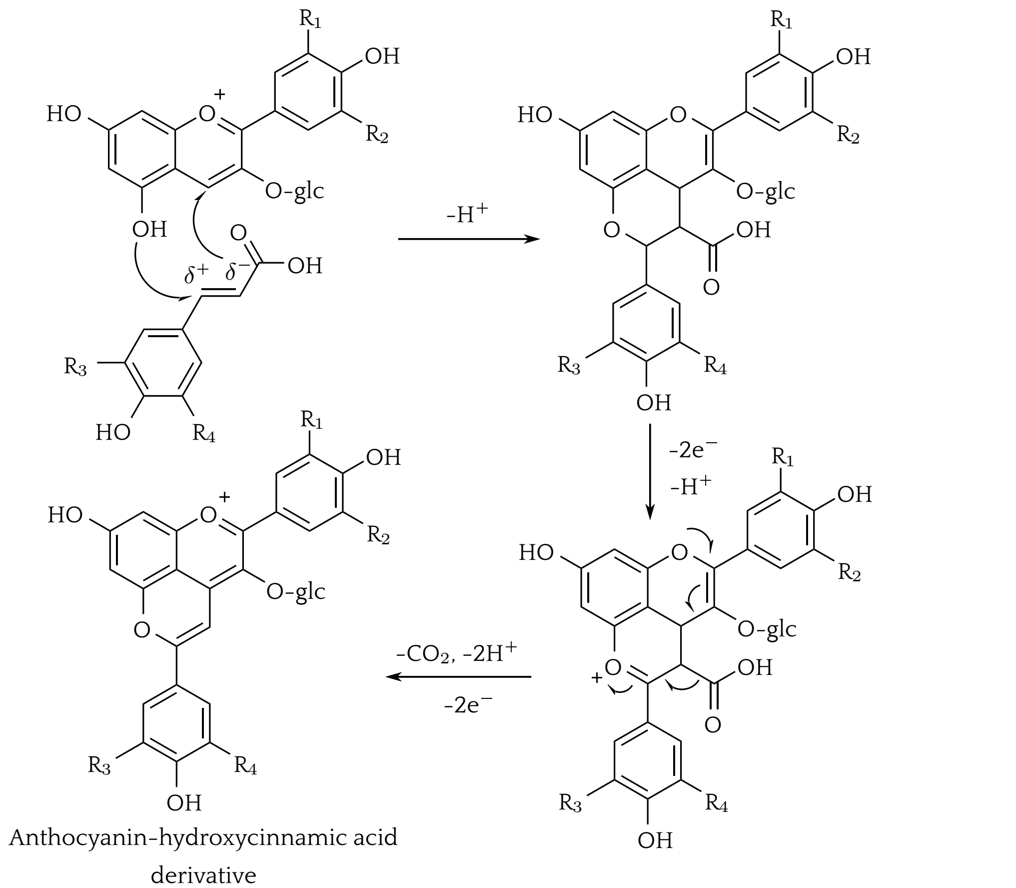


Figure 1.16. Formation scheme of the anthocyanin-decarboxylated hydroxycinnamic acid derivatives.

The formation of pyranoanthocyanin derivatives with hydroxycinnamic acids, especially those with vinylphenol and vinylguaiacol, can be observed in relatively young wines; after an initial increase in their concentration, they remain stable during the first two years of aging. After two or three years of aging, the concentration of these compounds increases again due to the direct reaction of anthocyanins with hydroxycinnamic acid [74].

b3) Derivatives with vinylflavanols. Anthocyanins react with vinylflavanols to produce derivatives that also have in their structure the pyran ring D (Figure 1.11). The vinylflavanols may consist of one or more monomers of flavanol. Such compounds have stereoisomers for two reasons: first, the flavanol can be (+)-(gallo)catechin or (-)-epi(gallo)catechin, and second, the binding position of anthocyanin-flavanol can be from C6 or C8 of the flavanol [92].

The formation of this type of derivatives begins once the acetaldehyde protonation has occurred, as in the case of anthocyanin derivatives with flavanols formed by acetaldehyde-mediated condensation. After that, the addition of the resulting cation to a nucleophilic position of the flavanol A ring takes place on the C6 or C8 of the phloroglucinol ring, yielding an unstable product which protonates to produce ethylidene-flavanol cation (Figure 1.17). The vinylflavanols can also result from the breaking of anthocyanin-ethylidene-flavanol pigments [93]. The vinylflavanol formed undergoes a nucleophilic cycloaddition reaction with the anthocyanin in a mechanism similar to that previously described for other pyranoanthocyanin derivatives (Figure 1.18).

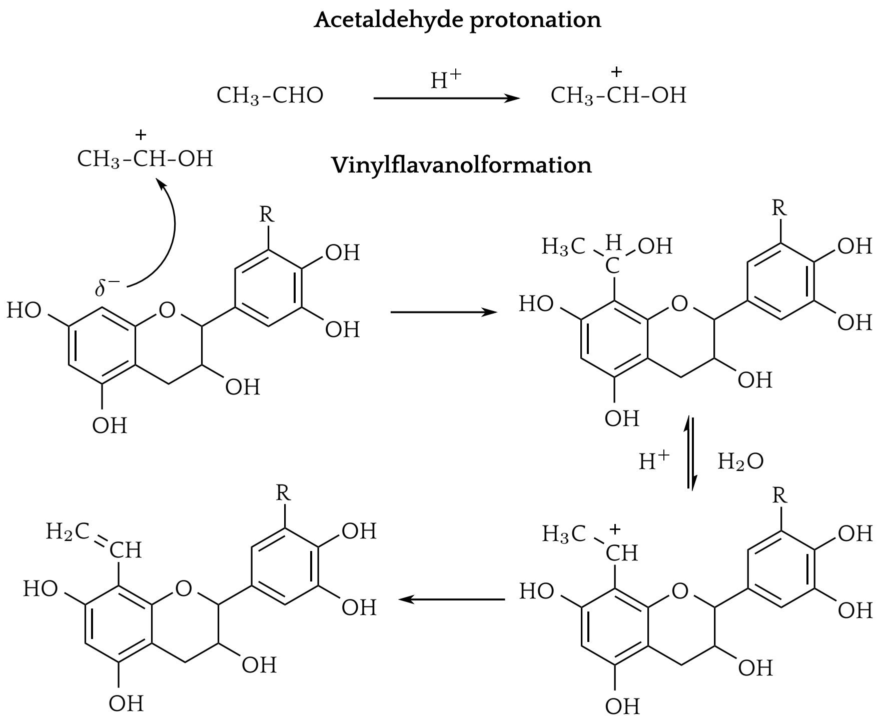


Figure 1.17. Acetaldehyde protonation and vinylflavanol formation.

The pyranoanthocyanin derivatives with vinylflavanols are responsible for the orange hue in wines, presenting a wavelength of maximum absorption in the UV-Vis spectrum at 500-511 nm (Band I). The substitution present in C4 makes them more resistant to discoloring by the medium pH and by the presence of SO_2 than the ethylidene-bridged pigments [94]. If the flavanol is a dimer, the pigment presents a bathochromic shift of *ca.* 9 nm compared to those containing a monomer. This highlights the importance of the flavanol in the pigment color, and suggests that a phenomenon of intramolecular co-pigmentation occurs between the flavanol part and the chromophore group of the pyranoanthocyanin.

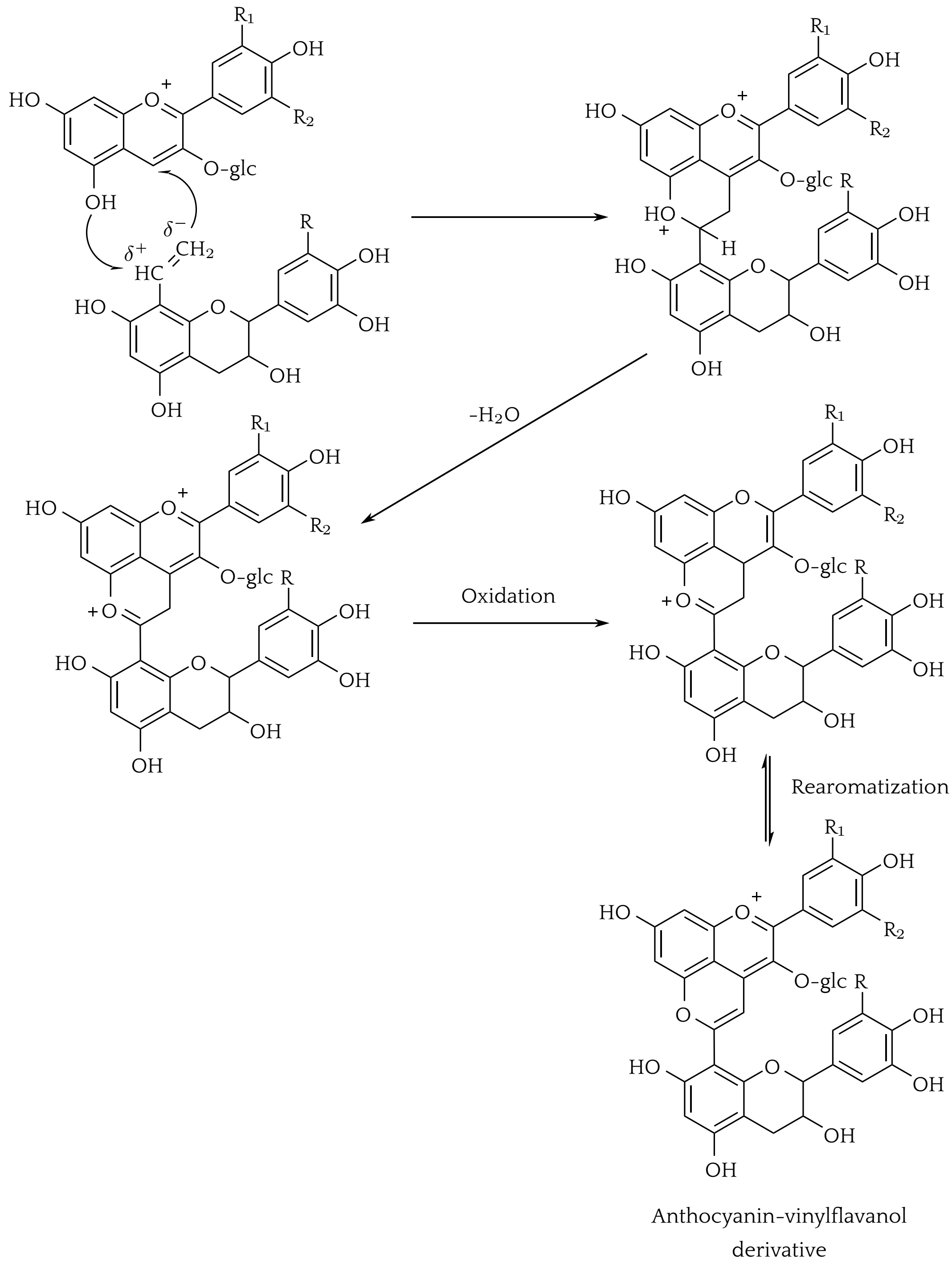


Figure 1.18. Acetaldehyde protonation and vinylflavanol formation.

b4) Portisins. Portisins are the result of the interactions between derivatives of anthocyanins with pyruvic acid, vinylflavanols or derivatives of hydroxycinnamic acids. The formation schemes of these type of derivatives are shown in Figures 1.19 and 1.20, respectively.

The broad conjugation of π electrons provides high stability to the pigment, producing bathochromic shifts in the wavelength of maximum absorption of the UV-Vis spectrum (Band I), giving the wine violet hues. An increment on the hydroxylation of the phenolic ring B of the portisin structure contributes to a bathochromic shift in Band I. The wavelength of maximum absorption of the spectrum is 572 nm for the Mv-3-*O*-glc derivatives [95].

These derivatives have a high resistance to discoloration caused by the high protection of the chromophore group against nucleophilic attack of water or SO_2. This resistance is greater for portisins of vinylflavanol derivatives than for portisins of hydroxycinnamic acid derivatives because the hydroxycinnamic acid residue is smaller and does not protect the chromophore as efficiently as the vinylflavanol one [96].

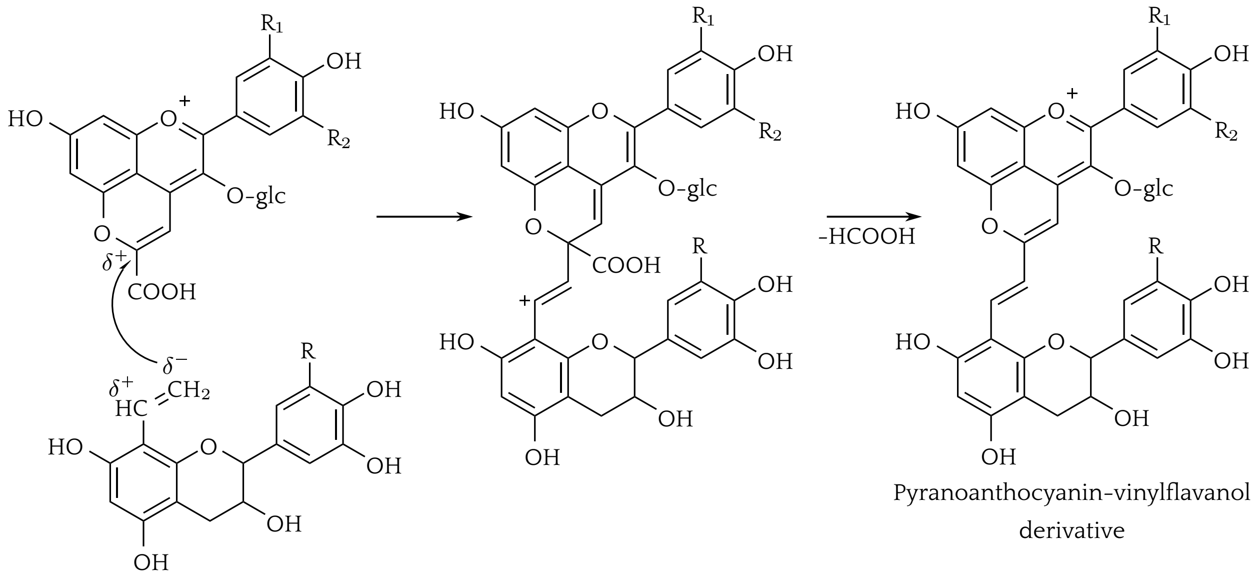


Figure 1.19. Reaction scheme of anthocyanin-pyruvic derivative with vinylflavanol to yield the pyranoanthocyanin-vinylflavanol compound type.

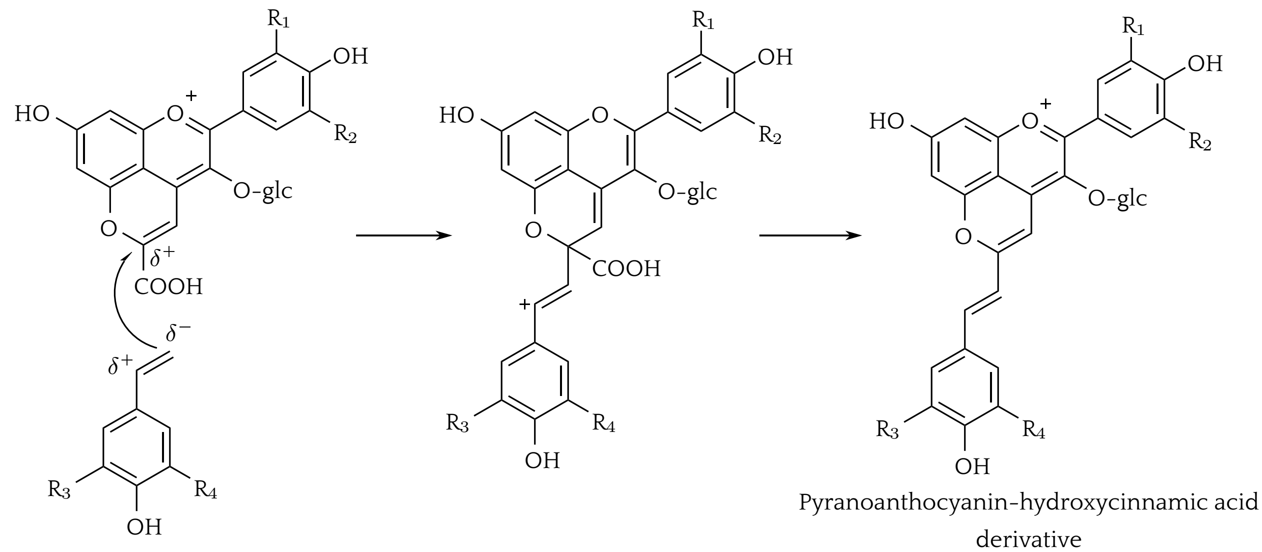


Figure 1.20. Reaction scheme of anthocyanin-pyruvic derivative with hydroxycinnamic acid derivative to form the pyranoanthocyanin-hydroxycinnamic acid compound type.

1.1.3.3 Condensed tannins

Condensed tannins are polymers of flavan-3-ols and are also known as proanthocyanidins. They can produce stable combinations with proteins and other polymers like polysaccharides, and are responsible for the sensory attribute of astringency in wine, as a result of their interaction with saliva proteins [97].

Procyanidins are constituted of cat and epicat monomers, and prodelphinidins, of gallocat and epigallocat monomers. Mixed proanthocyanidins are formed by both units (epi)cat and (+)-Gallocatechin or (-)-Epigallocatechin, unknown isomer ((epi)gallocat), which are present in grape skin and seeds [98].

Flavan-3-ol monomers and proanthocyanidins have both a clear tendency towards polymerization, which can take place directly, through a interflavanoid bond type B and type A, and indirectly, mediated by acetaldehyde, glyoxylic acid or furfural.

Tannins formed by direct condensation: B bond type B-type procyanidins are linked by a single interflavonoid bond [99, 100, 101, 102]. This can occur between two or more flavan-3-ols, forming from dimers, trimers or tetramers to tannins that may contain 30 units of flavan-3-ol, reaching mass to charge ratio (m/z) higher than 6000.

Among type B procyanidin dimers, there are eight best known made of two (epi)cat moieties, which differ in spatial configuration and interflavonoid link positions. In four of them, the interflavonoid link is formed between C4 and C8 (Figure 1.21), whereas in the other four is between C4 and C6 (Figure 1.22). The same occurs for prodelphinidins B1 to B8, which are formed by two units of (epi)gallocat. Mixed dimers with one unit of each type of flavan-3-ol can also be formed.

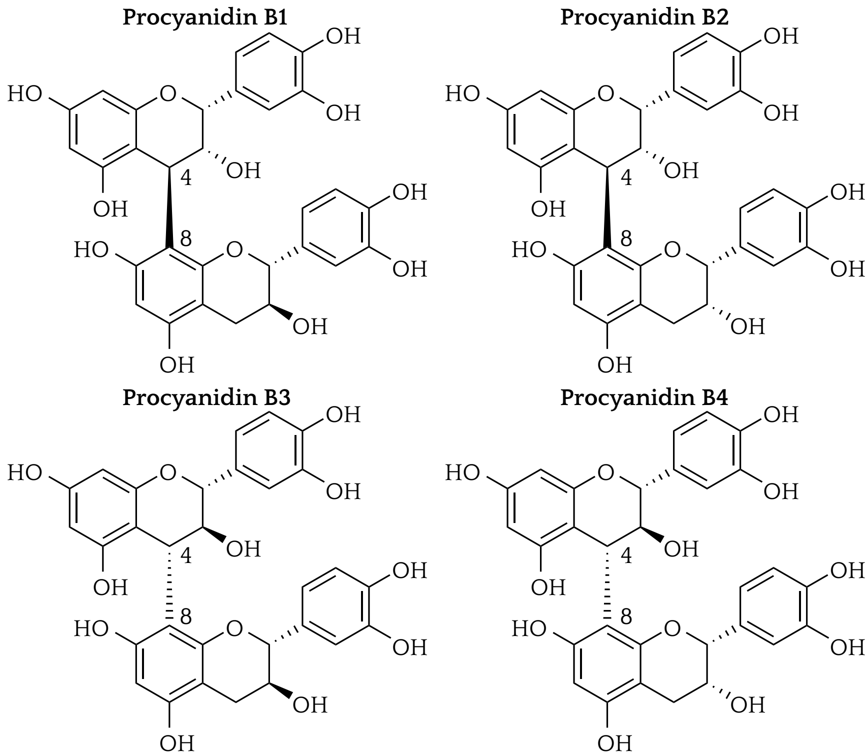


Figure 1.21. Chemical structure of procyanidins B1 to B4.

The polymerization mechanism to form proanthocyanidins is not clear [103, 104], even though all proposed condensation mechanisms agree that a nucleophilic addition of C6 or C8 positions of the bottom flavan-3-ol to the C4 position of the upper unit occurs, which is in an electrophile state after its conversion in different reaction intermediates [105].

Proanthocyanidins from B9 to B16 are known as dehydrodicatechins since they result from an enzymatic chemical oxidation of the flavan-3-ols. These oxidation products contain bonds between C6' and C8 or C6' and C6 in their structures (Figure 1.23), which are the result of the condensation between ring B of the upper flavan-3-ol and ring A of the bottom unit [106, 107, 108]. Similarly to other proanthocyanidins, they differ on their spatial configuration.

Tannins formed by direct condensation: A bond type A-type proanthocyanidins differ from B-type ones because the formers have an additional interflavanoid ether link between C2 and C5 or C2 and C7 (Figure 1.24). This link is originated from an intramolecular link in its precursor B-type

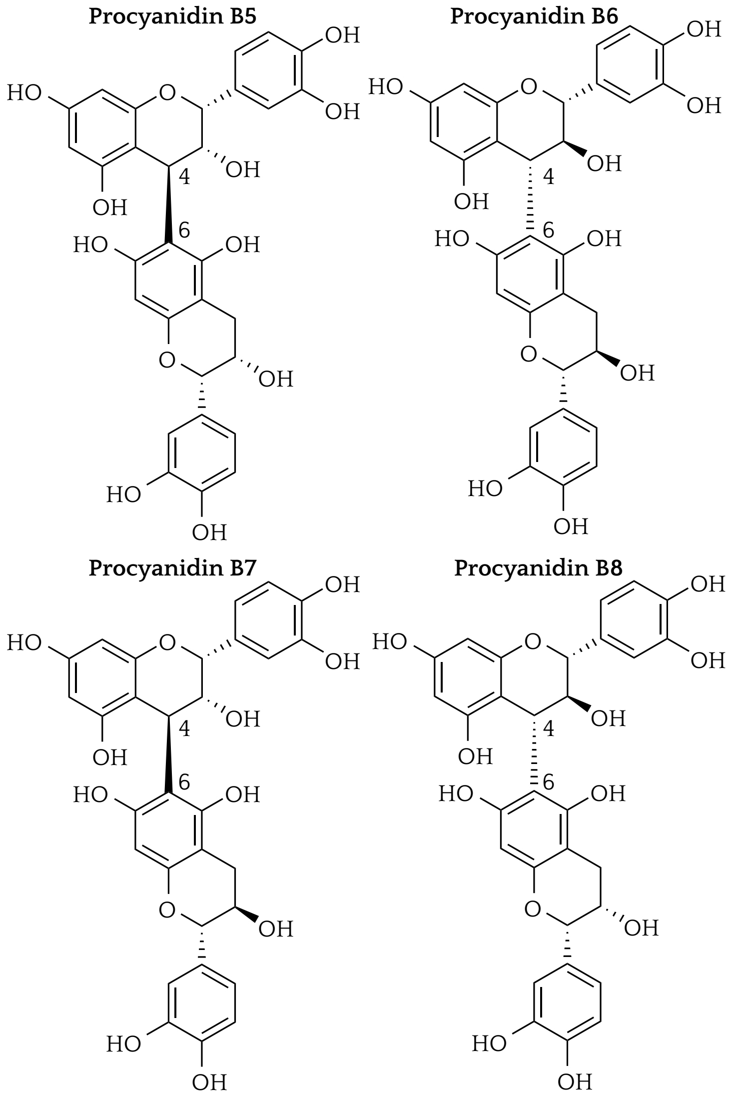


Figure 1.22. Chemical structure of procyanidins B5 to B8.

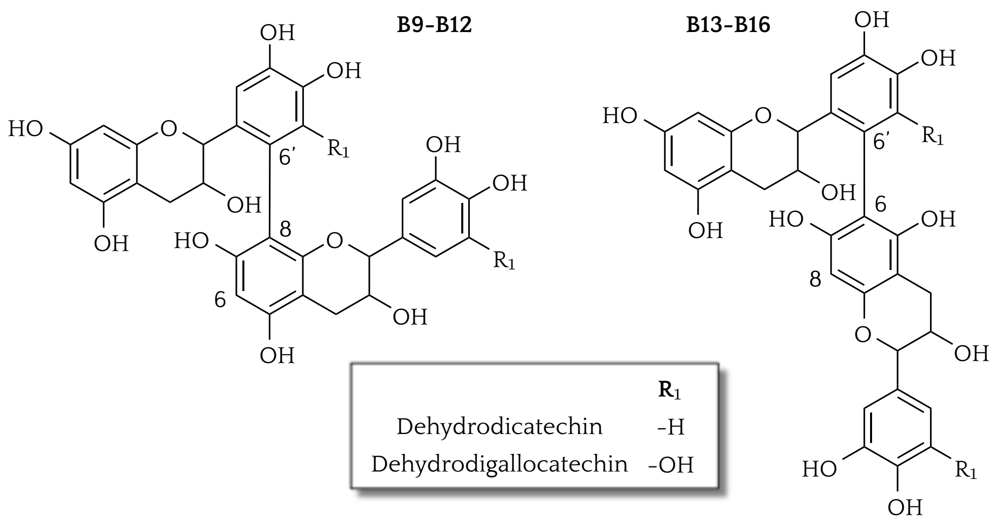


Figure 1.23. Chemical structures of dehydrodicatechins B9 to B16.

proanthocyanidin. Thus, procyanidin A2 comes from procyanidin B 2 (PCB2) when an intramolecular bond is formed between C2 and C7 [109]. Proanthocyanidins A type have been detected in some plants [110], cranberries [111], grapes [112] and wine [113].

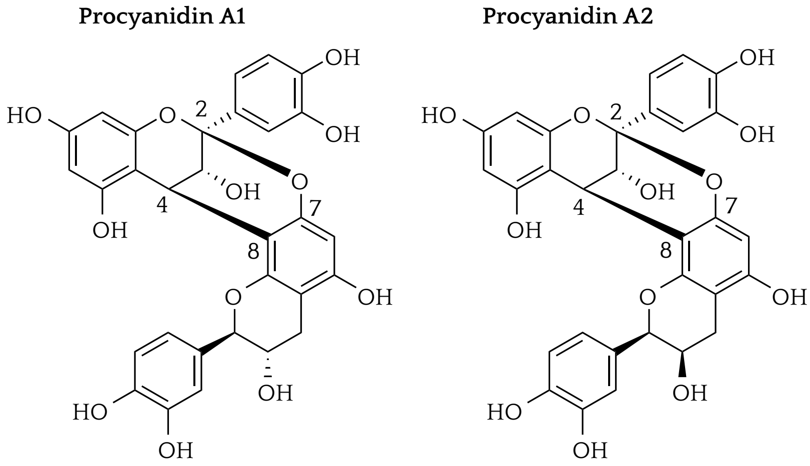


Figure 1.24. Chemical structures of procyanidins A1 and A2.

Proanthocyanidin trimers with one A-type interflavonoid bond and two B-type bonds have been detected in plums [110], peanut skin [114] or berries [115] (Figure 1.25), and are also called proanthocyanidins of type A [39].

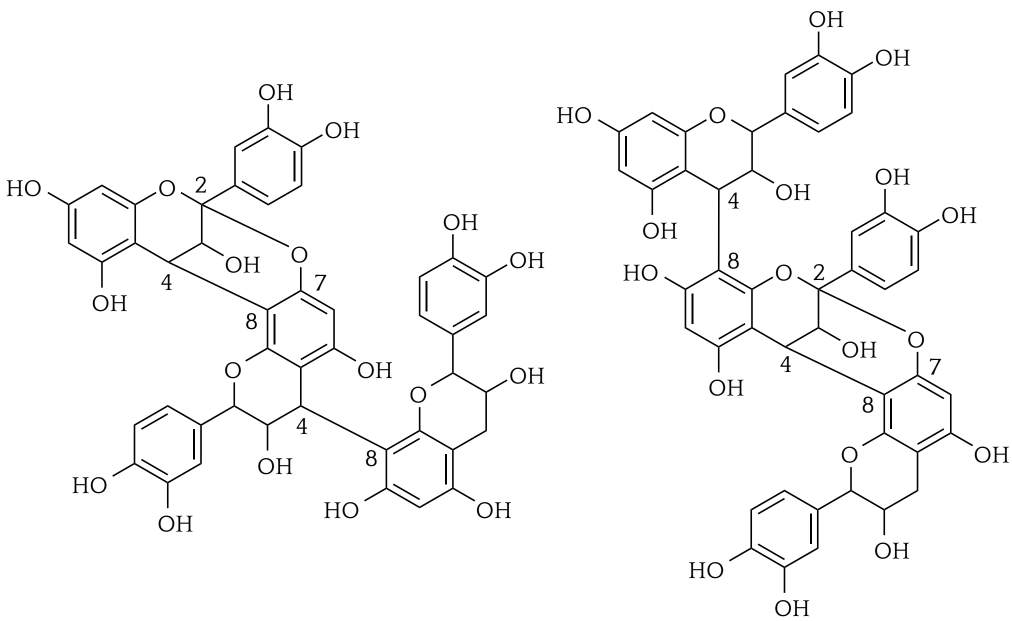


Figure 1.25. Chemical structure of the trimers of type A. Left: (epi)cat-(4→8, 2→O→7)-(epi)cat-(4→8)-(epi)cat, and right: (epi)cat-(4→8)-(epi)cat-(4→8, 2→O→7)-(epi)cat.

Tannins formed by indirect condensation Tannins formed by indirect condensation are those in which the condensation of two or more flavan-3-ols occurs through the chemical action of another molecule, such as acetaldehyde, glyoxylic acid or furfural. The presence of acetaldehyde in wine can have two origins: its biochemical production by yeast metabolism during AF [116], and the oxidation of EtOH. This compound plays an important role during wine aging [117]. Glyoxylic acid is the product of tartaric acid oxidation [118], and furfurals are either formed during grape juice preparation [119] or extracted from the wood barrels during wine aging, contributing directly to wine aroma and flavor [120].

The first step of the formation mechanism of this type of tannins is a nucleophilic addition of the C8 or C6 position of the flavan-3-ol to the carbocation of the intermediate molecule (*i.e.* acetaldehyde, glyoxylic acid, furfural...) [57]. Then, the adduct formed loses a water molecule to yield another carbocation, which suffers a nucleophilic addition from C8 or C6 of a second flavan-3-ol unit [121]. This reaction can take place between positions C6 to C8 or C6 to C6, yielding different positional isomers (Figure 1.26). The condensed tannin with a link between positions C6 and C8 is asymmetric, thus the compound presents two isomers, *R* and *S*, whereas in the other cases (link between C8 and C8, and link between C6 and C6) it is not asymmetric.

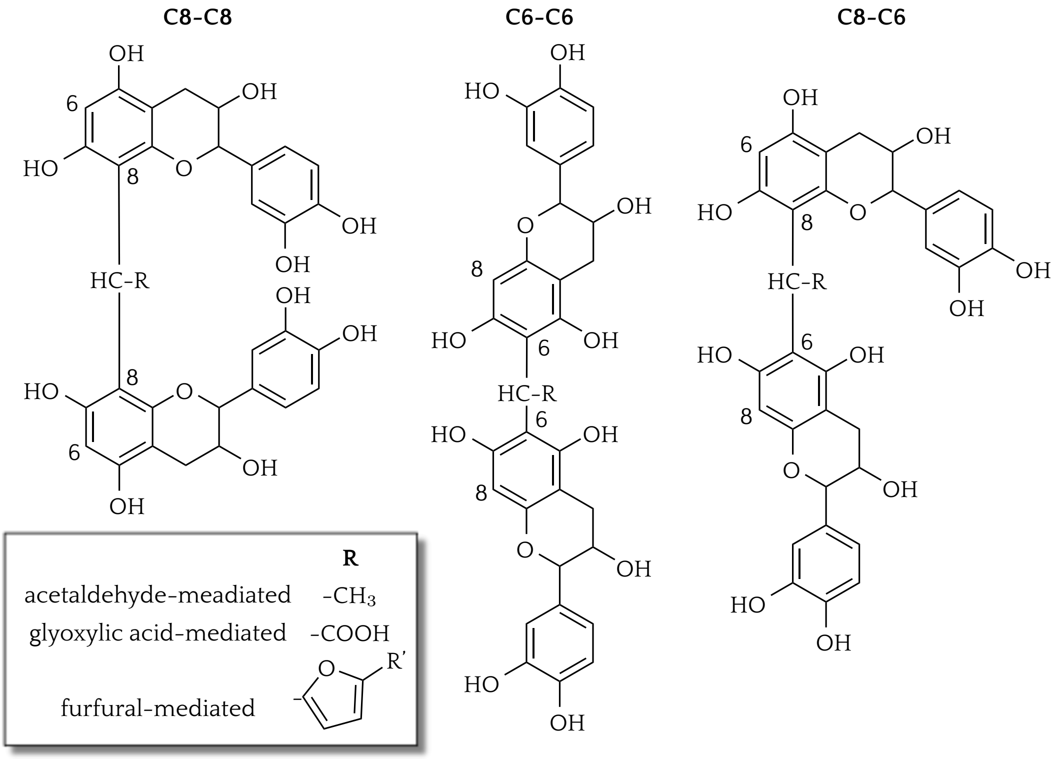


Figure 1.26. Chemical structure of the different positional isomers of tannins formed by indirect condensation.

In the case of acetaldehyde-mediated condensed tannins, a depolymerization reaction or a dehydration of the ethyl alcohol-flavan-3-ol adducts formed during the condensation process can lead to the formation of vinyl-flavan-3-ols [122] (Figure 1.27).

1.1.3.4 Hydrolyzable tannins

Hydrolyzable tannins are polyesters derived from sugar (D-glucose) which are formed by condensation of several units of gallic or ellagic acid esterified with one or more sugar molecules. Gallotannins are formed when gallic acid forms the ester bond, and ellagitannins, when ellagic acid forms it (Figure 1.28). Hydrolyzable tannins are present in oak wood [123]; the quantities of non-volatile ones vary according to the toasting level of oak [124]. Gallotannins are polygalloylated glucose esters present in the galls of oak which are allowed to be added to wine as commercial products. Ellagitannins are believed to be formed from gallotannins by oxidative coupling between two neighboring galloyl groups.

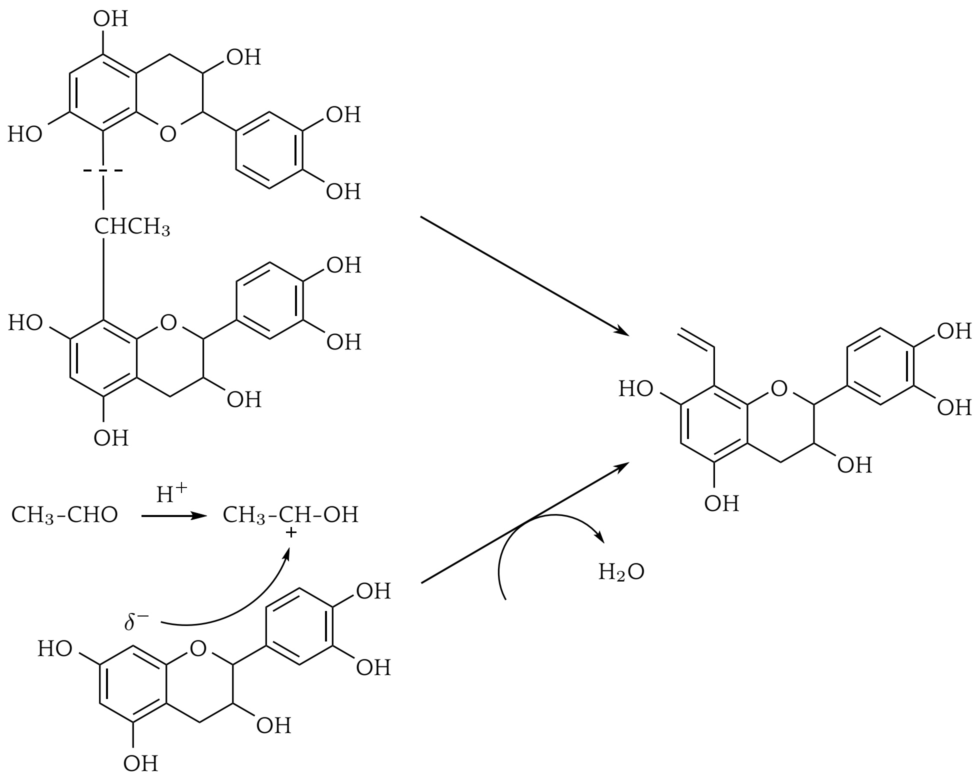


Figure 1.27. Formation scheme of a vinyl-flavan-3-ol: vinyl-(epi)catechin.

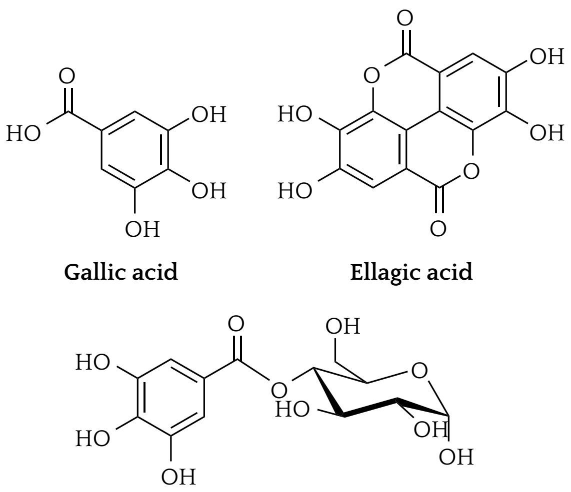


Figure 1.28. Chemical structures of gallic and ellagic acids and one gallotannin, galloyl-glucose.

1.2 Analytical methods for phenolic compounds

Structural characterization of phenolic compounds requires the use of rapid and reliable methods for the separation and identification of these natural compounds present in wine, grape berries and grape pomace.

Anthocyanins are generally highly water soluble and easily extracted from the grape berries by solid-liquid extraction with polar solvents such as methanol (MeOH). It is important that the pH of the extracting solvent is lowered with small amounts of acid, making it suitable for preventing the degradation of anthocyanins [125].

Anthocyanins have the ability of transforming their structure and being involved in complexation reactions, which difficult their determination independently from other flavonoids due to their similar structure and characteristics [126].

1.2.1 High Performance Liquid Chromatography

Separation techniques allow the identification of the components of complex mixtures, such as wine. Liquid chromatography is a technique frequently used for the separation of phenolic compounds, which is achieved according to their polarity and molecular weight [127]. Low pressure chromatography [128] has been employed for the identification of anthocyanins, however, it does not manage to separate complex mixtures.

High-performance liquid chromatography (HPLC) coupled to spectrophotometry UV-Vis and MS results a very suitable technique for phenolic analysis, since it provides on-line structural information of the compounds in complex mixtures. HPLC is the separation technique most commonly used for the identification and quantification of anthocyanins [129] and tannins [130]. Reverse phase chromatography using C18 columns allows excellent separations for anthocyanins and other phenolic compounds, providing high sensitivity and relatively short analysis time [131]. This technique is also widely used to study the profile of the tannins in grapes and wines [132].

Regarding the detection system for HPLC, UV-Vis spectrophotometry using a diode array detector (DAD) is the most common technique, which allows to distinguish the type of the different anthocyanin pigments, as the UV-Vis spectrum provides information on the nature of the aglycone, the presence of glycosyl and acyl residues in the compound structure. However, it does not allow the complete structural elucidation of the anthocyanin compounds. Besides, it is difficult to obtain reference compounds.

MS is currently one of the most widely used techniques for the identification of phenolic compounds, since it enables structure elucidation by the recognition of the molecular ions and the fragmentation patterns [133, 134]. Moreover, it is a very sensitive detection technique that allows the study of compositional changes during wine aging, as well as to follow the polymerizations and reactions with other flavonoids taking place during wine-making.

The online coupling of liquid chromatography with UV-Vis and MS allows the analysis of a complex mixture of anthocyanins in a sample, affording the structural characterization of its constituents [135].

1.2.2 Mass Spectrometry

MS is based on the separation of ions (positive or negative) produced from the analyzed molecules depending on their m/z, thereby obtaining a mass spectrum. It is a technique based on the classical principles of the ions movement through magnetic and electric fields and is mainly used to identify unknown compounds, quantify known substances and elucidating the structural and physical properties of the ions. The most important parts of a mass spectrometer are the ion source, the analyzer and the detector.

In MS, the formation of ions in gas phase is an essential requirement. When coupling of HPLC with MS, the analyte molecules that are dissolved in the mobile phase must be transformed into ions in the gas phase without thermal degradation, and also eliminate the large amount of gas molecules of the mobile phase prior to entering to the high vacuum region of the analyzer. Ions are generated in the ion source. A large majority of analytical applications of HPLC-MS use atmospheric pressure ionization (API) sources, such as electrospray ionization (ESI) or atmospheric pressure chemical ionization (APCI). ESI is often used for compounds of medium and high polarity, and the APCI for those with an average low polarity [136].

The transmission of the ions in gas phase from the atmospheric pressure region, where the spray is generated, to the high vacuum, where the mass analyzer and detector are located, is critical and is the stage in which the loss of the analyte can occur. Different geometries for the API sources have been designed, including the geometry Z-spray, in which the ions are extracted in an orthogonal path to that generated at the source, thereby obtaining a higher sensitivity because it remove the spray neutral molecules, reducing background noise and favoring the removal of adducts in the ionization chamber. The ESI interface employed in this work consists of a Z-spray source geometry. The effluent of the chromatographic system enters in the interface through the sounding line. Applying a high voltage between the sample inlet capillary and sample cone, and with the aid of a coaxial flow of nitrogen gas (N_2), the effluent becomes a charged aerosol. A second flow of heated N_2 (desolvation gas) helps solvent evaporation. In the nebulization, the majority of the spray material is drawn to waste, while a small part is drawn into the sample cone. In this type of Z-spray source, there is an additional N_2 flow which comes from the sample cone in a contrary direction to the spray (gas cone). This N_2 flow prevents the entry of substances through the sample cone orifice.

The gas phase ions formed during ionization are extracted from the spray due to the potential difference between the capillary and the sample cone. Vacuum and voltage differences direct the ions through the sample cone, the extraction cone and the radio frequency (RF) lens towards the analyzer [137]. If the acceleration of the ions is increased (by increasing the potential difference) breaking of the ions can occur due to collisions with residual gas molecules from the mobile phase and the N_2 used as nebulization gas. The fragments produced by this phenomenon, called collision induced dissociation (CID) in the source, can be used for structure elucidation of molecules.

The gas phase ions are separated in the mass analyzer depending on their m/z ratio, using their different magnetic and electric properties. The analyzer is one of the most important components in a mass spectrometer, because its function is to classify the ions from the ion source based on their m/z ratio and the main resolution, sensitivity, range mass and mean residence time of the ions in the spectrometer depend on it. One of the most widely employed analyzer in MS is the quadrupole, mainly due to its low cost and robustness. The quadrupole consist in four molybdenum filter aligned in parallel to each other and equidistant from an imaginary central axis positioned on the Cartesian Z axis. By applying to each pair of opposed bars an overlapping variable direct current (DC) voltages and RF, the ions of selected mass can pass through the tunnel formed by the four pole rods following stable oscillating trajectories and leading them to the detector, while the other masses, following unstable trajectories do not reach the detector and are deflected out of the set of bars. Variation of the voltages allows to successively focus on different masses present and to obtain the corresponding mass spectrum [138]. Some other widely used MS analyzers used are the ion trap (IT), which confines the ions in closed orbits using RFs and the quadrupole time-of-flight (QToF) analyzer, which determine the m/z ratio depending on the time required for the ion to travel a distance [139].

Finally, the ions impact the detector, where the flow is converted into a proportional electric current. A data collection system records the magnitude of these electrical signals as a function of the m/z ratio and converts this information into a mass spectrum.

The ion generated during ionization are, as a rule, stable enough to reach the detector, so there is no need to couple analyzers in series unless the aim is to induce fragmentation between the ions. The usual technique for this is flight fragmentation which is induced by collision with high or low energy particles, in an analogous procedure to that which occurs in the ion source, but performed in specialized cells of collision with a collision gas, generally argon, at a controlled pressure. Collision cells are generally transmission quadrupoles, hexapoles or octapoles, which means that only

RFs are applied. The extension and the energy of the fragmentation in these collision cells are precisely controlled, unlike cone fragmentation. The effectiveness of this fragmentation may be very high, balancing out the general soft ionization in the interface.

There are many types of configurations of tandem MS; in this work a triple quadrupole (QqQ) configuration is used [140]. The second quadrupole acts as a collision cell, which is the most common configuration for trace analysis and screening of natural products. This equipment is easily automated, uses low voltages, and presents a resolution suitable for most applications and good levels of sensitivity and robustness. In a QqQ type configuration, the first and third quadrupole function as ion analyzers and therefore, DC voltage and RF are applied. While the intermediate quadrupole operates as collision cell in which only RF current are applied. This configuration is an arrangement of MS/MS, however the ionization is usually optimized to adjust the ionization produced in the source. In this type of HPLC-MS equipment, experiments of MS and MS/MS can be performed. In MS experiments, the first quadrupole (Q1) works only as analyzer, the valve of collision gas remains closed, and the collision cell (Q2) and the third quadrupole (Q3) act in transmission mode. Scan mode experiments can be performed, in which Q1 is scanning and mass spectra are obtained; or experiments in single ion monitoring (SIM) mode, in which Q1 is set in a m/z, achieving greater sensitivity.

In MS/MS experiments, the collision cell is activated. Dissociation of the molecules is induced by collision with an inert gas, usually argon (CID mechanism). In a configuration of this type, different experiments can be performed (Figure 1.29) [138], in which the quadrupoles Q1 and Q3 act as analyzers:

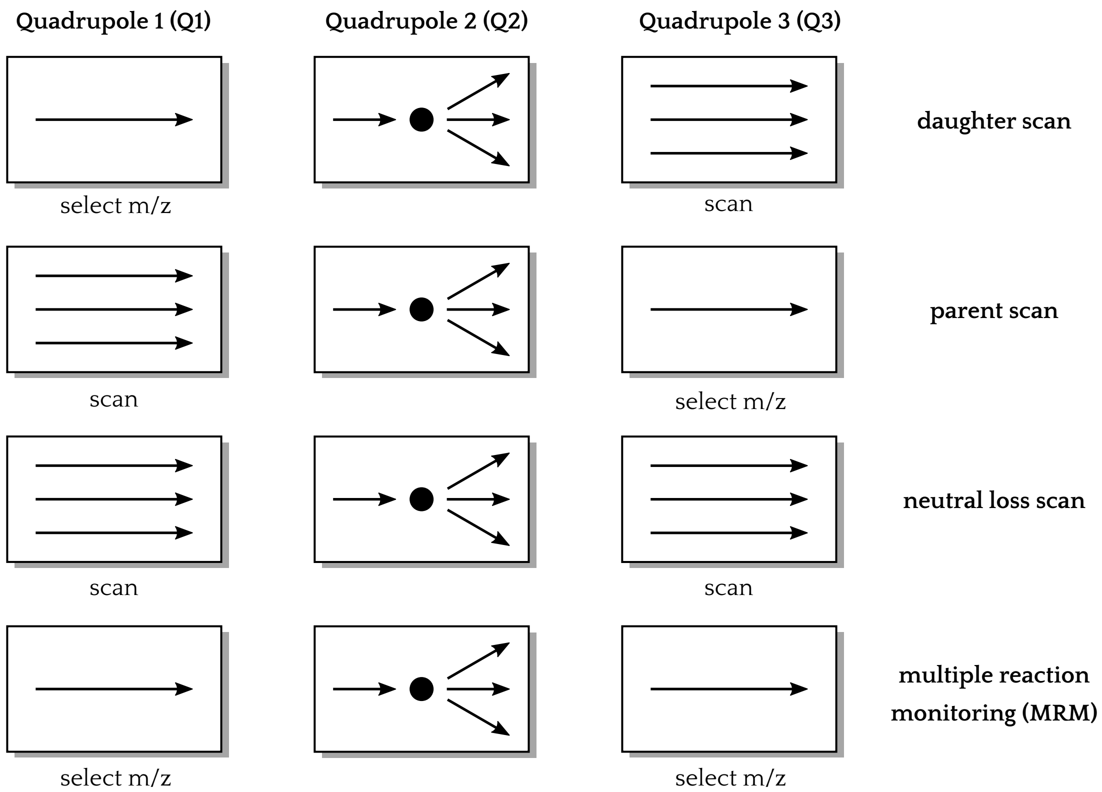


Figure 1.29. MS/MS experiments that can be performed in a QqQ configuration.

- **Product or daughter ion scan:** a precursor ion is selected in Q1, bypassing the rest of ions from ionization. This precursor ion breaks into the collision cell with a certain energy and Q3 is operating in scan mode to obtain the fragment ions spectrum from the selected precursor ion. This type of spectrum is very common in structural analysis because it creates high-quality spectra and allows structural characterization of the compounds studied.

- **Precursor or parent ion scan:** In this type of experiment, the precursors that are fragmented causing a particular fragment ion are studied. In this case Q1 makes a scan, ions are fragmented in the collision cell and Q3 let pass one specific fragment ion. Whereby the spectrometer records a signal only in the case that Q1 lets pass a precursor ion which can be fragmented giving the fragment ion selected in Q3.

- **Constant neutral loss scan:** In this case all ions which undergo fragmentation and loose the same neutral fragment are studied. Q1 and Q3 work in scanning mode, but with a gap between them equal to the neutral loss studied. Signal is observed when Q1 lets pass an ion that upon fragmentation suffers the loss of a neutral fragment with a m/z ratio equal to the gap between the quadrupoles, originating the fragment ion that Q3 is letting pass.

- **Multiple reaction monitoring (MRM):** the fragmentation of a precursor ion selected that produces a particular fragment ion is studied. Q1 selects a single precursor ion that is fragmented in the collision cell, Q3 lets pass only a specific fragment ion, so that the intensity caused by a specific fragmentation, called transition, is monitored. The two quadrupoles are fixed, so that the sensitivity is very high. Additionally, a signal is only originated by the compounds yielding a specific fragment with the same transition, so that the selectivity and specificity of the technique is very high, enabling even highly sensitive analysis in complex matrices. It is a technique that provides great advantages for the quantification of the analytes.

MS was a breakthrough in the structural elucidation of phenolics, including anthocyanin derivatives formed during wine elaboration and aging [141].

1.2.3 Color measurements

Color is one of the most important organoleptic parameters of wine, being a determining factor in its sensory evolution. The color of wine evolves progressively during aging and can be indicative of its age, its state of conservation and even some defects which will be perceived when it is consumed. Wine color is highly influenced by the anthocyanin content of the grapes used, as well as the different elaboration and conservation techniques employed.

Anthocyanins are responsible for the red color of grapes and young wines [142]. However, during aging several chemical reactions between anthocyanins and other molecules present in wine yield new pigments which modify wine color.

Wavelength of maximum absorption in the UV-Vis spectrum (Band I) for anthocyanins is around 525 nm, absorbing mainly green light and making human eye perceive a red color. As discussed in previous sections, the direct and indirect condensations between anthocyanins and flavan-3-ols result in a bathochromic shift of the wavelength of maximum absorption in the UV-Vis spectrum, causing violet hues in wine. Similarly, the formation of pyranoanthocyanin derivatives leads to hypsochromic shifts of the wavelength of maximum absorption, and leads to an orange hue to the wine.

Among the different methodologies to measure wine color, the measurement of the standard parameters and the chromatic coordinates are the most widely employed.

1.2.3.1 Standard Parameters

Standard parameters are CI, tonality (Ton) and yellow, red, blue components, and are determined following the methodology described by Glories [143, 144], which consists on the recording of the absorbance of each sample at 420, 520 and 620 nm. CI indicates how much color wine has, and is calculated as the sum of the absorbance at the recorded wavelengths (Equation 1.1).

$$CI = A_{420} + A_{520} + A_{620} \tag{1.1}$$

Ton indicates the relative importance of yellow over red, expressed in percentage (Equation 1.2).

$$Ton = (A_{420}/A_{520}) \times 100 \tag{1.2}$$

The yellow, red and blue components are determined as the ratio of each of them and the CI, expressed in percentage (Equations 1.3a, 1.3b and 1.3c). These parameters indicate the relative importance of each of the colors in the global color of wine.

$$Yellow\ (A_{420}) = (A_{420}/CI) \times 100 \tag{1.3a}$$

$$Red\ (A_{520}) = (A_{520}/CI) \times 100 \tag{1.3b}$$

$$Blue\ (A_{620}) = (A_{620}/CI) \times 100 \tag{1.3c}$$

1.2.3.2 Chromatic Coordinates

In 1986, the Commission Internationale de l'Èclairage (CIE) proposed a set of rules in order to properly define color [145, 146, 147]. These rules express color according to three luminous stimuli named X, Y and Z, which represent each of the basic colors (X: virtual red; Y virtual green; Z: virtual blue). By the combination of these factors, all colors can be reproduced. In other words, X, Y and Z coordinates are a numeric expression representing the relative proportion of each of the basic colors needed to represent a specific color for the observer's eye. They can be calculated by measuring the transmittance at specific wavelengths (450, 520, 570 and 630 nm) and applying the following Equations 1.4a, 1.4b and 1.4c.

$$X = 19.717\ T_{450} + 1.884\ T_{520} + 42.539\ T_{570} + 32.474\ T_{630} - 1.841 \tag{1.4a}$$

$$Y = 7.950\ T_{450} + 34.764\ T_{520} + 42.736\ T_{570} + 15.759\ T_{630} - 1.180 \tag{1.4b}$$

$$Z = 103.518\ T_{450} + 4.190\ T_{520} + 0.251\ T_{570} - 1.831\ T_{630} + 0.818 \tag{1.4c}$$

The CIE defined the CIELAB space, which attempts to represent spatially all colors. This definition of color is based on three coordinates: lightness (L*) has values ranging from 100 to 0, where 100 represent a perfect white sample and 0 a perfect black; a* represents the redness-greenness axis in the plane normal to L*, positive values of a* denote redness and negative ones greenness; and b* represents yellowness-blueness in an axis normal to both L* and a*, positive values indicate yellowness and negative ones blueness. The L*, a* and b* values are calculated from the X, Y and Z values according to Equations 1.5a, 1.5b and 1.5c.

$$L^* = 116\ (Y/100)^{1/3} - 16 \tag{1.5a}$$

$$a^* = 500\ [(X/94.825)^{1/3} - (Y/100)^{1/3}] \tag{1.5b}$$

$$b^* = 200\ [(Y/100)^{1/3} - (Z/107.383)^{1/3}] \tag{1.5c}$$

In order to simplify the color expression, the coordinates a* and b* from the CIELAB space can be transformed into the spherical coordinates hue (H*) and chroma (C*) according to Equations 1.6a and 1.6b. This way the color of any object is defined within the CIELAB space by the three coordinates L*, H* and C*.

$$H^* = \arctan(b^*/a^*) \tag{1.6a}$$

$$C^* = (a^{*2} + b^{*2})^{1/2} \tag{1.6b}$$

1.3 Applications of phenolic compounds in cosmetics

The normal functioning of the body involves several biological reactions in cells and tissues that often generate species with unpaired electrons called free radicals, such as reactive oxygen species (ROS). These compounds are usually balanced by endogenous mechanisms, but an excessive accumulation can lead to oxidative stress in cells [148, 149]. In particular, the skin is continuously exposed to chemical, mechanical, and physical stress, which leads to an excess of ROS and other free radicals [150]. The accumulation of these species has been linked to the development of chronic inflammatory states and tumor initiation and promotion. An external intake of antioxidants has demonstrated an effect on counterbalancing these processes and restoring physiological conditions. Naturally occurring antioxidants include phenolics, which are present in fruits and plants and have been demonstrated to have antioxidant, anti-radical, antimicrobial, and anti-inflammatory properties *in vitro* that help protect and prevent chronic diseases and cancer [151].

The grape is one of the fruits with the highest content of phenolic antioxidants. As said in previous sections, its main components include anthocyanins, catechins, procyanidins, and tannins [152]. The grape has been employed for winemaking since ancient times, and wine consumption has been associated with an improvement in cardiovascular conditions [28, 25] amongst other benefits. Red grape pomace, defined as the residue of the red grape after the juice has been partially or thoroughly removed, before or after fermentation [153] is rich in anthocyanins, as well as other bioactive compounds [154]. Due to an incomplete extraction during winemaking, these compounds remain in the pomace, which is mostly composed of seeds, skins, and stems [155, 156]. These residues represent a waste problem, but also an opportunity to obtain a sustainable and low-cost source of antioxidants. Various industrial sectors, such as pharmaceuticals, foods, and cosmetics, can benefit from the valorization of wine-processing materials [157, 158].

To maximize the potential of the grape pomace, extraction method is an important factor to be considered. The efficacy and commercial feasibility of the extract depend highly on the use of convenient, inexpensive, and eco sustainable procedures that ensure the highest yield and quality of the active compounds of the extract [159].

Regarding their application, phenolic compounds present some limitations, such as a low *in vivo* bioavailability and easy degradation [160]. Their topical application has some potential advantages, such as the avoidance of hepatic first-pass metabolism and gastric degradation, a larger surface area for absorption, low proteolytic activity levels, and ease of accessibility [161]. In an attempt to improve the applicability of phenolic compounds, different innovative strategies have been used, including solid dispersions [162], nanosuspensions [163], microemulsions [164], solid lipid nanoparticles [165], and liposomes [166], the latter being one of the most successful.

Over the last years, liposomes have been the target of reformulating studies aimed at producing vesicles capable of delivering drugs to the deeper skin layers. Their use offers numerous advantages: nanoparticles can load a single drug or a multi-component extract increasing their solubility and bioavailability, provide protection against degradation, allow controlled rate of release, increase efficacy and reduce toxicity [167, 168].

Additionally, a number of additives have been explored in combination with conventional components of liposomes, producing new classes of vesicles, such as transfersomes. Transfersomes are composed of phospholipids and an edge activator, which is a membrane-softening agent (*e.g.*, polyoxyethylene (20) sorbitan mono-oleate (Tween 80), Span 80, and sodium cholate) that makes the vesicle ultra-deformable [169, 170]. Unlike conventional liposomes, when transfersomes reach skin pores, they are capable of changing their membrane flexibility and passing through the skin pores spontaneously, thus promoting the accumulation of a payload in the dermis. A number of transfersome-based formulations are currently being assessed at different stages of clinical trials [171].

The aim of the liposomal formulations is to (i) protect the phenolic compounds of the extracts, which are known to be prone to degradation; and (ii) increase the bioavailability of phenolics, which is generally poor due to their low solubility in water [172]. Furthermore, the liposomal formulations are expected not to interfere with the antioxidant properties of the phenolic compounds, and allow the development of a safe product that could be applied onto the skin for the treatment of oxidative stress-related disorders.

Characterization is an important step in order to ensure that the prepared particles are at a nanoscale. The term "characterization" refers to the process of analysis of the the properties and structure of the material explored. Among all the available characterization techniques, transmission electron microscopy (TEM), dynamic light scattering (DLS) and zeta potential offer several advantages to observe nanomaterials.

Optical microscopy helps to observe materials at a micron level with reasonable resolution. However, they show some limitations on achieving further resolution. Other techniques like TEM are more advanced and enable to detect materials in the nanoscale [173]. TEM is based on the interaction of an electron beam with the analyzed sample. Diffraction of the electron beam is produced and the transmitted electrons produce the image after passing through a focusing objective lens.

DLS measures light scattered from a laser that passes through a colloidal solution. This technique yields information on the size of the particles in solution [174]. Zeta potential is a measure of the "effective" electric charge on the nanoparticle surface, and quantifies the charge stability of colloidal nanoparticles [175].

Chapter 2

Objectives

The objectives of the present Ph.D. thesis are focused on different issues related to wine-making: (i) the study of the influence of different oenological techniques on the phenolic composition of wine during its elaboration, and (ii) the valorization of grape pomace waste resulting from wine elaboration.

The effect of several oenological techniques on the phenolic composition of red wine made at pilot scale in a winery were studied. In this context, the primary aims were the following:

- To investigate the kinetics of formation and evolution of the phenolic compounds during red wine elaboration.
- To study the influence of grape cultivar mixture, microoxygenation, tannin addition or ionic exchange on the phenolic composition of wine and on their formation and evolution kinetics during red wine elaboration.

The potential use of extracts from red grape pomace for the preparation of liposomal nanoformulations with antioxidant activity for cosmetic applications was studied. In this regard, the specific aims were:

- To characterize the phenolic profiles of the extracts obtained from the red grape pomace of *Tempranillo* and *Graciano* grape cultivars.
- To develop, optimize and characterize vesicle nanoformulations for grape pomace extracts of *Tempranillo* and *Graciano* grape varieties to be applied on human skin.
- To evaluate the antioxidant properties and the biocompatibility of the vesicle nanoformulations containing the phenolic extracts of *Tempranillo* and *Graciano* grape pomace.

Chapter 3

Methodology

The analytical methodology employed for the identification and quantification of anthocyanins, tannins and their derivatives in red wines had been optimized and validated by our research group in previous work [176, 177, 178, 179].

3.1 Standards, solvents and reagents

Malvidin-3-*O*-glucoside (Mv-3-*O*-glc) and (+)-catechin (cat) were purchased from Extrasynthèse (Genay, France). Acetonitrile (MeCN) and methanol (MeOH) were HPLC grade and were provided by Romil Chemical Ltd. (Heidelberg, Germany).

Trifluoroacetic acid (TFA) of spectroscopy grade, acetic acid (HAc), hydrochloric acid (HCl) 32%, L-(+)-tartaric acid of analytical grade, Folin–Ciocalteu's reagent, 2,2-diphenyl-1-picrylhydrazyl (DPPH), 6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid (Trolox) and 2,4,6-tris(pyridin-2-yl)-1,3,5-triazine (TPTZ) were supplied by Merck/Sigma-Aldrich (Darmstdt, Germany).

NaH_2PO_4 and Na_2HPO_4 of analytical grade were purchased from Fluka (Steinheim, Germany). Phospholipon 90G (P90G) and phospholipid lipoid S 75 (S75) were supplied by Lipoid GmbH (Ludwigshafen, Germany). Polyoxyethylene (20) sorbitan mono-oleate (Tween 80) was provided by Galeno (Carmignano, Prato, Italy). Human skin keratinocytes (HaCaT) were supplied by CLS–Cell Lines Service (Eppelheim, Germany).

Yeasts employed in the winery were Zymaflore® RX60 from Laffort (Bordeaux, France). Commercial tannins used in the winery were Fermotan AG tannins and ionic exchange resins were pH-Stab 2.0 from AEB Iberica (Barcelona, Spain).

Water was purified on a MilliQ system from Millipore (Bedford, MA, USA). All solvents were filtered through 0.45 μm nylon membranes (Lida, Kenosha, WI, USA) prior to use.

3.2 Samples

3.2.1 Wine-making process

3.2.1.1 Wine elaboration, experimental design and oenological variables

Wine elaborations were performed in winery Faustino (Oyón, Spain) in 2018 and 2019. Grape cultivars used were autochthonous from Rioja region, *i.e. Tempranillo*, *Graciano* and *Mazuelo*, and were grown in three sites in "La Rioja": Mendavia in 2018, and Alfaro and Laguardia in 2019.

The variables related to wine elaboration studied are: (i) the grape cultivar; (ii) the addition of tannins; (iii) the use of microoxygenation technique during malolactic fermentation; and (iiii) the use of ionic exchange resins to lower the pH of grape must. The levels of these variables are summarized in Table 3.1. The experimental designs performed in 2018 and 2019 are described in Tables 3.2 and 3.3, respectively. In 2019, the mixture of grape cultivars *Tempranillo* and *Mazuelo* was not included in the experimental design; instead grape cultivar *Tempranillo* was used in the experiments of tanks 17-24 (Table 3.3).

Table 3.1. Variables studied in wine elaborations.

Variables	Levels
Grape Cultivar	*Tempranillo* & *Graciano* / *Tempranillo*
	Tempranillo & *Mazuelo* / *Tempranillo*
Tannin addition	Yes / No
Microoxygenation	Yes / No
Ionic Exchange	Yes / No

Table 3.2. Experimental design for the wine elaborations in 2018.

Tank No.	Variety	Tannins	Microoxygenation	Ionic Exchange
1	*Tempranillo*	No	No	No
2	*Tempranillo*	No	Yes	No
3	*Tempranillo*	Yes	No	No
4	*Tempranillo*	Yes	Yes	No
5	*Tempranillo*	No	No	Yes
6	*Tempranillo*	No	Yes	Yes
7	*Tempranillo*	Yes	No	Yes
8	*Tempranillo*	Yes	Yes	Yes
9	*Tempranillo* & *Graciano*	No	No	No
10	*Tempranillo* & *Graciano*	No	Yes	No
11	*Tempranillo* & *Graciano*	Yes	No	No
12	*Tempranillo* & *Graciano*	Yes	Yes	No
13	*Tempranillo* & *Graciano*	No	No	Yes
14	*Tempranillo* & *Graciano*	No	Yes	Yes
15	*Tempranillo* & *Graciano*	Yes	No	Yes
16	*Tempranillo* & *Graciano*	Yes	Yes	Yes
17	*Tempranillo* & *Mazuelo*	No	No	No
18	*Tempranillo* & *Mazuelo*	No	Yes	No
19	*Tempranillo* & *Mazuelo*	Yes	No	No
20	*Tempranillo* & *Mazuelo*	Yes	Yes	No
21	*Tempranillo* & *Mazuelo*	No	No	Yes
22	*Tempranillo* & *Mazuelo*	No	Yes	Yes
23	*Tempranillo* & *Mazuelo*	Yes	No	Yes
24	*Tempranillo* & *Mazuelo*	Yes	Yes	Yes

Table 3.3. Experimental design for the wine elaborations in 2019.

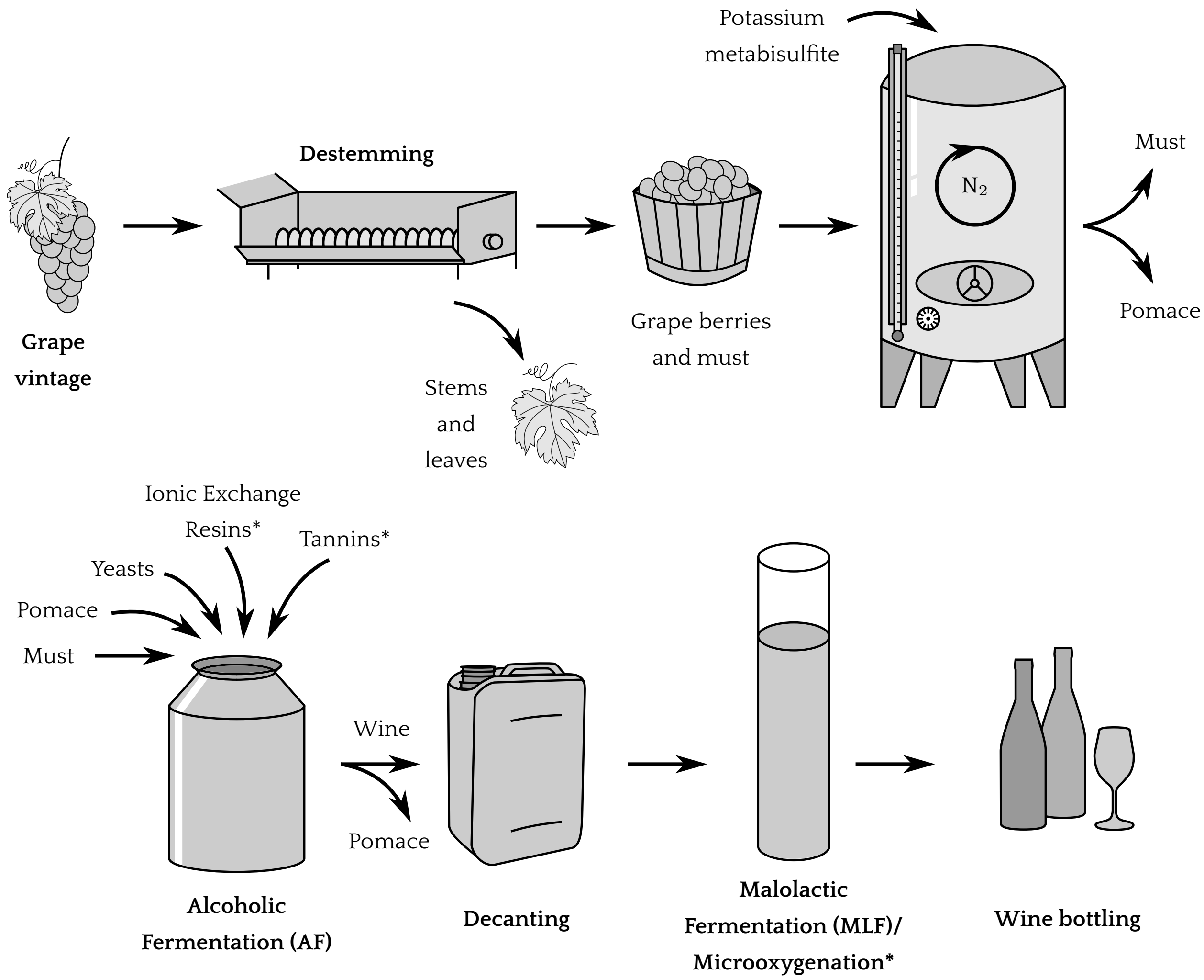
Tank No.	Variety	Tannins	Microoxygenation	Ionic Exchange
1	*Tempranillo*	No	No	No
2	*Tempranillo*	No	Yes	No
3	*Tempranillo*	Yes	No	No
4	*Tempranillo*	Yes	Yes	No
5	*Tempranillo*	No	No	Yes
6	*Tempranillo*	No	Yes	Yes
7	*Tempranillo*	Yes	No	Yes
8	*Tempranillo*	Yes	Yes	Yes
9	*Tempranillo* & *Graciano*	No	No	No
10	*Tempranillo* & *Graciano*	No	Yes	No
11	*Tempranillo* & *Graciano*	Yes	No	No
12	*Tempranillo* & *Graciano*	Yes	Yes	No
13	*Tempranillo* & *Graciano*	No	No	Yes
14	*Tempranillo* & *Graciano*	No	Yes	Yes
15	*Tempranillo* & *Graciano*	Yes	No	Yes
16	*Tempranillo* & *Graciano*	Yes	Yes	Yes
17	*Tempranillo*	No	No	No
18	*Tempranillo*	No	Yes	No
19	*Tempranillo*	Yes	No	No
20	*Tempranillo*	Yes	Yes	No
21	*Tempranillo*	No	No	Yes
22	*Tempranillo*	No	Yes	Yes
23	*Tempranillo*	Yes	No	Yes
24	*Tempranillo*	Yes	Yes	Yes

Grape vintage was done manually by the winery staff and each grape cultivar was processed individually. The whole wine elaboration process is summarized in Figure 3.1.

Grapes were destemmed and the resulting mixture consisting of must and grapes was transferred to a 500 L stainless steel tank, where 70 g of potassium metabisulfite were added. N_2 was flowed for 2 h to homogenize the mixture and break the grape skins. A day later, must was separated from the pomace (solid residue of grapes), and then transferred to 20 L stainless steel tanks in specific amounts. Each tank was filled with must and pomace from the different grape varieties studied according to Figure 3.2. Following to the experimental designs planned, 1.8 g of Fermotan AG tannins dissolved in warm water to a concentration of 1 g/20 mL and ionic exchange resins to achieve a final concentration of 10 g/L were added to the corresponding tanks. Yeast RX60 previously activated by mixing 40 g of the yeast with 500 mL of water and 30 g of sucrose was inoculated to all tanks in order to promote the start of AF.[1]

Completion of AF occurred around 10 to 13 days after the start, and was determined by the sugar content data obtained from density values from Winescan™ analyzer. Wine was separated from the pomace and transferred from the tanks to plastic decanters where they were left for

[1]In 2019, during the experiment with grapes from Alfaro the tank number 1 fell and the content was lost.



*Indicates dependency with experimental design for the indicated step of the process.

Figure 3.1. Scheme of the wine elaboration process used to obtain the wine elaborations of the experimental design.

2018	2019
Tanks 1-8 *Tempranillo* 9 kg *Tempranillo* must 5 kg *Tempranillo* pomace	**Tanks 1-8** *Tempranillo* 10 kg *Tempranillo* must 2 kg *Tempranillo* pomace
Tanks 9-16 *Tempranillo* + *Graciano* 9 kg *Tempranillo* + 2 kg *Graciano* musts 5 kg *Tempranillo* + 1 kg *Graciano* pomaces	**Tanks 9-16** *Tempranillo* + *Graciano* 8 kg *Tempranillo* + 2 kg *Graciano* musts 1.6 kg *Tempranillo* + 0.4 kg *Graciano* pomaces
Tanks 17-24 *Tempranillo* + *Mazuelo* 9 kg *Tempranillo* + 2 kg *Mazuelo* musts 5 kg *Tempranillo* + 1 kg *Mazuelo* pomaces	**Tanks 17-24** *Tempranillo* 10 kg *Tempranillo* must 2 kg *Tempranillo* pomace

Figure 3.2. Scheme of the amounts of grape must and pomace used for wine elaboration depending on the grape cultivar or mixture of grape cultivars employed.

4 days. Then, the liquid was carefully transferred to sealed methacrylate cylindrical tubes using a mechanical pump, discarding the decanted precipitate. The inside of the tubes had been previously purged with a flow of N_2. These tubes contained a total of five valves, three in the bottom part and two in the upper part (Figure 3.3). The wine from each tank was transferred to a separate tube. Afterwards, microoxygenation was performed, which consisted on bubbling a flow of O_2 from the bottom inlet valve of the tubes. Additionally, a larger flow of N_2 was bubbled in order to produce the mixture and homogenization of the wine. For the bubbling of both O_2 and N_2, an automated valve system was employed, which allowed programming of the bubbling system for 3 and 10 min, respectively, once per day everyday.[2] The end of MLF occurred around 25 to 30 days after it started. Wine was then extracted from the methacrylate tubes and bottled.

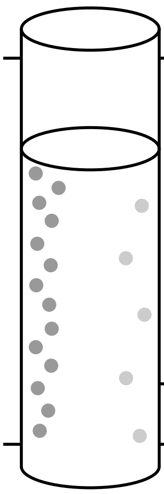


Figure 3.3. Scheme of the methacrylate tubes employed for the malolactic fermentation/microoxygenation process.

3.2.1.2 Sampling

In order to monitor the concentrations of phenolic compounds along the wine elaborations, samples of must and wine were taken from each tank at different stages of the elaboration process in both years of experiments.

During AF, technicians at the winery monitored the must/wine daily by infrared spectroscopy using Winescan^{TM} analyzer from Foss (Hillerød, Denmark). Wine in the tanks was punched prior to sampling, and a 20 mL aliquot was taken from each tank, centrifuged (3500 rpm, 30 min, r.t.) in a Digicen20 centrifuge from Orto Alresa (Madrid, Spain), filtered with quantitative filter paper from Filter-Lab (Barcelona, Spain), and analyzed in the Winescan^{TM} analyzer.

During MLF samples were taken every other day for the first week, and then, every 3-4 days, following the same protocol as for sampling during AF. During intermediate steps, like decanting no samples were taken. Figure 3.4 summarizes the number of samples collected from each wine elaboration.

For the analysis of phenolics the samples were an aliquot from t he sample collected by the technicians of the winery for the control of the elaboration process using Winescan^{TM} analyzer. After centrifuging and filtering each sample, approximately 8 mL of wine were taken with a syringe and filtered through an Acrodisc CR25 0.45 μm PTFE membrane (Pall, Port Washington, NY). Each

[2] In 2018, the automated valve for bubbling of O_2 was not available therefore the flow of O_2 was set manually for 10 min once a day every other day during the first two weeks of MLF.

sample was divided into four separate 2 mL amber-glass vials. All samples were frozen immediately and were kept at -80 °C until analysis.

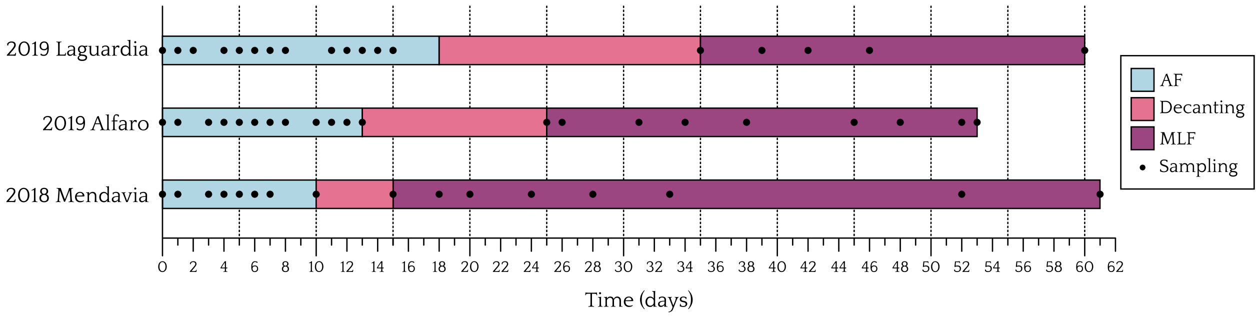


Figure 3.4. Chart of samples taken during the different elaborations performed during 2018 and 2019.

3.2.2 Grape pomace

Two pomaces from *Tempranillo* and *Graciano* red grape cultivars were supplied by Bodegas Faustino winery (Oyón, Spain), and stored at -20 °C. These pomaces were residues from the experiments of 2019 with grapes from Laguardia. Prior to extraction, the pomaces were freeze-dried and ground to a coarse powder using ø11 mm stainless steel balls in a rotary agitator. The freeze-dried powder of both pomaces was stored in a desecator at r.t. until their use.

3.3 Wine analysis

3.3.1 Analysis of anthocyanins by HPLC-DAD and HPLC-DAD-ESI(+)-MS/MS

The quantification of anthocyanins in red wines was carried out by HPLC coupled to a DAD. The HPLC-DAD conditions used in the analysis of wine samples had been previously optimized and validated by our research group [178, 179].

The HPLC-DAD analysis was performed in a Hewlett-Packard (Palo Alto, CA, USA) series 1100 chromatograph equipped with a vacuum degasser, a quaternary pump, an automatic and thermostated injector, an oven for the column and a DAD. A reverse-phase Phenomenex (Torrance, CA, USA) Luna C18 column (150 mm × 1.6 mm I.D., 3 μm) at 30 °C, protected with a guard column Phenomenex C18 (4 mm × 3.0 mm I.D.), was used. Data processing was performed by HP Chemstation v.6.01. The solvents used were aqueous solution of trifluoroacetic acid (TFA) 0.5% (v/v) as mobile phase A and acetonitrile (MeCN) as mobile phase B, and the elution gradient used was: 0-15 min, linear gradient from 12 to 15% B; 15-25 min, isocratic at 15% B; 25-40 min, linear gradient from 15 to 25% B; 40-50 min, linear gradient from 25 to 30% B; 50-55 min, linear gradient from 30 to 100% B; washing with 100% B and re-equilibration of the column. The flow rate was 0.8 mL/min and the injection volume was 50 μL. The sample vials in the automatic injector were kept at 4 °C to guarantee the preservation of the samples. Prior to injection into the HPLC instrument, wines samples were filtered through an Acrodisc CR13 0.45 μm polytetrafluoroethylene (PTFE) membrane (Pall, Port Washington, NY), and amber flask vials were used to avoid the light degradation of the anthocyanins. UV-Vis spectra were recorded from 250 to 600 nm, and quantification was carried out at 530 nm.

The anthocyanins analyzed are shown in Table 3.4 together with their retention time (t_R). Mv-3-*O*-glc was identified (Figure 3.5) by comparison of its t_R, UV-Vis absorption spectra with that of the commercial standard.

Table 3.4. List of anthocyanins analyzed in this work, their t_R and MS data.

#	Compound	t_R	m/z $[M]^+$	m/z $[Y_0]^+$
1	Dp-3-*O*-glc	9.0	465	303
2	Cy-3-*O*-glc	12.7	449	287
3	Pt-3-*O*-glc	14.6	479	317
4	Pn-3-*O*-glc	19.8	463	301
5	Mv-3-*O*-glc	21.7	493	331
6	Dp-3-*O*-(6-ac)-glc	28.8	507	303
7	Pt-3-*O*-(6-ac)-glc	36.4	521	317
8	Pn-3-*O*-(6-ac)-glc	39.8	505	301
9	Mv-3-*O*-(6-ac)-glc	40.4	535	331
10	Mv-3-*O*-(6-caff)-glc	42.0	655	331
11	Pt-3-*O*-(6-*p*-coum)-glc	43.2	625	317
12	Pn-3-*O*-(6-*p*-coum)-glc [1]	46.1	609	301
13	Mv-3-*O*-(6-*p*-coum)-glc [1]		639	331

[1] Coeluting compounds.

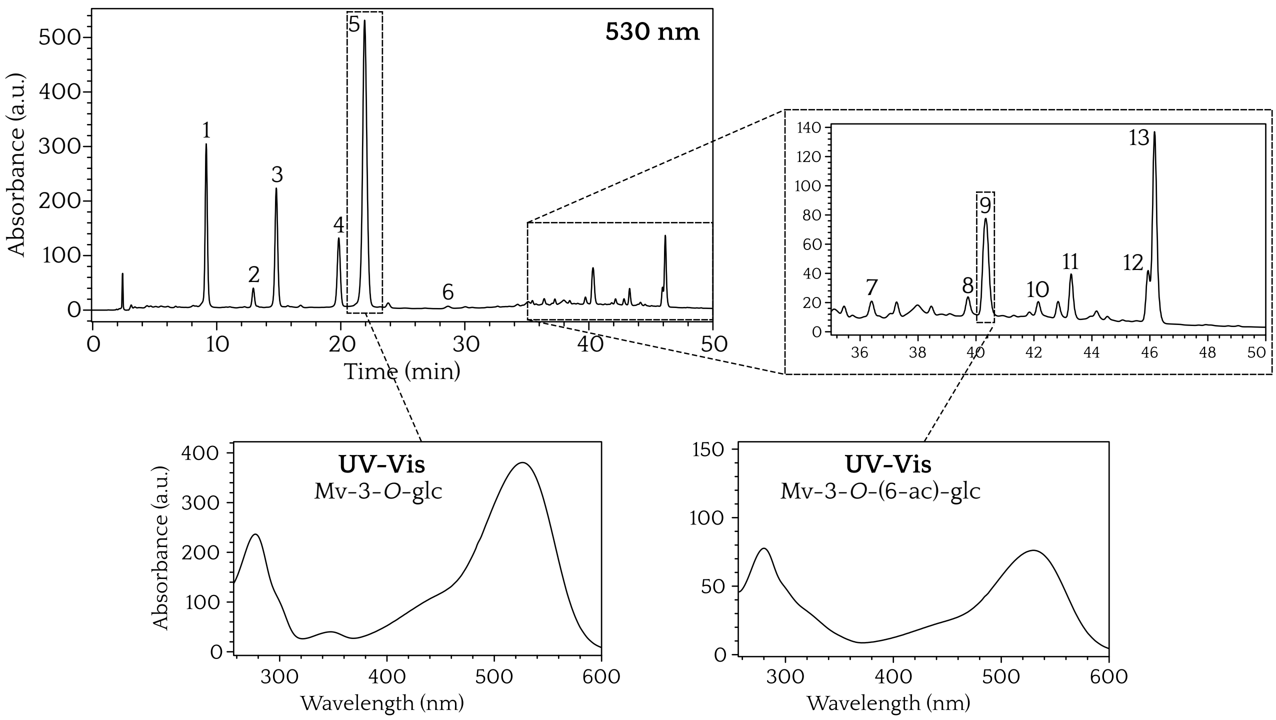


Figure 3.5. HPLC-DAD chromatogram at 530 nm corresponding to a wine sample and UV-Vis spectra of selected peaks.

Anthocyanins were quantified at 530 nm using Mv-3-*O*-glc as standard for the external calibration. The concentrations of detected compounds are expressed as equivalent concentrations in mg of Mv-3-*O*-glc/L of wine. Precision of the method was lower than 5% RSD, as calculated during method validation in previous works, and the limit of quantification was 0.01 mg of Mv-3-*O*-glc/L of wine [179].

The stock solution and the intermediate standard solutions were prepared in MeOH with hydrochloric acid (HCl) 0.1% (v/v). The final standard solutions to be injected in the HPLC system in the range 0.01-300 mg/L were prepared with ⩽20% of MeOH to avoid distortion of chromatographic peaks, and were preserved in dark vials at 4 °C.

Calibration curves of Mv-3-*O*-glc were carried out using 16 different concentration levels. Due to the wide concentration range, it was split into five linear range sections. Table 3.5 shows slope, intercept and regression coefficient of the calibration curves obtained during this work.

For the identification of the anthocyanins analyzed in the grape must and wine samples a Micromass (Milford, MA, USA) Quattro Micro QqQ mass spectrometer, coupled to HPLC-DAD and equipped with a Z-spray ESI source (HPLC-DAD-MS/MS) was used. Table 3.4 shows m/z values for each anthocyanin.

Table 3.5. Mv-3-*O*-glc calibration curves in the five linear ranges with their corresponding standard deviation (SD) for HPLC-DAD analysis.

Linear range (μg/mL)	Slope ± SD	Intercept ± SD	R^2
0.01-0.10	172 ± 2	0.2 ± 0.1	0.9997
0.10-1.0	180.5 ± 0.4	-0.7 ± 0.2	0.9999
1.0-10.0	190 ± 3	-17 ± 18	0.9995
10.0-100.0	183.2 ± 0.6	97 ± 33	0.99998
100.0-300.0	201 ± 4	-1624 ± 994	0.9991

3.3.2 Analysis of anthocyanin derivatives by HPLC-DAD-ESI(+)-MS/MS

The determination of anthocyanin derivatives is difficult not only due to the large number of compounds with great chemical diversity found in wine, but also because of their low concentrations. The analysis of anthocyanin derivatives by HPLC-DAD-ESI(+)-MS/MS requires a prior sample clean-up and preconcentration usually performed by solid phase extraction (SPE). A sample pretreatment by SPE had been previously optimized and validated by our group [176]. The SPE cartridges employed were StrataX (3 cc, 60 mg sorbent), from Phenomenex (Auckland, New Zealand), and the SPE of the wine samples was carried out as follows. Cartridges were connected to a vacuum manifold (20 kPa), activated with 100% MeOH (2 mL), and equilibrated first with MilliQ water (2 mL) and then, with an aqueous solution of synthetic wine (3.5 g/mL tartaric acid, 12% EtOH, pH = 3.5; 2 mL). Afterwards, the wine sample was loaded (1 mL), washed with phosphate buffer ($[HPO_4]^{2-}/[H_2PO_4]^-$, 0.1 M, pH = 7; 1 mL) and MilliQ water (1 mL), before eluted with MeOH-HCl (99.9:0.1, v/v; 4 mL). SPE eluents were evaporated to dryness with a N_2 flow using a Zymark TurboVap from Biotage (Uppsala, Sweden), reconstituted with 1 mL H_2O-TFA (99.5:0.5, v/v), and stored at 4 °C until analysis.

Anthocyanin derivatives in the wine extracts were analyzed on an Alliance 2695 liquid chromatography system from Waters (Milford, USA), equipped with a vacuum degasser, a binary pump, an automatic and thermostated injector and an oven for the column. The system was coupled to a DAD Waters 2996 and a QqQ mass spectrometer Micromass (Manchester, UK) Quattro micro with a Z-spray source coupled to an ESI sounding line controlled by the software MassLynx v. 4.0. A reversed-phase Onyx Monolithic C18 column (100 × 3.0 mm) from Phenomenex (Torrance, CA, USA) with a pre-column of the same material (5 × 4.6 mm) was used. Mobile phases consisting of aqueous TFA (0.5%, v/v; A) and MeCN (B) were delivered at a flow rate of 0.3 mL/min. A gradient program was used: 0-0.29 min, isocratic at 12% B; 0.29-4.29 min, linear gradient, 12 to 15% B; 4.29-9.17 min, linear gradient, 15 to 25% B; 9.17-12.72 min, linear gradient, 25-40% B; 12.72-13.17 min, isocratic 40% B; 13.17-13.63 min, linear gradient 40-100% B; 13.63-21.63 min, isocratic 100% B, and column reconditioning. The injector and column temperatures were 4 °C and 30 °C respectively, and the injection volume was 50 μL. UV-Vis spectra of the chromatographic peaks were registered each second in a 250-600 nm range. Mass spectrometer used N_2 at 300 °C and 450 L/h as desolvation gas. The capillary potential was 3.2 kV in positive ion mode and 120 °C was the source block temperature.

For the quantification of the anthocyanin derivatives found in red wines, study of MS spectra was used for structure elucidation. The acquisition in MS/MS was performed in MRM mode; thus, the precursor ion mass and the most intense fragment ion are fixed. Only those compounds with that particular mass transition show a signal in the detector, which lead to a high selectivity. Scan was performed in centroid mode in a range from 50 to 1500 *u* in positive mode. The scan time was 1.5 seconds with an interscan time of 0.1 seconds.

The anthocyanin derivatives quantified are listed in Table 3.6, where the corresponding transitions, collision energy (CE) and optimum cone voltage (CV) are summarized. Figures 3.6 and 3.7 show an example of the MRM chromatograms obtained in the analysis of red wine samples. Anthocyanin derivatives were quantified by the external calibration method using Mv-3-*O*-glc as standard. The concentrations of detected compounds are expressed as equivalent concentrations in mg of Mv-3-*O*-glc/L of wine. Limit of quantification was 0.001 mg og Mv-3-*O*-glc/L of wine. The stock solution and the intermediate standard solutions were prepared in MeOH with HCl 0.1% (v/v). The final standard solutions to be injected in the HPLC system in the range 0.001-100 mg/L were prepared with $\leqslant$20% of MeOH to avoid distortion of chromatographic peaks, and were preserved in dark vials at 4 °C.

Calibration curves of Mv-3-*O*-glc were carried out using 16 different concentration levels. Due to the wide concentration range, it was split into five linear range sections. Table 3.7 shows slope, intercept and regression coefficient of the calibration curves obtained during this work.

If the calibration curve is studied as a whole, linearity is not observed due to the drop saturation process, a phenomenon more pronounced in high concentration ranges. The first step in ESI is the formation of fine beads with an excess of ions (positive or negative, depending on the ionization mode) because of the voltage applied in the capillary of the probe. When the surface of the drop is fully occupied with charged molecules of the analyte, there is no gain in response with increasing concentration, because some of the analyte ions can not reach the surface and do not pass to gas phase. At this time the drop saturation is produced.

Calibration solutions were injected every 12 samples because of the variability of the mass spectrometer signal. The chromatographic method used for the standard solutions was shorter than that of the samples. Calibration solutions were injected in isocratic mode at 20.0% B in 8 min, using the same mobile phases, column and other experimental conditions described above.

3.3.3 Analysis of tannins by HPLC-DAD-ESI(+)-MS/MS

The determination of tannins in wine samples requires a sample pretreatment step, consisting on a SPE, prior to the analysis by HPLC-DAD-ESI(+)-MS/MS. The SPE method to extract and preconcentrate tannins in wines had been previously optimized and validated by our research group [177].

The SPE cartridges employed were Oasis HLB (3 cc, 60 mg sorbent), from Waters (Milford, MA, USA), and the SPE of the wine samples was carried out as follows. Cartridges were connected to a vacuum manifold (20 kPa), activated with 100% MeOH (2 mL), and equilibrated first with MilliQ water (2 mL) and then, with an aqueous solution of synthetic wine (3.5 g/mL tartaric acid, 12% EtOH,

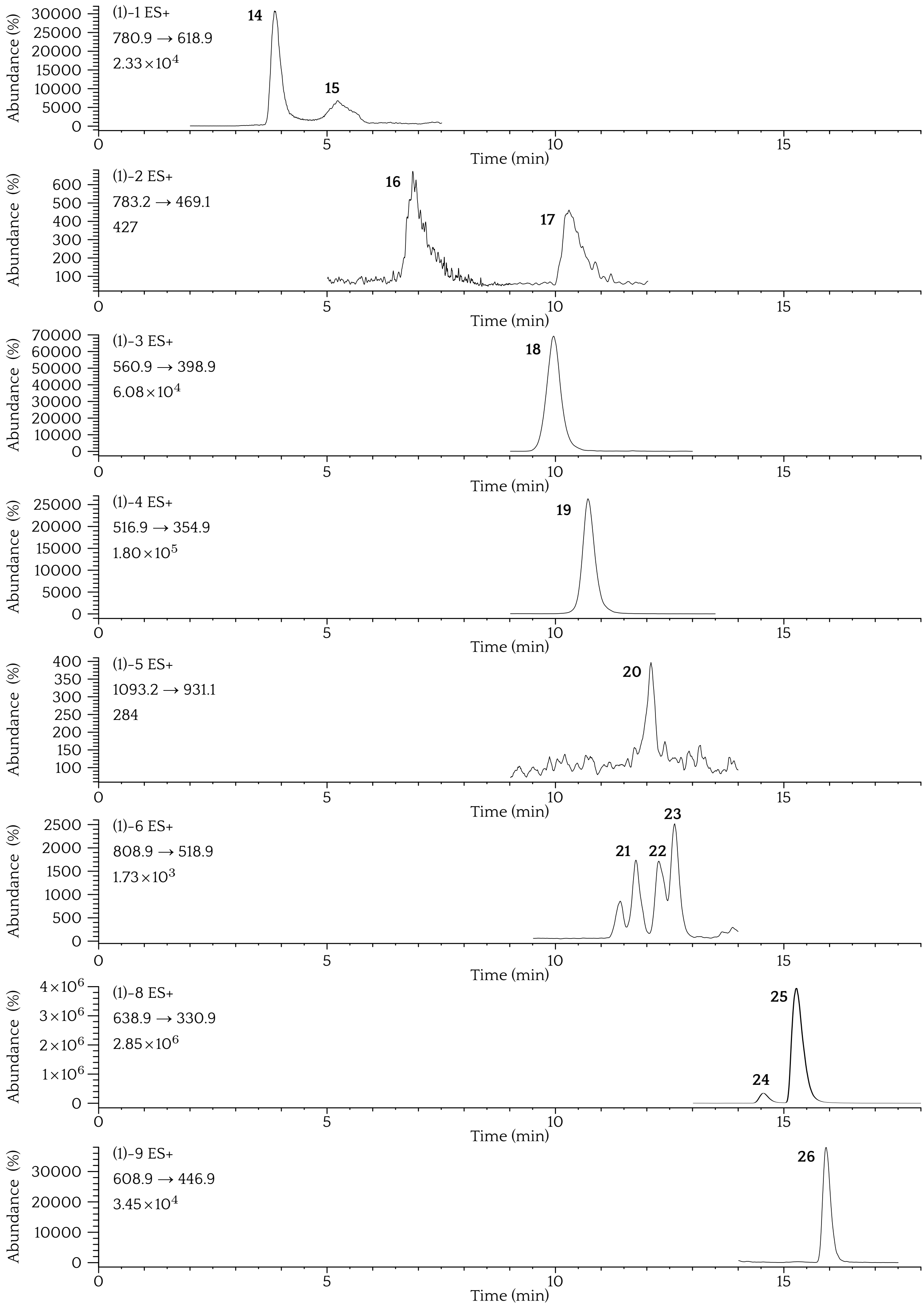


Figure 3.6. MRM chromatograms for anthocyanin derivatives (compounds 14-26).

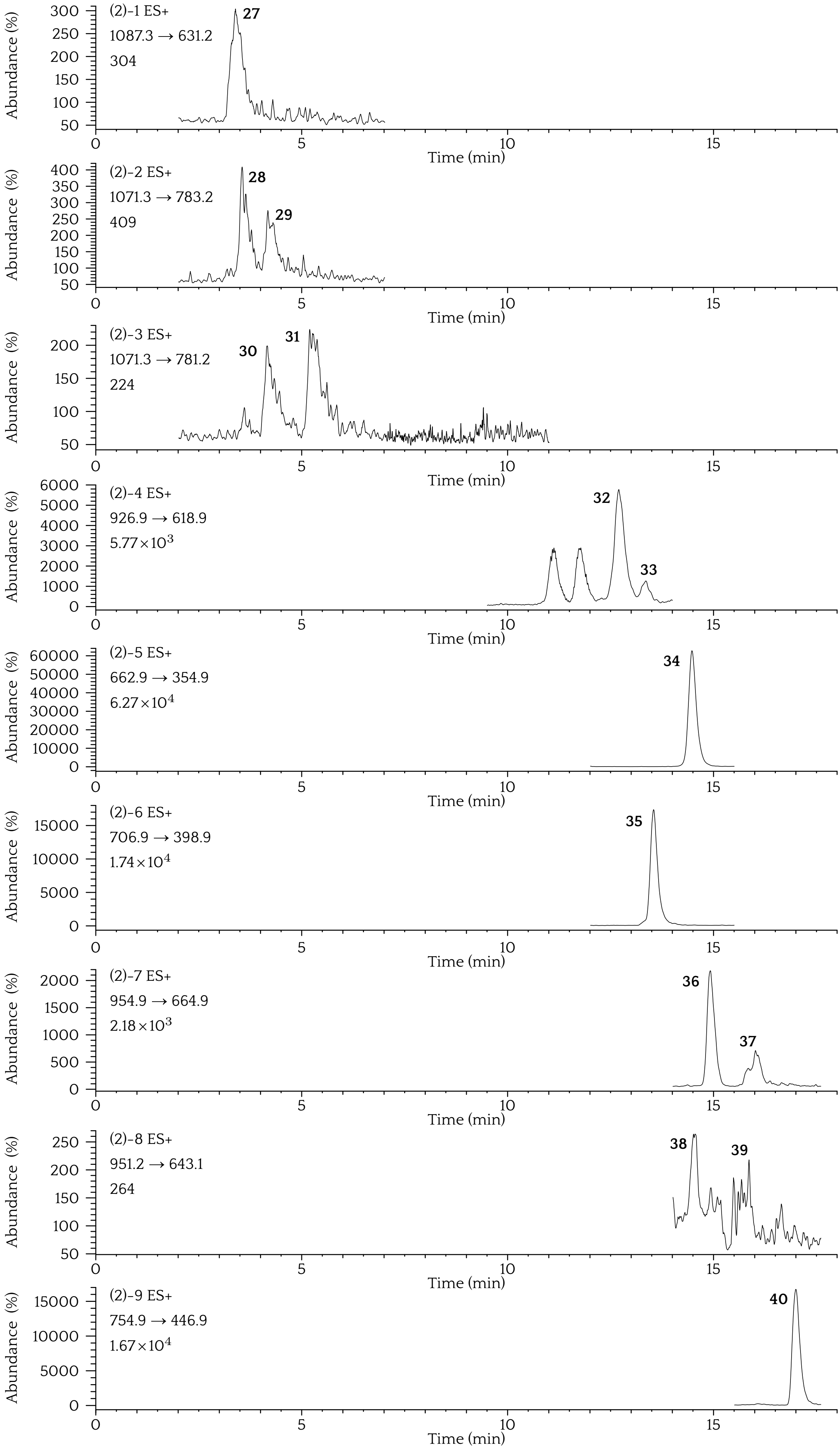


Figure 3.7. MRM chromatograms for anthocyanin derivatives (compounds 27-40).

Table 3.6. List of anthocyanin derivatives analyzed in this work, their retention time (t_R), mass transition in MRM mode, cone voltage (CV) and collision energy (CE).

#	Compound	t_R	Transition	CV (V)	CE (eV)
14	cat-Mv-3-*O*-glc	3.9	780.9 → 618.9	35	25
15	epicat-Mv-3-*O*-glc	5.3	780.9 → 618.9	35	25
16	Mv-3-*O*-glc-(epi)cat	6.9	783.2 → 469.1	30	20
17	Mv-3-*O*-glc-A-(epi)cat	10.3	783.2 → 469.1	30	20
18	Mv-3-*O*-glc-pyruvic	10.0	560.9 → 398.9	25	25
19	Mv-3-*O*-glc-acetaldehyde	10.7	516.9 → 354.9	25	25
20	pyruvic acid derivative-vinyl-cat-cat	12.1	1093.2 → 931.1	35	35
21	Mv-3-*O*-glc-8-ethyl-cat 1	11.8	808.9 → 518.9	35	25
22	Mv-3-*O*-glc-8-ethyl-cat 2	12.3	808.9 → 518.9	35	25
23	Mv-3-*O*-glc-8-ethyl-epicat	12.6	808.9 → 518.9	35	25
24	Mv-3-*O*-(6-*p*-coum)-glc *cis*	14.5	638.9 → 330.9	35	25
25	Mv-3-*O*-(6-*p*-coum)-glc *trans*	15.3	638.9 → 330.9	35	25
26	Mv-3-*O*-glc-4-vinylphenol	15.9	608.9 → 446.9	25	25
27	(epi)gallocat-Mv-3-*O*-glc-A-(epi)cat	3.4	1087.3 → 631.2	30	30
28	(epi)cat-Mv-3-*O*-glc-A-(epi)cat 1	3.6	1071.3 → 783.2	20	20
29	(epi)cat-Mv-3-*O*-glc-A-(epi)cat 2	4.2	1071.3 → 783.2	20	20
30	(epi)cat-A-(epi)cat-Mv-3-*O*-glc	4.2	1071.3 → 781.2	20	10
31	Mv-3-*O*-glc-(epi)cat-A-(epi)cat	5.2	1071.3 → 781.2	20	10
32	cat-Mv-3-*O*-(6-*p*-coum)-glc	12.7	926.9 → 618.9	35	25
33	epicat-Mv-3-*O*-(6-*p*-coum)-glc	13.4	926.9 → 618.9	35	25
34	Mv-3-*O*-(6-*p*-coum)-glc-acetaldehyde	14.5	662.9 → 354.9	35	25
35	Mv-3-*O*-(6-*p*-coum)-glc-pyruvic	13.5	706.9 → 398.9	35	25
36	Mv-3-*O*-(6-*p*-coum)-glc-8-ethyl-(epi)cat 1	14.9	954.9 → 664.9	35	25
37	Mv-3-*O*-(6-*p*-coum)-glc-8-ethyl-(epi)cat 2	16.0	954.9 → 664.9	35	25
38	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylcat	14.5	951.2 → 643.1	60	30
39	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylepicat	15.9	951.2 → 643.1	60	30
40	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylphenol	17.0	754.9 → 446.9	35	25

Table 3.7. Linear model for the five different ranges of Mv-3-*O*-glc calibration with their corresponding SD for HPLC-DAD-ESI(+)-MS/MS analysis.

Linear range (μg/mL)	Slope ± SD	Intercept ± SD	R^2
0.001-0.010	$(490 \pm 6)\times10^2$	-4 ± 4	0.9997
0.010-0.10	$(465 \pm 10)\times10^2$	91 ± 57	0.9992
0.10-1.0	$(448 \pm 16)\times10^2$	201 ± 937	0.9975
1.0-10.0	$(220 \pm 20)\times10^2$	$(33 \pm 12)\times10^3$	0.9836
10.0-100.0	$(83 \pm 5)\times10^2$	$(203 \pm 28)\times10^3$	0.9933

pH = 3.5; 2 mL). Afterwards, the wine sample was loaded (1 mL), washed with phosphate buffer ($[HPO_4]^{2-}/[H_2PO_4]^-$, 0.1 M, pH = 7; 1 mL) and MilliQ water (1 mL), before eluted with MeOH-HCl (99.9:0.1, v/v; 4 mL). SPE eluents were evaporated to dryness with a N_2 flow in a Zymark TurboVap from Biotage (Uppsala, Sweden), reconstituted in 1 mL H_2O-acetic acid (HAc) (99:1, v/v), and stored at 4 °C until analysis.

For the determination of tannins, the same HPLC-DAD-ESI(+)-MS/MS equipment used for the analysis of anthocyanin derivatives described in previous section was used. A reversed phase Onyx Monolithic C18 column from Phenomenex (Torrance, USA) (100 × 3 mm) with a precolumn of the same material (5 × 4.6 mm) was used.

The solvents used for the chromatographic separation of tannins were H_2O-HAc (99:1, v/v) as mobile phase A and MeOH-HAc (99:1, v/v) as mobile phase B. The reason for the use of HAc as an additive was to provide an acidic pH media in order to improve the separation of tannins from anthocyanins. The elution gradient used was: 0-1.03 min, isocratic, 19.3% B; 1.03-7.47 min, linear gradient, 19.3-20% B; 7.47-11.25 min, linear gradient, 20-25% B; 11.25-16.03 min, linear gradient, 25-45% B; 16.03-19.92 min, linear gradient, 45-75% B, 19.92-24.70 min, linear gradient, 75-100% B; 24.70-28.00 min, isocratic, 100% B; and column cleaning and reconditioning. The column and injector temperatures were 30 °C and 4 °C, respectively. The injection volume was 50 μL and the flow rate was 0.3 mL/min.

The acquisition in MS/MS was performed in MRM mode. Table 3.8 collects the t_R, optimum mass transitions, CV and CE for each tannin studied and Figures 3.8 and 3.9 show an example of the MRM chromatograms achieved.

Tannins were quantified using the external calibration method using (+)-cat as standard. The concentrations of detected compounds are expressed as equivalent concentrations in mg of (+)-cat/L of wine. Limit of quantification was 0.001 mg of (+)-cat/L of wine, as calculated in previous works.

The stock solution and the intermediate and standard solutions were prepared using H_2O-MeOH (80:20, v/v) as solvent. All standard solutions were preserved in dark vials at 4 °C, and injected in the range 0.025-150 mg of (+)-cat/L of wine. Calibration was carried out using 13 different concentration levels. Calibration curve was split into three linear range sections to avoid the effect of non linearity due to drop saturation process. Table 3.9 shows the slope, intercept and regression coefficient for the calibration curves performed in this work. In the case of the higher concentration range (10-150 mg/L),the effect of drop saturation was more pronounced and the fit of the experimental data fit better to a quadratic equation of the type $y = ax^2 + bx + c$.

Calibration solutions were injected every 12 samples because of the variability of the mass spectrometer signal. The chromatographic method used for the standard solutions was shorter than that of the samples; consisting in an isocratic run at 19.3% B in 7 min, using the same mobile phases, column and experimental conditions.

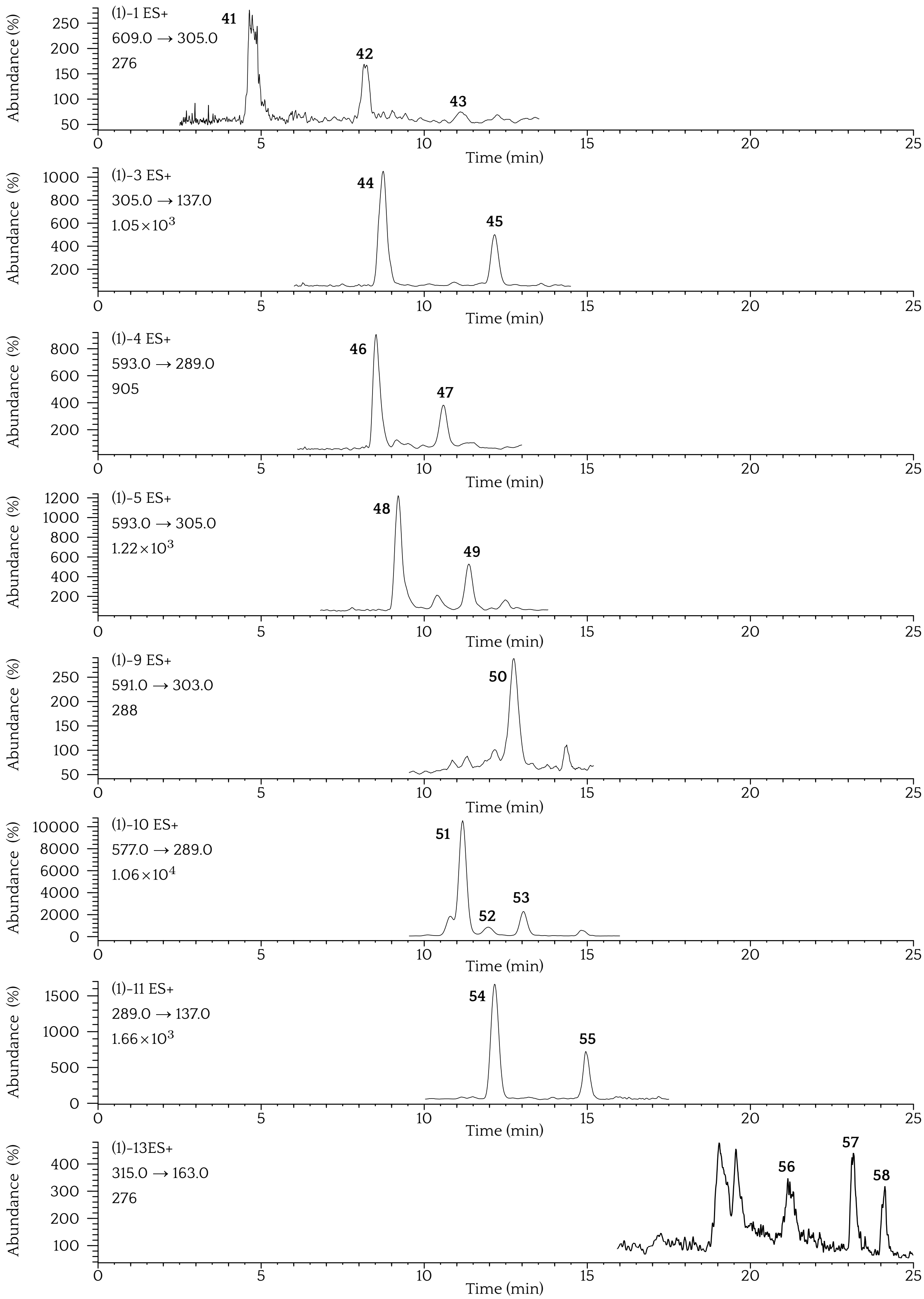


Figure 3.8. MRM chromatograms for tannins (compounds 41-58).

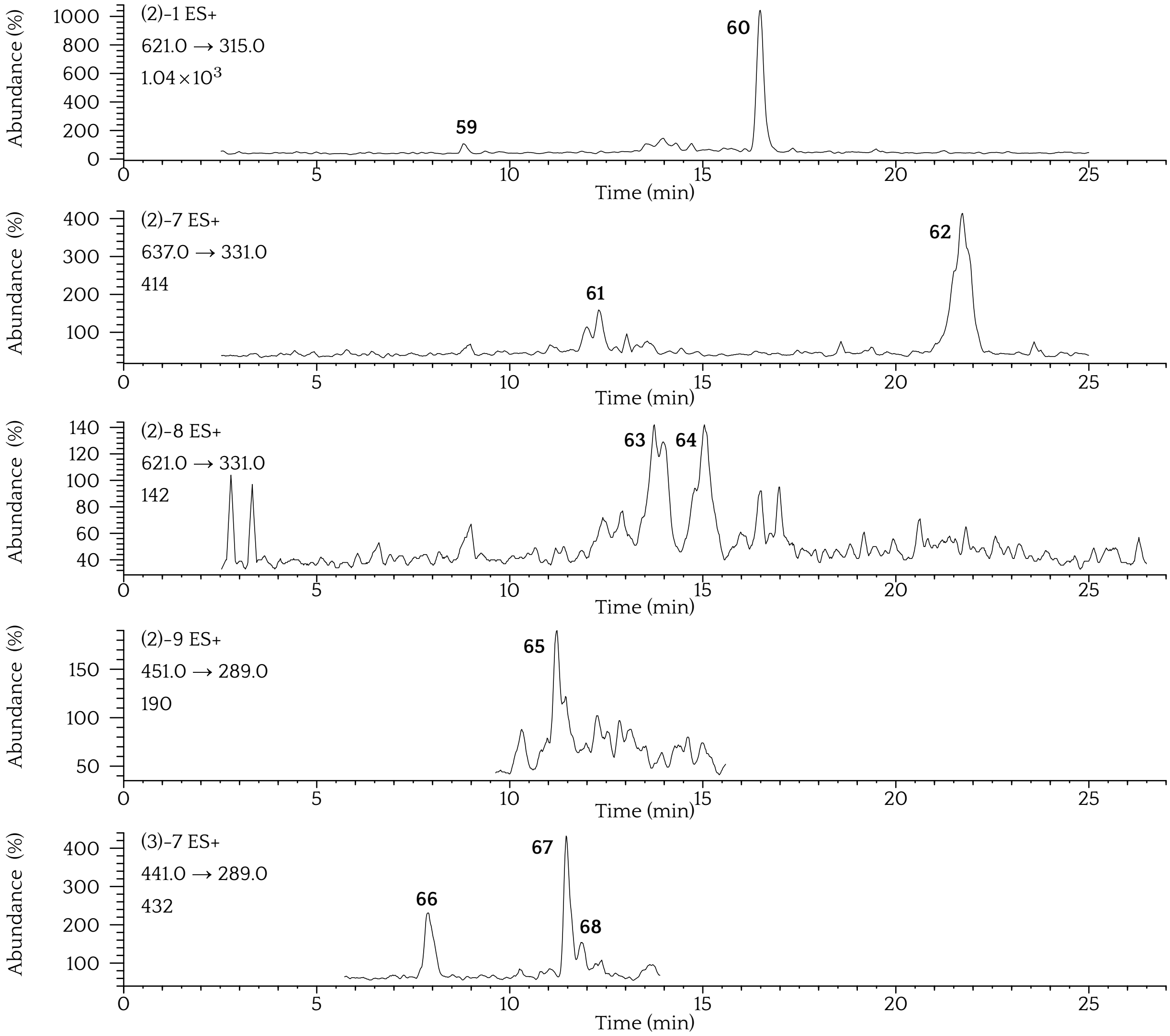


Figure 3.9. MRM chromatograms for tannins (compounds 59-68).

Table 3.8. List of tannins analyzed in this work, their retention time (t_R), mass transition in MRM mode, cone voltage (CV) and collision energy (CE).

#	Compound	t_R	Transition	CV (V)	CE (eV)
41	((epi)gallocat)$_2$ 1	4.0	609.0 → 305.0	25	25
42	((epi)gallocat)$_2$ 2	7.7	609.0 → 305.0	25	25
43	((epi)gallocat)$_2$ 3	11.1	609.0 → 305.0	25	25
44	gallocat	8.5	305.0 → 137.0	25	35
45	epigallocat	12.2	305.0 → 137.0	25	35
46	(epi)gallocat-(epi)cat 2	8.2	593.0 → 289.0	35	25
47	(epi)cat-(epi)gallocat 2	10.6	593.0 → 289.0	35	25
48	(epi)gallocat-(epi)cat 1	9.0	593.0 → 305.0	35	25
49	(epi)cat-(epi)gallocat 1	11.4	593.0 → 305.0	35	25
50	(epi)cat-(epi)gallocat A	12.9	591.0 → 303.0	55	25
51	((epi)cat)$_2$ 1	10.8	577.0 → 289.0	25	25
52	procyanidin B 1 (PCB1)	11.2	577.0 → 289.0	25	25
53	PCB2	13.1	577.0 → 289.0	25	25
54	cat	12.2	289.0 → 137.0	25	25
55	epicat	15.1	289.0 → 137.0	25	25
56	*p*-vinyl(epi)cat 1	19.0	315.0 → 163.0	55	25
57	*p*-vinyl(epi)cat 2	20.3	315.0 → 163.0	55	25
58	*p*-vinyl(epi)cat 3	23.1	315.0 → 163.0	55	25
59	gallocat-ethyl-cat	8.8	621.0 → 315.0	25	15
60	cat-ethyl-gallocat	16.5	621.0 → 315.0	25	15
61	(epi)gallocat-ethyl-(epi)gallocat	12.3	637.0 → 331.0	25	15
62	gallocat-ethyl-gallocat	21.7	637.0 → 331.0	25	15
63	gallocat-ethyl-cat	13.7	621.0 → 331.0	25	15
64	cat-ethyl-gallocat	15.0	621.0 → 331.0	25	15
65	(epi)cat-glycoside	11.2	451.0 → 289.0	55	25
66	((epi)cat)$_3$ 1	7.9	441.0 → 289.0	25	25
67	((epi)cat)$_3$ 2	11.5	441.0 → 289.0	25	25
68	procyanidin C 1 (PCC1)	11.9	441.0 → 289.0	25	25

Table 3.9. Model for the three different ranges of (+)-cat calibration with their corresponding SD for HPLC-DAD-ESI(+)-MS/MS analysis.

Linear range (μg/mL)	Slope ± SD	Intercept ± SD		R^2
0.025-1.00	269 ± 2	-5.4 ± 0.5		0.99996
1.00-10.0	369 ± 23	-154 ± 136		0.99619
Range (μg/mL)	**a ± SD**	**b ± SD**	**c ± SD**	**R^2**
10.0-150.0	-0.8 ± 0.1	269 ± 19	$(11 \pm 6)\times10^2$	0.99709

3.3.4 Color measurements

The chromatic properties of the red wine samples along the wine elaborations were measured out in order to characterize the wine color.

3.3.4.1 Standard parameters

The standard parameters CI, Ton, and yellow, red, blue components were determined following the methodology described by Glories [143, 144]. The absorbance (Abs) at 420, 520 and 620 nm of each sample was recorded in a 1 mm cuvette, using an UV-Vis spectrophotometer Lightwave II from Biochrom Ltd. (Cambridge, England). The results were multiplied by 10 in order to refer the result to a 10 mm standard cuvette. CI and Ton were calculated using Equations 1.1 and 1.2.

3.3.4.2 CIELAB parameters

The transmittance was recorded at 450, 520, 570 and 630 nm for each sample in a 2 mm cuvette using an UV-Vis spectrophotometer Lightwave II from Biochrom Ltd. (Cambridge, England). Then, the X, Y and Z values were calculated following Equations 1.4a, 1.4b and 1.4c. The L*, a* and b* values were calculated from the X, Y and Z values according to Equations 1.5a, 1.5b and 1.5c.

3.4 Nanoencapsulation of grape pomace extracts

3.4.1 Preparation of extracts of phenolic compounds from grape pomace

In this study, the extraction of bioactive compounds from two grape pomaces of *Tempranillo* and *Graciano* red grape cultivars was performed by using a simple procedure that involved the use of an EtOH-water mixture. An aliquot of the freeze-dried powder pomace (25 g) was soaked in 500 mL of ethanol-water (60:40, v/v), sonicated in an ultrasonic bath for 5 min (40 KHz) at r.t., and centrifuged (20 min, 8000 rpm, 4 °C) at r.t. to collect the supernatant. Then, the EtOH of the extract was evaporated at 30 °C under vacuum and these extracts were analyzed by ultra high-performance liquid chromatography (UHPLC) coupled to a DAD and an ESI QToF/MS and HPLC-DAD-ESI-QqQ in order to identify and quantify, respectively, their phenolic compounds.

The extracts were freeze-dried to obtain the freeze-dried extract (E). The yield was calculated as the % of freeze-dried extract weight respect to the starting freeze-dried material weight. The obtained *Tempranillo* extract (TE) and *Graciano* extract (GE) were used for preparing the nanoformulations (Figure 3.10).

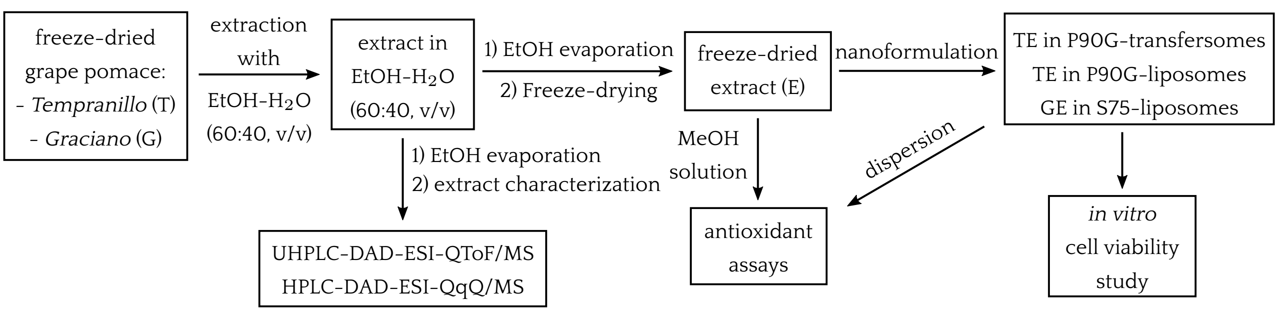


Figure 3.10. Scheme of extraction, characterization and nanoformulation of the grape pomace extracts.

3.4.2 Identification of phenolic compounds in grape pomace extracts

The phenolic profiles of the grape pomace extracts were characterized by UHPLC-DAD-ESI-QToF/MS using an ACQUITY UPLC^{TM} system coupled to DAD and a SYNAPT^{TM} G2 HDMS (Waters, Milford, MA, USA) with a QToF configuration, equipped with an ESI source. The separation was carried out using a reversed-phase Acquity UPLC BEH C18 column (100×2.1 mm, 1.7 μm) with a pre-column of the same material (VanGuard^{TM}) (Waters, Milford, USA), and the method described by Garrido *et al*. [180] with minor modifications. The separation was carried out using HAc in water (0.1%, v/v) and HAc in MeOH (0.1%, v/v) as mobile phases. Separation was carried out using the following elution gradient: 0.00–1.6 min, 2% B isocratic; 1.6–2.11 min, 15% B isocratic; 2.11–8.88 min, 8% B isocratic; 8.88–9.80 min, linear gradient, 8-10% B; 9.80–17.00 min, 10% B isocratic; 17.00–22.00 min, linear gradient, 10-20% B; 22.00–23.40 min, linear gradient, 20-23% B; 23.40–54.20 min, linear gradient, 23-60% B; 54.20–55.20 min, linear gradient, 60-100% B; and column cleaning and reconditioning. The column and injector temperatures were 40 °C and 4 °C, respectively. The injection volume was 5.0 μL and the flow rate was 0.35 mL/min. The extracts were filtered through an Acrodisc® filter with PTFE membrane (0.45 μm, ø13 mm, Pall Corporation, NY, USA) prior to injection. The wavelength range of the UV-Vis detector was 210–500 nm (20 Hz, 1.2 nm resolution). Flavan-3-ols were recorded at 280 nm, hydroxycinamic acids at 320 nm, and flavonols at 370 nm.

Mass spectral data was recorded in positive and negative ion modes. The capillary voltage was set to 1.0 kV for both ESI+ and ESI-. N_2 was used as the desolvation and cone gas at flow rates of 1000 L/h and 10 L/h, respectively. The source and desolvation temperatures were 120 °C and 400 °C, respectively. A leucine-enkephalin solution (2 ng/μL) in MeCN-water (50:50, v/v) with formic acid 0.1% was employed for the lock mass correction and the ions at m/z 556.2771 and 278.1141 in the positive ionization mode from this solution were monitored (0.3 s scan time, 10 s interval, 3 average scans, $\pm$0.5 Da mass window, 30 V CV, 10 μL/min flow rate). Data acquisition took place over the 50-1200 m/z mass range in resolution mode (FWHM $\approx$ 20,000) with a scan time of 0.1 s and an interscan delay of 0.024 s. All the acquired spectra were automatically corrected during acquisition based on the lock mass. Before analysis, the MS was calibrated with a sodium iodide solution.

Identification of phenolic compounds in grape pomace extracts was performed by comparison of their t_R, UV-Vis and MS spectra with literature results [180].

3.4.3 Analysis of anthocyanins in grape pomace extracts

Anthocyanins in the grape pomace extracts were determined by HPLC-DAD-ESI-QqQ/MS using an Alliance 2695 with a DAD and a Micromass Quattro micro^{TM} API tandem quadrupole system using a Z-spray ESI source (Waters) working in positive ion mode. A reversed-phase Luna C18 column (150×4.6 mm, 3 μm; Phenomenex, Torrance, USA) with a pre-column of the same material was used. Mobile phases consisting of aqueous TFA (0.5% v; A) and MeCN (B) delivered at a flow rate of 0.8 mL/min. A gradient program was used: 0-15 min, linear gradient, 12 to 15% B; 15-25 min, isocratic at 15% B; 25-40 min, linear gradient, 15 to 25% B; 40-50 min, linear gradient, 25 to 30% B; 50-55 min, linear gradient, 30 to 100% B; 55-60 min, isocratic, 100% B. An aliquot of 50 μL of extract was injected after filtration through an Acrodisc® filter with PTFE membrane (0.45 μm, ø13 mm, Pall Corporation, NY, USA). The injector and column temperatures were 4 °C and 30 °C, respectively. UV-Vis spectra of the chromatographic peaks were registered each second in a 250-600 nm range. Mass spectrometer used nitrogen at 300 °C and 450 L/h as desolvation gas. Capillary potential was 3.2 kV in positive ion mode and 120 °C was the source block temperature. Anthocyanins were quantified at 530 nm. Mv-3-*O*-glc, the major anthocyanin present in the extract, was used as standard for external calibration in the range 0.5-200 mg/L prepared with a stock solution in MeOH with HCl (0.1%, v/v). The concentrations of the detected compounds are expressed as equivalent concentrations of Mv-3-*O*-glc.

3.4.4 Preparation and characterization of vesicles for the encapsulation of grape pomace phenolics

To produce P90G-transfersomes containing TE, TE (10 mg/mL), P90G (120 mg/mL), and Tween 80 (10 mg/mL) were dispersed in 2 mL of water. The dispersions were sonicated (5 cycles of 5 s on/2 s off + 3 cycles 3 s on/2 s off; 13 μm of probe amplitude) with a Soniprep 150 (MSE Crowley, London, UK).

To produce S75-liposomes with GE, GE (10 mg/mL), S75 (120 mg/mL) were dispersed in 2 mL of water and sonicated (5 cycles of 5 s on/2 s off + 2 cycles 3 s on/2 s off; 13 μm of probe amplitude).

TE P90G-liposomes were obtained using the same procedure as P90G-transfersomes with TE without Tween 80. Empty P90G-transfersomes, P90G-liposomes and S75-liposomes (*i.e.* without TE or GE) were also prepared for an appropriate comparison.

To find an optimal nanoformulation for TE and GE, a pre-formulation study involving the evaluation of multiple candidates against selected endpoints was carried out. The study explored several processing conditions, such as type and concentration of phospholipid, phospholipid:edge activator (Tween 80) ratio, and sonication time, in order to identify the lead candidate with optimal features (*i.e.*, small size, high entrapment efficiency (EE), and physical stability). Furthermore, in order to evaluate the impact of the extract and the edge activator, TE P90G-transfersomes were compared with empty P90G-transfersomes and TE P90G-liposomes. In order to evaluate the impact of the extract on the vesicles' characteristics, the S75-liposomes loaded with GE were compared with empty S75-liposomes. The stability of the liposomal formulations was evaluated by monitoring the mean diameter (MD), the polydispersity index (PI) and the zeta potential (ZP) for two months at 4 $\pm$ 2 °C.

Cryogenic-transmission electron microscopy (cryo-TEM) was employed to examine the formation and morphologies of the vesicles. Three μL of the corresponding dispersion was placed on a glow-discharged 300-mesh Quantifoil grid and plunge frozen into liquid ethane in an FEI Vitrobot Mark IV (Eindhoven, The Netherlands). The frozen grid was transferred first to a 626 DH Single Tilt Cryo-Holder (Gatan, France), where it was kept below -180 °C, and then to a TECNAI G2 20 TWIN (FEI), operating at a 200 KeV accelerating voltage in a bright-field low-dose image mode.

Dynamic and electrophoretic light scattering techniques were used to measure the MD, PI and ZP of the vesicles. The dispersions were diluted with water (1:30, v/v) and analyzed using a Zetasizer nano-ZS (Malvern Panalytical, Worcestershire, UK). The above parameters were monitored over two months at 4 $\pm$ 2 °C to evaluate the storage stabilities of the formulations.

Dialysis was performed to remove the non-incorporated extract constituents from the vesicle dispersions. One mL of sample was loaded into Spectra/Por® tubing (12,000–14,000 Da molecular weight cut-off (MWCO); Spectrum, DG Breda, The Netherlands) and kept in water (2 L) under gentle stirring for 2 h. Non-dialyzed and dialyzed vesicles were disrupted by diluting (1:50, v/v) them with MeOH-water (40:60, v/v) and analyzed by HPLC-DAD-ESI-QqQ/MS to determine the amounts of anthocyanins. The EE was calculated as the percentages of the anthocyanins detected in dialyzed respect to non-dialyzed samples.

3.4.5 Assays to determine the total phenolic content and antioxidant activity

3.4.5.1 Folin-Ciocalteu assay

The total phenolic contents (TPC) of TE and GE methanolic solutions and in vesicle dispersions were determined by the Folin-Ciocalteu method with minor modifications [181].

The vesicle dispersions were sonicated (6 cycles with 10 s on and 2 s off) to disrupt the vesicles and free the components from TE and GE. An amount of 10 μL of each sample was mixed with 50 μL of Folin-Ciocalteu's reagent (2 N) and 790 μL of water. After 1 min, 150 μL of 20% aqueous solution of sodium carbonate was added. After 45 min of incubation at r.t. in the dark, the samples were centrifuged, and the Abs of the supernatant was read at 750 nm.

The TE and GE methanolic solutions were processed according to the above procedure, but without the sonication and centrifugation steps. The TPC was expressed as μg of gallic acid equivalents (GAE)/mL of solution.

3.4.5.2 DPPH assay

The 2,2-diphenyl-1-picrylhydrazyl (DPPH) assay was used to asses the antioxidant activity (AA) of TE and GE methanolic solutions, TE P90G-transfersomes, TE P90G-liposomes and GE S75-liposomes, and the corresponding empty vesicle preparations. Forty μL of each sample was mixed with 2 mL of a 25 μM DPPH methanolic solution. After 30 min of incubation at r.t. in the dark, Abs was recorded at 517 nm. The discoloration of the DPPH solution corresponds to a decrease in Abs, which is correlated to the antioxidant power and the concentration of the sample. The AA was expressed as Trolox equivalents (TrEq) and calculated according to Equation 3.1:

$$AA = ((Abs_{DPPH} - Abs_{sample})/Abs_{DPPH}) \times 100 \tag{3.1}$$

The TrEq values of the samples expressed as μg TrEq/mL solution, were calculated using a calibration curve (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid (Trolox) concentration range: 0-250 μg/mL).

3.4.5.3 FRAP assay

The ferric reducing antioxidant power (FRAP) assay was used to asses the AAs of TE and GE methanolic solutions, TE P90G-transfersomes and GE S75-liposomes, and the corresponding empty vesicle preparations. FRAP assay is based on the reduction of Fe^{3+}-2,4,6-tris(pyridin-2-yl)-1,3,5-triazine (TPTZ) to Fe^{2+}-TPTZ that causes an increase in absorption [182]. Twenty μL of each sample was mixed with 2 mL of the TPTZ-ferric solution. After 4 min of incubation at r.t. in the dark, the Abs was read at 593 nm. The results, expressed as μg Fe^{2+} equivalents (FE)/mL solution, were calculated using a calibration curve ($FeSO_4$ concentration range: 0-1200 μg/mL).

3.4.6 Cell culture viability to determine the toxicity of grape pomace extracts

Human skin keratinocytes (HaCaT) were cultivated at 37 °C in a humidified atmosphere of 5% CO_2 in Dulbecco's Modified Eagle's Medium (DMEM) supplemented with 10% fetal bovine serum (FBS) (Gibco, NY, USA) and 1% penicillin/streptomycin. Cell viability was estimated by the 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) assay as previously described [183]. In short, HaCaT cells were seeded in 96-well plates (104 cells/well) and incubated with the samples diluted to achieve the desired concentrations of TE and GE (0.1, 1 and 10 μg/mL). After 24 h, the cells were incubated with the MTT solution at 37 °C for 3 h. The formed purple formazan crystals were dissolved in dimethyl sulfoxide (DMSO) and the Abs was read at 590 nm.

3.4.7 Determination of intracellular ROS levels inhibition by the liposomal formulations with grape pomace extracts

The cellular ROS levels were determined with the 20,70-dichlorofuorescein diacetate (DCFH-DA) method [183]. HaCaT cells were incubated with the TE methanolic solution and with the liposomal formulations containing TE, diluted to achieve the desired concentrations of the extract (0.1, 1, and 10 μg/mL) for 24 h. Then, the cells were incubated with 10 μM of DCFH-DA for 30 min. After the incubation, 1 mM of H_2O_2 was added to each well, and the fluorescence intensity of ROS-oxidized 20,70-dichlorofuorescein (DCF) was measured at 485/530 nm (excitation/emission wavelengths), recording data every 5 min for 60 min.

3.5 Data analysis

3.5.1 Statistical data analysis

The results were expressed as the mean $\pm$ the SD. Student's t-test was performed to find significant differences between groups. For intracellular AA data, a two-way analysis of variance (ANOVA) was performed, followed by Tukey's test. Differences were considered statistically significant for p values below 0.05.

3.5.2 Kinetic study of the wine-making process

The concentration data of anthocyanins, anthocyanin derivatives and tannins in the samples during wine elaboration obtained by HPLC-DAD and HPLC-DAD-ESI(+)-MS/MS analyses were used to plot the concentration profiles over time for each of the compounds analyzed. An example of these profiles is shown in Figure 3.11 for Mv-3-*O*-glc-pyruvic (Vitisin A).

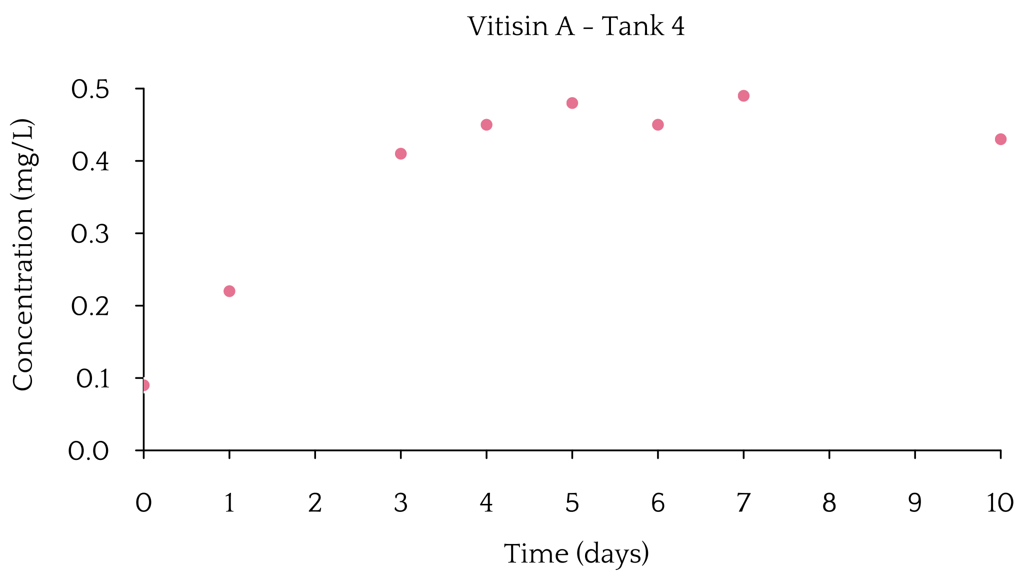


Figure 3.11. Example of a concentration evolution profile for Vitisin A.

The kinetics of the evolution of the concentration of the anthocyanins and anthocyanin derivatives studied during AF were studied. Among the analytes, two classes of compounds were distinguished:

1. Compounds originally present in grapes and were extracted from the pomace to the must at early stages of maceration and AF.
2. Compounds formed in the must from a precursor compound by reaction with other phenolic compounds or with other molecules present in the media.

Moreover, two preliminary conditions were assumed: (i) the kinetic order of the extraction process of all degradation processes and of the chemical reactions was considered to be 1; and (ii) for the compounds formed by chemical reactions of a precursor phenolic compound and a small molecule, such as acetaldehyde, this molecule was supposed to be present in the media in excess relative to the concentration of the precursor phenolic compound.

3.5.2.1 Phenolic compounds originally present in grape

Mv-3-*O*-glc is used as example of compounds originally present in grape. These compounds are extracted from pomace to must, increasing their concentrations in must. Then, their content decreases due to different degradation processes, some of them to yield anthocyanin derived pigments. Concentration of Mv-3-*O*-glc in grape berries (G) and in must (M) is differentiated, the kinetic equations being:

$$\frac{dG}{dt} = -k_e \cdot G \tag{3.2}$$

$$\frac{dM}{dt} = k_e \cdot G - k_d \cdot M \tag{3.3}$$

where k_e and k_d are the extraction and degradation kinetic constants, respectively.

Integrating Equation 3.2:

$$\int_0^t \frac{dG}{G} = -k_e \int_0^t dt \tag{3.4a}$$

$$\ln\left(\frac{G}{G_0}\right) = -k_e \cdot (t-0) \tag{3.4b}$$

$$G = G_0 \cdot e^{-k_e \cdot t} \tag{3.4c}$$

The Laplace transform [184] was applied to Equation 3.3:

$$\mathscr{L}\left[\frac{dM}{dt}\right] = \mathscr{L}\left[k_e \cdot G - k_d \cdot M\right] \tag{3.5}$$

Substituting Equation 3.4c in 3.5:

$$\mathscr{L}\left[\frac{dM}{dt}\right] = \mathscr{L}\left[k_e \cdot G_0 \cdot e^{-k_e \cdot t} - k_d \cdot M\right] \tag{3.6a}$$

$$\mathscr{L}\left[\frac{dM}{dt}\right] = k_e \cdot G_0 \cdot \mathscr{L}\left[e^{-k_e \cdot t}\right] - k_d \cdot \mathscr{L}\left[M\right] \tag{3.6b}$$

Applying the Laplace transform to Equation 3.6b:

$$s \cdot \mathscr{L}[M] - M_0 = \frac{k_e \cdot G_0}{s + k_e} - k_d \cdot \mathscr{L}[M] \tag{3.7}$$

As the initial concentration of Mv-3-*O*-glc in must is 0, then M_0 = 0:

$$(s + k_d) \cdot \mathscr{L}[M] = \frac{k_e \cdot G_0}{s + k_e} \tag{3.8a}$$

$$\mathscr{L}[M] = \frac{k_e \cdot G_0}{(s + k_e)(s + k_d)} \tag{3.8b}$$

Applying the inverse Laplace transform to 3.8b and reorganizing:

$$M = \frac{k_e \cdot G_0}{k_d - k_e} \cdot \left(e^{-k_e t} - e^{-k_d t}\right) \tag{3.9a}$$

$$M = \frac{k_e \cdot G_0}{k_e - k_d} \cdot \left(e^{-k_d t} - e^{-k_e t}\right) \tag{3.9b}$$

Equation 3.9b is similar to a pharmacokinetic equation.

3.5.2.2 Phenolic derivatives formed by chemical reactions during wine elaboration

Mv-3-*O*-glc-acetaldehyde (Vitisin B) is used as an example of derivatives formed by chemical reactions (Equation 3.10).

$$Mv\text{-}3\text{-}O\text{-}glc + CH_3CHO \xrightarrow{\mathrm{k}_f} Vitisin\ B \tag{3.10}$$

The rate of this reaction can be expressed as differential of each of the components (Equation 3.11a), or as the product of the formation constant (k_f) and the concentration of the components (Equation 3.11b), where m and n are the reaction orders of each species.

$$v = -\frac{dM}{dt} = -\frac{d[CH_3CHO]}{dt} = \frac{dD}{dt} \tag{3.11a}$$

$$v = k_f \cdot [Mv\text{-}3\text{-}O\text{-}glc]^m \cdot [CH_3CHO]^n \tag{3.11b}$$

Assuming that both reaction orders are 1 and that the concentration of acetaldehyde is in excess with respect to that of Mv-3-*O*-glc, and taking into account the concentration of Mv-3-*O*-glc in grape berries (G) and in must (M), and the concentration of the derivative Vitisin B in must (D), then the kinetic reactions can be expressed as follows:

Extraction of the precursor from grape berries:

$$\frac{dG}{dt} = -k_e \cdot G \tag{3.12a}$$

Extraction of the precursor to the must, and degradation of the precursor due to the formation of a derivative:

$$\frac{dM}{dt} = k_e \cdot G - k_f \cdot M \tag{3.12b}$$

Formation and degradation of the derivative:

$$\frac{dD}{dt} = k_f \cdot M - k_d \cdot D \tag{3.12c}$$

Integrating Equation 3.12a (similar to integration of Equation 3.2) and substituting in Equation 3.12b:

$$\frac{dM}{dt} = k_e \cdot G - k_f \cdot M = k_e \cdot G_0 \cdot e^{-k_e \cdot t} \tag{3.13}$$

Integrating Equation 3.13 (similar to integration of Equation 3.3):

$$M = \frac{k_e \cdot G_0}{k_e - k_f} \cdot \left(e^{-k_f t} - e^{-k_e t}\right) \tag{3.14}$$

Substituting Equation 3.14 in Equation 3.12c:

$$\frac{dD}{dt} = \frac{k_f \cdot k_e \cdot G_0}{k_e - k_f} \cdot \left(e^{-k_f t} - e^{-k_e t}\right) - k_d \cdot D \tag{3.15}$$

Applying Laplace transform to Equation 3.15 and rearranging:

$$\mathscr{L}\left[\frac{dD}{dt}\right] = \frac{k_f \cdot k_e \cdot G_0}{k_e - k_f} \cdot \left(\mathscr{L}\left[e^{-k_f t}\right] - \mathscr{L}\left[e^{-k_e t}\right]\right) - k_d \cdot \mathscr{L}[D] \tag{3.16a}$$

$$s \cdot \mathscr{L}[D] = \frac{k_f \cdot k_e \cdot G_0}{k_e - k_f} \cdot \left(\frac{1}{s + k_f} - \frac{1}{s + k_e}\right) - k_d \cdot \mathscr{L}[D] \tag{3.16b}$$

$$\mathscr{L}[D] = \frac{k_f \cdot k_e \cdot G_0}{(k_e - k_f)} \cdot \frac{\frac{(s+k_e)-(s+k_f)}{(s+k_f)\cdot(s+k_e)}}{s + k_d} = \frac{k_f \cdot k_e \cdot G_0}{(k_e - k_f)} \cdot \frac{(k_e - k_f)}{(s + k_f)(s + k_e)(s + k_d)} \tag{3.16c}$$

Applying inverse Laplace transform to Equation 3.16c:

$$D = k_f \cdot k_e \cdot G_0 \cdot \left(\frac{e^{-k_e t}}{(k_f - k_e) \cdot (k_d - k_e)} + \frac{e^{-k_f t}}{(k_e - k_f) \cdot (k_d - k_f)} + \frac{e^{-k_d t}}{(k_e - k_d) \cdot (k_f - k_d)}\right) \tag{3.17}$$

Equation 3.17 is similar to a pharmacokinetic equation. Moreover, regarding only experimental points at high values of time in the profile, when the extraction of the precursor can be considered nearly completed, the first term of this equation summatory is negligible and can be omitted, and thus the equation is similar to Equation 3.9b.

3.5.2.3 Pharmacokinetics of phenolic compounds in red wine

Pharmacokinetics studies the process of the uptake of drugs by the body, the biotransformations that the drugs undergo, the distribution of the drugs in the tissues and the elimination of drug metabolites from the body over a period of time. Indeed, pharmacokinetics studies how the drug is affected by the organism, in contrast to pharmacodynamics, which studies how the drug affects the organism [185].

Rapid intravenous (IV) injection is the simplest way of drug administration from a modeling perspective. Since pharmacokinetics study the absorption, distribution and elimination of drugs, IV administration simplifies drug absorption, allowing the study of distribution and elimination processes in a more simple manner. One of the simplest ways to describe the process of drug distribution and elimination is the one-compartment model, which assumes that the drug can enter and leave the body (*i.e.* open model), and considers the body as a single, uniform compartment (*i.e.* one compartment) [186]. The simplest drug administration, known as an IV bolus, is when the totality of the drug is given in a rapid IV injection. Therefore, the one-compartment open model with IV bolus administration is the simplest pharmacokinetic model. It assumes that the drug distributes instantaneously and rapidly throughout the body (compartment) and drug elimination also begins to occur immediately after the injection. Considering that distribution processes of the drug through the different organs of the body occur rapidly enough, the process can be simplified as if the drug distributed into a single compartment of fluid. The volume of this compartment is referred to as volume of distribution (V_d), and it is a theoretical volume that the drug uniformly distributes immediately after injection. The apparent volume of distribution is a proportion between the dose (Do) and the concentration of drug in plasma (C_p^0), immediately after injection. All of the processes of drug elimination or degradation can be described by the elimination constant rate (k), which represents the proportion between the rate of drug elimination and the amount of drug in the body. Since the amount of drug in the body is time dependent, the rate of elimination also changes over time; however, k is a constant value [187].

For the case of our study, oral administration will be considered, since the absorption process is of interest. The one-compartment model with extravascular oral administration dosing describes the distribution and elimination after oral administration and is shown in Figure 3.12.

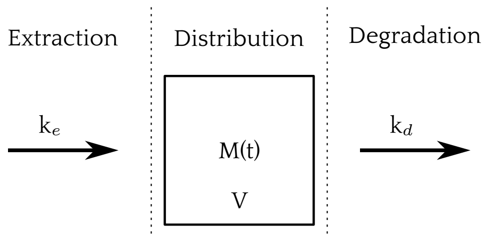


Figure 3.12. Pharmacokinetic model for a drug administered by rapid intravenous injection.

Assuming that the elimination processes follow a first order kinetics, the rate of the process can be expressed as [188]:

$$\frac{dM}{dt} = -k \cdot M \tag{3.18}$$

Integrating with respect to time:

$$M = M_0 \cdot e^{-k \cdot t} \tag{3.19}$$

Considering the premises of the model, the concentration of drug can be expressed as:

$$C = \frac{Do}{V_d} \cdot e^{-k \cdot t} \tag{3.20}$$

The one-compartment model can also be applied for extravascular drug administration. In this case, in contrast to IV injection, it is frequent to find incomplete absorption and latency periods. The integrated differential equation for the one-compartment model excluding latency period is as follows:

$$M = \frac{F \cdot D \cdot k_e}{(k_e - k_d)} \cdot (e^{-k_d \cdot t} - e^{-k_e \cdot t}) \tag{3.21}$$

This work examines the application of pharmacokinetic equations for the study of the concentration profiles for the phenolic compounds during wine elaboration. In this approach, the phenolic compounds in the samples play the role of the drug, whereas the must/wine is considered the compartment in the model. In our case, the input in the one-compartment model are the phenolic compounds extracted from the grape pomace to the must proportionally to a extraction constant (k_e). M is the amount of phenolic compounds in the must (compartment), V is the volume of must, equivalent to V_d and the degradation rate expressed in mg/day is proportional to M and a degradation constant (k_d) expressed in days^{-1}.

For the compounds formed by chemical reaction, the same model can be considered, with the assumption that the chemical reaction takes place within the compartment (Figure 3.13). D represents the derivatives formed by reaction of the original phenolic compounds (M) with other molecules in a rate proportional to a formation constant (k_f). These secondary compounds can undergo degradation at a rate proportional to a k_d. Additionally, M can undergo alternative degradation routes yielding different compounds, with a rate proportional to a degradation constant k_{Md}.

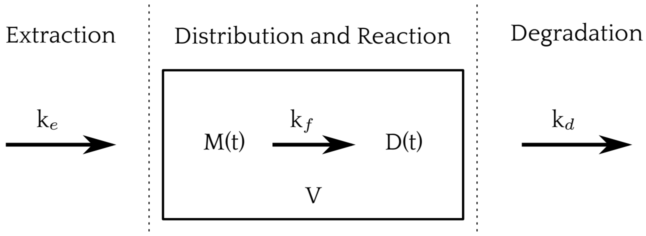


Figure 3.13. Pharmacokinetic model for a drug administered by extravascular/oral administration considering chemical transformation within the compartment.

3.5.2.4 Residuals method for pharmacokinetic calculations

Because there are two processes occurring at the same time (*i.e.* extraction or formation and degradation), the residuals method is a mathematical tool for the analysis of the process by the decomposition of the curve in each of its components. This method assumes that the kinetic order of all processes is one [188].

In this method, the first step is to calculate the degradation parameters using the points at high time values, when the extraction/formation component will approach to zero, while the degradation component will still have a value. The linear regression of the time values against the logarithm of the concentration allows the calculation of the degradation parameters (Figure 3.14). k_d is calculated following Equation 3.22a using the data from the regression of degradation component.

Then, using the calculated degradation data the concentration values are extrapolated as if only degradation process existed. The original experimental data points are then subtracted from the extrapolated values and the logarithms of the residuals are plotted *versus* time (Figure 3.14), allowing the calculation of the extraction/formation parameters using the data from the regression of extraction/formation component (Equation 3.22b) [189].

$$k_d = -slope_d \cdot \ln(10) \tag{3.22a}$$

$$k_{e/f} = -slope_{e/f} \cdot \ln(10) \tag{3.22b}$$

Other parameters can be calculated from these regressions. C_0, or the theoretical concentration at the beginning if only degradation occurred (Equation 3.23a), which is calculated using the intercept of the regression of the degradation component; and A_0, which is the calculated with intercept of the regression of the extraction/formation component (Equation 3.23b).

$$C_0 = 10^{intercept} \tag{3.23a}$$

$$A_0 = 10^{intercept} \tag{3.23b}$$

Following Equation 3.24, the theoretical concentration values are calculated using the constant values, and being plotted *versus* time, along with the experimental concentration values. An example of the profile obtained is shown in Figure 3.15.

$$C_{calc} = C_0 \cdot e^{-k_d \cdot t} - A_0 \cdot e^{-k_{e/f} \cdot t} \tag{3.24}$$

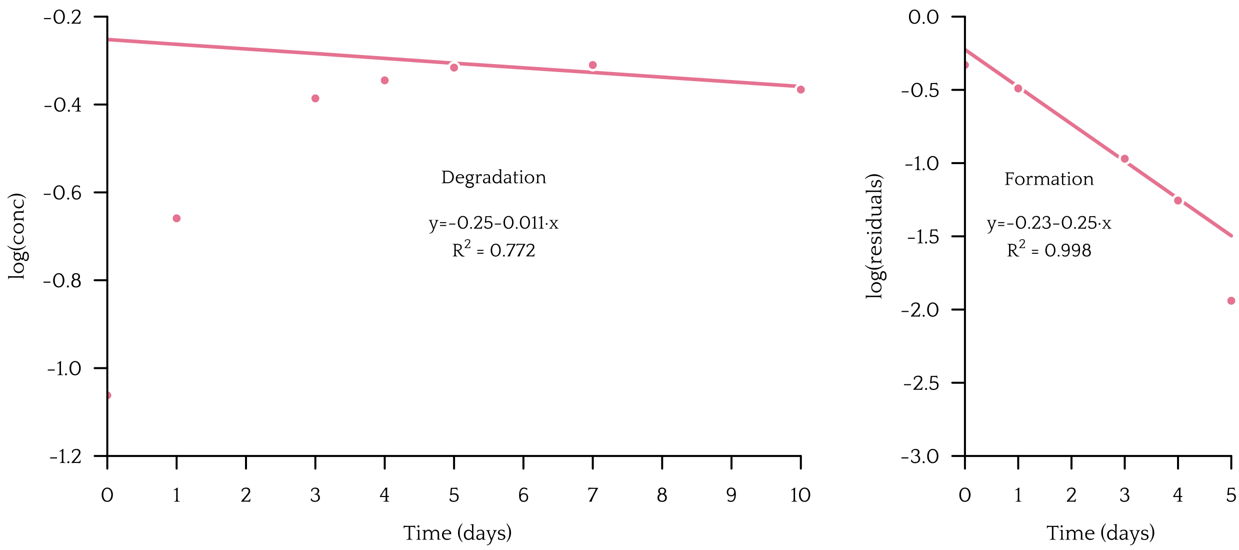


Figure 3.14. Example of the residuals method for the calculation of the degradation constant (k_d) (left) and formation constant (k_f) (right) for Vitisin A data.

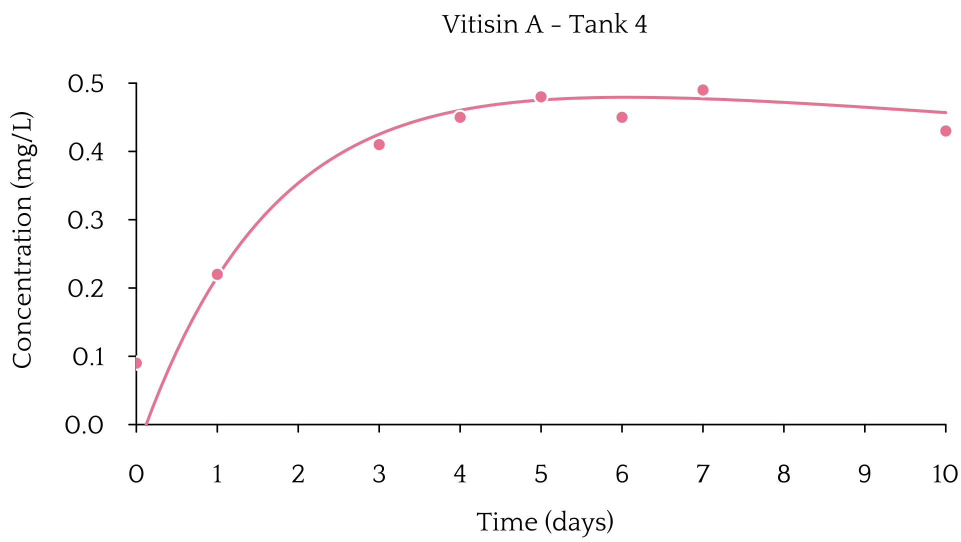


Figure 3.15. Example of the profile obtained by the residuals method along with experimental concentration values found for Vitisin A data.

The error associated to the calculated constants is obtained from the propagation of uncertainties of the slopes and intercepts of the regressions in the residuals method.

The residuals method was employed for the calculation of the kinetic constants for the concentration profiles during AF of the 8 most important anthocyanins and anthocyanin derivatives (Table 3.10):

3.5.2.5 Statistical data analysis of kinetic results

Once the corresponding values of k_e, k_f and k_d were obtained, paired difference Student's t-test was performed to substantiate differences between compounds on one hand, and between oenological conditions applied during wine elaboration on the other hand. The t-values were calcu-

Table 3.10. Selected anthocyanins and anthocyanin derivatives for the kinetic study.

#	Compound
5	Mv-3-*O*-glc
14	cat-Mv-3-*O*-glc
15	epicat-Mv-3-*O*-glc
16	Mv-3-*O*-glc-(epi)cat
18	Mv-3-*O*-glc-pyruvic
19	Mv-3-*O*-glc-acetaldehyde
21	Mv-3-*O*-glc-8-ethyl-cat 1
26	Mv-3-*O*-glc-vinylphenol

lated using Equation 3.25, where Δ is the average difference of all the pairs, n is the number of pairs, and the SD was calculated from the differences of each pair. Additionally, data from the concentration at the end of AF and MLF was also used for this statistic analysis.

$$t_{calc} = \frac{|\Delta|}{SD/\sqrt{n}} \tag{3.25}$$

From the calculated t-values, p-values were obtained and when lower than 0.05 differences were considered as statistically significant.

Chapter 4

Influence of oenological variables on the phenolic composition of wine during the wine-making process

4.1 Determination of anthocyanins, anthocyanin derivatives and tannins in grape must and wine

Grape must and wine samples obtained from the wine-making experiments of 2018 and 2019 performed at pilot scale by the winery Faustino were analyzed by HPLC-DAD and HPLC-DAD-ESI(+)-MS/MS following the methods described in Section 3.3, in order to identify and quantify anthocyanins, anthocyanin derivatives and tannins. Results of the elaborations from 2018 are shown in Tables S1, S2, S3 and S4 of Supplementary Material. Results of the elaborations from 2019 are shown in Tables S5, S6, S7 and S8 of Supplementary Material.

Additionally, data corresponding to wine elaborations at industrial scale from a previous work of our research group was used for comparison purposes. The concentrations of the six anthocyanin derivatives compared during AF is shown in Table 4.1. This data had been included in the Ph.D. dissertation of Prieto Perea [179].

Color measurements for all the grape must and red wine samples of the experiments of Mendavia from 2018 and Alfaro and Laguardia from 2019 are shown in Tables S9, S10 and S11 of the Supplementary Material.

4.2 Kinetics of the wine-making process

The residuals method was applied to the data of the concentration profiles of the selected anthocyanins and anthocyanin derivatives during AF (Table 3.10). The calculated kinetic constants of the process, *i.e.* k_e, k_f and k_d, are shown in Tables S12 and S13 of the Supplementary Material.

The concentration data of the selected anthocyanin derivatives from the experiments at industrial scale was also treated following the residuals method in order to obtain the corresponding constant values (Table 4.2), and to elaborate their evolution profiles.

Table 4.1. Concentration of selected anthocyanin derivatives during AF of the experiments at industrial scale.

Time (days)	Vitisin B	Vitisin A	Mv-3-*O*-glc-8-ethyl-cat 1	Mv-3-*O*-glc-vinylphenol	Cat-Mv-3-*O*-glc	Epicat-Mv-3-*O*-glc
0	0.008	0.017	0.001	-[b]	0.035	0.005
1	0.014	0.036	0.001	0.001	0.035	0.007
2	0.098	0.087	0.001	0.001	0.047	0.006
3	0.284	0.211	0.001	0.002	0.052	0.029
4	2.717	0.617	0.012	0.088	0.115	0.038
5	3.299	0.799	0.013	0.106	0.131	0.052
6	3.531	0.915	0.019	0.101	0.161	0.048
7	4.067	1.031	0.017	0.088	0.175	0.050
8	3.940	1.158	0.022	0.092	0.162	0.056
9	2.955	0.919	0.017	0.090	0.150	0.054
10	1.818	1.652	0.016	0.124	0.153	0.040
11	2.438	0.959	0.014	0.103	0.156	0.046
12	2.071	0.971	0.014	0.116	0.144	0.040

[a] Concentrations are expressed in mg of Mv-3-*O*-glc equiv./L.
[b] No data available.

Table 4.2. Results of k_f and k_d (mean $\pm$ SD) calculated by the residuals method with the concentration profiles of the selected anthocyanins and anthocyanin derivatives from the wine-making experiments at industrial scale.

#	Compound	k_f	k_d
14	Cat-Mv-3-*O*-glc	0.7 ± 0.1	0.03 ± 0.01
15	Epicat-Mv-3-*O*-glc	0.37 ± 0.01	0.08 ± 0.01
18	Vitisin A	0.47 ± 0.03	0.05 ± 0.02
19	Vitisin B	0.56 ± 0.02	0.14 ± 0.02
21	Mv-3-*O*-glc-8-ethyl-cat 1	0.9 ± 0.1	0.04 ± 0.01
26	Mv-3-*O*-glc-vinylphenol	0.9 ± 0.5	0.04 ± 0.02

[a] Constants are expressed in $days^{-1}$.

4.3 Statistical analysis of the kinetic constants

The constant values (k_e or k_f and k_d) and the concentrations found in the wine at the end of AF and MLF were statistically compared according to the phenolics and the oenological variables considered. Thus, the *p*-values were calculated using the paired difference Student's t-test (Tables 4.3 and 4.4) in order to determine significant differences between compounds (Table 4.3) and oenological conditions employed during wine elaboration (Table 4.4).

For comparisons between compounds, concentrations were normalized against the maximum value of the adjusted curve of each concentration profile. Hence, the comparisons between compounds consider the variation relative to the maximum value of each profile curve.

Table 4.3. *p*-values from the paired difference Student's t-test comparing compounds using data of the k_f and k_d calculated by the residuals method coupled to the concentration profiles of the selected anthocyanins and anthocyanin derivatives, and the normalized concentration data of these compounds at the end of AF and MLF.

	k_f		k_d		Norm. conc. end AF	Norm. conc. end MLF
Compounds	**n**	***p*-value**	**n**	***p*-value**	***p*-value (n=23)**	***p*-value (n=24)**
Vitisin A *vs* Vitisin B	24	0.63	12	†**$1.5 \cdot 10^{-2}$**	•**$5.3 \cdot 10^{-3}$**	•**$2.0 \cdot 10^{-7}$**
Mv-3-*O*-glc-vinylphenol *vs* Vitisin A	20	0.27	16	†**$5.5 \cdot 10^{-7}$**	0.10	•**$2.0 \cdot 10^{-3}$**
Mv-3-*O*-glc-vinylphenol *vs* Vitisin B	20	0.31	16	†**$2.1 \cdot 10^{-7}$**	0.54	•**$5.6 \cdot 10^{-8}$**
Mv-3-*O*-glc-8-ethyl-cat 1 *vs* cat-Mv-3-*O*-glc	16	0.94	10	•**$4.8 \cdot 10^{-2}$**	0.88	•**$3.6 \cdot 10^{-8}$**
Mv-3-*O*-glc-8-ethyl-cat 1 *vs* epicat-Mv-3-*O*-glc	21	0.87	11	0.90	•**$7.2 \cdot 10^{-5}$**	•**$2.3 \cdot 10^{-7}$**
Mv-3-*O*-glc-8-ethyl-cat 1 *vs* Mv-3-*O*-glc-(epi)cat	18	0.43	12	†**$4.5 \cdot 10^{-2}$**	•**$4.4 \cdot 10^{-3}$**	0.11
epicat-Mv-3-*O*-glc *vs* cat-Mv-3-*O*-glc	18	0.73	11	•**$1.5 \cdot 10^{-3}$**	0.11	•**$1.7 \cdot 10^{-3}$**
cat-Mv-3-*O*-glc *vs* Mv-3-*O*-glc-(epi)cat	15	0.94	10	†**$1.0 \cdot 10^{-5}$**	0.11	†**$1.9 \cdot 10^{-7}$**
epicat-Mv-3-*O*-glc *vs* Mv-3-*O*-glc-(epi)cat	19	0.66	10	†**$4.7 \cdot 10^{-2}$**	0.83	†**$1.2 \cdot 10^{-5}$**

[a] *p*-values $\leqslant 0.05$ indicate significant difference between the data compared and are highlighted in bold.
[b] • indicates that the compound on the left has a higher value.
[c] † indicates that the compound on the left has a lower value.

Table 4.4. p-values of the paired difference Student's t-test comparing the oenological variables employed during wine elaboration using data of the k_e, k_f and k_d calculated by the residuals method with the concentration profiles of the selected anthocyanins and anthocyanin derivatives, and the concentration data at the end of AF and MLF.

Variable	Vitisin A	Vitisin B	Mv-3-*O*-glc-vinylphenol	Mv-3-*O*-glc	Mv-3-*O*-glc-8-ethyl-cat 1	Mv-3-*O*-glc-(epi)cat	cat-Mv-3-*O*-glc	epicat-Mv-3-*O*-glc
k_e or k_f								
Cultivar *Graciano*	0.10	**•0.019**	0.32	0.15	**†0.046**	0.42	0.87	**†0.006**
Cultivar *Mazuelo*	**•0.035**	0.12	**•0.033**	**•0.023**	**†0.003**	**†0.020**	0.41	**†0.022**
Addition of Tannins	0.71	0.70	0.95	0.12	0.98	0.14	**†0.027**	0.12
Microoxygenation	0.73	0.72	0.81	0.26	0.58	0.23	**†0.033**	0.44
Ionic Exchange	0.95	0.44	0.26	0.13	0.23	0.18	0.27	0.69
k_d								
Cultivar *Graciano*	0.93	0.26	0.43	0.066	0.98	0.55	0.75	0.96
Cultivar *Mazuelo*	0.43	0.091	0.44	0.052	**•0.020**	0.066	0.14	0.18
Addition of Tannins	**†0.045**	0.30	0.91	0.65	0.57	0.74	0.64	0.27
Microoxygenation	0.78	0.73	0.089	0.59	0.33	0.18	**•0.037**	0.75
Ionic Exchange	0.32	0.56	0.23	0.78	0.20	0.60	0.83	0.16
Concentration at the end of AF								
Cultivar *Graciano*	0.35	0.40	0.72	1.0	**•$2.4 \cdot 10^{-4}$**	0.18	0.26	0.31
Cultivar *Mazuelo*	**†0.001**	0.86	0.29	0.051	**•0.001**	0.7	0.4	0.054
Addition of Tannins	0.53	0.89	0.38	0.12	0.15	**•0.046**	0.25	0.47
Microoxygenation	0.25	0.73	0.11	0.56	0.75	0.65	0.31	0.28
Ionic Exchange	**†0.015**	0.44	0.81	**†$6.6 \cdot 10^{-4}$**	**•0.045**	0.18	**•0.014**	0.46
Concentration at the end of MLF								
Cultivar *Graciano*	0.99	0.54	0.33	**†0.017**	**•0.020**	**•0.040**	0.85	0.082
Cultivar *Mazuelo*	0.14	0.16	**•$5.5 \cdot 10^{-7}$**	**†$4.0 \cdot 10^{-5}$**	**•0.006**	**•0.049**	0.78	**†$6.5 \cdot 10^{-4}$**
Addition of Tannins	0.45	0.82	0.51	0.12	0.09	0.43	**•0.030**	**•0.038**
Microoxygenation	0.10	**•0.050**	0.12	0.64	0.63	0.79	0.16	0.10
Ionic Exchange	0.10	0.15	**†0.010**	**†$2.9 \cdot 10^{-6}$**	**•0.004**	0.83	0.51	0.55

[a] Values of $p \leqslant 0.05$ indicate statistical difference between the data compared are highlighted in bold.
[b] • indicates that positive value of the oenological variable produces a higher value.
[c] † indicates that positive value of the oenological variable produces a lower value.

4.4 Stability of vitisin A and vitisin B

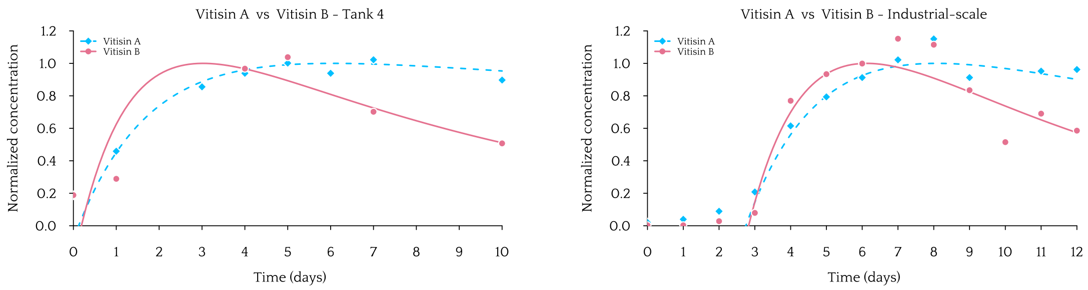
Vitisins are pyranoanthocyanin derivatives originated from the cycloaddition reaction between an anthocyanin and a molecule such as pyruvic acid or acetaldehyde, among others. These compounds are mainly formed during wine elaboration. Among the vitisins, Vitisin A and Vitisin B were the ones studied in this work.

At the end of AF, the concentration of Vitisin A is significantly lower than that of Vitisin B ($p = 5.3 \cdot 10^{-3}$). Both compounds compete for consuming Mv-3-*O*-glc for their formation. Mv-3-*O*-glc is present in grape and is extracted to the must at an early stage of the wine-making process. The formation of the vitisins depends on the extraction rate of Mv-3-*O*-glc from grapes. It is assumed that the other two compounds involved in the reaction, *i.e.* pyruvic acid and acetaldehyde, are in excess compared to Mv-3-*O*-glc, and do not impose any restriction or control to the kinetics of the formation reaction of the vitisins. Moreover, is logical that the compound with the highest k_f value of the pair, *i.e.* Vitisin B, consumes more reactant and finally is present in higher concentrations.

Vitisin A and Vitisin B show no significant differences in their k_f values when considering data from all tanks overall ($p = 0.63$). However, in the cases where only *Tempranillo* grape cultivar was employed (tanks 1-8), Vitisin A shows significantly lower k_f values than Vitisin B ($p = 0.011$) (Figure 4.1a). The same fact is found for the industrial-scale elaboration (Table 4.2 and Figure 4.1b), for which only *Tempranillo* single grape cultivar was employed.

Regarding their stability, Vitisin B has a significantly higher k_d value than Vitisin A ($p = 0.015$) when considering data from all tanks overall, which results in Vitisin B showing a significantly greater decrease in concentration at the end of both AF and MLF compared to Vitisin A (Figure 4.1a). This observation was evident in the data from the industrial-scale wine-making experiments (Figure 4.1b).

As a matter of fact, it is foreseeable to observe a higher degradation of Vitisin B in the long term, leading to even lower concentrations than of Vitisin A in the final wine.



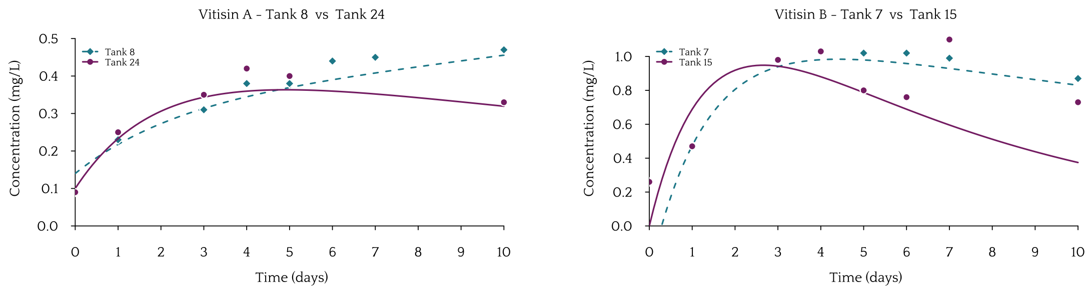
(a) Tank 4 - *Tempranillo* single grape cultivar. (b) Industrial-scale elaboration.

Figure 4.1. Normalized concentration profiles obtained for Vitisin A and Vitisin B in different tanks of the experiments from Mendavia 2018 and the industrial-scale elaboration. (a) In the presence of the single grape cultivar *Tempranillo*. (b) In the industrial-scale experiments only *Tempranillo* single grape cultivar was employed.

4.4.1 Influence of oenological variables on the contents of vitisins A and B

Regarding the specific oenological variables studied, the presence of *Mazuelo* grape cultivar mixed with *Tempranillo* (tanks 17-24) produces a significant increase in the k_f values of Vitisin A compared to the elaborations in which only *Tempranillo* grape cultivar was employed (tanks 1-8) ($p = 0.04$), as shown in Figure 4.2a. The average k_f values for Vitisin A of these wine elaborations were 0.5 $\pm$ 0.2 days^{-1} when *Tempranillo* grapes were used, and 0.8 $\pm$ 0.4 days^{-1} when a mixture of *Mazuelo* and *Tempranillo* grapes were employed. Additionally, a significant decrease in the concentration of Vitisin A was observed at the end of AF (p = 0.001).

In the case of Vitisin B, the presence of the grape cultivar *Graciano* mixed with *Tempranillo* (tanks 9-16) produces a significant increase in the k_f values compared to the elaborations in which only *Tempranillo* grape cultivar was employed (p = 0.019), as shown in Figure 4.2b.



(a) Profile of Vitisin A in tanks 8 and 24.

(b) Profile of Vitisin B in tanks 7 and 15.

Figure 4.2. Concentration profiles obtained for Vitisin A (left) and Vitisin B (right) in different tanks of the experiments from Mendavia 2018. (a) In the presence of the secondary grape cultivar *Mazuelo* (tank 24) in comparison to the single grape cultivar *Tempranillo* (tank 8). (b) In the presence of the secondary grape cultivar *Graciano* (tank 15) in comparison to the single grape cultivar *Tempranillo* (tank 7).

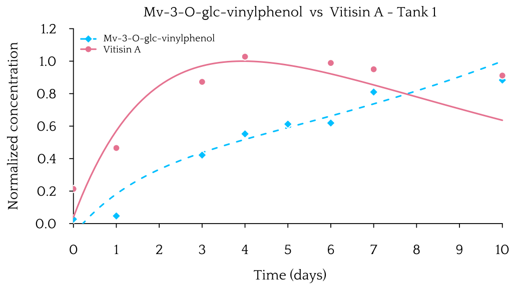
From the other oenological variables studied (i) the addition of tannins produced a significant decrease in the k_d values of Vitisin A (p = 0.045), (ii) the use of ionic exchange also produced a significant decrease in the concentration of Vitisin A at the end of AF (p = 0.015), and (iii) the use of microoxygenation caused a significant increase in the concentration of Vitisin B at the end of MLF (p = 0.049). The other variables did not produce any significant changes in the constant or concentration values for the vitisins.

4.5 Evolution of vinylphenols and vitisins A and B

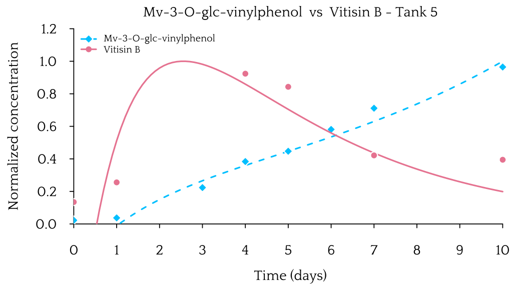
The comparison of the compound Mv-3-*O*-glc-vinylphenol with both Vitisin A and Vitisin B resulted in the following observations:

- The concentration of Mv-3-*O*-glc-vinylphenol increases until the end of AF, having negative values of k_d, since degradation has not started yet at this stage of wine elaboration. As a result, Mv-3-*O*-glc-vinylphenol has a significantly lower k_d value than vitisins when compared individually (Figures 4.3a and 4.3b). Consequently, Mv-3-*O*-glc-vinylphenol has a significantly higher stability and thus, a significantly lower concentration loss at the end of MLF.

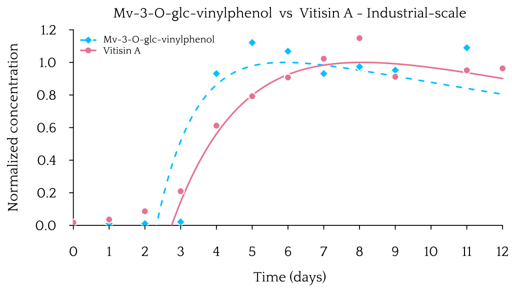
- However, considering the industrial-scale elaboration, Mv-3-*O*-glc-vinylphenol and Vitisin A show similar k_d values (0.04 $\pm$ 0.02 *vs* 0.05 $\pm$ 0.02 days^{-1}) (Figure 4.3c), while Vitisin B has a higher k_d value than the other two compounds (0.14 $\pm$ 0.02 days^{-1}) (Figure 4.3d). The k_d of Mv-3-*O*-glc-vinylphenol has a positive value, since the compound starts degrading before the end of AF under this elaboration conditions.



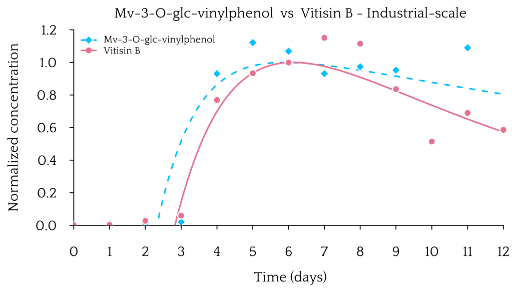
(a) Tank 1 of experiments from Mendavia 2018.



(b) Tank 5 of experiments from Mendavia 2018.



(c) Industrial-scale elaboration.



(d) Industrial-scale elaboration.

Figure 4.3. Concentration profiles obtained for Mv-3-*O*-glc-vinylphenol compared to Vitisin A (a, c) and Vitisin B (b, d) in different tanks of the experiments from Mendavia 2018 (a, b) and the industrial-scale elaboration (c, d).

4.5.1 Influence of oenological variables on the contents of malvidin-3-*O*-glucoside-vinylphenol

The presence of the secondary grape cultivar *Mazuelo* (tanks 17-24) produces a significant increase in the k_f of Mv-3-*O*-glc-vinylphenol compared to the use of the single grape cultivar *Tempranillo* (tanks 1-8) (p = 0.033) (Figure 4.4). Furthermore, the use of the grape mixture of *Mazuelo* and *Tempranillo* produces a significant increase in the concentration of Mv-3-*O*-glc-vinylphenol at the end of MLF ($p = 5.5 \cdot 10^{-5}$). Moreover, the use of ionic exchange technology also increases the concentration of this phenolic compound significantly (p = 0.010).

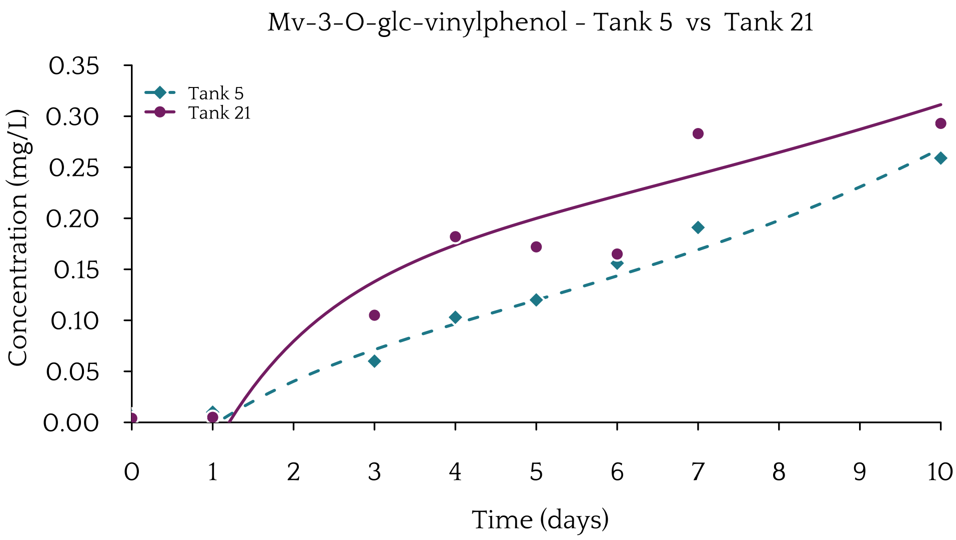


Figure 4.4. Concentration profiles obtained for Mv-3-*O*-glc-vinylphenol using *Tempranillo* grape cultivar (tank 5) and the mixture of *Tempranillo* and *Mazuelo* (tank 21) of the wine-making experiments from Mendavia 2018.

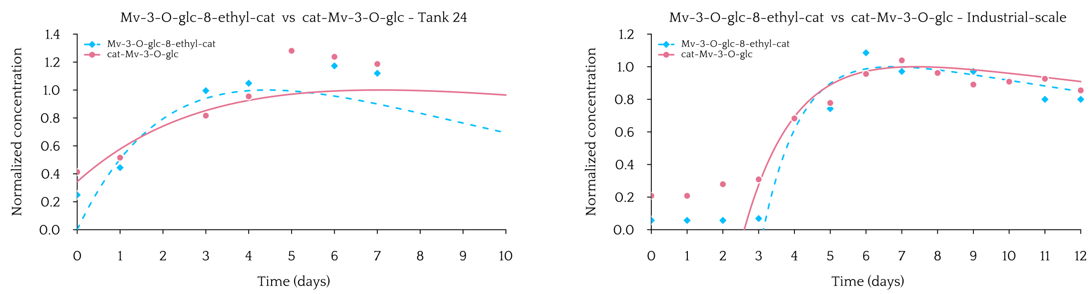
4.6 Stability of direct and indirect condensation products

The derivatives formed by condensation with flavan-3-ols can occur directly [59] or indirectly, mediated by acetaldehyde and generating an ethyl bridge in the structure [60]. Direct anthocyanin-flavan-3-ol condensation products have a similar behavior towards pH changes than anthocyanins. On the contrary, indirect condensation products are more resistant than the precursor anthocyanins, leading to more stable aged wines.

The indirect condensation product, Mv-3-*O*-glc-8-ethyl-cat, was compared to three different direct condensation products: cat-Mv-3-*O*-glc (F-A^+), epicat-Mv-3-*O*-glc (F-A^+) and Mv-3-*O*-glc-(epi)cat (A^+-F). Additionally, the direct condensation products were compared among themselves to find differences in their behavior and stability.

4.6.1 Comparison of the evolution of indirect *vs* direct F-A^+ condensation products

The comparison of the k_d of the indirect condensation product, Mv-3-*O*-glc-8-ethyl-cat, with the direct condensation (F-A^+) product cat-Mv-3-*O*-glc (Figures 4.5a and 4.5b) showed that the former has a significantly higher value and thus, lower stability than the direct condensation product. This fact was observed with all the oenological conditions studied in the wine-making experiments at pilot scale and at industrial-scale. This more unstable behavior of indirect condensation derivatives has been previously reported [72, 190].



(a) Tank 24 of experiments from Mendavia 2018. (b) Industrial-scale elaboration.

Figure 4.5. Concentration profiles of Mv-3-*O*-glc-8-ethyl-cat and cat-Mv-3-*O*-glc (a) in tank 24 of the wine-making experiments from Mendavia 2018 at pilot scale and (b) in the industrial-scale elaboration.

4.6.2 Comparison of the evolution of indirect *vs* direct A^+-F condensation products

The comparison of k_d of the indirect condensation product Mv-3-*O*-glc-8-ethyl-cat and the direct A^+-F product, Mv-3-*O*-glc-(epi)cat indicated that the former is lower (p = 0.045) (Figure 4.6). Therefore, the indirect condensation products are more stable than the direct A^+-F ones.

4.6.3 Comparison of the evolution of direct condensation products

Both direct (F-A^+) condensation products, cat-Mv-3-*O*-glc and epicat-Mv-3-*O*-glc, present similar k_f. However, their k_d are significantly different, cat-Mv-3-*O*-glc exhibiting a lower constant value and thus, a higher stability than epicat-Mv-3-*O*-glc (Figures 4.7a and 4.7b).

4.6.4 Comparison of the evolution of direct condensation products F-A^+ *vs* A^+-F

The influence of the relative position of the flavan-3-ol and the anthocyanin in the condensation product on the kinetic constants was studied. The F-A^+ compounds (cat-Mv-3-*O*-glc and

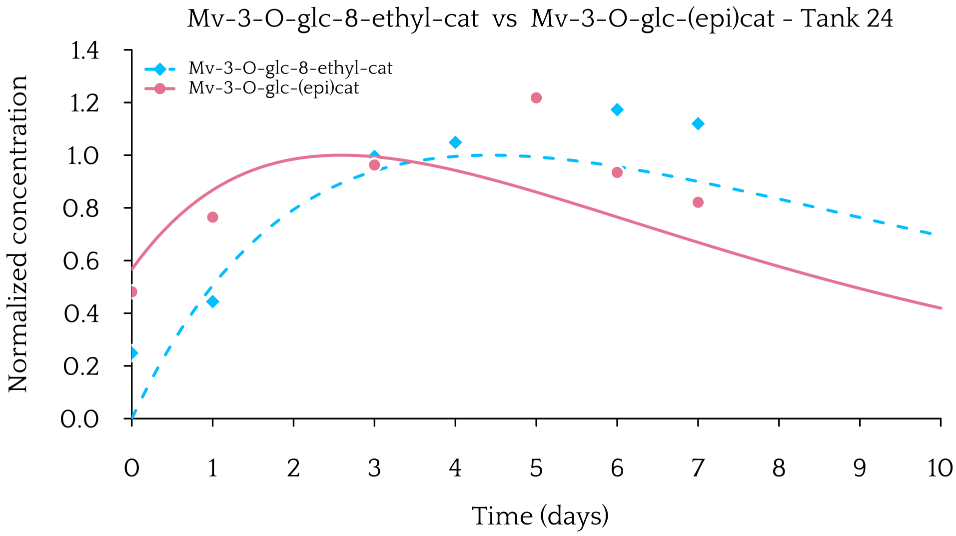
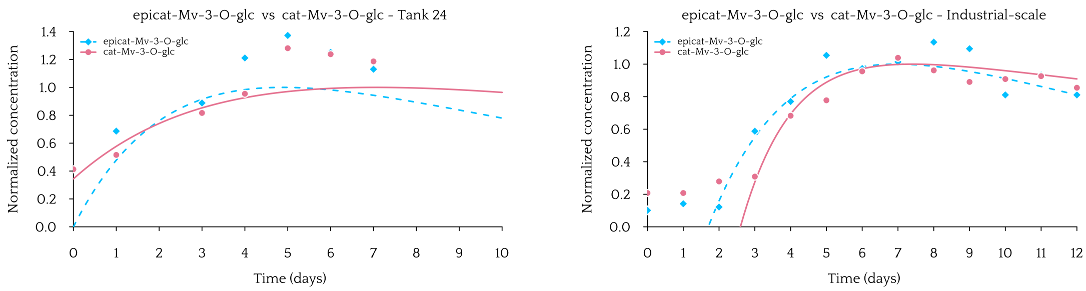


Figure 4.6. Concentration profiles of Mv-3-*O*-glc-8-ethyl-cat and Mv-3-*O*-glc-(epi)cat in tank 24 of the wine-making experiments from Mendavia 2018.



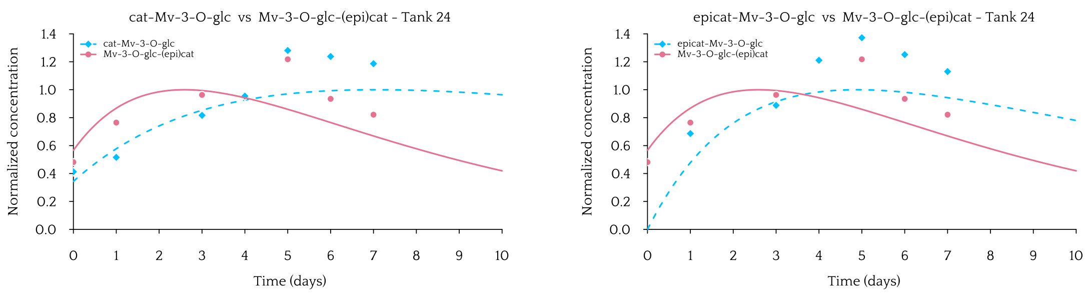
(a) Tank 24 of experiments from Mendavia 2018.

(b) Industrial-scale elaboration.

Figure 4.7. Concentration profiles of epicat-Mv-3-*O*-glc and cat-Mv-3-*O*-glc (a) in tank 24 of the wine-making experiments from Mendavia 2018 at pilot scale and (b) in the industrial-scale elaboration.

epicat-Mv-3-*O*-glc) have a significantly lower k_d than the A^+-F compound (Mv-3-*O*-glc-(epi)cat) ($p = 1.0 \cdot 10^{-5}$) (Figures 4.8a and 4.8b).

Table 4.1 shows that in the industrial-scale elaboration, the concentration of A^+-F compound cat-Mv-3-*O*-glc (0.144) is four times higher than that of epicat-Mv-3-*O*-glc (0.040) and ten times higher than that of the indirect condensation product Mv-3-*O*-glc-8-ethyl-cat (0.014). The same is observed for the experiments of Mendavia 2018, in all tanks when considered overall.



(a) *vs* cat-Mv-3-*O*-glc.

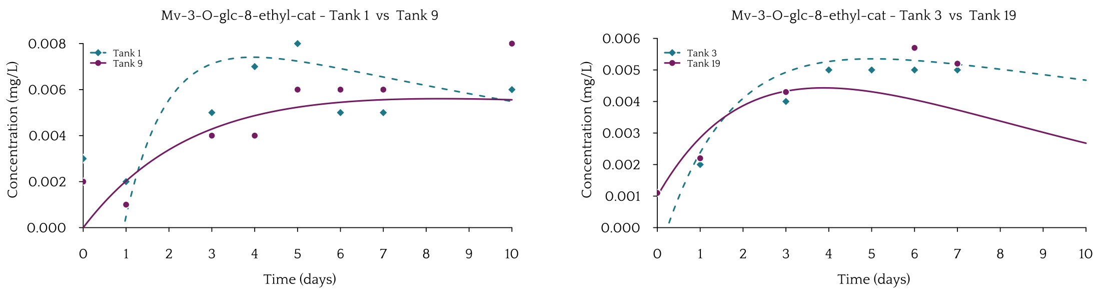
(b) *vs* epicat-Mv-3-*O*-glc.

Figure 4.8. Concentration profiles obtained for Mv-3-*O*-glc-(epi)cat compared to (a) cat-Mv-3-*O*-glc and (b) epicat-Mv-3-*O*-glc in tank 24 of the experiments from Mendavia 2018.

4.6.5 Influence of oenological variables on the contents of direct and indirect condensation products

4.6.5.1 Mv-3-*O*-glc-8-ethyl-cat

In the presence of the secondary grape cultivar *Graciano* k_f values decrease significantly respect to k_f obtained in the wine-making experiments using the single grape cultivar *Tempranillo* (p = 0.046) (Figure 4.9a). The use of *Mazuelo* as secondary grape cultivar also resulted in significantly lower k_f values (p = 0.003), and higher k_d values then when only *Tempranillo* cultivar was employed (p = 0.02) (Figure 4.9b).



(a) With (tank 9) and wihtout (tank 1) *Graciano*.

(b) With (tank 19) and without (tank 3) *Mazuelo*.

Figure 4.9. Concentration profiles of Mv-3-*O*-glc-8-ethyl-cat in different tanks of the wine-making experiments from Mendavia 2018 at pilot scale. (a) In the presence of *Graciano* (tank 9) grape cultivar compared to the single grape cultivar *Tempranillo* (tank 1). (b) In the presence of grape cultivar *Mazuelo* (tank 19) compared to the single grape cultivar *Tempranillo* (tank 3).

4.6.5.2 Mv-3-*O*-glc-(epi)cat

In the presence of the secondary grape cultivar *Mazuelo*, the k_f values significantly decrease in comparison with the use of the single grape cultivar *Tempranillo* (p = 0.02) (Figure 4.10).

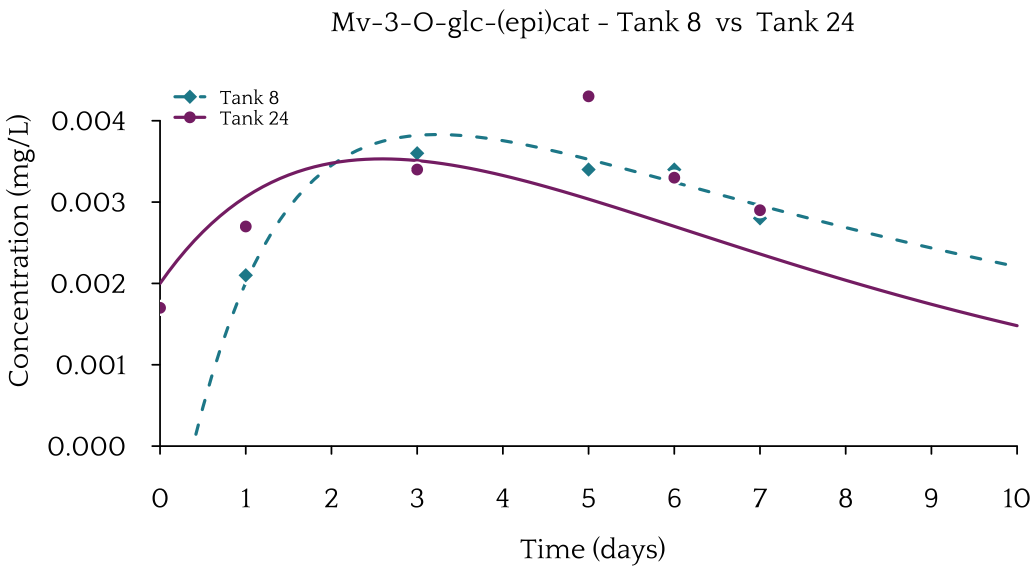
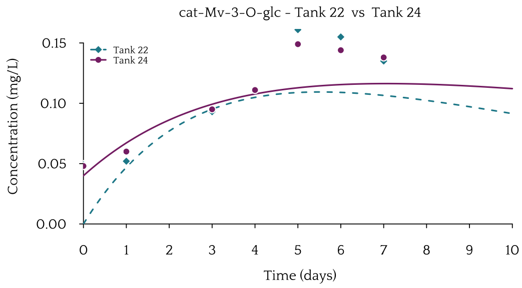


Figure 4.10. Concentration profiles of Mv-3-*O*-glc-(epi)cat using the single grape cultivar *Tempranillo* (tank 8) and using mixture of *Mazuelo* and *Tempranillo* (tank 24) of the wine-elaboration experiments from Mendavia 2018 at pilot scale.

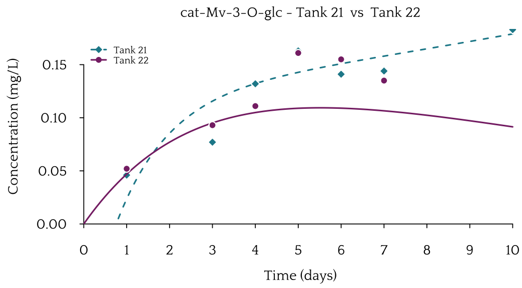
4.6.5.3 Cat-Mv-3-*O*-glc

For this condensation product, the grape cultivar used in the wine-making experiment did not influence significantly the kinetic constants or concentrations. However, the other three studied oenlogical variables, *i.e.* addition of tannins, microoxygenation and ionic exchange, had a significant impact on the kinetic constants.

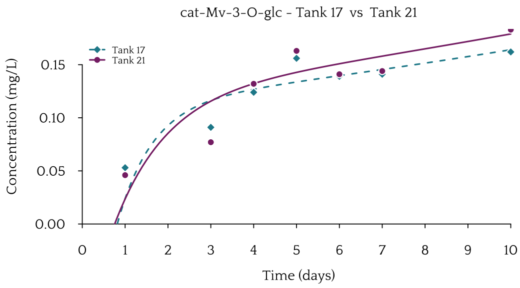
The addition of tannins (tank 24) produced a significant decrease in the k_f (Figure 4.11a). Similarly, microoxygenation during MLF (tank 22) induced a significant decrease in k_f, and a significant increase in k_d values (Figure 4.11b). The use of ionic exchange at the beginning of AF (tank 21) resulted in a significant increase in the concentration of this compound at the end of AF (Figure 4.11c). This increase is not observed at the end of MLF (p = 0.51).



(a) Tannins Yes (tank 24) *vs* No (tank 22).



(b) Microoxygenation Yes (tank 22) *vs* No (tank 21).

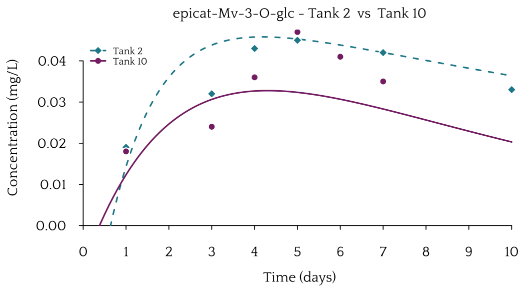


(c) Ionic Exchange Yes (tank 21) *vs* No (tank 17).

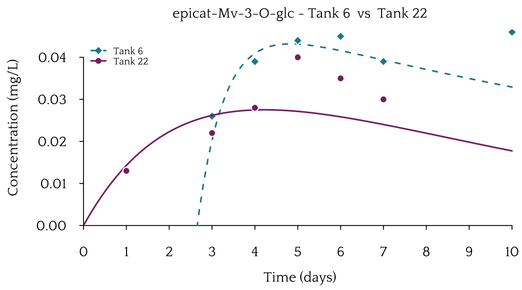
Figure 4.11. Concentration profiles of cat-Mv-3-*O*-glc in different tanks of the wine-making experiments from Mendavia 2018 at pilot scale, studying (a) the addition of tannins (tank 24), (b) the use of microoxygenation (tank 22), and (c) the use of ionic exchange (Tank 21).

4.6.5.4 Epicat-Mv-3-*O*-glc

In the presence of either secondary grape cultivar *Graciano* (tanks 9-16) or *Mazuelo* (tanks 17-24), the k_f values are significantly lower than in the case that the single grape cultivar *Tempranillo* was used (tanks 1-8) (Figures 4.12a and 4.12b).



(a) With (tank 10) and wihtout (tank 2) *Graciano*.



(b) With (tank 22) and without (tank 6) *Mazuelo*.

Figure 4.12. Concentration profiles of epicat-Mv-3-*O*-glc in different tanks of the wine-making experiments from Mendavia 2018 at pilot scale: using a secondary grape cultivar (a) *Graciano* (tank 10) or (b) *Mazuelo* (tank 22), and using single grape cultivar *Tempranillo* (tanks 2 and 6).

Chapter 5

Nanoencapsulation of grape pomace extracts for cosmetic applications

5.1 Phenolic compounds in grape pomace extracts

The TE and GE of phenolic compounds were obtained as a purple paste following a green extraction procedure described in Section 3.4.1. The yield of the extraction procedure was 38.7% and 42.4% in terms of dry weight, respectively. Considering a previous research [191], anthocyanins are the major components in red grape pomace, while the other phenolic components have been reported in significantly smaller amounts. For this reason, in this study only the former were quantified. The phenolic profiles of the grape pomace extracts were characterized by UHPLC-DAD-ESI(+/-)-QToF/MS. Phenolic compounds were identified based on their t_R, UV-Vis and MS spectra (Table 5.1). The anthocyanins in TE and GE were quantified by HPLC-DAD-ESI(+)-QqQ/MS (Table 5.2).

Fourteen flavan-3-ols, monomers, and trimers of (-)-epicat and (+)-cat; 10 flavonols, derivatives of quercetin (quer) and kaempferol; 1 hydroxycinnamic acid, a derivative of *p*-coumaric acid; 1 hydroxybenzoic acid; 1 dihydroflavonol, derivative of quer; and 13 anthocyanins, 3-*O*-glycosides of Mv, Pt, Cy, Pn, and Dp, were identified in the extract. Anthocyanins were the major components, in accordance with previously reported findings; Mv-3-*O*-glc being the most important in red grape skin extracts [192, 193]. Regarding the other phenolic families, the most abundant were reported to be phenolic acids, flavan-3-ols and flavonols [194]. In addition, oligomers, such as (-)-epicat and (+)-cat, and polymers of flavan-3-ols have also been found in grape seeds [195].

Table 5.1. Identification of phenolic compounds in TE and GE by UHPLC-DAD-ESI-QToF/MS analysis.

#	Compound	t_R (min)	Max. UV-Vis Bands (nm)	Molecular formula $[M+H]^+$	$[M+H]^+$ m/z (error)	Molecular formula $[M-H]^-$	$[M-H]^-$ m/z (error)
	Flavan-3-ols						
1	((epi)cat)$_3$ (1)	3.28	283	$C_{45}H_{39}O_{18}$	867.199 (0.8)	$C_{45}H_{37}O_{18}$	865.199 (0.8)
2	procyanidin B I	5.52	280	$C_{30}H_{27}O_{12}$	579.151 (0.5)	$C_{30}H_{25}O_{12}$	577.135 (0.5)
3	((epi)cat)$_3$ (2)	5.73	283	$C_{45}H_{39}O_{18}$	867.213 (0.8)	$C_{45}H_{37}O_{18}$	865.199 (0.8)
4	procyanidin B II	6.43	280	$C_{30}H_{27}O_{12}$	579.150 (-0.7)	$C_{30}H_{25}O_{12}$	577.136 (1.2)
5	cat [a]	7.53	278	$C_{15}H_{15}O_6$	291.087 (0.4)	$C_{15}H_{13}O_6$	289.072 (0.5)
6	((epi)cat)$_3$ (3) [a]	7.56	283	$C_{45}H_{39}O_{18}$	867.212 (-1.5)	$C_{45}H_{37}O_{18}$	865.199 (0.8)
7	procyanidin B III	8.24	280	$C_{30}H_{27}O_{12}$	579.150 (-0.3)	$C_{30}H_{25}O_{12}$	577.135 (0.3)
8	((epi)cat)$_3$ (4)	8.65	283	$C_{45}H_{39}O_{18}$	867.214 (-1.5)	$C_{45}H_{37}O_{18}$	865.199 (0.8)
9	procyanidin B IV	12.08	280	$C_{30}H_{27}O_{12}$	579.151 (0.6)	$C_{30}H_{25}O_{12}$	577.135 (0.3)
10	((epi)cat)$_3$ (5)	12.91	283	$C_{45}H_{39}O_{18}$	867.214 (-1.5)	$C_{45}H_{37}O_{18}$	865.199 (0.8)
11	epicat	16.25	278	$C_{15}H_{15}O_6$	291.087 (0.0)	$C_{15}H_{13}O_6$	289.072 (0.7)
12	((epi)cat)$_3$ (6)	17.39	283	$C_{45}H_{39}O_{18}$	867.216 (-1.5)	$C_{45}H_{37}O_{18}$	865.199 (0.8)
13	procyanidin B-gallate	19.40	280	$C_{37}H_{31}O_{16}$	731.160 (-1.3)	$C_{37}H_{29}O_{16}$	729.140 (-5.8)
14	((epi)cat)$_3$ (7)	20.50	283	$C_{45}H_{39}O_{18}$	867.216 (2.8)	$C_{45}H_{37}O_{18}$	865.199 (0.8)
	Flavonols						
15	quer-hexosyl-hexoside-1	23.80	264, 344	$C_{27}H_{31}O_{17}$	627.157 (1.1)	$C_{27}H_{29}O_{17}$	625.137 (-3.5)
16	quer-hexosyl-hexoside-2	25.20	264, 344	$C_{27}H_{31}O_{17}$	627.156 (0.1)	$C_{27}H_{29}O_{17}$	625.140 (-0.4)
17	quer-3-*O*-gal	27.61	255, 353	n.d. [b]	n.d. [b]	$C_{21}H_{19}O_{12}$	463.082 (-5.3)
18	quer-3-*O*-glu	27.87	255, 352	$C_{21}H_{19}O_{13}$	479.082 (-0.2)	$C_{21}H_{17}O_{13}$	477.067 (-0.2)
19	quer-3-*O*-glc	28.36	255, 352	n.d. [b]	n.d. [b]	$C_{21}H_{19}O_{12}$	463.092 (4.1)
20	Kaempferol-3-*O*-gal	30.21	265, 345	$C_{21}H_{21}O_{11}$	449.108 (-0.3)	$C_{21}H_{19}O_{11}$	447.093 (0.2)

continued

Table 5.1. Identification of phenolic compounds in TE and GE by UHPLC-DAD-ESI-QToF/MS analysis.

#	Compound	t_R (min)	Max. UV-Vis Bands (nm)	Molecular formula $[M+H]^+$	$[M+H]^+$ m/z (error)	Molecular formula $[M-H]^-$	$[M-H]^-$ m/z (error)
21	Kaempferol-3-*O*-glu	30.98	265, 345	$C_{21}H_{19}O_{12}$	463.088 (0.1)	$C_{21}H_{17}O_{12}$	461.070 (-1.9)
22	Kaempferol-3-*O*-glc	31.50	265, 348	$C_{21}H_{21}O_{11}$	449.108 (-0.4)	$C_{21}H_{19}O_{11}$	447.093 (0.7)
23	Isorhamnetin-3-*O*-gal	31.83	254, 352	$C_{22}H_{23}O_{12}$	479.119 (0.2)	$C_{22}H_{21}O_{12}$	477.103 (0.0)
24	Isorhamnetin-3-*O*-glc	32.39	254, 352	$C_{22}H_{23}O_{12}$	479.119 (-0.2)	$C_{22}H_{21}O_{12}$	477.104 (0.9)
	Hydroxycinnamic acids						
25	*p*-coum hexoside	10.48	313	n.d. [b]	n.d. [b]	$C_{15}H_{17}O_8$	325.092 (0.2)
	Hydroxybenzoic acids						
23	Galloyl rhamnoside	3.23	279	n.d. [b]	n.d. [b]	$C_{13}H_{15}O_9$	315.0717 (0.1)
	Dihydroflavonols						
24	Dihydroquer-3-*O*-rhamnoside	26.92	255, 352	$C_{21}H_{23}O_{11}$	451.1241 (0.1)	$C_{21}H_{21}O_{11}$	449.1086 (0.2)

[a] Coeluting compounds.
[b] n.d.: not detected.

Table 5.2. Determination of anthocyanins in TE and GE by HPLC-DAD-ESI-QqQ/MS analysis.

#	Compound	t_R (min)	Max. UV-Vis Bands (nm)	Parent ion $[M]^+$ m/z	Daughter ion $[Y_0]^+$ m/z	Conc. (μg Mv-3-*O*-glc equiv./g freeze-dried grape pomace) TE	GE
1	Dp-3-*O*-glc	8.97	276, 526	465	303	235.02	252.82
2	Cy-3-*O*-glc	12.63	279, 519	449	287	49.39	66.05
3	Pt-3-*O*-glc	14.48	276, 526	479	317	201.99	224.84
4	Pn-3-*O*-glc	19.43	278, 519	463	301	118.26	517.50
5	Mv-3-*O*-glc	21.54	276, 526	493	331	585.04	917.45
6	Dp-3-*O*-(6-*O*-ac)-glc	28.24	275, 529	507	303	5.25	10.26
7	Pt-3-*O*-(6-*O*-ac)-glc	36.10	273, 526	521	317	6.19	12.69
8	Pn-3-*O*-(6-*O*-ac)-glc	39.43	278, 526	505	301	<5 [1]	25.42
9	Mv-3-*O*-(6-*O*-ac)-glc	40.05	279, 526	535	331	47.04	111.41
10	Mv-3-*O*-(6-*O*-caff)-glc	41.87	279, 543	655	331	10.81	15.61
11	Pt-3-*O*-(6-*O*-coum)-glc	43.00	279, 531	625	317	22.10	20.92
12	Pn-3-*O*-(6-*p*-coum)-glc [b]	45.76	279, 531	609	301	134.44	252.19
13	Mv-3-*O*-(6-*p*-coum)-glc [b]	45.88	281, 532	639	331	-	-

[a] <5 μg of Mv-3-*O*-glc equiv./g freeze-dried grape pomace: below lower limit of calibration.
[b] Coeluting compounds.

5.2 Design and characterization of vesicles for the encapsulation of grape pomace phenolics

This study aimed to develop nanoformulations of the TE and GE for cosmetic applications. With this purpose, we examined whether liposomes and transfersomes would allow the production of a safe and stable formulation to be applied on the skin, as well as enhance the bioactivity of TE and GE constituents, providing protection from oxidative damage at the cellular level.

MD, PI and ZP measured by light scattering for the different formulations assayed are reported in Table 5.3.

Table 5.3. Mean diameter (MD), polydispersity index (PI), zeta potential (ZP) and entrapment efficiency (EE) of TE P90G-transfersomes, TE P90G-liposomes, empty P90G-liposomes, empty P90G-transfersomes, GE S75-liposomes and empty S75-liposomes. MD, PI, ZP and EE are expressed as the mean ± SD (n = 6).

Formulation	MD (nm)	PI	ZP (mV)	EE (%)
TE P90G-transfersomes	**105 ± 8	**0.29 ± 0.03	$^{**••}$-9 ± 2	66 ± 9
TE P90G-liposomes	$^{◇◇}$155 ± 16	$^{◇◇}$0.59 ± 0.04	$^{◇◇}$-4 ± 1	-
Empty P90G-transfersomes	$^{≀≀}$106 ± 17	$^{≀}$0.29 ± 0.02	$^{≀≀}$-16 ± 2	-
Empty P90G-liposomes	128 ± 2	0.33 ± 0.03	-9 ± 2	-
GE S75-liposomes	††104 ± 4	††0.29 ± 0.01	-65 ± 4	75 ± 30
Empty S75-liposomes	116 ± 7	0.25 ± 0.01	-62 ± 3	-

[a] Values significantly different:

TE P90G-transfersomes *vs* TE P90G-liposomes: $^{**}p < 0.01$.
TE P90G-transfersomes *vs* empty P90G-transfersomes: $^{••}p < 0.01$.
TE P90G-liposomes *vs* empty P90G-liposomes: $^{◇◇}p < 0.01$.
empty P90G-transfersomes *vs* empty P90G-liposomes: $^{≀}p < 0.05$, $^{≀≀}p < 0.01$.
GE S75-liposomes *vs* empty S75-liposomes: $^{††}p < 0.01$.

For the experiments with TE P90G-liposomes were studied. The results showed that the empty P90G-liposomes were approximately 130 nm in diameter, slightly polydisperse (PI 0.33 ± 0.3), and negatively charged (ZP -9 ± 2). The loading of the TE extract significantly increased the average size (*ca.* 150 nm) and the PI (0.6). The modification of the liposomal formulation with the addition of Tween 80 leading to a transfersome formulation, resulted in a marked improvement in the above features. Both the empty and TE P90G-transfersomes were smaller, around 100 nm in diameter. These vesicles were also characterized by a good homogeneity (PI 0.29), and maintained negative ZP values. These results pointed out the crucial role of Tween 80 in the formulations. Indeed, the presence of Tween 80 promoted a better arrangement of the phospholipids of the vesicle, and a better solubilization and distribution of the extract constituents within the vesicles. As a result, the transfersomes improved the physico-chemical and technological characteristics of the vesicle, such as size, homogeneity, storage stability monitored for two months, and the EE.

Regarding the experiments with GE, S75-liposomes were assayed (Table 5.3). The empty S75-liposomes were approximately 116 nm in diameter, fairly monodispersed (PI 0.25 ± 0.01) and negatively charged (ZP -62 ± 3). The loading of the GE extract significantly decreased the average size (*ca.* 104 nm) and increased the PI (0.29); however, the ZP values were unaltered. The stability of these liposomal formulations was evaluated by monitoring the mean diameter, PI and ZP for two months; no significant alterations were detected during this time period. Due to the dilution prepared in order to disrupt the vesicles for the analysis of the GE inside the S75-liposomes, phenolic compounds were found at trace levels. Since anthocyanins, being the major components, were contained in the GE in higher concentrations, they were still detectable and quantifiable.

Entrapment efficiency (EE) was calculated based on the amount of the major anthocyanins detected in the extract (Table 5.2): (i) In TE, Dp-3-*O*-glc (1), Mv-3-*O*-glc (5), and the coeluting compounds Pn-3-*O*-(6-*p*-coum)-glc (12) + Mv-3-*O*-(6-*p*-coum)-glc (13); and (ii) In GE, the coeluting compounds Pn-3-*O*-(6-*p*-coum)-glc (12) + Mv-3-*O*-(6-*p*-coum)-glc (13).

The formation of vesicular structures of small sizes was confirmed by cryo-TEM. Figures 5.1 and 5.2 show spherical, unilamellar vesicles of *ca.* 100 nm in diameter. These observations were aligned with the light scattering data of TE and GE, respectively. Some multivesicular structures were also observed in the case of GE S75-liposomes (Figure 5.2 (left) bottom-right corner).

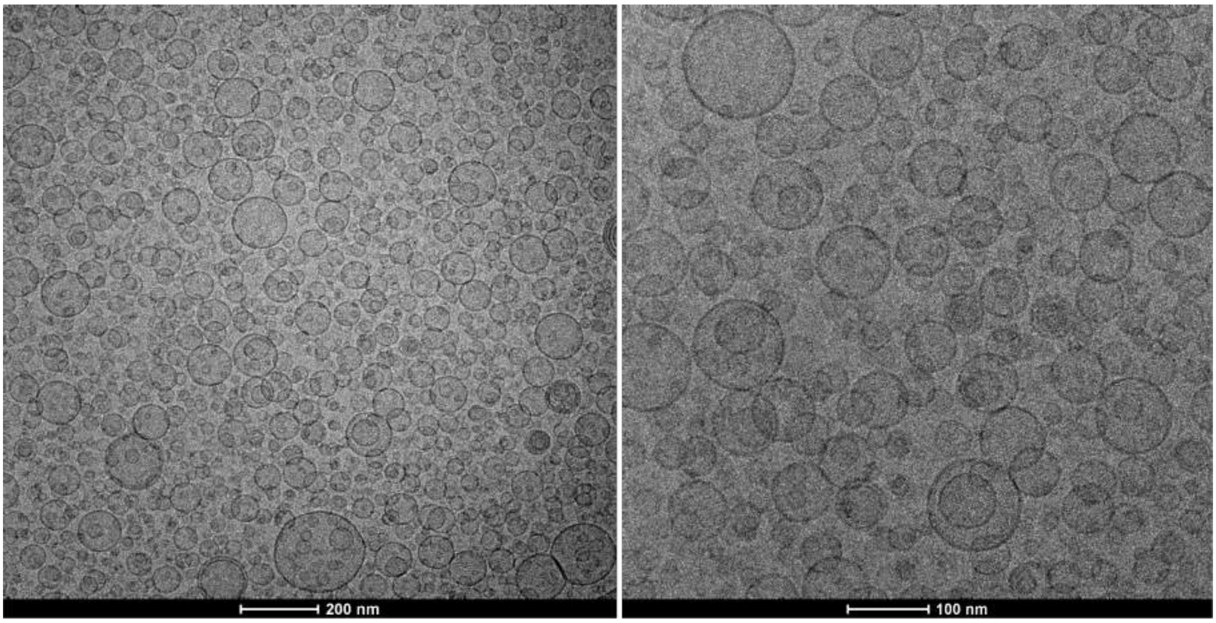


Figure 5.1. Cryo-TEM images of TE P90G-transfersomes. Two magnifications are shown: 29.000× (left) and 62.000× (right).

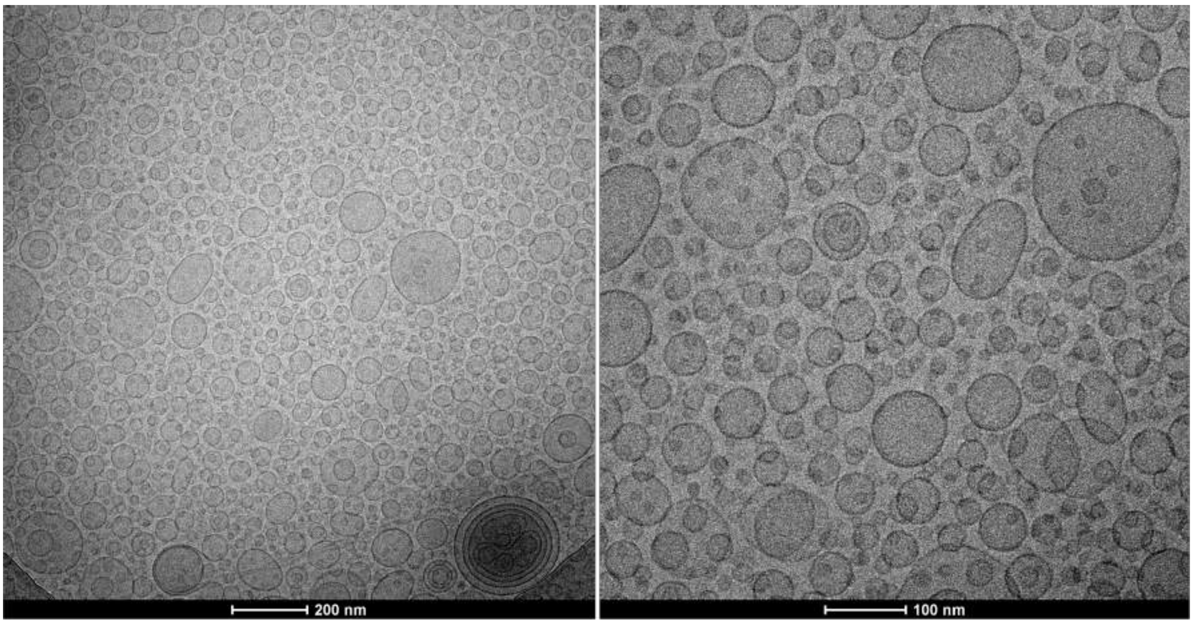


Figure 5.2. Cryo-TEM images of GE S75-liposomes. Two magnifications are shown: 29.000× (left) and 62.000× (right).

5.3 Antioxidant activity of grape pomace extract and its nanoformulations

The assays to determine the TPC and the AA of the methanolic solutions of TE and GE and the liposomal formulations containing the grape pomace extracts were performed as described in section 3.4.5, and the results are shown in Table 5.4.

Table 5.4. Total phenolic contents (TPC) and antioxidant activity (AA) of *Tempranillo* extract (TE) and *Graciano* extract (GE) methanolic solutions and of the liposomal formulations (mean ± SD).

Formulation	Folin-Ciocalteu	DPPH assay		FRAP assay
	TPC (μg GAE/mL)	AA (%)	AA (μg TrEq/mL)	AA (μg FE/mL)
TE methanolic solution	257 ± 36	81 ± 2	287 ± 18	1011 ± 65
GE methanolic solution	217 ± 10	61 ± 3	201 ± 9	819 ± 77
TE P90G-transfersomes	180 ± 34	85 ± 3	297 ± 13	865 ± 41
TE P90G-liposomes	–[b]	87 ± 5	288 ± 22	1037 ± 25
Empty P90G-transfersomes	30 ± 4	38 ± 3	138 ± 9	355 ± 19
Empty P90G-liposomes	–[b]	36 ± 4	133 ± 12	474 ± 28
GE S75-liposomes	191 ± 20	79 ± 2	254 ± 9	741 ± 63
Empty S75-liposomes	92 ± 9	38 ± 3	131 ± 11	339 ± 42

[a] Abbreviations: gallic acid equivalents (GAE), Trolox equivalents (TrEq), Fe^{2+} equivalents (FE).
[b] Not analyzed.

The phenolic content of TE and GE was estimated by the Folin–Ciocalteu assay. The TE methanolic solution contained 257 ± 36 μg GAE/mL, and the GE methanolic solution, 217 ± 104 μg GAE/mL. The analysis of the TE vesicle formulation TE P90G-transfersomes showed lower TPC (180 ± 34 μg GAE/mL), which was likely due to the procedure employed. The approach to disrupt the vesicles and free their content did not involve the use of organic solvents and, apparently, the sonication step included for this purpose was not effective enough. The TPC of the GE S75-liposomes also were lower (191 ± 20 μg GAE/mL) than that of the GE methanolic solution.

The AA of TE and GE methanolic solutions and the liposomal formulations of TE and GE were estimated as a function of their radical scavenging ability (DPPH assay) and ferric reducing ability (FRAP assay). The TE methanolic solution scavenged the DPPH radical almost completely (81 ± 2%; 287 ± 18 μg TrEq/mL), in agreement with the well-known antioxidant power of the compounds identified in the extract. The GE methanolic solution showed lower AA (61%; ∼200 μg TrEq/mL).

The AA of TE in the P90G-transfersomes was slightly higher (85 ± 3%; 297 ± 13 μg TrEq/mL; $p < 0.01$), than the TE methanolic solution. The AA of GE S75-liposomes was also higher (79 ± 2 %; 254 ± 9 μg TrEq/mL; $p < 0.01$) than that of the GE methanolic solution. The higher AA of the liposomal formulations of TE and GE is due to the contribution of the vesicle carrier to the total AA. Indeed, the empty vesicles possessed slight AA themselves (36-38%), due to the presence of phosphatidylcholine in the liposomes and transfersomes.

The AA results of the FRAP assay followed the same trend. The TE transfersomes (865 ± 41 μg FE/mL) showed a reducing power close to that of the TE methanolic extract (1011 ± 65 μg FE/mL). The GE S75-liposomes showed a strong reducing power (741 ± 63 μg FE/mL), which was not statistically different from that of GE methanolic solution (819 ± 77 μg FE/mL). These findings demonstrated that the liposomal formulations in the vesicles preserved the intrinsic properties of the TE and GE extracts.

5.4 Cell culture viability and inhibition of intracellular ROS of nanoformulations of extract

Whether TE transfersomes exert an antioxidant effect by inhibiting H_2O_2-induced ROS generation in cells was examined . Firstly, the cytocompatibility of the TE methanolic solution and TE transfersomes was assessed by evaluating their effects on the viability of human keratinocytes. After 24 h of exposure of the cells to various concentrations of the samples, *i.e.* TE methanolic solution and TE P90G-transfersomes, the viability was examined using an MTT test. The results indicated that none of the samples were cytotoxic (Figure 5.3A). Indeed, cell viability remained around 85% when the highest concentration of TE transfersomes was tested, showing no statistical significant differences respect to the untreated control cells.

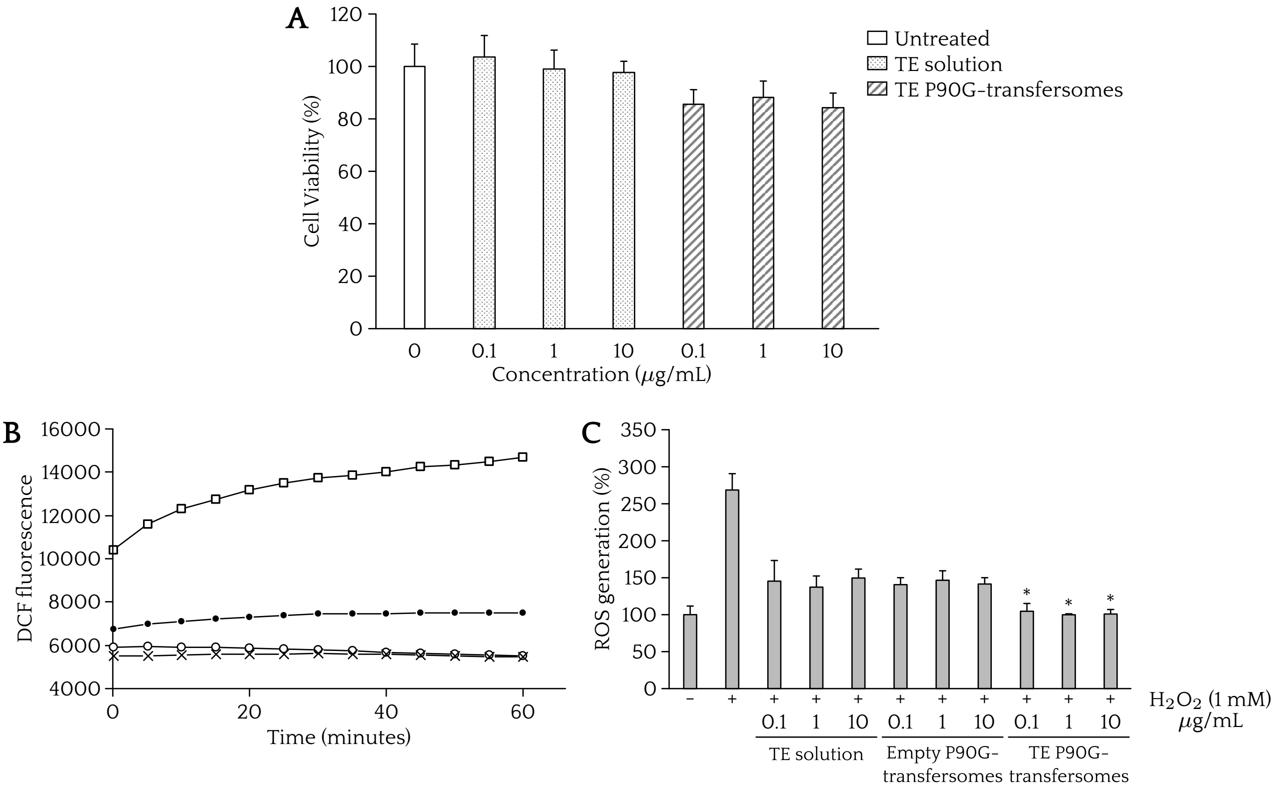


Figure 5.3. (**A**) Effects of TE, in solution and in P90G-transfersomes, on HaCaT cell viability. (**B**) ROS levels (expressed as DCF fluorescence) in HaCaT cells pre-treated with TE, in solution and in P90G-transfersomes (extract concentration: 1 μg/mL), and incubated with 1 mM of H_2O_2 for 60 min. (○): Untreated cells; (□): 1 mM H_2O_2; (●): TE + H_2O_2; (×): TE P90G-transfersomes + H_2O_2. (**C**) Effects of TE, in solution and in P90G-transfersomes, on ROS production in HaCaT cells after a 1 h treatment with 1 mM of H_2O_2. Means $\pm$ SD of three independent experiments, each performed in triplicate, are shown. Asterisks (*) indicate significant statistical difference between TE P90G-transfersomes and TE solution at each concentration: $^{*}p < 0.05$, $^{**}p < 0.005$.

To investigate the protective effects of TE P90G-transfersomes against oxidative stress, intracellular ROS levels were estimated using the DCFH-DA method. DCFH-DA is a non-fluorescent probe that is hydrolyzed to DCFH-DA by intracellular esterases. The oxidation of DCFH-DA by ROS leads to the formation of DCF, displaying an increase in the fluorescence intensity [196]. Figure 5.3B shows the increase in fluorescence due to the exposure of the HaCaT cells to H_2O_2, as well as how it decreased as a function of time when HaCaT cells were incubated with TE methanolic solution or with TE P90G-transfersomes (1 μg/mL). TE P90G-transfersomes restored basal ROS levels, since the curve for the vesicle formulation was essentially superimposed on that of untreated cells (*i.e.*, not exposed to H_2O_2). As shown in Figure 5.3C, the exposure of the HaCaT cells to H_2O_2 significantly increased the ROS levels in these cells, as expected. Both the TE in the solution and the TE P90G-transfersomes succeeded in reducing the ROS levels already at a concentration of 0.1 μg/mL. However, the TE P90G-transfersomes reduced H_2O_2-induced ROS production with a statistically significant effect with respect to the TE solution (Figure 5.3C). These findings suggested the incorporation of TE to liposomal vesicles results in a greater antioxidant effect in a cellular system.

The effect of the methanolic GE solution and the GE S75-liposomes on the viability of HaCaT was studied to determine the safety of these samples. After 24 h of exposure of the cells to various concentrations of the samples (0, 0.1 and 10 μg/mL), the viability was assessed using the MTT test. The results indicated that none of the samples were cytotoxic (Figure 5.4). Indeed, cell viability was $\geqslant$ 90% for all the tested samples, regardless of their concentration, and displaying no statistically significant differences from the untreated control cells.

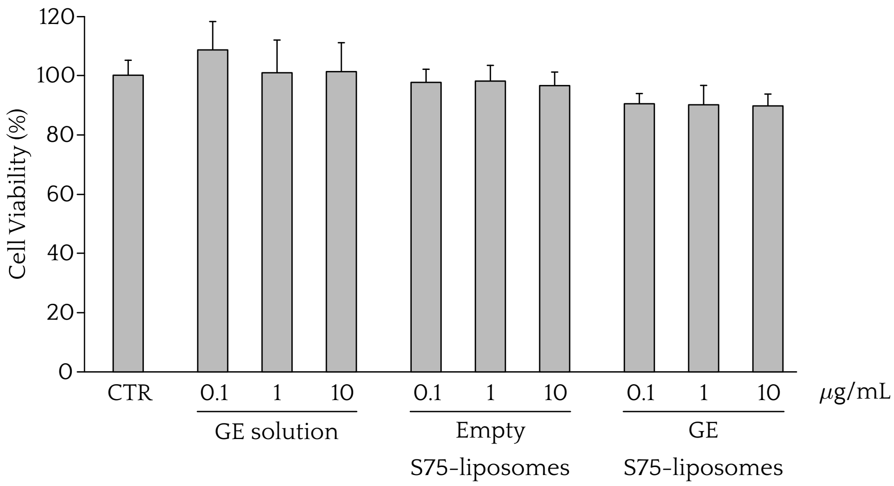


Figure 5.4. Effect of GE, in solution or in S75-liposomes, and empty S75-liposomes on HaCaT cell viability. Cells were untreated (CTR) or treated with different concentrations of samples (0–10 μg/mL) and studied by MTT assay. Data are expressed as a percentage of the control.

Chapter 6

Conclusions

Application of pharmacokinetics to the profiles of phenolic compounds in grape must and wine.

1. The mathematical treatment derived from pharmacokinetics performed on the experimental concentration data of the wine-making experiments, allowed the calculation of the kinetic constants of extraction or formation and degradation of the studied phenolic compounds involved in the wine-making process.

Kinetic study of the evolution of phenolic compounds during wine elaboration.

2. Extraction of anthocyanins from grape occurs in the early stage of maceration and AF, increasing their contents in must rapidly. Afterwards, a progressive and continuous decrease of anthocyanin contents during fermentation takes place.

3. Formation of anthocyanin derivatives starts quickly and in parallel as anthocyanins are extracted from grape. Consequently, maximum concentrations of anthocyanin derivatives are reached just a few days (2-3 days) after the highest contents of anthocyanins have been extracted to the must.

4. Direct condensation derivatives represent about 10% of total anthocyanin derivatives at the end of MLF, and among them, Cat-Mv-3-*O*-glc is the major one. Indirect condensation derivatives formed by ethylidene bridges are minor derivatives.

5. Within pyranoanthocyanins, Vitisin A and Vitisin B are the major ones, being each one around 40% of total anthocyanin derivatives, at the end of MLF. The remaining 10% of total anthocyanin derivatives are pyranoanthocyanins with vinylphenol.

6. Vitisin B has a more unstable behavior than Vitisin A during fermentations, with a quicker formation along AF but a more rapid degradation. So, although the contents of Vitisin B are higher than those of Vitisin A during fermentations, one or two weeks after the end of MLF the concentrations of both vitisins are similar.

7. Mv-3-*O*-glc-vinylphenol has an important contribution to wine color due to its high stability, comparable or even higher than that of Vitisin A.

8. Stability order of condensation derivatives can be established as: F-A^+ > ethyl-bridged compounds > A^+-F. Among them, cat-Mv-3-*O*-glc is the most important for contribution to wine color in the long term.

Effect of oenological variables employed during wine elaboration on the kinetics of phenolic compounds.

9. The use of a secondary red grape cultivar, *Mazuelo* or *Graciano*, mixed with the main grape cultivar *Tempranillo* produced significant changes in the kinetic constants of formation and degradation of the phenolic compounds studied. In general, an increase in the formation constants of pyranoanthocyanins (*i.e.* Vitisin A, Vitisin B, and Mv-3-*O*-glc-vinylphenol), and a decrease in the formation constant values for anthocyanin-flavanol condensation products, both direct and indirect, was observed.

10. The addition of tannins during wine-making and the application of microoxygenation during MLF had little influence on the concentration profiles and the kinetic constants of formation and degradation of the phenolic compounds studied.

11. The use of ionic exchange to lower the pH of the grape must at the beginning of AF produced significant changes in the concentration profiles of the phenolic compounds studied. The concentrations of pyranoanthocyanins were negatively affected, whereas an increase was observed on the concentrations of anthocyanin-flavanol condensation products.

Development of nanoformulation containing red grape pomace extract.

12. The green extraction method employed was proven useful for obtaining an extract rich in antioxidants from food processing residues (*e.g.*, red grape pomace).

13. Nanotechnologies were demonstrated to be crucial for developing a formulation complying with standards regarding safety, effectiveness and usability. Liposomes and transfersomes were able to incorporate, protect, and deliver *Tempranillo* and *Graciano* red grape pomace extracts to cells, without interfering with their antioxidant properties, and were proved to be non-toxic when tested in a cellular system.

14. The *in vitro* studies highlighted the ability of the vesicle formulations to counteract ROS over-production, enhancing the effect of the extract in the cells.

15. The proposed liposomes and transfersomes formulations present a great potential for the treatment of skin under oxidative stress conditions.

Chapter 7

Bibliography

[1] P. McGovern, M. Jalabadze, S. Batiuk, M. P. Callahan, K. E. Smith, G. R. Hall, E. Kvavadze, D. Maghradze, N. Rusishvili, L. Bouby, O. Failla, G. Cola, L. Mariani, E. Boaretto, R. Bacilieri, P. This, N. Wales, and D. Lordkipanidze, "Early Neolithic wine of Georgia in the South Caucasus," *Proceedings of the National Academy of Sciences*, vol. 114, no. 48, E10309–E10318, 2017. DOI: 10.1073/pnas.1714728114.

[2] P. Goufo, R. K. Singh, and I. Cortez, "A reference list of phenolic compounds (including stilbenes) in grapevine (*Vitis vinifera* L.) roots, woods, canes, stems, and leaves," *Antioxidants*, vol. 9, no. 5, p. 398, 2020. DOI: 10.3390/antiox9050398.

[3] S. D. Santo, M. Fasoli, S. Negri, E. D'Incá, N. Vicenzi, F. Guzzo, G. B. Tornielli, M. Pezzotti, and S. Zenoni, "Plasticity of the berry ripening program in a white grape variety," *Frontiers in Plant Science*, vol. 7, 2016. DOI: 10.3389/fpls.2016.00970.

[4] H. Xie, M. Konate, N. Sai, K. G. Tesfamicael, T. Cavagnaro, M. Gilliham, J. Breen, A. Metcalfe, J. R. Stephen, R. D. Bei, C. Collins, and C. M. R. Lopez, "Global DNA methylation patterns can play a role in defining terroir in grapevine (*Vitis vinifera* cv. Shiraz)," *Frontiers in Plant Science*, vol. 8, 2017. DOI: 10.3389/fpls.2017.01860.

[5] D. O. Adams, "Phenolics and ripening in grape berries," *American Journal of Enology and Viticulture*, vol. 57, no. 3, pp. 249–256, 2006.

[6] M. O. Downey, N. K. Dokoozlian, and M. P. Krstic, "Cultural practice and environmental impacts on the flavonoid composition of grapes and wine: A review of recent research," *American Journal of Enology and Viticulture*, vol. 57, no. 3, pp. 257–268, 2006.

[7] C. S. Parra, J. Aguirreolea, M. Sánchez-Díaz, J. J. Irigoyen, and F. Morales, "Effects of climate change scenarios on Tempranillo grapevine (*Vitis vinifera* L.) ripening: Response to a combination of elevated CO_2 and temperature, and moderate drought," *Plant and Soil*, vol. 337, no. 1-2, pp. 179–191, 2010. DOI: 10.1007/s11104-010-0514-z.

[8] A. Martínez-Gil, M. del Alamo-Sanza, and I. Nevares, "Evolution of red wine in oak barrels with different oxygen transmission rates. Phenolic compounds and colour," *LWT*, vol. 158, p. 113 133, 2022. DOI: 10.1016/j.lwt.2022.113133.

[9] A. Razungles, J. Blouin, J. Boulet, J. Escudier, M. Feuillat, C. Flanzy, and D. Peyron, "Vinificación en tinto," in *Enología fundamentos cientificos y tecnólogicos*, 1st ed., Madrid: A. Madrid Vicente, 2000, ch. 17.1, pp. 418–442, ISBN: 84-89922-19-5.

[10] Y. Yang, R. Deed, L. Araujo, A. Waterhouse, and P. Kilmartin, "Effect of microoxygenation applied before and after malolactic fermentation on monomeric phenolics and tannin composition of Pinot Noir wine," *Australian Journal of Grape and Wine Research*, vol. 28, no. 1, pp. 95–106, 2021. DOI: 10.1111/ajgw.12520.

[11] P. Ribéreau-Gayon, D. Dubourdieu, B. Donèche, and A. Lonvaud, "Red winemaking," in *Handbook of Enology: The Microbiology of Wine and Vinifications*, 2nd ed., vol. 1, Chichester: John Wiley & Sons Ltd., 2006, ch. 12, pp. 431–512, ISBN: 0-470-01034-7. DOI: 10.1002/9781119588320.ch12.

[12] A. Chaïb, O. Claisse, E. Delbarre, J. Bosviel, and C. L. Marrec, "Assessment of the lysogenic status in the lactic acid bacterium *O. oeni* during the spontaneous malolactic fermentation of red wines," *Food Microbiology*, vol. 103, p. 103 947, 2022. DOI: 10.1016/j.fm.2021.103947.

[13] U. Vrhovsek, A. Vanzo, and J. Nemanic, "Effect of red wine maceration techniques on oligomeric and polymeric proanthocyanidins in wine, cv. Blaufrankisch," en, *VITIS - Journal of Grapevine Research*, vol. 41, no. 1, pp. 47–51, 2015. DOI: 10.5073/VITIS.2002.41.47-51.

[14] M. Cano-López, J. López-Roca, F. Pardo-Minguez, and E. G. Plaza, "Oak barrel maturation vs. micro-oxygenation: Effect on the formation of anthocyanin-derived pigments and wine colour," *Food Chemistry*, vol. 119, no. 1, pp. 191–195, 2010. DOI: 10.1016/j.foodchem.2009.06.018.

[15] M. De Rosso, A. Panighel, A. Dalla Vedova, L. Stella, and R. Flamini, "Changes in chemical composition of a red wine aged in acacia, cherry, chestnut, mulberry, and oak wood barrels," *Journal of Agricultural and Food Chemistry*, vol. 57, no. 5, pp. 1915–1920, 2009, ISSN: 0021-8561. DOI: 10.1021/jf803161r. [Online]. Available: https://doi.org/10.1021/jf803161r.

[16] L. Rustioni, G. Cola, J. VanderWeide, P. Murad, O. Failla, and P. Sabbatini, "Utilization of a freeze-thaw treatment to enhance phenolic ripening and tannin oxidation of grape seeds in red (*Vitis vinifera* L.) cultivars," *Food Chemistry*, vol. 259, pp. 139–146, 2018. DOI: 10.1016/j.foodchem.2018.03.120.

[17] R. Alonso-Salces, K. Héberger, M. Holland, J. Moreno-Rojas, C. Mariani, G. Bellan, F. Reniero, and C. Guillou, "Multivariate analysis of NMR fingerprint of the unsaponifiable fraction of virgin olive oils for authentication purposes," *Food Chemistry*, vol. 118, no. 4, pp. 956–965, 2010. DOI: 10.1016/j.foodchem.2008.09.061.

[18] R. del Barrio-Galán, H. del Valle-Herrero, M. Bueno-Herrera, P. López-de-la-Cuesta, and S. Pérez-Magariño, "Volatile and non-volatile characterization of white and rosé wines from different Spanish Protected Designations of Origin," *Beverages*, vol. 7, no. 3, p. 49, 2021. DOI: 10.3390/beverages7030049.

[19] Consejo Regulador de la Denominación de Origen Calificada (D.O.Ca) Rioja, *Denominación de origen calificada*, Spanish, Online, Jan. 2021. [Online]. Available: https://www.riojawine.com/doca-rioja/.

[20] Ministerio de Agricultura, Pesca y Alimentación, *Pliego de condiciones de la denominación de origen protegida (Denominación de Origen Calificada) "RIOJA"*, Online, 2020. [Online]. Available: https://bit.ly/3u8ujdE.

[21] A. (para el Desarrollo de La Rioja Alta), *Uvas y vinos de rioja*, Jun. 2022. [Online]. Available: https://www.rutasdelvinorioja.com/uvas-y-vinos-de-rioja/.

[22] A. L. Klatsky, G. D. Friedman, and A. B. Siegelaub, "Alcohol consumption before myocardial infarction," *Annals of Internal Medicine*, vol. 81, no. 3, pp. 294–301, 1974, ISSN: 0003-4819. DOI: 10.7326/0003-4819-81-3-294. [Online]. Available: https://www.acpjournals.org/doi/abs/10.7326/0003-4819-81-3-294.

[23] A. Evans, P. Marques-Vidal, P. Ducimetière, M. Montaye, D. Arveiler, A. Bingham, J.-B. Ruidavets, P. Amouyel, B. Haas, J. Yarnell, J. Ferrières, F. Fumeron, G. Luc, F. Kee, and F. Cambien, "Patterns of alcohol consumption and cardiovascular risk in Northern Ireland and France," *Annals of Epidemiology*, vol. 17, no. 5, S75–S80, 2007. DOI: 10.1016/j.annepidem.2007.01.017.

[24] M. L. Burr, "Explaining the French paradox," *Journal of the Royal Society of Health*, vol. 115, no. 4, pp. 217–219, 1995, ISSN: 0264-0325. DOI: 10.1177/146642409511500404. [Online]. Available: https://doi.org/10.1177/146642409511500404.

[25] Z. Rasines-Perea and P.-L. Teissedre, "Grape polyphenols' effects in human cardiovascular diseases and diabetes," *Molecules*, vol. 22, no. 1, p. 68, 2017. DOI: 10.3390/molecules22010068.

[26] M. M. Markoski, J. Garavaglia, A. Oliveira, J. Olivaes, and A. Marcadenti, "Molecular properties of red wine compounds and cardiometabolic benefits," *Nutrition and Metabolic Insights*, vol. 9, pp. 51–57, 2016. DOI: 10.4137/nmi.s32909.

[27] M. Butnariu and A. Butu, “Qualitative and quantitative chemical composition of wine,” in *Quality Control in the Beverage Industry*, Elsevier, 2019, pp. 385–417. DOI: 10.1016/b978-0-12-816681-9.00011-4.

[28] D. de Lange, “From red wine to polyphenols and back: A journey through the history of the French Paradox,” *Thrombosis Research*, vol. 119, no. 4, pp. 403–406, 2007. DOI: 10.1016/j.thromres.2006.06.001.

[29] N. F. Santos-Sánchez, R. Salas-Coronado, B. Hernández-Carlos, and C. Villanueva-Cañongo, “Shikimic acid pathway in biosynthesis of phenolic compounds,” in *Plant Physiological Aspects of Phenolic Compounds*, IntechOpen, 2019. DOI: 10.5772/intechopen.83815.

[30] F. Buiarelli, F. Coccioli, M. Merolle, R. Jasionowska, and A. Terracciano, “Identification of hydroxycinnamic acid-tartaric acid esters in wine by HPLC-tandem mass spectrometry,” *Food Chemistry*, vol. 123, no. 3, pp. 827–833, 2010. DOI: 10.1016/j.foodchem.2010.05.017.

[31] F. Chinnici, F. Sonni, N. Natali, S. Galassi, and C. Riponi, “Colour features and pigment composition of Italian carbonic macerated red wines,” *Food Chemistry*, vol. 113, no. 2, pp. 651–657, 2009. DOI: 10.1016/j.foodchem.2008.07.055.

[32] K. Chira, N. Pacella, M. Jourdes, and P.-L. Teissedre, “Chemical and sensory evaluation of Bordeaux wines (Cabernet-Sauvignon and Merlot) and correlation with wine age,” *Food Chemistry*, vol. 126, no. 4, pp. 1971–1977, 2011. DOI: 10.1016/j.foodchem.2010.12.056.

[33] M. García-Falcón, P.-L. C., E. Martínez-Carballo, and J. Simal-Gándara, “Determination of phenolic compounds in wines: Influence of bottle storage of young red wines on their evolution,” *Food Chemistry*, vol. 105, no. 1, pp. 248–259, 2007. DOI: 10.1016/j.foodchem.2006.11.006.

[34] L. Zhu, Y. Zhang, J. Deng, H. Li, and J. Lu, “Phenolic concentrations and antioxidant properties of wines made from North American grapes grown in China,” *Molecules*, vol. 17, no. 3, pp. 3304–3323, 2012. DOI: 10.3390/molecules17033304.

[35] J.-M. Souquet, B. Labarbe, C. L. Guernevé, V. Cheynier, and M. Moutounet, “Phenolic composition of grape stems,” *Journal of Agricultural and Food Chemistry*, vol. 48, no. 4, pp. 1076–1080, 2000. DOI: 10.1021/jf991171u.

[36] A. Buettner, “Investigation of potent odorants and afterodor development in two chardonnay wines using the buccal odor screening system (BOSS),” *Journal of Agricultural and Food Chemistry*, vol. 52, no. 8, pp. 2339–2346, 2004. DOI: 10.1021/jf035322b.

[37] X. Wei, Y. Ju, T. Ma, J. Zhang, Y. Fang, and X. Sun, “New perspectives on the biosynthesis, transportation, astringency perception and detection methods of grape proanthocyanidins,” *Critical Reviews in Food Science and Nutrition*, vol. 61, no. 14, pp. 2372–2398, 2020. DOI: 10.1080/10408398.2020.1777527.

[38] J.-J. Macheix, A. Fleuriet, and J. Billot, “The main phenolics of fruits,” in *Fruit Phenolics*, CRC Press, 2018, pp. 1–378. DOI: 10.1201/9781351072175.

[39] R. Flamini, “Mass spectrometry in grape and wine chemistry. Part I: Polyphenols,” *Mass Spectrometry Reviews*, vol. 22, no. 4, pp. 218–250, 2003, ISSN: 0277-7037. DOI: 10.1002/mas.10052. [Online]. Available: https://doi.org/10.1002/mas.10052.

[40] G. Sontag, M. I. Pinto, J. P. Noronha, and H. D. Burrows, “Analysis of food by high performance liquid chromatography coupled with coulometric detection and related techniques: A review,” *Journal of Agricultural and Food Chemistry*, vol. 67, no. 15, pp. 4113–4144, 2019. DOI: 10.1021/acs.jafc.9b00003.

[41] X.-X. Cheng, C.-C. Guo, Q. Yang, X.-M. Tang, and C.-R. Zhang, “Isolation and identification of radical scavenging components of seeds of *Desmodium styracifolium*,” *Chemistry of Natural Compounds*, vol. 53, no. 1, pp. 36–39, 2017. DOI: 10.1007/s10600-017-1905-7.

[42] I. Fernandes, A. Faria, C. Calhau, V. de Freitas, and N. Mateus, “Bioavailability of anthocyanins and derivatives,” *Journal of Functional Foods*, vol. 7, pp. 54–66, 2014. DOI: 10.1016/j.jff.2013.05.010.

[43] M. Sohail Akh and W. Ali Shehata, "Phytochemical and pharmacological aspects of anthocyanins," *Asian Journal of Applied Sciences*, vol. 13, no. 3, pp. 94–99, 2020. DOI: 10.3923/ajaps.2020.94.99.

[44] E. García-Beneytez, F. Cabello, and E. Revilla, "Analysis of grape and wine anthocyanins by HPLC-MS," *Journal of Agricultural and Food Chemistry*, vol. 51, no. 19, pp. 5622–5629, 2003. DOI: 10.1021/jf0302207.

[45] S. Saha, J. Singh, A. Paul, R. Sarkar, Z. Khan, and K. Banerjee, "Anthocyanin profiling using UV-Vis spectroscopy and liquid chromatography mass spectrometry," *Journal of AOAC INTERNATIONAL*, vol. 103, no. 1, pp. 23–39, 2020. DOI: 10.5740/jaoacint.19-0201.

[46] P. Mazzuca, P. Ferranti, G. Picariello, L. Chianese, and F. Addeo, "Mass spectrometry in the study of anthocyanins and their derivatives: Differentiation of *Vitis vinifera* and hybrid grapes by liquid chromatography/electrospray ionization mass spectrometry and tandem mass spectrometry," *Journal of Mass Spectrometry*, vol. 40, no. 1, pp. 83–90, 2005. DOI: 10.1002/jms.778.

[47] D. Durner, "Improvement and stabilization of red wine color," in *Handbook on Natural Pigments in Food and Beverages*, Elsevier, 2016, pp. 239–264. DOI: 10.1016/b978-0-08-100371-8.00012-9.

[48] I. Álvarez, J. L. Aleixandre, M. J. García, V. Lizama, and J. L. Aleixandre-Tudó, "Effect of the prefermentative addition of copigments on the polyphenolic composition of tempranillo wines after malolactic fermentation," *European Food Research and Technology*, vol. 228, no. 4, pp. 501–510, 2008. DOI: 10.1007/s00217-008-0957-0.

[49] S. González-Manzano, N. Mateus, V. de Freitas, and C. Santos-Buelga, "Influence of the degree of polymerisation in the ability of catechins to act as anthocyanin copigments," *European Food Research and Technology*, vol. 227, no. 1, pp. 83–92, 2007. DOI: 10.1007/s00217-007-0696-7.

[50] M. Edgley, D. C. Close, P. F. Measham, and D. S. Nichols, "Physiochemistry of blackberries (*Rubus* L. subgenus *Rubus* Watson) affected by red drupelet reversion," *Postharvest Biology and Technology*, vol. 153, pp. 183–190, 2019. DOI: 10.1016/j.postharvbio.2019.04.012.

[51] C. Escott, A. Morata, I. Loira, W. Tesfaye, and J. Suarez-Lepe, "Characterization of polymeric pigments and pyranoanthocyanins formed in microfermentations of non-*Saccharomyces* yeasts," *Journal of Applied Microbiology*, vol. 121, no. 5, pp. 1346–1356, 2016. DOI: 10.1111/jam.13255.

[52] S. González-Manzano, M. Dueñas, J. Rivas-Gonzalo, M. T. Escribano-Bailón, and C. Santos-Buelga, "Studies on the copigmentation between anthocyanins and flavan-3-ols and their influence in the colour expression of red wine," *Food Chemistry*, vol. 114, no. 2, pp. 649–656, 2009. DOI: 10.1016/j.foodchem.2008.10.002.

[53] S. González-Manzano, C. Santos-Buelga, M. Dueñas, J. C. Rivas-Gonzalo, and T. Escribano-Bailón, "Colour implications of self-association processes of wine anthocyanins," *European Food Research and Technology*, vol. 226, no. 3, pp. 483–490, 2007. DOI: 10.1007/s00217-007-0560-9.

[54] G. Miyagusuku-Cruzado, D. M. Voss, and M. M. Giusti, "Influence of the anthocyanin and cofactor structure on the formation efficiency of naturally derived pyranoanthocyanins," *International Journal of Molecular Sciences*, vol. 22, no. 13, p. 6708, 2021. DOI: 10.3390/ijms22136708.

[55] I. H. Gutiérrez, E. S.-P. Lorenzo, and A. V. Espinosa, "Phenolic composition and magnitude of copigmentation in young and shortly aged red wines made from the cultivars, Cabernet Sauvignon, Cencibel, and Syrah," *Food Chemistry*, vol. 92, no. 2, pp. 269–283, 2005. DOI: 10.1016/j.foodchem.2004.07.023.

[56] A. Marquez, M. P. Serratosa, and J. Merida, "Influence of bottle storage time on colour, phenolic composition and sensory properties of sweet red wines," *Food Chemistry*, vol. 146, pp. 507–514, 2014. DOI: 10.1016/j.foodchem.2013.09.103.

[57] L. Cruz, N. Basílio, N. Mateus, V. de Freitas, and F. Pina, "Natural and synthetic flavylium-based dyes: The chemistry behind the color," *Chemical Reviews*, vol. 122, no. 1, pp. 1416–1481, 2021. DOI: 10.1021/acs.chemrev.1c00399.

[58] E. Salas, C. L. Guernevé, H. Fulcrand, C. Poncet-Legrand, and V. Cheynier, "Structure determination and colour properties of a new directly linked flavanol-anthocyanin dimer," *Tetrahedron Letters*, vol. 45, no. 47, pp. 8725–8729, 2004. DOI: 10.1016/j.tetlet.2004.09.127.

[59] C. M. Willemse, M. A. Stander, J. Vestner, A. G. J. Tredoux, and A. de Villiers, "Comprehensive two-dimensional hydrophilic interaction chromatography (HILIC) × reversed-phase liquid chromatography coupled to high-resolution mass spectrometry (RP-LC-UV-MS) analysis of anthocyanins and derived pigments in red wine," *Analytical Chemistry*, vol. 87, no. 24, pp. 12 006–12 015, 2015. DOI: 10.1021/acs.analchem.5b03615.

[60] D. F. Lee, E. E. Swinny, and G. P. Jones, "NMR identification of ethyl-linked anthocyanin-flavanol pigments formed in model wine ferments," *Tetrahedron Letters*, vol. 45, no. 8, pp. 1671–1674, 2004. DOI: 10.1016/j.tetlet.2003.12.110.

[61] G. A. Macz-Pop, A. M. González-Paramás, J. J. Pérez-Alonso, and J. C. Rivas-Gonzalo, "New flavanol-anthocyanin condensed pigments and anthocyanin composition in Guatemalan beans (*Phaseolus* spp.)," *Journal of Agricultural and Food Chemistry*, vol. 54, no. 2, pp. 536–542, 2005. DOI: 10.1021/jf051913l.

[62] J. E. Laitila, "Composition and evolution of oligomeric proanthocyanidin-malvidin glycoside adducts in commercial red wines," *Food Chemistry*, vol. 340, p. 127 905, 2021. DOI: 10.1016/j.foodchem.2020.127905.

[63] A. M. González-Paramás, F. L. da Silva, P. Martín-López, G. Macz-Pop, S. González-Manzano, C. Alcalde-Eon, J. J. Pérez-Alonso, M. Escribano-Bailón, J. C. Rivas-Gonzalo, and C. Santos-Buelga, "Flavanol-anthocyanin condensed pigments in plant extracts," *Food Chemistry*, vol. 94, no. 3, pp. 428–436, 2006. DOI: 10.1016/j.foodchem.2004.11.037.

[64] M. Dueñas, H. Fulcrand, and V. Cheynier, "Formation of anthocyanin-flavanol adducts in model solutions," *Analytica Chimica Acta*, vol. 563, no. 1-2, pp. 15–25, 2006. DOI: 10.1016/j.aca.2005.10.062.

[65] E. Salas, M. Dueñas, M. Schwarz, P. Winterhalter, V. Cheynier, and H. Fulcrand, "Characterization of pigments from different high speed countercurrent chromatography wine fractions," *Journal of Agricultural and Food Chemistry*, vol. 53, no. 11, pp. 4536–4546, 2005. DOI: 10.1021/jf0478096.

[66] J. A. Kennedy, "Wine color," in *Managing Wine Quality*, Elsevier, 2022, pp. 97–132. DOI: 10.1016/b978-0-08-102067-8.00016-6.

[67] H. Ye, L. Luo, J. Wang, K. Jiang, T. Yue, and H. Yang, "Highly galloylated and A-type prodelphinidins and procyanidins in persimmon (*Diospyros kaki* L.) peel," *Food Chemistry*, vol. 378, p. 131 972, 2022. DOI: 10.1016/j.foodchem.2021.131972.

[68] J. Pissarra, S. Lourenço, A. M. González-Paramás, N. Mateus, C. S. Buelga, A. M. S. Silva, and V. de Freitas, "Structural characterization of new malvidin 3-glucoside-catechin aryl/alkyl-linked pigments," *Journal of Agricultural and Food Chemistry*, vol. 52, no. 17, pp. 5519–5526, 2004. DOI: 10.1021/jf0494433.

[69] V. de Freitas and N. Mateus, "Chemical transformations of anthocyanins yielding a variety of colours (Review)," *Environmental Chemistry Letters*, vol. 4, no. 3, pp. 175–183, 2006. DOI: 10.1007/s10311-006-0060-3.

[70] H. Wang, E. J. Race, and A. J. Shrikhande, "Anthocyanin transformation in Cabernet Sauvignon wine during aging," *Journal of Agricultural and Food Chemistry*, vol. 51, no. 27, pp. 7989–7994, 2003. DOI: 10.1021/jf034501q.

[71] S. Prat-García, J. Oliveira, M. del Alamo-Sanza, V. de Freitas, I. Nevares, and N. Mateus, "Characterization of anthocyanins and anthocyanin-derivatives in red wines during ageing in custom oxygenation oak wood barrels," *Molecules*, vol. 26, no. 1, p. 64, 2020. DOI: 10.3390/molecules26010064.

[72] M. Cano-López, F. Pardo-Mínguez, G. Schmauch, C. Saucier, P.-L. Teissedre, J. M. López-Roca, and E. Gómez-Plaza, "Effect of micro-oxygenation on color and anthocyanin-related compounds of wines with different phenolic contents," *Journal of Agricultural and Food Chemistry*, vol. 56, no. 14, pp. 5932–5941, 2008. DOI: 10.1021/jf8006147.

[73] M. Fanzone, A. Catania, M. Assof, V. Jofré, J. Prieto, D. G. Quiroga, J. L. Sottano, and S. Sari, "Application of vine-shoot chips during winemaking and aging of Malbec and Bonarda wines," *Beverages*, vol. 7, no. 3, p. 51, 2021. DOI: 10.3390/beverages7030051.

[74] M. Rentzsch, M. Schwarz, and P. Winterhalter, "Pyranoanthocyanins - an overview on structures, occurrence, and pathways of formation," *Trends in Food Science & Technology*, vol. 18, no. 10, pp. 526–534, 2007. DOI: 10.1016/j.tifs.2007.04.014.

[75] C. Alcalde-Eon, M.-T. Escribano-Bailón, and I. García-Estévez, "Role of Oak ellagitannins in the synthesis of Vitisin A and in the degradation of malvidin 3-*O*-glucoside: An approach in wine-like model systems," *Journal of Agricultural and Food Chemistry*, 2022. DOI: 10.1021/acs.jafc.2c00615.

[76] C. Benabdeljalil, V. Cheynier, H. Fulcrand, A. Hafiki, M. Mosaddak, and M. Moutounet, "Mise en èvidence de nouveaux pigments formés par réaction des anthocyanes avec des métabolites de levure," *Sciences des Aliments*, vol. 20, no. 2, pp. 203–220, 2000. DOI: 10.3166/sda.20.203-220.

[77] A. L. Waterhouse and J. Zhu, "A quarter century of wine pigment discovery," *Journal of the Science of Food and Agriculture*, vol. 100, no. 14, pp. 5093–5101, 2019. DOI: 10.1002/jsfa.9840.

[78] A. Morata, M. Gómez-Cordovés, F. Calderón, and J. Suárez, "Effects of pH, temperature and SO_2 on the formation of pyranoanthocyanins during red wine fermentation with two species of *Saccharomyces*," *International Journal of Food Microbiology*, vol. 106, no. 2, pp. 123–129, 2006. DOI: 10.1016/j.ijfoodmicro.2005.05.019.

[79] N. Mateus, A. M. S. Silva, J. C. Rivas-Gonzalo, C. Santos-Buelga, and V. de Freitas, "A new class of blue anthocyanin-derived pigments isolated from red wines," *Journal of Agricultural and Food Chemistry*, vol. 51, no. 7, pp. 1919–1923, 2003. DOI: 10.1021/jf020943a.

[80] N. Mateus, J. Oliveira, A. M. González-Paramás, C. Santos-Buelga, and V. de Freitas, "Screening of portisins (vinylpyranoanthocyanin pigments) in Port wine by LC/DAD-MS," *Food Science and Technology International*, vol. 11, no. 5, pp. 353–358, 2005. DOI: 10.1177/1082013205057940.

[81] H. Fulcrand, C. Benabdeljalil, J. Rigaud, V. Cheynier, and M. Moutounet, "A new class of wine pigments generated by reaction between pyruvic acid and grape anthocyanins," *Phytochemistry*, vol. 47, no. 7, pp. 1401–1407, 1998, ISSN: 0031-9422. DOI: 10.1016/S0031-9422(97)00772-3. [Online]. Available: https://www.sciencedirect.com/science/article/pii/S0031942297007723.

[82] A. Morata, F. Calderón, M. González, M. Gómez-Cordovés, and J. Suárez, "Formation of the highly stable pyranoanthocyanins (vitisins A and B) in red wines by the addition of pyruvic acid and acetaldehyde," *Food Chemistry*, vol. 100, no. 3, pp. 1144–1152, 2007. DOI: 10.1016/j.foodchem.2005.11.024.

[83] J. Bakker and C. F. Timberlake, "Isolation, identification, and characterization of new color-stable anthocyanins occurring in some red wines," *Journal of Agricultural and Food Chemistry*, vol. 45, no. 1, pp. 35–43, 1997, ISSN: 0021-8561. DOI: 10.1021/jf960252c. [Online]. Available: https://doi.org/10.1021/jf960252c.

[84] J. Oliveira, M. A. da Silva, N. Teixeira, V. D. Freitas, and E. Salas, "Screening of anthocyanins and anthocyanin-derived pigments in red wine grape pomace using LC-DAD/MS and MALDI-TOF techniques," *Journal of Agricultural and Food Chemistry*, vol. 63, no. 35, pp. 7636–7644, 2015. DOI: 10.1021/acs.jafc.5b00256.

[85] T. Dipalmo, P. Crupi, S. Pati, M. L. Clodoveo, and A. D. Luccia, "Studying the evolution of anthocyanin-derived pigments in a typical red wine of Southern Italy to assess its resistance to aging," *LWT - Food Science and Technology*, vol. 71, pp. 1–9, 2016. DOI: 10.1016/j.lwt.2016.03.012.

[86] C. Alcalde-Eon, M. T. Escribano-Bailón, C. Santos-Buelga, and J. C. Rivas-Gonzalo, "Changes in the detailed pigment composition of red wine during maturity and ageing: A comprehensive study," *Analytical Chimica Acta*, vol. 563, no. 1-2, pp. 238–254, 2006. DOI: 10.1016/j.aca.2005.11.028.

[87] E. Boido, C. Alcalde-Eon, F. Carrau, E. Dellacassa, and J. C. Rivas-Gonzalo, "Aging effect on the pigment composition and color of *Vitis vinifera* L. Cv. tannat wines. Contribution of the main pigment families to wine color," *Journal of Agricultural and Food Chemistry*, vol. 54, no. 18, pp. 6692–6704, 2006. DOI: 10.1021/jf061240m.

[88] F. Cosme, L. Filipe-Ribeiro, and F. M. Nunes, "Wine stabilisation: An overview of defects and treatments," in *Chemistry and Biochemistry of Winemaking, Wine Stabilization and Aging*, F. Cosme, F. M. Nunes, and L. Filipe-Ribeiro, Eds., Rijeka: IntechOpen, 2021, ch. 8. DOI: 10.5772/intechopen.95245. [Online]. Available: https://doi.org/10.5772/intechopen.95245.

[89] M. Schwarz, G. Jerz, and P. Winterhalter, "Isolation and structure of Pinotin A, a new anthocyanin derivative from Pinotage wine," en, *VITIS - Journal of Grapevine Research*, vol. 42, no. 2, pp. 105–106, 2015. DOI: 10.5073/VITIS.2003.42.105-106.

[90] M. Schwarz, T. C. Wabnitz, and P. Winterhalter, "Pathway leading to the formation of anthocyanin-vinylphenol adducts and related pigments in red wines," *Journal of Agricultural and Food Chemistry*, vol. 51, no. 12, pp. 3682–3687, 2003. DOI: 10.1021/jf0340963.

[91] J. Sun, X. Li, H. Luo, L. Ding, X. Jiang, X. Li, R. Jiao, and W. Bai, "Comparative study on the stability and antioxidant activity of six pyranoanthocyanins based on malvidin-3-glucoside," *Journal of Agricultural and Food Chemistry*, vol. 68, no. 9, pp. 2783–2794, 2020. DOI: 10.1021/acs.jafc.9b06734.

[92] S. Pati, I. Losito, G. Gambacorta, E. La Notte, F. Palmisano, and P. G. Zambonin, "Simultaneous separation and identification of oligomeric procyanidins and anthocyanin-derived pigments in raw red wine by HPLC-UV-ESI-MS^n," *Journal of Mass Spectrometry*, vol. 41, no. 7, pp. 861–871, 2006. DOI: 10.1002/jms.1044.

[93] V. A. P. de Freitas and N. Mateus, "Structural changes of anthocyanins during red wine aging: Portisins: A new class of blue anthocyanin-derived pigments," in *ACS Symposium Series*, American Chemical Society, 2004, pp. 160–178. DOI: 10.1021/bk-2004-0886.ch010.

[94] C. Gómez-Cordovés, "New pigments produced in red wines via different enological processes," in *ACS Symposium Series*, American Chemical Society, 2004, pp. 89–124. DOI: 10.1021/bk-2004-0886.ch007.

[95] N. Mateus, J. Oliveira, C. Santos-Buelga, A. M. Silva, and V. de Freitas, "NMR structure characterization of a new vinylpyranoanthocyanin-catechin pigment (a portisin)," *Tetrahedron Letters*, vol. 45, no. 17, pp. 3455–3457, 2004. DOI: 10.1016/j.tetlet.2004.03.007.

[96] J. Oliveira, V. de Freitas, A. M. S. Silva, and N. Mateus, "Reaction between hydroxycinnamic acids and anthocyanin-pyruvic acid adducts yielding new portisins," *Journal of Agricultural and Food Chemistry*, vol. 55, no. 15, pp. 6349–6356, 2007. DOI: 10.1021/jf070968f.

[97] P. Ribéreau-Gayon, Y. Glories, A. Maujean, D. Dubourdieu, P. Darriet, and J. Towey, "Phenolic compounds," in *Handbook of Enology: The Microbiology of Wine and Vinifications*, 3rd ed., vol. 2, Wiley, 2021, ch. 6, pp. 161–241. DOI: 10.1002/9781119588320.ch20.

[98] S. González-Manzano, J. C. Rivas-Gonzalo, and C. Santos-Buelga, "Extraction of flavan-3-ols from grape seed and skin into wine using simulated maceration," *Analytica Chimica Acta*, vol. 513, no. 1, pp. 283–289, 2004. DOI: 10.1016/j.aca.2003.10.019.

[99] J. Hellström, J. Sinkkonen, M. Karonen, and P. Mattila, "Isolation and structure elucidation of procyanidin oligomers from saskatoon berries (*Amelanchier alnifolia*)," *Journal of Agricultural and Food Chemistry*, vol. 55, no. 1, pp. 157–164, 2006. DOI: 10.1021/jf062441t.

[100] L. M. de Souza, T. R. Cipriani, M. Iacomini, P. A. Gorin, and G. L. Sassaki, "HPLC/ESI-MS and NMR analysis of flavonoids and tannins in bioactive extract from leaves of *Maytenus ilicifolia*," *Journal of Pharmaceutical and Biomedical Analysis*, vol. 47, no. 1, pp. 59–67, 2008. DOI: 10.1016/j.jpba.2007.12.008.

[101] B. Bartolomé, M. Monagas, I. Garrido, C. Gómez-Cordovés, P. J. Martín-Álvarez, R. Lebrón-Aguilar, M. Urpí-Sardà, R. Llorach, and C. Andrés-Lacueva, "Almond (*Prunus dulcis* (Mill.) D.A. Webb) polyphenols: From chemical characterization to targeted analysis of phenolic metabolites in humans," *Archives of Biochemistry and Biophysics*, vol. 501, no. 1, pp. 124–133, 2010. DOI: 10.1016/j.abb.2010.03.020.

[102] M. Monagas, R. Suárez, C. Gómez-Cordovés, and B. Bartolomé, “Simultaneous determination of nonanthocyanin phenolic compounds in red wines by HPLC-DAD/ESI-MS,” *American Journal of Enology and Viticulture*, vol. 56, no. 2, p. 139, 2005. [Online]. Available: http://www.ajevonline.org/content/56/2/139.abstract.

[103] D.-Y. Xie and R. A. Dixon, “Proanthocyanidin biosynthesis - still more questions than answers?” *Phytochemistry*, vol. 66, no. 18, pp. 2127–2144, 2005. DOI: 10.1016/j.phytochem.2005.01.008.

[104] M. A. S. Marles, H. Ray, and M. Y. Gruber, “New perspectives on proanthocyanidin biochemistry and molecular regulation,” *Phytochemistry*, vol. 64, no. 2, pp. 367–383, 2003. DOI: 10.1016/s0031-9422(03)00377-7.

[105] F. He, Q.-H. Pan, Y. Shi, and C.-Q. Duan, “Biosynthesis and genetic regulation of proanthocyanidins in plants,” *Molecules*, vol. 13, no. 10, pp. 2674–2703, 2008. DOI: 10.3390/molecules13102674.

[106] F. He, Q.-H. Pan, Y. Shi, X.-T. Zhang, and C.-Q. Duan, “Identification of autoxidation oligomers of flavan-3-ols in model solutions by HPLC-MS/MS,” *Journal of Mass Spectrometry*, vol. 44, no. 5, pp. 633–640, 2009. DOI: 10.1002/jms.1536.

[107] S. Deshaies, C. le Guernevé, L. Suc, L. Mouls, F. Garcia, and C. Saucier, “Unambiguous NMR structural determination of (+)-catechin-laccase dimeric reaction products as potential markers of grape and wine oxidation,” *Molecules*, vol. 26, no. 20, p. 6165, 2021. DOI: 10.3390/molecules26206165.

[108] R. Kawazoe, Y. Matsuo, Y. Saito, and T. Tanaka, “Stereochemistry of a cyclic epicatechin trimer with C_3 symmetry produced by oxidative coupling,” *European Journal of Organic Chemistry*, vol. 2021, no. 5, pp. 777–781, 2021. DOI: 10.1002/ejoc.202001579.

[109] P. Poupard, P. Sanoner, A. Baron, C. M. G. C. Renard, and S. Guyot, “Characterization of procyanidin B2 oxidation products in an apple juice model solution and confirmation of their presence in apple juice by high-performance liquid chromatography coupled to electrospray ion trap mass spectrometry,” *Journal of Mass Spectrometry*, vol. 46, no. 11, pp. 1186–1197, 2011. DOI: 10.1002/jms.2007.

[110] L. Gu, M. A. Kelm, J. F. Hammerstone, Z. Zhang, G. Beecher, J. Holden, D. Haytowitz, and R. L. Prior, “Liquid chromatographic/electrospray ionization mass spectrometric studies of proanthocyanidins in foods,” *Journal of Mass Spectrometry*, vol. 38, no. 12, pp. 1272–1280, 2003. DOI: 10.1002/jms.541.

[111] S. Suriyaprom, P. Mosoni, S. Leroy, T. Kaewkod, M. Desvaux, and Y. Tragoolpua, “Antioxidants of fruit extracts as antimicrobial agents against pathogenic bacteria,” *Antioxidants*, vol. 11, no. 3, p. 602, 2022. DOI: 10.3390/antiox11030602.

[112] C. P. Passos, S. M. Cardoso, M. R. M. Domingues, P. Domingues, C. M. Silva, and M. A. Coimbra, “Evidence for galloylated type-A procyanidins in grape seeds,” *Food Chemistry*, vol. 105, no. 4, pp. 1457–1467, 2007. DOI: 10.1016/j.foodchem.2007.05.026.

[113] Z. Wang, M. Ashraf-Khorassani, and L. T. Taylor, “Feasibility study of online Supercritical Fluid Extraction-Liquid Chromatography-UV absorbance-Mass Spectrometry for the determination of proanthocyanidins in grape seeds,” *Journal of Chromatographic Science*, vol. 43, no. 3, pp. 109–115, 2005. DOI: 10.1093/chromsci/43.3.109.

[114] P. J. Sarnoski, J. V. Johnson, K. A. Reed, J. M. Tanko, and S. F. O’Keefe, “Separation and characterisation of proanthocyanidins in Virginia type peanut skins by LC-MS^n,” *Food Chemistry*, vol. 131, no. 3, pp. 927–939, 2012. DOI: 10.1016/j.foodchem.2011.09.081.

[115] Z. Lofft, A. Taibi, P. Massara, T. Tokar, I. Paetau-Robinson, C. Khoo, and E. M. Comelli, “Cranberry proanthocyanidin and its microbial metabolite 3,4-dihydroxyphenylacetic acid, but not 3-(4-hydroxyphenyl)-propionic acid, partially reverse pro-inflammatory microRNA responses in human intestinal epithelial cells,” *Molecular Nutrition & Food Research*, vol. 66, no. 8, p. 2 100 853, 2022. DOI: 10.1002/mnfr.202100853.

[116] J. Drinkine, Y. Glories, and C. Saucier, “(+)-catechin-aldehyde condensations: Competition between acetaldehyde and glyoxylic acid,” *Journal of Agricultural and Food Chemistry*, vol. 53, no. 19, pp. 7552–7558, 2005. DOI: 10.1021/jf0504723.

[117] A. Marrufo-Curtido, V. Ferreira, and A. Escudero, “Can aldehyde accumulation rates of red wines undergoing oxidation be predicted in accelerated conditions? the controverted role of aldehyde-polyphenol reactivity,” *Journal of the Science of Food and Agriculture*, 2022. DOI: 10.1002/jsfa.11736.

[118] H. Fulcrand, V. Cheynier, J. Oszmianski, and M. Moutounet, “An oxidized tartaric acid residue as a new bridge potentially competing with acetaldehyde in flavan-3-ol condensation,” *Phytochemistry*, vol. 46, no. 2, pp. 223–227, 1997. DOI: 10.1016/s0031-9422(97)00276-8.

[119] N.-E. Es-Safi, V. Cheynier, and M. Moutounet, “Study of the reactions between (+)-catechin and furfural derivatives in the presence or absence of anthocyanins and their implication in food color change,” *Journal of Agricultural and Food Chemistry*, vol. 48, no. 12, pp. 5946–5954, 2000. DOI: 10.1021/jf000394d.

[120] M. N. Bourden, N. Vivas, C. Absalon, C. Vitry, E. Fouquet, and N. V. de Gaulejac, “Structural diversity of nucleophilic adducts from flavanols and oak wood aldehydes,” *Food Chemistry*, vol. 107, no. 4, pp. 1494–1505, 2008. DOI: 10.1016/j.foodchem.2007.10.012.

[121] N.-E. Es-Safi, V. Cheynier, and M. Moutounet, “Role of aldehydic derivatives in the condensation of phenolic compounds with emphasis on the sensorial properties of fruit-derived foods,” *Journal of Agricultural and Food Chemistry*, vol. 50, no. 20, pp. 5571–5585, 2002. DOI: 10.1021/jf025503y.

[122] C. Saucier, C. Guerra, I. Pianet, M. Laguerre, and Y. Glories, “(+)-catechin-acetaldehyde condensation products in relation to wine-ageing,” *Phytochemistry*, vol. 46, no. 2, pp. 229–234, 1997. DOI: 10.1016/s0031-9422(97)00268-9.

[123] C. Saucier, M. Jourdes, Y. Glories, and S. Quideau, “Extraction, detection, and quantification of flavano-ellagitannins and ethylvescalagin in a Bordeaux red wine aged in oak barrels,” *Journal of Agricultural and Food Chemistry*, vol. 54, no. 19, pp. 7349–7354, 2006. DOI: 10.1021/jf061724i.

[124] A. Glabasnia and T. Hofmann, “Identification and sensory evaluation of dehydro- and deoxy-ellagitannins formed upon toasting of oak wood (*Quercus alba* L.),” *Journal of Agricultural and Food Chemistry*, vol. 55, no. 10, pp. 4109–4118, 2007. DOI: 10.1021/jf070151m.

[125] A. Amr and E. Al-Tamimi, “Stability of the crude extracts of *Ranunculus asiaticus* anthocyanins and their use as food colourants,” *International Journal of Food Science & Technology*, vol. 42, no. 8, pp. 985–991, 2007. DOI: 10.1111/j.1365-2621.2006.01334.x.

[126] H. A. Mohammed and R. A. Khan, “Anthocyanins: Traditional uses, structural and functional variations, approaches to increase yields and products’ quality, hepatoprotection, liver longevity, and commercial products,” *International Journal of Molecular Sciences*, vol. 23, no. 4, p. 2149, 2022. DOI: 10.3390/ijms23042149.

[127] F. Pomar, M. Novo, and A. Masa, “Varietal differences among the anthocyanin profiles of 50 red table grape cultivars studied by high performance liquid chromatography,” *Journal of Chromatography A*, vol. 1094, no. 1-2, pp. 34–41, 2005. DOI: 10.1016/j.chroma.2005.07.096.

[128] M. B. Sousa, J. R. Santos, P. Almeida, and J. Rodrigues, “Low pressure ion pair chromatography with amperometric detection for the determination of trigonelline in coffee samples,” *Food Research International*, vol. 114, pp. 223–229, 2018. DOI: 10.1016/j.foodres.2018.07.068.

[129] C. T. da Costa, D. Horton, and S. A. Margolis, “Analysis of anthocyanins in foods by liquid chromatography, liquid chromatography-mass spectrometry and capillary electrophoresis,” *Journal of Chromatography A*, vol. 881, no. 1-2, pp. 403–410, 2000. DOI: 10.1016/s0021-9673(00)00328-9.

[130] A. Versari, R. B. Boulton, and G. P. Parpinello, “A comparison of analytical methods for measuring the color components of red wines,” *Food Chemistry*, vol. 106, no. 1, pp. 397–402, 2008. DOI: 10.1016/j.foodchem.2007.05.073.

[131] M. O. Downey and S. Rochfort, “Simultaneous separation by reversed-phase high-performance liquid chromatography and mass spectral identification of anthocyanins and flavonols in Shiraz grape skin,” *Journal of Chromatography A*, vol. 1201, no. 1, pp. 43–47, 2008. DOI: 10.1016/j.chroma.2008.06.002.

[132] C. Mané, J. M. Souquet, D. Ollé, C. Verriés, F. Véran, G. Mazerolles, V. Cheynier, and H. Fulcrand, "Optimization of simultaneous flavanol, phenolic acid, and anthocyanin extraction from grapes using an experimental design: Application to the characterization of Champagne grape varieties," *Journal of Agricultural and Food Chemistry*, vol. 55, no. 18, pp. 7224–7233, 2007. DOI: 10.1021/jf071301w.

[133] S. Pati, M. T. Liberatore, G. Gambacorta, D. Antonacci, and E. L. Notte, "Rapid screening for anthocyanins and anthocyanin dimers in crude grape extracts by high performance liquid chromatography coupled with diode array detection and tandem mass spectrometry," *Journal of Chromatography A*, vol. 1216, no. 18, pp. 3864–3868, 2009. DOI: 10.1016/j.chroma.2009.02.068.

[134] Z. Huang, B. Wang, P. Williams, and R. D. Pace, "Identification of anthocyanins in muscadine grapes with HPLC-ESI-MS," *LWT - Food Science and Technology*, vol. 42, no. 4, pp. 819–824, 2009. DOI: 10.1016/j.lwt.2008.11.005.

[135] I. J. Košir, B. Lapornik, S. Andrenšek, A. G. Wondra, U. Vrhovšek, and J. Kidri, "Identification of anthocyanins in wines by liquid chromatography, liquid chromatography-mass spectrometry and nuclear magnetic resonance," *Analytica Chimica Acta*, vol. 513, no. 1, pp. 277–282, 2004. DOI: 10.1016/j.aca.2003.12.013.

[136] R. E. Ardrey, "Applications of high performance liquid chromatography-mass spectrometry," in *Liquid Chromatography-Mass Spectrometry: An Introduction*, 1st, Kent, U.K.: John Wiley & Sons, Ltd., 2003, ch. 5, pp. 129–332, ISBN: 9780470867297. DOI: 10.1002/0470867299.ch5.

[137] F. Lemière, "Interfaces for lc-ms," in *Guide to LC-MS*, vol. 12, 2001, pp. 2–8.

[138] R. E. Ardrey, "Mass spectrometry," in *Liquid Chromatography-Mass Spectrometry: An Introduction*, 1st, John Wiley & Sons, Ltd., 2003, ch. 3, pp. 33–74, ISBN: 9780470867297. DOI: 10.1002/0470867299.ch3.

[139] J. C. Fjeldsted, "Accurate mass measurements with orthogonal axis time-of-flight mass spectrometry," in *Liquid Chromatography Time-of-Flight Mass Spectrometry*, I. Ferrer and E. M. Thurman, Eds., vol. 173, Hoboken, New Jersey: John Wiley & Sons, Inc., 2009, ch. 1, pp. 1–15, ISBN: 9780470429969. DOI: 10.1002/9780470429969.ch1.

[140] R. Flamini and T. Pietro, "MS/MS methodologies," in *Mass Spectrometry in Grape and Wine Chemistry*, Hoboken, New Jersey: John Wiley & Sons Inc., 2009, ch. 3, pp. 76–93, ISBN: 0470392479. DOI: 10.1002/9780470552926.ch3. [Online]. Available: https://www.ebook.de/de/product/9338723/riccardo_flamini_mass_spectrometry_in_grape_and_wine_chemistry.html.

[141] N. Mateus, S. de Pascual-Teresa, J. C. Rivas-Gonzalo, C. Santos-Buelga, and V. de Freitas, "Structural diversity of anthocyanin-derived pigments in port wines," *Food Chemistry*, vol. 76, no. 3, pp. 335–342, 2002. DOI: 10.1016/s0308-8146(01)00281-3.

[142] P. Dugo, O. Favoino, M. L. Presti, R. Luppino, G. Dugo, and L. Mondello, "Deterrmination of anthocyanins and related components in red wines by micro- and capillary HPLC," *Journal of Separation Science*, vol. 27, no. 17-18, pp. 1458–1466, 2004. DOI: 10.1002/jssc.200401822.

[143] Y. Glories, "La couleur des vins rouges. lre partie : Les équilibres des anthocyanes et des tanins," *OENO One*, vol. 18, no. 3, p. 195, 1984. DOI: 10.20870/oeno-one.1984.18.3.1751.

[144] Y. Glories, "La couleur des vins rouges. 2e partie : Mesure, origine et interprétation," *OENO One*, vol. 18, no. 4, p. 253, 1984. DOI: 10.20870/oeno-one.1984.18.4.1744.

[145] C. I. de l'Eclairage (CIE), *Colorimetry*, 2nd ed. Vienna: Commission Internationale de l'Eclairage, 1986.

[146] I. Esparza, C. Santamaría, I. Calvo, and J. M. Fernández, "Significance of CIELAB parameters in the routine analysis of red wines relevancia de los parámetros CIELAB en el análisis de rutina de vinos tintos," *CyTA - Journal of Food*, vol. 7, no. 3, pp. 189–199, 2009. DOI: 10.1080/19476330903068001.

[147] M. Monagas, P. J. Martín-Álvarez, C. Gómez-Cordovés, and B. Bartolomé, "Time course of the colour of young red wines from *Vitis vinifera* L. during ageing in bottle," *International Journal of Food Science and Technology*, vol. 41, no. 8, pp. 892–899, 2006. DOI: 10.1111/j.1365-2621.2005.01132.x.

[148] O. Taofiq, A. M. González-Paramás, A. Martins, M. F. Barreiro, and I. C. F. R. Ferreira, "Mushrooms extracts and compounds in cosmetics, cosmeceuticals and nutricosmetics-A review.," English, *Industrial Crops and Products*, vol. 90, A. C. S. (ACS), Ed., pp. 38–48, 2016, ISSN: 0926-6690. DOI: 10.1016/j.indcrop.2016.06.012.

[149] M. Carocho and I. C. F. R. Ferreira, "A review on antioxidants, prooxidants and related controversy: Natural and synthetic compounds, screening and analysis methodologies and future perspectives.," English, *Food and Chemical Toxicology*, vol. 51, A. C. S. (ACS), Ed., pp. 15–25, 2013, ISSN: 0278-6915. DOI: 10.1016/j.fct.2012.09.021.

[150] M. M. Santoro and G. Gaudino, "Cellular and molecular facets of keratinocyte reepithelialization during wound healing.," English, *Experimental Cell Research*, vol. 304, no. 1, pp. 274–286, 2005, ISSN: 0014-4827. DOI: 10.1016/j.yexcr.2004.10.033.

[151] M. Kelkel, C. Jacob, M. Dicato, and M. Diederich, "Potential of the dietary antioxidants resveratrol and curcumin in prevention and treatment of hematologic malignancies," English, *Molecules*, vol. 15, no. 10, pp. 7035–7074, 2010, ISSN: 1420-3049. DOI: 10.3390/molecules15107035.

[152] A. R. Fontana, A. Antoniolli, and R. Bottini, "Grape pomace as a sustainable source of bioactive compounds: Extraction, characterization, and biotechnological applications of phenolics.," English, *Journal of Agricultural and Food Chemistry*, vol. 61, no. 38, pp. 8987–9003, 2013, ISSN: 0021-8561. DOI: 10.1021/jf402586f.

[153] J. R. Eoff, "Pomace wines: Their composition and detection," *Journal of Industrial and Engineering Chemistry*, vol. 8, no. 8, pp. 723–726, 1916. DOI: 10.1021/i500008a014.

[154] A. Teixeira, N. Baenas, R. Dominguez-Perles, A. Barros, E. Rosa, D. A. Moreno, and C. Garcia-Viguera, "Natural bioactive compounds from winery by-products as health promoters: A review.," English, *International Journal of Molecular Sciences*, vol. 15, no. 9, pp. 15 638–15 678, 2014, ISSN: 1422-0067. DOI: 10.3390/ijms150915638.

[155] C. Drosou, K. Kyriakopoulou, A. Bimpilas, D. Tsimogiannis, and M. Krokida, "A comparative study on different extraction techniques to recover red grape pomace polyphenols from vinification byproducts.," English, *Industrial Crops and Products*, vol. 75, no. Part B, pp. 141–149, 2015, ISSN: 0926-6690. DOI: 10.1016/j.indcrop.2015.05.063.

[156] J. Portu, I. López-Alfaro, S. Gómez-Alonso, R. López, and T. Garde-Cerdán, "Changes on grape phenolic composition induced by grapevine foliar applications of phenylalanine and urea.," English, *Food Chemistry*, vol. 180, A. C. S. (ACS), Ed., pp. 171–180, 2015, ISSN: 0308-8146. DOI: 10.1016/j.foodchem.2015.02.042.

[157] A. S. Ferreira, C. Nunes, A. Castro, P. Ferreira, and M. A. Coimbra, "Influence of grape pomace extract incorporation on chitosan films properties.," English, *Carbohydrate Polymers*, vol. 113, A. C. S. (ACS), Ed., pp. 490–499, 2014, ISSN: 0144-8617. DOI: 10.1016/j.carbpol.2014.07.032.

[158] F. J. Barba, Z. Zhu, M. Koubaa, A. S. Sant'Ana, and V. Orlien, "Green alternative methods for the extraction of antioxidant bioactive compounds from winery wastes and by-products: A review.," English, *Trends in Food Science & Technology*, vol. 49, A. C. S. (ACS), Ed., pp. 96–109, 2016, ISSN: 0924-2244. DOI: 10.1016/j.tifs.2016.01.006.

[159] Q.-W. Zhang, L.-G. Lin, and W.-C. Ye, "Techniques for extraction and isolation of natural products: A comprehensive review," English, *Chinese Medicine*, vol. 13, no. 1, p. 20, 2018, ISSN: 1749-8546. DOI: 10.1186/s13020-018-0177-x. [Online]. Available: https://doi.org/10.1186/s13020-018-0177-x.

[160] A. Gillet, B. Evrard, and G. Piel, "Liposomes and parameters affecting their skin penetration behaviour," English, *Journal of Drug Delivery Science and Technology*, vol. 21, no. 1, pp. 35–42, 2011, ISSN: 1773-2247. DOI: 10.1016/S1773-2247(11)50004-8. [Online]. Available: https://www.sciencedirect.com/science/article/pii/S1773224711500048.

[161] S. E. Cross and M. S. Roberts, "Physical enhancement of transdermal drug application: Is delivery technology keeping up with pharmaceutical development?" English, *Current Drug Delivery*, vol. 1, no. 1, pp. 81–92, 2004, ISSN: 1567-2018/1875-5704. DOI: 10.2174/1567201043480045. [Online]. Available: http://www.eurekaselect.com/node/63045/article.

[162] M. Kakran, N. G. Sahoo, and L. Li, "Dissolution enhancement of quercetin through nanofabrication, complexation, and solid dispersion.," English, *Colloids and Surfaces, B: Biointerfaces*, vol. 88, no. 1, pp. 121–130, 2011, ISSN: 0927-7765. DOI: 10.1016/j.colsurfb.2011.06.020.

[163] L. Gao, G.-Y. Liu, X.-Q. Wang, F. Liu, Y.-F. Xu, and J. Ma, "Preparation of a chemically stable quercetin formulation using nanosuspension technology.," English, *International Journal of Pharmaceutics*, vol. 404, no. 1-2, pp. 231–237, 2011, ISSN: 0378-5173. DOI: 10.1016/j.ijpharm.2010.11.009.

[164] Y. Gao, Y. Wang, Y. Ma, A. Yu, F. Cai, W. Shao, and G. Zhai, "Formulation optimization and in situ absorption in rat intestinal tract of quercetin-loaded microemulsion.," English, *Colloids and Surfaces, B: Biointerfaces*, vol. 71, no. 2, pp. 306–314, 2009, ISSN: 0927-7765. DOI: 10.1016/j.colsurfb.2009.03.005.

[165] H. L. Li, X. B. Zhao, Y. K. Ma, G. X. Zhai, L. B. Li, and H. X. Lou, "Enhancement of gastrointestinal absorption of quercetin by solid lipid nanoparticles.," English, *Journal of Controlled Release*, vol. 133, no. 3, pp. 238–244, 2009, ISSN: 0168-3659. DOI: 10.1016/j.jconrel.2008.10.002.

[166] C. Caddeo, O. Díez-Sales, R. Pons, C. Carbone, G. Ennas, G. Puglisi, A. M. Fadda, and M. Manconi, "Cross-linked chitosan/liposome hybrid system for the intestinal delivery of quercetin.," English, *Journal of Colloid and Interface Science*, vol. 461, A. C. S. (ACS), Ed., pp. 69–78, 2016, ISSN: 0021-9797. DOI: 10.1016/j.jcis.2015.09.013.

[167] H. Daraee, A. Etemadi, M. Kouhi, S. Alimirzalu, and A. Akbarzadeh, "Application of liposomes in medicine and drug delivery," *Artificial Cells, Nanomedicine, and Biotechnology*, vol. 44, no. 1, pp. 381–391, 2016, ISSN: 2169-1401. DOI: 10.3109/21691401.2014.953633. [Online]. Available: https://doi.org/10.3109/21691401.2014.953633.

[168] M.-K. Lee, "Liposomes for enhanced bioavailability of water-insoluble drugs: In vivo evidence and recent approaches," *Pharmaceutics*, vol. 12, no. 3, p. 264, 2020, ISSN: 1999-4923. DOI: 10.3390/pharmaceutics12030264.

[169] G. Cevc, "Material transport across permeability barriers by means of lipid vesicles," in *Handbook of Biological Physics*, vol. I, Elsevier, 1995, pp. 465–490. DOI: 10.1016/s1383-8121(06)80026-6.

[170] S. Rai, V. Pandey, and G. Rai, "Transfersomes as versatile and flexible nanovesicular carriers in skin cancer therapy: The state of the art.," English, *Nano Reviews & Experiments*, vol. 8, no. 1, pp. 1325708/1–1325708/19, 2017, ISSN: 2002-2727. DOI: 10.1080/20022727.2017.1325708.

[171] S. A. T. Opatha, V. Titapiwatanakun, and R. Chutoprapat, "Transfersomes: A promising nanoencapsulation technique for transdermal drug delivery," *Pharmaceutics*, vol. 12, no. 9, p. 855, 2020. DOI: 10.3390/pharmaceutics12090855.

[172] M. G. Nava-Arzaluz, E. Piñón-Segundo, A. Ganem-Rondero, and A. M. Grumezescu, "Lipid nanocarriers as skin drug delivery systems," in *Nanoparticles in Pharmacotherapy*, William Andrew Publishing, 2019, ch. 11, pp. 311–390. DOI: 10.1016/B978-0-12-816504-1.00007-7. [Online]. Available: https://www.sciencedirect.com/science/article/pii/B9780128165041000077.

[173] D. Titus, E. J. J. Samuel, and S. M. Roopan, "Nanoparticle characterization techniques," in *Green Synthesis, Characterization and Applications of Nanoparticles*, Elsevier, 2019, pp. 303–319. DOI: 10.1016/b978-0-08-102579-6.00012-5.

[174] P. M. Carvalho, M. R. Felício, N. C. Santos, S. Gonçalves, and M. M. Domingues, "Application of light scattering techniques to nanoparticle characterization and development," *Frontiers in Chemistry*, vol. 6, 2018. DOI: 10.3389/fchem.2018.00237.

[175] nanoComposix, *Nanoparticle characterization techniques*, 2022. [Online]. Available: https://nanocomposix.com/pages/nanoparticle-characterization-techniques#dls.

[176] M. B. Sánchez-Ilárduya, "Pigmentos derivados antociánicos de los vinos tintos de Rioja. Estudio analítico, influencia en el color y evolución durante la crianza," Ph.D. dissertation, Universidad del País Vasco-Euskal Herriko Unibersitatea, 2010.

[177] C. Sánchez-Fernández, "Búsqueda de marcadores de tipo tanino en vinos tintos de Rioja: Estudio cualitativo y cuantitativo por HPLC-MS/MS," Ph.D. dissertation, Universidad del País Vasco-Euskal Herriko Unibersitatea, 2012.

[178] Z. Rasines Perea, "Study of the evolution of anthocyanins, tannins and derivatives during making and ageing of red wine from Rioja by FT-IR and HPLC-MS/MS," Ph.D. dissertation, Universidad del País Vasco-Euskal Herriko Unibersitatea, 2014.

[179] N. Prieto Perea, "Anthocyanin derivatives and tannins of red wine by HPLC-DAD-MS/MS. Evolution along winemaking and comparision between Rioja and Bordeaux wines," Ph.D. dissertation, Universidad del País Vasco-Euskal Herriko Unibersitatea, 2018.

[180] T. Garrido, M. Gizdavic-Nikolaidis, I. Leceta, M. Urdanpilleta, P. Guerrero, K. de la Caba, and P. A. Kilmartin, "Optimizing the extraction process of natural antioxidants from chardonnay grape marc using microwave-assisted extraction," English, *Waste Management*, vol. 88, pp. 110–117, 2019, ISSN: 0956-053X. DOI: 10.1016/j.wasman.2019.03.031. [Online]. Available: https://www.sciencedirect.com/science/article/pii/S0956053X19301631.

[181] F. Pintus, D. Spanò, C. Mascia, A. Macone, G. Floris, and R. Medda, "Acetylcholinesterase inhibitory and antioxidant properties of *Euphorbia characias* latex," English, *Records of Natural Products*, 2013, ISSN: 1307-6167.

[182] C. Caddeo, D. Lucchesi, X. Fernàndez-Busquets, D. Valenti, G. Penno, A. M. Fadda, and L. Pucci, "Efficacy of a resveratrol nanoformulation based on a commercially available liposomal platform," *International Journal of Pharmaceutics*, vol. 608, p. 121 086, 2021. DOI: 10.1016/j.ijpharm.2021.121086.

[183] B. Era, S. Floris, V. Sogos, C. Porcedda, A. Piras, R. Medda, A. Fais, and F. Pintus, "Anti-aging potential of extracts from *Washingtonia filifera* seeds," English, *Plants*, vol. 10, no. 1, 2021, ISSN: 2223-7747. DOI: 10.3390/plants10010151.

[184] A. V. Oppenheim, A. S. Willsky, and S. H. Nawab, "The laplace transform," English, in *Signals and Systems*, 2nd ed., Upper Saddle River, NJ: Prentice-Hall, 1997, ch. 9, pp. 654–740.

[185] M. Nordberg, J. Duffus, and D. M. Templeton, "Glossary of terms used in toxicokinetics (IUPAC recommendations 2003)," *Pure and Applied Chemistry*, vol. 76, no. 5, pp. 1033–1082, 2004. DOI: 10.1351/pac200476051033.

[186] L. Shargel, S. Wu-Pong, and A. B. C. Yu, "Chapter 3. One-compartment open model: Intravenous bolus administration," in Book, Section, New York, NY: The McGraw-Hill Companies, 2012. [Online]. Available: https://accesspharmacy.mhmedical.com/content.aspx?bookid=513&sectionid=41488021.

[187] D. S. H. Lee, "One-compartment open model: Intravenous bolus administration," in *Applied Biopharmaceutics & Pharmacokinetics*, L. Shargel and A. B. Yu, Eds., 7th ed. New York, NY: McGraw-Hill Education, 2016, ch. 4. [Online]. Available: accesspharmacy.mhmedical.com/content.aspx?aid=1117896709.

[188] A. Aguilar Ros, M. Caamaño Somoza, and F. R. Martín Martín, *Biofarmacia y farmacocinética: Ejercicios y problemas resueltos*, 2nd ed. Barcelona: Elsevier, 2014, ISBN: 8490222606.

[189] T. A. Ahmed, "Pharmacokinetics of drugs following IV bolus, IV infusion, and oral administration," in *Basic Pharmacokinetic Concepts and Some Clinical Applications*, InTech, 2015. DOI: 10.5772/61573.

[190] T. Escribano-Bailón, M. Álvarez-García, J. C. Rivas-Gonzalo, F. J. Heredia, and C. Santos-Buelga, "Color and stability of pigments derived from the acetaldehyde-mediated condensation between malvidin 3-*O*-glucoside and (+)-catechin," *Journal of Agricultural and Food Chemistry*, vol. 49, no. 3, pp. 1213–1217, 2001. DOI: 10.1021/jf001081l.

[191] I. I. Rockenbach, L. V. Gonzaga, V. M. Rizelio, A. E. de Souza Schmidt Gonçalves, M. I. Genovese, and R. Fett, "Phenolic compounds and antioxidant activity of seed and skin extracts of red grape (*Vitis vinifera* and *Vitis labrusca*) pomace from Brazilian winemaking," *Food Research International*, vol. 44, no. 4, pp. 897–901, 2011. DOI: 10.1016/j.foodres.2011.01.049.

[192] Q. Yan, L. Zhang, X. Zhang, X. Liu, F. Yuan, Z. Hou, and Y. Gao, "Stabilization of grape skin anthocyanins by copigmentation with enzymatically modified isoquercitrin (EMIQ) as a copigment," *Food Research International*, vol. 50, no. 2, pp. 603–609, 2013. DOI: 10.1016/j.foodres.2011.04.007.

[193] C. Negro, A. Aprile, A. Luvisi, L. D. Bellis, and A. Miceli, "Antioxidant activity and polyphenols characterization of four monovarietal grape pomaces from salento (apulia, italy)," *Antioxidants*, vol. 10, no. 9, p. 1406, 2021. DOI: 10.3390/antiox10091406.

[194] F. Campos, A. F. Peixoto, P. A. R. Fernandes, M. A. Coimbra, N. Mateus, V. de Freitas, I. Fernandes, and A. Fernandes, "The antidiabetic effect of grape pomace polysaccharide-polyphenol complexes," *Nutrients*, vol. 13, no. 12, p. 4495, 2021. DOI: 10.3390/nu13124495.

[195] C. Beres, G. N. Costa, I. Cabezudo, N. K. da Silva-James, A. S. Teles, A. P. Cruz, C. Mellinger-Silva, R. V. Tonon, L. M. Cabral, and S. P. Freitas, "Towards integral utilization of grape pomace from winemaking process: A review," *Waste Management*, vol. 68, pp. 581–594, 2017. DOI: 10.1016/j.wasman.2017.07.017.

[196] W. Shi, B. Hass, M. A. Kuss, H. Zhang, S. Ryu, D. Zhang, T. Li, Y.-l. Li, and B. Duan, "Fabrication of versatile dynamic hyaluronic acid-based hydrogels," *Carbohydrate Polymers*, vol. 233, p. 115 803, 2020, ISSN: 0144-8617. DOI: 10.1016/j.carbpol.2019.115803. [Online]. Available: https://www.sciencedirect.com/science/article/pii/S0144861719314717.

Supplementary material

Table S1. Anthocyanin concentrations determined by HPLC-DAD in red wine samples from Mendavia 2018, expressed in mg of Mv-3-*O*-glc equiv./L.

This table is provided as a supplementary file in the appendix.

Table S2. Anthocyanin derivatives concentrations determined by HPLC-DAD-ESI(+)-MS/MS in red wine samples from Mendavia 2018, expressed in mg of Mv-3-*O*-glc equiv./L. Compounds 14 to 26.

This table is provided as a supplementary file in the appendix.

Table S3. Anthocyanin derivatives concentrations determined by HPLC-DAD-ESI(+)-MS/MS in red wine samples from Mendavia 2018, expressed in mg of Mv-3-*O*-glc equiv./L. Compounds 27 to 40.

This table is provided as a supplementary file in the appendix.

Table S4. Tannin concentrations determined by HPLC-DAD-ESI(+)-MS/MS in red wine samples from Mendavia 2018, expressed in mg of (+)-cat equiv./L.

This table is provided as a supplementary file in the appendix.

Table S5. Anthocyanin concentrations determined by HPLC-DAD in red wine samples from Alfaro 2019, expressed in mg of Mv-3-*O*-glc equiv./L.

This table is provided as a supplementary file in the appendix.

Table S6. Tannin concentrations determined by HPLC-DAD-ESI(+)-MS/MS in red wine samples from Alfaro 2019, expressed in mg of (+)-cat equiv./L. Compounds 41 to 58.

This table is provided as a supplementary file in the appendix.

Table S7. Tannin concentrations determined by HPLC-DAD-ESI(+)-MS/MS in red wine samples from Alfaro 2019, expressed in mg of (+)-cat equiv./L. Compounds 59 to 68.

This table is provided as a supplementary file in the appendix.

Table S8. Anthocyanin concentrations determined by HPLC-DAD in red wine samples from Laguardia 2019, expressed in mg of Mv-3-*O*-glc equiv./L.

This table is provided as a supplementary file in the appendix.

Table S9. Results of the chromatic coordinates obtained for wine of Mendavia 2018.

This table is provided as a supplementary file in the appendix.

Table S10. Results of the chromatic coordinates obtained for wine of Alfaro 2019.

This table is provided as a supplementary file in the appendix.

Table S11. Results of the chromatic coordinates obtained for wine of Laguardia 2019.

This table is provided as a supplementary file in the appendix.

Table S12. Results of k_e, k_f and k_d (mean ± SD) calculated by the residuals method with the concentration profiles of the selected anthocyanins and anthocyanin derivatives from the wine-making experiments of 2018 with grapes from Mendavia at pilot scale (part 1).

	Vitisin B		Vitisin A		Mv-3-*O*-glc		Mv-3-*O*-glc-vinylphenol	
Tank	k_f	k_d	k_f	k_d	k_e	k_d	k_f	k_d
1	0.7 ± 0.2	0.3 ± 0.1	0.45 ± 0.05	0.12 ± 0.05	3 ± 1	0.0191 ± 0.0001	0.7 ± 0.2	-0.10 ± 0.02
2	0.72 ± 0.08	0.2 ± 0.1	0.42 ± 0.05	- [c]	1.3 ± 0.7	0.052 ± 0.002	0.4 ± 0.2	-0.09 ± 0.02
3	1.5 ± 0.7	0.206 ± 0.004	0.9 ± 0.2	- [c]	0.8 ± 0.5	0.02 ± 0.01	0.40 ± 0.06	-0.08 ± 0.01
4	0.8 ± 0.1	0.12 ± 0.02	0.59 ± 0.03	0.02 ± 0.01	0.8 ± 0.1	0.047 ± 0.009	- [c]	-0.18 ± 0.01
5	0.8 ± 0.3	0.27 ± 0.06	0.37 ± 0.03	0.023 ± 0.003	0.67 ± 0.07	0.015 ± 0.005	0.6 ± 0.3	-0.15 ± 0.03
6	1.0 ± 0.4	0.22 ± 0.02	0.28 ± 0.03	0.022 ± 0.008	1.3 ± 0.8	0.039 ± 0.007	- [c]	-0.31 ± 0.01
7	0.7 ± 0.2	0.035 ± 0.005	0.8 ± 0.1	-0.012 ± 0.004	0.9 ± 0.5	0.05 ± 0.02	0.18 ± 0.02	-0.08 ± 0.04
8	0.43 ± 0.03	0.18 ± 0.03	0.41 ± 0.05	-0.03 ± 0.02	0.204 ± 0.008	0.025 ± 0.003	0.18 ± 0.01	-0.08 ± 0.04
9	1.0 ± 0.2	0.008 ± 0.002	0.9 ± 0.3	0.10 ± 0.03	0.5 ± 0.1	0.03 ± 0.01	- [c]	-0.18 ± 0.02
10	0.9 ± 0.2	- [c]	1.0 ± 0.4	0.03 ± 0.01	0.7 ± 0.2	- [c]	- [c]	-0.18 ± 0.03
11	1.7 ± 0.5	- [c]	0.52 ± 0.03	-0.028 ± 0.004	0.375 ± 0.007	0.018 ± 0.003	0.3 ± 0.2	-0.20 ± 0.04
12	0.8 ± 0.2	0.18 ± 0.01	0.54 ± 0.08	- [c]	1.02 ± 0.07	0.007 ± 0.002	0.4 ± 0.2	-0.18 ± 0.01
13	0.9 ± 0.3	0.03 ± 0.01	1.5 ± 0.3	0.03 ± 0.01	0.7 ± 0.2	0.008 ± 0.002	0.3 ± 0.1	- [c]
14	1.4 ± 0.8	0.0275 ± 0.0005	0.70 ± 0.08	0.016 ± 0.006	0.32 ± 0.02	0.007 ± 0.005	0.3 ± 0.1	-0.13 ± 0.05
15	0.7 ± 0.1	0.16 ± 0.06	0.49 ± 0.01	- [c]	0.7 ± 0.1	0.016 ± 0.002	1.7 ± 0.7	-0.17 ± 0.02
16	0.56 ± 0.05	- [c]	1.3 ± 0.5	-0.007 ± 0.003	0.42 ± 0.08	0.0181 ± 0.0005	1.1 ± 0.4	-0.09 ± 0.05
17	0.37 ± 0.07	0.035 ± 0.003	0.7 ± 0.1	0.02 ± 0.01	1.2 ± 0.2	0.021 ± 0.005	0.8 ± 0.3	-0.128 ± 0.008
18	0.32 ± 0.05	- [c]	1.0 ± 0.3	-0.008 ± 0.004	0.52 ± 0.07	0.033 ± 0.003	1.1 ± 0.3	-0.28 ± 0.06
19	0.32 ± 0.01	- [c]	0.55 ± 0.02	- [c]	0.6 ± 0.1	0.015 ± 0.005	0.4 ± 0.1	-0.19 ± 0.05
20	0.9 ± 0.2	- [c]	1.2 ± 0.5	-0.036 ± 0.006	0.277 ± 0.009	0.005 ± 0.004	0.4 ± 0.2	-0.300 ± 0.004
21	0.60 ± 0.08	0.04 ± 0.03	0.54 ± 0.06	- [c]	0.29 ± 0.03	0.027 ± 0.005	0.7 ± 0.4	-0.08 ± 0.04
22	0.34 ± 0.03	- [c]	0.57 ± 0.06	- [c]	0.664 ± 0.004	0.023 ± 0.002	0.810 ± 0.005	-0.09 ± 0.03
23	0.43 ± 0.05	0.04 ± 0.03	1.5 ± 0.4	-0.057 ± 0.003	0.7 ± 0.3	0.0171 ± 0.0009	0.68 ± 0.06	-0.10 ± 0.03
24	0.9 ± 0.3	0.06 ± 0.01	0.51 ± 0.04	0.037 ± 0.001	0.20 ± 0.06	0.009 ± 0.002	0.7 ± 0.4	-0.18 ± 0.08

[a] Constants are expressed in days^{-1}.
[b] See in Figure 3.2 the grape cultivars used in each tank.
[c] Not enough data available for the calculation of the constant.

Table S13. Results of k_e, k_f and k_d (mean ± SD) calculated by the residuals method with the concentration profiles of the selected anthocyanins and anthocyanin derivatives from the wine-making experiments of 2018 with grapes from Mendavia at pilot scale (part 2).

	cat-Mv-3-*O*-glc		**epicat-Mv-3-*O*-glc**		**Mv-3-*O*-glc-8-ethyl-cat 1**		**Mv-3-*O*-glc-(epi)cat**	
Tank	k_f	k_d	k_f	k_d	k_f	k_d	k_f	k_d
1	- [c]	-0.19 ± 0.02	1.5 ± 1.1	0.055 ± 0.007	1.0 ± 0.5	0.06 ± 0.05	0.28 ± 0.03	- [1]
2	0.5 ± 0.1	- [c]	0.9 ± 0.4	0.05 ± 0.01	- [c]	0.04 ± 0.02	1.0 ± 0.1	0.04 ± 0.02
3	- [c]	-0.070 ± 0.006	1.1 ± 0.8	- [c]	0.61 ± 0.01	0.044 ± 0.008	1.1 ± 0.2	0.05 ± 0.04
4	- [c]	-0.04 ± 0.01	0.18 ± 0.06	0.008 ± 0.007	0.64 ± 0.06	- [c]	1.2 ± 0.2	0.06 ± 0.01
5	- [c]	-0.06 ± 0.01	0.69 ± 0.09	- [c]	0.7 ± 0.4	- [c]	0.4 ± 0.2	-0.009 ± 0.004
6	1.195 ± 0.003	- [c]	1.6 ± 0.3	0.06 ± 0.04	1.3 ± 0.8	0.07 ± 0.02	0.7 ± 0.2	0.05 ± 0.03
7	0.3 ± 0.1	- [c]	0.890 ± 0.002	- [c]	1.6 ± 1.0	-0.08 ± 0.03	0.8 ± 0.2	- [c]
8	0.3 ± 0.2	- [c]	0.5 ± 0.2	- [c]	1.3 ± 0.2	-0.083 ± 0.007	0.85 ± 0.07	0.10 ± 0.05
9	- [c]	-0.08 ± 0.02	0.5 ± 0.1	0.04 ± 0.03	0.37 ± 0.05	0.023 ± 0.002	- [c]	0.10 ± 0.01
10	0.9 ± 0.6	- [c]	0.4 ± 0.1	0.146 ± 0.004	0.48 ± 0.05	0.18 ± 0.02	1.2 ± 0.6	0.13 ± 0.01
11	1.2 ± 0.7	-0.08 ± 0.01	0.5 ± 0.2	0.07 ± 0.05	0.42 ± 0.03	- [c]	- [c]	0.047 ± 0.008
12	1.0 ± 0.5	-0.06 ± 0.02	- [c]	0.010 ± 0.006	- [c]	- [c]	- [c]	0.100 ± 0.007
13	0.8 ± 0.7	-0.10 ± 0.01	0.5 ± 0.2	-0.033 ± 0.002	0.6 ± 0.3	-0.10 ± 0.04	0.11 ± 0.07	- [c]
14	0.5 ± 0.2	-0.049 ± 0.002	0.53 ± 0.07	-0.02 ± 0.01	- [c]	-0.15 ± 0.02	- [c]	0.054 ± 0.006
15	0.5 ± 0.2	-0.075 ± 0.008	0.21 ± 0.08	- [c]	0.28 ± 0.02	-0.07 ± 0.02	- [c]	0.070 ± 0.003
16	0.2856 ± 0.0001	- [c]	0.4 ± 0.2	- [c]	0.32 ± 0.01	0.04 ± 0.03	0.297 ± 0.004	0.04 ± 0.02
17	1.2 ± 0.8	-0.043 ± 0.003	0.4 ± 0.2	- [c]	0.4002 ± 0.0005	- [c]	0.4 ± 0.1	- [c]
18	0.5 ± 0.2	- [c]	0.5 ± 0.2	- [c]	0.414 ± 0.003	- [c]	0.460 ± 0.002	0.23 ± 0.09
19	0.194 ± 0.008	- [c]	0.8 ± 0.2	0.12 ± 0.05	0.33 ± 0.02	0.16 ± 0.04	0.40 ± 0.02	0.15 ± 0.08
20	0.27 ± 0.03	0.12 ± 0.03	0.29 ± 0.02	0.14 ± 0.03	0.29 ± 0.07	- [c]	0.366 ± 0.006	- [c]
21	0.8 ± 0.6	-0.04 ± 0.02	0.5 ± 0.2	- [c]	0.36 ± 0.08	-0.0314 ± 0.0008	0.5 ± 0.4	0.009 ± 0.002
22	0.32 ± 0.03	0.09 ± 0.03	0.37 ± 0.06	0.136 ± 0.001	0.4 ± 0.1	0.18 ± 0.07	0.29 ± 0.03	- [c]
23	0.4 ± 0.1	-0.07 ± 0.02	0.30 ± 0.04	0.12 ± 0.01	0.39 ± 0.01	0.20 ± 0.02	0.407 ± 0.004	- [c]
24	0.28 ± 0.03	0.041 ± 0.001	0.39 ± 0.09	0.094 ± 0.004	0.38 ± 0.02	0.12 ± 0.05	0.403 ± 0.008	0.19 ± 0.03

[a] Constants are expressed in $days^{-1}$.
[b] See in Figure 3.2 the grape cultivars used in each tank.
[c] Not enough data available for the calculation of the constant.

Appendix

Table S1. Anthocyanin concentrations determined by HPLC-DAD in red wine samples from Mendavia 2018, expressed in mg of Mv-3- *O*-glc equiv./L.

Tank 01

#	Time (days)	0	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
1	Dp-3-*O*-glc	28.64	22.94	18.13	15.71	14.37	16.55	14.71	12.31	11.87	12.63	12.64	12.60	10.81	10.22	10.31	10.54
2	Cy-3-*O*-glc	7.81	3.96	1.82	2.87	2.61	2.53	2.61	2.45	2.12	2.30	2.33	2.27	1.99	2.51	1.86	2.22
3	Pt-3-*O*-glc	30.24	24.31	34.83	30.31	28.41	30.78	29.39	25.51	24.88	25.74	24.81	24.87	21.65	20.46	19.99	20.20
4	Pn-3-*O*-glc	20.07	12.96	6.40	8.51	8.62	9.12	8.38	7.28	6.33	6.49	7.44	6.81	5.79	7.58	4.84	5.84
5	Mv-3-*O*-glc	143.94	125.34	185.52	170.90	169.78	175.27	171.86	158.80	155.15	157.45	155.14	151.88	142.04	134.13	129.53	126.35
6	Dp-3-*O*-(6-ac)-glc	1.78	2.04	4.21	3.70	3.78	3.81	3.92	3.58	3.41	3.34	3.25	3.27	1.70	2.73	1.67	2.85
7	Pt-3-*O*-(6-ac)-glc	2.57	2.45	4.72	4.19	5.41	5.13	4.37	4.70	4.68	4.84	4.78	4.87	3.88	4.33	3.76	2.21
8	Pn-3-*O*-(6-ac)-glc	2.13	2.00	4.28	3.95	2.67	3.85	4.10	3.70	3.65	3.75	3.61	3.76	3.22	3.68	3.20	2.65
9	Mv-3-*O*-(6-ac)-glc	12.14	11.01	23.51	21.80	19.97	20.34	20.05	17.59	17.24	16.84	16.70	16.41	14.62	13.81	13.46	13.88
10	Mv-3-*O*-(6-caff)-glc	2.49	2.20	5.90	5.54	6.20	6.99	6.64	7.27	6.00	6.49	6.69	7.99	5.85	7.37	6.72	5.97
11	Pt-3-*O*-(6-*p*-coum)-glc	2.42	1.95	8.28	7.67	6.09	7.36	6.21	4.95	4.87	5.55	5.45	5.42	4.67	4.52	4.14	4.51
12	Pn-3-*O*-(6-*p*-coum)-glc	19.19	11.84	51.31	44.44	42.83	47.06	42.36	33.95	30.92	32.91	32.48	31.48	28.92	29.80	24.34	24.39
13	Mv-3-*O*-(6-*p*-coum)-glc	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Tank 02

#	Time (days)	0	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
1	Dp-3-*O*-glc	28.64	19.03	12.60	17.30	15.43	14.60	14.57	11.75	12.63	12.21	12.86	12.55	10.65	8.60	10.04	10.41
2	Cy-3-*O*-glc	7.81	3.01	2.55	2.93	2.76	2.42	2.64	2.44	2.23	2.24	2.30	2.29	1.93	1.96	1.78	2.14
3	Pt-3-*O*-glc	30.24	20.60	25.17	33.25	30.09	27.61	29.07	24.41	25.63	24.48	24.71	24.16	20.94	18.35	18.54	18.70
4	Pn-3-*O*-glc	20.07	10.10	6.74	9.10	8.75	8.76	8.37	7.23	6.51	7.32	7.36	6.60	5.70	5.97	4.71	5.81
5	Mv-3-*O*-glc	143.94	107.90	155.64	183.26	174.66	165.16	171.05	155.40	157.56	153.42	154.48	148.65	137.90	125.20	122.47	119.40
6	Dp-3-*O*-(6-ac)-glc	1.78	1.94	3.47	4.18	3.89	3.53	3.90	3.48	3.69	3.28	3.24	3.22	1.72	1.54	1.61	2.89
7	Pt-3-*O*-(6-ac)-glc	2.57	2.21	3.82	5.81	5.44	4.69	4.30	4.56	4.91	4.75	3.23	4.91	4.01	3.74	3.76	4.31
8	Pn-3-*O*-(6-ac)-glc	2.13	1.81	3.82	3.16	4.02	3.69	4.04	3.58	3.80	3.74	3.45	3.87	3.40	3.42	2.47	2.72
9	Mv-3-*O*-(6-ac)-glc	12.14	10.26	17.15	21.94	21.20	20.04	20.12	17.14	18.10	16.88	17.34	16.60	14.78	13.14	13.32	13.48
10	Mv-3-*O*-(6-caff)-glc	2.49	2.03	4.28	6.08	6.03	6.21	7.82	5.59	7.71	7.75	5.31	8.09	6.00	6.85	6.80	5.94
11	Pt-3-*O*-(6-*p*-coum)-glc	2.42	1.95	4.72	8.43	6.82	6.34	6.27	4.69	5.29	5.50	5.73	5.48	4.74	4.19	4.12	4.27
12	Pn-3-*O*-(6-*p*-coum)-glc	19.19	12.11	36.04	50.37	44.85	43.15	42.79	33.68	32.79	32.60	33.30	31.55	30.37	27.81	24.06	23.38
13	Mv-3-*O*-(6-*p*-coum)-glc	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Tank 03

#	Time (days)	0	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
1	Dp-3-*O*-glc	32.74	18.32	15.70	15.93	13.25	13.84	13.79	12.56	10.91	11.82	11.11	11.54	9.85	9.08	9.34	9.76
2	Cy-3-*O*-glc	8.28	3.18	2.53	2.71	2.51	2.30	2.43	2.34	2.02	2.02	1.99	2.14	1.89	2.32	1.67	1.96
3	Pt-3-*O*-glc	32.84	19.99	31.32	31.24	26.73	26.86	28.13	26.17	23.32	23.88	22.31	22.91	19.70	18.59	17.91	18.00
4	Pn-3-*O*-glc	20.88	10.36	5.37	8.65	8.15	8.49	8.04	7.11	6.11	6.82	6.62	6.54	5.92	7.59	4.96	5.44
5	Mv-3-*O*-glc	146.20	104.02	170.60	173.20	159.18	160.76	164.19	158.21	146.80	147.95	142.98	142.13	132.32	125.35	118.37	115.56
6	Dp-3-*O*-(6-ac)-glc	2.00	1.95	3.81	3.93	3.54	3.39	3.70	3.53	3.41	3.04	2.88	3.08	1.63	2.56	1.54	1.95
7	Pt-3-*O*-(6-ac)-glc	2.64	2.11	4.32	5.47	4.64	4.56	4.10	4.71	4.54	4.47	4.36	4.60	3.65	4.08	3.46	3.94
8	Pn-3-*O*-(6-ac)-glc	2.11	1.70	3.94	4.02	3.69	3.51	3.85	3.57	3.54	3.47	3.27	3.62	3.12	3.53	3.01	2.42
9	Mv-3-*O*-(6-ac)-glc	12.50	9.62	21.03	21.97	18.60	17.45	19.11	17.81	15.10	15.89	15.40	15.62	13.68	12.98	12.45	12.72
10	Mv-3-*O*-(6-caff)-glc	2.54	1.82	3.98	4.86	5.71	6.09	4.73	7.35	5.84	6.14	6.00	7.81	6.81	5.86	6.38	6.64
11	Pt-3-*O*-(6-*p*-coum)-glc	2.64	1.70	7.06	7.75	5.73	5.65	5.97	5.30	4.63	5.17	4.94	5.22	4.39	4.28	3.86	4.03
12	Pn-3-*O*-(6-*p*-coum)-glc	20.29	10.33	46.58	48.79	39.81	38.69	40.73	35.94	30.51	30.56	29.36	30.08	29.16	27.83	22.73	21.95
13	Mv-3-*O*-(6-*p*-coum)-glc	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Tank 04

#	Time (days)	0	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
1	Dp-3-*O*-glc	19.87	19.11	15.18	17.22	16.84	17.02	14.83	12.11	15.00	15.32	15.48	14.89	13.17	12.59	11.83	12.38
2	Cy-3-*O*-glc	6.86	3.33	2.93	3.20	3.01	2.97	2.83	2.28	2.78	2.66	2.79	2.80	2.37	2.87	2.08	2.46
3	Pt-3-*O*-glc	24.14	20.80	28.18	32.05	31.80	30.89	28.68	22.15	28.60	28.16	27.80	27.28	24.24	23.81	21.32	21.55
4	Pn-3-*O*-glc	17.39	10.31	5.95	7.36	9.77	10.02	8.87	7.30	7.66	7.95	8.32	7.81	6.65	8.57	5.30	6.52
5	Mv-3-*O*-glc	123.18	107.48	169.54	179.84	181.83	178.53	168.83	137.99	166.97	160.51	162.13	156.10	146.73	140.52	130.20	126.79
6	Dp-3-*O*-(6-ac)-glc	1.55	2.06	3.74	4.13	4.15	3.76	4.00	3.32	4.03	3.44	3.53	3.54	2.22	3.20	1.82	3.15
7	Pt-3-*O*-(6-ac)-glc	2.27	2.03	4.24	5.94	5.53	5.22	4.39	4.37	5.32	5.15	5.32	5.39	4.47	5.03	4.26	4.87
8	Pn-3-*O*-(6-ac)-glc	1.98	1.77	4.14	4.36	4.32	4.05	4.19	3.39	4.13	3.94	3.97	4.19	3.77	4.28	2.69	2.97
9	Mv-3-*O*-(6-ac)-glc	10.25	9.73	19.16	22.27	21.94	19.88	19.28	15.77	19.29	17.72	18.24	17.69	16.07	15.41	14.43	14.76
10	Mv-3-*O*-(6-caff)-glc	2.51	2.03	3.61	4.80	6.75	6.77	6.53	6.91	8.27	6.88	7.28	7.31	6.60	6.83	7.58	6.60
11	Pt-3-*O*-(6-*p*-coum)-glc	2.08	1.78	5.56	8.40	6.88	6.73	5.68	4.35	5.66	6.08	6.28	6.17	5.54	5.31	4.70	5.01
12	Pn-3-*O*-(6-*p*-coum)-glc	16.07	10.32	41.36	49.33	46.45	45.09	38.74	29.14	34.55	33.16	34.45	33.23	32.56	31.01	25.45	24.75
13	Mv-3-*O*-(6-*p*-coum)-glc	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Tank 05

#	Time (days)	0	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
1	Dp-3-*O*-glc	26.79	13.42	11.97	13.83	14.74	14.61	13.71	14.46	11.27	12.31	11.64	12.07	10.48	9.66	9.72	9.94
2	Cy-3-*O*-glc	7.32	2.30	2.82	2.38	2.41	1.97	2.16	2.96	1.95	2.05	2.06	2.07	1.78	2.22	1.62	1.89
3	Pt-3-*O*-glc	28.53	17.32	22.71	24.55	25.82	24.96	24.74	28.76	21.23	22.06	20.76	21.27	18.70	17.81	16.82	16.63
4	Pn-3-*O*-glc	18.73	8.89	11.49	8.61	8.73	8.80	8.10	8.48	6.35	7.16	7.07	6.51	5.62	6.69	4.67	5.51
5	Mv-3-*O*-glc	134.34	100.55	138.29	146.75	152.84	149.29	148.37	171.01	133.65	135.66	132.32	130.69	122.86	116.41	109.19	105.20
6	Dp-3-*O*-(6-ac)-glc	1.92	1.51	2.79	3.41	3.50	3.18	3.53	4.10	3.22	2.87	2.76	2.79	1.54	2.46	1.48	2.49
7	Pt-3-*O*-(6-ac)-glc	2.49	1.93	3.44	5.05	5.24	4.57	5.19	5.20	4.41	4.42	4.26	4.41	3.63	4.02	3.47	3.84
8	Pn-3-*O*-(6-ac)-glc	2.07	1.75	3.37	3.72	3.66	3.50	3.76	4.05	3.41	3.35	3.22	3.36	2.91	3.32	2.19	2.34
9	Mv-3-*O*-(6-ac)-glc	11.73	9.51	15.69	18.46	18.47	17.05	17.50	19.20	13.98	14.72	14.24	14.38	12.91	13.46	11.67	11.60
10	Mv-3-*O*-(6-caff)-glc	2.57	2.05	4.15	7.02	7.43	7.64	7.58	6.55	7.14	7.43	7.31	6.10	6.72	6.82	6.32	6.48
11	Pt-3-*O*-(6-*p*-coum)-glc	2.48	1.68	4.33	5.97	5.57	5.68	5.18	5.54	4.30	4.78	4.49	4.71	4.07	3.84	3.61	3.68
12	Pn-3-*O*-(6-*p*-coum)-glc	17.73	10.26	32.26	40.47	38.11	37.49	35.25	37.62	26.29	27.50	26.41	26.53	24.11	21.86	19.90	19.05
13	Mv-3-*O*-(6-*p*-coum)-glc	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

continued

Table S1. Anthocyanin concentrations determined by HPLC-DAD in red wine samples from Mendavia 2018, expressed in mg of Mv-3- *O*-glc equiv./L.

Tank 06

#	Time (days)	0	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
1	Dp-3-*O*-glc	26.79	16.71	13.03	15.75	15.06	13.76	12.77	12.97	12.29	12.02	12.45	12.47	10.57	10.25	9.85	9.99
2	Cy-3-*O*-glc	7.32	2.51	2.67	2.51	2.37	2.08	2.16	2.26	2.04	1.94	1.98	2.02	2.14	2.23	1.58	1.86
3	Pt-3-*O*-glc	28.53	19.30	21.06	27.44	26.35	23.72	23.11	23.26	22.27	21.35	21.40	21.28	20.30	18.59	16.16	16.12
4	Pn-3-*O*-glc	18.73	9.22	10.48	8.95	8.65	8.51	7.68	7.42	6.56	6.05	7.04	6.18	7.20	6.63	4.44	5.00
5	Mv-3-*O*-glc	134.34	105.02	125.72	156.54	154.09	143.61	140.53	141.14	135.78	132.60	133.05	129.42	124.66	117.73	105.16	102.27
6	Dp-3-*O*-(6-ac)-glc	1.92	1.01	2.81	3.58	3.51	2.99	3.30	3.35	3.33	2.76	2.76	2.72	2.77	2.57	1.48	2.49
7	Pt-3-*O*-(6-ac)-glc	2.49	2.08	3.27	4.92	4.76	4.32	4.45	4.39	4.47	4.21	4.31	4.39	4.27	4.16	3.48	3.89
8	Pn-3-*O*-(6-ac)-glc	2.07	1.77	3.22	3.82	3.65	3.34	3.44	3.41	3.35	3.22	2.76	3.33	3.52	3.38	2.22	2.39
9	Mv-3-*O*-(6-ac)-glc	11.73	10.39	14.39	19.89	18.79	16.07	16.34	16.18	14.53	14.25	14.56	14.35	13.40	12.67	11.51	11.64
10	Mv-3-*O*-(6-caff)-glc	2.57	2.34	4.99	7.43	7.45	7.12	6.92	7.05	5.91	7.05	7.36	7.43	7.22	7.05	6.32	6.63
11	Pt-3-*O*-(6-*p*-coum)-glc	2.48	2.34	4.20	6.71	5.89	5.27	4.75	4.68	4.64	4.51	4.70	4.68	4.40	4.09	3.59	3.81
12	Pn-3-*O*-(6-*p*-coum)-glc	17.73	16.11	31.40	44.40	40.19	35.51	32.78	30.92	27.88	26.63	27.44	26.48	25.28	22.96	20.03	19.67
13	Mv-3-*O*-(6-*p*-coum)-glc	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Tank 07

#	Time (days)	0	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
1	Dp-3-*O*-glc	32.90	17.61	12.96	16.59	16.77	9.77	12.45	13.36	12.12	12.23	12.53	12.19	11.58	9.68	10.21	10.40
2	Cy-3-*O*-glc	8.24	3.04	2.48	2.51	2.45	1.40	2.10	2.15	1.92	1.92	1.93	1.94	2.16	2.20	1.61	1.90
3	Pt-3-*O*-glc	33.53	21.12	20.55	28.32	28.62	14.79	22.27	23.70	21.97	21.66	21.34	20.81	20.65	18.61	16.89	17.15
4	Pn-3-*O*-glc	20.79	10.71	10.28	9.18	9.12	6.08	7.58	7.52	6.46	7.07	7.17	6.26	7.44	6.99	4.77	5.65
5	Mv-3-*O*-glc	148.12	110.50	120.95	158.27	161.05	98.57	136.29	141.48	133.96	132.34	131.11	126.52	124.58	116.75	106.72	104.71
6	Dp-3-*O*-(6-ac)-glc	2.40	1.95	2.68	3.66	3.64	2.08	3.17	3.34	3.08	2.80	2.78	2.72	2.78	2.54	1.46	2.53
7	Pt-3-*O*-(6-ac)-glc	2.81	2.38	3.17	4.98	4.97	2.93	4.32	4.46	4.31	4.28	4.23	4.31	4.25	4.11	3.40	3.87
8	Pn-3-*O*-(6-ac)-glc	2.28	1.97	3.09	3.79	3.77	2.38	3.38	3.45	3.26	3.26	3.17	3.26	3.40	3.34	2.19	2.34
9	Mv-3-*O*-(6-ac)-glc	13.26	11.01	13.93	20.43	19.87	10.31	15.76	16.39	14.14	14.39	14.42	14.02	13.58	12.63	11.62	11.95
10	Mv-3-*O*-(6-caff)-glc	2.90	2.29	2.84	6.31	6.67	4.68	6.65	5.96	5.66	5.86	7.26	7.25	7.28	7.02	6.20	6.60
11	Pt-3-*O*-(6-*p*-coum)-glc	3.06	2.57	4.15	7.00	6.39	3.22	4.48	4.77	4.41	4.66	4.71	4.63	4.56	4.19	3.64	3.92
12	Pn-3-*O*-(6-*p*-coum)-glc	20.89	17.48	30.36	44.25	42.28	22.45	31.23	30.92	26.53	27.08	27.02	26.09	25.75	23.69	20.36	20.28
13	Mv-3-*O*-(6-*p*-coum)-glc	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Tank 08

#	Time (days)	0	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
1	Dp-3-*O*-glc	18.82	18.61	13.44	16.30	15.22	14.49	11.50	12.77	11.26	12.31	11.97	12.10	11.01	9.01	9.65	9.50
2	Cy-3-*O*-glc	6.08	2.57	2.78	2.50	2.39	2.03	2.07	2.12	2.08	1.92	1.91	1.98	2.08	2.12	1.53	1.76
3	Pt-3-*O*-glc	22.04	22.25	20.62	28.36	27.01	25.25	21.29	22.87	20.96	21.82	20.82	21.15	20.07	17.75	16.17	15.61
4	Pn-3-*O*-glc	15.30	10.41	5.71	9.01	8.75	8.53	7.29	7.13	7.69	6.85	6.83	6.12	6.97	6.41	4.35	5.27
5	Mv-3-*O*-glc	111.69	118.00	128.40	159.50	157.52	149.33	134.34	137.87	138.82	134.48	131.19	129.37	124.03	114.91	105.01	100.54
6	Dp-3-*O*-(6-ac)-glc	1.13	1.86	2.76	3.67	3.53	3.11	3.10	3.38	3.28	2.82	2.71	2.87	2.71	2.52	1.48	2.41
7	Pt-3-*O*-(6-ac)-glc	1.92	2.49	3.34	4.97	4.82	4.49	4.54	3.73	4.29	4.32	4.24	4.51	4.27	4.03	3.46	3.77
8	Pn-3-*O*-(6-ac)-glc	1.57	2.03	3.29	3.81	3.66	3.36	3.25	3.60	3.78	3.26	2.73	3.40	3.46	3.30	2.21	2.32
9	Mv-3-*O*-(6-ac)-glc	9.15	11.86	15.19	20.55	19.27	16.89	15.27	15.84	14.72	14.71	14.34	14.52	13.49	12.32	11.59	11.23
10	Mv-3-*O*-(6-caff)-glc	1.79	2.35	2.98	6.28	7.61	6.13	6.37	5.77	5.33	7.31	7.27	6.13	7.28	6.82	6.37	6.35
11	Pt-3-*O*-(6-*p*-coum)-glc	1.62	2.78	4.39	7.04	6.05	5.69	4.20	4.58	4.16	4.77	4.59	4.81	4.42	3.93	3.69	3.57
12	Pn-3-*O*-(6-*p*-coum)-glc	12.41	19.25	32.61	46.21	41.05	37.67	29.91	29.74	28.41	27.48	26.69	26.77	25.11	22.08	20.29	18.38
13	Mv-3-*O*-(6-*p*-coum)-glc	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Tank 09

#	Time (days)	0	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
1	Dp-3-*O*-glc	32.90	16.89	13.80	15.15	17.54	14.09	14.15	12.99	12.81	12.85	12.41	12.64	11.00	10.31	10.44	10.44
2	Cy-3-*O*-glc	8.24	3.45	2.28	2.42	2.76	2.36	2.46	2.43	2.12	2.22	2.22	2.20	2.31	2.41	2.15	1.96
3	Pt-3-*O*-glc	33.53	20.45	23.39	27.03	30.56	24.63	25.77	24.26	23.05	23.09	21.90	22.38	20.78	19.14	18.58	17.45
4	Pn-3-*O*-glc	20.79	17.36	6.67	10.91	12.19	10.86	10.76	10.06	9.06	9.87	9.68	8.97	9.55	9.07	8.02	7.27
5	Mv-3-*O*-glc	148.12	115.26	143.06	165.35	182.49	158.83	164.32	157.58	149.40	151.05	147.19	144.28	138.39	129.78	122.86	116.26
6	Dp-3-*O*-(6-ac)-glc	2.40	1.49	3.17	3.54	3.79	3.01	3.53	3.55	3.38	3.09	2.91	2.97	2.78	2.56	2.56	2.54
7	Pt-3-*O*-(6-ac)-glc	2.81	2.26	3.54	4.64	5.04	4.22	4.72	3.83	4.47	4.52	4.35	4.52	4.25	4.11	3.94	3.88
8	Pn-3-*O*-(6-ac)-glc	2.28	2.47	4.08	4.52	4.75	4.09	4.50	4.44	4.15	4.24	3.97	4.10	4.12	4.01	3.74	3.01
9	Mv-3-*O*-(6-ac)-glc	13.26	11.38	17.26	21.20	22.46	17.75	19.78	18.44	16.34	17.01	15.53	16.33	15.01	14.05	13.70	13.34
10	Mv-3-*O*-(6-caff)-glc	2.90	2.35	2.90	4.00	4.83	4.17	4.53	5.58	5.51	5.87	4.59	5.72	5.37	3.81	4.95	4.86
11	Pt-3-*O*-(6-*p*-coum)-glc	3.06	2.19	4.67	6.53	6.52	4.95	5.41	4.88	4.74	5.09	4.80	4.92	4.43	4.15	3.93	3.89
12	Pn-3-*O*-(6-*p*-coum)-glc	20.89	16.80	31.01	45.04	45.58	36.61	40.12	35.82	32.61	32.48	31.31	30.87	30.34	27.86	23.74	22.06
13	Mv-3-*O*-(6-*p*-coum)-glc	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Tank 10

#	Time (days)	0	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
1	Dp-3-*O*-glc	32.90	16.14	15.59	15.69	16.68	13.60	13.26	13.10	12.67	12.21	12.41	12.47	11.16	10.23	10.04	10.31
2	Cy-3-*O*-glc	8.24	2.91	2.39	2.47	2.76	2.40	2.42	2.51	2.22	2.22	2.15	2.16	2.36	2.46	1.76	2.08
3	Pt-3-*O*-glc	33.53	19.45	24.84	27.93	29.33	23.91	24.24	24.53	23.63	22.29	22.06	21.76	20.68	19.16	16.98	17.05
4	Pn-3-*O*-glc	20.79	16.47	7.43	11.18	12.22	11.07	10.74	10.36	9.48	9.94	9.90	9.04	9.56	8.84	6.47	7.47
5	Mv-3-*O*-glc	148.12	116.77	156.32	170.61	179.75	157.69	159.34	159.77	154.14	149.08	148.41	144.26	138.88	130.87	119.18	114.95
6	Dp-3-*O*-(6-ac)-glc	2.40	1.69	3.35	3.65	3.75	3.06	3.49	3.63	3.43	3.03	2.96	2.97	2.94	2.84	1.16	2.56
7	Pt-3-*O*-(6-ac)-glc	2.81	2.31	3.84	4.81	4.99	4.33	4.67	3.90	4.65	2.68	4.46	4.58	4.41	4.30	3.51	3.96
8	Pn-3-*O*-(6-ac)-glc	2.28	2.54	4.32	4.64	4.76	4.27	4.50	4.52	4.34	4.22	4.07	4.22	4.41	4.28	3.57	3.10
9	Mv-3-*O*-(6-ac)-glc	13.26	11.75	19.16	21.96	22.26	18.26	19.15	18.66	17.01	16.55	16.74	16.42	16.84	14.48	13.31	13.32
10	Mv-3-*O*-(6-caff)-glc	2.90	2.34	3.21	4.00	4.61	4.35	4.43	5.71	5.88	5.74	5.89	5.90	5.63	5.41	4.84	5.05
11	Pt-3-*O*-(6-*p*-coum)-glc	3.06	2.35	5.59	6.80	6.43	5.34	5.09	4.89	4.94	4.79	4.89	4.80	4.44	4.22	3.69	3.90
12	Pn-3-*O*-(6-*p*-coum)-glc	20.89	18.33	39.16	47.10	45.67	38.32	38.39	35.94	32.88	30.84	31.34	30.28	28.53	26.62	22.83	21.73
13	Mv-3-*O*-(6-*p*-coum)-glc	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

continued

Table S1. Anthocyanin concentrations determined by HPLC-DAD in red wine samples from Mendavia 2018, expressed in mg of Mv-3- *O*-glc equiv./L.

Tank 11

#	Time (days)	0	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
1	Dp-3-*O*-glc	10.31	18.53	13.03	14.96	14.71	13.88	12.91	11.98	11.33	11.69	11.50	11.37	10.26	8.58	9.19	9.97
2	Cy-3-*O*-glc	4.90	3.44	2.14	2.12	2.49	2.30	2.31	2.27	2.05	2.06	2.03	1.98	2.21	2.26	2.05	1.92
3	Pt-3-*O*-glc	13.63	21.71	21.37	27.12	26.68	24.98	24.17	22.91	21.71	21.65	20.86	20.68	19.51	17.85	17.82	16.62
4	Pn-3-*O*-glc	19.01	18.32	8.17	10.93	11.36	10.81	10.33	9.75	9.02	9.44	9.33	8.63	9.47	8.86	7.91	7.14
5	Mv-3-*O*-glc	95.75	120.11	143.46	166.76	168.30	160.29	157.08	151.33	145.57	144.76	141.44	138.48	132.80	124.62	120.12	112.10
6	Dp-3-*O*-(6-ac)-glc	0.42	1.80	2.57	3.51	3.51	3.11	3.46	3.41	2.94	2.92	2.82	2.71	2.82	2.53	2.70	2.49
7	Pt-3-*O*-(6-ac)-glc	1.51	2.32	3.26	4.68	4.68	4.41	4.52	3.71	4.38	4.32	4.25	4.24	4.17	3.98	3.96	3.75
8	Pn-3-*O*-(6-ac)-glc	1.94	2.53	3.90	4.57	4.57	4.29	4.44	4.39	4.17	4.16	3.98	3.92	4.18	3.98	3.83	2.94
9	Mv-3-*O*-(6-ac)-glc	8.49	11.96	16.84	21.15	20.59	18.47	18.75	17.62	15.87	16.09	15.73	15.35	14.22	13.38	13.41	12.82
10	Mv-3-*O*-(6-caff)-glc	1.72	2.43	3.85	4.51	4.82	4.82	5.88	5.76	5.70	5.86	5.79	5.62	5.48	5.15	5.18	4.87
11	Pt-3-*O*-(6-*p*-coum)-glc	1.26	2.33	4.35	6.32	5.70	5.46	4.98	4.54	4.44	4.68	4.50	4.40	4.12	3.85	3.83	3.72
12	Pn-3-*O*-(6-*p*-coum)-glc	11.37	18.20	33.39	43.87	40.54	37.89	36.95	33.29	29.48	30.05	28.93	27.42	28.06	25.99	22.84	20.46
13	Mv-3-*O*-(6-*p*-coum)-glc	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Tank 12

#	Time (days)	0	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
1	Dp-3-*O*-glc	10.86	14.19	14.99	15.96	15.80	16.90	14.80	14.65	12.65	13.05	13.13	12.59	12.24	10.64	10.82	12.31
2	Cy-3-*O*-glc	5.16	2.94	2.46	2.40	2.73	2.64	2.63	2.64	2.26	2.31	2.27	2.20	2.43	2.49	2.22	2.02
3	Pt-3-*O*-glc	14.89	17.24	26.91	28.17	27.64	28.80	26.71	26.54	23.06	23.21	22.45	21.89	21.85	19.64	18.33	17.23
4	Pn-3-*O*-glc	20.70	15.87	8.15	11.65	11.99	12.34	11.37	10.87	9.76	10.33	10.23	9.36	10.02	8.93	8.18	7.59
5	Mv-3-*O*-glc	101.48	105.18	163.44	169.88	172.54	176.77	168.38	166.15	150.85	150.72	148.11	142.40	141.12	130.90	121.24	111.44
6	Dp-3-*O*-(6-ac)-glc	1.10	1.81	3.46	3.67	3.62	3.39	3.67	3.73	3.06	3.06	2.98	2.97	3.02	2.68	2.62	2.65
7	Pt-3-*O*-(6-ac)-glc	1.77	2.18	3.99	4.82	4.84	4.84	4.11	4.11	4.59	4.57	4.48	4.61	4.49	4.20	4.05	4.06
8	Pn-3-*O*-(6-ac)-glc	2.21	2.43	4.61	4.69	4.70	4.56	4.82	4.69	4.31	4.29	4.18	4.23	4.44	4.09	3.91	3.85
9	Mv-3-*O*-(6-ac)-glc	9.03	10.65	19.54	22.09	21.46	20.49	20.39	19.81	16.60	16.93	16.73	16.36	15.63	14.33	13.67	13.13
10	Mv-3-*O*-(6-caff)-glc	1.98	2.29	3.64	4.38	4.66	5.15	6.15	6.17	5.73	5.92	5.93	5.85	5.77	3.92	5.14	5.10
11	Pt-3-*O*-(6-*p*-coum)-glc	1.49	2.01	5.98	6.83	6.06	6.24	5.58	5.46	4.71	5.03	4.88	4.89	4.64	3.98	3.88	4.05
12	Pn-3-*O*-(6-*p*-coum)-glc	12.96	15.18	39.83	47.01	43.16	43.76	41.36	38.24	32.56	32.09	31.16	29.97	29.11	24.94	22.98	21.58
13	Mv-3-*O*-(6-*p*-coum)-glc	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Tank 13

#	Time (days)	0	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
1	Dp-3-*O*-glc	10.86	14.05	15.75	15.81	14.68	13.26	15.16	13.48	11.91	11.82	11.09	12.18	10.96	10.23	9.51	9.05
2	Cy-3-*O*-glc	5.16	2.66	1.24	2.40	2.34	1.98	2.31	2.21	1.92	1.92	1.91	2.01	2.12	2.17	1.91	2.67
3	Pt-3-*O*-glc	14.89	17.22	24.56	23.86	24.02	21.73	23.13	22.91	20.53	19.81	18.39	20.02	18.52	17.41	16.16	15.21
4	Pn-3-*O*-glc	20.70	14.87	11.95	10.95	11.34	10.59	10.77	10.31	9.11	9.68	9.42	9.35	9.47	8.69	7.97	6.99
5	Mv-3-*O*-glc	101.48	105.43	147.87	146.70	150.64	141.64	147.05	144.27	133.86	131.20	127.09	128.69	122.21	116.44	106.77	99.40
6	Dp-3-*O*-(6-ac)-glc	1.10	1.51	3.05	3.25	3.27	2.78	3.40	3.38	2.81	2.73	2.60	2.83	2.71	2.46	2.45	3.62
7	Pt-3-*O*-(6-ac)-glc	1.77	2.02	3.67	4.30	4.46	4.03	3.72	3.70	4.27	4.17	4.05	4.35	4.13	3.97	3.80	2.58
8	Pn-3-*O*-(6-ac)-glc	2.21	2.17	4.24	4.14	4.23	3.82	4.31	4.18	3.85	3.84	3.25	4.06	3.98	3.73	3.60	2.60
9	Mv-3-*O*-(6-ac)-glc	9.03	10.15	18.40	18.81	18.98	16.16	17.98	17.50	15.06	14.81	14.27	14.71	13.79	13.08	12.40	10.87
10	Mv-3-*O*-(6-caff)-glc	1.98	1.92	4.41	4.11	5.73	5.13	5.78	5.77	5.57	5.54	5.36	5.62	5.43	5.09	4.99	3.91
11	Pt-3-*O*-(6-*p*-coum)-glc	1.49	1.63	5.16	5.62	5.31	4.55	4.85	4.82	4.45	4.31	3.97	4.39	4.09	3.79	3.66	3.49
12	Pn-3-*O*-(6-*p*-coum)-glc	12.96	10.58	36.52	38.54	38.86	32.02	35.14	32.99	28.22	27.04	25.36	26.08	25.12	22.66	20.94	16.98
13	Mv-3-*O*-(6-*p*-coum)-glc	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Tank 14

#	Time (days)	0	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
1	Dp-3-*O*-glc	11.82	17.64	13.52	15.20	14.03	13.31	14.18	12.96	13.07	11.89	12.01	12.29	10.79	10.15	10.34	9.10
2	Cy-3-*O*-glc	5.08	3.54	3.03	2.36	2.36	2.06	2.28	2.17	1.90	1.93	1.94	2.00	2.07	2.17	2.01	2.60
3	Pt-3-*O*-glc	15.15	20.18	21.55	23.06	23.24	21.69	23.87	22.48	19.86	20.13	19.78	20.54	18.52	17.08	16.48	15.52
4	Pn-3-*O*-glc	20.03	16.87	7.50	10.51	11.02	10.52	10.54	10.03	9.02	9.67	9.57	9.22	9.03	8.38	7.97	6.31
5	Mv-3-*O*-glc	99.72	115.44	130.25	143.25	147.64	139.69	148.56	142.67	130.06	132.59	131.59	129.61	122.25	115.68	107.84	101.08
6	Dp-3-*O*-(6-ac)-glc	1.02	1.80	2.81	3.27	3.25	2.85	3.46	3.36	2.74	2.79	2.72	2.85	2.56	2.44	2.60	3.72
7	Pt-3-*O*-(6-ac)-glc	1.70	2.26	3.30	4.37	4.39	4.18	3.80	3.71	4.16	4.22	4.21	4.35	4.02	3.90	3.91	2.64
8	Pn-3-*O*-(6-ac)-glc	2.02	2.34	3.81	4.11	4.12	3.88	4.29	4.13	3.76	3.79	3.27	3.96	3.79	3.68	3.70	2.62
9	Mv-3-*O*-(6-ac)-glc	8.89	10.87	16.13	18.97	18.68	16.71	18.47	17.32	14.66	14.89	14.98	14.82	13.53	12.97	12.67	11.10
10	Mv-3-*O*-(6-caff)-glc	1.74	2.20	2.84	4.12	5.59	5.57	5.93	5.74	5.41	5.59	5.69	5.73	5.22	5.01	5.18	4.03
11	Pt-3-*O*-(6-*p*-coum)-glc	1.41	2.00	4.45	5.91	5.29	5.13	5.26	4.80	4.27	4.39	4.42	4.57	3.95	3.71	3.89	3.69
12	Pn-3-*O*-(6-*p*-coum)-glc	12.43	12.54	31.17	40.19	38.36	36.00	36.82	32.81	27.18	27.08	27.48	27.19	23.92	21.26	21.65	17.85
13	Mv-3-*O*-(6-*p*-coum)-glc	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Tank 15

#	Time (days)	0	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
1	Dp-3-*O*-glc	13.33	12.26	15.09	15.29	14.04	14.02	12.97	11.79	11.17	11.51	10.78	12.09	10.66	9.90	9.19	8.59
2	Cy-3-*O*-glc	5.36	2.81	2.59	2.22	2.19	2.14	2.15	2.04	1.83	1.78	1.79	1.82	2.01	2.01	1.78	2.49
3	Pt-3-*O*-glc	16.29	15.19	23.85	23.37	23.28	23.03	22.47	20.75	19.37	19.21	17.92	18.14	18.19	16.55	15.68	14.01
4	Pn-3-*O*-glc	20.79	15.16	7.79	10.22	10.28	10.55	10.20	9.32	8.69	8.94	8.72	8.37	8.93	8.05	7.38	6.26
5	Mv-3-*O*-glc	101.95	102.35	142.60	143.27	144.35	144.09	141.49	134.05	128.27	127.26	122.63	119.13	119.09	111.81	103.84	90.13
6	Dp-3-*O*-(6-ac)-glc	1.22	1.39	3.04	3.20	3.14	2.85	3.23	3.13	2.68	2.53	2.42	2.49	2.63	2.28	2.31	3.36
7	Pt-3-*O*-(6-ac)-glc	1.76	2.08	3.55	4.18	4.23	4.13	3.56	3.40	3.99	3.89	3.79	3.88	3.96	3.72	3.58	2.33
8	Pn-3-*O*-(6-ac)-glc	2.10	2.34	4.03	3.96	3.92	3.77	4.07	3.88	3.68	3.53	3.05	3.57	3.73	3.45	3.37	2.35
9	Mv-3-*O*-(6-ac)-glc	8.78	10.27	17.90	18.26	18.16	16.80	17.19	14.80	14.26	14.20	13.77	13.47	13.34	12.51	11.85	10.09
10	Mv-3-*O*-(6-caff)-glc	1.64	2.17	4.35	4.10	5.52	4.72	5.55	5.30	5.28	5.23	5.11	5.10	5.24	4.84	4.74	3.57
11	Pt-3-*O*-(6-*p*-coum)-glc	1.31	1.91	5.25	5.53	5.27	5.13	4.75	4.29	4.10	4.08	3.85	3.97	4.00	3.61	3.53	3.20
12	Pn-3-*O*-(6-*p*-coum)-glc	9.86	15.03	36.81	37.61	36.14	34.68	34.05	29.92	26.55	25.43	24.07	24.24	24.36	22.07	20.15	15.35
13	Mv-3-*O*-(6-*p*-coum)-glc	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

continued

Table S1. Anthocyanin concentrations determined by HPLC-DAD in red wine samples from Mendavia 2018, expressed in mg of Mv-3- *O*-glc equiv./L.

Tank 16

#	Time (days)	0	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
1	Dp-3-*O*-glc	11.43	12.31	14.79	16.10	15.88	14.97	14.75	13.17	12.37	12.10	12.79	12.73	11.80	11.00	9.07	9.36
2	Cy-3-*O*-glc	5.71	3.61	2.31	2.37	2.47	2.18	2.33	2.23	2.04	1.97	2.04	2.09	2.19	2.16	1.89	2.63
3	Pt-3-*O*-glc	15.74	15.40	23.44	23.87	25.77	24.23	24.59	22.62	20.97	19.66	20.56	20.97	19.55	18.00	15.19	15.64
4	Pn-3-*O*-glc	26.80	16.47	7.99	10.68	11.96	11.27	11.27	10.23	9.49	9.85	10.04	9.58	9.63	8.58	7.75	7.19
5	Mv-3-*O*-glc	108.75	103.58	139.53	148.74	158.52	150.76	153.22	144.82	136.56	131.43	135.66	132.96	127.36	119.72	103.91	101.75
6	Dp-3-*O*-(6-ac)-glc	1.20	1.64	2.92	3.33	3.33	2.95	3.49	3.31	2.84	2.74	2.78	2.86	2.77	2.48	2.36	3.71
7	Pt-3-*O*-(6-ac)-glc	1.92	2.00	3.48	4.40	4.51	4.32	3.83	3.66	4.22	4.13	4.27	4.39	4.19	3.96	3.63	2.66
8	Pn-3-*O*-(6-ac)-glc	2.65	2.38	4.05	4.25	4.29	4.00	4.47	4.17	3.87	3.82	3.41	4.08	4.03	3.75	2.82	2.72
9	Mv-3-*O*-(6-ac)-glc	9.69	10.36	17.60	19.34	20.12	17.74	19.14	17.73	15.66	15.15	15.97	15.67	14.72	13.84	12.13	11.46
10	Mv-3-*O*-(6-caff)-glc	1.93	2.12	4.01	3.67	4.35	4.77	5.55	5.31	5.39	5.17	5.50	5.57	5.27	4.90	4.53	3.87
11	Pt-3-*O*-(6-*p*-coum)-glc	1.34	1.78	4.88	5.75	5.77	5.41	5.34	4.82	4.54	4.36	4.70	4.76	4.34	3.95	3.46	3.79
12	Pn-3-*O*-(6-*p*-coum)-glc	10.75	13.18	34.69	40.38	40.71	37.21	38.95	34.43	29.67	27.72	29.91	29.22	27.02	24.31	20.37	18.87
13	Mv-3-*O*-(6-*p*-coum)-glc	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Tank 17

#	Time (days)	0	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
1	Dp-3-*O*-glc	8.25	10.70	15.27	15.86	14.58	13.51	14.81	13.39	12.14	11.44	11.65	12.21	10.85	9.53	10.16	8.72
2	Cy-3-*O*-glc	4.65	2.34	2.69	2.29	2.18	1.61	2.06	2.01	1.67	1.68	1.74	1.83	1.87	1.63	1.78	2.50
3	Pt-3-*O*-glc	12.55	14.11	27.44	26.44	24.85	22.90	23.39	23.97	21.49	20.19	20.32	21.52	19.54	16.85	17.07	16.00
4	Pn-3-*O*-glc	13.01	8.70	6.72	8.25	8.43	8.01	7.51	7.00	6.61	6.63	6.62	6.65	6.81	5.58	5.83	3.74
5	Mv-3-*O*-glc	95.89	90.18	156.96	155.23	154.23	144.43	146.09	148.07	137.89	134.22	134.38	135.37	127.13	116.30	112.24	104.16
6	Dp-3-*O*-(6-ac)-glc	0.33	1.40	3.28	3.29	3.14	2.69	3.21	3.19	2.70	2.51	2.50	2.75	2.50	1.31	2.30	3.54
7	Pt-3-*O*-(6-ac)-glc	1.47	1.68	3.72	3.66	4.19	3.90	3.47	3.58	4.01	3.81	3.84	4.12	3.80	3.13	3.48	2.49
8	Pn-3-*O*-(6-ac)-glc	1.55	1.58	3.59	3.32	3.25	3.04	3.42	3.27	3.08	2.92	2.45	3.20	3.03	2.64	2.24	1.96
9	Mv-3-*O*-(6-ac)-glc	7.77	8.11	17.97	19.00	16.52	15.41	16.20	15.28	14.25	13.60	13.79	14.23	12.87	11.41	11.60	10.30
10	Mv-3-*O*-(6-caff)-glc	1.65	1.62	3.36	4.82	4.82	4.86	5.61	5.85	4.67	5.50	5.65	4.78	5.61	4.95	5.35	3.22
11	Pt-3-*O*-(6-*p*-coum)-glc	1.36	1.40	6.45	6.54	5.44	4.92	4.81	5.01	4.56	4.19	4.30	4.68	4.12	3.58	3.69	3.52
12	Pn-3-*O*-(6-*p*-coum)-glc	13.49	9.71	43.12	40.50	36.54	31.25	31.55	30.01	25.40	23.02	23.50	24.79	22.12	19.79	19.08	15.91
13	Mv-3-*O*-(6-*p*-coum)-glc	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Tank 18

#	Time (days)	0	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
1	Dp-3-*O*-glc	5.21	13.86	14.56	16.47	14.98	12.34	15.03	13.56	11.60	11.58	11.60	12.14	10.76	9.91	10.33	8.92
2	Cy-3-*O*-glc	3.94	2.57	1.83	2.31	2.18	1.52	1.96	1.94	1.71	1.77	1.77	1.80	1.88	1.66	1.79	2.38
3	Pt-3-*O*-glc	9.01	17.97	24.01	28.15	25.81	21.50	23.88	24.32	20.59	20.46	20.25	21.42	19.42	17.29	17.15	14.98
4	Pn-3-*O*-glc	11.09	9.96	5.82	8.71	8.68	7.89	7.45	7.02	6.52	6.99	6.94	6.68	6.67	5.32	5.54	3.62
5	Mv-3-*O*-glc	81.20	103.63	145.62	163.62	157.03	140.19	147.95	148.73	134.52	134.84	133.77	134.78	126.80	117.93	111.82	98.66
6	Dp-3-*O*-(6-ac)-glc	0.19	1.36	1.85	3.40	3.15	2.62	3.16	3.14	2.61	2.64	2.65	2.73	2.47	1.36	2.34	3.42
7	Pt-3-*O*-(6-ac)-glc	1.09	1.85	2.84	4.51	4.25	3.86	3.51	3.57	3.93	3.90	3.93	4.14	3.79	3.18	3.57	2.42
8	Pn-3-*O*-(6-ac)-glc	1.20	1.57	2.73	3.43	3.26	3.05	3.45	3.24	3.07	3.07	3.05	3.21	3.01	2.67	2.27	1.95
9	Mv-3-*O*-(6-ac)-glc	6.04	9.35	15.07	19.57	16.93	14.90	16.54	15.30	13.71	13.93	13.89	14.22	12.95	11.77	11.80	10.01
10	Mv-3-*O*-(6-caff)-glc	1.14	1.69	2.75	4.17	5.27	5.26	4.96	3.34	4.72	6.03	4.88	5.02	5.86	5.19	5.61	3.26
11	Pt-3-*O*-(6-*p*-coum)-glc	0.74	1.80	4.79	6.68	5.75	4.83	5.03	5.09	4.30	4.45	4.43	4.70	4.13	3.62	3.78	3.37
12	Pn-3-*O*-(6-*p*-coum)-glc	7.91	13.71	33.46	42.21	38.38	32.44	33.15	30.81	24.92	25.30	24.95	25.56	23.04	20.36	19.54	15.28
13	Mv-3-*O*-(6-*p*-coum)-glc	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Tank 19

#	Time (days)	0	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
1	Dp-3-*O*-glc	7.87	15.58	15.95	15.65	13.57	14.23	14.41	12.78	11.92	11.40	11.64	11.59	10.50	10.01	10.35	9.28
2	Cy-3-*O*-glc	4.72	2.89	2.17	2.10	2.05	1.71	2.09	1.98	1.72	1.67	1.64	1.63	1.83	1.96	1.79	1.96
3	Pt-3-*O*-glc	12.27	19.59	25.90	27.53	23.78	24.43	25.39	22.78	21.23	20.26	20.01	20.47	18.83	17.75	17.39	15.72
4	Pn-3-*O*-glc	13.10	10.32	6.34	8.17	8.21	8.25	7.61	6.85	6.36	6.58	6.38	6.15	6.57	6.69	5.48	3.53
5	Mv-3-*O*-glc	92.80	107.91	146.03	156.94	147.71	148.64	152.24	142.40	136.34	132.25	129.44	129.07	122.51	116.19	111.47	98.38
6	Dp-3-*O*-(6-ac)-glc	0.77	1.77	2.97	3.34	3.00	2.86	3.34	3.09	2.69	2.64	2.46	2.51	2.38	2.32	2.34	3.48
7	Pt-3-*O*-(6-ac)-glc	1.51	1.96	3.50	4.74	4.02	4.16	3.68	4.11	4.02	3.95	3.82	3.92	3.72	3.68	3.60	2.44
8	Pn-3-*O*-(6-ac)-glc	1.52	1.75	3.37	3.54	3.13	3.21	3.45	3.17	3.07	3.02	2.36	3.05	2.97	3.05	2.22	1.94
9	Mv-3-*O*-(6-ac)-glc	7.14	9.72	17.65	19.06	15.70	16.45	17.34	14.62	13.94	13.71	13.34	13.41	12.45	11.81	11.73	10.14
10	Mv-3-*O*-(6-caff)-glc	1.49	1.97	3.17	4.88	4.74	5.63	5.07	4.78	4.76	5.94	4.64	5.96	5.66	5.75	5.62	3.30
11	Pt-3-*O*-(6-*p*-coum)-glc	1.11	1.86	5.96	6.61	5.14	5.69	5.41	4.70	4.42	4.39	4.27	4.40	4.01	3.87	3.76	3.53
12	Pn-3-*O*-(6-*p*-coum)-glc	10.21	12.04	40.28	41.13	35.13	36.54	34.94	29.37	25.54	24.77	23.59	23.97	22.27	21.31	19.51	15.71
13	Mv-3-*O*-(6-*p*-coum)-glc	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Tank 20

#	Time (days)	0	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
1	Dp-3-*O*-glc	7.93	16.55	13.09	17.70	15.86	13.10	14.30	14.89	12.29	12.93	12.45	12.04	11.29	10.58	8.39	9.15
2	Cy-3-*O*-glc	4.77	3.49	2.28	2.18	2.26	1.76	2.07	2.00	1.70	1.61	1.72	1.71	1.87	1.98	1.73	1.65
3	Pt-3-*O*-glc	12.38	19.54	21.38	27.24	26.12	20.95	24.65	25.79	21.54	19.87	21.12	21.00	19.69	18.53	15.19	15.38
4	Pn-3-*O*-glc	13.31	11.98	5.51	8.31	8.84	6.89	7.66	7.27	6.64	6.38	5.97	6.47	6.76	6.52	5.24	2.47
5	Mv-3-*O*-glc	94.94	110.77	128.52	154.01	157.64	134.07	150.15	151.19	135.70	126.16	131.86	131.50	125.81	119.62	103.31	103.45
6	Dp-3-*O*-(6-ac)-glc	0.78	2.16	1.77	3.42	3.19	2.98	3.24	3.24	2.70	2.47	2.70	2.71	2.54	2.35	2.18	2.97
7	Pt-3-*O*-(6-ac)-glc	1.54	2.27	2.59	4.78	4.31	3.27	3.60	3.72	4.02	3.73	4.10	4.10	3.82	3.72	3.28	2.37
8	Pn-3-*O*-(6-ac)-glc	1.60	2.15	2.53	3.57	3.30	3.28	3.44	3.24	3.05	2.81	3.09	3.14	3.06	3.03	2.06	1.88
9	Mv-3-*O*-(6-ac)-glc	7.29	10.77	13.53	19.25	17.08	15.34	16.94	16.00	14.17	13.05	13.93	13.79	12.97	12.28	10.49	10.37
10	Mv-3-*O*-(6-caff)-glc	1.50	2.26	2.29	4.96	5.22	4.46	4.98	6.25	4.77	5.51	4.79	4.85	5.86	5.74	4.99	3.28
11	Pt-3-*O*-(6-*p*-coum)-glc	1.19	2.59	3.90	6.68	5.70	4.56	5.12	5.45	4.58	4.21	4.61	4.54	4.17	3.99	3.16	3.52
12	Pn-3-*O*-(6-*p*-coum)-glc	10.35	18.62	28.41	41.34	38.06	30.67	33.54	31.46	25.43	22.37	24.70	24.27	22.68	21.50	16.43	16.39
13	Mv-3-*O*-(6-*p*-coum)-glc	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

continued

Table S1. Anthocyanin concentrations determined by HPLC-DAD in red wine samples from Mendavia 2018, expressed in mg of Mv-3- *O*-glc equiv./L.

Tank 21

#	Time (days)	0	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
1	Dp-3-*O*-glc	10.36	12.78	12.38	16.00	15.56	13.98	14.15	13.77	11.47	10.92	11.13	11.27	11.51	9.73	10.17	8.71
2	Cy-3-*O*-glc	4.82	2.82	1.72	2.04	1.98	1.43	1.76	1.67	1.54	1.53	1.55	1.61	1.69	1.75	1.62	2.32
3	Pt-3-*O*-glc	14.30	16.73	19.96	24.40	23.34	22.01	21.72	21.20	19.49	18.18	18.73	18.54	17.15	16.10	15.51	14.75
4	Pn-3-*O*-glc	13.19	10.39	9.44	7.70	8.22	6.77	7.03	6.44	6.27	6.29	5.57	6.10	6.34	6.17	5.36	4.71
5	Mv-3-*O*-glc	96.50	103.76	120.14	143.02	140.39	133.85	132.76	128.74	122.23	118.18	118.73	115.82	110.13	104.89	98.65	92.10
6	Dp-3-*O*-(6-ac)-glc	1.08	1.12	1.79	3.11	2.89	2.89	2.98	2.91	2.49	2.33	2.34	2.37	2.21	2.11	2.15	3.33
7	Pt-3-*O*-(6-ac)-glc	1.72	1.80	2.55	3.53	4.03	3.39	3.33	3.96	3.80	3.58	3.77	3.73	3.48	3.44	3.31	2.30
8	Pn-3-*O*-(6-ac)-glc	1.32	1.55	2.41	3.28	3.02	3.23	3.17	2.94	2.83	2.68	2.79	2.80	2.68	2.73	1.96	1.82
9	Mv-3-*O*-(6-ac)-glc	8.15	9.12	13.34	17.28	15.41	15.62	15.14	13.54	12.86	12.27	12.52	12.26	11.30	10.78	10.50	9.61
10	Mv-3-*O*-(6-caff)-glc	1.84	2.03	2.29	4.98	6.36	4.58	5.02	6.04	4.94	5.80	4.79	4.78	5.61	5.59	4.32	3.41
11	Pt-3-*O*-(6-*p*-coum)-glc	1.63	1.92	4.06	5.89	5.30	4.99	4.68	4.56	4.33	4.00	4.15	4.11	3.70	3.58	3.49	3.34
12	Pn-3-*O*-(6-*p*-coum)-glc	14.40	14.77	28.34	39.47	35.18	32.18	30.88	27.97	24.83	23.00	23.46	22.81	20.68	19.99	18.36	15.60
13	Mv-3-*O*-(6-*p*-coum)-glc	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Tank 22

#	Time (days)	0	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
1	Dp-3-*O*-glc	21.17	12.42	14.87	14.85	14.10	13.01	12.81	12.62	11.60	10.65	11.19	10.91	10.35	9.23	9.89	8.72
2	Cy-3-*O*-glc	6.49	4.01	1.78	2.01	1.98	1.50	1.76	1.62	1.46	1.49	1.58	1.53	1.70	1.48	1.61	1.83
3	Pt-3-*O*-glc	23.96	15.29	23.54	22.88	23.39	22.44	21.85	19.81	17.89	17.76	18.76	18.10	17.14	15.20	15.26	14.81
4	Pn-3-*O*-glc	17.58	11.95	4.94	7.61	8.37	6.94	7.13	6.41	5.69	5.34	5.69	5.85	6.22	4.68	5.21	4.70
5	Mv-3-*O*-glc	126.79	99.63	132.23	136.00	140.97	135.79	133.86	125.08	115.55	117.56	119.43	114.55	110.96	103.44	98.48	93.06
6	Dp-3-*O*-(6-ac)-glc	1.30	1.74	3.21	3.01	2.85	2.92	2.94	2.81	2.30	2.29	2.35	2.32	2.30	1.22	1.58	3.34
7	Pt-3-*O*-(6-ac)-glc	2.05	2.04	3.48	4.37	4.03	3.40	4.30	3.83	3.71	3.54	3.75	3.65	3.56	2.93	3.30	2.34
8	Pn-3-*O*-(6-ac)-glc	1.72	2.03	3.33	3.22	3.01	3.21	3.17	2.86	2.73	2.14	2.75	2.73	2.72	2.37	2.00	1.85
9	Mv-3-*O*-(6-ac)-glc	10.43	9.84	15.80	16.73	15.51	14.66	15.26	12.95	11.93	12.13	12.52	12.08	11.58	10.47	10.52	9.74
10	Mv-3-*O*-(6-caff)-glc	2.01	2.28	4.03	4.97	6.48	4.82	5.23	5.99	4.64	4.72	4.89	4.80	5.84	5.09	5.51	3.54
11	Pt-3-*O*-(6-*p*-coum)-glc	2.43	2.17	5.71	5.76	5.40	5.08	4.71	4.22	3.89	3.87	4.11	4.02	3.78	3.26	3.47	3.39
12	Pn-3-*O*-(6-*p*-coum)-glc	20.91	16.15	35.79	36.93	36.04	32.95	30.63	26.75	22.66	22.52	23.35	22.27	21.22	18.50	18.17	15.69
13	Mv-3-*O*-(6-*p*-coum)-glc	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Tank 23

#	Time (days)	0	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
1	Dp-3-*O*-glc	15.95	13.11	15.83	14.80	15.93	13.49	14.74	12.65	12.75	11.34	11.25	12.30	10.20	11.49	9.12	10.10
2	Cy-3-*O*-glc	5.51	3.84	1.94	1.95	1.99	1.40	1.74	1.67	1.56	1.35	1.42	1.51	1.66	1.73	1.54	1.81
3	Pt-3-*O*-glc	18.64	16.02	24.36	22.31	23.66	20.98	22.38	21.04	19.55	17.18	18.33	18.15	16.60	16.65	14.85	14.41
4	Pn-3-*O*-glc	14.83	11.63	5.52	7.57	8.38	6.75	7.17	6.61	6.65	5.99	5.54	5.99	6.25	5.98	5.21	4.72
5	Mv-3-*O*-glc	107.40	99.29	138.10	132.01	140.59	129.20	135.33	129.03	122.10	114.75	116.56	114.11	106.70	105.56	93.97	88.37
6	Dp-3-*O*-(6-ac)-glc	1.26	1.46	2.84	2.88	2.80	2.75	2.91	2.88	2.73	2.15	2.21	2.29	2.24	2.14	2.08	3.25
7	Pt-3-*O*-(6-ac)-glc	1.44	1.78	3.02	4.18	4.01	3.23	4.27	3.26	3.75	3.42	3.58	3.65	3.50	3.44	3.25	2.28
8	Pn-3-*O*-(6-ac)-glc	1.16	1.69	2.16	3.11	2.99	3.12	3.08	2.97	2.88	2.55	2.68	2.74	2.70	2.70	1.96	1.85
9	Mv-3-*O*-(6-ac)-glc	9.35	8.98	16.13	16.25	15.58	13.99	15.56	13.50	12.72	11.88	12.21	12.05	11.31	11.14	10.43	9.45
10	Mv-3-*O*-(6-caff)-glc	1.81	1.79	3.10	4.64	6.27	4.34	5.01	4.87	4.76	5.41	4.53	4.61	5.63	5.59	5.30	3.38
11	Pt-3-*O*-(6-*p*-coum)-glc	2.03	1.72	5.82	5.66	5.51	4.87	4.91	4.58	4.26	3.80	4.02	4.00	3.79	3.76	3.47	3.37
12	Pn-3-*O*-(6-*p*-coum)-glc	17.53	11.80	36.94	36.21	36.37	31.82	31.50	28.20	24.48	21.93	22.63	22.07	20.83	20.35	17.59	15.06
13	Mv-3-*O*-(6-*p*-coum)-glc	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Tank 24

#	Time (days)	0	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
1	Dp-3-*O*-glc	9.28	13.74	11.43	15.86	14.65	14.14	12.05	12.82	11.60	5.39	11.64	12.68	11.53	10.14	10.19	8.93
2	Cy-3-*O*-glc	4.49	2.53	1.63	2.08	1.90	1.42	1.75	1.74	1.54	0.73	1.54	1.50	1.60	1.70	1.55	1.77
3	Pt-3-*O*-glc	14.17	17.17	17.00	23.47	21.59	21.76	18.57	21.14	19.40	8.69	18.89	18.63	17.16	16.28	15.09	14.47
4	Pn-3-*O*-glc	13.32	9.34	5.76	7.86	7.95	6.90	6.64	6.52	5.80	2.51	5.78	5.94	5.57	5.79	5.29	4.62
5	Mv-3-*O*-glc	101.80	101.54	114.27	135.86	132.84	132.91	120.52	127.97	121.57	57.82	118.49	116.21	109.28	105.10	96.58	89.22
6	Dp-3-*O*-(6-ac)-glc	0.69	1.94	2.19	2.99	2.54	2.83	2.72	2.93	2.50	1.16	2.32	2.30	2.23	2.09	2.12	3.21
7	Pt-3-*O*-(6-ac)-glc	1.63	2.18	2.77	4.25	3.69	3.28	3.61	3.23	3.68	1.74	3.65	3.65	3.51	3.36	3.28	2.26
8	Pn-3-*O*-(6-ac)-glc	1.23	1.99	2.81	3.14	2.81	3.18	2.83	2.90	2.83	1.09	2.69	2.73	2.72	2.61	1.97	1.80
9	Mv-3-*O*-(6-ac)-glc	8.18	9.92	13.13	16.39	14.46	14.14	13.50	13.38	12.62	6.00	12.39	12.23	11.31	10.85	10.32	9.42
10	Mv-3-*O*-(6-caff)-glc	1.76	1.87	4.10	4.59	4.66	4.22	5.10	4.62	5.66	2.65	4.51	5.65	5.31	5.23	5.26	3.26
11	Pt-3-*O*-(6-*p*-coum)-glc	1.60	2.15	3.96	5.62	4.87	4.84	3.90	4.49	4.18	1.89	4.07	4.07	3.69	3.52	3.48	3.35
12	Pn-3-*O*-(6-*p*-coum)-glc	14.97	14.13	26.25	35.81	32.96	31.92	26.60	27.69	24.30	10.30	23.06	22.45	20.66	19.19	18.14	15.23
13	Mv-3-*O*-(6-*p*-coum)-glc	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Table S2. Anthocyanin derivatives concentrations determined by HPLC-DAD-ESI(+)-MS/MS in red wine samples from Mendavia 2018, expressed in mg of Mv-3-*O*-glc equiv./L.

Tank 01

#	Time (days)	0	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
14	Catechin-Mv-3-*O*-glc	0.080	0.066	0.101	0.160	0.153	0.176	0.138	0.160	0.161	0.093	0.064	0.074	0.048	0.074	0.083	0.062
15	Epicatechin-Mv-3-*O*-glc	0.019	0.022	0.028	0.048	0.046	0.042	0.041	0.037	0.051	0.030	0.018	0.030	0.013	0.020	0.023	0.020
16	Mv-3-*O*-glc-(epi)catechin	0.003	0.003	0.004	0.004	0.003	0.004	0.004	0.003	0.004	0.003	0.001	0.002	0.001	0.002	0.001	0.002
17	Mv-3-*O*-glc-A-catechin	0.002	0.003	0.003	0.004	0.003	0.002	0.003	0.002	0.002	0.001	0.001	0.001	0.001	0.001	0.001	0.001
18	Mv-3-*O*-glc-pyruvic	0.114	0.240	0.450	0.529	0.626	0.512	0.490	0.470	0.530	0.477	0.308	0.471	0.301	0.417	0.377	0.351
19	Mv-3-*O*-glc-acetaldehyde	0.372	0.671	0.905	2.083	2.269	1.174	0.924	0.920	1.392	1.425	0.594	1.503	0.487	0.306	0.525	0.325
20	Pyruvic acid derivative-vinyl-catechin-catechin	0.000	0.000	0.000	0.001	0.001	0.001	0.001	0.001	0.002	0.001	0.001	0.001	0.001	0.001	0.001	0.001
21	Mv-3-*O*-glc-8-ethyl-catechin 1	0.003	0.002	0.005	0.007	0.008	0.005	0.005	0.006	0.011	0.006	0.004	0.007	0.004	0.004	0.004	0.003
22	Mv-3-*O*-glc-8-ethyl-catechin 2	0.003	0.003	0.005	0.008	0.008	0.006	0.007	0.009	0.010	0.007	0.004	0.007	0.004	0.005	0.005	0.004
23	Mv-3-*O*-glc-8-ethyl-epicatechin	0.003	0.004	0.007	0.010	0.016	0.009	0.009	0.010	0.013	0.010	0.005	0.009	0.005	0.006	0.004	0.003
24	Mv-3-*O*-(6-*p*-coum)-glc *cis*	1.500	0.789	1.157	1.866	1.887	1.128	0.896	0.673	0.000	0.702	0.422	0.496	0.358	0.480	0.476	0.265
25	Mv-3-*O*-(6-*p*-coum)-glc *trans*	65.851	61.821	89.625	110.899	100.513	82.624	75.043	47.981	0.031	50.894	38.326	58.694	30.438	37.967	34.764	28.597
26	Mv-3-*O*-glc-4-vinylphenol	0.008	0.014	0.126	0.165	0.183	0.185	0.242	0.264	0.001	0.437	0.237	0.449	0.198	0.353	0.335	0.277

Tank 02

#	Time (days)	0	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
14	Catechin-Mv-3-*O*-glc	0.098	0.063	0.101	0.149	0.133	0.163	0.144	0.162	0.171	0.095	0.067	0.069	0.048	0.073	0.080	0.064
15	Epicatechin-Mv-3-*O*-glc	0.025	0.019	0.032	0.043	0.045	0.041	0.042	0.033	0.052	0.029	0.022	0.025	0.012	0.018	0.020	0.016
16	Mv-3-*O*-glc-(epi)catechin	0.004	0.002	0.004	0.004	0.003	0.003	0.004	0.003	0.004	0.002	0.002	0.002	0.001	0.001	0.002	0.002
17	Mv-3-*O*-glc-A-catechin	0.003	0.002	0.003	0.002	0.002	0.001	0.002	0.002	0.002	0.001	0.001	0.001	0.001	0.001	0.001	0.001
18	Mv-3-*O*-glc-pyruvic	0.106	0.210	0.400	0.576	0.436	0.516	0.500	0.450	0.529	0.447	0.341	0.491	0.295	0.498	0.424	0.390
19	Mv-3-*O*-glc-acetaldehyde	0.403	0.562	0.683	2.101	1.412	1.102	1.118	0.823	1.661	2.264	1.782	3.154	1.953	2.074	0.873	0.609
20	Pyruvic acid derivative-vinyl-catechin-catechin	0.000	0.000	0.000	0.001	0.001	0.001	0.002	0.001	0.002	0.001	0.001	0.001	0.001	0.001	0.001	0.002
21	Mv-3-*O*-glc-8-ethyl-catechin 1	0.003	0.002	0.005	0.007	0.006	0.005	0.005	0.005	0.013	0.006	0.004	0.007	0.004	0.004	0.004	0.003
22	Mv-3-*O*-glc-8-ethyl-catechin 2	0.004	0.002	0.005	0.007	0.007	0.006	0.006	0.007	0.011	0.006	0.005	0.007	0.004	0.005	0.006	0.005
23	Mv-3-*O*-glc-8-ethyl-epicatechin	0.003	0.002	0.007	0.010	0.008	0.007	0.008	0.008	0.015	0.009	0.006	0.009	0.005	0.006	0.005	0.004
24	Mv-3-*O*-(6-*p*-coum)-glc *cis*	1.544	0.838	0.962	1.344	0.930	0.772	0.937	0.728	0.846	0.850	0.561	0.832	0.289	0.450	0.418	0.247
25	Mv-3-*O*-(6-*p*-coum)-glc *trans*	59.302	40.170	83.928	112.070	82.020	84.610	77.422	45.301	67.176	46.182	43.506	57.010	26.616	34.483	29.746	26.113
26	Mv-3-*O*-glc-4-vinylphenol	0.008	0.011	0.101	0.181	0.149	0.185	0.256	0.242	0.465	0.335	0.199	0.375	0.142	0.287	0.246	0.219

Tank 03

#	Time (days)	0	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
14	Catechin-Mv-3-*O*-glc	0.082	0.055	0.095	0.152	0.131	0.166	0.147	0.185	0.171	0.088	0.067	0.066	0.049	0.073	0.079	0.066
15	Epicatechin-Mv-3-*O*-glc	0.029	0.016	0.025	0.043	0.045	0.054	0.042	0.048	0.043	0.023	0.018	0.021	0.014	0.020	0.021	0.023
16	Mv-3-*O*-glc-(epi)catechin	0.003	0.002	0.003	0.004	0.003	0.004	0.003	0.005	0.004	0.002	0.001	0.002	0.002	0.002	0.002	0.002
17	Mv-3-*O*-glc-A-catechin	0.002	0.002	0.003	0.003	0.002	0.002	0.002	0.004	0.003	0.001	0.001	0.001	0.001	0.001	0.001	0.001
18	Mv-3-*O*-glc-pyruvic	0.102	0.229	0.421	0.500	0.454	0.544	0.493	0.498	0.555	0.481	0.347	0.452	0.314	0.467	0.405	0.375
19	Mv-3-*O*-glc-acetaldehyde	0.400	0.553	0.975	1.702	1.394	1.128	0.950	0.789	1.905	2.106	1.198	1.997	1.201	1.091	0.656	0.398
20	Pyruvic acid derivative-vinyl-catechin-catechin	0.000	0.000	0.001	0.001	0.001	0.001	0.001	0.001	0.002	0.001	0.001	0.001	0.001	0.001	0.002	0.002
21	Mv-3-*O*-glc-8-ethyl-catechin 1	0.003	0.002	0.004	0.005	0.005	0.005	0.005	0.008	0.013	0.006	0.004	0.006	0.004	0.005	0.005	0.004
22	Mv-3-*O*-glc-8-ethyl-catechin 2	0.003	0.003	0.005	0.008	0.006	0.006	0.007	0.009	0.011	0.007	0.004	0.006	0.005	0.005	0.006	0.005
23	Mv-3-*O*-glc-8-ethyl-epicatechin	0.004	0.003	0.005	0.009	0.007	0.008	0.007	0.012	0.012	0.008	0.004	0.008	0.006	0.007	0.004	0.004
24	Mv-3-*O*-(6-*p*-coum)-glc *cis*	1.006	0.858	1.029	1.258	0.767	0.719	0.983	0.735	1.003	0.873	0.522	0.695	0.449	0.578	0.545	0.461
25	Mv-3-*O*-(6-*p*-coum)-glc *trans*	62.486	41.915	80.892	95.038	77.257	92.005	76.711	67.978	67.313	47.519	41.231	52.640	38.679	45.584	35.610	40.150
26	Mv-3-*O*-glc-4-vinylphenol	0.008	0.011	0.100	0.144	0.152	0.210	0.240	0.296	0.441	0.400	0.237	0.359	0.209	0.359	0.284	0.276

Tank 04

#	Time (days)	0	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
14	Catechin-Mv-3-*O*-glc	0.063	0.052	0.090	0.149	0.143	0.177	0.146	0.175	0.183	0.096	0.065	0.068	0.050	0.072	0.081	0.063
15	Epicatechin-Mv-3-*O*-glc	0.015	0.015	0.027	0.046	0.043	0.045	0.034	0.043	0.056	0.030	0.020	0.023	0.017	0.022	0.020	0.018
16	Mv-3-*O*-glc-(epi)catechin	0.002	0.003	0.004	0.004	0.003	0.003	0.003	0.003	0.007	0.002	0.002	0.002	0.002	0.002	0.002	0.002
17	Mv-3-*O*-glc-A-catechin	0.002	0.002	0.003	0.004	0.002	0.003	0.002	0.004	0.004	0.001	0.001	0.001	0.001	0.001	0.001	0.001
18	Mv-3-*O*-glc-pyruvic	0.087	0.219	0.412	0.451	0.483	0.454	0.489	0.430	0.577	0.484	0.335	0.411	0.293	0.429	0.383	0.358
19	Mv-3-*O*-glc-acetaldehyde	0.320	0.494	0.606	1.642	1.761	1.033	1.189	0.858	2.786	3.036	2.275	3.148	1.911	1.924	0.876	0.658
20	Pyruvic acid derivative-vinyl-catechin-catechin	0.000	0.000	0.001	0.001	0.001	0.001	0.001	0.001	0.002	0.001	0.002	0.002	0.002	0.002	0.002	0.002
21	Mv-3-*O*-glc-8-ethyl-catechin 1	0.002	0.001	0.005	0.005	0.006	0.006	0.006	0.008	0.012	0.007	0.005	0.007	0.005	0.006	0.005	0.004
22	Mv-3-*O*-glc-8-ethyl-catechin 2	0.003	0.002	0.005	0.008	0.007	0.007	0.008	0.009	0.012	0.009	0.007	0.007	0.006	0.007	0.006	0.005
23	Mv-3-*O*-glc-8-ethyl-epicatechin	0.003	0.002	0.006	0.010	0.008	0.008	0.009	0.012	0.015	0.011	0.007	0.010	0.007	0.007	0.006	0.004
24	Mv-3-*O*-(6-*p*-coum)-glc *cis*	1.009	0.750	1.023	1.284	1.134	0.962	0.900	0.781	1.011	0.930	0.480	0.685	0.373	0.487	0.413	0.211
25	Mv-3-*O*-(6-*p*-coum)-glc *trans*	53.872	37.222	76.298	102.558	86.148	94.625	79.548	47.956	76.941	53.033	46.034	54.552	36.943	38.616	31.334	23.451
26	Mv-3-*O*-glc-4-vinylphenol	0.004	0.009	0.091	0.138	0.133	0.192	0.235	0.196	0.463	0.339	0.180	0.308	0.122	0.258	0.244	0.186

Tank 05

#	Time (days)	0	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
14	Catechin-Mv-3-*O*-glc	0.083	0.059	0.094	0.130	0.134	0.171	0.140	0.189	0.168	0.101	0.068	0.074	0.049	0.072	0.079	0.069
15	Epicatechin-Mv-3-*O*-glc	0.020	0.020	0.025	0.039	0.049	0.057	0.039	0.045	0.046	0.030	0.021	0.025	0.014	0.022	0.023	0.020
16	Mv-3-*O*-glc-(epi)catechin	0.002	0.002	0.003	0.003	0.004	0.004	0.002	0.004	0.005	0.002	0.002	0.002	0.001	0.002	0.002	0.002
17	Mv-3-*O*-glc-A-catechin	0.002	0.002	0.002	0.003	0.002	0.002	0.001	0.003	0.004	0.001	0.001	0.001	0.001	0.001	0.001	0.001
18	Mv-3-*O*-glc-pyruvic	0.095	0.251	0.368	0.513	0.494	0.477	0.478	0.444	0.474	0.368	0.263	0.339	0.235	0.345	0.330	0.268
19	Mv-3-*O*-glc-acetaldehyde	0.296	0.574	0.938	2.056	1.876	0.771	0.936	0.878	1.637	1.355	0.674	1.250	0.803	0.682	0.650	0.431
20	Pyruvic acid derivative-vinyl-catechin-catechin	0.000	0.000	0.000	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.002	0.002	0.002
21	Mv-3-*O*-glc-8-ethyl-catechin 1	0.002	0.001	0.004	0.006	0.008	0.006	0.006	0.008	0.010	0.008	0.005	0.008	0.004	0.006	0.005	0.004
22	Mv-3-*O*-glc-8-ethyl-catechin 2	0.003	0.002	0.006	0.008	0.008	0.007	0.007	0.010	0.011	0.009	0.007	0.009	0.005	0.007	0.006	0.005
23	Mv-3-*O*-glc-8-ethyl-epicatechin	0.002	0.002	0.006	0.010	0.009	0.009	0.009	0.011	0.015	0.011	0.007	0.010	0.006	0.008	0.004	0.004
24	Mv-3-*O*-(6-*p*-coum)-glc *cis*	0.590	0.786	0.929	0.628	1.017	0.651	0.712	0.851	0.832	0.863	0.378	0.701	0.241	0.462	0.424	0.187
25	Mv-3-*O*-(6-*p*-coum)-glc *trans*	52.578	38.756	62.966	88.145	78.372	83.615	65.753	59.706	54.505	45.055	34.625	47.005	27.514	35.244	26.141	19.066
26	Mv-3-*O*-glc-4-vinylphenol	0.006	0.010	0.060	0.103	0.120	0.156	0.191	0.259	0.368	0.304	0.161	0.291	0.165	0.297	0.283	0.211

Tank 06

#	Time (days)	0	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
14	Catechin-Mv-3-*O*-glc	0.087	0.066	0.094	0.130	0.142	0.158	0.147	0.190	0.165	0.092	0.000	0.075	0.052	0.075	0.088	0.072
15	Epicatechin-Mv-3-*O*-glc	0.026	0.020	0.026	0.039	0.044	0.045	0.039	0.046	0.051	0.027	0.000	0.028	0.013	0.023	0.021	0.021
16	Mv-3-*O*-glc-(epi)catechin	0.003	0.003	0.004	0.003	0.003	0.003	0.003	0.004	0.005	0.001	0.000	0.003	0.002	0.002	0.002	0.002
17	Mv-3-*O*-glc-A-catechin	0.003	0.002	0.003	0.002	0.002	0.002	0.002	0.002	0.003	0.001	0.000	0.001	0.001	0.001	0.001	0.001
18	Mv-3-*O*-glc-pyruvic	0.098	0.213	0.306	0.484	0.450	0.432	0.452	0.413	0.468	0.294	0.000	0.378	0.243	0.378	0.339	0.355
19	Mv-3-*O*-glc-acetaldehyde	0.321	0.497	0.859	1.777	1.512	0.874	0.935	0.855	1.992	1.383	0.000	2.519	1.884	1.786	0.918	0.659
20	Pyruvic acid derivative-vinyl-catechin-catechin	0.000	0.000	0.000	0.001	0.001	0.001	0.001	0.002	0.003	0.001	0.000	0.002	0.001	0.002	0.003	0.003
21	Mv-3-*O*-glc-8-ethyl-catechin 1	0.003	0.001	0.005	0.008	0.007	0.007	0.008	0.008	0.013	0.007	0.000	0.008	0.005	0.006	0.005	0.004
22	Mv-3-*O*-glc-8-ethyl-catechin 2	0.003	0.003	0.005	0.008	0.008	0.007	0.008	0.010	0.012	0.008	0.000	0.008	0.006	0.007	0.006	0.006
23	Mv-3-*O*-glc-8-ethyl-epicatechin	0.003	0.002	0.006	0.009	0.008	0.009	0.009	0.011	0.015	0.009	0.000	0.010	0.006	0.007	0.004	0.004
24	Mv-3-*O*-(6-*p*-coum)-glc *cis*	1.237	0.735	0.913	1.026	1.053	0.787	0.895	0.861	0.792	0.628	0.000	0.686	0.232	0.413	0.340	0.268
25	Mv-3-*O*-(6-*p*-coum)-glc *trans*	56.542	35.175	57.232	97.312	76.241	77.872	66.864	54.453	58.999	34.866	0.002	51.172	27.481	34.276	22.239	27.197
26	Mv-3-*O*-glc-4-vinylphenol	0.008	0.010	0.057	0.110	0.105	0.149	0.191	0.205	0.367	0.198	-	0.281	0.137	0.267	0.194	0.212

continued

Table S2. Anthocyanin derivatives concentrations determined by HPLC-DAD-ESI(+)-MS/MS in red wine samples from Mendavia 2018, expressed in mg of Mv-3-*O*-glc equiv./L.

Tank 07

#	Time (days)	0	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
14	Catechin-Mv-3-*O*-glc	0.096	0.059	0.102	0.138	0.139	0.183	0.161	0.208	0.189	0.102	0.078	0.086	0.063	0.086	0.100	0.079
15	Epicatechin-Mv-3-*O*-glc	0.028	0.019	0.024	0.038	0.044	0.048	0.029	0.046	0.045	0.027	0.022	0.026	0.017	0.023	0.025	0.021
16	Mv-3-*O*-glc-(epi)catechin	0.003	0.002	0.003	0.003	0.003	0.003	0.003	0.004	0.006	0.002	0.002	0.002	0.002	0.002	0.001	0.002
17	Mv-3-*O*-glc-A-catechin	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.003	0.001	0.001	0.001	0.001	0.001	0.001	0.001
18	Mv-3-*O*-glc-pyruvic	0.097	0.222	0.268	0.379	0.409	0.418	0.431	0.435	0.438	0.389	0.280	0.331	0.213	0.328	0.364	0.264
19	Mv-3-*O*-glc-acetaldehyde	0.264	0.467	0.654	0.725	1.022	1.017	0.986	0.865	1.234	1.475	1.243	1.175	0.637	0.838	0.796	0.409
20	Pyruvic acid derivative-vinyl-catechin-catechin	0.000	0.000	0.001	0.001	0.001	0.001	0.001	0.002	0.002	0.001	0.001	0.001	0.001	0.001	0.002	0.002
21	Mv-3-*O*-glc-8-ethyl-catechin 1	0.003	0.002	0.004	0.005	0.006	0.005	0.006	0.008	0.011	0.006	0.005	0.007	0.005	0.006	0.005	0.004
22	Mv-3-*O*-glc-8-ethyl-catechin 2	0.003	0.002	0.005	0.006	0.007	0.006	0.007	0.011	0.011	0.008	0.006	0.007	0.005	0.006	0.006	0.005
23	Mv-3-*O*-glc-8-ethyl-epicatechin	0.004	0.002	0.005	0.007	0.008	0.007	0.008	0.010	0.012	0.008	0.007	0.008	0.006	0.007	0.004	0.003
24	Mv-3-*O*-(6-*p*-coum)-glc *cis*	0.881	0.674	0.760	0.893	0.676	0.952	0.789	0.882	0.821	0.704	0.508	0.640	0.308	0.496	0.518	0.190
25	Mv-3-*O*-(6-*p*-coum)-glc *trans*	58.056	35.210	50.966	70.246	63.967	69.671	64.245	54.637	57.584	42.854	40.261	47.393	28.221	36.216	32.282	19.700
26	Mv-3-*O*-glc-4-vinylphenol	0.006	0.007	0.052	0.075	0.087	0.133	0.168	0.190	0.317	0.283	0.202	0.206	0.001	0.207	0.273	0.158

Tank 08

#	Time (days)	0	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
14	Catechin-Mv-3-*O*-glc	0.067	0.054	0.090	0.124	0.114	0.162	0.144	0.180	0.171	0.093	0.064	0.071	0.054	0.070	0.086	0.069
15	Epicatechin-Mv-3-*O*-glc	0.024	0.018	0.027	0.033	0.040	0.047	0.039	0.045	0.046	0.029	0.018	0.025	0.016	0.019	0.020	0.021
16	Mv-3-*O*-glc-(epi)catechin	0.003	0.002	0.004	0.003	0.003	0.003	0.003	0.004	0.005	0.002	0.001	0.002	0.002	0.002	0.002	0.002
17	Mv-3-*O*-glc-A-catechin	0.002	0.002	0.002	0.001	0.002	0.003	0.002	0.003	0.004	0.001	0.001	0.001	0.001	0.001	0.001	0.001
18	Mv-3-*O*-glc-pyruvic	0.090	0.227	0.312	0.384	0.380	0.439	0.449	0.468	0.478	0.379	0.327	0.377	0.259	0.394	0.378	0.322
19	Mv-3-*O*-glc-acetaldehyde	0.273	0.470	0.767	1.096	0.966	0.770	0.695	1.077	1.300	1.879	2.157	2.160	1.734	1.723	0.884	0.505
20	Pyruvic acid derivative-vinyl-catechin-catechin	0.000	0.000	0.001	0.001	0.001	0.001	0.001	0.001	0.002	0.001	0.001	0.002	0.003	0.002	0.003	0.003
21	Mv-3-*O*-glc-8-ethyl-catechin 1	0.002	0.001	0.004	0.005	0.006	0.006	0.006	0.008	0.010	0.007	0.004	0.007	0.006	0.006	0.006	0.005
22	Mv-3-*O*-glc-8-ethyl-catechin 2	0.003	0.002	0.005	0.006	0.007	0.007	0.007	0.010	0.012	0.008	0.006	0.008	0.007	0.007	0.007	0.006
23	Mv-3-*O*-glc-8-ethyl-epicatechin	0.002	0.002	0.005	0.007	0.007	0.008	0.009	0.010	0.017	0.009	0.006	0.009	0.007	0.007	0.005	0.004
24	Mv-3-*O*-(6-*p*-coum)-glc *cis*	0.878	0.684	0.838	0.839	0.763	0.828	0.882	0.855	0.707	0.720	0.455	0.687	0.463	0.469	0.452	0.223
25	Mv-3-*O*-(6-*p*-coum)-glc *trans*	41.064	38.753	53.981	67.286	62.434	74.027	63.299	52.128	58.069	43.540	31.993	46.066	31.140	34.300	28.643	25.237
26	Mv-3-*O*-glc-4-vinylphenol	0.005	0.010	0.062	0.081	0.100	0.149	0.188	0.211	0.404	0.299	0.225	0.235	0.141	0.263	0.252	0.201

Tank 09

#	Time (days)	0	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
14	Catechin-Mv-3-*O*-glc	0.067	0.045	0.092	0.117	0.111	0.143	0.138	0.186	0.173	0.103	0.066	0.070	0.056	0.079	0.088	0.069
15	Epicatechin-Mv-3-*O*-glc	0.022	0.015	0.029	0.036	0.041	0.041	0.038	0.048	0.045	0.033	0.018	0.023	0.014	0.026	0.029	0.017
16	Mv-3-*O*-glc-(epi)catechin	0.002	0.002	0.003	0.003	0.003	0.004	0.002	0.004	0.005	0.003	0.002	0.002	0.002	0.002	0.002	0.002
17	Mv-3-*O*-glc-A-catechin	0.002	0.001	0.003	0.003	0.002	0.002	0.001	0.003	0.004	0.002	0.001	0.001	0.001	0.002	0.001	0.002
18	Mv-3-*O*-glc-pyruvic	0.093	0.183	0.340	0.448	0.430	0.370	0.422	0.513	0.482	0.430	0.293	0.423	0.306	0.405	0.405	0.324
19	Mv-3-*O*-glc-acetaldehyde	0.321	0.418	0.992	0.950	0.956	0.959	0.890	0.924	1.082	1.140	0.911	1.329	0.902	0.462	0.714	0.346
20	Pyruvic acid derivative-vinyl-catechin-catechin	0.000	0.000	0.001	0.001	0.001	0.001	0.001	0.001	0.003	0.001	0.001	0.001	0.001	0.001	0.001	0.002
21	Mv-3-*O*-glc-8-ethyl-catechin 1	0.002	0.001	0.004	0.004	0.006	0.006	0.006	0.008	0.012	0.009	0.005	0.007	0.005	0.007	0.006	0.004
22	Mv-3-*O*-glc-8-ethyl-catechin 2	0.003	0.002	0.005	0.006	0.007	0.007	0.007	0.010	0.011	0.008	0.007	0.007	0.005	0.007	0.007	0.005
23	Mv-3-*O*-glc-8-ethyl-epicatechin	0.002	0.002	0.007	0.009	0.009	0.009	0.009	0.015	0.018	0.014	0.009	0.012	0.008	0.009	0.006	0.005
24	Mv-3-*O*-(6-*p*-coum)-glc *cis*	1.016	0.669	0.828	0.884	0.848	0.738	0.716	0.885	0.842	0.870	0.726	0.818	0.370	0.687	0.551	0.226
25	Mv-3-*O*-(6-*p*-coum)-glc *trans*	31.368	35.326	59.629	76.205	66.165	72.538	59.672	59.120	60.154	47.715	39.914	45.045	29.987	46.500	37.738	22.684
26	Mv-3-*O*-glc-4-vinylphenol	0.004	0.007	0.070	0.110	0.086	0.143	0.205	0.309	0.471	0.437	0.262	0.382	0.271	0.408	0.371	0.295

Tank 10

#	Time (days)	0	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
14	Catechin-Mv-3-*O*-glc	0.071	0.049	0.076	0.117	0.120	0.145	0.124	0.181	0.158	0.096	0.062	0.068	0.062	0.075	0.084	0.060
15	Epicatechin-Mv-3-*O*-glc	0.026	0.018	0.024	0.036	0.047	0.041	0.035	0.054	0.044	0.032	0.020	0.023	0.016	0.022	0.025	0.016
16	Mv-3-*O*-glc-(epi)catechin	0.003	0.002	0.003	0.003	0.003	0.004	0.002	0.005	0.005	0.002	0.001	0.002	0.002	0.002	0.002	0.002
17	Mv-3-*O*-glc-A-catechin	0.003	0.002	0.002	0.003	0.002	0.002	0.002	0.004	0.004	0.002	0.001	0.002	0.002	0.001	0.001	0.001
18	Mv-3-*O*-glc-pyruvic	0.082	0.199	0.329	0.446	0.447	0.414	0.410	0.513	0.497	0.389	0.299	0.419	0.346	0.434	0.413	0.318
19	Mv-3-*O*-glc-acetaldehyde	0.290	0.396	0.989	0.892	0.936	1.024	0.883	0.916	1.168	1.280	1.025	1.814	1.044	1.054	0.770	0.442
20	Pyruvic acid derivative-vinyl-catechin-catechin	0.000	0.000	0.001	0.001	0.001	0.001	0.001	0.001	0.002	0.001	0.001	0.001	0.001	0.001	0.002	0.002
21	Mv-3-*O*-glc-8-ethyl-catechin 1	0.002	0.001	0.004	0.005	0.007	0.005	0.005	0.009	0.013	0.007	0.005	0.006	0.005	0.006	0.005	0.004
22	Mv-3-*O*-glc-8-ethyl-catechin 2	0.003	0.002	0.005	0.006	0.007	0.006	0.007	0.010	0.011	0.009	0.005	0.007	0.006	0.007	0.006	0.005
23	Mv-3-*O*-glc-8-ethyl-epicatechin	0.002	0.002	0.006	0.009	0.010	0.010	0.009	0.015	0.017	0.012	0.008	0.012	0.009	0.009	0.006	0.004
24	Mv-3-*O*-(6-*p*-coum)-glc *cis*	0.868	0.616	0.618	0.935	1.422	1.000	0.719	1.005	0.829	0.725	0.382	0.670	0.405	0.557	0.429	0.158
25	Mv-3-*O*-(6-*p*-coum)-glc *trans*	32.574	35.574	59.013	82.278	77.240	67.240	63.014	66.249	58.926	45.289	29.607	39.047	27.882	36.572	30.510	15.125
26	Mv-3-*O*-glc-4-vinylphenol	0.004	0.007	0.070	0.116	0.087	0.131	0.200	0.316	0.503	0.362	0.240	0.353	0.263	0.355	0.346	0.227

Tank 11

#	Time (days)	0	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
14	Catechin-Mv-3-*O*-glc	0.077	0.042	0.082	0.111	0.107	0.137	0.136	0.181	0.164	0.088	0.064	0.069	0.054	0.079	0.086	0.077
15	Epicatechin-Mv-3-*O*-glc	0.024	0.014	0.023	0.033	0.039	0.033	0.034	0.051	0.039	0.025	0.020	0.022	0.015	0.025	0.030	0.022
16	Mv-3-*O*-glc-(epi)catechin	0.004	0.002	0.003	0.003	0.003	0.003	0.002	0.004	0.004	0.001	0.001	0.002	0.002	0.002	0.001	0.003
17	Mv-3-*O*-glc-A-catechin	0.003	0.001	0.002	0.002	0.001	0.003	0.002	0.003	0.004	0.001	0.001	0.002	0.001	0.001	0.001	0.002
18	Mv-3-*O*-glc-pyruvic	0.078	0.200	0.358	0.442	0.389	0.463	0.468	0.524	0.490	0.445	0.289	0.413	0.287	0.391	0.414	0.331
19	Mv-3-*O*-glc-acetaldehyde	0.302	0.379	1.014	0.884	0.837	1.045	1.002	1.056	1.238	1.350	0.774	1.301	0.876	0.482	0.646	0.394
20	Pyruvic acid derivative-vinyl-catechin-catechin	0.001	0.000	0.001	0.001	0.001	0.001	0.001	0.002	0.001	0.001	0.001	0.001	0.001	0.002	0.002	0.003
21	Mv-3-*O*-glc-8-ethyl-catechin 1	0.002	0.001	0.004	0.004	0.005	0.006	0.005	0.010	0.012	0.006	0.004	0.007	0.005	0.006	0.006	0.004
22	Mv-3-*O*-glc-8-ethyl-catechin 2	0.003	0.001	0.004	0.005	0.007	0.007	0.006	0.010	0.012	0.006	0.006	0.007	0.006	0.007	0.007	0.006
23	Mv-3-*O*-glc-8-ethyl-epicatechin	0.002	0.002	0.005	0.007	0.008	0.009	0.009	0.015	0.015	0.011	0.007	0.012	0.008	0.009	0.006	0.005
24	Mv-3-*O*-(6-*p*-coum)-glc *cis*	0.990	0.575	0.682	0.757	0.899	0.842	0.740	0.850	0.747	0.436	0.395	0.692	0.334	0.726	0.650	0.358
25	Mv-3-*O*-(6-*p*-coum)-glc *trans*	32.253	36.119	53.320	69.416	59.712	76.177	62.311	60.164	51.342	33.339	23.262	43.531	30.690	44.153	36.778	30.095
26	Mv-3-*O*-glc-4-vinylphenol	0.004	0.008	0.059	0.090	0.093	0.142	0.209	0.276	0.461	0.400	0.221	0.403	0.222	0.370	0.406	0.342

Tank 12

#	Time (days)	0	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
14	Catechin-Mv-3-*O*-glc	0.071	0.048	0.096	0.124	0.097	0.152	0.140	0.179	0.171	0.097	0.061	0.067	0.054	0.072	0.095	0.067
15	Epicatechin-Mv-3-*O*-glc	0.025	0.016	0.028	0.038	0.036	0.035	0.036	0.035	0.052	0.025	0.020	0.023	0.015	0.022	0.034	0.021
16	Mv-3-*O*-glc-(epi)catechin	0.003	0.002	0.003	0.004	0.003	0.003	0.003	0.004	0.006	0.002	0.002	0.002	0.002	0.002	0.002	0.002
17	Mv-3-*O*-glc-A-catechin	0.002	0.002	0.002	0.003	0.002	0.002	0.002	0.004	0.004	0.002	0.001	0.002	0.002	0.001	0.001	0.001
18	Mv-3-*O*-glc-pyruvic	0.088	0.182	0.367	0.447	0.434	0.444	0.407	0.429	0.507	0.422	0.322	0.407	0.249	0.447	0.420	0.364
19	Mv-3-*O*-glc-acetaldehyde	0.331	0.338	0.994	0.972	0.821	0.672	0.920	0.731	1.456	1.503	1.156	1.698	0.920	1.148	0.770	0.462
20	Pyruvic acid derivative-vinyl-catechin-catechin	0.000	0.000	0.001	0.001	0.001	0.001	0.001	0.002	0.003	0.001	0.002	0.002	0.002	0.002	0.003	0.003
21	Mv-3-*O*-glc-8-ethyl-catechin 1	0.002	0.001	0.005	0.006	0.006	0.005	0.006	0.010	0.012	0.007	0.005	0.008	0.006	0.007	0.007	0.004
22	Mv-3-*O*-glc-8-ethyl-catechin 2	0.003	0.002	0.006	0.006	0.006	0.007	0.007	0.011	0.013	0.008	0.006	0.008	0.007	0.008	0.008	0.006
23	Mv-3-*O*-glc-8-ethyl-epicatechin	0.003	0.002	0.007	0.009	0.009	0.010	0.010	0.014	0.019	0.012	0.009	0.012	0.010	0.010	0.008	0.005
24	Mv-3-*O*-(6-*p*-coum)-glc *cis*	0.902	0.565	0.859	0.629	0.891	0.906	0.708	0.000	1.026	0.625	0.420	0.627	0.351	0.469	0.585	0.231
25	Mv-3-*O*-(6-*p*-coum)-glc *trans*	35.781	28.241	64.882	89.466	62.644	71.024	58.141	0.037	67.879	40.303	35.370	48.138	33.761	41.772	36.616	21.317
26	Mv-3-*O*-glc-4-vinylphenol	0.004	0.006	0.071	0.103	0.079	0.145	0.179	0.002	0.458	0.334	0.250	0.287	0.177	0.329	0.313	0.266

continued

Table S2. Anthocyanin derivatives concentrations determined by HPLC-DAD-ESI(+)-MS/MS in red wine samples from Mendavia 2018, expressed in mg of Mv-3-*O*-glc equiv./L.

Tank 13

#	Time (days)	0	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
14	Catechin-Mv-3-*O*-glc	0.072	0.056	0.103	0.111	0.124	0.154	0.152	0.199	0.145	0.097	-	0.066	0.058	0.071	0.130	0.071
15	Epicatechin-Mv-3-*O*-glc	0.022	0.018	0.027	0.035	0.031	0.041	0.042	0.046	0.037	0.038	-	0.025	0.016	0.026	0.050	0.018
16	Mv-3-*O*-glc-(epi)catechin	0.003	0.003	0.003	0.004	0.003	0.003	0.003	0.005	0.003	0.003	-	0.003	0.002	0.002	0.004	0.003
17	Mv-3-*O*-glc-A-catechin	0.002	0.003	0.003	0.003	0.002	0.003	0.002	0.005	0.003	0.002	-	0.002	0.001	0.001	0.002	0.002
18	Mv-3-*O*-glc-pyruvic	0.076	0.223	0.461	0.462	0.401	0.421	0.498	0.406	0.474	0.398	-	0.423	0.217	0.339	0.409	0.357
19	Mv-3-*O*-glc-acetaldehyde	0.289	0.408	0.969	1.227	0.816	0.654	1.196	1.031	1.303	1.743	-	2.273	0.728	1.712	0.926	0.651
20	Pyruvic acid derivative-vinyl-catechin-catechin	0.000	0.000	0.001	0.001	0.001	0.002	0.002	0.001	0.001	0.002	-	0.002	0.002	0.002	0.006	0.003
21	Mv-3-*O*-glc-8-ethyl-catechin 1	0.002	0.002	0.005	0.006	0.006	0.007	0.007	0.011	0.011	0.010	-	0.010	0.007	0.008	0.015	0.005
22	Mv-3-*O*-glc-8-ethyl-catechin 2	0.003	0.003	0.006	0.006	0.008	0.009	0.009	0.012	0.011	0.009	-	0.004	0.008	0.009	0.018	0.007
23	Mv-3-*O*-glc-8-ethyl-epicatechin	0.003	0.004	0.006	0.009	0.009	0.010	0.012	0.017	0.016	0.014	-	0.010	0.008	0.011	0.015	0.006
24	Mv-3-*O*-(6-*p*-coum)-glc *cis*	0.936	0.645	0.523	0.833	0.630	0.816	0.885	0.812	0.512	0.659	-	0.641	0.318	0.554	0.527	0.301
25	Mv-3-*O*-(6-*p*-coum)-glc *trans*	35.877	35.132	60.555	76.987	60.407	59.081	61.509	52.197	37.742	39.349	-	37.525	25.308	35.984	35.674	23.555
26	Mv-3-*O*-glc-4-vinylphenol	0.005	0.008	0.080	0.087	0.087	0.136	0.209	0.208	0.358	0.314	-	0.247	0.110	0.227	0.310	0.261

Tank 14

#	Time (days)	0	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
14	Catechin-Mv-3-*O*-glc	0.071	0.054	0.109	0.116	0.140	0.146	0.152	0.178	0.157	0.097	0.059	0.072	0.060	0.074	0.124	0.059
15	Epicatechin-Mv-3-*O*-glc	0.023	0.020	0.034	0.033	0.034	0.036	0.038	0.040	0.040	0.030	0.017	0.031	0.017	0.022	0.043	0.014
16	Mv-3-*O*-glc-(epi)catechin	0.003	0.003	0.004	0.004	0.003	0.003	0.003	0.003	0.005	0.003	0.002	0.003	0.002	0.001	0.003	0.002
17	Mv-3-*O*-glc-A-catechin	0.002	0.002	0.003	0.003	0.002	0.002	0.003	0.003	0.004	0.002	0.001	0.002	0.001	0.001	0.002	0.002
18	Mv-3-*O*-glc-pyruvic	0.076	0.214	0.400	0.454	0.429	0.420	0.434	0.404	0.471	0.406	0.238	0.404	0.225	0.338	0.406	0.308
19	Mv-3-*O*-glc-acetaldehyde	0.300	0.477	0.729	1.187	0.910	0.668	1.096	1.006	1.365	1.542	0.892	2.047	0.622	1.341	0.868	0.465
20	Pyruvic acid derivative-vinyl-catechin-catechin	0.000	0.000	0.001	0.002	0.002	0.002	0.001	0.002	0.002	0.002	0.001	0.002	0.002	0.002	0.007	0.003
21	Mv-3-*O*-glc-8-ethyl-catechin 1	0.002	0.002	0.005	0.005	0.006	0.006	0.007	0.010	0.013	0.008	0.005	0.010	0.006	0.007	0.015	0.004
22	Mv-3-*O*-glc-8-ethyl-catechin 2	0.003	0.003	0.006	0.007	0.008	0.007	0.008	0.012	0.013	0.010	0.006	0.010	0.008	0.008	0.018	0.006
23	Mv-3-*O*-glc-8-ethyl-epicatechin	0.003	0.003	0.008	0.008	0.009	0.009	0.011	0.014	0.019	0.013	0.007	0.008	0.010	0.010	0.014	0.004
24	Mv-3-*O*-(6-*p*-coum)-glc *cis*	0.913	0.652	0.963	0.956	0.798	0.721	0.757	0.764	0.753	0.632	0.266	0.635	0.372	0.484	0.580	0.196
25	Mv-3-*O*-(6-*p*-coum)-glc *trans*	37.526	40.617	69.293	79.827	62.702	57.786	60.716	53.098	44.296	37.959	26.707	33.999	25.500	34.115	36.852	15.953
26	Mv-3-*O*-glc-4-vinylphenol	0.005	0.007	0.082	0.080	0.091	0.132	0.166	0.191	0.376	0.341	0.132	0.239	0.106	0.241	0.292	0.138

Tank 15

#	Time (days)	0	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
14	Catechin-Mv-3-*O*-glc	0.054	0.051	0.086	0.113	0.136	0.171	0.152	0.197	0.136	0.102	0.050	0.070	0.057	0.067	0.118	0.070
15	Epicatechin-Mv-3-*O*-glc	0.016	0.018	0.025	0.031	0.037	0.048	0.038	0.049	0.034	0.034	0.012	0.029	0.016	0.020	0.044	0.014
16	Mv-3-*O*-glc-(epi)catechin	0.002	0.003	0.003	0.003	0.003	0.004	0.003	0.005	0.002	0.003	0.001	0.002	0.002	0.002	0.004	0.002
17	Mv-3-*O*-glc-A-catechin	0.002	0.002	0.003	0.002	0.003	0.004	0.003	0.004	0.003	0.002	0.001	0.002	0.001	0.001	0.002	0.001
18	Mv-3-*O*-glc-pyruvic	0.071	0.212	0.367	0.467	0.437	0.458	0.482	0.448	0.477	0.385	0.210	0.480	0.279	0.370	0.430	0.292
19	Mv-3-*O*-glc-acetaldehyde	0.257	0.473	0.976	1.035	0.797	0.759	1.104	0.726	1.196	1.369	0.993	1.778	0.894	1.415	0.806	0.378
20	Pyruvic acid derivative-vinyl-catechin-catechin	0.001	0.000	0.001	0.001	0.002	0.002	0.001	0.001	0.001	0.002	0.001	0.002	0.002	0.002	0.006	0.003
21	Mv-3-*O*-glc-8-ethyl-catechin 1	0.002	0.002	0.004	0.005	0.006	0.007	0.007	0.009	0.010	0.009	0.003	0.010	0.007	0.007	0.014	0.004
22	Mv-3-*O*-glc-8-ethyl-catechin 2	0.003	0.003	0.006	0.006	0.007	0.008	0.008	0.010	0.010	0.010	0.004	0.003	0.007	0.008	0.016	0.005
23	Mv-3-*O*-glc-8-ethyl-epicatechin	0.002	0.003	0.006	0.008	0.009	0.009	0.011	0.015	0.013	0.011	0.005	0.008	0.010	0.010	0.013	0.004
24	Mv-3-*O*-(6-*p*-coum)-glc *cis*	0.904	0.669	0.641	0.775	0.776	1.333	0.861	0.820	0.511	0.687	0.157	0.686	0.455	0.506	0.465	0.198
25	Mv-3-*O*-(6-*p*-coum)-glc *trans*	39.225	34.964	56.868	73.764	59.539	64.912	61.018	52.853	30.415	36.693	4.593	41.228	27.607	36.441	34.471	17.181
26	Mv-3-*O*-glc-4-vinylphenol	0.004	0.007	0.062	0.081	0.091	0.125	0.183	0.227	0.352	0.277	0.099	0.325	0.164	0.253	0.260	0.127

Tank 16

#	Time (days)	0	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
14	Catechin-Mv-3-*O*-glc	0.072	0.050	0.096	0.110	0.154	0.159	0.151	0.195	0.163	0.097	0.061	0.068	0.058	0.072	0.125	0.074
15	Epicatechin-Mv-3-*O*-glc	0.028	0.018	0.025	0.035	0.040	0.040	0.038	0.048	0.050	0.035	0.014	0.026	0.016	0.023	0.043	0.019
16	Mv-3-*O*-glc-(epi)catechin	0.002	0.003	0.003	0.002	0.004	0.004	0.004	0.005	0.005	0.003	0.001	0.003	0.002	0.002	0.004	0.003
17	Mv-3-*O*-glc-A-catechin	0.002	0.002	0.002	0.003	0.003	0.004	0.003	0.004	0.004	0.002	0.001	0.002	0.002	0.001	0.002	0.002
18	Mv-3-*O*-glc-pyruvic	0.080	0.206	0.362	0.441	0.452	0.443	0.448	0.462	0.481	0.386	0.224	0.437	0.253	0.366	0.287	0.387
19	Mv-3-*O*-glc-acetaldehyde	0.276	0.502	0.959	0.934	1.004	1.024	0.984	1.039	1.209	1.329	0.621	2.038	0.970	1.592	0.515	0.586
20	Pyruvic acid derivative-vinyl-catechin-catechin	0.001	0.000	0.001	0.001	0.001	0.001	0.001	0.002	0.003	0.002	0.001	0.003	0.002	0.003	0.007	0.004
21	Mv-3-*O*-glc-8-ethyl-catechin 1	0.002	0.002	0.004	0.005	0.007	0.007	0.007	0.009	0.014	0.009	0.004	0.010	0.008	0.008	0.013	0.006
22	Mv-3-*O*-glc-8-ethyl-catechin 2	0.002	0.003	0.005	0.006	0.009	0.007	0.008	0.012	0.014	0.010	0.005	0.004	0.008	0.008	0.015	0.007
23	Mv-3-*O*-glc-8-ethyl-epicatechin	0.003	0.003	0.007	0.008	0.011	0.010	0.011	0.018	0.019	0.013	0.007	0.011	0.009	0.013	0.014	0.006
24	Mv-3-*O*-(6-*p*-coum)-glc *cis*	0.798	0.637	0.717	0.821	0.720	1.040	0.893	1.004	0.961	0.718	0.299	0.765	0.545	0.595	0.408	0.348
25	Mv-3-*O*-(6-*p*-coum)-glc *trans*	36.231	30.364	62.208	75.388	73.757	60.870	61.529	60.932	51.635	34.933	16.877	37.789	27.478	36.792	30.733	29.251
26	Mv-3-*O*-glc-4-vinylphenol	0.004	0.006	0.085	0.107	0.094	0.120	0.166	0.245	0.389	0.270	0.115	0.260	0.145	0.238	0.235	0.236

Tank 17

#	Time (days)	0	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
14	Catechin-Mv-3-*O*-glc	0.057	0.053	0.091	0.124	0.156	0.139	0.141	0.162	0.152	0.090	0.051	0.063	0.051	0.071	0.121	0.068
15	Epicatechin-Mv-3-*O*-glc	0.014	0.016	0.021	0.032	0.042	0.029	0.032	0.035	0.037	0.032	0.014	0.024	0.012	0.022	0.036	0.017
16	Mv-3-*O*-glc-(epi)catechin	0.002	0.003	0.003	0.004	0.005	0.002	0.002	0.004	0.004	0.002	0.002	0.002	0.001	0.002	0.004	0.002
17	Mv-3-*O*-glc-A-catechin	0.001	0.002	0.003	0.003	0.003	0.002	0.002	0.002	0.002	0.002	0.001	0.001	0.001	0.001	0.002	0.002
18	Mv-3-*O*-glc-pyruvic	0.070	0.186	0.365	0.407	0.387	0.388	0.475	0.383	0.436	0.404	0.233	0.404	0.251	0.309	0.355	0.288
19	Mv-3-*O*-glc-acetaldehyde	0.298	0.402	0.772	1.046	0.692	0.959	1.066	0.845	0.977	1.012	0.990	1.173	0.402	0.968	0.562	0.382
20	Pyruvic acid derivative-vinyl-catechin-catechin	0.000	0.000	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.002	0.001	0.001	0.004	0.002
21	Mv-3-*O*-glc-8-ethyl-catechin 1	0.002	0.002	0.005	0.005	0.007	0.005	0.006	0.008	0.011	0.007	0.004	0.007	0.004	0.006	0.011	0.004
22	Mv-3-*O*-glc-8-ethyl-catechin 2	0.002	0.003	0.006	0.006	0.009	0.006	0.008	0.010	0.011	0.009	0.005	0.009	0.005	0.007	0.013	0.005
23	Mv-3-*O*-glc-8-ethyl-epicatechin	0.002	0.003	0.006	0.007	0.010	0.008	0.009	0.010	0.014	0.009	0.005	0.010	0.006	0.006	0.009	0.004
24	Mv-3-*O*-(6-*p*-coum)-glc *cis*	0.821	0.683	0.989	0.000	2.028	0.937	1.038	0.749	0.846	0.777	0.489	0.879	0.488	0.600	0.502	0.413
25	Mv-3-*O*-(6-*p*-coum)-glc *trans*	41.531	29.923	72.479	0.038	75.194	52.677	62.299	44.529	34.257	36.523	21.631	33.652	29.215	35.044	31.393	24.451
26	Mv-3-*O*-glc-4-vinylphenol	0.005	0.010	0.119	0.003	0.225	0.267	0.459	0.433	0.746	0.832	0.371	0.734	0.549	0.664	0.616	0.681

Tank 18

#	Time (days)	0	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
14	Catechin-Mv-3-*O*-glc	0.051	0.055	0.088	0.118	0.156	0.139	0.139	0.174	0.148	0.095	0.059	0.061	0.050	0.071	0.120	0.065
15	Epicatechin-Mv-3-*O*-glc	0.018	0.016	0.023	0.030	0.043	0.032	0.029	0.037	0.032	0.028	0.016	0.022	0.012	0.021	0.037	0.013
16	Mv-3-*O*-glc-(epi)catechin	0.003	0.003	0.003	0.003	0.004	0.003	0.003	0.003	0.003	0.003	0.002	0.003	0.001	0.002	0.004	0.002
17	Mv-3-*O*-glc-A-catechin	0.001	0.002	0.003	0.002	0.003	0.002	0.002	0.002	0.002	0.001	0.001	0.002	0.001	0.001	0.002	0.002
18	Mv-3-*O*-glc-pyruvic	0.066	0.193	0.329	0.386	0.401	0.390	0.467	0.408	0.485	0.418	0.239	0.423	0.250	0.320	0.376	0.317
19	Mv-3-*O*-glc-acetaldehyde	0.279	0.424	0.600	0.941	0.823	0.995	1.114	0.862	1.272	1.253	0.619	1.441	0.703	0.727	0.657	0.775
20	Pyruvic acid derivative-vinyl-catechin-catechin	0.001	0.000	0.001	0.001	0.002	0.001	0.001	0.001	0.001	0.002	0.001	0.002	0.001	0.002	0.006	0.003
21	Mv-3-*O*-glc-8-ethyl-catechin 1	0.002	0.002	0.005	0.005	0.008	0.005	0.006	0.008	0.009	0.008	0.004	0.008	0.005	0.006	0.010	0.004
22	Mv-3-*O*-glc-8-ethyl-catechin 2	0.002	0.003	0.006	0.005	0.009	0.007	0.008	0.010	0.011	0.008	0.006	0.009	0.005	0.007	0.013	0.006
23	Mv-3-*O*-glc-8-ethyl-epicatechin	0.002	0.003	0.006	0.006	0.009	0.007	0.009	0.012	0.012	0.009	0.006	0.004	0.006	0.006	0.009	0.004
24	Mv-3-*O*-(6-*p*-coum)-glc *cis*	0.488	0.641	0.983	0.852	1.647	0.879	0.878	0.030	0.733	0.779	0.545	0.812	0.485	0.646	0.453	0.323
25	Mv-3-*O*-(6-*p*-coum)-glc *trans*	41.554	34.965	69.092	74.885	76.637	50.417	56.259	0.000	34.408	37.273	24.617	37.610	24.239	33.950	27.906	18.910
26	Mv-3-*O*-glc-4-vinylphenol	0.005	0.012	0.114	0.164	0.239	0.247	0.410	0.000	0.765	0.786	0.366	0.710	0.451	0.617	0.414	0.584

continued

Table S2. Anthocyanin derivatives concentrations determined by HPLC-DAD-ESI(+)-MS/MS in red wine samples from Mendavia 2018, expressed in mg of Mv-3-*O*-glc equiv./L.

Tank 19

#	Time (days)	0	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
14	Catechin-Mv-3-*O*-glc	0.048	0.066	0.101	0.000	0.171	0.171	0.159	0.184	0.168	0.099	0.068	0.089	0.061	0.089	0.151	0.083
15	Epicatechin-Mv-3-*O*-glc	0.014	0.019	0.027	0.000	0.041	0.040	0.032	0.043	0.035	0.026	0.021	0.030	0.016	0.024	0.047	0.023
16	Mv-3-*O*-glc-(epi)catechin	0.002	0.003	0.004	0.000	0.005	0.004	0.004	0.004	0.004	0.003	0.002	0.002	0.001	0.002	0.004	0.002
17	Mv-3-*O*-glc-A-catechin	0.001	0.002	0.003	0.000	0.003	0.003	0.002	0.002	0.003	0.001	0.001	0.002	0.001	0.001	0.002	0.001
18	Mv-3-*O*-glc-pyruvic	0.062	0.234	0.337	0.000	0.380	0.453	0.457	0.445	0.445	0.377	0.279	0.409	0.174	0.276	0.403	0.313
19	Mv-3-*O*-glc-acetaldehyde	0.246	0.432	0.702	0.000	0.734	0.829	0.993	0.998	0.987	1.212	1.292	1.928	0.448	0.822	0.792	0.543
20	Pyruvic acid derivative-vinyl-catechin-catechin	0.000	0.000	0.001	0.000	0.002	0.001	0.001	0.002	0.002	0.002	0.002	0.002	0.001	0.002	0.006	0.003
21	Mv-3-*O*-glc-8-ethyl-catechin 1	0.001	0.002	0.004	0.000	0.007	0.006	0.005	0.009	0.010	0.006	0.005	0.009	0.005	0.006	0.014	0.005
22	Mv-3-*O*-glc-8-ethyl-catechin 2	0.002	0.004	0.006	0.000	0.008	0.007	0.007	0.009	0.011	0.007	0.006	0.010	0.006	0.007	0.015	0.006
23	Mv-3-*O*-glc-8-ethyl-epicatechin	0.001	0.003	0.007	0.000	0.009	0.008	0.007	0.011	0.014	0.009	0.007	0.006	0.007	0.007	0.012	0.004
24	Mv-3-*O*-(6-*p*-coum)-glc *cis*	0.674	0.892	0.615	0.972	1.752	0.944	0.898	0.770	0.742	0.000	0.585	0.806	0.490	0.742	0.676	0.588
25	Mv-3-*O*-(6-*p*-coum)-glc *trans*	37.807	40.828	71.528	75.030	71.872	65.998	59.859	51.006	39.734	0.000	30.396	45.721	28.069	38.888	42.868	31.891
26	Mv-3-*O*-glc-4-vinylphenol	0.004	0.012	0.113	0.142	0.182	0.299	0.364	0.448	0.625	0.000	0.401	0.683	0.303	0.480	0.702	0.665

Tank 20

#	Time (days)	0	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
14	Catechin-Mv-3-*O*-glc	0.054	0.056	0.086	0.106	0.165	0.156	0.130	-	0.149	0.097	0.047	0.056	0.051	0.077	0.125	0.066
15	Epicatechin-Mv-3-*O*-glc	0.015	0.018	0.023	0.027	0.041	0.038	0.031	-	0.035	0.028	0.011	0.017	0.013	0.023	0.039	0.014
16	Mv-3-*O*-glc-(epi)catechin	0.002	0.003	0.004	0.004	0.004	0.004	0.003	-	0.004	0.002	0.001	0.002	0.002	0.002	0.004	0.002
17	Mv-3-*O*-glc-A-catechin	0.001	0.002	0.003	0.002	0.004	0.004	0.002	-	0.003	0.002	0.001	0.001	0.001	0.001	0.002	0.001
18	Mv-3-*O*-glc-pyruvic	0.063	0.178	0.327	0.413	0.399	0.450	0.459	-	0.413	0.401	0.226	0.388	0.180	0.322	0.412	0.315
19	Mv-3-*O*-glc-acetaldehyde	0.238	0.428	0.734	1.073	0.879	0.965	1.055	-	0.879	1.072	0.801	1.880	0.960	0.689	0.704	0.504
20	Pyruvic acid derivative-vinyl-catechin-catechin	0.000	0.000	0.001	0.002	0.001	0.001	0.001	-	0.002	0.002	0.001	0.002	0.001	0.002	0.007	0.003
21	Mv-3-*O*-glc-8-ethyl-catechin 1	0.002	0.002	0.005	0.005	0.008	0.008	0.005	-	0.011	0.006	0.003	0.008	0.005	0.007	0.013	0.004
22	Mv-3-*O*-glc-8-ethyl-catechin 2	0.003	0.004	0.006	0.005	0.009	0.009	0.007	-	0.011	0.007	0.004	0.008	0.006	0.008	0.015	0.005
23	Mv-3-*O*-glc-8-ethyl-epicatechin	0.003	0.003	0.005	0.006	0.010	0.009	0.008	-	0.013	0.009	0.005	0.010	0.007	0.008	0.011	0.004
24	Mv-3-*O*-(6-*p*-coum)-glc *cis*	0.548	0.729	0.947	0.030	1.909	1.743	0.767	-	0.744	0.826	0.351	0.785	0.484	0.743	0.685	0.384
25	Mv-3-*O*-(6-*p*-coum)-glc *trans*	42.856	38.871	62.551	0.000	80.157	71.934	58.289	-	38.413	37.345	15.345	32.415	26.096	41.485	41.055	19.973
26	Mv-3-*O*-glc-4-vinylphenol	0.005	0.010	0.102	0.002	0.213	0.286	0.388	-	0.651	0.710	0.337	0.647	0.349	0.610	0.669	0.585

Tank 21

#	Time (days)	0	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
14	Catechin-Mv-3-*O*-glc	0.051	0.046	0.077	0.132	0.163	0.141	0.144	0.183	0.155	0.090	0.058	0.059	0.041	0.072	0.120	0.066
15	Epicatechin-Mv-3-*O*-glc	0.015	0.014	0.019	0.037	0.044	0.029	0.032	0.041	0.043	0.028	0.017	0.027	0.012	0.021	0.036	0.016
16	Mv-3-*O*-glc-(epi)catechin	0.002	0.003	0.003	0.003	0.005	0.003	0.003	0.004	0.005	0.002	0.002	0.002	0.002	0.001	0.004	0.002
17	Mv-3-*O*-glc-A-catechin	0.002	0.003	0.003	0.002	0.003	0.003	0.002	0.003	0.003	0.002	0.001	0.001	0.001	0.001	0.002	0.001
18	Mv-3-*O*-glc-pyruvic	0.070	0.178	0.336	0.460	0.407	0.362	0.462	0.363	0.434	0.397	0.233	0.386	0.169	0.299	0.321	0.275
19	Mv-3-*O*-glc-acetaldehyde	0.228	0.428	0.872	1.324	1.017	0.698	1.081	0.856	1.234	1.369	1.336	1.622	0.990	0.892	0.511	0.493
20	Pyruvic acid derivative-vinyl-catechin-catechin	0.000	0.000	0.001	0.001	0.002	0.002	0.001	0.002	0.003	0.003	0.002	0.002	0.001	0.002	0.005	0.002
21	Mv-3-*O*-glc-8-ethyl-catechin 1	0.002	0.002	0.004	0.005	0.008	0.006	0.006	0.010	0.012	0.008	0.006	0.009	0.006	0.007	0.012	0.004
22	Mv-3-*O*-glc-8-ethyl-catechin 2	0.003	0.003	0.006	0.006	0.010	0.007	0.008	0.011	0.014	0.009	0.006	0.003	0.007	0.008	0.015	0.006
23	Mv-3-*O*-glc-8-ethyl-epicatechin	0.002	0.003	0.005	0.007	0.009	0.008	0.009	0.013	0.016	0.009	0.007	0.004	0.007	0.007	0.010	0.003
24	Mv-3-*O*-(6-*p*-coum)-glc *cis*	0.901	0.589	0.830	0.957	1.703	0.849	0.839	0.764	0.863	0.773	0.577	0.734	0.454	0.633	0.527	0.313
25	Mv-3-*O*-(6-*p*-coum)-glc *trans*	42.732	21.637	67.054	78.658	74.987	51.382	57.381	45.904	48.339	40.746	30.480	39.390	26.451	39.729	31.755	20.550
26	Mv-3-*O*-glc-4-vinylphenol	0.004	0.005	0.105	0.182	0.172	0.165	0.283	0.293	0.612	0.581	0.351	0.551	0.276	0.526	0.425	0.484

Tank 22

#	Time (days)	0	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
14	Catechin-Mv-3-*O*-glc	0.049	0.052	0.093	0.111	0.161	0.155	0.135	0.181	0.146	0.101	0.055	0.062	0.048	0.072	0.119	0.068
15	Epicatechin-Mv-3-*O*-glc	0.016	0.013	0.022	0.028	0.040	0.035	0.030	0.040	0.036	0.034	0.015	0.025	0.012	0.020	0.039	0.018
16	Mv-3-*O*-glc-(epi)catechin	0.002	0.003	0.003	0.003	0.004	0.004	0.003	0.004	0.004	0.003	0.002	0.002	0.001	0.002	0.005	0.002
17	Mv-3-*O*-glc-A-catechin	0.001	0.002	0.003	0.002	0.003	0.003	0.002	0.002	0.003	0.002	0.001	0.001	0.001	0.001	0.003	0.001
18	Mv-3-*O*-glc-pyruvic	0.063	0.136	0.346	0.450	0.373	0.425	0.473	0.375	0.426	0.335	0.253	0.431	0.200	0.301	0.393	0.303
19	Mv-3-*O*-glc-acetaldehyde	0.195	0.381	0.685	1.472	0.948	1.031	1.161	0.935	1.183	1.118	1.151	2.097	0.482	1.096	0.842	0.579
20	Pyruvic acid derivative-vinyl-catechin-catechin	0.000	0.001	0.001	0.001	0.002	0.002	0.002	0.001	0.002	0.002	0.002	0.002	0.002	0.002	0.008	0.003
21	Mv-3-*O*-glc-8-ethyl-catechin 1	0.002	0.002	0.004	0.006	0.009	0.007	0.006	0.009	0.012	0.010	0.006	0.010	0.005	0.007	0.014	0.005
22	Mv-3-*O*-glc-8-ethyl-catechin 2	0.003	0.004	0.006	0.006	0.010	0.009	0.007	0.011	0.012	0.010	0.006	0.004	0.006	0.008	0.016	0.006
23	Mv-3-*O*-glc-8-ethyl-epicatechin	0.002	0.002	0.006	0.007	0.009	0.009	0.010	0.013	0.014	0.009	0.007	0.007	0.006	0.008	0.012	0.003
24	Mv-3-*O*-(6-*p*-coum)-glc *cis*	0.700	0.662	0.901	1.106	1.496	0.818	0.805	0.832	0.708	0.809	0.594	0.794	0.429	0.678	0.662	0.397
25	Mv-3-*O*-(6-*p*-coum)-glc *trans*	46.329	35.451	69.438	81.846	70.105	64.342	55.486	47.662	38.141	38.106	26.130	45.286	27.887	39.355	37.844	25.224
26	Mv-3-*O*-glc-4-vinylphenol	0.004	0.007	0.148	0.180	0.153	0.224	0.301	0.306	0.567	0.465	0.334	0.602	0.305	0.495	0.565	0.511

Tank 23

#	Time (days)	0	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
14	Catechin-Mv-3-*O*-glc	0.055	0.065	0.089	0.109	0.159	0.143	0.145	0.167	0.146	0.089	0.056	0.094	0.047	0.069	0.130	0.062
15	Epicatechin-Mv-3-*O*-glc	0.016	0.019	0.022	0.027	0.038	0.033	0.030	0.038	0.033	0.026	0.014	0.019	0.012	0.021	0.038	0.016
16	Mv-3-*O*-glc-(epi)catechin	0.002	0.003	0.004	0.003	0.005	0.004	0.003	0.004	0.004	0.003	0.002	0.002	0.001	0.002	0.004	0.002
17	Mv-3-*O*-glc-A-catechin	0.002	0.003	0.003	0.002	0.003	0.002	0.002	0.004	0.003	0.002	0.001	0.001	0.001	0.001	0.003	0.001
18	Mv-3-*O*-glc-pyruvic	0.063	0.144	0.363	0.394	0.410	0.436	0.459	0.361	0.405	0.384	0.208	0.358	0.206	0.307	0.408	0.335
19	Mv-3-*O*-glc-acetaldehyde	0.212	0.373	0.775	1.232	0.979	1.019	1.106	0.896	1.152	1.562	1.196	2.063	1.016	1.346	0.894	0.809
20	Pyruvic acid derivative-vinyl-catechin-catechin	0.000	0.000	0.002	0.002	0.002	0.002	0.002	0.002	0.003	0.003	0.002	0.003	0.002	0.003	0.009	0.004
21	Mv-3-*O*-glc-8-ethyl-catechin 1	0.002	0.002	0.005	0.005	0.009	0.007	0.006	0.009	0.011	0.010	0.005	0.008	0.006	0.007	0.015	0.006
22	Mv-3-*O*-glc-8-ethyl-catechin 2	0.003	0.003	0.006	0.007	0.009	0.008	0.008	0.010	0.011	0.009	0.006	0.003	0.007	0.009	0.017	0.007
23	Mv-3-*O*-glc-8-ethyl-epicatechin	0.002	0.003	0.006	0.008	0.010	0.009	0.010	0.011	0.014	0.011	0.007	0.003	0.007	0.008	0.012	0.004
24	Mv-3-*O*-(6-*p*-coum)-glc *cis*	0.797	0.790	0.842	0.882	1.776	1.280	0.910	0.703	0.676	0.000	0.480	0.573	0.426	0.725	0.623	0.369
25	Mv-3-*O*-(6-*p*-coum)-glc *trans*	47.749	38.931	70.144	74.982	74.955	67.286	57.173	41.417	31.882	0.000	20.790	31.573	26.975	36.698	36.159	24.670
26	Mv-3-*O*-glc-4-vinylphenol	0.005	0.009	0.128	0.167	0.203	0.255	0.338	0.321	0.542	0.000	0.287	0.466	0.329	0.450	0.552	0.615

Tank 24

#	Time (days)	0	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
14	Catechin-Mv-3-*O*-glc	0.048	0.060	0.095	0.111	0.149	0.144	0.138	0.179	0.143	0.103	0.059	-	0.051	0.070	0.119	0.072
15	Epicatechin-Mv-3-*O*-glc	0.015	0.017	0.022	0.030	0.034	0.031	0.028	0.041	0.032	0.034	0.016	-	0.012	0.018	0.036	0.017
16	Mv-3-*O*-glc-(epi)catechin	0.002	0.003	0.003	0.003	0.004	0.003	0.003	0.005	0.004	0.003	0.002	-	0.002	0.002	0.004	0.002
17	Mv-3-*O*-glc-A-catechin	0.001	0.003	0.003	0.002	0.003	0.002	0.002	0.003	0.003	0.002	0.001	-	0.001	0.001	0.003	0.002
18	Mv-3-*O*-glc-pyruvic	0.088	0.253	0.348	0.417	0.399	0.345	0.431	0.334	0.420	0.373	0.204	-	0.223	0.270	0.399	0.309
19	Mv-3-*O*-glc-acetaldehyde	0.262	0.587	1.014	1.252	0.875	1.003	1.107	0.877	1.319	1.298	0.930	-	0.951	1.104	0.828	0.654
20	Pyruvic acid derivative-vinyl-catechin-catechin	0.001	0.001	0.002	0.001	0.002	0.001	0.001	0.003	0.002	0.003	0.002	-	0.002	0.003	0.009	0.004
21	Mv-3-*O*-glc-8-ethyl-catechin 1	0.001	0.003	0.006	0.006	0.008	0.007	0.006	0.010	0.011	0.009	0.005	-	0.006	0.007	0.015	0.006
22	Mv-3-*O*-glc-8-ethyl-catechin 2	0.003	0.004	0.007	0.007	0.009	0.007	0.007	0.013	0.012	0.010	0.006	-	0.007	0.009	0.017	0.008
23	Mv-3-*O*-glc-8-ethyl-epicatechin	0.002	0.004	0.007	0.008	0.009	0.009	0.009	0.012	0.013	0.010	0.007	-	0.008	0.009	0.012	0.004
24	Mv-3-*O*-(6-*p*-coum)-glc *cis*	0.875	0.667	0.894	0.917	1.134	1.021	0.832	0.807	0.722	0.997	0.466	-	0.605	0.601	0.624	0.452
25	Mv-3-*O*-(6-*p*-coum)-glc *trans*	34.690	38.690	55.406	75.037	67.760	52.009	50.494	42.527	32.937	42.161	18.526	-	31.786	37.283	38.676	27.323
26	Mv-3-*O*-glc-4-vinylphenol	0.004	0.013	0.066	0.129	0.179	0.185	0.311	0.303	0.590	0.632	0.324	-	0.422	0.561	0.656	0.623

Table S3. Anthocyanin derivatives concentrations determined by HPLC-DAD-ESI(+)-MS/MS in red wine samples from Mendavia 2018, expressed in mg of Mv-3-*O*-glc equiv./L.

Tank 01

#	Time (days)	0	6	10	20	61
27	(Epi)gallocatechin-Mv-3-*O*-glc-A-(epi)catechin 1	<LQ	0.002	0.001	<LQ	<LQ
28	(Epi)catechin-Mv-3-*O*-glc-A-(epi)catechin 1	<LQ	0.001	0.001	<LQ	<LQ
29	(Epi)catechin-Mv-3-*O*-glc-A-(epi)catechin 2	<LQ	0.001	0.000	<LQ	<LQ
30	(Epi)catechin-A-(epi)catechin-Mv-3-*O*-glc	<LD	<LQ	<LD	<LQ	<LD
31	Mv-3-*O*-glc-(epi)catechin-A-(epi)catechin	<LD	0.001	<LD	<LQ	<LQ
32	Catechin-Mv-3-*O*-(6-*p*-coum)-glc	0.014	0.040	0.037	0.015	0.012
33	Epicatechin-Mv-3-*O*-(6-*p*-coum)-glc	0.004	0.004	0.005	0.001	0.002
34	Mv-3-*O*-(6-*p*-coum)-glc-acetaldehyde	0.142	0.372	<LD	0.242	0.048
35	Mv-3-*O*-(6-*p*-coum)-glc-pyruvic	0.022	0.100	0.082	0.042	0.036
36	Mv-3-*O*-(6-*p*-coum)-glc-8-ethyl-(epi)catechin 1	0.004	0.012	<LD	0.007	0.003
37	Mv-3-*O*-(6-*p*-coum)-glc-8-ethyl-(epi)catechin 2	0.001	0.004	<LD	0.002	0.002
38	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylcatechin	<LD	<LQ	<LD	<LD	<LD
39	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylepicatechin	<LD	<LQ	<LD	<LD	<LQ
40	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylphenol	0.003	0.095	<LD	0.099	0.001

Tank 02

#	Time (days)	0	6	10	20	61
27	(Epi)gallocatechin-Mv-3-*O*-glc-A-(epi)catechin 1	<LQ	0.001	0.001	<LQ	<LQ
28	(Epi)catechin-Mv-3-*O*-glc-A-(epi)catechin 1	<LQ	0.001	<LQ	<LQ	<LQ
29	(Epi)catechin-Mv-3-*O*-glc-A-(epi)catechin 2	<LQ	0.001	<LQ	<LQ	<LQ
30	(Epi)catechin-A-(epi)catechin-Mv-3-*O*-glc	<LQ	<LD	<LQ	<LD	<LD
31	Mv-3-*O*-glc-(epi)catechin-A-(epi)catechin	<LQ	<LD	<LQ	<LQ	<LQ
32	Catechin-Mv-3-*O*-(6-*p*-coum)-glc	0.017	0.038	0.037	0.018	0.011
33	Epicatechin-Mv-3-*O*-(6-*p*-coum)-glc	0.003	0.004	0.002	0.002	0.002
34	Mv-3-*O*-(6-*p*-coum)-glc-acetaldehyde	0.141	0.387	0.339	0.484	0.007
35	Mv-3-*O*-(6-*p*-coum)-glc-pyruvic	0.017	0.113	0.088	0.052	0.044
36	Mv-3-*O*-(6-*p*-coum)-glc-8-ethyl-(epi)catechin 1	0.004	0.010	0.011	0.008	0.004
37	Mv-3-*O*-(6-*p*-coum)-glc-8-ethyl-(epi)catechin 2	0.001	0.003	0.003	0.003	0.002
38	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylcatechin	<LD	0.001	<LQ	<LD	<LD
39	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylepicatechin	<LD	<LD	<LD	<LQ	0.002
40	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylphenol	<LQ	0.115	0.131	0.101	0.001

Tank 03

#	Time (days)	0	6	10	20	61
27	(Epi)gallocatechin-Mv-3-*O*-glc-A-(epi)catechin 1	<LQ	0.001	0.001	<LQ	<LQ
28	(Epi)catechin-Mv-3-*O*-glc-A-(epi)catechin 1	<LQ	0.001	0.001	<LQ	<LQ
29	(Epi)catechin-Mv-3-*O*-glc-A-(epi)catechin 2	<LQ	<LQ	0.000	<LQ	<LQ
30	(Epi)catechin-A-(epi)catechin-Mv-3-*O*-glc	<LD	<LQ	<LD	<LD	<LD
31	Mv-3-*O*-glc-(epi)catechin-A-(epi)catechin	<LD	<LD	<LQ	<LQ	<LQ
32	Catechin-Mv-3-*O*-(6-*p*-coum)-glc	0.017	0.043	0.061	0.016	0.017
33	Epicatechin-Mv-3-*O*-(6-*p*-coum)-glc	0.003	0.006	0.007	0.002	0.002
34	Mv-3-*O*-(6-*p*-coum)-glc-acetaldehyde	0.148	0.425	0.513	0.388	0.005
35	Mv-3-*O*-(6-*p*-coum)-glc-pyruvic	0.022	0.138	0.152	0.049	0.051
36	Mv-3-*O*-(6-*p*-coum)-glc-8-ethyl-(epi)catechin 1	0.005	0.011	0.017	0.007	0.005
37	Mv-3-*O*-(6-*p*-coum)-glc-8-ethyl-(epi)catechin 2	0.001	0.004	0.003	0.002	0.002
38	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylcatechin	<LD	<LD	<LD	<LD	<LD
39	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylepicatechin	<LD	<LD	<LD	<LQ	0.001
40	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylphenol	0.003	0.146	0.213	0.101	0.007

Tank 04

#	Time (days)	0	6	10	20	61
27	(Epi)gallocatechin-Mv-3-*O*-glc-A-(epi)catechin 1	<LQ	0.001	0.001	<LQ	<LQ
28	(Epi)catechin-Mv-3-*O*-glc-A-(epi)catechin 1	<LQ	0.001	0.001	<LQ	<LQ
29	(Epi)catechin-Mv-3-*O*-glc-A-(epi)catechin 2	<LQ	0.001	0.000	<LQ	<LQ
30	(Epi)catechin-A-(epi)catechin-Mv-3-*O*-glc	<LD	<LD	<LD	<LD	<LD
31	Mv-3-*O*-glc-(epi)catechin-A-(epi)catechin	<LD	0.001	<LQ	<LQ	<LQ
32	Catechin-Mv-3-*O*-(6-*p*-coum)-glc	0.011	0.051	0.041	0.017	0.011
33	Epicatechin-Mv-3-*O*-(6-*p*-coum)-glc	0.003	0.004	0.004	0.003	0.002
34	Mv-3-*O*-(6-*p*-coum)-glc-acetaldehyde	0.096	0.449	0.402	0.530	0.009
35	Mv-3-*O*-(6-*p*-coum)-glc-pyruvic	0.018	0.121	0.100	0.047	0.038
36	Mv-3-*O*-(6-*p*-coum)-glc-8-ethyl-(epi)catechin 1	0.004	0.013	0.016	0.009	0.005
37	Mv-3-*O*-(6-*p*-coum)-glc-8-ethyl-(epi)catechin 2	0.001	0.004	0.004	0.003	0.002
38	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylcatechin	<LQ	<LD	<LD	<LD	<LD
39	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylepicatechin	<LD	<LD	<LD	<LD	0.002
40	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylphenol	0.001	0.119	0.122	0.090	0.001

Tank 05

#	Time (days)	0	6	10	20	61
27	(Epi)gallocatechin-Mv-3-*O*-glc-A-(epi)catechin 1	<LQ	0.001	0.001	<LQ	<LQ
28	(Epi)catechin-Mv-3-*O*-glc-A-(epi)catechin 1	<LQ	0.001	0.001	<LQ	<LQ
29	(Epi)catechin-Mv-3-*O*-glc-A-(epi)catechin 2	<LQ	0.001	0.001	<LQ	<LQ
30	(Epi)catechin-A-(epi)catechin-Mv-3-*O*-glc	<LD	<LQ	<LQ	<LQ	<LQ
31	Mv-3-*O*-glc-(epi)catechin-A-(epi)catechin	<LQ	0.001	<LQ	<LQ	<LQ
32	Catechin-Mv-3-*O*-(6-*p*-coum)-glc	0.017	0.044	0.049	0.016	0.012
33	Epicatechin-Mv-3-*O*-(6-*p*-coum)-glc	0.003	0.004	0.002	0.002	0.002
34	Mv-3-*O*-(6-*p*-coum)-glc-acetaldehyde	0.118	0.408	0.412	0.261	0.000
35	Mv-3-*O*-(6-*p*-coum)-glc-pyruvic	0.021	0.117	0.118	0.038	0.031
36	Mv-3-*O*-(6-*p*-coum)-glc-8-ethyl-(epi)catechin 1	0.004	0.012	0.015	0.009	0.004
37	Mv-3-*O*-(6-*p*-coum)-glc-8-ethyl-(epi)catechin 2	0.001	0.005	0.006	0.003	0.002
38	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylcatechin	<LD	<LD	<LD	<LD	<LD
39	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylepicatechin	<LD	<LD	<LD	<LQ	0.001
40	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylphenol	0.002	0.094	0.150	0.069	0.002

Tank 06

#	Time (days)	0	6	10	20	61
27	(Epi)gallocatechin-Mv-3-*O*-glc-A-(epi)catechin 1	<LQ	0.001	0.001	<LD	<LQ
28	(Epi)catechin-Mv-3-*O*-glc-A-(epi)catechin 1	<LQ	0.001	0.002	<LD	<LQ
29	(Epi)catechin-Mv-3-*O*-glc-A-(epi)catechin 2	<LQ	0.001	0.001	<LD	<LQ
30	(Epi)catechin-A-(epi)catechin-Mv-3-*O*-glc	<LQ	<LQ	<LQ	<LD	<LQ
31	Mv-3-*O*-glc-(epi)catechin-A-(epi)catechin	<LQ	0.001	<LQ	<LD	<LQ
32	Catechin-Mv-3-*O*-(6-*p*-coum)-glc	0.018	0.039	0.050	<LD	0.013
33	Epicatechin-Mv-3-*O*-(6-*p*-coum)-glc	0.003	0.003	0.002	<LD	0.002
34	Mv-3-*O*-(6-*p*-coum)-glc-acetaldehyde	0.124	0.377	0.435	<LD	0.011
35	Mv-3-*O*-(6-*p*-coum)-glc-pyruvic	0.020	0.116	0.120	<LD	0.048
36	Mv-3-*O*-(6-*p*-coum)-glc-8-ethyl-(epi)catechin 1	0.004	0.011	0.018	<LD	0.005
37	Mv-3-*O*-(6-*p*-coum)-glc-8-ethyl-(epi)catechin 2	0.001	0.004	0.005	<LD	0.003
38	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylcatechin	<LD	0.001	<LD	<LD	<LD
39	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylepicatechin	<LD	<LD	<LD	<LD	0.002
40	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylphenol	0.003	0.088	0.134	<LD	0.004

Tank 07

#	Time (days)	0	6	10	20	61
27	(Epi)gallocatechin-Mv-3-*O*-glc-A-(epi)catechin 1	<LQ	0.001	0.001	<LQ	<LQ
28	(Epi)catechin-Mv-3-*O*-glc-A-(epi)catechin 1	<LQ	0.002	0.002	<LQ	<LQ
29	(Epi)catechin-Mv-3-*O*-glc-A-(epi)catechin 2	<LQ	0.001	0.001	<LQ	<LQ
30	(Epi)catechin-A-(epi)catechin-Mv-3-*O*-glc	<LQ	<LQ	<LQ	<LQ	<LQ
31	Mv-3-*O*-glc-(epi)catechin-A-(epi)catechin	<LQ	0.001	<LQ	<LQ	<LQ
32	Catechin-Mv-3-*O*-(6-*p*-coum)-glc	0.019	0.043	0.056	0.017	0.013
33	Epicatechin-Mv-3-*O*-(6-*p*-coum)-glc	0.002	0.005	0.005	0.001	0.002
34	Mv-3-*O*-(6-*p*-coum)-glc-acetaldehyde	0.136	0.343	0.477	0.423	0.006
35	Mv-3-*O*-(6-*p*-coum)-glc-pyruvic	0.023	0.103	0.130	0.047	0.038
36	Mv-3-*O*-(6-*p*-coum)-glc-8-ethyl-(epi)catechin 1	0.005	0.011	0.017	0.009	0.005
37	Mv-3-*O*-(6-*p*-coum)-glc-8-ethyl-(epi)catechin 2	0.001	0.004	0.007	0.003	0.003
38	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylcatechin	<LD	0.001	<LQ	<LQ	<LD
39	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylepicatechin	<LD	<LQ	<LQ	<LQ	0.002
40	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylphenol	0.002	0.084	0.136	0.098	0.003

Tank 08

#	Time (days)	0	6	10	20	61
27	(Epi)gallocatechin-Mv-3-*O*-glc-A-(epi)catechin 1	<LQ	0.001	0.001	<LQ	<LQ
28	(Epi)catechin-Mv-3-*O*-glc-A-(epi)catechin 1	<LQ	0.001	0.001	<LQ	<LQ
29	(Epi)catechin-Mv-3-*O*-glc-A-(epi)catechin 2	<LQ	<LQ	<LQ	<LQ	<LQ
30	(Epi)catechin-A-(epi)catechin-Mv-3-*O*-glc	<LD	<LQ	<LQ	<LD	<LQ
31	Mv-3-*O*-glc-(epi)catechin-A-(epi)catechin	<LD	0.001	0.001	<LQ	<LQ
32	Catechin-Mv-3-*O*-(6-*p*-coum)-glc	0.013	0.044	0.049	0.015	0.016
33	Epicatechin-Mv-3-*O*-(6-*p*-coum)-glc	0.002	0.004	0.003	0.001	0.002
34	Mv-3-*O*-(6-*p*-coum)-glc-acetaldehyde	0.101	0.391	0.483	0.438	0.010
35	Mv-3-*O*-(6-*p*-coum)-glc-pyruvic	0.017	0.128	0.132	0.044	0.048
36	Mv-3-*O*-(6-*p*-coum)-glc-8-ethyl-(epi)catechin 1	0.003	0.011	0.016	0.009	0.007
37	Mv-3-*O*-(6-*p*-coum)-glc-8-ethyl-(epi)catechin 2	0.001	0.004	0.005	0.003	0.003
38	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylcatechin	<LQ	0.001	<LQ	<LQ	<LQ
39	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylepicatechin	<LD	0.001	<LQ	<LQ	0.002
40	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylphenol	0.001	0.116	0.141	0.090	0.006

Tank 09

#	Time (days)	0	6	10	20	61
27	(Epi)gallocatechin-Mv-3-*O*-glc-A-(epi)catechin 1	<LQ	0.001	0.001	<LQ	<LQ
28	(Epi)catechin-Mv-3-*O*-glc-A-(epi)catechin 1	<LQ	0.001	0.001	<LQ	<LQ
29	(Epi)catechin-Mv-3-*O*-glc-A-(epi)catechin 2	<LQ	0.001	0.001	<LQ	<LQ
30	(Epi)catechin-A-(epi)catechin-Mv-3-*O*-glc	<LD	<LQ	<LQ	<LD	<LD
31	Mv-3-*O*-glc-(epi)catechin-A-(epi)catechin	<LD	<LQ	<LQ	<LQ	<LQ
32	Catechin-Mv-3-*O*-(6-*p*-coum)-glc	0.011	0.043	0.049	0.017	0.014
33	Epicatechin-Mv-3-*O*-(6-*p*-coum)-glc	0.002	0.002	0.003	0.002	0.002
34	Mv-3-*O*-(6-*p*-coum)-glc-acetaldehyde	0.084	0.326	0.465	0.335	0.061
35	Mv-3-*O*-(6-*p*-coum)-glc-pyruvic	0.015	0.091	0.138	0.046	0.036
36	Mv-3-*O*-(6-*p*-coum)-glc-8-ethyl-(epi)catechin 1	0.003	0.012	0.018	0.010	0.006
37	Mv-3-*O*-(6-*p*-coum)-glc-8-ethyl-(epi)catechin 2	<LQ	0.005	0.006	0.003	0.003
38	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylcatechin	<LQ	<LQ	0.001	<LQ	<LQ
39	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylepicatechin	<LD	<LD	<LD	<LQ	0.002
40	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylphenol	<LQ	0.082	0.192	0.117	0.007

Tank 10

#	Time (days)	0	6	10	20	61
27	(Epi)gallocatechin-Mv-3-*O*-glc-A-(epi)catechin 1	<LQ	0.001	0.001	<LQ	<LQ
28	(Epi)catechin-Mv-3-*O*-glc-A-(epi)catechin 1	<LQ	0.001	0.001	<LQ	<LQ
29	(Epi)catechin-Mv-3-*O*-glc-A-(epi)catechin 2	<LQ	<LQ	0.000	<LQ	<LQ
30	(Epi)catechin-A-(epi)catechin-Mv-3-*O*-glc	<LD	<LQ	<LQ	<LD	<LD
31	Mv-3-*O*-glc-(epi)catechin-A-(epi)catechin	<LD	<LQ	<LQ	<LQ	<LQ
32	Catechin-Mv-3-*O*-(6-*p*-coum)-glc	0.014	0.038	0.054	0.015	0.011
33	Epicatechin-Mv-3-*O*-(6-*p*-coum)-glc	0.002	0.003	0.004	0.002	0.002
34	Mv-3-*O*-(6-*p*-coum)-glc-acetaldehyde	0.091	0.313	0.485	0.249	0.002
35	Mv-3-*O*-(6-*p*-coum)-glc-pyruvic	0.014	0.084	0.144	0.035	0.035
36	Mv-3-*O*-(6-*p*-coum)-glc-8-ethyl-(epi)catechin 1	0.004	0.011	0.019	0.008	0.005
37	Mv-3-*O*-(6-*p*-coum)-glc-8-ethyl-(epi)catechin 2	<LQ	0.004	0.007	0.003	0.003
38	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylcatechin	<LD	<LQ	0.000	<LQ	<LD
39	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylepicatechin	<LD	<LD	<LD	<LQ	0.002
40	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylphenol	0.001	0.071	0.209	0.095	0.004

continued

Table S3. Anthocyanin derivatives concentrations determined by HPLC-DAD-ESI(+)-MS/MS in red wine samples from Mendavia 2018, expressed in mg of Mv-3-*O*-glc equiv./L.

Tank 11

#	Time (days)	0	6	10	20	61
27	(Epi)gallocatechin-Mv-3-*O*-glc-A-(epi)catechin 1	<LQ	0.001	0.000	<LQ	<LQ
28	(Epi)catechin-Mv-3-*O*-glc-A-(epi)catechin 1	<LQ	0.001	0.000	<LQ	<LQ
29	(Epi)catechin-Mv-3-*O*-glc-A-(epi)catechin 2	<LQ	<LQ	<LQ	<LQ	<LQ
30	(Epi)catechin-A-(epi)catechin-Mv-3-*O*-glc	<LD	<LQ	<LD	<LQ	<LQ
31	Mv-3-*O*-glc-(epi)catechin-A-(epi)catechin	<LD	<LQ	<LQ	<LQ	<LQ
32	Catechin-Mv-3-*O*-(6-*p*-coum)-glc	0.015	0.032	0.045	0.015	0.018
33	Epicatechin-Mv-3-*O*-(6-*p*-coum)-glc	0.002	0.004	0.004	0.002	0.002
34	Mv-3-*O*-(6-*p*-coum)-glc-acetaldehyde	0.094	0.346	0.504	0.209	0.004
35	Mv-3-*O*-(6-*p*-coum)-glc-pyruvic	0.013	0.126	0.147	0.033	0.047
36	Mv-3-*O*-(6-*p*-coum)-glc-8-ethyl-(epi)catechin 1	0.003	0.012	0.018	0.008	0.008
37	Mv-3-*O*-(6-*p*-coum)-glc-8-ethyl-(epi)catechin 2	<LQ	0.005	0.006	0.002	0.004
38	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylcatechin	<LD	<LQ	<LQ	<LQ	<LD
39	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylepicatechin	<LD	<LD	<LQ	<LQ	0.002
40	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylphenol	0.001	0.089	0.178	0.068	0.015

Tank 12

#	Time (days)	0	6	10	20	61
27	(Epi)gallocatechin-Mv-3-*O*-glc-A-(epi)catechin 1	<LQ	0.001	0.001	<LQ	<LQ
28	(Epi)catechin-Mv-3-*O*-glc-A-(epi)catechin 1	<LQ	0.001	0.000	<LQ	<LQ
29	(Epi)catechin-Mv-3-*O*-glc-A-(epi)catechin 2	<LQ	<LQ	<LQ	<LQ	<LQ
30	(Epi)catechin-A-(epi)catechin-Mv-3-*O*-glc	<LD	<LQ	<LQ	<LD	<LQ
31	Mv-3-*O*-glc-(epi)catechin-A-(epi)catechin	<LD	<LQ	<LQ	<LQ	<LQ
32	Catechin-Mv-3-*O*-(6-*p*-coum)-glc	0.014	0.036	0.046	0.015	0.014
33	Epicatechin-Mv-3-*O*-(6-*p*-coum)-glc	0.002	0.003	0.003	0.001	0.002
34	Mv-3-*O*-(6-*p*-coum)-glc-acetaldehyde	0.093	0.324	0.423	0.343	0.003
35	Mv-3-*O*-(6-*p*-coum)-glc-pyruvic	0.013	0.091	0.131	0.043	0.041
36	Mv-3-*O*-(6-*p*-coum)-glc-8-ethyl-(epi)catechin 1	0.004	0.011	0.017	0.010	0.006
37	Mv-3-*O*-(6-*p*-coum)-glc-8-ethyl-(epi)catechin 2	0.001	0.004	0.007	0.003	0.003
38	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylcatechin	<LD	<LQ	<LQ	<LQ	<LQ
39	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylepicatechin	<LD	<LQ	<LD	<LQ	0.002
40	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylphenol	<LQ	0.079	0.156	0.080	0.005

Tank 13

#	Time (days)	0	6	10	20	61
27	(Epi)gallocatechin-Mv-3-*O*-glc-A-(epi)catechin 1	<LQ	0.002	0.001	-	<LQ
28	(Epi)catechin-Mv-3-*O*-glc-A-(epi)catechin 1	<LQ	0.001	0.001	-	<LQ
29	(Epi)catechin-Mv-3-*O*-glc-A-(epi)catechin 2	<LQ	0.001	0.001	-	<LQ
30	(Epi)catechin-A-(epi)catechin-Mv-3-*O*-glc	<LD	<LQ	<LQ	-	<LQ
31	Mv-3-*O*-glc-(epi)catechin-A-(epi)catechin	<LD	<LQ	0.001	-	<LQ
32	Catechin-Mv-3-*O*-(6-*p*-coum)-glc	0.015	0.039	0.048	-	0.017
33	Epicatechin-Mv-3-*O*-(6-*p*-coum)-glc	0.002	0.003	0.004	-	0.002
34	Mv-3-*O*-(6-*p*-coum)-glc-acetaldehyde	0.073	0.338	0.411	-	0.012
35	Mv-3-*O*-(6-*p*-coum)-glc-pyruvic	0.013	0.104	0.128	-	0.045
36	Mv-3-*O*-(6-*p*-coum)-glc-8-ethyl-(epi)catechin 1	0.003	0.013	0.017	-	0.009
37	Mv-3-*O*-(6-*p*-coum)-glc-8-ethyl-(epi)catechin 2	0.001	0.005	0.005	-	0.004
38	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylcatechin	<LD	0.001	<LQ	-	<LD
39	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylepicatechin	<LD	<LQ	<LQ	-	0.002
40	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylphenol	0.001	0.075	0.145	-	0.007

Tank 14

#	Time (days)	0	6	10	20	61
27	(Epi)gallocatechin-Mv-3-*O*-glc-A-(epi)catechin 1	<LQ	0.002	<LQ	<LQ	<LQ
28	(Epi)catechin-Mv-3-*O*-glc-A-(epi)catechin 1	<LQ	0.001	0.001	<LQ	<LQ
29	(Epi)catechin-Mv-3-*O*-glc-A-(epi)catechin 2	<LQ	0.001	<LQ	<LQ	<LQ
30	(Epi)catechin-A-(epi)catechin-Mv-3-*O*-glc	<LD	<LQ	<LD	<LQ	<LQ
31	Mv-3-*O*-glc-(epi)catechin-A-(epi)catechin	<LD	<LQ	<LQ	<LQ	<LQ
32	Catechin-Mv-3-*O*-(6-*p*-coum)-glc	0.013	0.035	0.041	0.017	0.015
33	Epicatechin-Mv-3-*O*-(6-*p*-coum)-glc	0.002	0.002	0.003	0.002	0.002
34	Mv-3-*O*-(6-*p*-coum)-glc-acetaldehyde	0.075	0.327	0.407	0.321	0.010
35	Mv-3-*O*-(6-*p*-coum)-glc-pyruvic	0.013	0.101	0.131	0.045	0.045
36	Mv-3-*O*-(6-*p*-coum)-glc-8-ethyl-(epi)catechin 1	0.003	0.011	0.016	0.010	0.007
37	Mv-3-*O*-(6-*p*-coum)-glc-8-ethyl-(epi)catechin 2	0.001	0.004	0.005	0.003	0.003
38	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylcatechin	<LD	<LD	<LQ	<LQ	<LD
39	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylepicatechin	<LD	<LD	<LD	<LQ	0.002
40	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylphenol	0.001	0.078	0.130	0.075	0.004

Tank 15

#	Time (days)	0	6	10	20	61
27	(Epi)gallocatechin-Mv-3-*O*-glc-A-(epi)catechin 1	<LQ	0.002	0.002	<LQ	<LQ
28	(Epi)catechin-Mv-3-*O*-glc-A-(epi)catechin 1	<LQ	0.002	0.001	<LQ	<LQ
29	(Epi)catechin-Mv-3-*O*-glc-A-(epi)catechin 2	<LQ	0.002	0.001	<LQ	<LQ
30	(Epi)catechin-A-(epi)catechin-Mv-3-*O*-glc	<LD	<LQ	<LQ	<LD	<LQ
31	Mv-3-*O*-glc-(epi)catechin-A-(epi)catechin	<LD	0.001	<LQ	<LQ	<LQ
32	Catechin-Mv-3-*O*-(6-*p*-coum)-glc	0.011	0.054	0.049	0.010	0.015
33	Epicatechin-Mv-3-*O*-(6-*p*-coum)-glc	0.002	0.003	0.002	0.001	0.002
34	Mv-3-*O*-(6-*p*-coum)-glc-acetaldehyde	0.068	0.387	0.429	0.132	0.009
35	Mv-3-*O*-(6-*p*-coum)-glc-pyruvic	0.013	0.134	0.139	0.023	0.049
36	Mv-3-*O*-(6-*p*-coum)-glc-8-ethyl-(epi)catechin 1	0.003	0.013	0.017	0.005	0.007
37	Mv-3-*O*-(6-*p*-coum)-glc-8-ethyl-(epi)catechin 2	0.001	0.005	0.006	0.001	0.003
38	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylcatechin	<LD	<LQ	0.001	<LQ	<LD
39	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylepicatechin	<LD	<LD	<LQ	<LQ	0.002
40	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylphenol	0.001	0.078	0.153	0.046	0.006

Tank 16

#	Time (days)	0	6	10	20	61
27	(Epi)gallocatechin-Mv-3-*O*-glc-A-(epi)catechin 1	<LD	0.001	<LQ	<LQ	<LQ
28	(Epi)catechin-Mv-3-*O*-glc-A-(epi)catechin 1	<LD	0.001	0.001	<LQ	<LQ
29	(Epi)catechin-Mv-3-*O*-glc-A-(epi)catechin 2	<LD	0.001	0.001	<LQ	<LQ
30	(Epi)catechin-A-(epi)catechin-Mv-3-*O*-glc	<LD	<LD	<LQ	<LQ	<LQ
31	Mv-3-*O*-glc-(epi)catechin-A-(epi)catechin	<LD	<LQ	0.001	<LQ	<LQ
32	Catechin-Mv-3-*O*-(6-*p*-coum)-glc	0.015	0.039	0.050	0.015	0.019
33	Epicatechin-Mv-3-*O*-(6-*p*-coum)-glc	0.001	0.003	0.004	0.001	0.002
34	Mv-3-*O*-(6-*p*-coum)-glc-acetaldehyde	0.074	0.343	0.449	0.217	0.011
35	Mv-3-*O*-(6-*p*-coum)-glc-pyruvic	0.013	0.122	0.145	0.035	0.052
36	Mv-3-*O*-(6-*p*-coum)-glc-8-ethyl-(epi)catechin 1	0.003	0.011	0.018	0.009	0.010
37	Mv-3-*O*-(6-*p*-coum)-glc-8-ethyl-(epi)catechin 2	<LQ	0.005	0.006	0.003	0.004
38	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylcatechin	<LD	<LQ	<LQ	<LQ	<LD
39	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylepicatechin	<LD	<LD	<LD	<LQ	0.003
40	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylphenol	0.001	0.072	0.171	0.069	0.004

Tank 17

#	Time (days)	0	6	10	20	61
27	(Epi)gallocatechin-Mv-3-*O*-glc-A-(epi)catechin 1	<LQ	0.001	0.001	<LQ	<LQ
28	(Epi)catechin-Mv-3-*O*-glc-A-(epi)catechin 1	<LQ	0.001	0.001	<LQ	<LQ
29	(Epi)catechin-Mv-3-*O*-glc-A-(epi)catechin 2	<LQ	0.001	<LQ	<LQ	<LQ
30	(Epi)catechin-A-(epi)catechin-Mv-3-*O*-glc	<LD	<LQ	<LQ	<LD	<LQ
31	Mv-3-*O*-glc-(epi)catechin-A-(epi)catechin	<LD	<LD	<LQ	<LQ	<LQ
32	Catechin-Mv-3-*O*-(6-*p*-coum)-glc	0.011	0.034	0.041	0.016	0.017
33	Epicatechin-Mv-3-*O*-(6-*p*-coum)-glc	0.003	0.003	0.004	0.003	0.002
34	Mv-3-*O*-(6-*p*-coum)-glc-acetaldehyde	0.091	0.289	0.358	0.199	0.000
35	Mv-3-*O*-(6-*p*-coum)-glc-pyruvic	0.014	0.088	0.090	0.040	0.041
36	Mv-3-*O*-(6-*p*-coum)-glc-8-ethyl-(epi)catechin 1	0.003	0.011	0.015	0.009	0.005
37	Mv-3-*O*-(6-*p*-coum)-glc-8-ethyl-(epi)catechin 2	0.001	0.003	0.004	0.003	0.002
38	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylcatechin	<LQ	0.002	0.001	<LQ	<LD
39	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylepicatechin	<LD	<LD	<LD	<LQ	0.002
40	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylphenol	0.001	0.144	0.222	0.115	0.024

Tank 18

#	Time (days)	0	6	10	20	61
27	(Epi)gallocatechin-Mv-3-*O*-glc-A-(epi)catechin 1	<LQ	0.002	0.001	<LQ	<LQ
28	(Epi)catechin-Mv-3-*O*-glc-A-(epi)catechin 1	<LQ	0.001	0.001	<LQ	<LQ
29	(Epi)catechin-Mv-3-*O*-glc-A-(epi)catechin 2	<LQ	<LQ	0.001	<LQ	<LQ
30	(Epi)catechin-A-(epi)catechin-Mv-3-*O*-glc	<LQ	<LD	<LQ	<LQ	<LD
31	Mv-3-*O*-glc-(epi)catechin-A-(epi)catechin	<LQ	<LQ	<LQ	<LQ	<LQ
32	Catechin-Mv-3-*O*-(6-*p*-coum)-glc	0.011	0.033	0.041	0.020	0.014
33	Epicatechin-Mv-3-*O*-(6-*p*-coum)-glc	0.002	0.004	0.002	0.003	0.002
34	Mv-3-*O*-(6-*p*-coum)-glc-acetaldehyde	0.089	0.296	0.369	0.259	0.008
35	Mv-3-*O*-(6-*p*-coum)-glc-pyruvic	0.015	0.085	0.102	0.044	0.036
36	Mv-3-*O*-(6-*p*-coum)-glc-8-ethyl-(epi)catechin 1	0.003	0.011	0.013	0.010	0.005
37	Mv-3-*O*-(6-*p*-coum)-glc-8-ethyl-(epi)catechin 2	0.001	0.004	0.003	0.003	0.002
38	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylcatechin	<LD	0.001	0.001	<LQ	<LD
39	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylepicatechin	<LD	<LD	<LD	<LQ	0.001
40	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylphenol	0.001	0.130	0.210	0.146	0.011

Tank 19

#	Time (days)	0	6	10	20	61
27	(Epi)gallocatechin-Mv-3-*O*-glc-A-(epi)catechin 1	<LD	0.001	0.001	<LQ	<LQ
28	(Epi)catechin-Mv-3-*O*-glc-A-(epi)catechin 1	<LD	0.002	0.001	<LQ	0.001
29	(Epi)catechin-Mv-3-*O*-glc-A-(epi)catechin 2	<LD	0.001	0.001	<LQ	<LQ
30	(Epi)catechin-A-(epi)catechin-Mv-3-*O*-glc	<LD	<LQ	<LQ	<LD	<LD
31	Mv-3-*O*-glc-(epi)catechin-A-(epi)catechin	<LD	<LQ	<LQ	<LQ	<LQ
32	Catechin-Mv-3-*O*-(6-*p*-coum)-glc	0.008	0.045	0.042	0.019	0.020
33	Epicatechin-Mv-3-*O*-(6-*p*-coum)-glc	0.003	0.003	0.004	0.003	0.002
34	Mv-3-*O*-(6-*p*-coum)-glc-acetaldehyde	0.079	0.394	0.446	0.320	0.009
35	Mv-3-*O*-(6-*p*-coum)-glc-pyruvic	0.014	0.126	0.136	0.048	0.048
36	Mv-3-*O*-(6-*p*-coum)-glc-8-ethyl-(epi)catechin 1	0.003	0.012	0.016	0.010	0.007
37	Mv-3-*O*-(6-*p*-coum)-glc-8-ethyl-(epi)catechin 2	<LQ	0.005	0.005	0.003	0.003
38	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylcatechin	<LQ	0.001	0.002	<LD	<LD
39	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylepicatechin	<LD	<LD	<LD	<LQ	0.002
40	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylphenol	<LQ	0.196	0.239	0.130	0.026

Tank 20

#	Time (days)	0	6	10	20	61
27	(Epi)gallocatechin-Mv-3-*O*-glc-A-(epi)catechin 1	<LQ	0.001	-	<LQ	<LQ
28	(Epi)catechin-Mv-3-*O*-glc-A-(epi)catechin 1	<LQ	0.002	-	<LQ	<LQ
29	(Epi)catechin-Mv-3-*O*-glc-A-(epi)catechin 2	<LQ	0.001	-	<LQ	<LQ
30	(Epi)catechin-A-(epi)catechin-Mv-3-*O*-glc	<LD	<LQ	-	<LD	<LD
31	Mv-3-*O*-glc-(epi)catechin-A-(epi)catechin	<LD	<LQ	-	<LQ	<LQ
32	Catechin-Mv-3-*O*-(6-*p*-coum)-glc	0.012	0.050	-	0.013	0.015
33	Epicatechin-Mv-3-*O*-(6-*p*-coum)-glc	0.003	0.003	-	0.002	0.002
34	Mv-3-*O*-(6-*p*-coum)-glc-acetaldehyde	0.093	0.417	-	0.170	0.001
35	Mv-3-*O*-(6-*p*-coum)-glc-pyruvic	0.015	0.133	-	0.032	0.037
36	Mv-3-*O*-(6-*p*-coum)-glc-8-ethyl-(epi)catechin 1	0.004	0.015	-	0.007	0.005
37	Mv-3-*O*-(6-*p*-coum)-glc-8-ethyl-(epi)catechin 2	0.002	0.006	-	0.002	0.002
38	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylcatechin	<LD	<LQ	-	<LQ	<LD
39	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylepicatechin	<LD	0.001	-	<LQ	0.002
40	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylphenol	0.002	0.190	-	0.063	0.010

continued

Table S3. Anthocyanin derivatives concentrations determined by HPLC-DAD-ESI(+)-MS/MS in red wine samples from Mendavia 2018, expressed in mg of Mv-3-*O*-glc equiv./L.

Tank 21

#	Time (days)	0	6	10	20	61
27	(Epi)gallocatechin-Mv-3-*O*-glc-A-(epi)catechin 1	<LQ	0.001	0.001	<LQ	<LQ
28	(Epi)catechin-Mv-3-*O*-glc-A-(epi)catechin 1	<LQ	0.002	0.001	<LQ	<LQ
29	(Epi)catechin-Mv-3-*O*-glc-A-(epi)catechin 2	<LQ	0.001	0.001	<LQ	<LQ
30	(Epi)catechin-A-(epi)catechin-Mv-3-*O*-glc	<LQ	<LD	<LQ	<LD	<LQ
31	Mv-3-*O*-glc-(epi)catechin-A-(epi)catechin	<LD	<LQ	0.001	<LQ	<LQ
32	Catechin-Mv-3-*O*-(6-*p*-coum)-glc	0.010	0.037	0.046	0.019	0.015
33	Epicatechin-Mv-3-*O*-(6-*p*-coum)-glc	0.004	0.003	0.004	0.003	0.001
34	Mv-3-*O*-(6-*p*-coum)-glc-acetaldehyde	0.083	0.276	0.391	0.346	0.004
35	Mv-3-*O*-(6-*p*-coum)-glc-pyruvic	0.014	0.074	0.097	0.045	0.038
36	Mv-3-*O*-(6-*p*-coum)-glc-8-ethyl-(epi)catechin 1	0.004	0.011	0.015	0.011	0.006
37	Mv-3-*O*-(6-*p*-coum)-glc-8-ethyl-(epi)catechin 2	0.001	0.004	0.005	0.004	0.003
38	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylcatechin	<LD	<LQ	<LQ	<LQ	<LD
39	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylepicatechin	<LD	<LD	<LD	<LQ	0.002
40	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylphenol	0.002	0.052	0.194	0.129	0.014

Tank 22

#	Time (days)	0	6	10	20	61
27	(Epi)gallocatechin-Mv-3-*O*-glc-A-(epi)catechin 1	<LD	0.002	0.001	<LQ	<LQ
28	(Epi)catechin-Mv-3-*O*-glc-A-(epi)catechin 1	<LD	0.001	0.002	<LQ	<LQ
29	(Epi)catechin-Mv-3-*O*-glc-A-(epi)catechin 2	<LD	0.001	0.001	<LQ	<LQ
30	(Epi)catechin-A-(epi)catechin-Mv-3-*O*-glc	<LD	<LD	<LD	<LQ	<LQ
31	Mv-3-*O*-glc-(epi)catechin-A-(epi)catechin	<LD	<LQ	<LQ	<LQ	<LQ
32	Catechin-Mv-3-*O*-(6-*p*-coum)-glc	0.010	0.044	0.052	0.019	0.018
33	Epicatechin-Mv-3-*O*-(6-*p*-coum)-glc	0.004	0.002	0.005	0.003	0.002
34	Mv-3-*O*-(6-*p*-coum)-glc-acetaldehyde	0.077	0.421	0.460	0.326	0.010
35	Mv-3-*O*-(6-*p*-coum)-glc-pyruvic	0.013	0.132	0.129	0.045	0.049
36	Mv-3-*O*-(6-*p*-coum)-glc-8-ethyl-(epi)catechin 1	0.004	0.014	0.019	0.011	0.008
37	Mv-3-*O*-(6-*p*-coum)-glc-8-ethyl-(epi)catechin 2	0.001	0.005	0.006	0.004	0.003
38	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylcatechin	<LD	<LQ	<LQ	<LQ	<LD
39	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylepicatechin	<LD	<LD	<LD	<LQ	0.002
40	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylphenol	0.002	0.142	0.204	0.131	0.021

Tank 23

#	Time (days)	0	6	10	20	61
27	(Epi)gallocatechin-Mv-3-*O*-glc-A-(epi)catechin 1	<LQ	0.001	0.001	<LQ	<LQ
28	(Epi)catechin-Mv-3-*O*-glc-A-(epi)catechin 1	<LQ	0.001	0.001	<LQ	<LQ
29	(Epi)catechin-Mv-3-*O*-glc-A-(epi)catechin 2	<LQ	0.001	0.001	<LQ	<LQ
30	(Epi)catechin-A-(epi)catechin-Mv-3-*O*-glc	<LD	<LQ	<LD	<LD	<LQ
31	Mv-3-*O*-glc-(epi)catechin-A-(epi)catechin	<LQ	<LQ	<LQ	<LQ	<LQ
32	Catechin-Mv-3-*O*-(6-*p*-coum)-glc	0.013	0.040	0.042	0.017	0.016
33	Epicatechin-Mv-3-*O*-(6-*p*-coum)-glc	0.003	0.004	0.002	0.002	0.001
34	Mv-3-*O*-(6-*p*-coum)-glc-acetaldehyde	0.073	0.420	0.388	0.302	0.013
35	Mv-3-*O*-(6-*p*-coum)-glc-pyruvic	0.014	0.135	0.095	0.037	0.049
36	Mv-3-*O*-(6-*p*-coum)-glc-8-ethyl-(epi)catechin 1	0.004	0.015	0.015	0.010	0.008
37	Mv-3-*O*-(6-*p*-coum)-glc-8-ethyl-(epi)catechin 2	0.001	0.006	0.005	0.003	0.003
38	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylcatechin	<LD	0.001	<LQ	<LQ	<LD
39	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylepicatechin	<LD	<LD	<LQ	<LQ	0.002
40	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylphenol	0.002	0.157	0.183	0.081	0.018

Tank 24

#	Time (days)	0	6	10	20	61
27	(Epi)gallocatechin-Mv-3-*O*-glc-A-(epi)catechin 1	<LQ	0.002	0.001	<LQ	<LQ
28	(Epi)catechin-Mv-3-*O*-glc-A-(epi)catechin 1	<LQ	0.002	0.001	<LQ	<LQ
29	(Epi)catechin-Mv-3-*O*-glc-A-(epi)catechin 2	<LD	0.001	<LQ	<LQ	<LQ
30	(Epi)catechin-A-(epi)catechin-Mv-3-*O*-glc	<LD	<LQ	<LD	<LQ	<LQ
31	Mv-3-*O*-glc-(epi)catechin-A-(epi)catechin	<LD	<LQ	<LD	<LQ	<LQ
32	Catechin-Mv-3-*O*-(6-*p*-coum)-glc	0.009	0.040	0.048	0.020	0.018
33	Epicatechin-Mv-3-*O*-(6-*p*-coum)-glc	0.002	0.002	0.004	0.003	0.002
34	Mv-3-*O*-(6-*p*-coum)-glc-acetaldehyde	0.081	0.315	0.404	0.282	0.011
35	Mv-3-*O*-(6-*p*-coum)-glc-pyruvic	0.021	0.090	0.095	0.039	0.048
36	Mv-3-*O*-(6-*p*-coum)-glc-8-ethyl-(epi)catechin 1	0.004	0.011	0.016	0.010	0.009
37	Mv-3-*O*-(6-*p*-coum)-glc-8-ethyl-(epi)catechin 2	<LQ	0.004	0.005	0.003	0.004
38	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylcatechin	<LD	0.001	<LQ	<LQ	<LD
39	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylepicatechin	<LD	<LD	<LQ	<LQ	0.002
40	Mv-3-*O*-(6-*p*-coum)-glc-4-vinylphenol	0.001	0.099	0.194	0.105	0.023

Table S4. Tannin concentrations determined by HPLC-DAD-ESI(+)-MS/MS in red wine samples from Mendavia 2018, expressed in mg of (+)-cat equiv./L.

Tank 01

#	Time (days)	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
41	((Epi)gallocatechin)$_2$ 1	1.09	2.67	1.74	1.73	0.63	1.39	1.51	1.61	2.05	2.74	1.18	1.57	0.57	0.66	1.42
42	((Epi)gallocatechin)$_2$ 2	0.35	0.68	0.53	0.46	0.22	0.29	0.29	0.39	0.46	0.57	0.29	0.39	0.17	0.21	0.44
43	((Epi)gallocatechin)$_2$ 3	0.06	0.11	0.09	0.15	0.05	0.08	0.05	0.09	0.12	0.10	0.04	0.11	<LQ	0.05	0.05
44	Gallocatechin	0.84	1.49	1.48	1.75	0.80	1.48	1.50	0.82	1.53	1.59	1.13	1.13	0.66	0.61	1.23
45	Epigallocatechin	0.38	0.49	0.50	0.54	0.27	0.38	0.35	0.26	0.49	0.32	0.33	0.41	0.34	0.21	0.41
46	((Epi)gallocatechin-(epi)catechin) 2	0.34	0.99	1.46	1.46	0.82	1.33	1.36	1.36	1.50	1.97	0.93	1.17	0.45	0.57	1.30
47	((Epi)catechin-(epi)gallocatechin) 2	0.70	1.39	1.45	1.39	0.86	0.88	0.93	0.85	0.93	1.59	0.79	1.11	0.42	0.57	1.14
48	((Epi)gallocatechin-(epi)catechin) 1	2.35	5.57	3.98	3.86	2.27	3.36	3.08	4.20	5.19	6.80	3.15	3.94	1.65	2.04	3.67
49	((Epi)catechin-(epi)gallocatechin) 1	2.69	5.57	4.57	4.31	2.68	4.43	3.39	4.18	5.52	7.07	3.51	4.49	2.15	2.25	3.84
50	((Epi)catechin-(epi)gallocatechin) A	0.06	0.15	0.51	0.43	0.42	0.16	0.11	<LD	<LD	<LD	0.04	0.05	<LD	<LD	<LD
51	((Epi)catechin)$_2$ 1	3.38	7.05	5.01	4.45	3.16	6.44	4.65	3.95	7.46	8.66	4.98	5.57	2.76	2.98	5.00
52	Procyanidin B 1	15.11	42.14	24.94	22.73	12.40	28.26	20.42	30.96	44.63	62.01	28.69	33.64	16.14	11.17	28.97
53	Procyanidin B 2	3.18	6.60	5.66	5.50	3.61	5.71	5.81	6.56	10.60	13.07	6.78	8.76	5.08	4.38	7.18
54	Catechin	1.45	2.28	2.16	2.73	2.00	2.83	2.34	2.03	2.63	2.99	2.18	2.32	1.89	1.54	2.31
55	Epicatechin	0.45	0.60	0.69	0.93	0.70	0.68	1.37	0.76	1.27	1.27	0.88	0.84	0.77	0.63	1.17
56	*p*-vinyl(epi)catechin 1	2.19	3.43	3.28	3.03	2.67	3.14	1.73	1.47	1.72	1.65	1.27	1.29	0.76	0.84	1.18
57	*p*-vinyl(epi)catechin 2	<LD	0.20	<LD	0.26	<LD	0.26	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
58	*p*-vinyl(epi)catechin 3	0.07	0.48	0.53	0.82	<LD	1.33	0.86	0.42	0.54	0.58	0.27	0.42	0.17	0.27	0.24

Tank 02

#	Time (days)	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
41	((Epi)gallocatechin)$_2$ 1	0.51	0.52	1.64	1.74	0.90	0.89	1.45	1.61	1.82	2.04	1.21	1.28	0.53	0.65	0.88
42	((Epi)gallocatechin)$_2$ 2	0.18	0.18	0.55	0.46	0.33	0.23	0.33	0.41	0.47	0.54	0.27	0.39	0.16	0.20	0.32
43	((Epi)gallocatechin)$_2$ 3	<LQ	0.14	0.12	0.15	0.33	0.04	0.07	0.11	0.06	0.12	0.07	0.06	0.04	0.05	0.08
44	Gallocatechin	0.80	0.70	1.52	1.75	1.25	1.26	1.49	1.39	1.36	1.97	0.73	1.15	0.58	0.54	1.20
45	Epigallocatechin	0.36	0.21	0.50	0.54	0.35	0.31	0.41	0.44	0.62	0.42	0.31	0.35	0.33	0.23	0.43
46	((Epi)gallocatechin-(epi)catechin) 2	0.26	0.41	1.45	1.46	0.76	0.72	0.94	1.44	1.20	1.66	0.82	1.12	0.37	0.54	0.92
47	((Epi)catechin-(epi)gallocatechin) 2	0.44	0.33	1.44	1.39	0.98	0.63	0.76	0.93	1.19	1.46	0.66	0.95	0.41	0.52	0.96
48	((Epi)gallocatechin-(epi)catechin) 1	1.40	1.57	3.73	3.86	2.67	3.02	2.99	4.06	4.82	5.14	2.68	3.52	1.38	1.93	2.55
49	((Epi)catechin-(epi)gallocatechin) 1	1.87	1.85	4.65	4.31	3.28	4.02	3.06	4.57	5.28	6.29	2.89	3.91	1.91	2.16	3.09
50	((Epi)catechin-(epi)gallocatechin) A	0.08	0.19	0.40	0.43	0.37	0.13	<LD	<LD	<LD	<LD	0.06	<LD	<LD	<LD	<LD
51	((Epi)catechin)$_2$ 1	2.46	2.64	5.10	4.45	3.78	5.17	3.95	5.61	8.02	9.46	4.09	5.04	2.42	2.64	3.86
52	Procyanidin B 1	8.38	9.93	23.50	22.73	17.69	24.21	19.23	33.60	44.46	48.18	24.46	28.65	12.34	10.16	20.75
53	Procyanidin B 2	2.33	1.76	5.05	5.50	3.98	4.53	5.25	8.56	9.64	10.68	5.57	7.22	4.22	3.90	5.48
54	Catechin	1.40	1.65	2.09	2.73	1.91	2.20	2.23	2.37	2.62	3.46	1.97	2.40	1.56	1.41	2.24
55	Epicatechin	0.46	0.26	0.58	0.93	0.50	0.59	0.85	0.87	1.21	1.27	0.70	0.83	0.59	0.61	0.96
56	*p*-vinyl(epi)catechin 1	2.04	3.04	3.25	2.97	2.59	3.01	1.78	1.69	1.60	1.56	1.42	1.31	0.79	1.13	1.40
57	*p*-vinyl(epi)catechin 2	<LD	0.63	<LD	0.27	<LD	0.35	0.23	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
58	*p*-vinyl(epi)catechin 3	<LD	0.29	0.69	0.83	0.33	0.84	0.75	0.44	0.47	0.59	0.30	0.31	0.14	0.28	0.25

Tank 03

#	Time (days)	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
41	((Epi)gallocatechin)$_2$ 1	0.41	3.04	1.47	1.48	1.46	1.76	0.97	1.31	1.51	1.92	1.23	0.93	0.57	0.61	1.22
42	((Epi)gallocatechin)$_2$ 2	0.17	0.80	0.33	0.48	0.40	0.35	0.28	0.25	0.36	0.56	0.33	0.28	0.16	0.22	0.33
43	((Epi)gallocatechin)$_2$ 3	0.07	0.17	0.15	0.07	0.08	0.12	0.08	<LQ	0.04	0.25	0.04	0.04	<LQ	<LQ	0.08
44	Gallocatechin	0.82	1.63	1.54	1.56	1.31	1.49	1.48	1.29	1.46	1.44	0.99	0.98	0.65	0.63	1.22
45	Epigallocatechin	0.35	0.73	0.59	0.42	0.45	0.33	0.38	0.35	0.52	0.33	0.40	0.28	0.26	0.29	0.48
46	((Epi)gallocatechin-(epi)catechin) 2	0.19	1.60	1.62	0.99	1.27	0.99	0.91	1.25	1.21	1.39	1.18	0.76	0.43	0.49	1.22
47	((Epi)catechin-(epi)gallocatechin) 2	0.43	1.49	1.42	1.37	1.46	0.93	0.69	0.82	0.93	0.91	0.79	0.79	0.45	0.56	1.00
48	((Epi)gallocatechin-(epi)catechin) 1	1.32	6.58	3.46	3.26	3.47	4.52	2.60	3.13	3.77	5.07	3.12	2.55	1.59	1.89	3.10
49	((Epi)catechin-(epi)gallocatechin) 1	1.79	6.38	4.08	3.91	4.03	5.08	2.82	3.35	4.78	5.60	3.63	3.25	1.98	2.22	3.37
50	((Epi)catechin-(epi)gallocatechin) A	0.06	0.40	0.35	0.38	0.44	0.19	0.11	<LD	<LD	<LD	0.08	0.04	<LD	<LD	<LD
51	((Epi)catechin)$_2$ 1	1.98	6.98	4.22	3.71	4.14	5.01	3.53	3.61	6.64	9.08	4.50	4.65	2.44	2.84	3.66
52	Procyanidin B 1	8.58	49.40	21.18	19.04	21.46	28.84	17.37	25.13	37.95	51.11	25.38	24.59	12.54	9.51	22.44
53	Procyanidin B 2	2.17	7.41	4.66	4.68	4.95	6.32	4.63	5.98	9.63	12.43	6.33	6.44	4.39	3.90	5.99
54	Catechin	1.34	2.91	2.04	2.25	2.04	2.47	2.20	1.95	2.76	2.86	2.48	1.99	1.76	1.71	2.28
55	Epicatechin	0.43	0.77	0.64	0.85	0.68	0.65	0.81	0.73	1.24	1.40	1.16	0.77	0.69	0.67	1.00
56	*p*-vinyl(epi)catechin 1	1.94	3.29	3.05	2.91	2.34	2.12	1.75	1.51	1.65	1.66	1.28	1.13	0.62	1.09	0.99
57	*p*-vinyl(epi)catechin 2	<LD	0.18	<LD	<LD	<LD	0.41	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
58	*p*-vinyl(epi)catechin 3	<LD	0.56	0.60	0.56	0.60	0.63	0.70	0.30	0.37	0.43	0.32	0.38	0.14	0.25	0.22

continued

Table S4. Tannin concentrations determined by HPLC-DAD-ESI(+)-MS/MS in red wine samples from Mendavia 2018, expressed in mg of (+)-cat equiv./L.

#	Tank 04															
#	**Time (days)**	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
41	((Epi)gallocatechin)$_2$ 1	0.73	3.51	1.79	1.87	0.36	4.80	1.38	2.53	2.47	2.42	1.47	1.38	0.80	0.92	1.40
42	((Epi)gallocatechin)$_2$ 2	0.24	0.80	0.52	0.51	0.10	0.94	0.31	0.47	0.58	0.72	0.34	0.38	0.23	0.26	0.43
43	((Epi)gallocatechin)$_2$ 3	0.06	0.14	0.09	0.14	0.07	0.19	<LQ	0.16	0.08	0.11	0.07	0.11	0.03	0.08	0.14
44	Gallocatechin	0.77	1.87	1.50	1.59	0.74	1.93	1.39	1.48	1.58	1.78	0.93	0.95	0.64	0.74	1.18
45	Epigallocatechin	0.28	0.69	0.49	0.52	0.16	0.40	0.41	0.51	0.37	0.42	0.35	0.29	0.29	0.29	0.34
46	((Epi)gallocatechin-(epi)catechin) 2	0.28	1.73	1.44	1.58	0.56	2.49	0.99	2.20	1.78	1.91	1.24	1.16	0.51	0.73	1.43
47	((Epi)catechin-(epi)gallocatechin) 2	0.53	1.64	1.38	1.41	0.41	2.10	0.81	1.49	1.43	1.79	1.11	0.80	0.48	0.69	1.16
48	((Epi)gallocatechin-(epi)catechin) 1	1.94	7.20	4.04	4.21	1.52	10.04	2.95	6.50	6.08	6.37	4.04	3.68	2.04	2.56	3.72
49	((Epi)catechin-(epi)gallocatechin) 1	2.31	7.17	4.58	4.58	2.00	10.47	3.20	6.37	6.14	6.78	3.84	3.69	2.41	2.72	3.80
50	((Epi)catechin-(epi)gallocatechin) A	0.07	0.57	0.48	0.25	0.32	0.22	<LD	<LD	<LD	<LD	0.06	<LD	<LD	<LD	<LD
51	((Epi)catechin)$_2$ 1	2.75	7.72	4.79	5.00	1.82	9.51	4.50	4.88	8.28	9.49	5.13	5.85	2.81	3.59	4.35
52	Procyanidin B 1	11.78	50.97	23.79	25.64	8.93	54.71	21.40	42.80	45.12	57.48	29.75	32.17	15.21	14.17	25.62
53	Procyanidin B 2	3.00	8.11	4.73	5.92	1.93	10.31	6.26	8.64	11.20	13.38	7.31	8.11	5.08	4.82	6.77
54	Catechin	1.28	2.72	1.97	2.52	1.69	2.80	2.23	2.71	3.00	3.85	2.29	2.50	1.84	1.90	2.26
55	Epicatechin	0.46	0.86	0.59	0.87	0.42	1.38	0.97	0.94	1.51	1.70	1.13	0.97	0.79	0.84	1.15
56	*p*-vinyl(epi)catechin 1	2.03	3.65	3.25	3.11	2.57	2.93	1.74	2.03	1.89	1.90	1.43	1.29	0.86	1.35	1.41
57	*p*-vinyl(epi)catechin 2	<LD	<LD	<LD	<LD	<LD	0.51	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
58	*p*-vinyl(epi)catechin 3	<LD	0.43	0.53	0.95	0.53	0.89	0.52	0.51	0.49	0.89	0.30	0.45	0.20	0.25	0.29
	Tank 05															
#	**Time (days)**	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
41	((Epi)gallocatechin)$_2$ 1	0.48	2.47	1.46	1.45	1.46	0.99	1.75	1.27	1.68	2.05	1.18	1.00	0.53	0.67	0.90
42	((Epi)gallocatechin)$_2$ 2	0.12	0.64	0.38	0.31	0.32	0.31	0.44	0.23	0.39	0.49	0.27	0.27	0.15	0.18	0.27
43	((Epi)gallocatechin)$_2$ 3	0.06	0.13	0.13	0.16	0.09	0.03	0.06	0.06	0.10	0.10	<LQ	0.06	<LQ	0.07	0.09
44	Gallocatechin	0.70	1.56	1.43	1.62	1.00	1.29	1.58	0.73	1.54	1.67	0.94	1.10	0.58	0.70	1.17
45	Epigallocatechin	0.22	0.54	0.47	0.40	0.38	0.29	0.44	0.26	0.30	0.37	0.39	0.33	0.26	0.24	0.30
46	((Epi)gallocatechin-(epi)catechin) 2	0.22	1.26	1.45	1.42	1.42	0.83	1.62	1.28	1.45	1.56	0.84	0.96	0.49	0.70	1.33
47	((Epi)catechin-(epi)gallocatechin) 2	0.38	1.30	0.97	1.36	1.33	0.68	0.96	0.77	1.41	1.33	0.83	0.76	0.44	0.55	0.80
48	((Epi)gallocatechin-(epi)catechin) 1	1.56	5.43	3.40	3.08	3.43	3.25	3.74	3.41	4.34	5.71	3.01	3.19	1.45	2.09	2.76
49	((Epi)catechin-(epi)gallocatechin) 1	2.03	5.63	4.06	3.53	4.42	4.24	3.98	3.57	5.07	5.96	3.41	3.71	1.93	2.21	2.98
50	((Epi)catechin-(epi)gallocatechin) A 2	0.06	0.39	0.17	0.16	0.49	0.14	0.17	0.09	<LD	<LD	<LD	0.06	<LD	<LD	<LD
51	((Epi)catechin)$_2$ 1	2.47	6.42	4.83	4.12	4.50	5.05	4.66	4.02	7.60	9.57	4.44	5.02	2.33	2.93	3.22
52	Procyanidin B 1	9.28	43.73	23.96	20.09	22.92	27.30	23.69	30.91	42.17	52.85	27.01	32.25	11.99	11.00	19.82
53	Procyanidin B 2	2.85	7.67	5.31	5.27	5.53	6.76	6.35	6.17	10.66	12.19	6.78	8.05	4.44	4.10	5.63
54	Catechin	1.33	2.66	2.18	2.34	2.14	2.44	2.43	2.02	2.71	3.24	2.28	2.14	1.65	<LD	2.06
55	Epicatechin	0.36	0.69	0.76	0.95	0.69	0.61	1.38	0.59	1.49	1.41	0.87	0.78	0.69	<LD	0.93
56	*p*-vinyl(epi)catechin 1	1.97	2.92	3.30	2.91	2.22	1.94	1.87	1.46	1.93	1.73	1.36	1.32	0.61	0.99	1.22
57	*p*-vinyl(epi)catechin 2	<LD	<LD	<LD	<LD	<LD	<LD	0.18	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
58	*p*-vinyl(epi)catechin 3	<LD	0.45	0.70	0.44	0.32	0.45	0.73	0.36	0.29	0.55	0.22	0.26	0.13	0.17	0.16
	Tank 06															
#	**Time (days)**	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
41	((Epi)gallocatechin)$_2$ 1	0.41	2.35	1.54	1.45	0.98	1.62	1.43	0.94	1.99	2.31	0.97	1.31	0.49	0.65	1.23
42	((Epi)gallocatechin)$_2$ 2	0.18	0.59	0.36	0.35	0.25	0.42	0.27	0.20	0.51	0.59	0.26	0.34	0.16	0.16	0.33
43	((Epi)gallocatechin)$_2$ 3	0.06	0.17	0.12	0.09	<LD	<LD	0.04	0.06	0.06	0.07	0.04	0.05	<LQ	<LQ	0.10
44	Gallocatechin	0.72	1.48	1.52	1.51	1.34	1.43	1.38	0.75	1.59	1.53	0.89	1.11	0.63	0.57	1.14
45	Epigallocatechin	0.20	0.56	0.45	0.45	0.44	0.39	0.37	0.21	0.36	0.49	0.40	0.30	0.25	0.21	0.40
46	((Epi)gallocatechin-(epi)catechin) 2	0.23	1.22	1.53	1.35	0.70	1.32	1.37	0.98	1.31	1.79	0.76	1.01	0.34	0.61	0.97
47	((Epi)catechin-(epi)gallocatechin) 2	0.38	1.00	1.53	1.34	0.88	0.97	0.84	0.68	1.45	1.46	0.64	0.90	0.46	0.66	0.87
48	((Epi)gallocatechin-(epi)catechin) 1	1.18	5.18	3.58	3.05	2.72	4.59	2.94	2.84	4.99	5.92	2.60	3.63	1.50	2.04	3.00
49	((Epi)catechin-(epi)gallocatechin) 1	1.59	5.89	4.17	3.75	3.89	5.24	3.10	2.99	5.36	6.81	3.12	4.07	1.97	2.32	3.37
50	((Epi)catechin-(epi)gallocatechin) A	0.11	0.23	0.19	0.20	0.30	<LD	0.08	<LD	<LD	0.06	<LD	<LD	<LQ	<LD	<LD
51	((Epi)catechin)$_2$ 1	2.13	6.34	4.68	4.05	4.71	6.39	4.26	3.35	7.97	9.94	4.44	5.07	2.67	3.06	4.38
52	Procyanidin B 1	8.15	42.89	22.92	20.51	21.04	35.29	19.87	25.58	48.41	58.64	24.02	33.23	12.81	13.44	26.56
53	Procyanidin B 2	1.87	7.54	4.57	5.11	5.50	6.61	5.45	5.31	9.75	11.85	5.75	7.69	4.20	4.28	6.15
54	Catechin	1.20	2.32	2.28	2.06	2.22	2.38	2.16	1.77	2.76	3.05	1.92	2.05	1.47	1.67	2.10
55	Epicatechin	0.36	0.74	0.57	0.68	0.83	0.69	0.82	0.52	1.24	1.29	0.75	0.81	0.63	0.64	0.84
56	*p*-vinyl(epi)catechin 1	1.92	2.83	3.15	2.67	2.39	2.59	1.79	1.54	1.64	1.91	1.38	1.41	0.73	0.95	1.19
57	*p*-vinyl(epi)catechin 2	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
58	*p*-vinyl(epi)catechin 3	<LD	0.37	0.72	0.36	<LD	0.46	0.48	0.37	0.31	0.45	0.27	0.22	0.11	0.17	0.16

continued

Table S4. Tannin concentrations determined by HPLC-DAD-ESI(+)-MS/MS in red wine samples from Mendavia 2018, expressed in mg of (+)-cat equiv./L.

Tank 07

#	Time (days)	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
41	((Epi)gallocatechin)$_2$ 1	0.48	2.37	2.01	1.79	1.41	<LD	1.55	1.37	1.96	2.27	1.25	1.34	0.22	0.78	0.98
42	((Epi)gallocatechin)$_2$ 2	0.20	0.70	0.46	0.36	0.33	<LD	0.30	0.40	0.54	0.55	0.26	0.35	0.07	0.21	0.28
43	((Epi)gallocatechin)$_2$ 3	0.07	0.16	0.11	0.07	0.05	<LD	0.09	0.12	0.07	0.06	0.06	0.08	<LQ	0.05	0.13
44	Gallocatechin	0.73	1.32	1.76	1.71	1.47	<LD	1.70	1.61	1.61	1.83	1.15	1.16	0.32	0.67	1.29
45	Epigallocatechin	0.28	0.74	0.53	0.46	0.52	<LD	0.39	0.38	0.44	0.45	0.24	0.27	0.11	0.23	0.35
46	((Epi)gallocatechin-(epi)catechin) 2	0.22	0.99	1.66	1.46	1.31	<LD	1.35	0.87	1.31	1.87	0.94	0.88	0.19	0.69	1.18
47	((Epi)catechin-(epi)gallocatechin) 2	0.38	1.27	1.45	1.44	0.85	<LD	0.94	0.89	1.40	1.59	0.71	0.85	0.20	0.49	0.87
48	((Epi)gallocatechin-(epi)catechin) 1	1.65	4.82	3.92	3.36	3.18	<LD	2.89	3.12	4.79	5.87	3.10	3.53	0.70	2.24	2.75
49	((Epi)catechin-(epi)gallocatechin) 1	2.12	5.32	4.87	3.83	4.11	<LD	3.57	3.82	5.53	6.50	3.50	4.04	0.97	2.39	3.07
50	((Epi)catechin-(epi)gallocatechin) A 2	<LQ	0.26	0.18	0.17	0.42	<LD	0.12	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
51	((Epi)catechin)$_2$ 1	2.82	6.65	5.72	4.31	4.65	<LD	5.11	5.68	7.57	9.80	4.66	5.43	1.29	3.09	4.29
52	Procyanidin B 1	11.92	40.21	26.79	21.95	21.96	<LD	22.73	29.89	45.59	65.57	24.92	33.18	6.97	13.03	22.13
53	Procyanidin B 2	2.73	6.24	5.41	4.72	5.22	<LD	5.91	7.09	9.57	13.44	6.18	7.85	1.86	4.26	6.10
54	Catechin	1.25	2.45	2.54	2.33	2.19	<LD	2.53	2.81	2.99	3.57	2.03	2.06	0.89	1.54	2.22
55	Epicatechin	0.38	0.61	0.79	0.82	0.70	<LD	0.89	0.85	1.32	1.38	0.85	0.75	0.28	0.62	0.95
56	*p*-vinyl(epi)catechin 1	1.69	3.29	3.52	2.79	2.55	<LD	1.85	1.87	1.81	1.96	1.26	1.15	0.63	0.99	1.25
57	*p*-vinyl(epi)catechin 2	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
58	*p*-vinyl(epi)catechin 3	<LD	0.33	0.77	0.64	0.27	<LD	0.36	0.32	0.30	0.38	0.20	0.30	0.09	0.17	0.15

Tank 08

#	Time (days)	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
41	((Epi)gallocatechin)$_2$ 1	0.43	2.90	1.93	0.52	1.28	1.26	1.48	1.30	2.24	2.16	0.83	0.95	0.64	0.62	0.87
42	((Epi)gallocatechin)$_2$ 2	0.14	0.66	0.55	0.17	0.35	0.28	0.33	0.30	0.45	0.47	0.21	0.25	0.14	0.21	0.30
43	((Epi)gallocatechin)$_2$ 3	<LQ	0.14	0.10	<LD	0.10	0.04	0.05	0.04	0.05	0.06	0.04	0.07	<LQ	0.07	0.09
44	Gallocatechin	0.68	1.58	1.58	0.95	1.38	1.47	1.43	1.34	1.55	1.60	0.78	1.14	0.50	0.62	1.23
45	Epigallocatechin	0.22	0.59	0.55	0.32	0.43	0.30	0.34	0.37	0.37	0.45	0.32	0.31	0.22	0.21	0.27
46	((Epi)gallocatechin-(epi)catechin) 2	0.29	1.77	1.55	0.63	0.97	0.90	1.37	1.34	1.44	1.75	0.63	0.84	0.44	0.57	0.82
47	((Epi)catechin-(epi)gallocatechin) 2	0.41	1.40	1.67	0.50	1.33	0.90	0.93	0.89	1.32	1.52	0.76	0.78	0.45	0.50	0.94
48	((Epi)gallocatechin-(epi)catechin) 1	1.25	6.63	4.40	1.81	3.08	3.86	3.04	3.00	5.06	6.15	2.52	3.03	1.58	1.86	2.62
49	((Epi)catechin-(epi)gallocatechin) 1	1.53	6.94	5.02	2.09	4.11	4.43	3.69	3.61	5.60	6.97	2.86	3.67	2.05	2.02	2.92
50	((Epi)catechin-(epi)gallocatechin) A 2	0.09	0.48	0.15	0.22	0.24	0.10	0.10	0.11	<LD	<LD	0.03	0.12	<LD	<LD	<LD
51	((Epi)catechin)$_2$ 1	2.35	7.44	5.80	2.59	4.53	6.85	4.21	4.74	8.87	9.18	4.30	4.94	2.34	2.53	3.58
52	Procyanidin B 1	8.91	49.15	28.02	9.49	22.64	28.01	20.50	28.50	47.41	60.62	22.71	29.83	10.75	8.60	20.49
53	Procyanidin B 2	2.10	8.10	5.80	2.75	5.63	6.20	5.40	7.49	11.41	14.53	5.77	7.26	3.96	3.81	5.73
54	Catechin	1.11	2.74	2.15	1.82	2.31	2.55	2.43	2.65	2.91	3.10	2.07	2.25	1.34	1.43	2.02
55	Epicatechin	0.28	0.86	0.69	0.52	0.78	0.77	0.86	1.43	1.27	1.47	0.72	0.87	0.59	0.59	0.86
56	*p*-vinyl(epi)catechin 1	1.89	2.96	2.93	2.73	2.20	3.04	1.85	1.70	1.72	1.68	1.28	1.29	0.64	0.87	1.17
57	*p*-vinyl(epi)catechin 2	<LD	<LD	<LD	<LD	<LD	0.12	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
58	*p*-vinyl(epi)catechin 3	<LD	0.36	0.72	0.56	0.37	0.62	0.44	0.66	0.33	0.44	0.16	0.34	0.11	0.19	0.18

Tank 09

#	Time (days)	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
41	((Epi)gallocatechin)$_2$ 1	0.48	2.38	1.49	1.54	1.50	1.72	1.43	1.23	1.70	1.96	1.33	1.26	0.55	1.07	1.56
42	((Epi)gallocatechin)$_2$ 2	0.18	0.69	0.46	0.44	0.44	0.42	0.39	0.35	0.51	0.49	0.36	0.45	0.17	0.34	0.49
43	((Epi)gallocatechin)$_2$ 3	<LD	0.10	0.08	0.08	0.08	0.04	0.05	0.06	0.13	0.14	0.07	0.09	0.05	0.06	0.13
44	Gallocatechin	0.70	2.41	1.66	1.70	1.47	1.52	1.70	1.54	1.62	1.97	0.84	1.22	0.60	0.76	1.30
45	Epigallocatechin	0.32	0.64	0.47	0.58	0.45	0.32	0.56	0.40	0.63	0.63	0.37	0.36	0.31	0.32	0.44
46	((Epi)gallocatechin-(epi)catechin) 2	0.25	2.34	1.79	1.51	1.67	1.62	1.72	1.95	2.11	2.94	0.89	1.16	0.45	0.99	1.51
47	((Epi)catechin-(epi)gallocatechin) 2	0.41	1.78	1.49	1.35	1.43	1.31	0.98	1.26	1.42	1.59	0.87	0.97	0.47	0.73	1.19
48	((Epi)gallocatechin-(epi)catechin) 1	1.40	6.31	3.60	3.55	3.61	4.73	3.13	3.49	4.92	5.90	3.29	3.55	1.50	2.59	3.76
49	((Epi)catechin-(epi)gallocatechin) 1	1.76	6.93	4.11	4.07	4.21	5.69	3.63	3.96	5.35	6.24	3.70	4.04	1.84	2.65	3.90
50	((Epi)catechin-(epi)gallocatechin) A 2	<LD	0.49	0.46	0.27	0.40	0.21	0.11	<LD	<LD	0.20	0.04	0.08	0.04	<LD	<LD
51	((Epi)catechin)$_2$ 1	2.87	6.92	4.40	4.30	4.70	6.43	5.02	5.00	6.62	8.01	4.80	5.18	<LD	3.17	4.53
52	Procyanidin B 1	10.80	51.15	21.42	23.91	22.27	36.84	23.75	31.43	40.04	47.34	27.89	33.13	<LD	14.67	28.49
53	Procyanidin B 2	2.69	10.60	6.23	6.09	6.94	8.86	7.90	9.67	13.26	15.23	8.02	9.58	<LD	5.82	8.69
54	Catechin	1.14	3.95	2.36	2.42	2.57	2.72	2.63	2.97	3.61	4.21	2.03	2.61	1.68	1.75	2.49
55	Epicatechin	0.41	1.62	1.36	1.39	1.38	1.30	1.71	1.51	1.88	2.20	1.32	1.43	0.97	1.09	1.43
56	*p*-vinyl(epi)catechin 1	1.78	2.92	2.97	2.35	2.23	2.05	1.73	1.55	1.53	1.76	0.81	0.92	0.57	0.73	0.81
57	*p*-vinyl(epi)catechin 2	<LD	<LD	<LD	<LD	0.42	0.13	0.30	0.37	<LD	<LD	<LD	<LD	<LD	<LD	<LD
58	*p*-vinyl(epi)catechin 3	<LD	0.20	0.87	1.35	0.99	1.64	1.60	0.95	0.79	0.87	0.49	0.78	0.19	0.29	0.23

continued

Table S4. Tannin concentrations determined by HPLC-DAD-ESI(+)-MS/MS in red wine samples from Mendavia 2018, expressed in mg of (+)-cat equiv./L.

Tank 10

#	Time (days)	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
41	((Epi)gallocatechin)$_2$ 1	0.55	0.40	2.44	1.72	1.61	1.80	1.49	1.30	1.44	1.67	1.10	1.47	0.54	1.09	1.41
42	((Epi)gallocatechin)$_2$ 2	0.21	0.17	0.70	0.52	0.52	0.56	0.45	0.39	0.42	0.47	0.25	0.38	0.17	0.31	0.44
43	((Epi)gallocatechin)$_2$ 3	<LQ	0.07	0.11	0.12	0.11	0.04	0.06	0.07	0.18	0.11	0.04	0.10	<LQ	0.06	0.10
44	Gallocatechin	0.67	1.33	1.53	1.58	1.47	1.49	1.71	1.57	1.74	2.06	0.72	1.21	0.53	0.71	1.15
45	Epigallocatechin	0.22	0.41	0.60	0.55	0.58	0.39	0.47	0.50	0.44	0.38	0.22	0.31	0.23	0.27	0.39
46	((Epi)gallocatechin-(epi)catechin) 2	0.27	0.62	1.94	1.55	1.78	1.54	1.59	1.72	2.07	2.73	0.76	1.25	0.48	0.80	1.32
47	((Epi)catechin-(epi)gallocatechin) 2	0.40	0.43	1.76	1.35	1.72	1.38	1.40	1.30	1.41	1.49	0.83	0.90	0.43	0.74	1.24
48	((Epi)gallocatechin-(epi)catechin) 1	1.40	1.77	5.35	3.79	3.92	4.97	3.19	3.66	4.20	5.40	2.74	3.82	1.43	2.53	3.38
49	((Epi)catechin-(epi)gallocatechin) 1	2.01	2.32	5.31	3.77	4.52	5.14	3.52	3.87	4.11	5.42	3.04	4.29	1.85	2.61	3.68
50	((Epi)catechin-(epi)gallocatechin) A 2	<LD	0.21	0.26	0.25	0.51	0.13	0.14	<LD	<LD	0.11	<LD	<LD	<LD	<LD	<LD
51	((Epi)catechin)$_2$ 1	2.34	3.38	5.46	4.92	4.83	6.23	4.75	5.94	5.84	8.60	3.54	5.71	2.30	3.22	4.62
52	Procyanidin B 1	9.13	15.04	27.30	24.77	25.08	36.42	22.04	32.40	35.22	45.67	22.73	36.33	10.12	15.25	26.87
53	Procyanidin B 2	2.58	4.48	6.65	6.36	6.57	8.93	7.07	8.49	11.22	14.14	6.59	8.41	4.26	5.83	8.11
54	Catechin	1.50	2.58	2.41	2.45	2.56	2.62	2.70	3.14	3.31	4.57	1.82	2.63	1.47	1.65	2.13
55	Epicatechin	0.45	0.82	0.91	1.35	1.39	1.43	1.65	1.79	1.86	1.98	0.79	1.24	0.78	0.87	1.25
56	*p*-vinyl(epi)catechin 1	1.69	2.75	2.54	2.33	2.16	1.95	1.68	1.41	1.43	1.91	0.79	0.92	0.45	0.69	0.79
57	*p*-vinyl(epi)catechin 2	<LD	<LD	0.28	<LD	0.48	0.18	0.27	0.31	<LD	<LD	<LD	<LD	<LD	<LD	<LD
58	*p*-vinyl(epi)catechin 3	<LD	0.33	1.39	1.46	1.00	1.72	1.56	0.80	0.72	0.79	0.53	0.61	0.20	0.26	0.27

Tank 11

#	Time (days)	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
41	((Epi)gallocatechin)$_2$ 1	0.50	1.19	2.27	1.51	0.48	0.99	1.42	1.25	1.28	1.86	1.13	0.94	0.41	0.80	1.23
42	((Epi)gallocatechin)$_2$ 2	0.19	0.47	0.75	0.43	0.17	0.33	0.38	0.35	0.48	0.47	0.29	0.27	0.15	0.31	0.42
43	((Epi)gallocatechin)$_2$ 3	<LQ	0.13	0.16	0.05	0.05	0.03	0.06	0.11	0.08	0.21	0.06	0.06	0.04	0.07	0.08
44	Gallocatechin	0.73	1.97	1.60	1.66	0.87	1.45	1.57	1.61	1.74	1.86	1.10	1.18	0.59	0.68	1.31
45	Epigallocatechin	0.23	0.68	0.61	0.53	0.29	0.42	0.50	0.46	0.48	0.43	0.37	0.37	0.21	0.30	0.37
46	((Epi)gallocatechin-(epi)catechin) 2	0.23	0.98	1.99	1.55	0.61	1.44	1.48	1.66	1.97	2.40	0.99	1.11	0.49	0.70	1.42
47	((Epi)catechin-(epi)gallocatechin) 2	0.39	1.51	1.76	1.44	0.76	1.25	0.99	0.99	1.45	1.51	0.85	0.83	0.43	0.67	1.00
48	((Epi)gallocatechin-(epi)catechin) 1	1.41	3.27	5.08	3.33	1.67	3.75	2.88	3.53	3.79	5.59	2.94	3.06	1.25	2.23	3.09
49	((Epi)catechin-(epi)gallocatechin) 1	1.74	3.69	5.40	3.94	2.10	4.79	3.22	3.86	4.15	5.84	3.08	3.65	1.52	2.44	3.33
50	((Epi)catechin-(epi)gallocatechin) A 2	<LD	0.43	0.34	0.30	0.43	0.20	0.09	<LD	<LD	0.18	0.07	0.07	0.06	<LD	<LD
51	((Epi)catechin)$_2$ 1	2.42	4.31	5.40	4.61	2.08	5.51	4.59	5.52	6.36	8.00	4.23	4.73	1.96	3.05	4.18
52	Procyanidin B 1	8.38	20.81	27.13	21.95	8.47	30.52	20.02	30.59	32.30	48.64	24.36	31.13	6.31	12.33	22.43
53	Procyanidin B 2	2.22	6.14	6.93	6.24	2.79	7.17	6.73	8.66	10.09	13.53	7.26	8.62	4.31	5.34	7.23
54	Catechin	1.15	3.14	2.37	2.51	1.97	2.68	2.55	3.13	3.45	3.62	2.24	2.73	1.67	1.75	2.33
55	Epicatechin	0.33	1.18	1.31	1.42	0.59	0.90	1.53	1.56	1.79	1.87	1.26	1.23	0.83	0.99	1.38
56	*p*-vinyl(epi)catechin 1	1.68	2.86	2.70	2.22	1.84	2.00	1.53	1.38	1.23	1.45	0.72	0.87	0.36	0.58	0.69
57	*p*-vinyl(epi)catechin 2	<LD	<LD	0.34	<LD	0.28	<LD	<LD	0.29	<LD	<LD	<LD	<LD	<LD	<LD	<LD
58	*p*-vinyl(epi)catechin 3	<LD	0.45	1.43	1.39	0.72	1.47	1.39	0.91	0.74	0.85	0.47	0.66	0.18	0.30	0.24

Tank 12

#	Time (days)	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
41	((Epi)gallocatechin)$_2$ 1	0.46	0.90	2.11	1.77	1.58	1.70	1.66	1.29	1.32	<LD	1.25	1.60	0.62	0.73	1.32
42	((Epi)gallocatechin)$_2$ 2	0.22	0.34	0.62	0.53	0.47	0.38	0.46	0.28	0.46	<LD	0.32	0.35	0.18	0.23	0.37
43	((Epi)gallocatechin)$_2$ 3	0.07	0.08	0.17	0.08	0.05	0.07	0.04	0.05	0.11	<LD	0.03	0.07	<LQ	0.05	0.07
44	Gallocatechin	0.60	1.64	1.65	1.53	1.51	1.42	1.68	1.63	1.70	<LD	0.85	1.27	0.56	0.73	1.19
45	Epigallocatechin	0.24	0.39	0.43	0.52	0.41	0.47	0.50	0.36	0.50	<LD	0.28	0.34	0.24	0.21	0.33
46	((Epi)gallocatechin-(epi)catechin) 2	0.35	1.53	1.91	1.48	1.59	1.52	1.60	1.85	1.97	<LD	0.90	1.48	0.46	0.75	1.40
47	((Epi)catechin-(epi)gallocatechin) 2	0.36	0.79	1.53	1.47	1.45	1.41	1.38	1.49	1.31	<LD	0.76	0.95	0.43	0.54	0.95
48	((Epi)gallocatechin-(epi)catechin) 1	1.26	3.31	4.92	3.82	3.50	4.89	3.61	3.67	4.08	<LD	3.18	4.36	1.70	2.14	3.35
49	((Epi)catechin-(epi)gallocatechin) 1	1.88	3.88	4.91	4.37	4.36	5.09	4.03	4.02	4.28	<LD	3.53	4.08	2.23	2.31	3.56
50	((Epi)catechin-(epi)gallocatechin) A 2	<LD	0.49	0.33	0.32	0.38	0.22	0.12	0.13	<LD	<LD	<LD	0.06	<LD	<LD	<LD
51	((Epi)catechin)$_2$ 1	2.40	5.70	5.32	4.58	4.77	6.76	5.36	4.99	6.00	<LD	4.71	5.43	2.48	2.97	3.83
52	Procyanidin B 1	9.07	30.86	25.40	24.62	24.75	34.34	24.74	30.39	32.60	<LD	25.54	32.97	10.96	12.40	24.96
53	Procyanidin B 2	2.68	7.85	6.01	6.40	6.39	9.22	8.21	9.42	10.52	<LD	7.79	9.00	5.03	5.05	7.20
54	Catechin	1.19	2.62	2.53	2.30	2.46	2.55	2.52	3.25	3.27	<LD	2.03	2.57	1.37	1.77	1.92
55	Epicatechin	0.44	1.17	0.99	1.00	1.30	1.37	1.72	1.78	1.82	<LD	1.20	1.31	0.85	0.95	1.25
56	*p*-vinyl(epi)catechin 1	1.68	3.24	2.66	2.48	2.20	2.30	1.65	1.56	1.36	<LD	0.75	1.13	0.45	0.78	0.84
57	*p*-vinyl(epi)catechin 2	<LD	<LD	0.39	<LD	<LD	<LD	<LD	0.32	<LD	<LD	<LD	<LD	<LD	<LD	<LD
58	*p*-vinyl(epi)catechin 3	<LD	0.42	1.57	1.42	0.77	1.44	1.50	0.90	0.81	<LD	0.43	0.71	0.22	0.30	0.22

continued

Table S4. Tannin concentrations determined by HPLC-DAD-ESI(+)-MS/MS in red wine samples from Mendavia 2018, expressed in mg of (+)-cat equiv./L.

Tank 13

#	Time (days)	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
41	((Epi)gallocatechin)$_2$ 1	0.59	1.48	1.76	1.66	1.58	1.42	1.48	0.92	1.22	1.58	1.83	1.31	1.13	0.92	1.33
42	((Epi)gallocatechin)$_2$ 2	0.22	0.49	0.53	0.48	0.44	0.37	0.34	0.33	0.41	0.27	0.50	0.36	0.33	0.27	0.35
43	((Epi)gallocatechin)$_2$ 3	0.05	0.19	0.07	0.08	0.12	0.02	0.05	0.12	0.09	0.16	0.06	0.06	0.09	0.08	0.10
44	Gallocatechin	0.85	1.97	1.74	1.73	1.53	1.56	1.72	1.54	1.70	1.61	1.30	1.26	0.81	0.81	0.96
45	Epigallocatechin	0.30	0.72	0.48	0.54	0.59	0.53	0.57	0.43	0.45	0.43	0.38	0.46	0.33	0.31	0.30
46	((Epi)gallocatechin-(epi)catechin) 2	0.24	1.75	1.75	1.65	1.75	1.61	1.43	1.63	1.53	2.14	1.49	1.15	0.90	0.76	1.23
47	((Epi)catechin-(epi)gallocatechin) 2	0.45	1.38	1.61	1.45	1.46	1.26	1.36	1.26	1.38	1.49	1.30	0.91	0.75	0.69	0.95
48	((Epi)gallocatechin-(epi)catechin) 1	1.74	4.22	4.18	3.74	3.82	4.03	3.15	3.26	3.92	5.57	4.20	3.89	2.93	2.47	3.22
49	((Epi)catechin-(epi)gallocatechin) 1	2.52	4.32	4.68	4.18	4.48	5.19	3.44	3.73	4.45	5.38	4.57	4.51	3.32	2.78	3.18
50	((Epi)catechin-(epi)gallocatechin) A	0.05	0.45	0.15	0.19	0.46	0.14	0.09	<LD	<LD	0.07	<LD	<LD	<LD	<LD	<LD
51	((Epi)catechin)$_2$ 1	3.03	5.41	4.87	4.45	5.17	5.20	4.82	5.10	5.84	7.43	5.60	5.82	3.53	3.28	3.40
52	Procyanidin B 1	12.89	27.03	28.08	23.46	26.89	35.36	23.19	30.70	34.57	48.05	36.76	38.51	20.87	13.73	22.77
53	Procyanidin B 2	3.42	7.05	6.47	6.00	7.49	7.56	6.83	9.35	10.74	10.65	8.12	10.07	6.26	5.49	6.53
54	Catechin	1.60	3.19	2.47	2.44	2.83	2.56	2.59	2.84	3.56	3.85	2.62	2.59	1.89	1.78	1.86
55	Epicatechin	0.53	1.12	0.89	1.36	1.52	1.21	1.58	1.43	1.88	1.89	1.56	1.25	1.02	0.92	0.94
56	*p*-vinyl(epi)catechin 1	1.92	3.06	2.94	2.38	2.24	2.13	1.67	1.47	1.57	1.72	1.33	1.21	0.61	0.85	0.68
57	*p*-vinyl(epi)catechin 2	<LD	<LD	<LD	<LD	<LD	<LD	<LD	0.15	<LD	<LD	<LD	<LD	<LD	<LD	<LD
58	*p*-vinyl(epi)catechin 3	<LD	0.42	1.39	0.91	0.53	1.20	0.87	0.58	0.54	0.48	0.52	0.63	0.23	0.30	0.24

Tank 14

#	Time (days)	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
41	((Epi)gallocatechin)$_2$ 1	0.74	1.28	2.70	1.63	0.91	1.35	0.91	1.35	1.58	1.35	1.49	1.38	0.69	0.90	0.98
42	((Epi)gallocatechin)$_2$ 2	0.23	0.50	0.76	0.52	0.36	0.29	0.29	0.39	0.40	0.36	0.40	0.40	0.23	0.27	0.32
43	((Epi)gallocatechin)$_2$ 3	0.13	0.19	0.22	0.03	0.14	0.03	0.12	0.11	0.13	0.12	0.02	0.08	0.06	0.07	0.07
44	Gallocatechin	0.79	1.84	1.87	1.68	1.62	1.52	1.65	1.74	1.61	1.33	1.23	1.17	0.72	0.75	1.14
45	Epigallocatechin	0.35	0.72	0.64	0.59	0.65	0.38	0.41	0.39	0.42	0.25	0.40	0.34	0.35	0.29	0.35
46	((Epi)gallocatechin-(epi)catechin) 2	0.35	1.42	2.32	1.49	1.37	1.45	1.41	2.03	1.66	1.77	0.97	0.99	0.51	0.77	1.00
47	((Epi)catechin-(epi)gallocatechin) 2	0.45	1.31	1.89	1.44	1.34	1.15	0.91	0.93	1.34	1.18	1.22	0.89	0.47	0.69	0.85
48	((Epi)gallocatechin-(epi)catechin) 1	2.13	3.77	6.73	3.60	2.93	3.98	2.53	3.69	4.22	5.38	3.53	3.91	1.77	2.38	2.69
49	((Epi)catechin-(epi)gallocatechin) 1	2.61	4.35	6.75	4.39	3.77	5.14	3.05	3.88	4.57	5.66	4.26	4.41	2.36	2.72	2.99
50	((Epi)catechin-(epi)gallocatechin) A	<LD	0.55	0.18	0.20	0.35	0.24	0.04	<LD	0.12	<LD	<LD	<LD	<LD	<LD	<LD
51	((Epi)catechin)$_2$ 1	3.00	5.28	6.24	4.87	4.40	5.75	4.38	5.10	5.80	7.28	5.43	6.03	2.94	3.15	3.57
52	Procyanidin B 1	15.11	28.14	34.40	25.32	22.29	32.93	19.19	32.98	38.29	48.49	33.25	38.79	14.99	14.02	21.37
53	Procyanidin B 2	3.65	7.30	7.74	6.63	6.27	7.96	6.38	9.21	10.14	10.97	9.09	9.22	5.30	5.02	6.44
54	Catechin	1.55	3.28	2.73	2.55	2.63	2.87	2.70	3.13	3.45	3.77	2.56	2.33	1.76	1.55	1.82
55	Epicatechin	0.43	1.27	1.52	1.43	1.27	1.42	1.55	1.60	1.76	1.53	1.44	1.30	0.89	0.81	0.83
56	*p*-vinyl(epi)catechin 1	2.27	2.95	3.08	2.58	2.16	2.34	1.73	1.54	1.63	1.75	1.26	1.14	0.70	0.88	0.68
57	*p*-vinyl(epi)catechin 2	<LD	<LD	0.46	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
58	*p*-vinyl(epi)catechin 3	0.09	0.46	1.34	0.82	0.67	1.14	0.79	0.61	0.57	0.58	0.49	0.50	0.24	0.30	0.20

Tank 15

#	Time (days)	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
41	((Epi)gallocatechin)$_2$ 1	0.51	1.20	1.96	1.37	0.91	0.89	1.48	0.72	0.86	1.22	1.35	1.22	0.74	0.79	0.74
42	((Epi)gallocatechin)$_2$ 2	0.09	0.39	0.59	0.32	0.36	0.21	0.29	0.30	0.40	0.37	0.36	0.37	0.24	0.24	0.29
43	((Epi)gallocatechin)$_2$ 3	0.05	0.16	0.07	0.05	0.14	<LD	0.02	0.10	0.15	0.12	0.05	0.04	0.05	0.05	0.08
44	Gallocatechin	0.74	1.81	1.92	1.66	1.62	1.63	1.57	1.57	1.70	1.72	1.28	1.33	0.74	0.80	1.16
45	Epigallocatechin	0.13	0.75	0.55	0.41	0.65	0.40	0.47	0.51	0.60	0.43	0.40	0.38	0.34	0.30	0.38
46	((Epi)gallocatechin-(epi)catechin) 2	0.26	1.45	2.16	1.36	1.37	1.20	1.52	1.42	1.72	1.50	1.23	1.21	0.73	0.82	0.85
47	((Epi)catechin-(epi)gallocatechin) 2	0.34	1.02	1.73	1.42	1.34	0.97	1.45	0.98	1.26	1.00	0.96	0.91	0.53	0.68	0.73
48	((Epi)gallocatechin-(epi)catechin) 1	1.53	3.60	4.76	3.23	2.93	3.39	3.08	2.79	3.20	3.83	3.22	3.39	1.93	2.22	2.31
49	((Epi)catechin-(epi)gallocatechin) 1	2.14	4.16	4.92	3.92	3.77	4.36	3.75	3.32	3.75	4.56	3.69	4.04	2.33	2.35	2.66
50	((Epi)catechin-(epi)gallocatechin) A	<LD	0.63	0.30	0.14	0.35	0.23	0.11	<LD	<LD	<LD	<LD	<LD	<LD	0.07	<LD
51	((Epi)catechin)$_2$ 1	2.81	4.97	5.50	4.65	4.40	5.35	5.13	4.91	5.93	7.81	4.92	5.78	2.81	2.97	3.51
52	Procyanidin B 1	11.17	25.56	28.39	20.44	22.29	30.91	22.74	25.48	30.49	41.61	29.75	32.89	12.49	11.99	17.98
53	Procyanidin B 2	3.30	7.01	7.06	6.18	6.27	7.60	8.08	8.15	9.15	10.44	8.61	9.95	5.16	5.20	6.05
54	Catechin	1.35	3.13	2.77	2.46	2.63	2.60	2.75	3.20	3.72	3.86	2.60	2.86	1.81	1.81	1.92
55	Epicatechin	0.43	1.10	1.49	1.49	1.27	1.23	1.57	1.81	1.96	1.93	1.38	1.47	1.04	0.92	1.19
56	*p*-vinyl(epi)catechin 1	1.98	3.01	2.94	2.43	2.16	2.00	1.68	1.45	1.45	1.27	1.23	0.96	0.55	0.79	0.69
57	*p*-vinyl(epi)catechin 2	<LD	<LD	0.26	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
58	*p*-vinyl(epi)catechin 3	<LD	0.50	1.35	0.82	0.67	0.91	0.80	0.51	0.56	0.58	0.43	0.51	0.21	0.27	0.16

continued

Table S4. Tannin concentrations determined by HPLC-DAD-ESI(+)-MS/MS in red wine samples from Mendavia 2018, expressed in mg of (+)-cat equiv./L.

Tank 16

#	Time (days)	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
41	((Epi)gallocatechin)$_2$ 1	0.59	1.81	1.37	1.56	0.48	1.69	0.87	1.48	1.68	1.19	1.60	0.96	0.75	0.76	1.18
42	((Epi)gallocatechin)$_2$ 2	0.12	0.71	0.42	0.41	0.17	0.45	0.25	0.44	0.48	0.44	0.48	0.30	0.25	0.26	0.28
43	((Epi)gallocatechin)$_2$ 3	0.02	0.19	0.07	0.04	0.10	0.04	0.04	0.07	0.11	0.12	0.04	0.10	0.05	0.08	0.07
44	Gallocatechin	0.73	1.90	1.81	1.64	0.96	1.65	1.63	1.67	1.79	1.71	1.33	1.26	0.83	0.68	0.95
45	Epigallocatechin	0.20	0.65	0.57	0.51	0.39	0.55	0.51	0.51	0.50	0.34	0.48	0.40	0.34	0.26	0.25
46	((Epi)gallocatechin-(epi)catechin) 2	0.34	1.88	1.79	1.60	0.70	1.82	1.57	1.79	2.16	2.07	1.46	1.12	0.83	0.64	1.29
47	((Epi)catechin-(epi)gallocatechin) 2	0.58	1.29	1.53	0.88	0.58	1.54	0.85	1.35	1.58	1.37	0.98	1.12	0.69	0.56	0.83
48	((Epi)gallocatechin-(epi)catechin) 1	1.77	5.09	3.59	3.32	1.67	4.70	2.92	3.99	4.85	4.98	3.86	4.05	2.13	1.95	2.66
49	((Epi)catechin-(epi)gallocatechin) 1	2.39	5.34	4.06	3.85	2.19	6.23	2.88	4.27	5.47	5.29	4.21	4.45	2.53	2.27	3.20
50	((Epi)catechin-(epi)gallocatechin) A	<LD	0.79	0.29	0.31	0.35	0.32	0.17	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
51	((Epi)catechin)$_2$ 1	2.94	5.68	5.39	4.84	2.87	6.88	3.87	6.40	7.50	8.51	5.82	7.41	3.21	2.92	3.76
52	Procyanidin B 1	12.44	35.18	25.49	22.34	10.56	35.19	19.02	34.43	42.21	46.78	35.45	44.77	17.04	10.88	20.34
53	Procyanidin B 2	3.57	8.92	6.20	6.43	3.13	8.78	6.42	10.23	13.93	14.24	9.73	14.09	6.21	5.29	6.92
54	Catechin	1.45	3.39	2.53	2.64	2.21	3.24	2.71	3.38	3.84	4.54	2.56	3.02	1.94	1.47	1.86
55	Epicatechin	0.45	1.39	1.39	1.60	0.72	1.52	1.67	1.96	2.10	2.02	1.62	1.62	1.14	0.92	1.15
56	*p*-vinyl(epi)catechin 1	1.83	3.09	3.31	2.93	2.45	2.35	1.59	1.59	1.78	1.85	1.45	1.23	0.77	0.86	0.72
57	*p*-vinyl(epi)catechin 2	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
58	*p*-vinyl(epi)catechin 3	<LD	0.38	1.42	0.84	0.59	1.18	0.95	0.73	0.75	0.62	0.56	0.49	0.23	0.33	0.20

Tank 17

#	Time (days)	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
41	((Epi)gallocatechin)$_2$ 1	0.91	3.18	1.93	1.50	1.82	1.77	1.58	1.00	2.03	2.30	1.68	1.89	0.54	1.30	0.93
42	((Epi)gallocatechin)$_2$ 2	0.27	0.85	0.48	0.40	0.44	0.53	0.33	0.32	0.50	0.65	0.43	0.46	0.18	0.41	0.35
43	((Epi)gallocatechin)$_2$ 3	0.03	0.10	0.06	0.04	0.08	0.00	0.06	0.07	0.09	0.10	0.09	0.04	<LQ	0.06	0.04
44	Gallocatechin	0.94	1.70	1.54	1.55	1.38	1.74	1.57	1.41	1.71	1.60	1.38	1.19	0.59	0.73	1.14
45	Epigallocatechin	0.29	0.62	0.33	0.53	0.44	0.32	0.33	0.33	0.35	0.46	0.35	0.39	0.23	0.30	0.29
46	((Epi)gallocatechin-(epi)catechin) 2	0.20	1.37	1.57	0.88	1.57	1.56	1.55	1.53	1.69	1.99	1.51	1.23	0.40	0.84	0.72
47	((Epi)catechin-(epi)gallocatechin) 2	0.65	1.36	1.43	1.37	1.45	1.54	0.97	0.87	1.61	1.79	1.38	1.01	0.50	0.85	0.78
48	((Epi)gallocatechin-(epi)catechin) 1	2.44	6.59	4.68	3.02	4.62	4.92	3.39	3.17	5.15	6.68	4.24	4.88	1.53	3.07	2.39
49	((Epi)catechin-(epi)gallocatechin) 1	3.17	6.35	5.24	3.47	4.94	6.38	3.63	3.32	5.78	7.38	4.43	5.34	1.97	3.10	2.67
50	((Epi)catechin-(epi)gallocatechin) A	<LD	0.28	0.23	0.24	0.25	0.12	0.14	<LD	<LD	<LD	0.07	<LD	<LD	0.07	<LD
51	((Epi)catechin)$_2$ 1	3.55	7.38	5.32	4.21	5.47	6.92	4.61	3.44	7.84	8.87	5.61	6.95	2.85	3.84	2.97
52	Procyanidin B 1	18.83	50.43	31.42	20.31	30.09	41.61	23.65	24.96	51.00	58.10	34.38	46.49	12.51	18.39	17.12
53	Procyanidin B 2	4.38	8.65	6.13	5.04	6.73	9.08	6.62	6.24	12.51	14.67	8.55	11.55	4.92	6.03	5.35
54	Catechin	1.58	2.77	2.30	2.21	2.49	2.71	2.51	2.81	3.09	3.45	2.58	2.62	1.45	1.64	1.82
55	Epicatechin	0.53	0.81	0.75	0.63	0.77	1.13	1.33	0.86	1.36	1.33	1.28	0.99	0.61	0.81	0.76
56	*p*-vinyl(epi)catechin 1	1.73	3.06	3.06	2.53	2.21	2.44	1.64	1.30	1.56	1.72	1.36	0.88	0.46	0.69	0.48
57	*p*-vinyl(epi)catechin 2	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
58	*p*-vinyl(epi)catechin 3	<LD	0.57	0.51	0.52	0.41	0.85	0.68	0.42	0.46	0.55	0.34	0.41	0.17	0.29	0.16

Tank 18

#	Time (days)	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
41	((Epi)gallocatechin)$_2$ 1	0.79	3.43	2.55	1.42	1.50	1.43	0.74	1.37	1.81	1.72	1.35	1.39	1.02	1.12	1.41
42	((Epi)gallocatechin)$_2$ 2	0.28	0.82	0.52	0.35	0.40	0.42	0.26	0.37	0.62	0.48	0.43	0.38	0.29	0.31	0.47
43	((Epi)gallocatechin)$_2$ 3	0.03	0.26	0.09	0.04	0.10	<LD	0.09	0.13	0.12	0.24	0.05	0.07	0.04	0.07	0.11
44	Gallocatechin	0.81	1.68	1.60	1.55	1.43	1.68	1.55	1.77	1.67	1.74	1.35	1.28	0.67	0.86	1.16
45	Epigallocatechin	0.36	0.53	0.36	0.31	0.36	0.51	0.29	0.36	0.35	0.49	0.35	0.41	0.22	0.27	0.38
46	((Epi)gallocatechin-(epi)catechin) 2	0.32	1.91	1.69	0.88	1.36	1.24	1.36	1.76	1.68	1.64	1.34	1.11	0.58	0.92	1.36
47	((Epi)catechin-(epi)gallocatechin) 2	0.55	1.65	1.60	0.89	1.33	1.25	1.37	1.26	1.60	1.42	0.99	0.85	0.62	0.79	1.15
48	((Epi)gallocatechin-(epi)catechin) 1	2.13	7.48	5.58	3.06	4.04	4.90	2.72	3.72	5.02	5.27	3.42	3.70	2.28	2.61	3.11
49	((Epi)catechin-(epi)gallocatechin) 1	3.03	7.73	6.07	3.44	5.00	5.82	3.56	3.88	5.74	5.55	3.88	4.37	2.60	2.96	3.38
50	((Epi)catechin-(epi)gallocatechin) A	<LD	0.43	0.17	0.13	0.29	0.10	0.15	<LD	<LD	<LD	<LD	0.06	<LD	<LD	<LD
51	((Epi)catechin)$_2$ 1	2.90	7.45	5.46	4.05	5.44	7.18	3.65	5.33	8.31	9.05	4.92	5.73	2.90	3.59	4.13
52	Procyanidin B 1	15.83	60.08	32.53	20.25	30.77	43.29	19.38	28.83	49.84	54.42	27.96	38.56	16.61	17.48	24.24
53	Procyanidin B 2	3.99	9.81	6.67	5.02	6.57	8.25	5.31	8.39	13.21	11.65	7.84	9.41	4.98	5.70	7.14
54	Catechin	1.67	2.83	2.05	2.03	2.45	2.62	2.11	3.40	3.23	3.69	2.74	2.61	1.48	1.74	2.16
55	Epicatechin	0.50	0.94	0.60	0.65	0.84	0.84	1.34	1.52	1.38	1.33	1.21	0.97	0.57	0.80	1.16
56	*p*-vinyl(epi)catechin 1	1.94	2.74	2.64	2.42	2.10	2.16	1.58	1.48	1.60	1.37	1.25	0.85	0.49	0.85	0.56
57	*p*-vinyl(epi)catechin 2	<LD	<LD	0.16	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
58	*p*-vinyl(epi)catechin 3	<LD	0.52	0.58	0.61	0.21	1.14	0.59	0.40	0.41	0.54	0.41	0.53	0.18	0.29	<LD

continued

Table S4. Tannin concentrations determined by HPLC-DAD-ESI(+)-MS/MS in red wine samples from Mendavia 2018, expressed in mg of (+)-cat equiv./L.

Tank 19

#	Time (days)	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
41	((Epi)gallocatechin)$_2$ 1	1.38	3.70	1.99	1.52	1.93	1.65	1.73	1.28	2.01	2.10	1.61	1.64	0.71	1.01	0.64
42	((Epi)gallocatechin)$_2$ 2	0.33	0.82	0.54	0.36	0.51	0.48	0.36	0.29	0.50	0.51	0.43	0.44	0.23	0.32	0.18
43	((Epi)gallocatechin)$_2$ 3	0.08	0.19	0.05	0.08	0.08	0.05	0.09	0.13	<LD	0.09	0.13	0.11	0.05	0.07	0.06
44	Gallocatechin	1.19	1.66	1.80	1.68	1.65	2.00	1.91	1.81	1.73	1.94	1.33	1.47	0.77	0.79	0.79
45	Epigallocatechin	0.30	0.58	0.49	0.43	0.46	0.41	0.51	0.56	0.38	0.60	0.28	0.43	0.22	0.26	0.30
46	((Epi)gallocatechin-(epi)catechin) 2	0.45	1.72	1.64	1.44	1.49	1.31	1.53	1.92	1.59	1.89	1.34	1.20	0.57	0.75	0.65
47	((Epi)catechin-(epi)gallocatechin) 2	0.70	1.51	1.54	1.46	1.55	1.50	1.49	0.98	1.47	1.26	1.28	1.14	0.57	0.77	0.80
48	((Epi)gallocatechin-(epi)catechin) 1	3.23	7.81	4.16	3.37	4.63	4.76	3.75	3.50	4.90	6.10	3.99	4.52	2.01	2.54	1.97
49	((Epi)catechin-(epi)gallocatechin) 1	3.65	7.83	5.20	3.75	4.95	5.65	4.51	3.92	5.89	6.74	4.54	5.04	2.45	2.86	2.36
50	((Epi)catechin-(epi)gallocatechin) A	<LD	0.39	0.18	<LD	0.44	0.28	0.11	0.13	<LD	<LD	<LD	<LD	<LD	<LD	<LD
51	((Epi)catechin)$_2$ 1	3.80	7.94	5.70	4.95	5.91	7.35	6.13	5.29	7.95	8.33	5.86	7.38	2.86	3.50	3.06
52	Procyanidin B 1	20.80	60.80	31.75	22.98	33.27	39.14	26.27	27.22	51.62	56.09	32.77	45.33	12.82	17.55	17.68
53	Procyanidin B 2	4.37	9.30	6.09	5.41	6.96	7.66	7.31	7.93	11.44	12.81	8.64	10.35	4.63	5.38	5.62
54	Catechin	1.60	2.91	2.56	2.37	2.62	2.91	2.91	3.33	3.21	3.74	2.24	3.10	1.57	1.56	2.00
55	Epicatechin	0.45	0.90	0.72	0.75	0.84	1.31	1.37	1.53	1.42	1.42	0.95	1.11	0.74	0.69	0.93
56	*p*-vinyl(epi)catechin 1	1.91	2.62	3.07	2.40	2.14	2.64	1.84	1.48	1.46	1.68	0.96	1.12	0.55	0.78	0.75
57	*p*-vinyl(epi)catechin 2	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
58	*p*-vinyl(epi)catechin 3	<LD	0.28	0.50	0.59	0.43	0.88	0.84	0.37	0.41	0.39	0.29	0.45	0.16	0.25	0.16

Tank 20

#	Time (days)	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
41	((Epi)gallocatechin)$_2$ 1	1.49	2.73	1.92	1.52	1.56	1.65	1.56	0.90	2.16	2.30	2.04	<LD	0.90	1.21	0.70
42	((Epi)gallocatechin)$_2$ 2	0.37	0.73	0.47	0.45	0.41	0.37	0.39	0.33	0.56	0.54	0.53	<LD	0.22	0.38	0.24
43	((Epi)gallocatechin)$_2$ 3	0.08	0.17	0.05	0.06	0.10	0.01	0.03	0.13	0.09	0.12	0.10	<LD	0.08	0.08	0.07
44	Gallocatechin	1.28	1.68	1.61	1.53	1.42	1.53	1.84	1.72	1.63	1.70	1.32	<LD	0.64	0.76	0.91
45	Epigallocatechin	0.33	0.57	0.46	0.46	0.38	0.42	0.54	0.52	0.50	0.42	0.38	<LD	0.18	0.30	0.32
46	((Epi)gallocatechin-(epi)catechin) 2	0.57	1.29	1.60	1.37	1.32	1.47	1.59	1.72	1.83	1.86	1.49	<LD	0.70	0.93	0.73
47	((Epi)catechin-(epi)gallocatechin) 2	0.74	1.29	1.63	0.90	1.37	1.31	1.43	0.95	1.53	1.51	1.37	<LD	0.65	0.85	0.66
48	((Epi)gallocatechin-(epi)catechin) 1	3.32	6.62	4.89	3.31	4.02	5.07	3.19	3.14	5.78	6.78	4.94	<LD	2.32	3.01	2.03
49	((Epi)catechin-(epi)gallocatechin) 1	3.86	6.66	5.07	3.87	4.46	5.92	3.75	3.28	5.90	6.90	4.85	<LD	2.57	3.20	2.28
50	((Epi)catechin-(epi)gallocatechin) A	<LD	0.30	0.21	0.18	0.42	0.15	0.16	<LD	<LD	<LD	0.07	<LD	<LD	<LD	<LD
51	((Epi)catechin)$_2$ 1	4.05	6.32	5.13	4.42	4.57	6.44	4.77	5.28	7.80	8.86	5.62	<LD	2.88	3.47	2.90
52	Procyanidin B 1	19.81	45.42	31.83	20.90	26.23	39.83	23.06	24.97	53.81	55.24	37.16	<LD	15.78	18.35	15.10
53	Procyanidin B 2	4.64	8.88	6.03	5.30	5.80	7.83	6.63	7.36	12.99	14.09	8.81	<LD	4.41	5.66	5.45
54	Catechin	1.98	2.92	2.31	2.23	2.23	2.80	2.77	3.21	3.22	3.87	2.46	<LD	1.45	1.69	2.07
55	Epicatechin	0.61	1.27	0.69	0.82	0.66	0.92	1.58	1.49	1.53	1.39	1.23	<LD	0.60	0.78	0.94
56	*p*-vinyl(epi)catechin 1	2.11	2.86	3.13	2.60	2.03	2.52	1.78	1.51	1.63	1.64	1.27	<LD	0.54	0.89	0.76
57	*p*-vinyl(epi)catechin 2	<LD	<LD	<LD	<LD	<LD	<LD	0.35	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
58	*p*-vinyl(epi)catechin 3	<LD	0.34	0.51	0.54	0.41	0.70	0.74	0.40	0.32	0.42	0.37	<LD	0.16	0.26	0.19

Tank 21

#	Time (days)	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
41	((Epi)gallocatechin)$_2$ 1	0.64	2.13	1.62	0.97	1.43	1.18	1.59	0.82	1.90	1.79	1.44	2.55	0.56	0.84	0.68
42	((Epi)gallocatechin)$_2$ 2	0.13	0.71	0.50	0.26	0.35	0.30	0.35	0.27	0.40	0.49	0.37	0.52	0.18	0.30	0.21
43	((Epi)gallocatechin)$_2$ 3	0.03	0.14	0.05	0.07	0.07	0.04	0.08	0.17	0.12	0.10	0.11	0.11	0.05	<LQ	0.06
44	Gallocatechin	0.78	1.64	1.64	1.59	1.44	1.25	1.66	1.60	1.54	1.67	1.00	1.29	0.60	0.79	0.88
45	Epigallocatechin	0.18	0.63	0.54	0.41	0.40	0.50	0.47	0.32	0.36	0.42	0.36	0.30	0.22	0.23	0.29
46	((Epi)gallocatechin-(epi)catechin) 2	0.30	0.97	1.33	1.41	1.38	0.93	1.48	1.55	1.61	1.84	1.00	1.36	0.49	0.70	0.64
47	((Epi)catechin-(epi)gallocatechin) 2	0.42	0.93	1.54	1.37	1.36	1.13	1.33	0.84	1.36	1.53	0.74	1.12	0.61	0.72	0.61
48	((Epi)gallocatechin-(epi)catechin) 1	1.99	4.97	3.94	2.76	3.76	3.74	3.39	3.17	4.70	5.52	3.51	6.16	1.74	2.49	2.06
49	((Epi)catechin-(epi)gallocatechin) 1	2.76	5.55	4.62	3.32	4.60	4.49	3.87	3.31	5.31	6.41	3.83	6.06	2.30	2.73	2.31
50	((Epi)catechin-(epi)gallocatechin) A	<LD	0.16	<LD	0.17	0.48	0.16	0.11	<LD	<LD	<LD	0.06	0.04	<LD	<LD	<LD
51	((Epi)catechin)$_2$ 1	2.95	6.21	5.21	3.98	4.71	5.85	5.48	4.74	7.38	9.30	4.60	6.95	2.81	3.55	2.99
52	Procyanidin B 1	15.86	44.02	27.85	17.28	25.17	32.88	24.82	23.09	46.79	54.40	30.68	48.23	13.75	16.37	15.71
53	Procyanidin B 2	3.99	8.31	6.37	5.15	6.05	6.94	7.86	7.71	10.67	13.54	7.51	10.91	4.31	5.34	5.00
54	Catechin	1.70	2.82	2.25	2.23	2.46	2.24	2.87	3.01	2.95	3.65	2.28	2.27	1.42	1.73	1.90
55	Epicatechin	0.48	0.90	0.75	0.77	0.89	0.66	1.56	1.37	1.32	1.43	0.86	0.91	0.64	0.73	0.82
56	*p*-vinyl(epi)catechin 1	1.78	2.43	3.03	2.29	2.07	2.17	1.64	1.29	1.47	1.26	1.00	0.95	0.49	0.90	0.68
57	*p*-vinyl(epi)catechin 2	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
58	*p*-vinyl(epi)catechin 3	<LD	0.26	0.49	0.47	0.28	0.42	0.50	0.25	0.30	0.32	0.26	0.37	0.12	0.20	0.14

continued

Table S4. Tannin concentrations determined by HPLC-DAD-ESI(+)-MS/MS in red wine samples from Mendavia 2018, expressed in mg of (+)-cat equiv./L.

Tank 22

#	Time (days)	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
41	((Epi)gallocatechin)$_2$ 1	0.95	3.52	1.51	1.44	1.68	1.63	1.42	0.56	1.65	2.20	1.46	1.34	0.59	0.92	0.55
42	((Epi)gallocatechin)$_2$ 2	0.16	1.01	0.41	0.37	0.41	0.44	0.33	0.16	0.42	0.51	0.26	0.33	0.19	0.26	0.20
43	((Epi)gallocatechin)$_2$ 3	0.06	0.12	0.05	0.04	0.08	0.06	0.09	0.07	0.13	0.02	0.07	0.05	0.03	<LQ	0.10
44	Gallocatechin	0.77	1.90	1.51	1.64	1.45	1.57	1.52	1.41	1.59	1.61	0.95	1.19	0.58	0.77	0.91
45	Epigallocatechin	0.28	0.67	0.58	0.37	0.42	0.43	0.34	0.37	0.56	0.44	0.38	0.40	0.16	0.26	0.24
46	((Epi)gallocatechin-(epi)catechin) 2	0.40	1.63	0.84	1.44	1.44	1.46	1.46	1.28	1.42	1.72	1.18	0.81	0.34	0.79	0.54
47	((Epi)catechin-(epi)gallocatechin) 2	0.57	1.49	1.34	1.50	1.30	1.41	1.33	0.74	1.56	1.52	0.82	0.89	0.43	0.64	0.60
48	((Epi)gallocatechin-(epi)catechin) 1	2.59	7.60	3.48	3.25	4.00	5.25	3.13	2.29	4.72	5.99	3.61	3.72	1.56	2.26	1.72
49	((Epi)catechin-(epi)gallocatechin) 1	3.44	6.61	4.18	3.69	4.80	6.03	3.32	2.58	5.22	6.71	3.99	4.19	1.87	2.52	2.01
50	((Epi)catechin-(epi)gallocatechin) A	<LD	<LD	<LD	0.25	0.39	0.14	<LD	0.07	0.10	<LD	0.08	<LD	<LD	0.05	<LD
51	((Epi)catechin)$_2$ 1	3.19	7.70	4.66	4.34	5.28	6.74	4.14	3.51	8.15	9.87	4.49	5.58	2.26	3.31	2.69
52	Procyanidin B 1	20.34	56.36	26.41	21.55	28.19	40.19	21.36	19.04	51.69	64.61	30.77	38.76	9.85	13.39	8.93
53	Procyanidin B 2	4.51	9.88	6.03	5.63	6.71	8.28	6.24	5.44	12.79	15.75	7.54	9.97	3.86	5.04	4.60
54	Catechin	1.60	2.78	2.03	2.43	2.09	2.64	2.57	2.57	3.29	3.47	2.12	2.02	1.18	1.65	2.09
55	Epicatechin	0.54	0.91	0.61	0.93	0.70	0.92	1.40	0.89	1.37	1.32	0.86	0.91	0.48	0.76	0.82
56	*p*-vinyl(epi)catechin 1	1.90	3.22	2.79	2.58	2.07	2.26	1.72	1.40	1.56	1.68	1.25	0.91	0.45	0.71	0.66
57	*p*-vinyl(epi)catechin 2	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
58	*p*-vinyl(epi)catechin 3	<LD	0.39	0.58	0.39	0.30	0.59	0.48	0.30	0.31	0.38	0.26	0.32	0.14	0.24	0.15

Tank 23

#	Time (days)	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
41	((Epi)gallocatechin)$_2$ 1	0.98	3.19	2.19	1.44	1.73	1.39	1.47	0.57	1.56	1.70	1.27	1.40	0.61	0.93	0.63
42	((Epi)gallocatechin)$_2$ 2	0.24	0.87	0.53	0.33	0.42	0.36	0.33	0.27	0.40	0.42	0.32	0.36	0.18	0.31	0.22
43	((Epi)gallocatechin)$_2$ 3	<LD	0.17	0.07	<LQ	0.11	0.02	0.03	0.06	0.14	0.18	0.06	0.08	0.04	<LQ	0.05
44	Gallocatechin	0.81	1.65	1.71	1.55	1.38	1.43	1.47	1.52	1.65	1.85	1.21	1.16	0.64	0.82	0.85
45	Epigallocatechin	0.29	0.70	0.62	0.56	0.42	0.38	0.28	0.39	0.37	0.45	0.30	0.28	0.20	0.27	0.26
46	((Epi)gallocatechin-(epi)catechin) 2	0.46	1.51	1.78	0.94	1.45	1.22	0.92	0.88	1.56	1.49	0.91	1.09	0.45	0.76	0.63
47	((Epi)catechin-(epi)gallocatechin) 2	0.81	1.58	1.70	0.93	1.60	1.39	1.33	0.73	1.29	1.14	0.89	1.10	0.52	0.72	0.59
48	((Epi)gallocatechin-(epi)catechin) 1	2.69	6.62	4.75	3.01	4.32	4.27	2.83	2.44	4.07	4.96	3.12	4.13	1.95	2.43	1.91
49	((Epi)catechin-(epi)gallocatechin) 1	3.23	6.60	5.80	3.67	4.99	5.31	3.05	2.75	4.67	5.40	3.43	4.51	2.34	2.74	2.23
50	((Epi)catechin-(epi)gallocatechin) A	<LD	<LD	0.12	0.16	0.46	0.12	<LD	0.11	<LD	<LD	0.06	<LD	<LD	0.06	<LD
51	((Epi)catechin)$_2$ 1	3.32	6.72	6.02	4.52	5.11	6.54	4.04	4.34	7.20	8.32	4.79	5.94	2.44	3.29	2.88
52	Procyanidin B 1	18.96	52.62	35.53	20.18	27.95	35.71	21.97	19.44	41.62	47.63	24.92	37.00	11.13	15.85	12.49
53	Procyanidin B 2	4.61	8.97	7.17	5.18	6.90	6.86	5.62	5.68	10.20	12.59	7.50	9.55	4.21	5.26	5.06
54	Catechin	1.92	2.65	2.44	2.19	2.41	2.56	2.30	2.89	3.16	3.75	2.42	2.85	1.52	1.75	2.00
55	Epicatechin	0.59	0.95	0.85	0.78	0.92	0.82	0.83	1.31	1.64	1.38	1.22	1.14	0.65	0.80	0.93
56	*p*-vinyl(epi)catechin 1	2.17	3.07	3.17	2.42	2.05	2.28	1.57	1.45	1.54	1.41	1.38	1.15	0.53	0.82	0.66
57	*p*-vinyl(epi)catechin 2	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
58	*p*-vinyl(epi)catechin 3	<LD	0.34	0.47	0.45	0.29	0.39	0.49	0.25	0.22	0.37	0.28	0.34	0.12	0.19	0.15

Tank 24

#	Time (days)	1	3	4	5	6	7	10	15	18	20	24	28	33	52	61
41	((Epi)gallocatechin)$_2$ 1	1.46	3.28	1.87	1.45	1.38	1.50	1.55	0.93	1.80	1.91	1.60	1.54	0.64	0.97	0.77
42	((Epi)gallocatechin)$_2$ 2	0.35	0.75	0.57	0.29	0.40	0.36	0.33	0.21	0.46	0.49	0.34	0.36	0.19	0.33	0.20
43	((Epi)gallocatechin)$_2$ 3	0.07	0.11	0.06	0.14	0.10	<LD	0.03	0.10	0.09	0.05	0.09	0.05	0.06	0.08	0.06
44	Gallocatechin	0.98	1.61	1.75	1.60	1.45	1.48	1.57	1.70	1.62	1.76	0.99	1.24	0.63	0.82	0.92
45	Epigallocatechin	0.33	0.65	0.53	0.33	0.35	0.40	0.45	0.35	0.53	0.47	0.35	0.31	0.20	0.29	0.27
46	((Epi)gallocatechin-(epi)catechin) 2	0.26	1.66	1.52	0.80	1.32	1.67	1.36	1.47	1.57	1.70	1.31	1.15	0.48	0.77	0.76
47	((Epi)catechin-(epi)gallocatechin) 2	0.58	1.27	1.73	0.93	1.27	1.21	0.97	0.89	1.28	1.39	1.27	1.29	0.55	0.74	0.61
48	((Epi)gallocatechin-(epi)catechin) 1	3.17	7.23	4.85	3.16	3.28	4.00	3.32	3.04	4.37	5.67	3.90	4.24	1.79	2.62	2.17
49	((Epi)catechin-(epi)gallocatechin) 1	3.64	6.66	5.63	3.46	4.07	5.20	3.70	3.51	4.83	6.70	4.33	4.66	2.19	2.94	2.52
50	((Epi)catechin-(epi)gallocatechin) A	<LD	<LD	0.05	0.12	0.47	0.14	<LD	0.18	<LD	<LD	0.05	0.07	<LD	<LD	<LD
51	((Epi)catechin)$_2$ 1	3.69	7.43	6.23	4.35	4.23	6.43	5.28	4.47	6.81	8.81	5.45	6.35	2.67	3.52	3.14
52	Procyanidin B 1	21.74	57.33	34.88	19.82	21.53	34.89	24.81	23.72	43.67	58.67	33.21	42.01	12.70	16.95	16.44
53	Procyanidin B 2	4.62	8.74	7.72	4.67	5.70	7.62	7.49	7.36	10.64	13.55	9.02	9.92	4.65	5.32	5.38
54	Catechin	1.55	3.26	2.26	2.34	2.26	2.68	2.45	2.91	3.41	3.49	2.33	2.62	1.51	1.80	1.92
55	Epicatechin	0.59	0.92	0.74	0.65	0.78	0.83	1.33	1.58	1.59	1.56	1.18	1.09	0.68	0.73	0.91
56	*p*-vinyl(epi)catechin 1	2.11	2.46	2.86	2.30	2.06	2.02	1.50	1.27	1.00	1.32	0.84	0.94	0.45	0.65	0.55
57	*p*-vinyl(epi)catechin 2	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
58	*p*-vinyl(epi)catechin 3	<LD	0.57	0.48	0.45	0.26	0.55	0.40	0.27	0.29	0.38	0.20	0.33	0.12	0.17	0.14

Table S5. Anthocyanin concentrations determined by HPLC-DAD in red wine samples from Alfaro 2019, expressed in mg of Mv-3-*O*-glc equiv./L.

Tank 02

#	Time (days)	0	1	3	4	5	6	7	8	10	11	12	13	25	26	31	34	38	45	48	52	53
1	Dp-3-*O*-glc	20.67	24.46	19.77	14.38	13.16	11.07	10.99	10.25	9.58	8.54	9.08	8.02	6.65	7.14	6.05	5.48	5.02	4.04	4.36	4.94	4.74
2	Cy-3-*O*-glc	7.34	6.35	2.31	2.72	2.67	2.34	2.35	2.32	2.02	1.98	2.08	1.91	1.53	1.64	1.57	1.37	1.42	1.42	1.36	1.50	1.35
3	Pt-3-*O*-glc	18.28	21.84	23.36	24.82	23.87	21.92	22.10	21.52	19.61	18.14	19.01	17.47	14.93	15.66	13.22	11.69	10.89	8.85	9.48	11.00	10.67
4	Pn-3-*O*-glc	14.23	14.64	9.17	9.98	9.98	9.50	9.07	8.92	7.74	7.04	7.47	6.87	4.17	4.58	6.54	6.02	6.33	7.62	7.46	6.86	6.50
5	Mv-3-*O*-glc	78.70	95.15	110.92	120.04	119.13	114.56	117.23	119.12	112.74	111.23	114.66	109.58	105.69	104.47	92.32	83.63	72.43	64.46	66.91	72.44	72.56
6	Dp-3-*O*-(6-ac)-glc	0.61	0.78	0.90	2.26	2.32	1.97	1.97	1.99	1.26	1.23	1.27	1.89	0.92	1.84	2.05	1.20	0.75	0.75	0.82	1.78	0.86
7	Pt-3-*O*-(6-ac)-glc	1.24	1.55	2.13	2.95	3.08	3.00	3.03	3.06	2.54	2.52	2.58	2.93	2.59	2.96	3.00	2.62	2.39	1.83	1.80	2.19	2.38
8	Pn-3-*O*-(6-ac)-glc	0.66	0.82	2.28	3.02	3.07	3.06	2.97	3.02	2.41	2.35	2.36	2.59	1.60	2.24	2.42	2.28	2.21	2.28	2.17	2.42	2.16
9	Mv-3-*O*-(6-ac)-glc	5.21	6.79	10.24	11.89	12.27	11.91	12.23	12.15	11.05	10.72	11.03	10.71	10.40	10.38	9.39	8.58	7.78	7.00	7.28	8.08	7.82
10	Mv-3-*O*-(6-caff)-glc	1.09	1.09	2.30	3.22	3.40	3.55	3.64	3.73	3.27	4.15	3.34	3.54	3.25	3.43	4.48	4.29	4.11	4.04	3.89	4.36	3.94
11	Pt-3-*O*-(6-*p*-coum)-glc	1.27	1.73	4.05	5.12	5.36	5.37	5.38	5.28	4.45	4.07	4.25	4.06	3.19	3.43	3.16	3.10	2.93	2.77	2.78	3.06	2.83
12	Pn-3-*O*-(6-*p*-coum)-glc	8.09	11.02	27.68	32.69	33.76	33.88	33.97	33.28	28.06	26.34	26.78	25.10	17.86	17.83	16.94	16.51	15.52	17.55	14.92	15.65	15.03
13	Mv-3-*O*-(6-*p*-coum)-glc	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Tank 03

#	Time (days)	0	1	3	4	5	6	7	8	10	11	12	13	25	26	31	34	38	45	48	52	53
1	Dp-3-*O*-glc	20.33	24.82	21.03	14.63	14.14	12.03	12.11	10.74	10.23	8.56	9.07	8.45	6.15	6.49	5.90	5.08	5.00	3.79	4.17	4.54	3.61
2	Cy-3-*O*-glc	7.22	6.74	2.35	2.79	2.55	2.52	2.57	2.46	2.17	1.95	2.21	1.98	1.33	1.40	1.38	1.29	1.56	1.34	1.33	1.38	1.24
3	Pt-3-*O*-glc	17.69	21.38	23.80	24.32	23.91	22.83	23.51	21.62	20.59	18.12	18.90	17.76	13.37	14.37	12.85	10.97	11.01	8.20	8.88	9.65	8.95
4	Pn-3-*O*-glc	13.87	14.83	9.64	10.24	9.21	9.63	9.62	9.26	8.11	7.08	7.86	7.02	3.96	4.11	5.15	5.63	6.95	7.49	7.40	6.71	6.11
5	Mv-3-*O*-glc	75.33	91.39	109.22	115.39	117.47	117.99	122.57	120.04	111.84	107.31	112.42	107.47	96.41	102.91	94.91	83.01	75.47	61.41	65.03	67.02	64.05
6	Dp-3-*O*-(6-ac)-glc	0.59	0.80	0.90	2.22	0.97	2.07	2.07	2.04	1.91	1.18	1.72	2.10	0.80	0.84	1.27	1.15	1.78	0.77	0.88	1.73	0.78
7	Pt-3-*O*-(6-ac)-glc	1.20	1.54	2.21	2.83	2.61	3.08	3.18	3.07	2.97	2.43	2.82	3.03	2.47	2.60	2.84	2.65	2.23	1.79	1.87	2.09	1.75
8	Pn-3-*O*-(6-ac)-glc	0.63	0.83	2.36	2.99	2.74	3.21	3.14	3.11	2.76	2.27	2.61	2.68	1.56	2.09	2.36	2.35	2.62	2.30	2.33	2.44	2.04
9	Mv-3-*O*-(6-ac)-glc	4.94	6.93	10.41	11.37	11.96	12.42	12.93	12.32	11.77	10.45	10.98	10.66	9.47	10.02	9.55	8.44	8.18	6.76	7.24	7.59	7.01
10	Mv-3-*O*-(6-caff)-glc	0.99	1.29	2.46	3.03	3.90	4.80	3.74	3.72	4.78	3.98	3.48	4.67	3.06	4.07	4.51	4.44	4.72	4.02	4.18	4.37	3.77
11	Pt-3-*O*-(6-*p*-coum)-glc	1.22	1.98	4.24	4.90	5.24	5.65	5.74	5.38	5.03	4.04	4.33	4.09	2.91	3.08	3.11	2.94	3.07	2.67	2.78	2.88	2.54
12	Pn-3-*O*-(6-*p*-coum)-glc	7.24	12.62	28.75	31.73	33.72	36.15	35.98	34.57	31.34	26.07	28.25	25.58	16.28	17.01	17.27	16.08	16.44	16.97	17.28	14.72	13.51
13	Mv-3-*O*-(6-*p*-coum)-glc	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Tank 04

#	Time (days)	0	1	3	4	5	6	7	8	10	11	12	13	25	26	31	34	38	45	48	52	53
1	Dp-3-*O*-glc	23.10	26.15	21.82	15.76	15.07	12.55	12.02	10.34	10.54	8.61	9.16	8.74	6.94	7.89	6.31	5.89	5.51	4.91	4.90	5.28	5.18
2	Cy-3-*O*-glc	7.85	6.96	2.39	2.86	3.00	2.63	2.30	2.39	2.30	1.97	2.25	1.90	1.52	1.77	1.41	1.43	1.45	1.50	1.47	1.47	1.37
3	Pt-3-*O*-glc	19.74	22.49	24.40	25.66	26.27	23.79	23.09	21.07	21.11	18.28	18.75	18.56	15.23	17.11	13.51	12.77	12.00	10.68	10.70	11.39	11.24
4	Pn-3-*O*-glc	14.99	15.27	9.71	10.33	10.67	9.75	8.93	9.09	8.64	7.28	8.07	6.95	4.39	5.07	5.56	6.42	6.36	7.43	7.09	6.29	5.91
5	Mv-3-*O*-glc	82.63	95.24	110.17	118.65	124.47	120.29	120.00	114.19	113.39	106.46	108.96	112.08	103.85	109.57	92.44	90.12	77.31	70.60	70.42	73.77	73.71
6	Dp-3-*O*-(6-ac)-glc	0.68	0.85	0.94	2.50	2.77	2.05	0.99	1.79	2.26	1.20	1.86	1.16	0.86	1.94	1.30	1.25	0.84	0.87	0.96	1.62	0.93
7	Pt-3-*O*-(6-ac)-glc	1.33	1.60	2.21	3.03	3.43	3.05	2.80	2.85	3.15	2.44	2.88	2.50	2.61	3.10	2.79	2.78	2.51	2.46	2.46	2.58	2.37
8	Pn-3-*O*-(6-ac)-glc	0.71	0.86	2.40	3.15	3.50	3.26	2.96	2.99	3.01	2.31	2.72	2.30	2.13	1.85	2.35	2.48	2.38	2.37	2.29	2.32	2.12
9	Mv-3-*O*-(6-ac)-glc	5.66	7.21	10.32	12.28	13.59	12.76	12.97	11.72	12.26	10.59	10.88	10.86	10.45	11.04	9.53	9.26	8.47	7.69	7.82	7.96	8.06
10	Mv-3-*O*-(6-caff)-glc	1.13	1.33	2.31	3.02	4.70	2.61	3.34	4.36	4.79	3.79	4.41	3.84	3.95	3.44	4.28	4.47	4.22	4.06	4.00	4.01	3.73
11	Pt-3-*O*-(6-*p*-coum)-glc	1.47	2.03	4.37	5.46	6.17	5.91	5.89	5.21	5.33	4.20	4.42	4.13	3.36	3.70	3.28	3.35	3.23	3.02	3.03	2.84	2.84
12	Pn-3-*O*-(6-*p*-coum)-glc	8.90	13.08	29.40	34.57	38.30	37.74	36.83	33.56	32.41	27.02	28.79	25.74	18.70	19.90	18.15	18.61	17.13	18.73	18.20	15.37	15.30
13	Mv-3-*O*-(6-*p*-coum)-glc	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Tank 05

#	Time (days)	0	1	3	4	5	6	7	8	10	11	12	13	25	26	31	34	38	45	48	52	53
1	Dp-3-*O*-glc	23.05	28.38	22.65	21.41	20.95	16.69	17.25	15.29	16.38	15.40	15.83	15.46	12.54	13.86	12.23	12.44	11.65	11.01	9.46	9.11	8.47
2	Cy-3-*O*-glc	7.71	6.71	2.52	2.49	2.38	2.25	2.16	2.41	2.12	2.12	2.16	2.07	1.98	1.75	1.68	1.64	1.62	1.87	1.65	1.54	1.54
3	Pt-3-*O*-glc	19.83	23.26	24.58	25.02	24.04	23.40	23.70	21.83	22.95	21.96	22.86	22.16	18.83	19.47	17.97	17.69	16.27	15.82	14.16	13.44	12.66
4	Pn-3-*O*-glc	14.60	14.47	11.10	10.73	10.44	10.29	9.75	10.22	9.08	8.58	8.86	8.27	6.39	5.81	6.11	5.96	5.81	6.84	6.36	6.10	6.01
5	Mv-3-*O*-glc	84.11	100.59	107.63	111.37	109.27	109.68	109.89	103.53	115.28	115.69	113.34	115.84	103.49	103.87	97.73	94.18	81.79	80.69	74.25	69.27	66.86
6	Dp-3-*O*-(6-ac)-glc	0.69	1.02	0.96	0.99	1.08	0.96	1.03	1.90	1.03	0.93	0.98	1.00	1.77	0.95	1.45	1.45	1.16	1.90	1.16	0.84	0.99
7	Pt-3-*O*-(6-ac)-glc	1.35	1.88	2.30	2.76	2.76	2.84	2.89	3.03	2.67	2.68	2.75	2.92	3.16	2.93	3.18	3.22	2.85	3.31	2.86	2.77	2.81
8	Pn-3-*O*-(6-ac)-glc	0.70	1.03	2.31	2.83	2.77	2.94	2.76	2.90	2.41	2.32	2.39	2.49	2.32	2.17	2.35	2.32	2.19	2.43	2.20	2.17	2.24
9	Mv-3-*O*-(6-ac)-glc	5.74	8.77	10.82	12.25	12.13	12.04	12.33	11.37	11.84	11.89	11.89	11.98	10.69	10.81	10.48	10.42	9.26	9.33	8.49	8.20	7.91
10	Mv-3-*O*-(6-caff)-glc	1.18	1.57	1.73	2.90	3.23	3.60	3.59	3.54	3.42	3.47	3.47	3.79	4.58	3.46	4.74	4.75	4.30	4.74	4.36	4.47	4.42
11	Pt-3-*O*-(6-*p*-coum)-glc	1.42	2.82	4.52	5.28	5.18	5.22	5.30	4.72	4.66	4.42	4.52	4.52	3.54	3.70	3.69	3.65	3.33	3.32	3.05	3.08	2.99
12	Pn-3-*O*-(6-*p*-coum)-glc	8.67	16.60	29.34	33.54	33.17	34.09	32.87	29.56	28.01	26.28	26.52	26.34	18.05	18.70	18.35	17.72	15.91	15.39	15.38	15.65	15.43
13	Mv-3-*O*-(6-*p*-coum)-glc	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Tank 06

#	Time (days)	0	1	3	4	5	6	7	8	10	11	12	13	25	26	31	34	38	45	48	52	53
1	Dp-3-*O*-glc	21.26	25.55	21.01	19.70	18.97	15.65	16.35	14.74	15.96	15.10	14.36	12.99	13.22	13.74	11.70	11.94	10.95	9.96	9.16	8.81	8.24
2	Cy-3-*O*-glc	7.54	6.44	2.40	2.32	2.71	2.22	2.11	2.13	2.07	1.95	1.91	1.73	1.69	1.69	1.54	1.56	1.56	1.58	1.50	1.59	1.45
3	Pt-3-*O*-glc	19.04	20.86	22.85	22.86	25.04	21.75	22.30	20.66	21.98	20.66	20.01	18.08	18.38	18.86	16.48	16.62	15.21	14.12	13.01	12.74	11.79
4	Pn-3-*O*-glc	14.53	13.36	10.29	9.86	10.69	10.00	9.27	9.39	8.84	8.09	7.95	7.21	5.62	5.70	5.75	5.77	5.78	5.99	5.68	6.41	5.92
5	Mv-3-*O*-glc	80.52	89.54	99.53	100.80	107.57	100.93	102.75	98.61	104.03	106.10	97.50	93.92	98.88	99.01	87.34	87.42	76.34	71.57	64.93	64.36	60.03
6	Dp-3-*O*-(6-ac)-glc	0.65	0.88	0.87	0.94	2.28	0.87	0.91	0.88	0.98	0.93	1.61	0.82	0.93	0.93	1.34	1.40	0.99	1.13	0.99	1.59	0.91
7	Pt-3-*O*-(6-ac)-glc	1.31	1.60	2.15	2.50	3.17	2.67	2.49	2.64	2.53	2.65	2.39	2.41	2.82	2.85	2.95	3.11	2.80	2.79	2.71	2.79	2.56
8	Pn-3-*O*-(6-ac)-glc	0.69	0.85	2.20	2.57	3.00	2.83	2.40	2.66	2.30	2.35	2.12	2.06	2.07	2.11	2.18	2.27	2.11	2.17	2.12	2.29	2.04
9	Mv-3-*O*-(6-ac)-glc	5.47	7.21	10.15	10.75	12.11	11.26	11.12	10.76	11.17	11.07	10.27	9.79	10.32	10.25	9.68	9.72	8.60	8.32	7.82	7.62	7.05
10	Mv-3-*O*-(6-caff)-glc	1.20	1.22	1.62	2.56	3.24	3.20	2.93	3.13	3.05	3.22	2.82	2.99	4.11	4.16	4.26	4.45	4.10	4.17	4.23	4.37	3.89
11	Pt-3-*O*-(6-*p*-coum)-glc	1.40	2.03	4.18	4.73	5.40	5.02	4.77	4.62	4.53	4.31	3.90	3.73	3.54	3.58	3.37	3.48	3.09	3.04	3.01	2.94	2.72
12	Pn-3-*O*-(6-*p*-coum)-glc	8.48	11.13	27.11	30.29	33.91	32.46	29.27	30.18	27.26	25.87	22.78	21.91	18.01	18.00	16.53	16.72	14.88	14.46	15.21	15.01	13.78
13	Mv-3-*O*-(6-*p*-coum)-glc	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Tank 07

#	Time (days)	0	1	3	4	5	6	7	8	10	11	12	13	25	26	31	34	38	45	48	52	53
1	Dp-3-*O*-glc	23.16	30.24	21.39	18.99	16.70	14.24	14.99	15.58	13.57	13.75	12.76	14.98	11.31	11.09	10.35	10.25	9.44	8.48	8.18	7.71	7.39
2	Cy-3-*O*-glc	7.62	7.38	2.67	2.30	2.25	2.03	2.03	2.20	1.83	1.82	1.79	1.90	1.47	1.48	1.42	1.38	1.41	1.32	1.33	1.28	1.37
3	Pt-3-*O*-glc	19.57	24.04	23.00	21.72	21.57	19.48	20.64	21.54	18.59	18.80	17.97	20.88	15.75	15.57	14.90	14.03	13.32	11.92	11.80	11.06	10.85
4	Pn-3-*O*-glc	14.26	14.95	11.57	9.55	9.70	9.26	9.10	9.63	8.03	7.46	7.65	7.74	5.10	5.10	5.48	5.22	5.63	5.15	5.46	5.21	5.71
5	Mv-3-*O*-glc	81.37	98.80	97.18	95.10	96.60	91.06	96.38	103.47	94.46	96.13	88.86	105.93	85.54	84.69	81.02	76.69	67.63	60.74	59.95	56.46	55.79
6	Dp-3-*O*-(6-ac)-glc	0.71	1.02	1.58	0.85	0.86	0.77	0.84	0.86	0.83	0.77	0.77	0.98	0.82	0.78	1.23	1.18	0.90	0.87	0.90	0.71	0.81
7	Pt-3-*O*-(6-ac)-glc	1.32	1.75	2.35	2.23	2.32	2.43	2.34	2.68	2.23	2.26	2.22	2.69	2.49	2.46	2.72	2.66	2.48	2.39	2.39	2.24	2.33
8	Pn-3-*O*-(6-ac)-glc	0.70	0.91	2.25	2.23	2.32	2.56	2.26	2.63	2.04	1.92	1.96	2.29	1.50	1.84	1.96	1.94	1.94	1.80	1.87	1.82	1.91
9	Mv-3-*O*-(6-ac)-glc	5.61	8.52	9.83	10.32	10.32	10.25	10.24	11.23	9.74	9.98	9.43	10.94	9.12	8.97	8.89	8.44	7.72	7.10	7.10	6.63	6.67
10	Mv-3-*O*-(6-caff)-glc	1.08	1.37	2.06	2.37	2.72	3.08	2.93	3.33	2.80	2.88	2.76	3.23	3.72	3.67	3.95	3.84	3.82	3.52	3.64	3.60	3.72
11	Pt-3-*O*-(6-*p*-coum)-glc	1.45	2.80	4.01	4.40	4.53	4.51	4.43	4.72	3.85	3.81	3.60	4.27	3.06	3.01	3.06	2.93	2.86	2.58	2.65	2.51	2.54
12	Pn-3-*O*-(6-*p*-coum)-glc	8.53	16.08	25.23	27.84	28.74	29.84	27.50	30.53	23.50	21.73	21.29	24.65	15.58	15.37	15.33	14.50	14.14	12.22	12.64	13.04	13.33
13	Mv-3-*O*-(6-*p*-coum)-glc	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

continued

Table S5. Anthocyanin concentrations determined by HPLC-DAD in red wine samples from Alfaro 2019, expressed in mg of Mv-3-*O*-glc equiv./L.

Tank 08

#	Time (days)	0	1	3	4	5	6	7	8	10	11	12	13	25	26	31	34	38	45	48	52	53
1	Dp-3-*O*-glc	22.13	26.66	21.96	20.32	19.00	16.80	16.86	12.95	15.86	16.52	14.81	15.29	13.55	12.61	12.27	12.21	11.64	10.10	8.86	8.29	8.54
2	Cy-3-*O*-glc	7.66	6.84	2.81	2.43	2.42	2.25	2.14	1.87	1.98	2.03	1.97	1.90	1.61	1.60	1.59	1.53	1.52	1.61	1.39	1.34	1.38
3	Pt-3-*O*-glc	19.28	21.75	23.76	23.08	24.27	22.85	22.56	17.97	21.18	22.09	20.69	20.93	18.11	17.51	17.15	16.56	15.52	13.96	12.44	11.56	11.74
4	Pn-3-*O*-glc	14.91	14.24	11.66	10.23	10.41	10.37	9.68	8.42	8.50	8.55	8.37	7.80	5.49	5.42	5.75	5.56	5.31	5.72	5.46	5.35	5.82
5	Mv-3-*O*-glc	84.11	94.10	101.83	102.48	107.58	104.45	104.17	85.90	104.00	111.81	102.91	106.46	94.93	94.28	91.17	87.71	77.67	68.49	65.02	58.85	60.14
6	Dp-3-*O*-(6-ac)-glc	0.68	0.92	1.60	0.92	1.02	0.86	1.00	0.68	0.99	1.01	0.88	0.96	0.93	0.91	1.42	1.41	1.16	1.79	1.02	0.77	0.89
7	Pt-3-*O*-(6-ac)-glc	1.37	1.73	2.48	2.51	2.73	2.50	2.76	2.15	2.69	2.81	2.50	2.71	2.79	2.80	3.16	3.19	2.89	3.09	2.76	2.52	2.61
8	Pn-3-*O*-(6-ac)-glc	0.73	0.93	2.40	2.53	2.70	2.61	2.63	2.15	2.44	2.42	2.17	2.29	1.63	1.66	1.77	2.31	2.11	2.25	2.13	2.05	2.07
9	Mv-3-*O*-(6-ac)-glc	5.81	8.21	10.18	11.10	11.95	11.30	11.66	9.29	11.06	11.85	10.63	11.02	10.26	10.16	10.18	9.94	8.97	8.32	7.82	7.17	7.18
10	Mv-3-*O*-(6-caff)-glc	1.39	1.35	1.69	2.64	3.16	3.14	3.39	2.70	3.37	3.59	3.10	3.49	4.13	4.18	4.54	4.62	4.19	4.46	4.26	4.13	4.11
11	Pt-3-*O*-(6-*p*-coum)-glc	1.53	2.56	4.27	4.79	5.23	4.91	5.04	3.80	4.58	4.62	4.08	4.25	3.48	3.41	3.48	3.48	3.17	3.03	2.89	2.69	2.70
12	Pn-3-*O*-(6-*p*-coum)-glc	9.42	15.22	27.58	30.26	33.25	31.70	30.27	24.48	27.26	27.23	23.86	24.47	17.05	17.00	16.85	16.34	14.79	13.42	13.21	12.26	11.78
13	Mv-3-*O*-(6-*p*-coum)-glc	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Tank 09

#	Time (days)	0	1	3	4	5	6	7	8	10	11	12	13	25	26	31	34	38	45	48	52	53
1	Dp-3-*O*-glc	17.68	20.51	19.17	19.82	15.55	13.55	12.29	11.77	10.66	9.75	9.05	9.11	7.93	8.38	6.82	6.73	6.02	6.34	6.29	6.14	6.38
2	Cy-3-*O*-glc	6.46	5.90	1.97	2.17	2.56	2.48	2.39	2.25	2.22	2.16	1.98	2.07	1.84	1.82	1.57	1.53	1.73	1.68	1.45	1.37	1.46
3	Pt-3-*O*-glc	16.16	18.92	23.38	25.40	26.60	25.10	24.64	23.08	22.46	20.29	19.19	19.50	16.66	17.31	14.21	13.82	12.75	12.75	12.38	12.21	12.68
4	Pn-3-*O*-glc	14.99	16.07	14.74	9.57	10.25	11.04	10.24	10.07	9.21	8.62	8.29	8.32	5.82	5.79	6.88	7.22	8.40	7.85	6.88	6.02	6.41
5	Mv-3-*O*-glc	79.69	95.85	121.32	133.79	144.35	144.46	145.55	141.77	138.98	133.01	127.79	132.21	121.53	121.87	110.29	104.99	90.45	87.28	85.33	84.96	87.54
6	Dp-3-*O*-(6-ac)-glc	0.56	0.74	1.04	1.12	2.36	2.40	2.49	2.10	2.37	2.24	1.75	2.23	2.00	2.03	1.34	1.31	1.98	1.79	1.17	0.92	1.03
7	Pt-3-*O*-(6-ac)-glc	1.23	1.63	2.42	2.76	3.38	3.49	3.63	3.35	3.52	3.41	3.04	3.42	3.32	3.35	3.01	2.99	3.06	2.93	2.66	2.10	2.63
8	Pn-3-*O*-(6-ac)-glc	0.82	1.12	2.54	2.86	3.28	3.56	3.56	3.39	3.30	3.19	2.87	3.14	2.74	2.68	2.70	2.72	2.86	2.60	2.41	2.38	2.35
9	Mv-3-*O*-(6-ac)-glc	5.73	7.93	11.43	13.05	14.20	14.23	14.56	13.66	13.88	13.21	12.20	12.93	12.26	12.36	10.73	10.20	9.39	9.27	9.10	9.03	9.19
10	Mv-3-*O*-(6-caff)-glc	1.13	1.32	2.34	3.03	3.67	4.24	4.40	4.22	4.46	4.29	3.89	4.25	3.98	3.97	3.81	5.06	5.05	4.69	4.45	4.39	4.37
11	Pt-3-*O*-(6-*p*-coum)-glc	1.22	1.82	3.83	4.49	4.84	5.06	5.08	4.64	4.66	4.21	3.83	3.97	3.37	3.43	3.11	3.20	3.12	2.97	2.88	2.81	2.81
12	Pn-3-*O*-(6-*p*-coum)-glc	8.12	13.11	27.93	30.83	33.32	35.67	35.02	32.75	31.15	27.80	25.13	25.82	18.86	18.63	20.09	19.89	19.32	15.92	15.51	15.02	14.90
13	Mv-3-*O*-(6-*p*-coum)-glc	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Tank 10

#	Time (days)	0	1	3	4	5	6	7	8	10	11	12	13	25	26	31	34	38	45	48	52	53
1	Dp-3-*O*-glc	16.32	21.85	18.84	19.26	15.03	13.77	12.26	11.77	10.81	8.97	9.64	9.54	7.88	8.52	7.53	7.28	6.70	5.99	6.23	6.09	6.25
2	Cy-3-*O*-glc	6.37	6.00	2.00	2.20	2.68	2.56	2.27	2.44	2.22	2.01	2.22	2.12	1.86	1.82	1.85	1.75	1.53	1.55	1.52	1.44	1.58
3	Pt-3-*O*-glc	15.38	19.85	21.50	24.76	26.18	25.47	23.97	24.20	22.47	18.77	20.81	20.23	16.68	17.49	15.46	14.86	13.62	12.65	13.08	12.75	12.86
4	Pn-3-*O*-glc	14.67	16.49	7.95	9.61	10.57	10.91	10.11	10.19	9.19	8.31	9.25	8.32	5.87	5.86	7.21	7.26	6.03	6.91	6.80	6.20	6.66
5	Mv-3-*O*-glc	78.24	99.21	122.20	132.33	145.34	147.01	139.79	147.56	138.61	126.35	138.48	136.24	122.42	122.68	115.62	107.96	94.90	91.82	93.75	91.27	90.84
6	Dp-3-*O*-(6-ac)-glc	0.54	0.80	1.02	1.11	2.38	2.48	2.37	2.49	2.35	2.12	2.35	2.30	2.01	2.07	2.32	2.38	1.13	1.19	1.23	1.00	1.72
7	Pt-3-*O*-(6-ac)-glc	1.23	1.66	2.35	2.74	3.36	3.51	3.51	3.65	3.51	3.24	3.51	3.49	3.28	3.39	3.45	3.49	2.80	2.79	2.87	2.22	2.92
8	Pn-3-*O*-(6-ac)-glc	0.82	1.12	2.48	2.98	3.34	3.65	3.44	3.65	3.32	3.06	3.35	3.21	2.76	2.73	2.93	2.96	2.56	2.63	2.61	2.54	2.59
9	Mv-3-*O*-(6-ac)-glc	5.61	8.18	11.39	13.18	14.37	14.70	14.09	14.66	14.01	12.40	13.53	13.49	12.33	12.50	11.69	10.99	10.00	9.57	9.92	9.68	9.68
10	Mv-3-*O*-(6-caff)-glc	1.17	1.30	2.19	2.92	3.52	4.10	4.10	4.38	4.27	3.90	4.26	4.21	3.85	3.89	3.97	4.03	4.65	4.60	4.73	3.39	4.65
11	Pt-3-*O*-(6-*p*-coum)-glc	1.18	1.89	3.65	4.61	4.87	5.26	5.00	5.08	4.74	3.91	4.29	4.18	3.35	3.51	3.35	3.43	3.06	2.92	3.06	2.91	2.94
12	Pn-3-*O*-(6-*p*-coum)-glc	8.27	13.59	27.62	32.87	34.49	37.30	34.49	35.74	31.69	26.47	28.85	27.33	19.00	19.02	18.69	18.32	16.55	15.98	16.67	15.59	15.71
13	Mv-3-*O*-(6-*p*-coum)-glc	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Tank 11

#	Time (days)	0	1	3	4	5	6	7	8	10	11	12	13	25	26	31	34	38	45	48	52	53
1	Dp-3-*O*-glc	15.06	21.32	20.92	21.98	16.86	19.77	13.28	12.22	12.20	10.32	9.94	10.04	8.79	9.35	7.72	7.17	6.34	6.19	6.44	6.38	6.65
2	Cy-3-*O*-glc	5.90	6.03	2.19	2.83	2.81	2.30	2.44	2.44	2.33	2.36	2.19	2.12	1.98	2.01	1.93	1.60	1.54	1.60	1.59	1.48	1.50
3	Pt-3-*O*-glc	14.58	18.93	24.42	27.49	27.79	25.65	25.37	24.34	24.22	21.63	20.58	20.59	18.10	18.86	15.62	14.31	12.81	12.71	13.11	12.82	13.04
4	Pn-3-*O*-glc	14.07	16.20	10.29	11.60	11.71	11.85	10.67	10.54	9.88	9.47	9.25	8.60	5.41	6.58	8.47	7.89	7.50	8.30	7.98	6.93	6.97
5	Mv-3-*O*-glc	75.91	95.44	125.71	141.17	147.42	130.12	144.56	145.52	141.54	136.69	132.96	133.42	128.59	129.93	114.60	107.27	88.46	91.51	92.26	90.13	92.25
6	Dp-3-*O*-(6-ac)-glc	0.51	0.78	1.06	2.94	2.95	1.13	2.50	2.21	2.48	2.39	2.28	2.33	2.15	2.37	2.49	1.36	0.88	0.93	1.21	1.00	1.18
7	Pt-3-*O*-(6-ac)-glc	1.18	1.60	2.43	3.57	3.80	3.06	3.66	3.49	3.61	3.60	3.43	3.50	3.52	3.73	3.66	3.14	2.80	2.25	2.82	2.20	2.79
8	Pn-3-*O*-(6-ac)-glc	0.80	1.10	2.60	3.57	3.74	3.08	3.62	3.56	3.44	3.40	3.27	3.23	2.92	3.05	3.21	2.87	2.68	2.83	2.64	2.65	2.58
9	Mv-3-*O*-(6-ac)-glc	5.36	7.76	11.71	14.35	15.28	13.98	14.79	14.30	14.56	13.98	13.03	13.37	13.27	13.50	11.67	10.75	9.38	9.73	9.72	9.74	9.89
10	Mv-3-*O*-(6-caff)-glc	1.10	1.19	2.29	3.53	4.15	3.22	4.41	4.29	4.53	4.40	4.22	4.32	4.18	3.10	5.73	4.01	4.87	5.00	4.74	3.54	3.52
11	Pt-3-*O*-(6-*p*-coum)-glc	1.07	1.65	3.77	5.04	5.40	4.87	5.32	4.98	5.07	4.55	4.22	4.26	3.62	3.80	3.52	3.40	3.08	3.15	3.04	3.00	3.02
12	Pn-3-*O*-(6-*p*-coum)-glc	7.39	11.30	28.40	35.48	37.27	32.91	36.69	35.00	33.53	30.43	28.34	27.66	20.51	20.86	22.24	21.50	19.24	19.84	18.67	18.50	16.35
13	Mv-3-*O*-(6-*p*-coum)-glc	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Tank 12

#	Time (days)	0	1	3	4	5	6	7	8	10	11	12	13	25	26	31	34	38	45	48	52	53
1	Dp-3-*O*-glc	20.98	22.95	25.12	23.64	18.90	18.97	15.18	13.50	14.33	12.18	11.42	11.66	9.87	9.98	7.72	8.36	8.14	6.16	7.37	7.24	7.58
2	Cy-3-*O*-glc	7.11	6.55	2.97	2.62	4.31	2.56	2.66	2.71	2.69	2.48	2.50	2.42	2.22	2.14	1.93	1.94	2.04	1.62	1.69	1.71	1.63
3	Pt-3-*O*-glc	18.38	20.32	29.03	28.64	30.30	24.75	27.84	26.17	27.89	23.13	23.73	23.99	20.11	20.11	15.62	16.52	16.32	13.43	14.73	14.67	14.77
4	Pn-3-*O*-glc	16.05	16.95	20.99	11.05	12.02	12.89	10.77	11.05	10.55	9.87	9.77	9.43	6.80	6.63	8.47	8.36	8.49	7.55	7.71	6.88	6.41
5	Mv-3-*O*-glc	86.13	99.15	136.54	142.20	150.98	123.16	147.86	148.52	154.53	137.93	142.40	144.86	132.77	129.62	114.60	110.51	102.96	87.77	97.90	96.88	96.81
6	Dp-3-*O*-(6-ac)-glc	0.72	0.85	2.74	1.23	3.01	2.02	2.55	2.37	2.70	2.47	2.53	2.51	2.57	2.29	2.49	2.57	2.33	1.01	1.31	2.01	1.33
7	Pt-3-*O*-(6-ac)-glc	1.39	1.69	3.21	3.06	3.98	3.27	3.77	3.65	3.97	3.69	3.75	3.84	3.85	3.68	3.66	3.78	3.54	2.28	3.00	2.57	2.96
8	Pn-3-*O*-(6-ac)-glc	0.91	1.13	3.15	3.24	3.82	3.30	3.67	3.70	3.73	3.47	3.52	3.49	3.17	2.99	3.21	3.20	3.17	2.75	2.79	2.87	2.68
9	Mv-3-*O*-(6-ac)-glc	6.43	7.97	13.27	14.50	15.86	13.47	14.96	14.68	15.76	13.99	14.16	14.55	13.78	13.36	11.67	11.37	11.28	9.38	10.22	10.25	10.57
10	Mv-3-*O*-(6-caff)-glc	1.17	1.26	2.75	3.20	4.12	3.19	4.18	4.17	4.65	4.26	4.34	4.44	4.26	4.04	5.73	4.18	5.53	4.65	3.57	3.59	3.53
11	Pt-3-*O*-(6-*p*-coum)-glc	1.43	1.66	4.51	5.09	5.68	5.00	5.37	5.08	5.45	4.61	4.62	4.66	3.89	3.76	3.52	3.68	3.67	3.05	3.11	3.05	3.12
12	Pn-3-*O*-(6-*p*-coum)-glc	9.12	10.64	31.36	35.19	38.00	34.11	36.15	34.88	35.61	29.84	29.74	29.48	21.24	20.28	22.24	21.47	21.56	18.28	19.14	16.41	16.62
13	Mv-3-*O*-(6-*p*-coum)-glc	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Tank 13

#	Time (days)	0	1	3	4	5	6	7	8	10	11	12	13	25	26	31	34	38	45	48	52	53
1	Dp-3-*O*-glc	16.50	20.18	22.04	23.83	22.55	17.46	19.34	16.18	18.78	16.97	16.16	16.81	13.71	13.53	13.52	14.12	12.01	12.34	12.13	11.39	11.52
2	Cy-3-*O*-glc	6.14	5.22	2.60	2.78	2.65	2.88	2.40	1.99	2.42	1.98	1.96	1.95	1.91	1.62	1.59	1.58	1.47	1.48	1.42	1.35	1.40
3	Pt-3-*O*-glc	15.05	17.81	23.84	26.56	26.34	30.06	24.85	21.03	24.45	22.05	21.18	21.96	18.52	17.96	17.52	17.82	15.05	15.23	14.66	14.01	13.73
4	Pn-3-*O*-glc	14.45	14.26	10.67	12.98	12.51	12.06	12.22	10.61	11.47	10.17	9.98	9.73	7.79	6.99	7.23	6.94	6.33	6.03	5.81	5.24	5.53
5	Mv-3-*O*-glc	77.24	88.91	114.04	123.61	127.21	156.90	125.37	113.61	125.08	119.30	115.37	119.73	108.07	105.70	102.79	102.03	83.41	80.59	78.27	75.13	74.82
6	Dp-3-*O*-(6-ac)-glc	0.55	0.86	2.04	2.25	2.11	2.42	2.06	0.97	2.21	1.08	0.92	1.07	1.93	0.93	1.43	1.45	1.02	1.15	1.26	0.89	1.24
7	Pt-3-*O*-(6-ac)-glc	1.23	1.69	2.77	3.23	3.31	3.69	3.25	2.76	3.42	2.91	2.83	2.94	3.38	2.94	3.15	3.26	2.85	3.02	3.01	3.04	3.12
8	Pn-3-*O*-(6-ac)-glc	0.82	1.16	2.68	3.15	3.21	3.72	3.17	2.87	3.17	2.72	2.73	2.69	2.63	2.36	2.43	2.38	2.25	2.35	2.27	2.68	2.40
9	Mv-3-*O*-(6-ac)-glc	5.67	8.43	11.67	13.73	14.27	15.58	14.00	12.36	14.21	13.30	12.56	13.06	11.99	11.37	11.38	11.35	9.79	10.04	9.66	9.12	9.52
10	Mv-3-*O*-(6-caff)-glc	0.97	1.26	2.20	2.73	3.07	4.06	3.26	2.95	3.54	3.35	3.13	3.39	3.45	3.10	3.31	3.32	2.95	3.11	3.06	4.49	4.59
11	Pt-3-*O*-(6-*p*-coum)-glc	1.10	2.25	3.94	5.14	5.15	5.50	5.04	4.36	5.06	4.52	4.28	4.38	3.74	3.47	3.54	3.57	3.10	3.25	3.11	3.15	3.14
12	Pn-3-*O*-(6-*p*-coum)-glc	7.41	14.52	27.73	34.62	34.57	37.28	33.84	30.31	32.34	28.94	27.69	27.54	20.22	18.80	18.52	18.07	15.66	15.68	14.34	14.41	14.35
13	Mv-3-*O*-(6-*p*-coum)-glc	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

continued

Table S5. Anthocyanin concentrations determined by HPLC-DAD in red wine samples from Alfaro 2019, expressed in mg of Mv-3-*O*-glc equiv./L.

Tank 14

#	Time (days)	0	1	3	4	5	6	7	8	10	11	12	13	25	26	31	34	38	45	48	52	53
1	Dp-3-*O*-glc	16.85	23.72	25.19	24.93	24.15	14.34	20.39	18.09	21.20	19.64	17.17	17.13	15.22	14.13	13.54	14.69	14.31	12.18	12.83	11.53	11.50
2	Cy-3-*O*-glc	6.29	5.87	2.87	2.81	2.90	2.72	2.54	2.22	2.60	2.19	2.14	2.10	2.05	1.72	1.70	1.68	1.88	1.72	1.80	1.66	1.48
3	Pt-3-*O*-glc	15.38	20.77	26.84	28.14	28.31	26.63	26.76	23.71	27.64	25.70	23.22	22.97	20.68	18.89	17.57	18.71	18.20	15.25	16.23	14.61	14.08
4	Pn-3-*O*-glc	14.50	15.48	11.35	13.25	13.28	11.62	12.10	11.17	11.89	10.46	10.34	9.81	8.06	7.26	6.99	6.90	7.30	6.32	7.08	6.20	5.88
5	Mv-3-*O*-glc	78.36	100.42	123.81	137.26	136.20	149.78	132.58	123.45	142.68	133.60	123.57	124.82	114.68	107.98	103.06	104.12	94.34	79.50	83.35	74.39	73.81
6	Dp-3-*O*-(6-ac)-glc	0.57	0.97	2.17	1.85	2.30	2.70	2.14	1.03	2.28	1.23	1.11	1.10	1.90	1.49	1.48	1.56	2.13	1.84	2.12	1.79	1.27
7	Pt-3-*O*-(6-ac)-glc	1.31	1.86	3.07	3.05	3.66	3.78	3.53	3.03	3.65	3.27	3.12	2.92	3.63	3.14	3.43	3.67	3.67	3.48	3.84	3.70	3.49
8	Pn-3-*O*-(6-ac)-glc	0.89	1.22	2.90	2.90	3.45	3.83	3.27	3.06	3.24	2.94	2.89	2.51	2.80	2.48	2.64	2.75	2.79	2.81	2.95	3.20	2.73
9	Mv-3-*O*-(6-ac)-glc	6.15	9.46	12.93	13.99	15.47	15.26	14.81	13.38	15.33	14.80	13.43	13.27	12.68	11.83	11.72	11.98	11.44	9.86	10.83	9.39	9.59
10	Mv-3-*O*-(6-caff)-glc	1.18	1.36	2.49	2.64	3.53	4.39	3.61	3.32	3.91	3.84	3.50	3.30	3.73	3.38	4.86	5.22	3.69	4.73	5.57	5.52	5.31
11	Pt-3-*O*-(6-*p*-coum)-glc	1.40	2.46	4.44	4.76	5.52	5.47	5.22	4.58	5.25	4.90	4.47	4.08	3.91	3.59	3.62	3.80	3.63	3.26	3.62	3.45	3.43
12	Pn-3-*O*-(6-*p*-coum)-glc	10.00	15.82	29.48	31.13	36.42	38.67	33.60	30.56	32.16	30.04	27.69	24.70	19.81	18.57	18.07	18.38	16.69	13.98	15.57	14.30	14.04
13	Mv-3-*O*-(6-*p*-coum)-glc	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Tank 15

#	Time (days)	0	1	3	4	5	6	7	8	10	11	12	13	25	26	31	34	38	45	48	52	53
1	Dp-3-*O*-glc	20.35	26.88	26.05	26.07	24.71	13.30	22.81	18.87	21.28	19.55	18.44	17.06	16.58	14.05	14.23	15.87	14.38	13.02	12.53	10.72	12.13
2	Cy-3-*O*-glc	6.84	6.64	2.82	3.14	4.11	2.58	2.50	2.27	2.56	2.31	3.44	2.03	1.85	1.76	1.75	1.80	1.95	1.91	1.80	1.43	1.74
3	Pt-3-*O*-glc	17.81	22.45	26.70	28.94	28.41	25.63	26.40	24.09	27.57	25.67	23.94	21.58	20.85	18.53	18.37	19.75	18.03	16.38	15.69	13.30	15.07
4	Pn-3-*O*-glc	15.42	16.39	11.23	14.36	13.50	11.00	11.90	11.78	11.77	10.86	10.91	9.47	7.66	7.64	7.54	7.66	8.04	7.49	7.42	5.55	7.18
5	Mv-3-*O*-glc	84.48	104.01	123.13	132.70	134.26	148.03	127.23	122.55	131.38	135.99	121.82	115.69	115.00	106.94	103.94	107.22	92.90	84.77	80.94	72.22	77.30
6	Dp-3-*O*-(6-ac)-glc	0.68	1.08	1.15	2.37	2.28	2.61	1.95	1.10	2.11	1.20	2.00	1.01	1.08	1.49	1.51	1.69	2.04	2.19	0.95	0.81	1.87
7	Pt-3-*O*-(6-ac)-glc	1.40	1.99	2.68	3.55	3.59	3.66	3.41	3.07	3.51	3.33	3.40	2.93	3.35	3.19	3.39	3.71	3.57	3.69	3.58	3.01	3.51
8	Pn-3-*O*-(6-ac)-glc	0.91	1.30	2.67	3.32	3.36	3.72	3.08	3.06	3.06	2.95	2.99	2.57	2.60	2.52	2.62	2.75	2.69	2.52	2.69	2.41	2.74
9	Mv-3-*O*-(6-ac)-glc	6.52	9.92	13.00	14.83	14.94	14.82	14.17	13.48	14.56	14.79	13.41	12.48	12.66	11.80	11.64	12.21	11.16	10.73	10.17	8.70	9.82
10	Mv-3-*O*-(6-caff)-glc	1.18	1.57	2.51	3.35	3.68	4.13	3.69	3.57	3.96	4.12	3.90	3.52	3.74	3.53	4.96	3.95	3.70	3.84	3.71	4.67	5.29
11	Pt-3-*O*-(6-*p*-coum)-glc	1.50	2.78	4.65	5.39	5.29	5.21	5.10	4.78	5.23	5.02	4.53	4.04	3.91	3.59	3.67	3.92	3.60	3.57	3.42	2.97	3.40
12	Pn-3-*O*-(6-*p*-coum)-glc	9.71	17.29	31.22	35.32	34.61	37.26	31.77	31.86	31.28	30.91	27.76	24.51	20.34	18.86	18.52	19.10	16.96	16.33	15.41	13.38	14.61
13	Mv-3-*O*-(6-*p*-coum)-glc	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Tank 16

#	Time (days)	0	1	3	4	5	6	7	8	10	11	12	13	25	26	31	34	38	45	48	52	53
1	Dp-3-*O*-glc	19.04	25.17	25.06	25.14	24.44	12.74	20.70	17.49	20.07	18.90	17.12	16.20	15.80	14.55	14.29	14.83	14.06	12.07	11.77	11.45	12.27
2	Cy-3-*O*-glc	6.59	6.25	3.04	3.04	2.90	2.40	2.58	2.17	2.59	2.26	2.17	2.11	1.62	1.77	1.76	1.96	1.67	1.73	1.48	1.65	1.52
3	Pt-3-*O*-glc	17.21	21.33	26.60	27.98	28.21	24.87	27.12	22.52	26.59	25.01	22.91	21.66	18.28	19.22	18.32	18.78	17.15	15.18	14.37	14.28	14.92
4	Pn-3-*O*-glc	15.52	16.16	12.05	13.92	13.69	10.25	12.69	11.44	11.93	10.76	10.36	9.91	6.75	7.75	7.52	8.36	6.69	6.49	5.65	5.99	5.82
5	Mv-3-*O*-glc	83.88	102.82	123.32	131.40	136.27	144.02	133.96	120.24	133.03	135.94	124.03	124.49	103.41	110.05	105.55	103.11	90.23	81.76	77.70	75.22	78.39
6	Dp-3-*O*-(6-ac)-glc	0.63	1.01	2.19	2.40	2.30	2.15	2.03	1.02	2.14	1.17	1.02	1.07	0.93	1.49	1.51	2.31	1.34	1.77	1.30	1.78	1.33
7	Pt-3-*O*-(6-ac)-glc	1.37	1.95	3.06	3.55	3.65	3.32	3.55	2.97	3.53	3.23	3.13	3.08	2.89	3.15	3.46	3.86	3.22	3.45	3.28	3.56	3.50
8	Pn-3-*O*-(6-ac)-glc	0.93	1.30	2.89	3.36	3.41	3.37	3.25	3.05	3.14	2.86	2.86	2.73	2.29	2.48	2.62	2.79	2.48	2.52	2.58	3.09	3.00
9	Mv-3-*O*-(6-ac)-glc	6.52	9.84	12.94	14.67	15.17	13.91	14.82	13.13	14.73	14.63	13.45	13.14	11.15	11.95	11.90	11.69	10.75	9.81	9.84	9.29	9.69
10	Mv-3-*O*-(6-caff)-glc	1.22	1.49	2.55	3.30	3.73	3.95	3.95	3.54	4.03	4.04	3.89	3.78	3.39	3.52	3.77	3.95	3.45	5.13	4.96	5.33	5.27
11	Pt-3-*O*-(6-*p*-coum)-glc	1.51	2.60	4.33	5.20	5.27	4.79	5.18	4.46	5.00	4.73	4.35	4.06	3.50	3.52	3.60	3.76	3.32	3.20	3.20	3.20	3.31
12	Pn-3-*O*-(6-*p*-coum)-glc	10.28	16.62	29.14	34.51	34.52	33.84	33.42	30.35	30.79	29.40	27.42	25.20	18.14	18.59	18.18	17.77	15.59	14.40	14.05	13.44	14.02
13	Mv-3-*O*-(6-*p*-coum)-glc	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Tank 17

#	Time (days)	0	1	3	4	5	6	7	8	10	11	12	13	25	26	31	34	38	45	48	52	53
1	Dp-3-*O*-glc	24.55	29.63	23.93	16.42	14.95	16.09	11.97	10.46	9.99	9.72	8.56	8.17	7.17	7.06	6.01	5.60	4.84	4.34	4.49	4.75	5.02
2	Cy-3-*O*-glc	8.11	7.29	2.40	2.42	2.85	2.08	2.43	2.32	2.08	2.32	2.19	2.10	1.86	1.83	1.50	1.66	1.51	1.61	1.50	1.40	1.45
3	Pt-3-*O*-glc	21.05	25.05	27.46	27.19	27.92	21.23	23.92	22.58	21.46	21.50	19.69	18.59	16.81	16.73	13.88	12.69	11.16	9.72	10.07	11.02	11.24
4	Pn-3-*O*-glc	15.31	16.16	7.56	8.63	9.75	9.52	8.27	8.35	7.37	7.96	7.33	6.79	5.09	6.05	5.99	7.61	7.64	9.19	8.81	7.19	8.04
5	Mv-3-*O*-glc	88.93	105.74	120.85	129.06	137.97	98.21	125.67	123.72	122.45	128.44	122.59	117.63	110.85	113.05	100.23	90.02	77.34	68.12	71.42	74.92	76.07
6	Dp-3-*O*-(6-ac)-glc	0.76	0.98	1.14	1.21	2.48	0.88	2.42	1.98	1.35	2.57	2.18	2.35	2.35	2.48	1.41	2.32	0.90	1.67	0.96	0.82	1.00
7	Pt-3-*O*-(6-ac)-glc	1.45	1.78	2.53	2.96	3.57	2.39	3.55	3.23	2.84	3.73	3.42	3.43	3.56	3.57	3.07	3.40	2.74	2.23	2.66	2.10	2.69
8	Pn-3-*O*-(6-ac)-glc	0.77	0.95	2.47	2.88	3.29	2.40	3.17	3.03	2.54	3.21	2.99	2.93	2.06	2.66	2.55	2.83	2.59	2.77	2.52	2.43	2.43
9	Mv-3-*O*-(6-ac)-glc	6.31	8.03	11.93	13.70	14.61	10.50	13.36	12.91	12.58	13.76	12.53	12.04	11.76	11.63	10.32	9.67	8.47	7.91	8.10	8.40	8.53
10	Mv-3-*O*-(6-caff)-glc	1.16	1.34	2.53	3.48	4.15	2.88	4.37	4.22	3.95	4.78	5.71	5.61	4.19	5.25	5.06	5.43	4.78	4.90	4.67	4.57	4.55
11	Pt-3-*O*-(6-*p*-coum)-glc	1.65	2.09	4.66	5.73	6.04	4.51	5.55	5.33	4.92	5.37	4.75	4.47	4.03	3.83	3.49	3.60	3.29	3.27	3.22	3.20	3.22
12	Pn-3-*O*-(6-*p*-coum)-glc	10.28	13.35	30.33	35.05	37.03	28.81	34.81	32.62	29.54	31.86	28.96	26.87	20.32	20.07	21.00	21.07	20.01	19.91	19.70	19.20	16.74
13	Mv-3-*O*-(6-*p*-coum)-glc	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Tank 18

#	Time (days)	0	1	3	4	5	6	7	8	10	11	12	13	25	26	31	34	38	45	48	52	53
1	Dp-3-*O*-glc	21.40	28.48	22.96	16.99	16.02	15.04	12.04	10.27	9.59	9.20	9.07	7.37	7.65	7.19	6.39	5.36	5.06	4.33	4.85	4.93	4.87
2	Cy-3-*O*-glc	7.62	7.21	2.32	2.92	2.99	2.02	2.57	2.31	2.09	2.08	2.26	2.03	1.83	1.85	1.80	1.38	1.45	1.41	1.46	1.56	1.43
3	Pt-3-*O*-glc	19.38	24.68	26.39	28.43	28.31	20.12	24.87	21.65	20.89	20.43	20.13	17.85	16.80	17.04	14.87	12.16	11.74	9.85	11.07	11.51	11.36
4	Pn-3-*O*-glc	14.97	16.16	6.94	10.40	9.96	9.09	9.12	8.41	7.36	7.42	7.62	6.63	5.08	6.18	6.95	6.09	6.39	7.64	7.05	6.86	6.87
5	Mv-3-*O*-glc	84.62	105.00	117.79	132.92	137.15	92.80	133.36	120.42	121.17	124.40	126.59	114.43	113.85	115.34	104.44	90.17	80.39	70.32	76.26	77.33	77.35
6	Dp-3-*O*-(6-ac)-glc	0.66	0.94	1.10	2.99	2.91	0.82	2.56	2.06	1.31	1.41	1.40	2.24	2.13	2.63	2.50	1.32	0.99	0.79	1.00	1.66	1.19
7	Pt-3-*O*-(6-ac)-glc	1.35	1.76	2.44	3.62	3.80	2.27	3.67	3.23	2.79	2.89	2.92	3.32	3.42	3.73	3.59	2.93	2.72	1.98	2.16	2.77	2.68
8	Pn-3-*O*-(6-ac)-glc	0.73	0.95	2.37	3.38	3.46	2.27	3.41	3.07	2.53	2.59	2.64	2.86	2.63	2.76	2.86	2.51	2.45	2.52	2.54	2.45	2.36
9	Mv-3-*O*-(6-ac)-glc	5.73	8.11	11.43	14.31	14.63	10.23	14.36	12.64	12.15	12.55	12.40	11.55	11.89	12.02	10.71	9.44	8.74	7.89	8.58	8.47	8.60
10	Mv-3-*O*-(6-caff)-glc	1.17	1.43	2.50	3.89	4.02	2.80	4.49	4.05	3.75	3.91	4.99	4.06	4.08	4.25	5.50	4.85	4.63	4.50	4.66	4.55	4.53
11	Pt-3-*O*-(6-*p*-coum)-glc	1.44	2.30	4.44	6.03	6.14	4.34	6.10	5.32	4.79	4.73	4.59	4.31	4.03	4.04	3.73	3.34	3.22	3.11	3.29	3.11	3.17
12	Pn-3-*O*-(6-*p*-coum)-glc	9.16	15.29	29.26	36.71	37.86	27.49	38.35	33.00	29.93	28.75	28.23	26.77	21.01	21.28	19.98	17.78	16.94	18.94	17.23	16.30	16.76
13	Mv-3-*O*-(6-*p*-coum)-glc	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Tank 19

#	Time (days)	0	1	3	4	5	6	7	8	10	11	12	13	25	26	31	34	38	45	48	52	53
1	Dp-3-*O*-glc	24.79	29.09	24.59	16.61	15.48	12.92	11.93	11.05	10.43	9.85	8.32	8.62	7.38	7.56	6.77	5.98	4.92	3.47	4.65	5.18	-
2	Cy-3-*O*-glc	8.07	7.59	2.82	2.42	2.88	2.67	2.58	2.38	2.23	2.28	1.95	2.11	1.77	1.81	1.84	1.70	1.49	1.48	1.44	1.57	-
3	Pt-3-*O*-glc	20.98	24.31	27.25	26.23	27.16	25.13	24.14	22.90	21.69	20.91	19.18	18.90	16.41	17.00	15.06	12.70	11.00	9.01	10.09	11.41	-
4	Pn-3-*O*-glc	15.54	16.30	8.23	9.09	10.21	10.09	9.34	9.02	7.87	8.16	7.26	7.25	5.03	6.17	7.62	7.82	7.82	8.96	8.61	7.84	-
5	Mv-3-*O*-glc	88.27	102.97	116.43	123.75	129.94	128.85	127.47	128.22	121.88	120.76	116.16	116.38	107.04	110.78	102.86	86.88	73.65	65.23	69.87	73.59	-
6	Dp-3-*O*-(6-ac)-glc	0.75	0.97	2.19	1.11	2.80	2.52	2.47	1.47	1.36	2.42	1.29	2.32	2.00	2.48	2.45	2.27	0.92	0.71	0.81	1.64	-
7	Pt-3-*O*-(6-ac)-glc	1.43	1.73	2.91	2.79	3.67	3.54	3.60	2.91	2.88	3.51	2.69	3.40	3.23	3.55	3.57	3.34	2.64	1.91	1.97	2.21	-
8	Pn-3-*O*-(6-ac)-glc	0.78	0.94	2.72	2.82	3.41	3.45	3.36	2.86	2.61	3.09	2.46	2.92	2.48	2.60	2.87	2.78	2.51	2.59	2.51	2.50	-
9	Mv-3-*O*-(6-ac)-glc	6.22	7.90	11.52	12.92	13.99	13.79	13.76	12.94	12.50	12.85	11.35	11.97	11.09	11.61	10.58	9.48	8.23	7.53	8.04	8.44	-
10	Mv-3-*O*-(6-caff)-glc	1.19	1.32	2.85	4.21	4.22	5.91	4.55	5.27	4.02	4.55	3.76	4.32	3.91	4.12	5.59	5.32	4.68	4.54	4.55	4.68	-
11	Pt-3-*O*-(6-*p*-coum)-glc	1.67	2.15	4.54	5.46	6.00	6.04	5.91	5.36	5.02	5.11	4.30	4.56	3.77	3.94	3.79	3.57	3.22	3.09	3.18	3.27	-
12	Pn-3-*O*-(6-*p*-coum)-glc	10.05	13.28	29.64	34.31	36.45	38.83	36.18	34.38	30.95	30.93	27.08	27.89	19.40	20.42	22.43	20.84	19.54	19.12	19.29	16.76	-
13	Mv-3-*O*-(6-*p*-coum)-glc	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

continued

Table S5. Anthocyanin concentrations determined by HPLC-DAD in red wine samples from Alfaro 2019, expressed in mg of Mv-3-*O*-glc equiv./L.

Tank 20

#	Time (days)	0	1	3	4	5	6	7	8	10	11	12	13	25	26	31	34	38	45	48	52	53
1	Dp-3-*O*-glc	23.43	31.10	24.03	16.61	14.61	17.20	11.96	10.58	9.96	9.34	8.42	8.20	6.95	7.23	6.13	5.61	4.84	4.17	2.28	4.66	5.13
2	Cy-3-*O*-glc	8.06	8.07	2.75	2.90	2.88	2.18	2.56	2.48	2.30	2.24	2.09	2.03	1.67	1.76	1.70	1.62	1.47	1.42	4.58	1.32	1.58
3	Pt-3-*O*-glc	20.30	26.01	26.70	27.11	26.36	23.33	24.18	22.18	21.12	19.98	18.46	18.01	15.42	16.39	13.83	12.18	10.89	9.16	1.38	10.06	11.29
4	Pn-3-*O*-glc	15.47	17.13	8.64	10.18	10.26	9.90	9.42	8.96	7.66	7.85	7.33	6.76	4.83	5.86	7.11	7.53	7.20	8.51	9.99	6.33	7.59
5	Mv-3-*O*-glc	85.72	106.19	113.51	125.98	127.30	107.99	127.02	122.34	123.19	120.36	110.86	110.82	102.79	108.02	96.53	86.15	73.85	64.88	8.00	67.26	73.57
6	Dp-3-*O*-(6-ac)-glc	0.72	1.00	2.54	2.88	2.81	0.92	2.51	2.40	1.35	2.18	2.23	2.23	1.91	2.39	2.31	2.11	0.88	0.80	69.01	0.78	1.78
7	Pt-3-*O*-(6-ac)-glc	1.41	1.82	2.88	3.51	3.61	2.58	3.59	3.43	2.89	3.34	3.28	3.26	3.13	3.40	3.33	3.15	2.02	1.88	0.71	1.94	2.27
8	Pn-3-*O*-(6-ac)-glc	0.77	0.97	2.67	3.26	3.40	2.52	3.36	3.30	2.65	2.98	2.89	2.80	1.86	2.49	2.71	2.63	2.46	2.53	-	2.25	2.60
9	Mv-3-*O*-(6-ac)-glc	6.02	8.45	11.24	13.25	13.64	11.70	13.66	12.92	12.54	12.54	11.43	11.36	10.55	11.18	10.00	9.12	8.13	7.52	-	7.68	8.46
10	Mv-3-*O*-(6-caff)-glc	1.25	1.46	2.91	4.86	5.52	3.18	4.53	4.48	4.02	4.37	4.12	4.11	3.76	3.98	5.25	5.05	4.64	4.49	-	4.27	4.82
11	Pt-3-*O*-(6-*p*-coum)-glc	1.64	2.55	4.38	5.55	5.84	4.95	5.86	5.46	5.00	4.93	4.52	4.37	3.61	3.75	3.43	3.34	3.17	3.03	-	2.92	3.27
12	Pn-3-*O*-(6-*p*-coum)-glc	10.00	16.08	28.68	34.16	35.69	31.25	35.55	35.37	31.06	30.13	27.42	26.40	18.39	19.62	20.56	17.62	18.95	18.62	-	15.18	16.24
13	Mv-3-*O*-(6-*p*-coum)-glc	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Tank 21

#	Time (days)	0	1	3	4	5	6	7	8	10	11	12	13	25	26	31	34	38	45	48	52	53
1	Dp-3-*O*-glc	22.94	26.44	24.25	22.72	19.35	13.27	17.14	14.48	15.81	15.18	13.80	14.10	12.48	12.36	11.73	11.90	10.80	9.81	9.47	9.64	9.37
2	Cy-3-*O*-glc	7.68	6.50	2.81	2.79	2.27	2.70	2.06	1.89	2.56	1.88	1.80	1.79	1.54	1.54	1.47	1.51	1.68	1.41	1.40	1.63	1.42
3	Pt-3-*O*-glc	19.60	21.36	25.93	25.98	24.49	24.67	23.42	19.89	21.21	20.90	19.26	19.58	17.53	17.75	16.39	16.44	15.10	13.71	13.46	13.76	13.26
4	Pn-3-*O*-glc	14.74	13.67	11.04	10.67	9.62	10.07	9.11	8.57	7.92	7.90	7.69	7.14	5.32	5.88	5.60	5.73	6.58	5.33	5.20	6.27	5.90
5	Mv-3-*O*-glc	84.19	92.81	113.50	114.60	109.43	123.56	109.61	95.31	102.64	106.66	96.24	102.90	94.94	94.69	87.74	87.80	76.63	68.55	67.65	67.40	66.87
6	Dp-3-*O*-(6-ac)-glc	0.70	0.96	2.10	2.23	1.09	2.17	1.11	0.88	0.86	0.96	0.85	0.91	0.91	1.40	1.36	1.43	1.81	0.99	0.92	1.89	0.83
7	Pt-3-*O*-(6-ac)-glc	1.34	1.69	2.87	3.17	2.79	3.20	2.88	2.54	2.43	2.72	2.39	2.67	2.75	2.86	2.96	3.07	3.01	2.65	2.69	3.09	2.73
8	Pn-3-*O*-(6-ac)-glc	0.72	0.90	2.57	2.91	2.66	3.28	2.68	2.52	2.09	2.37	2.11	2.29	2.06	2.05	2.15	2.25	2.27	2.04	1.82	2.37	2.08
9	Mv-3-*O*-(6-ac)-glc	5.71	7.84	11.62	12.39	12.33	13.32	12.40	10.50	10.75	11.47	10.36	10.87	10.38	10.32	9.88	10.03	8.97	8.22	8.23	8.39	8.08
10	Mv-3-*O*-(6-caff)-glc	1.07	1.18	2.47	2.10	2.89	3.47	3.26	2.96	2.82	3.19	2.74	3.15	4.01	3.91	4.14	4.40	4.26	3.87	4.06	4.60	4.21
11	Pt-3-*O*-(6-*p*-coum)-glc	1.43	2.24	4.81	5.33	5.37	6.08	5.32	4.50	4.46	4.61	3.91	4.27	3.55	3.55	3.44	3.57	3.29	2.97	3.03	3.21	3.01
12	Pn-3-*O*-(6-*p*-coum)-glc	8.73	12.67	30.17	32.14	33.11	38.24	31.94	28.56	25.28	26.84	22.78	24.76	18.03	17.88	16.76	17.24	15.81	13.91	13.92	14.40	15.06
13	Mv-3-*O*-(6-*p*-coum)-glc	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Tank 22

#	Time (days)	0	1	3	4	5	6	7	8	10	11	12	13	25	26	31	34	38	45	48	52	53
1	Dp-3-*O*-glc	22.27	25.40	22.54	20.86	18.40	12.33	16.61	13.97	14.77	14.13	13.19	12.76	11.66	11.07	10.79	10.36	9.69	8.72	8.88	7.90	7.97
2	Cy-3-*O*-glc	7.61	6.34	2.64	2.31	2.31	2.43	2.05	2.12	1.86	1.81	1.92	1.93	1.49	1.54	1.55	1.41	1.41	1.36	1.32	1.28	1.33
3	Pt-3-*O*-glc	19.19	20.61	24.59	24.16	24.86	22.98	23.23	20.10	20.59	19.86	19.04	18.99	16.34	16.40	15.68	14.62	13.78	12.79	12.83	11.40	11.45
4	Pn-3-*O*-glc	14.74	13.38	8.83	9.67	9.53	9.10	8.77	9.06	7.49	7.47	7.82	7.46	5.04	5.72	5.46	5.05	5.10	4.66	4.70	4.75	5.00
5	Mv-3-*O*-glc	83.25	90.36	109.44	107.42	115.88	116.29	113.38	104.18	103.43	103.34	95.93	100.06	89.72	91.65	87.03	80.15	70.64	66.66	66.40	59.26	60.04
6	Dp-3-*O*-(6-ac)-glc	0.68	0.93	1.72	1.09	1.09	1.98	1.02	1.19	0.85	0.91	1.13	1.75	0.82	1.39	1.32	1.33	1.03	0.99	0.88	0.80	0.62
7	Pt-3-*O*-(6-ac)-glc	1.36	1.65	2.54	2.63	2.92	3.02	2.63	2.50	2.45	2.66	2.48	2.90	2.67	2.86	3.05	3.02	2.71	2.67	2.74	2.58	2.61
8	Pn-3-*O*-(6-ac)-glc	0.74	0.88	2.30	2.53	2.66	3.03	2.34	2.37	2.09	2.28	2.11	2.33	1.60	2.08	2.21	2.18	2.01	2.09	2.13	2.05	2.13
9	Mv-3-*O*-(6-ac)-glc	5.88	7.62	10.77	11.88	12.59	12.41	11.65	10.32	10.46	10.76	10.16	10.34	9.74	9.95	9.72	9.21	8.20	8.00	8.04	7.22	7.33
10	Mv-3-*O*-(6-caff)-glc	1.16	1.16	1.70	2.88	3.49	4.62	3.36	3.15	3.18	3.46	3.09	3.62	4.12	4.19	4.53	4.48	4.04	4.08	4.36	4.16	4.34
11	Pt-3-*O*-(6-*p*-coum)-glc	1.55	2.13	4.37	5.03	5.33	5.62	4.74	4.09	4.13	4.20	3.70	3.91	3.25	3.26	3.28	3.22	2.87	2.80	2.90	2.71	2.78
12	Pn-3-*O*-(6-*p*-coum)-glc	9.74	12.04	27.32	31.05	32.71	35.15	28.57	25.77	23.72	24.49	21.49	22.50	16.18	16.66	15.84	15.08	13.37	12.80	13.14	12.09	12.14
13	Mv-3-*O*-(6-*p*-coum)-glc	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Tank 23

#	Time (days)	0	1	3	4	5	6	7	8	10	11	12	13	25	26	31	34	38	45	48	52	53
1	Dp-3-*O*-glc	22.64	31.02	24.02	24.74	19.91	12.32	17.19	15.08	15.83	14.77	13.28	12.84	12.63	12.85	11.35	11.35	9.97	9.47	9.18	8.71	8.61
2	Cy-3-*O*-glc	7.77	7.59	2.88	2.87	2.37	2.52	2.14	2.02	1.97	1.86	2.03	1.77	1.57	1.64	1.51	1.43	1.44	1.52	1.66	1.42	1.55
3	Pt-3-*O*-glc	19.76	24.93	25.39	26.69	25.06	24.18	23.34	20.61	21.76	20.02	19.09	18.37	17.30	18.23	15.88	15.35	14.05	13.57	13.40	12.41	12.40
4	Pn-3-*O*-glc	14.96	15.96	11.56	11.39	9.83	9.38	9.51	9.22	8.31	7.68	8.48	7.24	5.49	6.44	5.72	5.59	5.90	6.09	6.55	6.00	6.82
5	Mv-3-*O*-glc	83.69	103.80	110.02	116.29	114.70	126.36	112.37	98.69	106.37	100.84	96.40	97.49	92.13	95.58	84.59	79.66	72.09	69.20	66.82	62.59	62.10
6	Dp-3-*O*-(6-ac)-glc	0.68	1.93	1.73	2.18	1.09	2.16	1.02	0.88	0.94	0.85	1.13	0.79	0.88	1.47	1.30	1.28	1.01	0.95	1.66	0.86	1.39
7	Pt-3-*O*-(6-ac)-glc	1.37	2.19	2.60	3.22	2.81	3.25	2.64	2.44	2.71	2.44	2.49	2.38	2.79	3.02	2.99	2.85	2.70	2.67	2.88	2.61	2.26
8	Pn-3-*O*-(6-ac)-glc	0.74	1.18	2.37	2.94	2.61	3.22	2.45	2.35	2.39	2.05	2.20	1.99	2.07	2.15	2.18	2.03	2.04	2.04	2.15	2.09	2.12
9	Mv-3-*O*-(6-ac)-glc	5.79	9.42	11.03	12.73	12.37	13.40	11.78	10.41	11.33	10.41	10.19	10.13	10.12	10.20	9.61	9.04	8.35	8.12	8.07	7.66	7.55
10	Mv-3-*O*-(6-caff)-glc	1.19	1.60	1.77	3.18	3.24	5.19	3.36	3.15	3.53	3.11	3.07	3.01	4.31	3.44	4.46	4.13	3.94	3.98	4.26	4.23	4.31
11	Pt-3-*O*-(6-*p*-coum)-glc	1.48	3.14	4.53	5.54	5.32	5.97	4.93	4.27	4.70	4.09	3.74	3.65	3.51	3.60	3.40	3.23	2.98	2.90	3.01	2.92	2.92
12	Pn-3-*O*-(6-*p*-coum)-glc	8.94	17.95	28.20	33.04	32.06	37.49	29.91	26.78	27.36	23.44	22.47	21.21	17.68	18.45	16.71	15.32	14.50	14.90	15.30	14.81	14.56
13	Mv-3-*O*-(6-*p*-coum)-glc	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Tank 24

#	Time (days)	0	1	3	4	5	6	7	8	10	11	12	13	25	26	31	34	38	45	48	52	53
1	Dp-3-*O*-glc	22.73	26.30	23.19	20.86	20.03	15.85	15.51	13.48	14.16	14.62	13.24	13.01	11.73	11.04	10.80	10.83	9.94	8.86	8.85	7.99	8.15
2	Cy-3-*O*-glc	7.61	6.63	2.76	2.57	2.24	2.08	1.95	1.94	1.85	1.84	1.77	1.67	1.48	1.43	1.47	1.42	1.38	1.32	1.54	1.33	1.44
3	Pt-3-*O*-glc	19.26	21.22	24.68	23.95	22.61	21.74	21.50	19.25	20.31	20.42	19.00	18.23	16.57	15.99	15.68	15.16	14.24	12.65	13.05	11.58	12.06
4	Pn-3-*O*-glc	14.50	13.70	18.09	10.34	9.53	9.46	8.92	8.84	7.74	7.82	7.72	6.85	5.20	5.47	5.53	4.21	5.37	5.09	5.82	5.44	6.01
5	Mv-3-*O*-glc	81.75	91.49	107.98	108.03	103.33	108.03	100.88	100.30	101.78	104.36	99.67	95.66	90.39	85.76	85.63	81.78	72.96	63.85	64.68	59.72	60.20
6	Dp-3-*O*-(6-ac)-glc	0.68	0.94	1.74	1.61	0.98	0.84	0.91	0.78	0.82	0.93	0.83	0.82	0.84	1.36	1.32	1.36	1.15	0.95	1.56	0.85	1.26
7	Pt-3-*O*-(6-ac)-glc	1.37	1.65	2.50	2.58	2.66	2.46	2.45	2.33	2.38	2.67	2.37	2.50	2.70	2.72	2.99	2.98	2.71	2.58	2.84	2.57	2.12
8	Pn-3-*O*-(6-ac)-glc	0.74	0.87	2.27	2.39	2.59	2.43	2.27	2.30	2.09	2.27	2.07	2.09	1.62	1.96	2.17	2.17	2.03	1.99	2.16	2.06	2.01
9	Mv-3-*O*-(6-ac)-glc	5.96	7.59	10.40	10.93	11.42	11.03	10.85	10.22	10.37	11.07	10.19	10.18	9.95	9.39	9.63	9.35	8.44	7.69	7.88	7.32	7.23
10	Mv-3-*O*-(6-caff)-glc	1.18	1.16	2.31	2.61	3.17	3.26	3.22	3.11	3.18	3.54	3.12	3.26	4.27	4.00	4.48	4.48	4.08	3.96	4.40	4.20	4.12
11	Pt-3-*O*-(6-*p*-coum)-glc	1.73	2.14	4.13	4.54	4.94	4.70	4.61	4.07	4.21	4.41	3.84	3.83	3.46	3.21	3.32	3.31	3.00	2.80	2.98	2.79	2.72
12	Pn-3-*O*-(6-*p*-coum)-glc	10.62	11.79	25.68	27.61	31.01	30.04	28.04	26.14	24.44	25.89	22.62	22.06	17.46	16.00	16.28	15.83	14.38	12.99	13.54	14.01	13.50
13	Mv-3-*O*-(6-*p*-coum)-glc	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Table S6. Tannin conc. determined by HPLC-DAD-ESI(+)-MS/MS in red wine samples from Alfaro 2019, expressed in mg of (+)-cat equiv./L.

Tank 02

#	Time (days)	0	1	3	4	5	6	7	8	10	11	12	13	25	26
41	((Epi)gallocatechin)$_2$ 1	<LD	0.08	0.27	0.29	0.26	0.26	0.61	0.54	0.73	1.73	1.54	1.60	0.52	0.13
42	((Epi)gallocatechin)$_2$ 2	<LD	0.07	0.14	0.17	0.16	0.16	0.49	0.41	0.59	1.57	1.43	1.45	0.49	0.06
43	((Epi)gallocatechin)$_2$ 3	<LD	<LD	0.05	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	1.39	<LD	<LD
44	Gallocatechin	0.27	0.49	0.97	1.84	0.95	1.00	1.22	1.20	1.20	2.17	2.02	2.09	0.94	0.61
45	Epigallocatechin	0.17	0.27	0.38	0.49	0.54	0.45	0.73	0.76	0.82	1.73	1.54	1.59	0.64	0.36
46	((Epi)gallocatechin-(epi)catechin) 2	0.06	0.18	0.62	1.71	1.01	0.85	1.00	0.94	1.34	2.28	1.89	2.05	0.66	0.34
47	((Epi)catechin-(epi)gallocatechin) 2	0.04	0.07	0.29	0.39	0.44	0.33	0.65	0.56	0.73	1.79	1.58	1.67	0.58	0.18
48	((Epi)gallocatechin-(epi)catechin) 1	0.13	0.38	0.97	2.11	1.99	1.87	1.28	1.29	1.64	2.59	2.05	2.15	0.80	0.38
49	((Epi)catechin-(epi)gallocatechin) 1	0.09	0.16	0.43	0.53	0.79	0.63	0.79	0.82	0.91	1.87	1.69	1.63	0.55	0.17
50	((Epi)catechin-(epi)gallocatechin) A	<LD	<LD	0.15	0.32	0.41	0.25	0.60	0.53	0.67	1.57	1.44	<LD	<LD	<LD
51	((Epi)catechin)$_2$ 1	0.32	0.42	1.84	2.32	2.21	2.34	1.53	1.79	2.26	3.18	2.49	2.69	1.16	0.69
52	Procyanidin B 1	1.72	2.71	6.11	10.07	9.44	9.67	8.35	8.64	9.89	8.26	8.96	9.21	4.28	4.93
53	Procyanidin B 2	0.50	0.65	1.96	2.65	2.61	2.79	2.02	2.33	2.79	4.00	3.22	3.71	1.74	2.03
54	Catechin	0.34	0.64	1.72	1.97	1.85	2.03	1.66	1.84	1.64	2.70	2.43	2.50	1.50	1.78
55	Epicatechin	0.13	0.21	0.43	0.48	0.62	0.59	0.86	0.86	0.96	1.96	1.83	1.89	0.85	0.52
56	*p*-vinyl(epi)catechin 1	0.35	0.51	0.87	1.82	0.61	0.57	0.93	0.51	0.62	1.57	1.42	1.43	0.56	0.27
57	*p*-vinyl(epi)catechin 2	<LD	<LD	<LD	<LD	<LD	<LD	0.58	0.47	0.67	<LD	<LD	<LD	<LD	<LD
58	*p*-vinyl(epi)catechin 3	<LD	<LD	<LD	<LD	0.21	0.18	0.58	0.53	0.70	1.61	1.56	1.60	0.71	0.37

Tank 03

#	Time (days)	0	1	3	4	5	6	7	8	10	11	12	13	25	26
41	((Epi)gallocatechin)$_2$ 1	<LD	0.11	0.28	0.34	0.27	0.36	0.55	0.55	0.72	1.74	1.74	1.60	0.54	0.29
42	((Epi)gallocatechin)$_2$ 2	<LD	0.05	0.21	0.18	0.15	0.25	0.50	0.42	0.62	1.57	1.61	1.44	0.47	0.10
43	((Epi)gallocatechin)$_2$ 3	<LD	<LD	0.05	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
44	Gallocatechin	0.51	0.70	1.54	1.73	0.79	1.71	0.90	1.09	1.09	2.18	2.30	2.01	0.98	0.66
45	Epigallocatechin	0.23	0.24	0.37	0.32	0.29	0.45	0.57	0.65	0.82	1.71	1.83	1.57	0.64	0.27
46	((Epi)gallocatechin-(epi)catechin) 2	0.15	0.30	0.98	1.81	0.94	1.83	0.88	1.03	1.42	2.37	2.21	2.08	0.80	0.75
47	((Epi)catechin-(epi)gallocatechin) 2	0.08	0.09	0.35	0.41	0.40	0.52	0.58	0.57	0.87	1.80	1.82	1.57	0.62	0.38
48	((Epi)gallocatechin-(epi)catechin) 1	0.38	0.44	2.11	2.17	1.68	2.21	1.01	1.36	1.78	2.74	2.36	2.25	0.88	0.86
49	((Epi)catechin-(epi)gallocatechin) 1	0.22	0.24	0.53	0.51	0.45	0.67	0.63	0.71	0.91	1.97	1.90	1.67	0.63	0.35
50	((Epi)catechin-(epi)gallocatechin) A	<LD	<LD	0.16	0.31	0.32	0.35	0.57	0.48	0.71	1.54	<LD	1.44	<LD	<LD
51	((Epi)catechin)$_2$ 1	0.67	0.89	2.25	2.65	1.93	2.42	1.20	1.95	2.18	3.19	3.00	2.79	1.62	1.95
52	Procyanidin B 1	3.42	4.15	9.54	9.13	6.75	9.69	5.94	9.65	10.50	8.38	10.30	9.83	5.29	8.19
53	Procyanidin B 2	1.28	1.66	2.54	2.72	1.94	2.79	1.47	2.78	2.77	3.88	3.79	3.61	2.16	3.40
54	Catechin	0.62	0.84	0.95	1.80	1.62	2.09	1.29	1.79	1.73	2.64	2.98	2.58	1.74	2.22
55	Epicatechin	0.25	0.31	0.44	0.53	0.44	0.67	0.67	0.85	0.87	2.01	2.06	1.85	0.93	0.78
56	*p*-vinyl(epi)catechin 1	0.25	0.48	0.86	1.75	0.54	0.53	0.65	0.49	0.59	<LD	<LD	<LD	0.55	0.24
57	*p*-vinyl(epi)catechin 2	<LD	<LD	<LD	<LD	<LD	<LD	0.59	0.45	0.58	<LD	<LD	<LD	<LD	<LD
58	*p*-vinyl(epi)catechin 3	<LD	0.06	<LD	<LD	0.25	0.24	0.55	0.51	0.65	1.62	1.72	1.53	0.72	0.35

Tank 04

#	Time (days)	0	1	3	4	5	6	7	8	10	11	12	13	25	26
41	((Epi)gallocatechin)$_2$ 1	<LD	0.12	0.34	0.50	0.35	0.26	0.50	0.79	0.69	1.74	1.50	1.66	0.54	0.19
42	((Epi)gallocatechin)$_2$ 2	<LD	0.08	0.21	0.22	0.20	0.11	0.45	0.49	0.61	1.58	1.43	1.46	0.49	0.08
43	((Epi)gallocatechin)$_2$ 3	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
44	Gallocatechin	<LD	0.65	1.55	1.95	0.94	0.80	0.93	1.14	1.18	2.12	1.98	2.02	0.93	0.75
45	Epigallocatechin	<LD	0.25	0.48	0.56	0.40	0.30	0.64	0.61	0.76	1.77	1.56	1.61	0.61	0.20
46	((Epi)gallocatechin-(epi)catechin) 2	<LD	0.36	0.91	2.02	1.57	0.89	0.79	1.54	1.40	2.45	1.92	2.14	0.82	0.58
47	((Epi)catechin-(epi)gallocatechin) 2	<LD	0.18	0.35	0.44	0.49	0.35	0.61	0.73	0.86	1.78	1.53	1.66	0.72	0.25
48	((Epi)gallocatechin-(epi)catechin) 1	<LD	0.42	1.90	2.41	2.00	1.78	0.95	1.68	1.90	2.75	2.22	2.46	0.91	0.65
49	((Epi)catechin-(epi)gallocatechin) 1	<LD	0.28	0.55	0.66	0.53	0.48	0.60	0.82	0.99	1.93	1.65	1.76	0.60	0.31
50	((Epi)catechin-(epi)gallocatechin) A	<LD	<LD	0.24	0.48	0.52	0.36	0.65	0.55	0.70	1.64	1.43	1.43	<LD	<LD
51	((Epi)catechin)$_2$ 1	<LD	0.91	2.19	2.69	2.16	2.22	1.20	2.19	2.29	3.35	2.68	3.00	1.64	1.70
52	Procyanidin B 1	1.93	4.52	8.86	9.45	8.67	8.17	5.65	12.17	10.87	9.68	10.07	10.15	6.24	7.23
53	Procyanidin B 2	0.53	1.69	2.34	2.98	2.45	2.56	1.54	2.67	2.85	4.22	3.55	4.00	2.57	3.00
54	Catechin	0.50	0.80	1.96	2.22	1.81	1.91	1.35	1.73	1.68	2.68	2.50	2.50	1.71	1.84
55	Epicatechin	0.12	0.27	0.49	0.68	0.63	0.51	0.73	0.82	0.93	2.00	1.79	1.89	0.95	0.66
56	*p*-vinyl(epi)catechin 1	<LD	0.50	0.80	1.85	0.77	0.44	0.70	0.49	0.62	1.57	1.48	<LD	0.52	0.29
57	*p*-vinyl(epi)catechin 2	<LD	<LD	<LD	<LD	<LD	<LD	0.58	0.51	0.61	<LD	<LD	<LD	<LD	<LD
58	*p*-vinyl(epi)catechin 3	<LD	0.06	<LD	<LD	0.23	0.19	0.48	0.48	0.70	1.64	1.57	1.58	0.75	0.37

continued

Table S6. Tannin conc. determined by HPLC-DAD-ESI(+)-MS/MS in red wine samples from Alfaro 2019, expressed in mg of (+)-cat equiv./L.

Tank 05

#	Time (days)	0	1	3	4	5	6	7	8	10	11	12	13	25	26
41	((Epi)gallocatechin)$_2$ 1	<LD	0.08	0.29	0.37	0.36	0.15	0.52	0.37	0.73	1.63	1.45	1.47	0.63	0.19
42	((Epi)gallocatechin)$_2$ 2	<LD	0.05	0.16	0.26	0.20	0.11	0.48	0.35	0.56	1.51	1.38	1.39	0.50	0.10
43	((Epi)gallocatechin)$_2$ 3	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
44	Gallocatechin	0.29	0.58	0.99	0.98	0.87	0.72	1.02	0.99	1.10	1.98	1.84	1.87	1.04	0.78
45	Epigallocatechin	0.07	0.30	0.46	0.27	0.39	0.29	0.57	0.54	0.68	1.63	1.51	1.52	0.57	0.32
46	((Epi)gallocatechin-(epi)catechin) 2	0.07	0.09	0.29	0.33	0.47	0.29	0.57	0.55	0.85	1.71	1.49	1.53	0.71	0.25
47	((Epi)catechin-(epi)gallocatechin) 2	0.08	0.20	0.46	0.56	0.45	0.39	0.57	0.44	0.78	1.65	1.48	1.49	0.65	0.30
48	((Epi)gallocatechin-(epi)catechin) 1	0.06	0.21	0.90	1.88	1.69	0.61	0.83	0.73	1.36	2.03	1.71	1.82	1.04	0.64
49	((Epi)catechin-(epi)gallocatechin) 1	0.21	0.39	1.95	2.24	2.00	1.00	0.91	0.76	1.56	2.28	1.88	1.86	1.11	0.86
50	((Epi)catechin-(epi)gallocatechin) A	<LD	<LD	0.17	0.29	0.30	0.29	0.59	0.52	0.70	1.59	1.45	1.40	<LD	<LD
51	((Epi)catechin)$_2$ 1	0.39	0.75	2.03	2.51	2.18	1.99	1.37	1.55	1.93	2.68	2.41	2.36	1.58	1.81
52	Procyanidin B 1	2.37	3.78	8.88	10.24	9.01	7.31	5.91	6.80	9.47	8.16	7.76	8.22	7.03	7.49
53	Procyanidin B 2	0.71	0.73	2.19	2.55	2.11	2.25	1.62	1.55	2.11	2.80	2.69	2.82	1.80	2.58
54	Catechin	0.55	0.62	1.68	1.83	1.64	1.73	1.44	1.65	1.66	2.46	2.34	2.37	1.62	1.93
55	Epicatechin	0.16	0.22	0.46	0.41	0.52	0.47	0.76	0.78	0.89	1.87	1.71	1.71	0.85	0.67
56	*p*-vinyl(epi)catechin 1	0.32	0.84	1.69	2.15	1.62	0.86	1.12	0.87	0.83	1.78	1.64	1.62	0.69	0.36
57	*p*-vinyl(epi)catechin 2	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
58	*p*-vinyl(epi)catechin 3	<LD	<LD	<LD	<LD	<LD	0.16	<LD	<LD	0.62	1.57	1.45	1.46	0.61	0.27

Tank 06

#	Time (days)	0	1	3	4	5	6	7	8	10	11	12	13	25	26
41	((Epi)gallocatechin)$_2$ 1	0.05	0.12	0.20	0.39	0.33	0.30	0.49	0.40	0.82	1.78	1.55	1.66	<LD	0.22
42	((Epi)gallocatechin)$_2$ 2	0.04	0.06	0.14	0.21	0.20	0.15	0.47	<LD	0.60	1.57	1.43	1.47	<LD	0.09
43	((Epi)gallocatechin)$_2$ 3	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
44	Gallocatechin	0.31	0.62	0.93	1.85	0.91	0.97	0.89	1.00	1.30	2.18	1.89	2.18	0.66	0.75
45	Epigallocatechin	0.15	0.35	0.31	0.37	0.33	0.28	0.54	0.58	0.72	1.79	1.51	1.58	0.49	0.29
46	((Epi)gallocatechin-(epi)catechin) 2	0.12	0.28	0.95	1.84	1.62	0.94	0.73	0.72	1.71	2.45	1.87	2.25	0.53	0.79
47	((Epi)catechin-(epi)gallocatechin) 2	0.06	0.15	0.28	0.40	0.50	0.39	0.51	0.52	0.94	1.87	1.57	1.64	0.48	0.29
48	((Epi)gallocatechin-(epi)catechin) 1	0.21	0.44	2.01	2.42	1.96	1.98	0.86	0.87	1.91	2.90	2.02	2.50	0.57	0.85
49	((Epi)catechin-(epi)gallocatechin) 1	0.14	0.20	0.53	0.57	0.62	0.55	0.58	0.49	0.99	1.95	1.61	1.72	0.47	0.33
50	((Epi)catechin-(epi)gallocatechin) A	<LD	<LD	0.20	0.38	0.39	0.30	0.66	0.45	0.77	1.58	1.43	1.49	<LD	<LD
51	((Epi)catechin)$_2$ 1	0.39	0.77	2.12	2.67	2.18	2.34	1.20	1.88	2.94	3.58	2.39	3.16	0.78	1.77
52	Procyanidin B 1	2.40	3.83	9.14	10.72	8.20	8.76	5.16	8.47	12.53	11.13	8.14	11.42	1.93	7.97
53	Procyanidin B 2	0.59	0.90	2.27	2.91	2.25	2.39	1.34	2.00	2.79	4.08	2.66	3.78	0.90	2.70
54	Catechin	0.36	0.78	0.91	1.91	1.60	1.85	1.38	1.65	1.97	2.76	2.38	2.70	1.00	1.79
55	Epicatechin	0.13	0.25	0.44	0.52	0.52	0.57	0.72	0.71	0.99	1.97	1.74	1.94	0.63	0.57
56	*p*-vinyl(epi)catechin 1	0.34	0.81	1.62	2.22	1.57	0.88	1.06	0.87	1.04	1.80	1.61	1.60	0.66	0.44
57	*p*-vinyl(epi)catechin 2	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
58	*p*-vinyl(epi)catechin 3	<LD	<LD	<LD	<LD	0.16	0.17	<LD	<LD	0.64	1.59	1.49	1.51	0.56	0.23

Tank 07

#	Time (days)	0	1	3	4	5	6	7	8	10	11	12	13	25	26
41	((Epi)gallocatechin)$_2$ 1	<LD	0.14	0.31	0.40	0.32	0.53	0.63	0.65	0.86	1.61	1.64	1.67	0.55	0.26
42	((Epi)gallocatechin)$_2$ 2	<LD	0.10	0.16	0.16	0.18	0.23	0.48	0.43	0.60	1.54	1.44	1.44	0.46	0.11
43	((Epi)gallocatechin)$_2$ 3	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
44	Gallocatechin	0.12	0.71	1.64	2.00	1.51	1.93	1.11	1.31	1.41	2.14	2.18	2.05	1.02	0.77
45	Epigallocatechin	0.06	0.36	0.49	0.40	0.37	0.54	0.70	0.66	0.71	1.72	1.65	1.57	0.62	0.23
46	((Epi)gallocatechin-(epi)catechin) 2	<LD	0.37	0.67	1.85	0.96	1.97	1.02	1.14	1.51	2.01	1.99	2.09	0.71	0.69
47	((Epi)catechin-(epi)gallocatechin) 2	<LD	0.13	0.39	0.47	0.46	0.56	0.67	0.63	0.84	1.79	1.64	1.64	0.64	0.27
48	((Epi)gallocatechin-(epi)catechin) 1	0.13	0.62	1.70	2.43	1.89	2.44	1.31	1.49	2.02	2.41	2.45	2.23	0.86	1.41
49	((Epi)catechin-(epi)gallocatechin) 1	0.05	0.29	0.51	0.71	0.72	0.82	0.72	0.68	1.02	1.84	1.68	1.69	0.56	0.25
50	((Epi)catechin-(epi)gallocatechin) A	<LD	<LD	0.21	0.42	0.37	0.24	0.56	0.47	0.65	1.55	1.44	<LD	<LD	<LD
51	((Epi)catechin)$_2$ 1	0.61	0.94	2.06	2.70	2.54	3.27	1.77	2.28	3.20	3.28	3.31	2.93	1.56	2.23
52	Procyanidin B 1	3.22	4.50	7.84	10.30	8.75	10.15	8.11	11.07	14.76	8.49	11.13	9.81	5.89	9.50
53	Procyanidin B 2	1.30	1.53	2.09	3.12	2.31	3.34	1.78	2.68	3.16	3.74	3.67	3.49	1.97	3.15
54	Catechin	0.74	0.90	1.89	2.04	1.67	2.21	1.55	2.03	1.97	2.66	2.66	2.46	1.54	2.17
55	Epicatechin	0.28	0.32	0.45	0.61	0.50	0.70	0.80	0.90	0.98	1.99	1.86	1.83	0.87	0.70
56	*p*-vinyl(epi)catechin 1	0.24	0.88	1.59	2.11	0.98	0.93	0.97	0.79	0.87	1.75	1.61	1.64	0.65	0.30
57	*p*-vinyl(epi)catechin 2	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
58	*p*-vinyl(epi)catechin 3	<LD	<LD	<LD	<LD	0.18	<LD	<LD	0.45	0.61	1.57	1.52	1.53	0.58	0.24

continued

Table S6. Tannin conc. determined by HPLC-DAD-ESI(+)-MS/MS in red wine samples from Alfaro 2019, expressed in mg of (+)-cat equiv./L.

Tank 08

#	Time (days)	0	1	3	4	5	6	7	8	10	11	12	13	25	26
41	((Epi)gallocatechin)$_2$ 1	0.14	0.11	0.29	0.36	0.42	0.32	0.54	0.40	1.04	1.77	1.53	1.66	0.58	0.21
42	((Epi)gallocatechin)$_2$ 2	0.05	0.06	0.15	0.19	0.22	0.19	0.46	0.36	0.71	1.61	1.42	1.47	0.48	0.08
43	((Epi)gallocatechin)$_2$ 3	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
44	Gallocatechin	0.43	0.74	1.58	1.71	<LD	1.65	0.88	1.12	1.34	2.15	2.06	2.19	0.94	0.72
45	Epigallocatechin	0.19	0.37	0.46	0.34	<LD	0.42	0.54	0.60	0.79	1.72	1.61	1.61	0.61	0.27
46	((Epi)gallocatechin-(epi)catechin) 2	0.26	0.34	0.86	1.91	1.83	1.66	0.81	0.82	2.01	2.49	1.94	2.24	0.86	0.60
47	((Epi)catechin-(epi)gallocatechin) 2	0.12	0.13	0.28	0.45	0.46	0.41	0.58	0.59	1.01	1.86	1.52	1.70	0.63	0.31
48	((Epi)gallocatechin-(epi)catechin) 1	0.51	0.50	1.79	2.14	2.32	1.97	1.00	0.85	2.36	2.90	2.15	2.48	1.03	0.81
49	((Epi)catechin-(epi)gallocatechin) 1	0.29	0.27	0.50	0.59	0.68	0.58	0.65	0.52	1.07	1.86	1.60	1.75	0.58	0.25
50	((Epi)catechin-(epi)gallocatechin) A	<LD	<LD	0.18	0.19	0.34	0.30	0.53	0.45	0.73	1.64	1.41	1.44	0.49	<LD
51	((Epi)catechin)$_2$ 1	0.66	1.54	1.97	2.40	2.41	2.48	1.54	1.87	2.69	3.32	2.72	3.18	1.87	1.95
52	Procyanidin B 1	3.72	4.41	8.07	10.44	9.88	9.38	7.49	7.96	14.19	10.53	9.38	10.98	6.71	7.80
53	Procyanidin B 2	0.99	1.69	2.25	2.78	2.45	2.82	1.77	2.04	3.09	3.84	3.11	3.85	1.96	2.60
54	Catechin	0.55	0.92	1.78	1.85	1.61	1.88	1.45	1.97	1.92	2.63	2.59	2.58	1.59	1.72
55	Epicatechin	0.19	0.36	0.53	0.57	0.54	0.65	0.68	0.92	1.01	1.95	1.87	1.88	0.90	0.69
56	*p*-vinyl(epi)catechin 1	0.42	0.90	0.98	2.03	1.02	0.84	1.00	0.75	0.89	1.77	1.64	1.58	0.71	0.32
57	*p*-vinyl(epi)catechin 2	<LD	<LD	<LD	<LD	<LD	<LD	<LD	0.43	<LD	<LD	<LD	<LD	<LD	<LD
58	*p*-vinyl(epi)catechin 3	<LD	<LD	<LD	<LD	0.15	<LD	0.50	0.43	0.60	1.61	1.46	1.51	0.65	0.32

Tank 09

#	Time (days)	0	1	3	4	5	6	7	8	10	11	12	13	25	26
41	((Epi)gallocatechin)$_2$ 1	0.06	0.14	0.28	0.25	0.20	0.24	0.51	0.64	0.72	1.72	1.57	1.52	0.52	0.24
42	((Epi)gallocatechin)$_2$ 2	<LD	0.05	0.15	0.11	0.14	0.14	0.47	0.47	0.58	1.55	1.43	1.44	0.47	0.12
43	((Epi)gallocatechin)$_2$ 3	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	0.45	<LD
44	Gallocatechin	0.45	0.64	1.71	1.84	0.90	1.66	0.85	1.30	1.31	2.19	2.10	2.02	0.89	0.73
45	Epigallocatechin	0.19	0.29	0.60	0.41	0.32	0.35	0.56	0.68	0.78	1.74	1.60	1.52	0.57	0.21
46	((Epi)gallocatechin-(epi)catechin) 2	0.06	0.12	0.36	0.33	0.39	0.37	0.55	0.65	0.86	1.82	1.58	1.62	0.56	0.23
47	((Epi)catechin-(epi)gallocatechin) 2	0.13	0.18	0.45	0.54	0.52	0.46	0.50	0.69	0.94	1.81	1.72	1.56	0.60	0.34
48	((Epi)gallocatechin-(epi)catechin) 1	0.15	0.31	0.81	0.80	0.77	0.76	0.61	1.10	1.38	2.28	1.92	1.85	0.79	0.55
49	((Epi)catechin-(epi)gallocatechin) 1	0.33	0.37	1.70	1.90	1.79	1.75	0.81	1.56	1.85	2.56	2.16	2.09	0.81	0.82
50	((Epi)catechin-(epi)gallocatechin) A	<LD	<LD	0.16	0.20	0.31	0.25	<LD	0.47	0.62	1.54	<LD	<LD	<LD	<LD
51	((Epi)catechin)$_2$ 1	0.52	0.45	1.77	2.13	1.74	1.90	1.18	2.10	2.74	3.13	2.56	2.50	1.53	1.61
52	Procyanidin B 1	3.16	2.96	7.22	9.47	7.11	8.18	5.13	10.49	12.23	8.56	9.71	9.95	5.67	8.06
53	Procyanidin B 2	0.88	0.74	2.37	2.69	2.27	2.91	1.60	3.10	3.91	4.28	4.00	4.19	2.76	3.60
54	Catechin	0.61	1.54	1.87	1.87	1.62	1.93	1.38	2.02	1.98	2.86	2.66	2.51	1.63	1.88
55	Epicatechin	0.24	0.32	0.55	0.56	0.46	0.65	0.73	1.12	1.23	2.06	2.00	1.95	1.00	0.82
56	*p*-vinyl(epi)catechin 1	0.30	0.61	0.94	1.85	0.58	0.70	0.70	0.55	0.70	1.59	<LD	<LD	<LD	<LD
57	*p*-vinyl(epi)catechin 2	<LD	<LD	<LD	<LD	<LD	<LD	0.54	0.41	<LD	<LD	<LD	<LD	<LD	<LD
58	*p*-vinyl(epi)catechin 3	<LD	<LD	<LD	<LD	0.24	0.14	0.49	0.55	0.70	1.68	1.55	1.58	0.85	0.50

Tank 10

#	Time (days)	0	1	3	4	5	6	7	8	10	11	12	13	25	26
41	((Epi)gallocatechin)$_2$ 1	0.07	0.14	0.38	0.30	0.43	0.44	0.50	0.79	1.01	1.71	1.75	1.59	0.47	0.29
42	((Epi)gallocatechin)$_2$ 2	<LD	0.06	0.20	0.18	0.19	0.22	0.46	0.52	0.66	1.56	1.50	1.43	0.45	0.16
43	((Epi)gallocatechin)$_2$ 3	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
44	Gallocatechin	0.35	0.73	2.13	2.08	1.00	1.84	1.04	1.42	1.55	2.21	2.08	2.07	0.70	1.44
45	Epigallocatechin	0.18	0.36	0.56	0.47	0.41	0.51	0.60	0.70	0.89	1.73	1.55	1.57	0.49	0.37
46	((Epi)gallocatechin-(epi)catechin) 2	0.13	0.25	0.98	1.74	1.68	1.81	0.76	1.46	1.98	2.13	2.24	2.04	0.56	1.49
47	((Epi)catechin-(epi)gallocatechin) 2	0.12	0.09	0.46	0.39	0.50	0.54	0.60	0.77	1.09	1.79	1.66	1.64	0.50	0.46
48	((Epi)gallocatechin-(epi)catechin) 1	0.28	0.51	2.31	2.50	2.03	2.33	0.90	1.74	2.52	2.47	2.37	2.29	0.60	1.69
49	((Epi)catechin-(epi)gallocatechin) 1	0.14	0.19	0.61	0.70	0.53	0.68	0.55	0.79	1.03	1.87	1.71	1.60	0.53	0.43
50	((Epi)catechin-(epi)gallocatechin) A	<LD	<LD	0.19	0.22	0.29	0.22	0.57	0.43	0.65	1.56	1.43	<LD	<LD	<LD
51	((Epi)catechin)$_2$ 1	0.39	0.54	2.06	2.52	2.23	2.54	1.26	2.44	2.91	2.97	2.78	2.80	0.95	2.08
52	Procyanidin B 1	2.08	3.02	8.85	10.50	8.94	8.02	5.44	12.51	15.61	7.43	9.16	9.65	2.93	10.78
53	Procyanidin B 2	0.72	0.83	2.68	3.21	2.53	3.17	1.72	3.61	4.29	4.32	4.28	4.29	1.35	5.09
54	Catechin	0.69	1.53	2.35	1.97	1.70	2.29	1.63	2.04	2.24	2.70	2.59	2.70	1.08	2.16
55	Epicatechin	0.21	0.41	0.70	0.64	0.59	0.77	0.94	1.15	1.36	2.11	1.97	1.95	0.63	1.55
56	*p*-vinyl(epi)catechin 1	0.37	0.56	1.13	1.72	0.56	0.60	0.70	0.59	0.69	1.61	1.44	<LD	0.52	0.23
57	*p*-vinyl(epi)catechin 2	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
58	*p*-vinyl(epi)catechin 3	<LD	<LD	<LD	<LD	0.26	0.20	0.52	0.59	0.74	1.64	1.61	1.65	0.83	0.54

continued

Table S6. Tannin conc. determined by HPLC-DAD-ESI(+)-MS/MS in red wine samples from Alfaro 2019, expressed in mg of (+)-cat equiv./L.

Tank 11

#	Time (days)	0	1	3	4	5	6	7	8	10	11	12	13	25	26
41	((Epi)gallocatechin)$_2$ 1	<LD	0.12	0.25	0.65	0.34	0.43	0.52	0.96	0.93	1.89	1.75	1.59	0.72	0.37
42	((Epi)gallocatechin)$_2$ 2	<LD	0.07	0.16	0.26	0.19	0.20	0.48	0.59	0.68	1.62	1.50	1.45	0.57	0.21
43	((Epi)gallocatechin)$_2$ 3	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
44	Gallocatechin	0.15	0.67	1.64	1.90	0.90	1.74	1.08	1.58	1.43	2.33	2.12	2.04	1.18	1.50
45	Epigallocatechin	0.05	0.27	0.37	0.41	0.40	0.40	0.62	0.76	0.85	1.77	1.62	1.61	0.68	0.26
46	((Epi)gallocatechin-(epi)catechin) 2	0.04	0.31	0.81	2.28	1.55	1.91	0.78	1.96	1.76	2.68	2.37	2.01	1.20	1.72
47	((Epi)catechin-(epi)gallocatechin) 2	<LQ	0.16	<LD	0.55	0.50	0.67	0.62	0.86	1.07	2.00	1.68	1.57	0.81	0.44
48	((Epi)gallocatechin-(epi)catechin) 1	0.14	0.41	1.78	2.88	1.89	2.38	0.92	2.55	2.20	2.83	2.64	2.31	1.43	1.84
49	((Epi)catechin-(epi)gallocatechin) 1	0.06	0.21	0.54	0.52	0.58	0.66	0.60	0.95	1.06	1.93	1.70	1.64	0.71	0.50
50	((Epi)catechin-(epi)gallocatechin) A	<LD	<LD	0.10	0.28	0.28	0.25	0.61	0.50	0.74	1.59	1.44	<LD	<LD	<LD
51	((Epi)catechin)$_2$ 1	0.38	0.64	1.92	2.60	2.21	2.59	1.24	2.64	2.63	3.50	3.23	2.64	2.22	2.48
52	Procyanidin B 1	2.42	3.20	8.06	11.75	8.19	10.60	6.06	17.65	13.23	11.69	11.84	10.07	9.39	10.48
53	Procyanidin B 2	0.95	0.91	2.30	3.17	2.38	3.26	1.85	4.01	3.74	4.74	4.63	3.89	3.96	4.76
54	Catechin	0.56	0.95	1.76	2.03	1.73	2.00	1.74	2.28	2.05	2.92	2.77	2.57	2.13	2.25
55	Epicatechin	0.20	0.33	0.51	0.49	0.63	0.74	0.87	1.26	1.26	2.20	2.03	1.90	1.36	1.60
56	*p*-vinyl(epi)catechin 1	0.22	0.56	0.84	1.93	0.61	1.92	0.70	0.56	0.68	1.57	<LD	1.47	0.57	0.27
57	*p*-vinyl(epi)catechin 2	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	0.57	<LD	<LD	<LD	<LD	<LD
58	*p*-vinyl(epi)catechin 3	<LD	<LD	<LD	<LD	0.14	0.14	0.54	0.56	0.73	1.69	1.59	1.65	0.94	0.46

Tank 12

#	Time (days)	0	1	3	4	5	6	7	8	10	11	12	13	25	26
41	((Epi)gallocatechin)$_2$ 1	0.08	0.11	0.29	0.44	0.46	0.32	0.55	0.72	1.21	1.84	1.66	1.77	0.48	0.48
42	((Epi)gallocatechin)$_2$ 2	<LD	0.06	0.18	0.19	0.24	0.17	0.47	0.52	0.77	1.62	1.47	1.52	<LD	0.21
43	((Epi)gallocatechin)$_2$ 3	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
44	Gallocatechin	0.41	0.53	1.79	1.81	0.91	1.70	0.98	1.36	1.42	2.19	2.10	2.13	0.65	1.41
45	Epigallocatechin	0.18	0.19	0.50	0.39	0.44	0.37	0.56	0.66	0.80	1.68	1.58	1.55	0.47	0.29
46	((Epi)gallocatechin-(epi)catechin) 2	0.19	0.26	0.87	1.95	1.80	0.89	0.91	1.45	2.48	2.75	2.15	2.45	0.57	1.77
47	((Epi)catechin-(epi)gallocatechin) 2	0.11	0.12	0.45	0.47	0.61	0.40	0.62	0.72	1.27	1.94	1.70	1.74	0.48	0.51
48	((Epi)gallocatechin-(epi)catechin) 1	0.42	0.43	1.89	2.65	2.24	2.05	1.00	1.95	2.92	3.13	2.45	2.70	0.59	2.12
49	((Epi)catechin-(epi)gallocatechin) 1	0.16	0.21	0.51	0.64	0.66	0.61	0.62	0.76	1.13	2.00	1.65	1.72	0.54	0.48
50	((Epi)catechin-(epi)gallocatechin) A	<LD	<LD	0.26	0.20	0.31	0.26	0.65	0.44	0.68	1.65	<LD	<LD	<LD	<LD
51	((Epi)catechin)$_2$ 1	0.73	0.68	1.96	2.80	2.42	2.30	1.74	2.63	3.58	3.68	3.04	3.51	1.00	2.88
52	Procyanidin B 1	3.33	2.99	7.38	10.99	9.79	9.03	7.31	15.49	18.65	13.57	9.89	15.42	2.71	14.00
53	Procyanidin B 2	1.36	0.93	2.39	3.44	2.72	2.59	2.10	3.95	4.52	5.37	4.42	5.28	1.33	6.09
54	Catechin	0.84	0.87	2.02	1.98	1.85	2.03	1.78	2.20	2.18	2.91	2.70	2.65	0.95	2.44
55	Epicatechin	0.28	0.33	0.66	0.62	0.66	0.65	0.89	1.19	1.30	2.17	2.04	2.09	0.59	1.63
56	*p*-vinyl(epi)catechin 1	0.50	0.74	1.62	1.85	0.82	1.73	0.73	0.55	0.71	1.66	1.49	1.50	<LD	0.29
57	*p*-vinyl(epi)catechin 2	<LD	<LD	<LD	<LD	<LD	<LD	<LD	0.44	<LD	<LD	<LD	<LD	<LD	<LD
58	*p*-vinyl(epi)catechin 3	<LD	<LD	<LD	<LD	0.22	0.16	0.50	0.51	0.71	1.69	1.58	1.67	0.84	0.55

Tank 13

#	Time (days)	0	1	3	4	5	6	7	8	10	11	12	13	25	26
41	((Epi)gallocatechin)$_2$ 1	0.09	0.14	0.33	0.45	0.43	0.56	0.54	0.70	0.80	1.59	1.62	1.63	0.61	0.32
42	((Epi)gallocatechin)$_2$ 2	<LD	0.09	0.17	0.23	0.18	0.36	0.47	0.50	0.51	1.33	1.39	1.39	0.51	0.17
43	((Epi)gallocatechin)$_2$ 3	<LD	<LD	0.04	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
44	Gallocatechin	0.48	0.83	1.83	1.98	1.53	1.92	1.06	1.47	1.44	2.23	2.24	2.17	1.20	1.65
45	Epigallocatechin	0.24	0.37	0.49	0.37	0.44	0.47	0.68	0.76	0.69	1.55	1.54	1.55	0.60	0.32
46	((Epi)gallocatechin-(epi)catechin) 2	0.10	0.12	0.36	0.47	0.47	0.84	0.62	0.74	0.78	1.64	1.59	1.64	0.64	0.51
47	((Epi)catechin-(epi)gallocatechin) 2	0.17	0.21	0.57	0.69	0.68	0.78	0.59	0.77	0.90	1.75	1.60	1.61	0.77	0.49
48	((Epi)gallocatechin-(epi)catechin) 1	0.20	0.36	0.86	2.03	1.69	2.26	0.78	1.14	1.56	2.22	2.10	2.16	1.02	1.68
49	((Epi)catechin-(epi)gallocatechin) 1	0.39	0.52	2.00	2.73	2.08	2.83	0.90	1.52	2.07	2.79	2.36	2.57	1.17	2.02
50	((Epi)catechin-(epi)gallocatechin) A	<LD	<LD	0.13	0.37	0.42	0.31	0.66	0.46	0.46	1.38	1.42	1.32	<LD	<LD
51	((Epi)catechin)$_2$ 1	0.68	0.79	1.94	2.35	2.04	3.33	1.29	2.20	2.56	3.35	2.60	3.11	1.78	2.34
52	Procyanidin B 1	2.88	4.26	8.19	10.93	8.40	11.69	6.42	12.15	8.39	11.63	10.39	12.56	8.47	11.30
53	Procyanidin B 2	0.92	1.00	2.45	3.10	2.43	4.06	1.66	3.08	3.13	3.90	3.43	4.10	3.03	4.61
54	Catechin	0.59	0.89	1.77	1.89	1.85	2.32	1.72	2.03	2.10	2.72	2.70	2.78	1.83	2.53
55	Epicatechin	0.24	0.34	0.52	0.61	0.67	0.89	0.88	1.12	1.07	1.92	1.97	1.97	1.07	1.54
56	*p*-vinyl(epi)catechin 1	0.47	0.94	1.94	2.48	1.77	0.73	1.19	1.06	0.90	1.65	1.65	1.54	0.71	0.43
57	*p*-vinyl(epi)catechin 2	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
58	*p*-vinyl(epi)catechin 3	<LD	<LD	<LD	<LD	<LD	0.41	0.54	0.50	0.48	1.37	1.49	1.45	0.61	0.26

continued

Table S6. Tannin conc. determined by HPLC-DAD-ESI(+)-MS/MS in red wine samples from Alfaro 2019, expressed in mg of (+)-cat equiv./L.

Tank 14

#	Time (days)	0	1	3	4	5	6	7	8	10	11	12	13	25	26
41	((Epi)gallocatechin)$_2$ 1	0.07	0.17	0.32	0.56	0.39	0.44	0.58	0.98	0.88	1.73	1.85	1.89	0.54	0.48
42	((Epi)gallocatechin)$_2$ 2	<LD	0.09	0.16	0.27	0.20	0.19	0.49	0.60	0.48	1.40	1.47	1.43	0.47	0.19
43	((Epi)gallocatechin)$_2$ 3	<LD	0.03	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
44	Gallocatechin	0.46	0.86	1.76	2.09	1.57	1.86	1.20	1.51	1.33	2.02	2.46	2.16	0.93	1.53
45	Epigallocatechin	0.22	0.43	0.42	0.54	0.36	0.33	0.67	0.82	0.68	1.53	1.64	1.53	0.53	0.27
46	((Epi)gallocatechin-(epi)catechin) 2	0.18	0.43	0.94	2.10	1.65	1.92	0.99	1.83	1.75	2.71	2.76	2.80	0.80	2.05
47	((Epi)catechin-(epi)gallocatechin) 2	0.08	0.21	0.33	0.72	0.68	0.64	0.69	1.02	0.88	1.78	1.85	1.85	0.61	0.60
48	((Epi)gallocatechin-(epi)catechin) 1	0.35	0.69	2.07	2.73	2.32	2.31	1.33	2.35	2.29	3.06	3.03	3.12	0.76	2.52
49	((Epi)catechin-(epi)gallocatechin) 1	0.16	0.31	0.58	0.76	0.65	0.64	0.74	0.97	0.93	1.77	1.79	1.74	0.59	0.51
50	((Epi)catechin-(epi)gallocatechin) A	<LD	<LD	0.15	0.20	0.40	0.35	0.71	0.54	0.45	1.35	1.47	1.40	<LD	<LD
51	((Epi)catechin)$_2$ 1	0.48	0.70	2.08	2.96	2.45	2.63	1.79	3.07	3.22	3.58	3.80	3.65	1.12	3.08
52	Procyanidin B 1	2.90	3.85	9.36	11.92	9.96	10.30	8.25	17.04	16.47	14.53	16.47	17.29	4.59	17.68
53	Procyanidin B 2	0.90	1.70	2.59	3.36	2.99	3.30	2.38	4.06	3.87	4.50	5.14	5.56	1.44	5.88
54	Catechin	0.64	0.99	1.99	2.11	1.86	2.14	2.02	2.39	2.03	2.53	3.14	2.96	1.51	2.32
55	Epicatechin	0.26	0.40	0.61	0.73	0.66	0.84	1.06	1.31	1.13	1.90	2.24	2.04	0.83	1.52
56	*p*-vinyl(epi)catechin 1	0.51	1.62	2.15	2.51	1.94	0.46	1.37	1.07	0.96	1.67	1.77	1.63	0.74	0.51
57	*p*-vinyl(epi)catechin 2	<LD	<LD	<LD	<LD	<LD	0.12	<LD	0.48	<LD	<LD	<LD	<LD	<LD	<LD
58	*p*-vinyl(epi)catechin 3	<LD	<LD	<LD	<LD	<LD	0.23	0.51	0.50	0.52	1.42	1.48	1.39	0.68	0.28

Tank 15

#	Time (days)	0	1	3	4	5	6	7	8	10	11	12	13	25	26
41	((Epi)gallocatechin)$_2$ 1	0.13	0.16	0.43	0.70	0.50	0.35	0.74	0.77	0.76	1.84	1.85	1.75	0.68	0.42
42	((Epi)gallocatechin)$_2$ 2	0.06	0.08	0.22	0.37	0.28	0.21	0.54	0.54	0.48	1.38	1.46	1.38	0.52	0.18
43	((Epi)gallocatechin)$_2$ 3	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
44	Gallocatechin	0.62	0.95	1.84	2.17	1.62	1.86	1.51	1.44	1.50	2.03	2.34	2.14	1.20	0.88
45	Epigallocatechin	0.26	0.39	0.47	0.49	0.37	0.34	0.73	0.71	0.80	1.52	1.56	1.56	0.61	0.20
46	((Epi)gallocatechin-(epi)catechin) 2	0.31	0.38	1.77	2.36	1.94	1.80	1.65	1.50	1.80	2.76	2.68	2.36	1.23	1.94
47	((Epi)catechin-(epi)gallocatechin) 2	0.18	0.23	0.59	0.68	0.72	0.50	0.93	0.81	0.90	1.83	1.83	1.63	0.66	0.35
48	((Epi)gallocatechin-(epi)catechin) 1	0.66	0.74	2.25	2.81	2.43	2.17	1.69	1.81	2.07	3.04	2.89	2.90	1.44	2.49
49	((Epi)catechin-(epi)gallocatechin) 1	0.30	0.38	0.63	0.69	0.84	0.56	0.76	0.72	0.87	1.66	1.74	1.71	0.70	0.42
50	((Epi)catechin-(epi)gallocatechin) A	<LD	<LD	0.20	0.33	0.49	0.25	0.80	0.50	0.54	1.34	1.46	<LD	<LD	<LD
51	((Epi)catechin)$_2$ 1	0.94	0.93	2.30	2.75	2.33	2.35	2.16	2.57	3.02	3.61	3.70	3.35	2.20	2.65
52	Procyanidin B 1	4.00	4.75	9.34	12.47	9.92	9.77	11.29	12.51	14.76	14.19	13.86	14.37	9.79	18.01
53	Procyanidin B 2	1.65	1.82	2.72	3.26	2.72	3.25	3.17	3.43	3.56	4.55	4.59	4.42	3.30	5.66
54	Catechin	0.95	1.83	2.09	2.12	1.90	2.16	2.13	2.08	2.20	2.84	3.03	2.89	1.89	2.18
55	Epicatechin	0.42	0.49	0.67	0.76	0.67	0.77	1.12	1.17	1.28	2.02	2.16	2.09	1.16	0.96
56	*p*-vinyl(epi)catechin 1	0.60	1.63	1.99	2.59	2.09	0.49	1.50	1.11	1.10	1.69	1.81	1.68	0.76	0.40
57	*p*-vinyl(epi)catechin 2	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
58	*p*-vinyl(epi)catechin 3	<LD	<LD	<LD	<LD	<LD	0.21	<LD	0.51	0.55	1.36	1.47	1.46	0.62	0.27

Tank 16

#	Time (days)	0	1	3	4	5	6	7	8	10	11	12	13	25	26
41	((Epi)gallocatechin)$_2$ 1	0.07	0.16	0.35	0.53	0.52	0.24	0.58	0.93	0.73	1.56	1.86	1.64	0.64	0.37
42	((Epi)gallocatechin)$_2$ 2	<LD	0.09	0.16	0.23	0.19	0.15	0.48	0.56	0.52	1.31	1.47	1.40	0.49	0.14
43	((Epi)gallocatechin)$_2$ 3	<LD	<LD	0.07	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
44	Gallocatechin	0.56	0.96	1.83	2.05	1.62	0.99	1.29	1.48	1.34	2.00	2.16	2.10	1.11	0.98
45	Epigallocatechin	0.19	0.40	0.50	0.41	0.42	0.42	0.66	0.76	0.70	1.44	1.55	1.50	0.57	0.22
46	((Epi)gallocatechin-(epi)catechin) 2	0.13	0.36	1.00	2.13	1.98	0.82	0.94	1.61	1.67	2.26	2.53	2.28	1.00	1.76
47	((Epi)catechin-(epi)gallocatechin) 2	0.09	0.18	0.38	0.59	0.74	0.37	0.73	0.86	0.87	1.61	1.81	1.71	0.63	0.50
48	((Epi)gallocatechin-(epi)catechin) 1	0.41	0.70	2.13	2.74	2.31	1.83	1.07	2.12	2.25	2.60	2.79	2.62	1.08	2.03
49	((Epi)catechin-(epi)gallocatechin) 1	0.21	0.26	0.56	0.64	0.75	0.48	0.68	0.79	0.79	1.61	1.72	1.67	0.64	0.54
50	((Epi)catechin-(epi)gallocatechin) A	<LD	<LD	0.11	0.27	0.39	0.24	0.63	0.46	0.49	1.29	<LD	<LD	<LD	<LD
51	((Epi)catechin)$_2$ 1	0.56	0.67	2.04	2.63	2.50	1.97	1.73	2.79	2.93	3.46	3.51	3.31	2.01	2.73
52	Procyanidin B 1	3.00	3.58	8.98	12.78	9.64	8.36	6.98	14.51	15.73	11.63	13.84	14.21	7.94	16.68
53	Procyanidin B 2	1.46	1.55	2.71	3.28	2.98	2.89	2.30	3.51	4.06	4.26	4.82	4.94	3.24	5.47
54	Catechin	0.76	1.61	1.89	2.06	1.88	1.97	1.79	2.16	1.99	2.61	2.75	2.68	1.92	2.34
55	Epicatechin	0.31	0.41	0.66	0.71	0.75	0.62	1.05	1.20	1.24	1.95	2.16	2.08	1.20	1.55
56	*p*-vinyl(epi)catechin 1	0.52	1.66	2.03	2.55	2.03	0.62	1.11	1.15	0.90	1.73	1.69	1.65	0.71	0.43
57	*p*-vinyl(epi)catechin 2	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
58	*p*-vinyl(epi)catechin 3	<LD	<LD	<LD	<LD	<LD	0.24	<LD	0.53	0.50	1.38	1.47	1.43	0.58	0.25

continued

Table S6. Tannin conc. determined by HPLC-DAD-ESI(+)-MS/MS in red wine samples from Alfaro 2019, expressed in mg of (+)-cat equiv./L.

Tank 17

#	Time (days)	0	1	3	4	5	6	7	8	10	11	12	13	25	26
41	((Epi)gallocatechin)$_2$ 1	0.08	0.10	0.38	0.75	0.52	0.43	0.57	0.71	0.73	1.57	1.62	1.60	0.66	0.60
42	((Epi)gallocatechin)$_2$ 2	0.05	0.06	0.21	0.36	0.25	0.22	0.51	0.53	0.49	1.31	1.45	1.39	0.52	0.25
43	((Epi)gallocatechin)$_2$ 3	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
44	Gallocatechin	0.38	0.43	1.00	1.94	0.98	1.76	1.03	1.27	1.18	1.89	2.13	2.12	1.00	1.17
45	Epigallocatechin	0.12	0.23	0.41	0.54	0.46	0.38	0.67	0.76	0.67	1.50	1.56	1.44	0.66	0.31
46	((Epi)gallocatechin-(epi)catechin) 2	0.04	0.06	0.31	0.68	0.60	0.54	0.66	0.75	0.79	1.55	1.61	1.67	0.73	0.49
47	((Epi)catechin-(epi)gallocatechin) 2	0.20	0.15	0.51	0.78	0.73	0.60	0.61	0.74	0.91	1.65	1.63	1.71	0.73	0.61
48	((Epi)gallocatechin-(epi)catechin) 1	0.27	0.28	1.73	2.42	2.02	2.03	1.00	1.42	1.54	2.24	2.24	2.22	1.10	2.13
49	((Epi)catechin-(epi)gallocatechin) 1	0.43	0.38	2.02	2.83	2.49	2.37	1.18	1.70	1.92	2.59	2.40	2.50	1.21	2.62
50	((Epi)catechin-(epi)gallocatechin) A	<LD	<LD	0.12	0.37	0.32	0.28	0.66	0.51	0.54	1.35	1.45	1.32	<LD	<LD
51	((Epi)catechin)$_2$ 1	0.39	0.46	2.24	3.15	2.34	2.71	1.54	2.06	2.70	3.09	2.83	3.04	1.91	3.00
52	Procyanidin B 1	2.75	3.12	9.37	13.84	10.40	10.31	7.26	11.46	12.52	10.41	8.91	12.10	8.77	12.45
53	Procyanidin B 2	0.88	0.59	2.58	3.52	2.71	2.95	2.14	2.91	3.37	4.18	3.96	5.11	3.45	6.28
54	Catechin	0.29	0.47	1.76	2.16	1.77	2.08	1.60	1.76	1.80	2.50	2.74	2.81	1.77	2.74
55	Epicatechin	0.19	0.19	0.45	0.69	0.54	0.63	0.86	0.98	0.97	1.70	1.94	1.96	1.08	1.04
56	*p*-vinyl(epi)catechin 1	0.55	0.21	0.97	1.85	0.67	0.94	0.75	0.62	0.55	1.33	<LD	1.40	0.61	0.33
57	*p*-vinyl(epi)catechin 2	<LD	<LD	<LD	<LD	<LD	<LD	0.60	0.54	<LD	<LD	<LD	<LD	<LD	<LD
58	*p*-vinyl(epi)catechin 3	<LD	<LD	<LD	<LD	0.28	0.12	0.50	0.58	0.59	1.47	1.57	1.54	0.88	0.58

Tank 18

#	Time (days)	0	1	3	4	5	6	7	8	10	11	12	13	25	26
41	((Epi)gallocatechin)$_2$ 1	0.11	0.24	0.27	0.72	0.44	0.31	0.50	0.72	0.80	1.60	1.70	1.65	0.55	0.36
42	((Epi)gallocatechin)$_2$ 2	0.06	0.13	0.14	0.30	0.27	0.18	0.48	0.56	0.56	1.42	1.44	1.42	0.47	0.12
43	((Epi)gallocatechin)$_2$ 3	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
44	Gallocatechin	0.58	0.88	1.68	1.95	1.63	1.75	1.19	1.38	1.26	1.95	2.10	2.09	1.01	0.79
45	Epigallocatechin	0.28	0.45	0.50	0.46	0.47	0.36	0.69	0.81	0.78	1.48	1.55	1.50	0.62	0.28
46	((Epi)gallocatechin-(epi)catechin) 2	0.21	0.52	0.82	2.33	1.97	1.89	0.83	1.45	1.80	2.51	2.30	2.24	0.88	1.55
47	((Epi)catechin-(epi)gallocatechin) 2	0.13	0.20	0.40	0.62	0.55	0.58	0.64	0.87	0.89	1.65	1.58	1.61	0.65	0.33
48	((Epi)gallocatechin-(epi)catechin) 1	0.41	0.96	1.87	2.94	2.60	2.30	1.03	1.69	2.29	2.90	2.62	2.53	0.95	1.69
49	((Epi)catechin-(epi)gallocatechin) 1	0.27	0.40	0.60	0.92	0.90	0.66	0.65	0.90	1.04	1.77	1.68	1.56	0.56	0.42
50	((Epi)catechin-(epi)gallocatechin) A	<LD	<LD	0.18	0.41	0.43	0.23	0.68	0.55	0.51	1.32	<LD	<LD	<LD	<LD
51	((Epi)catechin)$_2$ 1	0.55	1.83	1.00	2.89	2.33	2.61	1.53	1.81	3.03	3.16	2.92	2.93	1.38	2.18
52	Procyanidin B 1	2.87	6.52	7.24	13.89	7.85	9.88	6.64	9.63	15.35	13.04	11.02	11.36	5.17	12.04
53	Procyanidin B 2	0.82	1.92	2.31	3.04	2.66	2.71	1.86	2.50	4.10	4.36	3.87	4.33	2.03	4.65
54	Catechin	0.73	1.59	1.97	2.11	1.72	2.02	1.94	1.99	1.96	2.47	2.46	2.59	1.73	2.04
55	Epicatechin	0.26	0.33	0.47	0.55	0.62	0.65	0.95	0.95	1.06	1.72	1.81	1.87	0.93	0.69
56	*p*-vinyl(epi)catechin 1	0.42	0.70	0.91	1.88	0.69	0.74	0.84	0.56	0.45	1.39	1.44	<LD	0.58	0.19
57	*p*-vinyl(epi)catechin 2	<LD	<LD	<LD	<LD	<LD	<LD	0.63	0.48	<LD	<LD	<LD	<LD	<LD	<LD
58	*p*-vinyl(epi)catechin 3	<LD	<LD	<LD	<LD	0.24	0.13	0.58	0.65	0.57	1.50	1.57	1.57	0.81	0.51

Tank 19

#	Time (days)	0	1	3	4	5	6	7	8	10	11	12	13	25	26
41	((Epi)gallocatechin)$_2$ 1	0.12	0.38	0.34	0.58	0.88	0.44	0.56	0.78	0.92	1.81	1.81	1.86	0.54	0.70
42	((Epi)gallocatechin)$_2$ 2	0.06	0.16	0.21	0.25	0.35	0.26	0.50	0.55	0.59	1.47	1.49	1.43	0.46	0.33
43	((Epi)gallocatechin)$_2$ 3	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
44	Gallocatechin	0.63	0.94	1.78	1.95	1.70	1.93	1.28	1.53	1.56	2.19	2.24	2.13	1.11	<LD
45	Epigallocatechin	0.34	0.45	0.49	0.44	0.49	0.54	0.72	0.72	0.88	1.53	1.54	1.55	0.64	<LD
46	((Epi)gallocatechin-(epi)catechin) 2	0.31	0.91	0.90	2.10	2.46	2.09	0.91	1.44	1.96	2.84	2.42	2.52	0.86	2.23
47	((Epi)catechin-(epi)gallocatechin) 2	0.15	0.30	0.41	0.45	0.73	0.67	0.73	0.98	0.94	1.80	1.78	1.75	0.70	0.67
48	((Epi)gallocatechin-(epi)catechin) 1	0.57	1.72	2.03	2.58	3.10	2.47	1.10	2.03	2.34	3.29	2.68	2.71	0.85	2.60
49	((Epi)catechin-(epi)gallocatechin) 1	0.27	0.52	0.65	0.73	0.97	0.79	0.70	0.89	1.19	1.95	1.78	1.70	0.59	0.62
50	((Epi)catechin-(epi)gallocatechin) A	<LD	<LD	0.16	0.36	0.29	0.39	0.80	0.52	0.60	1.31	1.39	1.36	<LD	<LD
51	((Epi)catechin)$_2$ 1	1.38	2.16	2.46	3.19	3.13	2.82	1.61	2.35	3.20	4.13	3.13	3.66	1.61	3.93
52	Procyanidin B 1	4.45	8.61	10.19	12.65	12.15	9.03	6.34	12.40	17.22	17.23	13.01	14.21	6.98	22.18
53	Procyanidin B 2	1.60	2.36	2.57	3.19	3.08	3.21	1.77	3.24	3.93	5.14	4.24	4.73	2.76	7.77
54	Catechin	0.88	1.63	1.91	1.93	1.95	2.31	2.05	2.38	2.27	2.88	2.72	2.88	1.97	2.83
55	Epicatechin	0.29	0.38	0.48	0.57	0.67	0.68	0.98	1.09	1.03	1.86	1.83	1.88	1.02	1.67
56	*p*-vinyl(epi)catechin 1	0.53	0.79	0.86	1.75	0.66	0.64	0.76	0.55	<LD	1.42	1.44	<LD	0.57	0.18
57	*p*-vinyl(epi)catechin 2	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
58	*p*-vinyl(epi)catechin 3	<LD	<LD	<LD	<LD	0.26	0.29	0.58	0.61	0.57	1.41	1.58	1.54	0.76	0.37

continued

Table S6. Tannin conc. determined by HPLC-DAD-ESI(+)-MS/MS in red wine samples from Alfaro 2019, expressed in mg of (+)-cat equiv./L.

Tank 20

#	Time (days)	0	1	3	4	5	6	7	8	10	11	12	13	25	26
41	((Epi)gallocatechin)$_2$ 1	0.07	0.21	0.35	0.65	0.82	0.50	0.53	0.71	0.90	1.61	1.75	1.65	0.58	0.46
42	((Epi)gallocatechin)$_2$ 2	0.06	0.08	0.20	0.35	0.37	0.20	0.50	0.56	0.55	1.38	1.49	1.43	0.47	0.20
43	((Epi)gallocatechin)$_2$ 3	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
44	Gallocatechin	0.46	0.81	1.67	1.92	1.58	1.75	1.25	1.44	1.31	2.05	2.14	2.03	1.07	0.95
45	Epigallocatechin	0.24	0.46	0.51	0.54	0.51	0.51	0.70	0.74	0.72	1.51	1.64	1.55	0.70	0.44
46	((Epi)gallocatechin-(epi)catechin) 2	0.22	0.54	0.92	2.34	2.39	1.99	1.05	1.32	2.21	2.47	2.47	2.33	1.02	1.81
47	((Epi)catechin-(epi)gallocatechin) 2	0.12	0.21	0.39	0.64	0.65	0.49	0.78	0.72	0.92	1.56	1.73	1.62	0.70	0.42
48	((Epi)gallocatechin-(epi)catechin) 1	0.43	0.91	2.20	2.81	2.79	2.28	1.21	1.76	2.66	2.69	2.90	2.66	1.06	1.97
49	((Epi)catechin-(epi)gallocatechin) 1	0.23	0.44	0.48	0.75	0.90	0.58	0.74	0.94	1.05	1.65	1.79	1.74	0.63	0.55
50	((Epi)catechin-(epi)gallocatechin) A	<LD	<LD	0.15	0.26	0.31	0.33	0.70	0.55	0.51	1.28	1.39	<LD	<LD	<LD
51	((Epi)catechin)$_2$ 1	0.52	1.93	2.50	2.90	2.69	2.67	1.73	2.34	3.24	3.36	3.52	3.34	1.62	2.67
52	Procyanidin B 1	2.75	7.51	10.08	12.08	10.35	10.57	7.40	11.34	19.08	11.04	14.22	14.05	7.16	14.46
53	Procyanidin B 2	0.83	2.17	2.50	3.21	2.97	2.78	2.15	3.09	4.30	4.52	4.59	4.92	2.83	5.08
54	Catechin	0.75	1.62	1.91	2.12	1.96	2.04	2.00	2.19	2.00	2.86	2.71	2.81	2.17	2.29
55	Epicatechin	0.26	0.41	0.44	0.63	0.65	0.56	1.03	1.05	1.03	1.83	1.94	1.88	1.20	0.87
56	*p*-vinyl(epi)catechin 1	0.45	0.74	0.78	1.03	0.60	1.80	0.71	0.62	0.50	1.33	<LD	1.38	<LD	0.25
57	*p*-vinyl(epi)catechin 2	<LD	<LD	<LD	<LD	<LD	<LD	0.61	<LD	<LD	<LD	<LD	<LD	<LD	<LD
58	*p*-vinyl(epi)catechin 3	<LD	<LD	<LD	<LD	0.31	0.20	0.60	0.61	0.61	1.43	1.57	1.59	0.86	0.45

Tank 21

#	Time (days)	0	1	3	4	5	6	7	8	10	11	12	13	25	26
41	((Epi)gallocatechin)$_2$ 1	0.08	0.25	0.29	0.69	0.65	0.41	0.52	0.70	0.74	1.62	1.72	1.89	0.56	0.53
42	((Epi)gallocatechin)$_2$ 2	0.05	0.08	0.18	0.29	0.31	0.19	0.48	0.53	0.47	1.35	1.47	1.53	0.46	0.19
43	((Epi)gallocatechin)$_2$ 3	<LD	<LQ	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
44	Gallocatechin	0.52	0.88	1.74	1.96	0.97	1.82	1.29	1.52	1.21	2.05	2.11	2.42	1.17	0.90
45	Epigallocatechin	0.25	0.51	0.40	0.48	0.57	0.48	0.71	0.81	0.72	1.53	1.55	1.69	0.61	0.30
46	((Epi)gallocatechin-(epi)catechin) 2	0.12	0.16	0.42	0.69	0.70	0.48	0.73	0.78	0.81	1.63	1.74	1.83	0.67	0.41
47	((Epi)catechin-(epi)gallocatechin) 2	0.31	0.43	0.54	0.84	0.94	0.62	0.68	0.84	0.86	1.75	1.78	1.89	0.62	0.44
48	((Epi)gallocatechin-(epi)catechin) 1	0.19	0.73	1.68	2.35	2.20	2.02	0.98	1.31	1.71	2.53	2.45	3.06	0.91	1.88
49	((Epi)catechin-(epi)gallocatechin) 1	0.37	1.60	1.99	2.85	2.73	2.26	1.13	1.75	1.90	3.02	2.61	3.83	0.96	2.05
50	((Epi)catechin-(epi)gallocatechin) A	<LD	<LD	0.16	0.36	0.36	0.40	0.77	0.50	0.49	1.34	1.43	1.43	<LD	0.06
51	((Epi)catechin)$_2$ 1	0.67	1.95	2.18	2.84	2.77	2.51	1.78	2.19	2.39	3.57	2.93	3.89	1.61	2.40
52	Procyanidin B 1	3.24	8.14	9.11	11.38	9.71	9.88	7.24	12.18	12.26	13.51	11.19	22.16	6.88	13.16
53	Procyanidin B 2	0.84	2.11	2.43	2.96	2.79	3.00	1.67	2.76	2.69	3.79	3.48	5.76	2.14	3.56
54	Catechin	0.60	0.98	1.90	1.96	1.82	2.04	1.94	2.10	1.92	2.52	2.58	3.09	1.90	2.03
55	Epicatechin	0.20	0.37	0.47	0.62	0.58	0.65	0.96	1.03	0.87	1.70	1.82	2.02	0.90	0.67
56	*p*-vinyl(epi)catechin 1	0.53	0.99	1.84	2.26	1.71	0.67	1.19	0.94	0.90	1.57	1.61	1.75	0.73	0.37
57	*p*-vinyl(epi)catechin 2	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	1.34	<LD	<LD
58	*p*-vinyl(epi)catechin 3	<LD	<LD	<LD	<LD	<LD	0.26	0.54	0.52	0.49	1.34	1.47	1.39	0.58	0.30

Tank 22

#	Time (days)	0	1	3	4	5	6	7	8	10	11	12	13	25	26
41	((Epi)gallocatechin)$_2$ 1	0.09	0.36	0.39	-	0.53	0.41	0.50	0.71	0.76	1.79	1.80	1.68	0.74	0.25
42	((Epi)gallocatechin)$_2$ 2	0.05	0.15	0.20	-	0.23	0.19	<LD	0.52	0.45	1.39	1.44	1.41	0.50	0.09
43	((Epi)gallocatechin)$_2$ 3	<LD	<LD	<LD	-	<LD	<LD	0.47	<LD	<LD	<LD	<LD	<LD	<LD	<LD
44	Gallocatechin	0.52	0.90	1.72	-	0.95	1.71	1.15	1.45	1.20	1.99	2.03	2.10	1.07	0.72
45	Epigallocatechin	0.24	0.50	0.46	-	0.47	0.38	0.68	0.77	0.68	1.47	1.48	1.52	0.65	0.24
46	((Epi)gallocatechin-(epi)catechin) 2	0.22	0.91	1.77	-	1.98	1.87	0.80	1.32	1.62	2.69	2.38	2.48	1.34	0.79
47	((Epi)catechin-(epi)gallocatechin) 2	0.13	0.23	0.37	-	0.56	0.46	0.67	0.78	0.74	1.73	1.73	1.62	0.73	0.33
48	((Epi)gallocatechin-(epi)catechin) 1	0.44	1.62	2.09	-	2.61	2.20	0.97	1.68	2.23	2.99	2.76	2.84	1.47	1.63
49	((Epi)catechin-(epi)gallocatechin) 1	0.25	0.47	0.51	-	0.73	0.62	0.72	0.87	0.88	1.68	1.69	1.66	0.74	0.46
50	((Epi)catechin-(epi)gallocatechin) A	<LD	<LD	0.20	-	0.29	0.39	0.67	0.50	0.52	1.37	1.44	1.36	<LD	<LD
51	((Epi)catechin)$_2$ 1	0.59	2.04	2.21	-	2.76	2.35	1.61	2.09	2.77	3.33	3.17	3.39	1.83	2.29
52	Procyanidin B 1	2.78	8.62	9.98	-	8.34	9.66	6.05	9.72	14.26	12.93	12.50	13.61	9.87	11.66
53	Procyanidin B 2	0.79	2.23	2.40	-	2.52	2.65	1.77	2.51	3.16	3.76	3.64	4.26	2.80	3.53
54	Catechin	0.65	1.61	1.89	-	1.81	1.96	2.02	2.10	1.77	2.52	2.58	2.66	1.77	2.06
55	Epicatechin	0.29	0.38	0.46	-	0.57	0.53	0.95	1.06	0.93	1.69	1.80	1.81	0.95	0.70
56	*p*-vinyl(epi)catechin 1	0.53	0.91	1.74	-	1.55	0.40	1.07	0.83	0.79	1.57	1.58	1.51	0.66	0.36
57	*p*-vinyl(epi)catechin 2	<LD	<LD	<LD	-	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
58	*p*-vinyl(epi)catechin 3	<LD	<LD	<LD	-	0.14	0.33	<LD	0.52	0.49	1.33	1.43	1.43	0.59	0.24

continued

Table S6. Tannin conc. determined by HPLC-DAD-ESI(+)-MS/MS in red wine samples from Alfaro 2019, expressed in mg of (+)-cat equiv./L.

Tank 23

#	Time (days)	0	1	3	4	5	6	7	8	10	11	12	13	25	26
41	((Epi)gallocatechin)$_2$ 1	<LD	0.28	0.27	-	0.56	0.35	0.54	0.70	0.80	1.64	1.88	1.70	0.78	0.32
42	((Epi)gallocatechin)$_2$ 2	<LD	0.15	0.17	-	0.25	0.16	0.49	0.55	0.49	1.39	1.48	1.40	0.51	0.11
43	((Epi)gallocatechin)$_2$ 3	<LD	<LD	<LD	-	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
44	Gallocatechin	0.30	0.83	1.00	-	0.92	0.94	1.23	1.43	<LD	1.99	2.24	1.94	1.01	0.88
45	Epigallocatechin	0.06	0.52	0.42	-	0.43	0.32	0.72	0.73	<LD	1.44	1.59	1.45	0.56	0.29
46	((Epi)gallocatechin-(epi)catechin) 2	0.09	0.76	1.68	-	1.99	1.72	1.03	1.39	1.78	2.50	2.69	2.35	1.33	1.60
47	((Epi)catechin-(epi)gallocatechin) 2	0.05	0.29	0.37	-	0.64	0.37	0.74	0.82	0.89	1.74	1.73	1.63	0.74	0.39
48	((Epi)gallocatechin-(epi)catechin) 1	0.27	1.65	2.20	-	2.20	2.00	1.13	1.56	2.07	2.82	3.11	2.57	1.48	1.92
49	((Epi)catechin-(epi)gallocatechin) 1	0.09	0.44	0.55	-	0.85	0.38	0.72	0.77	0.84	1.70	1.74	1.63	0.69	0.39
50	((Epi)catechin-(epi)gallocatechin) A	<LD	<LD	0.16	-	0.32	0.25	0.67	0.51	0.54	1.34	1.50	<LD	<LD	<LD
51	((Epi)catechin)$_2$ 1	0.50	2.01	2.63	-	2.37	2.14	1.99	2.21	2.94	3.49	3.05	3.16	1.69	2.37
52	Procyanidin B 1	3.08	7.67	10.14	-	9.53	8.75	7.53	9.56	13.20	13.18	13.52	12.74	10.04	12.85
53	Procyanidin B 2	1.00	2.24	2.66	-	2.53	2.57	2.07	2.75	3.14	3.75	3.83	3.71	2.62	3.88
54	Catechin	0.91	1.67	2.03	-	1.82	1.92	1.98	2.11	2.18	2.46	2.61	2.54	1.40	1.99
55	Epicatechin	0.28	0.46	0.51	-	0.55	0.50	0.97	1.08	1.04	1.64	1.97	1.81	0.87	0.67
56	*p*-vinyl(epi)catechin 1	0.44	0.87	1.75	-	1.53	0.39	1.07	1.05	0.80	1.53	1.61	1.57	0.75	0.47
57	*p*-vinyl(epi)catechin 2	<LD	<LD	<LD	-	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
58	*p*-vinyl(epi)catechin 3	<LD	<LD	<LD	-	0.15	0.30	0.54	0.51	0.50	1.35	1.45	1.45	0.61	0.22

Tank 24

#	Time (days)	0	1	3	4	5	6	7	8	10	11	12	13	25	26
41	((Epi)gallocatechin)$_2$ 1	0.10	0.19	0.38	-	0.51	0.40	0.55	0.74	0.91	1.57	1.78	1.76	0.66	0.28
42	((Epi)gallocatechin)$_2$ 2	0.09	0.08	0.20	-	0.21	0.19	0.50	0.54	0.53	1.33	1.48	1.44	0.50	0.08
43	((Epi)gallocatechin)$_2$ 3	<LD	<LD	0.05	-	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
44	Gallocatechin	0.64	0.71	1.67	-	1.56	0.95	1.18	1.44	1.28	2.06	2.05	2.10	0.90	0.78
45	Epigallocatechin	0.35	0.42	0.46	-	0.42	0.36	0.74	0.79	0.78	1.47	1.55	1.48	0.58	0.27
46	((Epi)gallocatechin-(epi)catechin) 2	0.30	0.43	1.69	-	1.94	1.88	1.02	1.36	2.00	2.43	2.47	2.42	1.09	0.79
47	((Epi)catechin-(epi)gallocatechin) 2	0.17	0.16	0.40	-	0.59	0.47	0.68	0.74	0.85	1.62	1.66	1.66	0.66	0.30
48	((Epi)gallocatechin-(epi)catechin) 1	0.61	0.85	2.06	-	2.28	2.28	1.15	1.73	2.25	2.69	2.86	2.88	1.32	1.63
49	((Epi)catechin-(epi)gallocatechin) 1	0.36	0.32	0.55	-	0.69	0.54	0.68	0.78	0.92	1.74	1.74	1.61	0.62	0.36
50	((Epi)catechin-(epi)gallocatechin) A	<LD	<LD	0.12	-	0.33	0.22	0.69	0.55	0.48	1.44	<LD	<LD	<LD	<LD
51	((Epi)catechin)$_2$ 1	0.98	1.72	2.22	-	2.37	2.55	1.78	2.08	3.16	3.22	3.19	3.49	1.71	2.55
52	Procyanidin B 1	4.36	6.68	9.48	-	9.77	10.01	7.13	9.68	14.77	11.02	13.08	14.01	8.08	12.05
53	Procyanidin B 2	1.64	2.02	2.47	-	2.55	2.78	1.97	2.36	3.14	3.71	3.69	4.00	2.24	3.80
54	Catechin	0.93	1.60	1.97	-	1.87	1.81	1.85	1.99	1.96	2.55	2.50	2.59	1.42	1.98
55	Epicatechin	0.33	0.37	0.52	-	0.64	0.51	0.89	0.93	1.04	1.69	1.79	1.80	0.82	0.68
56	*p*-vinyl(epi)catechin 1	0.58	0.81	1.71	-	0.99	0.92	1.06	0.82	0.78	1.50	1.60	1.51	0.60	0.32
57	*p*-vinyl(epi)catechin 2	<LD	<LD	<LD	-	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
58	*p*-vinyl(epi)catechin 3	<LD	<LD	<LD	-	0.13	0.22	0.55	0.52	0.47	1.32	1.46	1.42	0.58	0.21

Table S7. Tannin conc. determined by HPLC-DAD-ESI(+)-MS/MS in red wine samples from Alfaro 2019, expressed in mg of (+)-cat equiv./L.

Tank 02

#	Time (days)	0	3	4	5	6	7	8	10	11	12	13	25
59	Gallocatechin-ethyl-catechin	<LD	<LD	0.10	0.14	0.05	<LD	-	<LD	1.55	-	<LD	<LD
60	Catechin-ethyl-gallocatechin	1.98	0.78	1.27	0.61	1.69	0.97	-	0.69	1.97	-	1.15	0.92
61	(Epi)gallocatechin-ethyl-(epi)gallocatechin	<LD	0.29	0.36	0.20	0.18	0.58	-	<LD	1.60	-	<LD	<LD
62	Gallocatechin-ethyl-gallocatechin	0.35	0.87	1.27	0.65	0.88	1.07	-	0.77	2.09	-	0.98	0.57
63	Gallocatechin-ethyl-catechin	<LD	<LD	0.28	0.12	0.22	0.63	-	0.18	1.73	-	0.47	<LD
64	Catechin-ethyl-gallocatechin	<LD	<LD	0.23	0.14	0.20	0.56	-	0.12	1.68	-	0.44	<LD
65	(Epi)catechin-glycoside	<LD	0.10	0.26	0.17	0.14	0.48	-	0.07	1.62	-	0.35	<LD
66	((Epi)catechin)$_3$ 1	<LD	0.15	<LD	0.23	0.66	-	0.55	1.19	-	0.55	0.48	0.10
67	((Epi)catechin)$_3$ 2	<LD	0.24	<LD	0.49	0.71	-	0.65	1.16	-	0.49	0.48	0.19
68	Procyanidin C 1	<LD	0.07	<LD	0.09	0.57	-	0.44	1.01	-	0.31	0.36	0.09

Tank 03

#	Time (days)	0	3	4	5	6	7	8	10	11	12	13	25
59	Gallocatechin-ethyl-catechin	<LD	1.32	0.46	0.12	0.12	<LD	-	<LD	1.55	-	<LD	<LD
60	Catechin-ethyl-gallocatechin	2.02	0.48	1.34	0.54	0.86	0.97	-	0.77	1.96	-	1.17	0.76
61	(Epi)gallocatechin-ethyl-(epi)gallocatechin	<LD	0.20	0.32	0.18	0.19	<LD	-	0.09	1.64	-	<LD	<LD
62	Gallocatechin-ethyl-gallocatechin	0.36	0.80	1.17	0.75	0.88	0.96	-	0.77	2.02	-	0.96	0.80
63	Gallocatechin-ethyl-catechin	<LD	<LD	0.22	<LD	0.26	0.52	-	0.17	1.71	-	0.46	<LD
64	Catechin-ethyl-gallocatechin	<LD	<LD	0.20	<LD	0.19	<LD	-	0.12	1.67	-	0.38	<LD
65	(Epi)catechin-glycoside	<LD	0.20	0.30	0.05	0.23	0.45	-	0.15	1.60	-	0.38	<LD
66	((Epi)catechin)$_3$ 1	<LD	0.25	<LD	0.31	0.65	-	0.56	1.17	-	0.49	0.51	0.12
67	((Epi)catechin)$_3$ 2	0.17	0.34	<LD	0.27	0.78	-	0.74	1.25	-	0.61	0.53	0.32
68	Procyanidin C 1	<LD	0.07	<LD	0.10	0.60	-	0.49	1.03	-	0.34	0.41	0.07

Tank 04

#	Time (days)	0	3	4	5	6	7	8	10	11	12	13	25
59	Gallocatechin-ethyl-catechin	<LD	<LD	0.14	0.20	0.07	<LD	-	<LD	1.54	-	<LD	<LD
60	Catechin-ethyl-gallocatechin	0.15	0.73	1.22	0.48	0.85	0.99	-	0.55	1.97	-	1.14	0.86
61	(Epi)gallocatechin-ethyl-(epi)gallocatechin	<LD	0.28	0.33	<LD	0.19	0.49	-	0.15	1.61	-	<LD	<LD
62	Gallocatechin-ethyl-gallocatechin	0.36	0.81	1.24	0.84	0.93	1.04	-	0.88	2.08	-	0.97	0.90
63	Gallocatechin-ethyl-catechin	<LD	0.14	0.33	<LD	0.15	0.55	-	0.14	1.72	-	0.45	<LD
64	Catechin-ethyl-gallocatechin	<LD	0.07	0.20	<LD	0.20	0.48	-	0.14	1.69	-	0.45	<LD
65	(Epi)catechin-glycoside	<LD	0.14	0.36	<LD	0.12	0.52	-	0.04	1.61	-	0.36	<LD
66	((Epi)catechin)$_3$ 1	<LD	0.22	<LD	0.26	0.66	-	0.82	1.15	-	0.50	0.57	0.15
67	((Epi)catechin)$_3$ 2	0.10	0.37	<LD	0.35	0.74	-	0.86	1.21	-	0.50	0.48	0.26
68	Procyanidin C 1	<LD	0.09	<LD	<LD	0.60	-	0.56	1.06	-	<LD	0.34	0.06

Tank 05

#	Time (days)	0	3	4	5	6	7	8	10	11	12	13	25
59	Gallocatechin-ethyl-catechin	<LD	0.53	0.39	0.21	0.11	<LD	-	<LD	<LD	-	<LD	<LD
60	Catechin-ethyl-gallocatechin	1.82	0.61	1.25	0.47	0.76	1.04	-	1.11	2.03	-	1.63	2.22
61	(Epi)gallocatechin-ethyl-(epi)gallocatechin	<LD	0.08	0.17	0.10	0.08	<LD	-	0.06	<LD	-	<LD	<LD
62	Gallocatechin-ethyl-gallocatechin	0.38	0.80	1.29	0.90	0.86	1.02	-	0.78	2.10	-	0.97	0.66
63	Gallocatechin-ethyl-catechin	<LD	0.11	0.17	0.09	0.20	0.56	-	0.11	1.62	-	0.41	<LD
64	Catechin-ethyl-gallocatechin	<LD	0.17	0.14	0.06	0.14	0.53	-	0.13	1.62	-	0.43	<LD
65	(Epi)catechin-glycoside	<LD	0.15	0.30	0.19	0.22	0.55	-	0.09	1.57	-	0.33	0.33
66	((Epi)catechin)$_3$ 1	<LD	0.21	<LD	0.39	0.61	-	0.52	1.20	-	0.42	0.46	0.30
67	((Epi)catechin)$_3$ 2	0.08	0.35	<LD	0.39	0.71	-	0.60	1.15	-	0.49	0.43	0.21
68	Procyanidin C 1	<LD	0.07	<LD	0.11	0.59	-	0.49	1.01	-	0.31	0.36	0.09

Tank 06

#	Time (days)	0	3	4	5	6	7	8	10	11	12	13	25
59	Gallocatechin-ethyl-catechin	<LD	1.93	0.47	0.59	0.43	<LD	-	<LD	<LD	-	<LD	<LD
60	Catechin-ethyl-gallocatechin	2.00	0.61	1.26	0.63	0.75	0.98	-	0.58	2.09	-	1.08	1.77
61	(Epi)gallocatechin-ethyl-(epi)gallocatechin	<LD	<LD	1.27	0.12	0.10	<LD	-	<LD	<LD	-	<LD	<LD
62	Gallocatechin-ethyl-gallocatechin	0.37	0.83	<LD	0.76	1.65	1.02	-	0.77	2.02	-	1.00	0.68
63	Gallocatechin-ethyl-catechin	<LD	0.19	0.33	0.08	0.19	0.50	-	0.20	1.70	-	0.48	<LD
64	Catechin-ethyl-gallocatechin	<LD	0.11	0.23	0.10	0.13	0.50	-	0.16	1.69	-	0.46	<LD
65	(Epi)catechin-glycoside	<LD	0.16	0.29	0.22	0.23	0.51	-	0.16	1.61	-	0.42	<LD
66	((Epi)catechin)$_3$ 1	<LD	0.24	<LD	0.30	0.62	-	0.54	1.31	-	0.52	0.61	0.06
67	((Epi)catechin)$_3$ 2	0.08	0.30	<LD	0.40	0.78	-	0.59	1.33	-	0.47	0.56	0.11
68	Procyanidin C 1	<LD	0.07	<LD	0.13	0.61	-	0.43	1.10	-	0.32	0.42	<LD

continued

Table S7. Tannin conc. determined by HPLC-DAD-ESI(+)-MS/MS in red wine samples from Alfaro 2019, expressed in mg of (+)-cat equiv./L.

Tank 07

#	Time (days)	0	3	4	5	6	7	8	10	11	12	13	25
59	Gallocatechin-ethyl-catechin	<LD	<LD	1.56	0.17	0.10	<LD	–	<LD	<LD	–	<LD	<LD
60	Catechin-ethyl-gallocatechin	1.48	0.96	1.27	0.83	0.83	1.05	–	0.76	2.33	–	2.03	1.53
61	(Epi)gallocatechin-ethyl-(epi)gallocatechin	<LD	<LD	<LD	0.10	0.16	0.49	–	<LD	<LD	–	<LD	<LD
62	Gallocatechin-ethyl-gallocatechin	0.20	0.70	0.90	0.65	0.85	0.93	–	0.67	1.99	–	0.90	0.83
63	Gallocatechin-ethyl-catechin	<LD	0.15	0.25	<LD	0.24	0.54	–	0.16	1.61	–	0.44	<LD
64	Catechin-ethyl-gallocatechin	<LD	0.13	0.27	0.12	0.25	0.49	–	0.13	1.63	–	0.39	<LD
65	(Epi)catechin-glycoside	<LD	<LD	0.46	0.11	0.21	0.46	–	0.08	1.58	–	0.40	0.33
66	((Epi)catechin)$_3$ 1	<LD	0.18	<LD	0.24	0.75	–	0.54	1.18	–	0.53	0.54	0.17
67	((Epi)catechin)$_3$ 2	0.18	0.30	<LD	0.47	0.82	–	0.70	1.22	–	0.56	0.46	0.23
68	Procyanidin C 1	<LD	0.10	<LD	0.11	0.57	–	0.52	1.02	–	0.36	<LD	0.10

Tank 08

#	Time (days)	0	3	4	5	6	7	8	10	11	12	13	25
59	Gallocatechin-ethyl-catechin	<LD	0.09	1.57	0.69	0.11	<LD	–	<LD	<LD	–	<LD	<LD
60	Catechin-ethyl-gallocatechin	2.18	0.66	0.96	0.55	0.84	1.10	–	0.82	2.13	–	1.31	1.23
61	(Epi)gallocatechin-ethyl-(epi)gallocatechin	<LD	0.13	<LD	0.09	0.07	<LD	–	<LD	<LD	–	<LD	<LD
62	Gallocatechin-ethyl-gallocatechin	0.34	0.82	1.21	0.79	0.88	0.99	–	0.80	2.06	–	0.97	0.86
63	Gallocatechin-ethyl-catechin	<LD	<LD	0.23	0.12	0.17	0.58	–	0.19	1.71	–	0.47	<LD
64	Catechin-ethyl-gallocatechin	<LD	0.14	0.15	0.12	0.17	0.52	–	0.12	1.67	–	0.46	<LD
65	(Epi)catechin-glycoside	<LD	0.14	0.30	0.10	0.18	0.51	–	0.15	1.59	–	0.41	0.37
66	((Epi)catechin)$_3$ 1	0.11	0.15	<LD	0.41	0.63	–	0.50	1.32	–	0.51	0.56	0.25
67	((Epi)catechin)$_3$ 2	0.18	0.31	<LD	0.54	0.75	–	0.64	1.41	–	0.43	0.52	0.28
68	Procyanidin C 1	0.06	0.08	<LD	0.14	0.61	–	0.47	1.11	–	<LD	0.35	0.10

Tank 09

#	Time (days)	0	3	4	5	6	7	8	10	11	12	13	25
59	Gallocatechin-ethyl-catechin	<LD	0.11	0.21	0.07	0.09	<LD	–	<LD	<LD	–	<LD	<LD
60	Catechin-ethyl-gallocatechin	1.95	0.52	0.80	0.51	0.68	1.13	–	0.65	2.05	–	1.22	1.02
61	(Epi)gallocatechin-ethyl-(epi)gallocatechin	<LD	<LD	0.20	0.16	0.11	<LD	–	<LD	1.61	–	<LD	<LD
62	Gallocatechin-ethyl-gallocatechin	0.41	0.79	1.20	0.72	1.66	0.96	–	0.79	2.03	–	0.83	0.60
63	Gallocatechin-ethyl-catechin	<LD	0.12	0.26	0.13	0.24	0.50	–	0.25	1.71	–	0.43	0.38
64	Catechin-ethyl-gallocatechin	<LD	0.18	0.24	0.10	0.21	0.52	–	0.20	1.71	–	0.44	0.36
65	(Epi)catechin-glycoside	<LD	0.19	0.19	0.12	0.11	0.49	–	0.10	1.62	–	0.38	0.34
66	((Epi)catechin)$_3$ 1	<LD	0.16	<LD	0.21	0.63	–	0.59	1.27	–	0.54	0.51	0.19
67	((Epi)catechin)$_3$ 2	0.11	0.36	<LD	0.35	0.68	–	0.65	1.20	–	0.48	0.40	0.24
68	Procyanidin C 1	<LD	0.07	<LD	0.11	0.59	–	0.44	1.04	–	0.34	0.34	0.09

Tank 10

#	Time (days)	0	3	4	5	6	7	8	10	11	12	13	25
59	Gallocatechin-ethyl-catechin	<LD	0.22	0.72	0.11	<LD	<LD	–	<LD	<LD	–	<LD	<LD
60	Catechin-ethyl-gallocatechin	1.70	0.76	0.99	0.43	0.82	0.80	–	0.51	1.90	–	1.11	1.20
61	(Epi)gallocatechin-ethyl-(epi)gallocatechin	<LD	<LD	0.28	0.12	0.17	<LD	–	<LD	<LD	–	<LD	<LD
62	Gallocatechin-ethyl-gallocatechin	0.38	0.94	1.20	0.83	0.86	1.04	–	0.75	2.08	–	0.99	0.69
63	Gallocatechin-ethyl-catechin	<LD	0.10	0.34	0.13	0.31	0.55	–	0.32	1.71	–	0.53	<LD
64	Catechin-ethyl-gallocatechin	<LD	0.09	0.20	0.08	0.20	0.57	–	0.35	1.72	–	0.47	<LD
65	(Epi)catechin-glycoside	<LD	0.25	0.47	0.18	0.11	0.51	–	0.14	1.58	–	0.38	0.32
66	((Epi)catechin)$_3$ 1	<LD	0.14	<LD	0.42	0.65	–	0.77	1.33	–	0.74	0.53	0.10
67	((Epi)catechin)$_3$ 2	0.11	0.40	<LD	0.38	0.83	–	0.80	1.36	–	0.60	0.47	0.12
68	Procyanidin C 1	<LD	<LD	<LD	0.16	0.61	–	0.52	1.12	–	0.39	0.35	<LQ

Tank 11

#	Time (days)	0	3	4	5	6	7	8	10	11	12	13	25
59	Gallocatechin-ethyl-catechin	<LD	0.11	0.21	0.06	0.14	<LD	–	<LD	<LD	–	<LD	<LD
60	Catechin-ethyl-gallocatechin	0.76	0.73	0.96	0.40	0.73	0.88	–	0.52	1.89	–	1.19	1.14
61	(Epi)gallocatechin-ethyl-(epi)gallocatechin	<LD	0.10	<LD	0.12	<LD	<LD	–	<LD	<LD	–	<LD	<LD
62	Gallocatechin-ethyl-gallocatechin	0.35	0.74	1.15	0.71	0.74	0.99	–	0.77	2.05	–	0.86	0.94
63	Gallocatechin-ethyl-catechin	<LD	0.12	0.19	<LD	0.32	0.56	–	0.34	1.82	–	0.44	0.34
64	Catechin-ethyl-gallocatechin	<LD	0.12	0.18	<LD	0.26	0.53	–	0.21	1.74	–	0.47	0.40
65	(Epi)catechin-glycoside	<LD	0.21	0.38	0.10	0.30	0.51	–	0.09	1.63	–	0.37	0.37
66	((Epi)catechin)$_3$ 1	<LD	0.15	<LD	0.25	0.71	–	0.89	1.22	–	0.67	0.50	0.33
67	((Epi)catechin)$_3$ 2	0.10	0.37	<LD	0.43	0.86	–	0.79	1.32	–	0.70	0.47	0.47
68	Procyanidin C 1	<LD	0.12	<LD	0.10	0.58	–	0.52	1.12	–	0.38	0.37	0.15

continued

Table S7. Tannin conc. determined by HPLC-DAD-ESI(+)-MS/MS in red wine samples from Alfaro 2019, expressed in mg of (+)-cat equiv./L.

Tank 12

#	Time (days)	0	3	4	5	6	7	8	10	11	12	13	25
59	Gallocatechin-ethyl-catechin	<LD	0.10	0.20	0.06	0.11	<LD	–	<LD	<LD	–	<LD	<LD
60	Catechin-ethyl-gallocatechin	1.89	0.51	1.28	0.38	0.66	0.94	–	0.47	1.87	–	1.35	1.55
61	(Epi)gallocatechin-ethyl-(epi)gallocatechin	<LD	0.13	0.11	0.13	<LD	<LD	–	<LD	<LD	–	<LD	<LD
62	Gallocatechin-ethyl-gallocatechin	0.36	0.68	1.17	0.74	0.96	0.97	–	0.75	2.00	–	0.80	0.60
63	Gallocatechin-ethyl-catechin	<LD	0.11	0.33	0.19	0.16	0.53	–	0.19	1.77	–	0.48	<LD
64	Catechin-ethyl-gallocatechin	<LD	0.11	0.28	0.12	0.22	0.54	–	0.29	1.72	–	0.51	<LD
65	(Epi)catechin-glycoside	<LD	0.16	0.41	0.29	0.21	0.47	–	0.11	1.65	–	0.39	<LD
66	((Epi)catechin)$_3$ 1	0.06	0.23	<LD	0.40	0.67	–	0.68	1.48	–	0.69	0.64	0.09
67	((Epi)catechin)$_3$ 2	0.13	0.37	<LD	0.42	0.80	–	0.80	1.47	–	0.64	0.68	0.14
68	Procyanidin C 1	0.07	0.12	<LD	0.17	0.61	–	0.52	1.07	–	0.37	0.44	0.04

Tank 13

#	Time (days)	0	3	4	5	6	7	8	10	11	12	13	25
59	Gallocatechin-ethyl-catechin	<LD	0.99	2.69	0.15	0.07	<LD	–	<LD	<LD	–	<LD	<LD
60	Catechin-ethyl-gallocatechin	1.97	0.57	0.89	0.45	0.74	1.03	–	0.77	0.91	–	1.31	1.74
61	(Epi)gallocatechin-ethyl-(epi)gallocatechin	<LD	<LD	<LD	0.14	0.11	<LD	–	<LD	<LD	–	<LD	<LD
62	Gallocatechin-ethyl-gallocatechin	0.39	0.94	1.32	0.83	0.91	1.12	–	1.12	1.13	–	0.94	0.75
63	Gallocatechin-ethyl-catechin	<LD	<LD	0.24	0.15	0.34	0.55	–	0.26	0.37	–	0.37	0.40
64	Catechin-ethyl-gallocatechin	<LD	0.16	0.26	0.13	0.30	0.54	–	0.29	0.42	–	0.35	0.40
65	(Epi)catechin-glycoside	<LD	0.15	0.28	0.12	0.32	0.48	–	0.13	0.25	–	0.25	0.43
66	((Epi)catechin)$_3$ 1	0.07	0.25	<LD	0.22	0.78	–	0.76	1.33	–	0.64	0.54	0.28
67	((Epi)catechin)$_3$ 2	0.10	0.30	<LD	0.40	0.89	–	0.89	1.24	–	0.59	0.60	0.31
68	Procyanidin C 1	0.05	0.08	<LD	0.12	0.52	–	0.63	1.09	–	0.42	0.37	0.07

Tank 14

#	Time (days)	0	3	4	5	6	7	8	10	11	12	13	25
59	Gallocatechin-ethyl-catechin	<LD	0.35	0.86	0.14	0.09	<LD	–	<LD	<LD	–	<LD	<LD
60	Catechin-ethyl-gallocatechin	2.30	0.57	1.28	0.41	0.55	0.93	–	1.06	1.28	–	1.17	1.03
61	(Epi)gallocatechin-ethyl-(epi)gallocatechin	<LD	<LD	<LD	<LD	0.18	<LD	–	<LD	<LD	–	<LD	<LD
62	Gallocatechin-ethyl-gallocatechin	0.25	0.80	1.29	0.75	0.97	1.16	–	1.05	0.97	–	0.82	0.91
63	Gallocatechin-ethyl-catechin	<LD	0.14	0.27	0.12	0.28	0.61	–	0.38	0.47	–	0.39	<LD
64	Catechin-ethyl-gallocatechin	<LD	0.14	0.23	0.19	0.22	0.55	–	0.35	0.45	–	0.45	0.36
65	(Epi)catechin-glycoside	<LD	0.23	0.33	0.16	0.20	0.54	–	0.20	0.31	–	0.32	0.35
66	((Epi)catechin)$_3$ 1	0.05	0.25	<LD	0.29	0.65	–	0.97	1.41	–	1.04	0.90	0.19
67	((Epi)catechin)$_3$ 2	0.13	0.48	<LD	0.43	0.77	–	1.02	1.38	–	0.97	0.80	0.13
68	Procyanidin C 1	0.04	0.15	<LD	0.06	0.51	–	0.70	1.12	–	0.41	0.50	<LD

Tank 15

#	Time (days)	0	3	4	5	6	7	8	10	11	12	13	25
59	Gallocatechin-ethyl-catechin	<LD	0.23	0.37	0.33	0.10	0.47	–	<LD	<LD	–	<LD	<LD
60	Catechin-ethyl-gallocatechin	2.00	0.74	0.95	0.50	0.56	0.82	–	0.79	0.98	–	0.32	1.15
61	(Epi)gallocatechin-ethyl-(epi)gallocatechin	<LD	<LD	<LD	0.12	<LD	<LD	–	<LD	<LD	–	<LD	<LD
62	Gallocatechin-ethyl-gallocatechin	0.43	0.74	1.34	0.80	0.89	1.19	–	1.06	0.99	–	0.83	0.86
63	Gallocatechin-ethyl-catechin	<LD	0.20	0.35	0.12	0.25	0.67	–	0.47	0.43	–	0.41	0.43
64	Catechin-ethyl-gallocatechin	<LD	0.15	0.39	0.06	0.24	0.63	–	0.24	0.37	–	0.38	0.41
65	(Epi)catechin-glycoside	<LD	0.23	0.34	0.20	0.19	0.60	–	0.17	0.32	–	0.29	0.46
66	((Epi)catechin)$_3$ 1	0.08	0.24	<LD	0.23	0.61	–	0.84	1.42	–	1.04	0.71	0.48
67	((Epi)catechin)$_3$ 2	0.24	0.49	<LD	0.45	0.66	–	0.99	1.33	–	0.78	0.54	0.34
68	Procyanidin C 1	0.10	0.13	<LD	0.15	0.50	–	0.71	1.15	–	0.41	0.37	0.07

Tank 16

#	Time (days)	0	3	4	5	6	7	8	10	11	12	13	25
59	Gallocatechin-ethyl-catechin	<LD	0.47	0.57	0.17	0.10	0.48	–	<LD	<LD	–	<LD	<LD
60	Catechin-ethyl-gallocatechin	1.95	0.63	0.93	0.47	0.59	0.79	–	0.81	1.18	–	0.95	1.12
61	(Epi)gallocatechin-ethyl-(epi)gallocatechin	<LD	0.08	<LD	<LD	0.13	<LD	–	<LD	<LD	–	<LD	<LD
62	Gallocatechin-ethyl-gallocatechin	0.39	0.75	1.30	0.75	1.79	0.95	–	1.10	0.97	–	0.79	0.85
63	Gallocatechin-ethyl-catechin	<LD	<LD	0.33	0.11	0.17	0.55	–	0.22	0.45	–	0.38	0.44
64	Catechin-ethyl-gallocatechin	<LD	0.11	0.34	0.14	0.18	0.54	–	0.23	0.44	–	0.33	0.41
65	(Epi)catechin-glycoside	<LD	0.09	0.37	0.22	0.16	0.48	–	0.15	0.23	–	0.35	0.37
66	((Epi)catechin)$_3$ 1	0.07	0.26	<LD	0.28	0.59	–	0.97	1.46	–	1.01	0.60	0.33
67	((Epi)catechin)$_3$ 2	0.10	0.37	<LD	0.44	0.64	–	0.96	1.33	–	0.74	0.58	0.26
68	Procyanidin C 1	0.05	0.07	<LD	0.15	0.48	–	0.67	1.12	–	0.54	0.36	0.08

continued

Table S7. Tannin conc. determined by HPLC-DAD-ESI(+)-MS/MS in red wine samples from Alfaro 2019, expressed in mg of (+)-cat equiv./L.

Tank 17

#	Time (days)	0	3	4	5	6	7	8	10	11	12	13	25
59	Gallocatechin-ethyl-catechin	2.20	0.33	0.24	0.09	0.11	<LD	-	<LD	<LD	-	<LD	<LD
60	Catechin-ethyl-gallocatechin	2.71	0.79	1.25	0.64	0.76	1.12	-	1.03	1.09	-	0.96	1.37
61	(Epi)gallocatechin-ethyl-(epi)gallocatechin	<LD	0.28	0.56	0.35	0.21	0.54	-	0.32	<LD	-	<LD	<LD
62	Gallocatechin-ethyl-gallocatechin	0.44	0.92	1.31	0.82	0.86	1.17	-	1.13	1.06	-	0.94	0.90
63	Gallocatechin-ethyl-catechin	<LD	<LD	0.47	0.22	0.23	0.58	-	0.35	0.51	-	0.57	0.41
64	Catechin-ethyl-gallocatechin	<LD	0.20	0.35	0.12	0.19	0.53	-	0.25	0.35	-	0.31	<LD
65	(Epi)catechin-glycoside	<LD	0.21	0.44	0.16	0.16	0.54	-	0.13	0.34	-	0.31	0.39
66	((Epi)catechin)$_3$ 1	0.07	0.31	<LD	0.31	0.68	-	0.84	1.40	-	0.74	0.71	0.42
67	((Epi)catechin)$_3$ 2	0.08	0.39	<LD	0.54	0.74	-	0.85	1.31	-	0.64	0.67	0.35
68	Procyanidin C 1	0.04	0.07	<LD	0.10	0.52	-	0.64	1.16	-	0.36	0.43	0.09

Tank 18

#	Time (days)	0	3	4	5	6	7	8	10	11	12	13	25
59	Gallocatechin-ethyl-catechin	<LD	0.37	0.19	0.12	0.09	<LD	-	<LD	<LD	-	<LD	<LD
60	Catechin-ethyl-gallocatechin	2.45	0.80	1.35	0.57	0.91	1.03	-	1.00	1.24	-	1.17	1.11
61	(Epi)gallocatechin-ethyl-(epi)gallocatechin	<LD	0.26	0.37	0.26	<LD	0.58	-	0.13	0.41	-	<LD	<LD
62	Gallocatechin-ethyl-gallocatechin	0.43	0.69	1.29	0.80	0.88	1.12	-	1.20	1.07	-	1.06	1.17
63	Gallocatechin-ethyl-catechin	<LD	0.16	0.63	0.14	0.23	0.67	-	0.41	0.53	-	0.43	0.35
64	Catechin-ethyl-gallocatechin	<LD	0.14	0.45	0.11	0.17	0.55	-	0.28	0.34	-	0.32	0.38
65	(Epi)catechin-glycoside	<LD	0.15	0.31	0.19	0.26	0.54	-	0.11	0.32	-	0.26	0.34
66	((Epi)catechin)$_3$ 1	0.06	0.20	<LD	0.27	0.59	-	0.81	1.39	-	0.81	0.62	0.20
67	((Epi)catechin)$_3$ 2	0.17	0.42	<LD	0.38	0.75	-	1.04	1.40	-	0.70	0.55	0.22
68	Procyanidin C 1	<LD	0.14	<LD	0.17	0.53	-	0.61	1.12	-	0.40	0.38	0.11

Tank 19

#	Time (days)	0	3	4	5	6	7	8	10	11	12	13	25
59	Gallocatechin-ethyl-catechin	<LD	0.09	0.66	<LD	0.10	<LD	-	<LD	<LD	-	<LD	<LD
60	Catechin-ethyl-gallocatechin	2.75	0.90	1.43	0.73	1.93	1.02	-	0.99	1.26	-	1.41	1.49
61	(Epi)gallocatechin-ethyl-(epi)gallocatechin	<LD	0.20	0.43	0.34	0.24	0.52	-	0.23	<LD	-	<LD	<LD
62	Gallocatechin-ethyl-gallocatechin	0.34	0.77	1.27	0.78	0.84	1.05	-	1.19	1.10	-	0.85	1.02
63	Gallocatechin-ethyl-catechin	0.13	0.15	0.37	0.16	0.29	0.66	-	0.45	0.52	-	0.45	<LD
64	Catechin-ethyl-gallocatechin	<LD	0.17	0.33	0.10	0.29	0.52	-	0.34	0.44	-	0.31	0.38
65	(Epi)catechin-glycoside	<LD	0.28	0.39	0.13	0.16	0.53	-	0.20	0.28	-	0.23	<LD
66	((Epi)catechin)$_3$ 1	0.07	0.25	<LD	0.51	0.60	-	0.78	1.43	-	0.77	0.59	0.19
67	((Epi)catechin)$_3$ 2	0.21	0.54	<LD	0.53	0.79	-	1.13	1.42	-	0.86	0.65	0.38
68	Procyanidin C 1	0.11	0.09	<LD	0.10	0.57	-	0.75	1.12	-	0.44	0.36	0.18

Tank 20

#	Time (days)	0	3	4	5	6	7	8	10	11	12	13	25
59	Gallocatechin-ethyl-catechin	<LD	0.20	0.21	0.06	0.11	<LD	-	<LD	<LD	-	<LD	<LD
60	Catechin-ethyl-gallocatechin	2.68	0.73	1.33	0.56	0.85	1.04	-	1.11	1.14	-	1.29	1.17
61	(Epi)gallocatechin-ethyl-(epi)gallocatechin	<LD	0.14	0.37	0.36	0.10	0.53	-	0.08	0.32	-	0.25	<LD
62	Gallocatechin-ethyl-gallocatechin	0.41	0.76	1.31	0.88	0.93	1.07	-	1.19	0.98	-	0.89	0.99
63	Gallocatechin-ethyl-catechin	0.06	0.11	0.34	0.13	0.21	0.65	-	0.34	0.48	-	0.41	<LD
64	Catechin-ethyl-gallocatechin	0.08	0.13	0.26	0.06	0.17	0.52	-	0.26	0.33	-	0.30	0.41
65	(Epi)catechin-glycoside	<LD	0.21	0.43	0.09	0.11	0.55	-	0.26	0.37	-	0.26	<LD
66	((Epi)catechin)$_3$ 1	0.08	0.25	<LD	0.49	0.69	-	0.72	1.46	-	0.88	0.65	0.23
67	((Epi)catechin)$_3$ 2	0.13	0.29	<LD	0.53	0.71	-	0.99	1.42	-	0.69	0.55	0.39
68	Procyanidin C 1	<LD	0.08	<LD	0.21	0.49	-	0.72	1.11	-	0.42	<LD	0.18

Tank 21

#	Time (days)	0	3	4	5	6	7	8	10	11	12	13	25
59	Gallocatechin-ethyl-catechin	<LD	0.26	1.46	0.06	0.17	<LD	-	0.03	<LD	-	<LD	<LD
60	Catechin-ethyl-gallocatechin	2.86	2.61	1.20	0.59	0.76	0.98	-	1.05	1.15	-	0.80	1.29
61	(Epi)gallocatechin-ethyl-(epi)gallocatechin	<LD	<LD	<LD	0.16	0.22	<LD	-	0.10	<LD	-	<LD	<LD
62	Gallocatechin-ethyl-gallocatechin	0.38	0.49	1.34	1.47	0.90	1.08	-	1.15	1.23	-	0.98	1.06
63	Gallocatechin-ethyl-catechin	0.07	<LD	0.35	0.17	0.38	0.63	-	0.32	0.59	-	0.44	0.37
64	Catechin-ethyl-gallocatechin	0.09	0.09	0.29	0.16	0.26	0.54	-	0.20	0.38	-	0.41	0.37
65	(Epi)catechin-glycoside	<LD	<LD	0.37	0.23	0.22	0.52	-	0.14	0.27	-	0.30	0.38
66	((Epi)catechin)$_3$ 1	0.04	0.27	<LD	0.45	0.59	-	0.72	1.34	-	0.79	0.68	0.18
67	((Epi)catechin)$_3$ 2	0.12	0.41	<LD	0.51	0.79	-	0.85	1.32	-	0.73	0.55	0.29
68	Procyanidin C 1	0.06	0.09	<LD	0.14	<LD	-	0.59	1.12	-	0.50	0.46	0.13

continued

Table S7. Tannin conc. determined by HPLC-DAD-ESI(+)-MS/MS in red wine samples from Alfaro 2019, expressed in mg of (+)-cat equiv./L.

Tank 22

#	Time (days)	0	3	4	5	6	7	8	10	11	12	13	25
59	Gallocatechin-ethyl-catechin	<LD	0.09	0.29	0.10	0.08	<LD	-	<LD	<LD	-	<LD	<LD
60	Catechin-ethyl-gallocatechin	2.70	0.95	1.42	0.64	0.82	0.97	-	1.07	1.21	-	1.05	1.36
61	(Epi)gallocatechin-ethyl-(epi)gallocatechin	<LD	0.26	<LD	0.12	0.15	<LD	-	0.03	<LD	-	<LD	<LD
62	Gallocatechin-ethyl-gallocatechin	0.45	0.79	1.31	0.86	0.91	1.03	-	1.07	1.07	-	0.86	0.94
63	Gallocatechin-ethyl-catechin	<LD	0.20	0.29	0.19	0.20	0.61	-	0.23	0.54	-	0.37	0.39
64	Catechin-ethyl-gallocatechin	0.09	0.15	0.18	0.13	0.16	0.61	-	0.17	0.40	-	0.35	0.38
65	(Epi)catechin-glycoside	<LD	0.23	0.32	0.14	0.10	0.52	-	0.16	0.40	-	0.24	0.37
66	((Epi)catechin)$_3$ 1	0.06	0.22	<LD	0.34	0.70	-	0.73	1.38	-	0.88	0.74	0.39
67	((Epi)catechin)$_3$ 2	0.14	0.33	<LD	0.41	0.67	-	0.97	1.33	-	0.72	0.61	0.32
68	Procyanidin C 1	0.05	0.06	<LD	0.07	0.52	-	0.63	1.12	-	0.42	0.42	0.13

Tank 23

#	Time (days)	0	3	4	5	6	7	8	10	11	12	13	25
59	Gallocatechin-ethyl-catechin	<LD	1.42	0.75	0.09	0.48	<LD	-	<LD	<LD	-	<LD	<LD
60	Catechin-ethyl-gallocatechin	1.92	0.63	1.62	0.62	0.86	1.03	-	1.03	1.60	-	1.48	1.69
61	(Epi)gallocatechin-ethyl-(epi)gallocatechin	<LD	0.12	<LD	0.18	0.20	<LD	-	<LD	<LD	-	<LD	0.36
62	Gallocatechin-ethyl-gallocatechin	0.45	0.85	1.29	0.85	0.93	1.13	-	1.07	0.94	-	0.74	0.88
63	Gallocatechin-ethyl-catechin	0.07	0.16	0.33	0.12	0.15	0.55	-	0.19	0.48	-	0.33	<LD
64	Catechin-ethyl-gallocatechin	0.06	0.16	0.18	0.09	0.15	0.67	-	0.22	0.37	-	0.27	0.41
65	(Epi)catechin-glycoside	0.18	0.19	0.34	0.14	0.16	0.52	-	0.13	0.29	-	0.28	0.40
66	((Epi)catechin)$_3$ 1	0.06	0.24	<LD	0.25	0.61	-	0.74	1.47	-	1.05	0.68	0.46
67	((Epi)catechin)$_3$ 2	0.13	0.49	<LD	0.52	0.66	-	1.02	1.31	-	0.76	0.56	0.20
68	Procyanidin C 1	<LD	0.10	<LD	0.13	0.51	-	0.61	1.11	-	0.43	0.36	0.08

Tank 24

#	Time (days)	0	3	4	5	6	7	8	10	11	12	13	25
59	Gallocatechin-ethyl-catechin	<LD	2.24	0.20	0.08	<LD	<LD	-	<LD	<LD	-	<LD	<LD
60	Catechin-ethyl-gallocatechin	2.46	0.65	1.30	0.54	1.87	1.00	-	0.99	0.92	-	1.15	1.65
61	(Epi)gallocatechin-ethyl-(epi)gallocatechin	<LD	<LD	<LD	0.09	<LD	<LD	-	<LD	<LD	-	<LD	<LD
62	Gallocatechin-ethyl-gallocatechin	0.39	0.94	1.34	0.78	0.88	1.06	-	1.14	1.01	-	0.89	0.85
63	Gallocatechin-ethyl-catechin	0.11	0.18	0.30	0.10	0.21	0.53	-	0.25	0.36	-	0.38	<LD
64	Catechin-ethyl-gallocatechin	0.09	0.20	0.22	0.08	0.20	0.54	-	0.24	0.35	-	0.30	<LD
65	(Epi)catechin-glycoside	0.20	0.17	0.38	0.12	0.25	0.52	-	0.10	0.32	-	0.26	0.38
66	((Epi)catechin)$_3$ 1	0.08	0.22	<LD	0.27	0.67	-	0.76	1.57	-	0.91	0.68	0.37
67	((Epi)catechin)$_3$ 2	0.16	0.54	<LD	0.52	0.79	-	1.00	1.39	-	0.73	0.62	0.23
68	Procyanidin C 1	<LD	0.10	<LD	0.09	0.51	-	0.67	1.17	-	0.41	0.39	0.11

Table S8. Anthocyanin conc. determined by HPLC-DAD in red wine samples from Laguardia 2019, expressed in mg of Mv-3-*O*-glc equiv./L.

Tank 01

#	Time (days)	0	1	2	4	5	6	7	8	11	12	13	14	15	19	21	25	28	32	35	39	42	46	60
1	Dp-3-*O*-glc	18.57	18.70	22.46	26.25	27.90	27.08	27.22	26.23	22.03	22.81	21.21	21.01	18.88	19.07	18.99	17.89	16.56	13.48	12.11	10.95	10.24	12.09	13.77
2	Cy-3-*O*-glc	8.01	4.65	2.32	2.45	2.77	2.77	2.76	2.65	2.47	2.44	2.33	2.39	1.97	2.15	2.08	2.07	2.04	1.61	1.83	1.70	1.68	1.89	1.88
3	Pt-3-*O*-glc	14.07	14.63	19.55	26.37	29.42	29.26	29.60	28.63	27.77	28.66	26.79	27.64	24.28	24.84	24.19	23.06	21.05	17.59	15.54	14.43	14.20	15.83	17.30
4	Pn-3-*O*-glc	13.57	11.96	8.66	8.26	9.19	9.14	9.19	8.60	8.14	8.07	7.80	7.86	6.51	6.87	6.81	6.72	7.12	6.45	7.95	7.29	7.24	8.06	6.68
5	Mv-3-*O*-glc	51.04	55.02	70.68	96.21	104.76	105.48	110.72	103.98	105.46	105.84	102.85	103.48	92.86	96.32	94.40	89.11	81.88	71.33	64.51	59.25	58.51	63.71	67.23
6	Dp-3-*O*-(6-ac)-glc	0.39	0.89	1.65	2.20	2.69	2.70	2.56	2.35	1.99	2.19	2.14	2.20	1.11	2.12	2.09	2.10	1.94	0.51	0.38	0.30	0.30	1.42	1.58
7	Pt-3-*O*-(6-ac)-glc	0.69	1.28	2.09	2.91	2.83	2.86	2.94	2.69	2.68	2.83	2.76	2.83	2.00	2.81	2.78	2.89	2.82	1.78	1.74	1.67	2.09	2.61	2.71
8	Pn-3-*O*-(6-ac)-glc	0.50	0.70	1.16	1.58	1.66	1.69	1.75	1.61	1.80	1.92	1.70	1.96	1.34	1.90	1.95	2.06	2.04	1.81	1.88	1.83	1.81	2.13	2.39
9	Mv-3-*O*-(6-ac)-glc	2.60	3.66	5.45	8.52	8.81	8.70	8.97	8.58	8.41	8.60	8.40	8.43	6.92	7.81	7.86	7.73	7.45	6.55	6.20	5.75	5.56	6.97	7.22
10	Mv-3-*O*-(6-caff)-glc	0.26	0.53	1.09	1.69	1.80	1.88	2.04	1.93	2.01	2.19	2.18	2.26	1.59	2.43	2.39	2.47	2.27	2.00	1.99	1.94	1.87	2.15	2.40
11	Pt-3-*O*-(6-*p*-coum)-glc	0.59	1.13	1.92	3.27	3.61	3.57	3.63	3.57	3.49	3.73	3.47	3.61	2.73	3.24	3.20	3.19	3.08	2.77	2.63	2.50	2.40	2.65	2.75
12	Pn-3-*O*-(6-*p*-coum)-glc	2.99	5.35	8.13	14.72	17.36	17.38	17.61	18.14	17.01	17.56	17.59	18.01	13.21	15.27	14.78	14.73	14.90	13.82	14.07	13.40	13.10	13.82	13.35
13	Mv-3-*O*-(6-*p*-coum)-glc	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Tank 02

#	Time (days)	0	1	2	4	5	6	7	8	11	12	13	14	15	19	21	25	28	32	35	39	42	46	60
1	Dp-3-*O*-glc	16.62	18.65	20.63	24.96	26.17	24.59	24.82	24.39	19.13	19.25	17.63	18.00	18.06	17.98	16.94	16.10	14.68	13.08	10.65	10.75	10.93	11.63	12.31
2	Cy-3-*O*-glc	7.45	3.14	1.98	2.32	2.67	2.49	2.49	2.55	2.22	2.19	1.80	1.83	2.01	2.03	2.00	1.95	1.95	1.60	1.68	1.67	1.88	1.84	1.78
3	Pt-3-*O*-glc	12.72	14.80	18.84	25.69	28.45	27.08	27.61	27.26	24.50	25.52	22.85	23.44	23.56	23.85	22.40	20.78	18.90	16.67	13.61	14.33	14.66	15.27	15.31
4	Pn-3-*O*-glc	12.79	10.74	7.70	7.83	8.65	8.21	8.31	8.20	7.31	7.16	6.07	6.13	6.51	6.39	6.45	6.35	6.93	6.25	7.16	6.91	7.32	7.30	6.36
5	Mv-3-*O*-glc	47.68	53.75	69.54	93.16	102.44	98.72	100.61	100.13	95.15	97.23	91.16	91.91	91.55	91.97	90.57	81.96	74.62	66.42	57.30	58.61	58.87	60.29	59.39
6	Dp-3-*O*-(6-ac)-glc	0.37	0.91	1.54	2.20	2.72	2.11	2.37	2.52	2.01	1.81	0.75	0.79	1.74	2.06	2.01	1.95	1.80	0.39	0.33	0.30	1.62	1.44	1.51
7	Pt-3-*O*-(6-ac)-glc	0.63	1.29	2.06	2.89	2.83	2.39	2.74	2.80	2.60	2.47	2.09	2.13	2.41	2.73	2.68	2.74	2.74	1.48	1.64	2.15	2.56	2.55	2.58
8	Pn-3-*O*-(6-ac)-glc	0.47	0.70	1.18	1.57	1.64	1.40	1.64	1.77	1.75	1.71	1.49	1.54	1.67	1.79	1.89	2.02	2.02	1.44	1.79	1.86	2.00	2.04	2.30
9	Mv-3-*O*-(6-ac)-glc	2.61	3.37	5.62	8.46	8.51	7.80	8.38	8.25	7.53	7.66	7.04	7.19	7.15	7.60	7.51	7.16	6.93	5.72	5.64	6.44	6.73	6.79	5.80
10	Mv-3-*O*-(6-caff)-glc	0.27	0.53	1.13	1.75	1.86	1.57	1.97	2.02	1.99	1.96	1.82	1.88	2.00	2.39	2.35	2.42	2.20	1.56	1.87	1.91	2.05	2.11	2.26
11	Pt-3-*O*-(6-*p*-coum)-glc	0.65	0.95	2.03	3.28	3.44	3.07	3.44	3.45	3.11	3.19	2.84	2.95	2.92	3.16	2.96	2.96	2.86	2.23	2.40	2.45	2.55	2.53	2.52
12	Pn-3-*O*-(6-*p*-coum)-glc	3.47	3.94	9.12	14.62	16.38	14.96	16.44	17.39	16.09	16.07	14.76	14.94	14.62	14.53	13.95	13.78	13.94	10.41	12.80	12.68	12.91	12.78	11.99
13	Mv-3-*O*-(6-*p*-coum)-glc	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Tank 03

#	Time (days)	0	1	2	4	5	6	7	8	11	12	13	14	15	19	21	25	28	32	35	39	42	46	60
1	Dp-3-*O*-glc	24.18	21.87	24.17	26.57	29.45	26.19	27.16	26.11	21.64	21.35	20.21	19.79	17.46	17.97	17.76	17.39	16.99	15.66	14.15	12.33	10.94	11.37	13.05
2	Cy-3-*O*-glc	10.74	5.91	2.39	2.23	2.95	2.71	2.73	2.75	2.43	2.51	2.41	2.06	1.96	2.19	1.82	2.07	2.01	2.05	2.16	2.12	2.09	1.72	1.99
3	Pt-3-*O*-glc	17.76	16.64	20.62	26.79	31.00	28.44	29.49	28.66	27.18	28.33	26.81	26.13	23.22	23.76	22.93	22.48	21.44	20.36	18.46	16.69	16.08	15.01	17.23
4	Pn-3-*O*-glc	16.88	13.61	9.21	7.99	9.70	8.97	9.12	8.89	8.04	8.17	7.81	6.83	6.36	6.96	6.06	6.72	6.54	7.04	7.66	7.57	7.73	6.63	6.53
5	Mv-3-*O*-glc	61.69	58.33	72.64	96.00	106.85	101.60	106.08	104.71	101.94	103.35	99.05	96.95	90.20	91.48	89.93	87.00	80.48	77.06	70.84	65.68	61.15	59.74	66.40
6	Dp-3-*O*-(6-ac)-glc	0.55	0.93	1.22	1.44	2.89	2.34	2.53	2.59	1.83	1.96	2.10	0.86	0.72	2.06	0.69	2.07	1.99	1.93	1.79	1.51	1.42	0.37	1.81
7	Pt-3-*O*-(6-ac)-glc	0.82	1.31	1.87	2.23	2.99	2.64	2.92	2.87	2.56	2.68	2.76	2.26	1.99	2.72	1.97	2.88	2.81	2.87	2.21	2.13	2.04	2.15	2.75
8	Pn-3-*O*-(6-ac)-glc	0.59	0.73	1.01	1.21	1.75	1.60	1.79	1.85	1.73	1.84	1.85	1.62	1.40	1.89	1.40	2.04	2.31	2.14	2.17	2.24	2.11	1.79	2.26
9	Mv-3-*O*-(6-ac)-glc	3.45	3.54	5.65	7.84	8.88	8.07	8.55	8.41	7.87	8.18	7.91	7.50	6.60	7.27	6.74	7.35	6.97	7.09	6.75	6.31	5.92	5.55	6.25
10	Mv-3-*O*-(6-caff)-glc	0.33	0.52	0.87	1.20	1.91	1.72	2.03	2.07	1.94	2.07	2.18	1.95	1.65	2.36	1.73	2.47	2.43	2.33	2.24	2.20	2.15	1.89	2.41
11	Pt-3-*O*-(6-*p*-coum)-glc	0.94	0.98	1.94	2.78	3.58	3.23	3.49	3.50	3.19	3.43	3.28	3.11	2.56	2.98	2.47	2.99	2.94	2.98	2.84	2.75	2.59	2.35	2.59
12	Pn-3-*O*-(6-*p*-coum)-glc	4.78	4.10	8.35	12.12	16.49	15.42	16.32	16.53	15.32	16.83	15.44	15.45	12.90	13.97	11.35	13.42	12.89	13.51	13.85	13.71	13.14	12.02	10.88
13	Mv-3-*O*-(6-*p*-coum)-glc	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Tank 04

#	Time (days)	0	1	2	4	5	6	7	8	11	12	13	14	15	19	21	25	28	32	35	39	42	46	60
1	Dp-3-*O*-glc	23.97	19.82	25.89	27.71	30.16	26.19	29.76	27.47	22.75	21.88	21.58	21.25	21.15	20.45	20.69	18.68	18.38	16.90	14.88	14.22	14.21	15.13	18.60
2	Cy-3-*O*-glc	10.09	5.11	2.61	2.27	2.95	2.71	2.82	2.93	2.57	2.56	2.48	2.57	2.64	2.50	2.51	2.35	2.51	2.05	2.77	2.94	2.00	2.25	2.25
3	Pt-3-*O*-glc	17.74	15.34	22.63	27.81	31.89	28.44	31.92	32.46	27.82	27.25	27.01	27.60	27.19	26.08	25.94	23.72	23.64	21.18	19.04	20.75	19.68	20.86	23.70
4	Pn-3-*O*-glc	16.33	12.28	10.01	8.14	9.85	8.97	9.57	9.64	8.83	8.75	8.61	9.07	9.14	8.82	8.92	8.14	8.80	7.46	7.97	7.98	7.01	7.35	6.84
5	Mv-3-*O*-glc	62.21	56.35	81.65	101.64	115.21	101.60	116.92	117.32	105.14	103.09	102.30	101.80	103.02	98.80	98.11	89.39	90.37	81.47	79.79	78.69	76.88	80.59	85.83
6	Dp-3-*O*-(6-ac)-glc	0.51	0.78	1.76	1.40	2.95	2.34	2.36	2.76	2.29	2.20	1.92	2.19	2.22	2.18	2.43	1.87	2.15	0.64	0.49	1.75	0.51	1.57	2.06
7	Pt-3-*O*-(6-ac)-glc	0.82	1.20	2.48	2.36	3.13	2.64	3.01	3.21	2.95	2.91	2.77	2.93	3.02	2.99	3.17	2.83	3.08	2.42	2.49	2.85	2.29	2.65	3.02
8	Pn-3-*O*-(6-ac)-glc	0.58	0.67	1.45	1.29	1.84	1.60	1.87	2.00	2.11	2.22	2.11	2.27	2.31	2.28	2.45	2.11	2.19	1.96	2.03	2.24	1.90	2.33	2.57
9	Mv-3-*O*-(6-ac)-glc	3.41	3.63	6.71	8.64	9.72	8.07	9.83	9.99	8.81	8.96	8.78	8.89	9.03	8.72	9.05	8.29	8.58	7.76	7.61	7.46	6.84	6.96	7.96
10	Mv-3-*O*-(6-caff)-glc	0.32	0.48	1.51	1.29	1.97	1.72	2.00	2.19	2.14	2.16	2.09	2.23	2.32	2.35	2.48	2.21	2.37	2.06	2.04	2.18	2.06	2.17	2.53
11	Pt-3-*O*-(6-*p*-coum)-glc	0.84	1.02	2.40	3.08	3.87	3.23	3.98	4.21	3.75	3.82	3.67	3.80	3.84	3.70	3.85	3.46	3.61	3.31	3.19	3.16	2.74	2.79	3.28
12	Pn-3-*O*-(6-*p*-coum)-glc	4.01	4.94	10.24	13.93	18.20	15.42	19.31	19.89	18.49	19.43	17.94	18.61	18.83	17.95	19.43	17.06	18.08	16.48	16.57	16.30	14.57	13.92	12.64
13	Mv-3-*O*-(6-*p*-coum)-glc	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Tank 05

#	Time (days)	0	1	2	4	5	6	7	8	11	12	13	14	15	19	21	25	28	32	35	39	42	46	60
1	Dp-3-*O*-glc	26.11	28.88	31.03	40.09	42.21	37.33	39.77	39.16	34.66	34.12	32.52	32.99	34.59	34.81	32.51	31.53	25.57	30.76	29.51	27.45	23.44	26.04	21.45
2	Cy-3-*O*-glc	11.56	11.20	7.51	4.78	6.16	5.74	5.92	6.02	5.36	5.65	5.47	4.72	5.45	4.97	4.59	4.55	3.66	4.40	4.34	4.66	4.30	4.44	3.74
3	Pt-3-*O*-glc	19.16	20.77	22.69	33.77	36.00	32.49	34.24	33.71	30.82	30.22	28.86	29.24	30.68	30.58	28.63	27.56	22.09	26.29	25.23	23.55	19.88	22.11	16.98
4	Pn-3-*O*-glc	17.85	18.16	15.46	14.93	16.17	14.85	15.48	15.47	14.87	14.71	14.23	14.38	14.82	15.37	13.54	13.08	10.03	12.34	13.05	12.08	10.21	10.68	9.09
5	Mv-3-*O*-glc	66.11	69.82	73.32	106.78	111.55	102.33	106.79	105.14	96.34	92.49	90.65	90.19	94.80	95.38	91.52	86.54	71.20	79.72	76.50	71.31	63.05	65.75	50.24
6	Dp-3-*O*-(6-ac)-glc	0.60	1.11	1.38	2.22	2.86	2.22	2.18	2.15	2.06	1.91	1.69	2.12	2.00	2.04	1.91	1.94	0.81	1.90	1.88	1.94	1.80	1.90	1.74
7	Pt-3-*O*-(6-ac)-glc	0.89	1.39	2.29	3.07	3.16	2.82	2.95	2.96	3.04	2.91	2.73	2.93	3.07	3.14	3.14	3.36	2.26	3.50	3.59	3.66	3.55	3.80	3.92
8	Pn-3-*O*-(6-ac)-glc	0.60	0.88	1.27	1.76	1.92	1.73	1.82	1.89	2.09	2.09	2.10	2.17	2.15	2.22	2.25	2.41	1.66	2.54	2.72	2.67	2.55	2.75	2.70
9	Mv-3-*O*-(6-ac)-glc	3.95	4.65	6.11	9.69	10.01	8.79	9.49	9.45	8.81	8.44	8.14	8.31	8.66	8.62	8.34	8.26	6.21	8.02	8.00	7.59	6.96	7.44	6.64
10	Mv-3-*O*-(6-caff)-glc	0.34	0.58	1.20	1.89	1.86	1.75	1.94	2.02	2.20	2.17	2.01	2.23	2.34	2.45	2.47	2.60	1.61	2.75	2.87	2.89	2.78	3.08	3.26
11	Pt-3-*O*-(6-*p*-coum)-glc	1.01	1.58	2.44	4.17	4.47	3.87	4.22	4.25	4.05	4.00	3.69	3.90	4.04	4.01	3.73	3.71	2.52	3.72	3.70	3.59	3.19	3.57	3.28
12	Pn-3-*O*-(6-*p*-coum)-glc	4.83	7.11	9.46	16.57	18.67	16.34	17.80	17.94	17.93	18.01	16.39	17.36	17.76	17.03	16.07	14.63	9.64	13.90	13.73	12.91	11.26	12.22	9.93
13	Mv-3-*O*-(6-*p*-coum)-glc	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Tank 06

#	Time (days)	0	1	2	4	5	6	7	8	11	12	13	14	15	19	21	25	28	32	35	39	42	46	60
1	Dp-3-*O*-glc	26.13	28.92	31.60	35.39	40.35	38.64	39.62	37.86	32.82	34.11	32.33	32.51	32.41	28.28	28.96	32.02	28.04	27.81	29.44	27.98	24.49	27.39	21.67
2	Cy-3-*O*-glc	11.22	11.00	6.94	4.30	5.92	5.81	5.85	5.79	5.41	4.91	5.41	4.53	4.91	3.95	4.09	4.45	3.79	3.98	4.24	4.69	4.33	4.49	3.82
3	Pt-3-*O*-glc	19.17	20.76	23.16	29.79	34.65	33.27	34.02	32.71	29.13	29.96	28.71	28.85	28.44	24.63	26.05	28.02	24.02	23.79	25.23	24.05	21.15	23.12	17.64
4	Pn-3-*O*-glc	17.39	17.91	15.08	13.33	15.60	14.96	15.21	14.96	14.12	14.11	14.23	14.04	13.43	12.35	12.33	12.89	10.94	10.96	12.90	11.50	10.55	10.89	9.33
5	Mv-3-*O*-glc	65.47	69.43	74.49	94.98	108.18	103.18	104.35	101.67	92.80	93.31	90.50	89.22	89.75	79.45	85.79	87.71	76.30	74.21	76.57	73.25	65.31	67.98	52.22
6	Dp-3-*O*-(6-ac)-glc	0.58	1.03	1.37	2.33	2.33	2.40	2.39	2.09	1.78	1.13	1.85	1.88	1.21	0.95	1.61	1.96	0.83	1.76	1.87	1.97	1.79	1.94	1.79
7	Pt-3-*O*-(6-ac)-glc	0.85	1.35	2.28	2.95	2.88	2.97	3.07	2.85	2.76	2.28	2.85	2.87	2.29	2.14	2.81	3.36	2.40	3.31	3.59	3.74	3.56	3.87	3.88
8	Pn-3-*O*-(6-ac)-glc	0.57	0.82	1.26	1.72	1.72	1.85	1.88	1.81	2.06	1.62	2.01	2.12	1.58	1.48	1.98	2.38	1.75	2.41	2.71	2.71	2.64	2.77	2.82
9	Mv-3-*O*-(6-ac)-glc	3.85	4.14	5.83	8.47	9.45	9.02	9.48	8.96	8.34	8.05	8.13	8.19	7.66	6.73	7.64	8.40	6.79	7.35	7.92	7.78	7.14	7.67	6.84
10	Mv-3-*O*-(6-caff)-glc	0.32	0.51	1.16	1.80	1.61	1.89	2.05	1.91	1.95	1.57	2.10	2.16	1.61	1.50	2.17	2.63	1.72	2.55	2.82	3.02	2.83	3.13	3.25
11	Pt-3-*O*-(6-*p*-coum)-glc	1.02	1.24	2.19	3.61	4.14	4.06	4.33	4.05	3.80	3.62	3.73	3.86	3.34	2.82	3.34	3.83	2.82	3.33	3.68	3.72	3.36	3.70	3.40
12	Pn-3-*O*-(6-*p*-coum)-glc	4.70	4.70	7.54	14.51	17.60	2.66	17.83	17.06	16.17	16.06	16.51	17.36	14.64	12.35	14.52	15.14	10.87	1.77	13.71	13.27	11.92	12.62	10.89
13	Mv-3-*O*-(6-*p*-coum)-glc	-	-	-	-	-	14.25	-	-	-	-	-	-	-	-	-	-	-	10.98	-	-	-	-	-

continued

Table S8. Anthocyanin conc. determined by HPLC-DAD in red wine samples from Laguardia 2019, expressed in mg of Mv-3-*O*-glc equiv./L.

Tank 07

#	Time (days)	0	1	2	4	5	6	7	8	11	12	13	14	15	19	21	25	28	32	35	39	42	46	60
1	Dp-3-*O*-glc	26.36	30.18	31.81	38.40	42.40	38.08	41.41	36.17	33.38	33.05	31.70	32.97	34.97	34.87	32.40	31.10	32.60	30.60	30.02	27.81	25.83	26.34	23.09
2	Cy-3-*O*-glc	11.52	11.58	7.95	4.88	6.42	6.05	6.28	5.50	5.76	5.25	5.44	5.30	5.43	5.63	5.49	4.47	4.70	4.94	4.99	4.77	4.57	4.53	4.06
3	Pt-3-*O*-glc	19.37	21.55	23.16	31.45	35.70	32.66	35.10	31.17	29.18	28.58	27.75	29.16	30.35	29.90	28.23	26.95	27.84	25.97	25.34	23.62	21.86	22.07	18.41
4	Pn-3-*O*-glc	17.88	18.57	15.92	14.73	16.68	15.51	16.38	15.27	14.94	14.04	14.19	14.74	14.87	13.95	13.73	13.04	13.40	12.56	12.11	12.39	11.10	10.99	9.34
5	Mv-3-*O*-glc	66.00	71.05	74.18	97.44	109.19	100.71	107.44	99.85	92.26	88.68	86.95	89.97	90.46	92.64	88.84	83.87	84.70	78.35	76.05	71.00	65.75	65.10	53.09
6	Dp-3-*O*-(6-ac)-glc	0.60	1.13	1.34	2.16	2.83	2.40	2.23	2.06	2.00	1.17	1.83	1.98	2.18	1.22	1.89	1.90	1.97	1.89	1.91	1.97	1.83	1.88	1.81
7	Pt-3-*O*-(6-ac)-glc	0.88	1.37	2.26	3.27	3.13	2.99	3.02	2.89	2.98	2.24	2.84	2.95	2.96	2.45	3.09	3.34	3.52	3.54	3.64	3.66	3.64	3.80	3.94
8	Pn-3-*O*-(6-ac)-glc	0.60	0.88	1.33	1.98	1.90	1.87	1.87	1.87	2.07	1.58	1.99	2.13	2.06	1.66	2.44	2.39	2.58	2.60	2.78	2.73	2.79	2.86	3.10
9	Mv-3-*O*-(6-ac)-glc	3.92	4.49	6.15	8.94	9.74	8.88	9.65	8.93	8.49	7.72	8.02	8.27	8.34	7.87	7.99	8.07	8.33	7.94	7.88	7.65	7.19	7.25	6.88
10	Mv-3-*O*-(6-caff)-glc	0.32	0.54	1.19	2.02	1.81	1.75	1.98	1.78	2.13	1.54	2.10	2.21	2.22	1.74	2.37	2.58	2.72	2.77	2.86	2.93	2.88	3.06	3.33
11	Pt-3-*O*-(6-*p*-coum)-glc	1.15	1.45	2.52	3.93	4.36	4.02	4.34	4.02	3.92	3.47	3.70	3.91	3.95	3.45	3.62	3.70	3.85	3.70	3.65	3.64	3.41	3.52	3.47
12	Pn-3-*O*-(6-*p*-coum)-glc	4.79	5.85	9.81	15.28	17.93	16.59	18.10	17.16	17.48	15.18	16.43	17.24	16.91	14.37	15.38	14.50	14.68	13.75	13.32	12.92	11.84	12.03	10.89
13	Mv-3-*O*-(6-*p*-coum)-glc	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Tank 08

#	Time (days)	0	1	2	4	5	6	7	8	11	12	13	14	15	19	21	25	28	32	35	39	42	46	60
1	Dp-3-*O*-glc	23.76	27.22	30.63	35.85	36.19	39.22	43.46	35.93	33.46	35.19	31.93	31.98	32.73	35.03	29.83	30.43	32.00	29.90	27.30	25.68	22.15	23.07	18.90
2	Cy-3-*O*-glc	10.78	10.45	6.76	4.53	5.79	6.12	5.98	5.97	5.24	5.41	5.44	4.92	5.31	5.20	5.22	4.41	4.56	4.85	4.61	4.47	4.01	4.06	3.49
3	Pt-3-*O*-glc	17.61	19.69	22.66	29.59	31.01	33.40	36.56	31.02	29.45	30.78	28.03	28.08	28.35	30.11	26.31	26.28	27.32	25.30	23.09	21.83	18.86	19.41	15.07
4	Pn-3-*O*-glc	16.70	17.22	14.95	13.55	14.67	15.54	16.63	15.23	14.56	14.96	13.97	13.58	13.61	13.74	12.75	12.50	12.91	12.20	12.26	10.92	9.50	10.13	8.41
5	Mv-3-*O*-glc	61.05	65.17	72.57	93.02	96.56	103.24	110.12	99.66	92.02	94.05	87.93	87.73	89.45	92.68	85.56	81.76	82.90	76.57	69.60	65.88	57.32	57.31	44.24
6	Dp-3-*O*-(6-ac)-glc	0.51	1.10	1.74	1.43	2.16	2.45	2.46	2.24	1.96	2.14	1.83	1.18	1.11	1.15	1.83	1.90	1.94	1.90	1.78	1.90	1.71	1.82	1.66
7	Pt-3-*O*-(6-ac)-glc	0.81	1.47	2.73	2.45	2.70	3.02	3.21	3.03	2.94	2.96	2.85	2.25	2.26	2.43	2.99	3.28	3.53	3.63	3.63	3.75	3.59	3.88	2.93
8	Pn-3-*O*-(6-ac)-glc	0.56	0.98	1.65	1.41	1.63	1.87	2.00	1.98	2.01	2.10	1.98	1.57	1.54	1.62	2.12	2.34	2.52	2.59	2.58	2.75	2.59	2.75	2.89
9	Mv-3-*O*-(6-ac)-glc	3.56	4.49	6.36	8.00	8.31	9.11	10.04	9.03	8.43	8.71	8.10	7.52	7.50	7.90	7.74	7.94	8.29	7.94	7.53	7.48	6.64	7.08	6.45
10	Mv-3-*O*-(6-caff)-glc	0.32	0.61	1.61	1.33	1.48	1.91	2.20	2.07	2.13	2.20	2.11	1.59	1.61	1.76	2.33	2.56	2.77	2.88	2.89	3.06	2.85	3.19	3.45
11	Pt-3-*O*-(6-*p*-coum)-glc	0.92	1.60	2.74	3.31	3.56	4.09	4.61	4.08	3.91	4.14	3.74	3.35	3.30	3.48	3.41	3.61	3.84	3.73	3.52	3.59	3.17	3.47	3.33
12	Pn-3-*O*-(6-*p*-coum)-glc	4.18	6.86	10.23	13.26	14.50	17.62	2.97	17.06	17.15	18.12	16.64	14.51	14.17	14.27	14.23	14.05	14.45	13.60	12.67	12.23	10.67	11.40	10.02
13	Mv-3-*O*-(6-*p*-coum)-glc	-	-	-	-	-	-	16.06	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Tank 09

#	Time (days)	0	1	2	4	5	6	7	8	11	12	13	14	15	19	21	25	28	32	35	39	42	46	60
1	Dp-3-*O*-glc	16.89	17.30	16.44	24.63	23.97	22.23	23.16	22.09	18.75	18.31	16.82	18.54	14.66	14.56	15.29	14.47	14.37	13.00	12.05	9.74	10.03	11.07	11.71
2	Cy-3-*O*-glc	7.59	4.28	1.81	2.47	2.51	2.31	2.46	2.39	2.13	2.14	2.01	2.15	1.63	1.71	1.85	1.50	1.68	1.52	1.87	1.50	1.48	1.66	1.74
3	Pt-3-*O*-glc	13.49	14.20	15.69	25.97	26.54	25.22	26.20	25.38	24.23	23.81	22.46	25.45	20.01	19.52	20.43	18.93	18.92	17.05	16.16	14.10	13.84	14.67	15.77
4	Pn-3-*O*-glc	20.36	16.98	9.96	10.50	10.68	9.92	10.43	9.96	9.27	9.12	8.54	9.13	7.24	7.28	7.66	6.62	7.24	7.01	8.47	7.10	7.31	7.41	7.11
5	Mv-3-*O*-glc	55.40	58.60	66.77	100.98	103.48	99.85	104.35	103.15	101.40	99.50	96.43	103.47	89.28	85.42	90.36	84.53	83.26	74.97	70.39	60.85	61.79	62.35	66.92
6	Dp-3-*O*-(6-ac)-glc	0.40	0.82	1.54	2.87	2.51	2.20	2.55	2.47	1.85	2.09	1.81	1.94	0.71	0.71	2.03	0.71	0.74	0.53	1.72	0.35	0.35	1.49	1.79
7	Pt-3-*O*-(6-ac)-glc	0.79	1.22	1.93	3.12	2.72	2.54	2.92	2.78	2.59	2.72	2.48	2.66	2.10	1.97	2.67	2.30	2.01	1.76	2.73	2.07	2.08	2.55	2.71
8	Pn-3-*O*-(6-ac)-glc	0.95	1.23	1.84	2.32	2.21	2.43	2.72	2.67	2.58	2.68	2.46	2.53	2.15	2.01	2.60	2.37	2.10	2.37	2.53	2.23	2.22	2.49	2.66
9	Mv-3-*O*-(6-ac)-glc	3.38	4.03	5.77	9.81	9.20	8.63	9.29	8.84	8.66	8.57	8.12	8.76	7.35	6.73	7.96	7.55	6.89	6.66	6.91	5.74	6.49	6.14	7.59
10	Mv-3-*O*-(6-caff)-glc	0.33	0.49	0.99	1.92	1.83	1.76	2.16	2.12	2.10	2.25	2.20	2.38	1.98	1.78	2.44	2.23	1.86	2.15	2.48	2.03	2.05	2.31	2.45
11	Pt-3-*O*-(6-*p*-coum)-glc	0.58	0.83	1.65	3.29	3.15	2.95	3.28	3.15	3.03	3.13	2.82	3.13	2.44	2.10	2.73	2.57	2.17	2.42	2.56	2.19	2.15	2.41	2.50
12	Pn-3-*O*-(6-*p*-coum)-glc	0.81	4.65	8.98	15.83	17.65	3.89	17.96	17.23	16.87	17.01	3.76	17.67	13.96	11.73	14.36	13.43	2.48	12.91	14.48	12.70	12.47	13.06	12.50
13	Mv-3-*O*-(6-*p*-coum)-glc	3.06	-	-	-	-	12.84	-	-	-	-	11.89	-	-	-	-	-	8.88	-	-	-	-	-	-

Tank 10

#	Time (days)	0	1	2	4	5	6	7	8	11	12	13	14	15	19	21	25	28	32	35	39	42	46	60
1	Dp-3-*O*-glc	16.41	16.37	17.93	25.71	25.55	24.14	25.11	23.64	19.78	19.06	19.03	17.24	15.63	15.69	16.13	15.76	15.58	14.94	13.87	12.68	11.11	11.71	12.62
2	Cy-3-*O*-glc	7.92	4.14	2.01	2.63	2.75	2.58	2.77	2.65	2.35	2.34	2.35	1.96	1.76	1.93	2.00	1.77	1.78	1.97	1.96	1.99	1.90	1.86	1.82
3	Pt-3-*O*-glc	12.98	13.26	16.74	26.53	27.81	26.57	27.74	26.45	24.96	24.73	24.76	23.12	20.73	21.17	21.37	20.41	20.02	19.48	18.02	16.85	15.06	15.54	16.29
4	Pn-3-*O*-glc	20.51	16.16	10.67	10.84	11.50	10.83	11.32	10.96	9.86	9.60	9.45	8.44	7.57	8.14	8.20	7.52	7.38	7.86	8.16	8.27	7.92	7.76	7.07
5	Mv-3-*O*-glc	52.70	54.47	67.52	98.79	105.37	100.20	106.46	103.09	99.79	99.77	99.15	95.03	87.52	92.41	90.50	87.44	84.40	79.41	74.13	69.63	63.79	64.54	66.15
6	Dp-3-*O*-(6-ac)-glc	0.40	0.81	1.65	2.84	2.69	2.31	2.65	2.56	2.14	1.90	2.18	0.79	0.72	2.02	2.04	0.85	0.80	2.02	1.86	1.64	1.74	1.59	1.91
7	Pt-3-*O*-(6-ac)-glc	0.78	1.21	2.20	3.13	2.92	2.62	2.97	2.87	2.75	2.58	2.79	2.22	2.09	2.65	2.72	2.11	2.09	2.92	2.87	2.87	2.06	2.72	2.77
8	Pn-3-*O*-(6-ac)-glc	0.98	1.24	2.07	2.34	2.34	2.19	2.80	2.76	2.70	2.55	2.67	2.31	2.13	2.56	2.61	2.08	2.08	2.76	2.81	2.82	2.65	2.64	2.65
9	Mv-3-*O*-(6-ac)-glc	3.34	3.94	6.15	9.47	9.17	8.62	9.22	8.89	8.54	8.31	8.44	7.75	7.08	7.93	7.87	7.22	6.97	7.39	7.00	6.67	6.02	6.29	6.62
10	Mv-3-*O*-(6-caff)-glc	0.33	0.49	1.19	1.86	1.87	1.73	2.08	2.08	2.12	2.02	2.35	1.94	1.89	2.43	2.38	1.79	1.77	2.53	2.55	2.55	2.34	2.38	2.41
11	Pt-3-*O*-(6-*p*-coum)-glc	0.62	0.87	1.87	3.22	3.18	3.00	3.22	3.21	3.07	2.95	3.06	2.68	2.39	2.72	2.70	2.19	2.14	2.75	2.64	2.62	2.30	2.42	2.45
12	Pn-3-*O*-(6-*p*-coum)-glc	0.95	1.14	2.17	3.27	16.88	16.34	17.20	17.17	16.34	15.74	4.10	14.75	13.36	14.82	13.81	2.09	2.04	12.93	13.22	13.15	3.51	12.16	10.24
13	Mv-3-*O*-(6-*p*-coum)-glc	3.37	4.20	7.69	11.58	-	-	-	-	-	-	11.86	-	-	-	-	8.71	8.24	-	-	-	8.27	-	-

Tank 11

#	Time (days)	0	1	2	4	5	6	7	8	11	12	13	14	15	19	21	25	28	32	35	39	42	46	60
1	Dp-3-*O*-glc	17.16	16.62	18.98	25.54	25.92	24.81	21.64	26.95	20.00	19.59	18.87	19.92	18.81	17.81	16.57	15.49	15.54	14.53	13.60	11.87	10.80	11.65	12.65
2	Cy-3-*O*-glc	8.15	4.51	2.12	2.70	2.78	2.71	2.62	2.77	2.36	2.31	2.31	2.38	2.22	2.04	1.79	1.92	1.77	1.91	2.03	1.72	1.65	1.88	1.80
3	Pt-3-*O*-glc	13.63	12.94	17.11	25.87	27.44	26.85	23.93	29.04	24.90	24.68	24.20	25.43	23.80	23.13	21.01	20.02	19.52	18.55	17.54	15.60	14.22	15.14	16.37
4	Pn-3-*O*-glc	21.66	17.37	11.72	11.39	11.80	11.65	11.02	11.82	10.54	10.02	9.83	10.09	9.48	8.60	7.88	8.07	7.76	8.45	9.08	8.13	8.10	8.55	7.30
5	Mv-3-*O*-glc	54.25	52.81	66.30	95.65	100.10	100.03	95.74	106.72	98.96	98.04	97.03	100.58	94.26	93.72	88.06	83.06	80.65	74.38	71.80	65.15	60.27	61.74	66.24
6	Dp-3-*O*-(6-ac)-glc	0.73	0.95	1.66	2.86	2.74	2.62	2.34	2.65	2.16	1.82	2.16	2.18	2.16	1.53	0.93	2.06	0.69	1.93	1.84	0.39	0.38	1.50	1.85
7	Pt-3-*O*-(6-ac)-glc	0.91	1.32	2.06	3.05	2.88	2.83	2.74	2.98	2.74	2.53	2.75	2.82	2.72	2.41	2.00	2.76	1.95	2.72	2.75	2.20	2.09	2.02	2.62
8	Pn-3-*O*-(6-ac)-glc	1.16	1.36	1.68	2.27	2.69	2.72	2.68	2.85	2.77	2.57	2.71	2.75	2.65	2.26	2.02	2.66	2.02	2.72	2.94	2.32	2.23	2.66	2.60
9	Mv-3-*O*-(6-ac)-glc	3.31	4.12	6.11	9.18	8.99	8.88	8.31	9.38	8.47	8.20	8.24	8.50	8.14	7.70	7.14	7.60	6.62	6.94	6.58	6.16	6.35	5.93	7.30
10	Mv-3-*O*-(6-caff)-glc	0.37	0.58	1.08	1.80	1.83	1.87	1.89	2.15	2.09	1.97	2.16	2.26	2.22	2.09	1.72	2.40	1.69	2.41	2.18	2.01	1.87	2.06	2.27
11	Pt-3-*O*-(6-*p*-coum)-glc	0.64	0.97	1.82	3.09	3.17	3.17	2.89	3.50	3.05	2.94	2.97	3.10	2.95	2.59	2.19	2.70	2.09	2.68	2.58	2.33	2.17	2.39	2.37
12	Pn-3-*O*-(6-*p*-coum)-glc	0.81	5.69	9.55	3.32	16.92	17.17	16.01	18.23	16.58	15.98	4.17	16.41	16.28	13.20	11.33	2.83	2.27	13.52	14.20	13.01	12.38	9.34	10.68
13	Mv-3-*O*-(6-*p*-coum)-glc	2.71	-	-	11.09	-	-	-	-	-	-	11.67	-	-	-	-	10.62	8.29	-	-	-	-	-	-

Tank 12

#	Time (days)	0	1	2	4	5	6	7	8	11	12	13	14	15	19	21	25	28	32	35	39	42	46	60
1	Dp-3-*O*-glc	16.85	18.02	19.39	25.14	25.08	23.16	25.30	26.50	20.39	20.06	19.08	18.85	20.19	17.89	17.79	16.12	24.24	14.91	13.09	11.93	12.02	12.19	13.31
2	Cy-3-*O*-glc	7.99	4.56	2.10	2.58	2.75	2.55	2.72	2.74	2.39	2.32	1.94	2.30	2.37	2.16	1.97	1.74	3.62	1.98	1.96	1.95	1.96	1.84	1.90
3	Pt-3-*O*-glc	12.98	14.05	17.37	25.54	26.70	25.39	27.49	28.74	25.62	25.22	24.12	24.36	26.21	23.05	22.71	20.49	21.77	19.19	16.99	15.86	15.84	15.68	16.94
4	Pn-3-*O*-glc	20.40	16.64	11.84	10.91	11.32	10.97	11.64	11.53	10.19	9.95	8.63	9.63	9.86	9.13	8.31	7.44	14.79	8.32	8.36	8.63	8.49	8.04	7.37
5	Mv-3-*O*-glc	53.33	55.26	66.37	94.98	99.43	97.11	104.34	106.22	100.50	100.06	96.76	97.53	102.52	93.28	93.23	84.30	75.36	77.59	68.71	64.42	64.14	62.43	66.03
6	Dp-3-*O*-(6-ac)-glc	0.40	0.88	1.01	2.71	2.63	2.18	2.66	2.63	2.21	1.89	0.84	2.17	2.28	2.14	1.50	0.81	1.73	1.96	1.80	1.53	1.75	1.57	1.93
7	Pt-3-*O*-(6-ac)-glc	0.82	1.33	1.65	3.04	2.84	2.54	2.93	2.96	2.79	2.62	2.31	2.73	2.90	2.77	2.43	2.08	3.13	2.92	2.13	2.09	2.73	2.68	2.82
8	Pn-3-*O*-(6-ac)-glc	0.99	1.29	1.32	2.21	2.21	2.43	2.74	2.77	2.69	2.53	2.31	2.63	2.69	2.66	2.30	1.98	3.02	2.65	2.50	2.80	2.76	2.56	2.70
9	Mv-3-*O*-(6-ac)-glc	3.45	4.07	5.10	9.01	8.68	8.33	9.12	9.20	8.50	8.31	8.12	8.23	8.68	8.07	7.84	7.08	7.57	7.39	6.73	6.13	6.20	6.18	7.68
10	Mv-3-*O*-(6-caff)-glc	0.37	0.57	0.66	1.79	1.82	1.68	2.06	2.15	2.15	2.04	2.08	2.31	2.48	2.39	2.10	1.76	2.52	2.53	2.44	2.22	2.37	2.30	2.50
11	Pt-3-*O*-(6-*p*-coum)-glc	0.72	0.97	1.23	3.08	3.09	2.89	3.25	3.44	3.09	2.97	2.89	2.99	3.16	2.87	2.61	2.23	3.00	2.79	2.55	2.51	2.48	2.47	2.60
12	Pn-3-*O*-(6-*p*-coum)-glc	1.15	1.12	5.53	13.98	16.21	15.91	17.06	17.73	16.18	15.82	3.13	3.92	16.37	3.02	13.12	2.04	2.44	13.68	3.70	3.80	13.18	12.12	11.01
13	Mv-3-*O*-(6-*p*-coum)-glc	3.90	4.22	-	-	-	-	-	-	-	-	11.69	12.74	-	10.85	-	8.59	10.75	-	8.96	8.83	-	-	-

continued

Table S8. Anthocyanin conc. determined by HPLC-DAD in red wine samples from Laguardia 2019, expressed in mg of Mv-3-*O*-glc equiv./L.

Tank 13

#	Time (days)	0	1	2	4	5	6	7	8	11	12	13	14	15	19	21	25	28	32	35	39	42	46	60
1	Dp-3-*O*-glc	18.22	18.20	26.38	34.42	30.92	30.56	31.97	28.64	30.02	29.47	28.61	26.86	28.56	30.22	29.08	24.98	28.01	25.33	23.83	22.70	22.32	19.30	16.71
2	Cy-3-*O*-glc	8.18	4.96	3.73	4.66	4.18	5.00	5.15	4.03	4.08	4.81	3.95	3.85	4.73	5.08	4.84	3.42	3.96	3.70	4.08	4.04	3.97	3.55	3.19
3	Pt-3-*O*-glc	14.09	14.00	21.45	29.33	28.37	28.03	29.12	26.47	27.85	27.23	26.58	25.17	26.32	27.82	26.67	22.73	25.32	22.89	21.36	20.47	20.03	17.36	14.65
4	Pn-3-*O*-glc	21.93	17.27	17.86	19.18	18.93	18.46	19.09	17.96	18.32	18.21	17.73	17.15	17.71	19.10	17.13	14.69	16.38	15.16	15.74	13.75	13.56	11.93	9.98
5	Mv-3-*O*-glc	56.89	53.15	79.92	103.60	99.02	97.73	101.20	94.26	96.30	94.04	93.39	88.62	93.05	95.88	93.63	81.54	85.94	78.90	72.81	70.07	67.68	59.20	48.04
6	Dp-3-*O*-(6-ac)-glc	0.79	0.91	1.22	2.75	2.83	2.06	2.31	2.48	2.23	1.70	1.78	2.04	1.80	2.24	1.71	0.83	1.89	1.85	1.75	1.85	1.78	1.72	1.61
7	Pt-3-*O*-(6-ac)-glc	1.02	1.33	2.20	3.40	3.03	2.75	3.06	2.91	2.94	2.73	2.65	2.80	2.64	3.10	2.90	2.32	3.30	3.39	3.32	3.48	3.54	3.41	3.53
8	Pn-3-*O*-(6-ac)-glc	1.20	0.99	1.76	2.62	2.55	2.40	2.84	2.77	2.84	2.68	2.58	2.76	2.58	2.92	2.78	2.26	3.08	3.26	3.22	3.31	2.97	2.80	2.80
9	Mv-3-*O*-(6-ac)-glc	3.76	3.55	7.13	10.18	9.45	9.02	9.65	8.95	9.17	8.80	8.59	8.42	8.40	9.05	8.69	7.46	8.51	8.15	7.70	7.73	7.58	6.85	6.33
10	Mv-3-*O*-(6-caff)-glc	0.43	0.49	1.15	2.23	2.04	1.89	2.22	2.16	2.31	2.15	2.09	2.28	2.14	2.57	2.37	1.83	2.70	2.79	2.79	2.88	2.94	2.85	2.98
11	Pt-3-*O*-(6-*p*-coum)-glc	0.80	0.76	2.25	3.83	3.57	3.37	3.73	3.46	3.64	3.46	3.28	3.32	3.22	3.57	3.27	2.62	3.39	3.32	3.20	3.20	3.19	2.95	2.88
12	Pn-3-*O*-(6-*p*-coum)-glc	0.98	0.68	2.04	17.22	3.72	16.98	18.36	17.20	17.77	3.66	3.42	3.56	15.71	3.50	2.81	2.20	2.69	2.59	2.41	12.90	12.56	11.43	1.90
13	Mv-3-*O*-(6-*p*-coum)-glc	3.24	2.40	8.79	-	14.03	-	-	-	-	13.50	12.81	12.57	-	12.96	12.85	9.90	12.11	11.82	11.02	-	-	-	8.18

Tank 14

#	Time (days)	0	1	2	4	5	6	7	8	11	12	13	14	15	19	21	25	28	32	35	39	42	46	60
1	Dp-3-*O*-glc	19.47	21.57	25.40	34.95	34.70	34.43	36.01	29.51	27.29	27.88	29.99	30.66	29.35	28.61	25.08	26.97	27.00	26.57	22.49	22.67	21.46	21.74	17.81
2	Cy-3-*O*-glc	8.73	5.75	3.68	4.84	5.62	5.63	4.71	4.24	4.70	4.86	4.29	4.29	5.11	4.74	3.56	3.79	4.19	4.86	4.09	4.06	3.96	3.90	3.36
3	Pt-3-*O*-glc	14.90	16.73	20.63	29.53	31.14	30.91	31.98	27.04	24.93	25.79	27.76	27.83	26.89	25.85	22.96	24.12	23.95	23.74	20.18	20.25	19.07	19.18	15.35
4	Pn-3-*O*-glc	22.57	20.32	16.71	19.31	20.64	20.59	20.82	18.42	17.52	18.08	18.73	18.84	18.53	17.26	15.99	15.73	16.00	15.72	14.00	13.78	13.87	12.96	11.11
5	Mv-3-*O*-glc	58.23	63.39	76.43	102.05	105.80	104.54	106.57	92.60	87.68	89.11	96.06	92.58	93.46	89.75	82.09	83.93	79.41	78.90	68.57	67.71	63.78	62.50	48.14
6	Dp-3-*O*-(6-ac)-glc	0.88	1.02	1.21	2.67	2.38	2.40	2.23	2.46	1.64	1.67	2.23	2.18	1.91	1.02	0.90	0.91	1.90	1.87	1.79	1.81	1.75	1.86	1.69
7	Pt-3-*O*-(6-ac)-glc	1.16	1.67	2.20	3.36	2.98	3.11	3.02	2.90	2.64	2.69	2.95	2.90	2.93	2.29	2.19	2.48	3.40	3.48	3.30	3.51	3.58	3.77	2.88
8	Pn-3-*O*-(6-ac)-glc	1.23	1.51	1.76	2.60	2.76	2.94	2.78	2.77	2.63	2.70	2.87	2.82	2.86	2.23	2.17	2.39	2.86	3.26	2.84	3.36	2.95	2.96	2.96
9	Mv-3-*O*-(6-ac)-glc	3.87	5.08	7.09	9.90	9.96	9.93	10.04	8.74	8.42	8.43	8.89	8.66	8.69	7.83	7.28	7.71	8.11	8.19	7.29	7.52	7.33	7.43	6.76
10	Mv-3-*O*-(6-caff)-glc	0.45	0.72	1.19	2.16	1.94	2.02	2.13	2.12	2.01	2.08	2.32	2.31	2.34	1.78	1.71	1.88	2.69	2.84	2.68	2.90	2.95	3.11	3.37
11	Pt-3-*O*-(6-*p*-coum)-glc	0.87	1.48	2.31	3.73	3.74	3.83	3.85	3.40	3.24	3.31	3.53	3.48	3.43	2.80	2.52	2.72	3.29	3.37	2.98	3.16	3.11	3.24	3.18
12	Pn-3-*O*-(6-*p*-coum)-glc	1.14	7.30	11.37	16.33	3.84	3.97	3.90	3.61	3.52	3.63	3.78	3.69	3.63	2.71	2.22	2.29	2.55	2.60	2.19	12.63	2.20	11.89	2.05
13	Mv-3-*O*-(6-*p*-coum)-glc	3.48	-	-	-	14.91	14.93	15.03	12.90	12.76	12.70	13.03	12.61	12.61	11.11	9.77	9.87	11.42	11.51	9.84	-	9.67	-	8.46

Tank 15

#	Time (days)	0	1	2	4	5	6	7	8	11	12	13	14	15	19	21	25	28	32	35	39	42	46	60
1	Dp-3-*O*-glc	20.22	22.25	24.93	32.22	37.02	32.96	35.62	29.80	31.79	30.19	28.36	30.69	31.82	32.15	27.03	29.72	24.00	27.56	24.63	20.72	21.85	20.71	19.02
2	Cy-3-*O*-glc	8.94	6.77	3.96	4.53	5.94	5.60	5.82	4.40	5.27	5.27	4.98	5.26	5.53	5.20	4.54	4.40	3.73	4.65	4.45	3.92	4.08	3.86	3.58
3	Pt-3-*O*-glc	15.22	16.87	19.94	27.36	32.46	29.51	31.51	26.90	28.65	27.39	26.08	27.63	28.65	28.94	24.15	26.48	21.30	24.11	21.73	18.40	19.11	18.14	16.11
4	Pn-3-*O*-glc	22.03	20.72	16.62	18.36	21.17	19.94	20.80	18.83	19.33	18.95	18.27	18.99	19.44	19.10	16.62	17.47	14.68	15.94	14.79	12.92	13.29	13.02	11.00
5	Mv-3-*O*-glc	57.74	61.61	71.73	94.25	107.24	99.86	104.27	93.31	95.36	91.16	90.13	91.92	95.95	95.50	84.32	87.64	72.39	78.11	71.38	61.41	61.99	58.12	48.99
6	Dp-3-*O*-(6-ac)-glc	0.93	1.13	0.99	2.38	2.43	2.35	2.41	2.23	1.97	1.91	1.89	1.72	2.00	2.07	0.91	2.03	1.76	1.93	1.87	1.72	1.80	1.79	1.76
7	Pt-3-*O*-(6-ac)-glc	1.17	1.73	2.19	3.37	3.06	3.02	3.21	2.81	2.84	2.94	2.73	2.80	3.08	3.20	2.27	3.49	3.19	3.62	3.59	3.41	3.64	3.74	3.04
8	Pn-3-*O*-(6-ac)-glc	1.21	1.38	1.71	2.57	2.53	2.56	2.64	2.65	2.69	2.83	2.62	2.69	2.92	2.70	2.19	2.86	2.69	2.96	2.98	2.87	2.96	2.97	3.17
9	Mv-3-*O*-(6-ac)-glc	3.85	4.85	6.60	9.34	10.13	9.45	9.98	8.77	8.95	8.71	8.29	8.51	9.00	9.04	7.42	8.78	7.43	8.25	7.80	6.87	7.13	7.05	6.86
10	Mv-3-*O*-(6-caff)-glc	0.46	0.79	1.12	2.14	1.96	2.04	2.24	1.97	2.10	2.22	2.05	2.14	2.40	2.54	1.70	2.77	2.50	2.91	2.88	2.76	2.94	3.07	3.47
11	Pt-3-*O*-(6-*p*-coum)-glc	0.93	1.45	2.15	3.59	3.87	3.66	3.91	3.36	3.52	3.51	3.21	3.32	3.59	3.63	2.53	3.53	2.97	3.42	3.26	2.90	3.07	3.15	3.34
12	Pn-3-*O*-(6-*p*-coum)-glc	1.13	6.66	1.89	15.13	18.68	17.58	3.84	16.42	3.57	16.43	3.34	16.43	3.63	3.49	2.18	2.73	2.33	2.53	2.34	11.20	11.39	11.42	2.10
13	Mv-3-*O*-(6-*p*-coum)-glc	3.56	-	7.88	-	-	-	14.62	-	13.16	-	12.06	-	12.86	12.49	9.77	12.38	10.28	11.23	10.80	-	-	-	8.67

Tank 16

#	Time (days)	0	1	2	4	5	6	7	8	11	12	13	14	15	19	21	25	28	32	35	39	42	46	60
1	Dp-3-*O*-glc	20.17	21.64	28.99	31.46	36.45	36.07	36.14	31.37	30.44	31.14	30.50	30.41	31.42	31.49	28.48	28.68	13.53	28.01	26.08	24.26	22.30	19.76	18.81
2	Cy-3-*O*-glc	9.12	6.54	4.64	4.55	6.10	5.92	5.93	4.68	4.51	4.60	5.44	5.43	5.16	5.59	4.11	4.12	1.59	4.76	4.71	4.47	4.22	3.86	3.62
3	Pt-3-*O*-glc	15.20	16.49	23.01	26.57	32.17	31.78	31.72	28.10	27.46	28.08	27.68	27.24	28.36	28.14	25.40	25.03	17.80	24.61	22.98	21.21	19.54	17.34	15.95
4	Pn-3-*O*-glc	22.26	20.48	19.65	17.95	21.21	20.84	20.78	19.34	18.93	19.25	18.97	18.91	19.29	18.63	17.39	16.06	5.53	16.08	15.44	14.34	13.39	12.20	10.94
5	Mv-3-*O*-glc	57.96	61.47	80.25	91.87	105.44	103.87	105.10	96.36	92.62	93.26	94.32	90.77	95.46	92.75	86.84	83.34	74.00	78.91	74.64	68.70	63.19	56.70	48.92
6	Dp-3-*O*-(6-ac)-glc	1.01	0.98	1.86	2.40	2.99	2.41	2.50	2.05	2.21	1.80	2.26	1.94	2.04	1.99	0.97	0.91	0.55	1.94	1.93	1.94	1.82	1.77	1.75
7	Pt-3-*O*-(6-ac)-glc	1.18	1.71	2.96	3.31	3.21	3.12	3.07	2.89	2.94	2.86	3.04	2.97	2.91	3.13	2.33	2.50	2.10	3.62	3.69	3.71	3.65	3.60	3.96
8	Pn-3-*O*-(6-ac)-glc	1.24	1.39	2.24	2.51	2.62	2.59	2.78	2.70	2.80	2.75	2.87	2.85	2.75	2.90	2.21	2.15	1.90	2.98	3.13	3.08	3.04	2.87	3.07
9	Mv-3-*O*-(6-ac)-glc	4.05	5.00	7.82	9.08	10.08	9.77	9.87	8.99	8.86	8.81	8.91	8.57	8.74	8.74	7.59	7.64	5.91	8.31	8.06	7.81	7.27	6.75	6.68
10	Mv-3-*O*-(6-caff)-glc	0.48	0.79	1.79	2.12	2.11	2.09	2.11	2.02	2.21	2.16	2.33	2.29	2.23	2.48	1.76	1.89	2.02	2.90	2.94	3.02	2.93	2.93	3.31
11	Pt-3-*O*-(6-*p*-coum)-glc	1.14	1.50	2.93	3.50	3.90	3.82	3.74	3.41	3.49	3.48	3.54	3.39	3.40	3.51	2.66	2.76	2.37	3.49	3.36	3.30	3.07	2.96	3.15
12	Pn-3-*O*-(6-*p*-coum)-glc	1.29	7.19	13.18	2.85	3.82	18.14	17.56	16.37	16.45	3.63	16.45	3.51	3.36	16.56	2.25	2.21	11.41	2.55	13.29	12.82	11.60	10.92	1.99
13	Mv-3-*O*-(6-*p*-coum)-glc	4.49	-	-	12.00	14.69	-	-	-	-	12.95	-	13.35	12.50	-	10.12	9.75	-	11.53	-	-	-	-	8.37

Tank 17

#	Time (days)	0	1	2	4	5	6	7	8	11	12	13	14	15	19	21	25	28	32	35	39	42	46	60
1	Dp-3-*O*-glc	19.66	15.93	21.56	26.00	27.18	25.60	27.93	24.68	20.22	21.30	18.96	18.45	18.38	18.01	17.00	16.84	15.47	14.76	12.38	11.63	10.03	11.55	12.28
2	Cy-3-*O*-glc	8.82	3.58	2.06	2.31	2.72	2.64	2.79	2.63	2.32	2.34	1.98	2.24	1.94	2.11	1.96	1.99	1.98	1.99	2.06	2.03	1.67	1.93	1.59
3	Pt-3-*O*-glc	14.75	12.79	19.57	26.68	29.20	28.28	30.44	27.63	25.97	27.10	24.71	25.17	24.89	24.11	22.57	22.33	20.71	19.66	17.81	15.83	13.92	15.74	16.14
4	Pn-3-*O*-glc	14.79	10.43	8.00	7.76	9.00	8.80	9.15	8.57	7.66	7.75	6.58	7.32	6.54	6.83	6.51	6.56	6.65	7.11	7.63	7.87	6.95	7.29	5.52
5	Mv-3-*O*-glc	52.98	48.71	70.58	95.14	102.80	102.50	108.59	102.86	99.64	101.19	95.94	97.39	96.35	94.02	89.90	87.88	82.12	76.31	69.10	63.13	57.93	62.81	64.40
6	Dp-3-*O*-(6-ac)-glc	0.42	0.76	1.64	1.55	2.70	2.23	2.63	2.42	1.83	1.88	0.79	1.81	0.81	2.11	2.05	2.10	1.66	1.85	1.60	1.41	0.31	1.50	0.44
7	Pt-3-*O*-(6-ac)-glc	0.72	1.22	2.21	2.24	2.82	2.55	2.96	2.77	2.50	2.54	2.20	2.48	2.22	2.70	2.69	2.87	2.61	2.23	2.72	2.66	1.58	2.58	2.14
8	Pn-3-*O*-(6-ac)-glc	0.51	0.68	1.26	1.22	1.66	1.57	1.77	1.78	1.72	1.76	1.59	1.74	1.57	1.87	1.85	2.16	2.08	2.15	2.20	2.05	1.79	2.05	1.82
9	Mv-3-*O*-(6-ac)-glc	2.57	3.16	5.73	7.75	8.39	7.90	8.78	8.08	7.54	7.83	7.22	7.09	7.20	7.26	7.29	7.49	6.66	6.87	6.30	6.82	5.21	5.81	5.67
10	Mv-3-*O*-(6-caff)-glc	0.25	0.50	1.19	1.23	1.86	1.72	2.14	2.03	1.97	2.03	1.94	1.99	2.08	2.39	2.40	2.53	2.29	2.33	2.31	2.18	1.87	2.18	2.05
11	Pt-3-*O*-(6-*p*-coum)-glc	0.55	0.88	2.11	2.80	3.44	3.10	3.64	3.37	3.08	3.29	2.97	2.84	2.88	2.98	2.93	3.02	2.70	2.92	2.73	2.64	2.24	2.53	2.31
12	Pn-3-*O*-(6-*p*-coum)-glc	2.70	4.16	1.47	12.10	16.03	14.99	17.04	16.09	14.99	16.14	15.14	14.83	14.80	13.79	13.50	13.47	12.48	13.90	13.79	13.34	12.02	12.83	9.89
13	Mv-3-*O*-(6-*p*-coum)-glc	-	-	9.17	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Tank 18

#	Time (days)	0	1	2	4	5	6	7	8	11	12	13	14	15	19	21	25	28	32	35	39	42	46	60
1	Dp-3-*O*-glc	21.19	17.33	22.06	26.99	25.96	24.88	27.04	24.63	20.40	18.41	19.68	17.68	18.62	17.91	16.59	16.89	15.87	14.35	12.53	11.92	10.88	11.16	13.04
2	Cy-3-*O*-glc	9.41	3.72	2.06	2.45	2.70	2.62	2.74	2.67	2.32	2.01	2.34	1.95	2.26	2.11	2.00	2.01	1.83	1.99	1.75	1.99	1.60	1.56	1.84
3	Pt-3-*O*-glc	15.87	13.95	19.84	27.40	28.14	27.57	29.72	27.61	25.76	23.89	25.75	23.53	24.80	23.83	22.08	22.26	20.36	19.29	16.75	16.32	14.61	14.98	17.05
4	Pn-3-*O*-glc	15.73	11.16	8.08	8.09	8.98	8.69	9.28	8.83	7.87	6.88	7.68	6.56	7.44	6.84	6.55	6.66	7.69	6.93	6.64	7.50	6.47	6.31	6.00
5	Mv-3-*O*-glc	56.76	52.16	71.74	96.42	100.32	98.73	106.69	102.96	98.18	93.97	98.52	93.46	95.91	92.26	89.21	87.27	83.63	75.49	67.61	65.67	60.01	60.84	65.99
6	Dp-3-*O*-(6-ac)-glc	0.47	0.81	1.25	1.55	2.40	2.50	2.55	2.44	2.05	0.79	2.15	0.74	2.09	2.07	1.98	2.10	0.72	1.89	0.41	1.50	0.36	0.37	1.61
7	Pt-3-*O*-(6-ac)-glc	0.79	1.32	1.91	2.32	2.61	2.70	2.95	2.79	2.66	2.13	2.72	2.14	2.69	2.70	2.69	2.87	2.07	2.79	2.23	2.69	2.05	2.06	2.67
8	Pn-3-*O*-(6-ac)-glc	0.58	0.73	1.03	1.24	1.58	1.62	1.76	1.83	1.80	1.57	1.89	1.62	1.86	1.89	2.19	1.99	2.06	2.20	1.90	2.22	1.79	1.76	2.19
9	Mv-3-*O*-(6-ac)-glc	3.04	3.52	5.49	8.04	8.05	8.03	8.83	8.10	7.72	7.02	7.70	6.93	7.50	7.30	7.19	7.50	6.90	6.83	6.03	6.95	5.31	6.09	5.99
10	Mv-3-*O*-(6-caff)-glc	0.32	0.57	0.91	1.31	1.73	1.90	2.19	2.09	2.13	1.85	2.23	1.93	2.26	2.41	2.41	2.56	1.81	2.31	2.14	2.41	1.86	1.92	2.36
11	Pt-3-*O*-(6-*p*-coum)-glc	0.78	1.11	1.85	2.95	3.18	3.28	3.67	3.38	3.22	2.85	3.22	2.82	3.12	3.04	2.88	3.10	2.22	2.90	2.51	2.66	2.25	2.26	2.44
12	Pn-3-*O*-(6-*p*-coum)-glc	4.10	5.20	7.98	12.69	14.99	15.75	17.33	16.16	15.61	15.00	15.29	14.76	15.67	13.98	13.51	13.85	2.20	13.39	12.74	13.44	11.72	11.60	10.03
13	Mv-3-*O*-(6-*p*-coum)-glc	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	8.45	-	-	-	-	-	-

continued

Table S8. Anthocyanin conc. determined by HPLC-DAD in red wine samples from Laguardia 2019, expressed in mg of Mv-3-*O*-glc equiv./L.

Tank 19

#	Time (days)	0	1	2	4	5	6	7	8	11	12	13	14	15	19	21	25	28	32	35	39	42	46	60
1	Dp-3-*O*-glc	21.80	22.78	22.30	27.51	29.44	25.47	27.19	25.42	20.63	20.62	20.45	18.55	18.31	18.12	17.40	17.16	16.51	15.29	13.59	12.09	10.57	11.37	13.39
2	Cy-3-*O*-glc	9.65	5.37	2.33	2.42	3.02	2.70	2.80	2.77	2.36	2.44	2.35	2.22	2.06	2.07	1.84	2.03	2.11	2.09	2.14	2.06	1.73	1.94	1.82
3	Pt-3-*O*-glc	16.20	17.73	19.65	27.43	31.02	27.69	29.37	28.12	25.89	26.33	26.09	24.39	23.69	23.95	22.32	22.23	21.52	20.05	18.11	16.41	14.06	15.45	17.20
4	Pn-3-*O*-glc	16.05	14.28	8.99	8.47	10.15	9.20	9.52	9.32	8.20	8.40	7.88	7.41	6.87	6.88	6.31	6.88	7.18	7.35	7.62	7.79	7.00	7.24	6.09
5	Mv-3-*O*-glc	56.43	63.65	69.36	94.58	104.85	97.47	103.92	102.69	96.66	97.78	95.34	92.47	89.63	90.65	86.58	83.94	82.01	75.60	69.50	63.10	56.16	59.57	63.73
6	Dp-3-*O*-(6-ac)-glc	0.47	0.92	1.48	1.50	2.82	2.49	2.58	2.49	1.83	2.11	2.15	1.50	1.08	1.48	0.90	2.07	2.03	1.94	1.60	1.67	0.32	1.39	1.61
7	Pt-3-*O*-(6-ac)-glc	0.82	1.55	2.14	2.29	2.98	2.74	2.93	2.86	2.52	2.74	2.74	2.26	2.02	2.34	2.03	2.89	2.88	2.87	2.79	2.74	2.09	2.57	2.62
8	Pn-3-*O*-(6-ac)-glc	0.62	0.87	1.26	1.27	1.78	1.71	1.85	1.87	1.75	1.92	1.87	1.58	1.37	1.64	1.44	1.92	2.41	2.20	2.13	2.16	1.82	2.06	2.22
9	Mv-3-*O*-(6-ac)-glc	3.11	3.60	5.67	7.88	8.76	7.95	8.49	8.09	7.47	7.73	7.68	6.84	6.56	6.88	6.66	7.43	7.01	7.01	6.53	7.04	5.27	5.73	5.94
10	Mv-3-*O*-(6-caff)-glc	0.36	0.59	1.16	1.26	1.95	1.87	2.10	2.07	1.95	2.15	2.19	1.82	1.66	2.06	1.76	2.52	2.50	2.35	2.33	2.18	1.87	2.18	2.30
11	Pt-3-*O*-(6-*p*-coum)-glc	0.88	0.92	2.08	2.88	3.57	3.28	3.55	3.36	3.07	3.29	3.29	2.74	2.51	2.74	2.45	3.08	2.96	2.98	2.75	2.66	2.27	2.50	2.48
12	Pn-3-*O*-(6-*p*-coum)-glc	4.20	3.38	8.95	12.23	16.25	15.48	16.62	15.91	3.18	16.48	16.07	13.63	11.75	12.57	10.98	13.46	13.52	13.56	13.63	13.32	11.89	12.51	9.86
13	Mv-3-*O*-(6-*p*-coum)-glc	-	-	-	-	-	-	-	-	11.72	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Tank 20

#	Time (days)	0	1	2	4	5	6	7	8	11	12	13	14	15	19	21	25	28	32	35	39	42	46	60
1	Dp-3-*O*-glc	22.88	17.74	23.17	27.75	27.23	27.49	26.56	25.56	21.76	20.12	20.00	19.62	18.97	18.60	17.22	16.98	3.18	15.71	14.31	12.78	10.75	11.39	12.33
2	Cy-3-*O*-glc	10.58	4.51	2.34	2.56	2.81	2.72	2.71	2.69	2.41	2.35	2.34	2.35	2.09	2.07	2.03	1.99	16.99	2.02	2.09	2.01	1.57	1.89	1.79
3	Pt-3-*O*-glc	16.97	13.56	20.67	27.53	29.10	29.44	28.88	28.13	27.21	25.57	25.87	25.65	24.68	24.28	22.57	21.99	2.06	20.53	18.81	16.99	14.06	15.23	16.06
4	Pn-3-*O*-glc	16.61	11.79	9.50	8.59	9.63	9.37	9.31	9.04	8.16	7.89	7.81	7.85	7.11	6.96	6.82	6.80	21.92	7.04	7.51	7.25	6.20	6.95	6.29
5	Mv-3-*O*-glc	59.03	50.84	74.40	93.81	103.81	103.62	103.74	101.55	99.24	95.21	96.19	96.35	93.05	91.96	87.38	84.82	6.93	76.80	71.57	64.33	55.47	59.46	60.82
6	Dp-3-*O*-(6-ac)-glc	0.50	0.89	1.52	1.65	2.68	2.62	2.55	2.49	2.15	2.09	2.13	2.13	1.13	1.50	2.04	2.05	82.84	1.98	1.83	1.74	0.34	1.53	1.52
7	Pt-3-*O*-(6-ac)-glc	0.84	1.34	2.23	2.31	2.83	2.83	2.88	2.83	2.75	2.64	2.72	2.70	2.06	2.36	2.72	2.84	2.02	2.87	2.84	2.70	2.03	2.55	2.57
8	Pn-3-*O*-(6-ac)-glc	0.64	0.77	1.32	1.26	1.66	1.76	1.82	1.85	1.86	1.85	1.87	1.90	1.42	1.61	1.94	2.02	2.88	2.19	2.29	2.15	1.68	2.06	2.16
9	Mv-3-*O*-(6-ac)-glc	3.28	3.20	5.78	7.69	8.15	8.36	8.39	8.03	7.92	7.51	7.60	7.47	6.80	6.98	7.12	7.14	2.18	7.06	6.64	6.15	5.82	5.56	6.56
10	Mv-3-*O*-(6-caff)-glc	0.37	0.54	1.19	1.22	1.79	1.90	2.01	1.99	2.09	2.02	2.11	2.13	1.64	2.01	2.32	2.43	7.05	2.28	2.43	2.11	1.78	2.04	2.25
11	Pt-3-*O*-(6-*p*-coum)-glc	0.90	0.90	2.06	2.81	3.25	3.49	3.48	3.36	3.37	3.18	3.22	3.14	2.65	2.75	2.89	2.93	2.46	2.97	2.82	2.65	2.17	2.40	2.37
12	Pn-3-*O*-(6-*p*-coum)-glc	4.62	0.64	8.88	11.94	15.15	16.31	16.54	15.85	15.87	16.03	15.08	15.88	12.53	12.88	13.33	13.21	2.96	13.44	13.15	13.02	11.19	12.14	9.77
13	Mv-3-*O*-(6-*p*-coum)-glc	-	3.09	-	-	-	-	-	-	-	-	-	-	-	-	-	-	13.14	-	-	-	-	-	-

Tank 21

#	Time (days)	0	1	2	4	5	6	7	8	11	12	13	14	15	19	21	25	28	32	35	39	42	46	60
1	Dp-3-*O*-glc	23.61	23.82	26.38	38.11	38.97	37.15	29.92	36.69	32.23	32.54	31.12	30.87	31.92	31.73	18.57	27.09	30.14	26.14	26.47	25.16	23.21	22.65	20.52
2	Cy-3-*O*-glc	10.17	6.79	3.90	4.99	5.64	5.77	4.33	6.11	4.85	5.56	4.45	5.05	5.48	4.89	2.99	4.12	4.24	4.57	4.70	4.54	4.27	4.17	3.71
3	Pt-3-*O*-glc	17.47	17.64	21.05	32.28	33.95	32.44	26.86	32.52	28.65	29.09	28.08	27.95	28.48	28.00	17.37	24.21	26.25	22.96	23.33	22.00	20.22	19.77	16.90
4	Pn-3-*O*-glc	16.46	13.66	11.78	14.83	15.94	15.15	13.32	15.49	13.85	14.44	13.54	13.89	14.02	13.11	9.04	12.10	11.93	11.50	11.63	11.14	10.26	9.89	8.51
5	Mv-3-*O*-glc	58.47	58.13	69.86	100.49	104.14	101.17	87.20	100.09	90.12	89.68	89.99	89.55	88.65	87.53	63.17	77.21	80.86	72.01	72.06	67.61	61.95	59.91	48.66
6	Dp-3-*O*-(6-ac)-glc	0.53	1.10	1.27	2.36	2.82	2.09	1.86	2.08	1.15	2.12	1.13	1.66	1.82	0.97	0.68	1.78	0.88	1.77	1.84	1.84	1.72	1.77	1.65
7	Pt-3-*O*-(6-ac)-glc	0.85	1.79	2.17	3.26	3.04	2.73	2.55	2.90	2.24	2.80	2.19	2.68	2.81	2.23	1.80	3.07	2.43	3.25	3.41	3.49	3.39	3.49	3.54
8	Pn-3-*O*-(6-ac)-glc	0.59	0.97	1.27	1.95	1.94	1.72	1.68	1.89	1.54	2.01	1.50	1.93	1.97	1.67	1.46	2.50	1.74	2.35	2.53	2.59	2.50	2.56	2.62
9	Mv-3-*O*-(6-ac)-glc	3.44	4.04	5.46	9.20	9.11	8.46	7.51	8.65	7.54	7.91	7.24	7.62	7.63	7.04	4.96	7.17	6.86	7.09	7.30	7.06	6.56	6.56	6.02
10	Mv-3-*O*-(6-caff)-glc	0.38	0.83	1.21	2.17	2.06	1.69	1.77	2.06	1.63	2.16	1.62	2.09	2.22	1.70	1.31	2.45	1.84	2.61	2.75	2.78	2.71	2.82	2.94
11	Pt-3-*O*-(6-*p*-coum)-glc	1.16	1.42	2.10	4.09	4.12	3.70	3.33	3.94	3.33	3.69	3.16	3.48	3.53	3.02	1.89	3.21	2.86	3.24	3.37	3.25	3.05	3.10	3.00
12	Pn-3-*O*-(6-*p*-coum)-glc	4.90	4.58	7.40	15.51	17.05	15.35	14.15	16.44	14.57	16.11	13.66	15.41	15.19	12.48	8.21	12.73	1.49	12.19	12.41	11.80	10.85	10.60	9.35
13	Mv-3-*O*-(6-*p*-coum)-glc	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	9.06	-	-	-	-	-	-

Tank 22

#	Time (days)	0	1	2	4	5	6	7	8	11	12	13	14	15	19	21	25	28	32	35	39	42	46	60
1	Dp-3-*O*-glc	24.45	23.93	30.51	34.41	40.42	35.70	39.06	34.59	33.15	32.40	34.77	33.41	32.44	31.76	31.92	25.60	30.82	27.15	24.84	21.67	23.54	21.41	18.73
2	Cy-3-*O*-glc	10.27	6.67	4.14	4.64	5.61	4.59	6.08	5.70	4.55	4.57	5.43	4.57	5.53	4.84	4.54	3.89	4.32	4.04	4.41	4.02	4.17	3.88	3.32
3	Pt-3-*O*-glc	17.92	17.65	23.95	30.04	35.27	31.67	34.22	30.83	30.25	29.27	31.85	30.04	29.44	28.55	29.06	23.25	27.20	24.22	22.26	19.34	20.87	18.76	15.35
4	Pn-3-*O*-glc	16.46	13.54	12.47	13.70	15.90	14.45	15.56	14.73	14.13	14.13	14.98	13.70	13.97	12.91	13.37	11.53	12.68	11.17	11.04	9.78	10.15	9.26	7.64
5	Mv-3-*O*-glc	60.95	59.93	78.99	98.66	112.60	103.14	108.46	101.40	98.66	94.75	102.27	97.91	97.32	93.73	95.18	79.02	85.87	77.43	71.59	62.97	65.25	58.41	45.08
6	Dp-3-*O*-(6-ac)-glc	0.57	1.02	1.54	2.39	2.37	2.00	2.40	2.00	1.73	2.11	2.25	1.25	1.74	1.01	1.92	1.74	1.93	1.83	1.79	1.71	1.79	1.77	1.63
7	Pt-3-*O*-(6-ac)-glc	0.85	1.73	2.54	3.06	3.01	2.68	3.11	2.80	2.74	2.85	3.05	2.31	2.80	2.29	3.10	3.12	3.44	3.50	3.52	3.50	3.81	3.85	2.95
8	Pn-3-*O*-(6-ac)-glc	0.57	0.91	1.44	1.79	1.84	1.66	1.95	1.83	1.85	2.04	2.09	1.56	1.93	1.53	2.16	2.15	2.35	2.37	2.44	2.43	2.65	2.62	2.86
9	Mv-3-*O*-(6-ac)-glc	3.34	4.02	6.53	8.46	9.58	8.33	9.26	8.49	8.22	8.05	8.72	7.69	7.93	7.22	7.98	7.08	7.82	7.45	7.10	6.58	7.08	6.77	6.24
10	Mv-3-*O*-(6-caff)-glc	0.35	0.78	1.43	1.98	2.00	1.79	2.25	2.06	2.11	2.24	2.42	1.77	2.23	1.81	2.53	2.50	2.81	2.86	2.88	2.84	3.16	3.19	3.53
11	Pt-3-*O*-(6-*p*-coum)-glc	0.92	1.43	2.62	3.61	4.22	3.58	4.11	3.76	3.73	3.64	4.02	3.29	3.51	3.01	3.48	3.08	3.54	3.35	3.21	2.99	3.36	3.17	3.27
12	Pn-3-*O*-(6-*p*-coum)-glc	3.92	4.64	9.83	2.06	18.09	15.32	17.03	16.34	16.61	16.42	16.58	14.53	15.64	12.69	14.98	12.54	13.46	12.44	11.65	10.72	11.46	10.52	9.49
13	Mv-3-*O*-(6-*p*-coum)-glc	-	-	-	13.30	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Tank 23

#	Time (days)	0	1	2	4	5	6	7	8	11	12	13	14	15	19	21	25	28	32	35	39	42	46	60
1	Dp-3-*O*-glc	23.77	24.51	30.54	42.09	38.29	37.66	40.96	37.38	38.33	38.25	36.85	34.02	37.33	30.77	35.02	30.27	31.26	29.55	26.50	25.66	24.49	18.43	20.44
2	Cy-3-*O*-glc	9.91	6.53	4.77	5.91	5.88	5.34	6.63	5.96	6.40	6.55	6.35	5.69	6.06	5.08	5.68	4.69	4.79	4.59	4.86	4.78	4.59	3.68	3.73
3	Pt-3-*O*-glc	17.15	18.22	24.02	33.92	33.41	32.54	35.02	32.68	33.58	33.61	32.57	30.12	32.89	26.87	31.06	26.60	27.13	25.54	22.99	22.37	21.28	15.28	16.35
4	Pn-3-*O*-glc	16.04	13.62	13.62	16.44	16.47	16.22	16.92	16.39	16.47	16.71	16.09	15.47	16.16	13.46	15.07	13.30	13.62	14.14	12.06	11.69	11.25	8.72	8.49
5	Mv-3-*O*-glc	59.15	60.56	79.23	106.06	105.38	105.11	109.06	104.26	104.48	103.83	102.81	97.64	103.24	88.77	99.03	85.59	84.99	79.28	72.13	69.85	66.00	50.57	46.82
6	Dp-3-*O*-(6-ac)-glc	0.55	1.23	1.83	2.82	2.41	2.26	2.25	2.08	2.25	2.09	2.06	1.94	2.32	0.99	2.04	1.89	1.92	1.90	1.83	1.86	1.83	1.40	1.66
7	Pt-3-*O*-(6-ac)-glc	0.90	1.99	2.74	3.64	3.01	2.84	3.01	2.93	3.03	3.09	3.05	2.95	3.09	2.26	3.25	3.32	3.48	3.62	3.56	3.76	3.81	3.22	2.96
8	Pn-3-*O*-(6-ac)-glc	0.61	1.18	1.67	2.20	1.88	1.78	1.90	1.91	2.07	2.14	2.04	2.06	2.10	1.51	2.20	2.30	2.40	2.46	2.49	2.62	2.66	2.26	2.83
9	Mv-3-*O*-(6-ac)-glc	3.18	4.58	6.67	9.77	8.85	8.80	9.34	8.80	8.81	8.93	8.63	8.07	8.53	6.77	8.43	7.68	7.82	7.66	7.12	7.17	6.96	5.44	6.33
10	Mv-3-*O*-(6-caff)-glc	0.37	1.01	1.68	2.40	2.02	1.79	2.13	2.10	2.32	2.39	2.39	2.30	2.42	1.73	2.64	2.65	2.81	2.93	2.87	3.05	3.10	2.54	3.43
11	Pt-3-*O*-(6-*p*-coum)-glc	0.91	1.79	2.84	4.42	3.94	3.84	4.21	3.96	4.07	4.15	3.96	3.63	3.90	2.78	3.76	3.42	3.56	3.56	3.29	3.33	3.33	2.48	3.21
12	Pn-3-*O*-(6-*p*-coum)-glc	3.45	6.88	11.04	17.78	16.69	16.36	17.68	16.91	16.87	18.27	16.28	16.21	16.72	11.91	15.45	13.50	13.65	13.14	11.96	11.91	11.45	8.16	9.39
13	Mv-3-*O*-(6-*p*-coum)-glc	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Tank 24

#	Time (days)	0	1	2	4	5	6	7	8	11	12	13	14	15	19	21	25	28	32	35	39	42	46	60
1	Dp-3-*O*-glc	19.34	19.97	27.69	30.08	32.83	33.36	31.45	31.22	26.80	25.13	27.17	27.84	23.61	28.19	25.59	25.44	24.65	23.42	22.00	20.82	19.96	18.16	16.33
2	Cy-3-*O*-glc	9.19	7.87	5.60	4.27	5.39	4.52	5.05	5.17	4.48	4.25	3.77	4.51	4.12	4.41	3.54	3.71	3.58	4.30	3.77	3.69	3.51	3.22	2.93
3	Pt-3-*O*-glc	14.82	15.34	20.90	24.37	28.11	28.52	26.87	26.85	23.09	21.83	23.46	23.94	20.88	24.20	21.89	21.77	20.85	19.77	18.57	17.16	16.32	14.75	12.29
4	Pn-3-*O*-glc	14.71	14.11	13.29	12.18	13.98	13.97	13.14	13.39	12.00	11.54	11.72	12.18	10.98	12.04	10.65	10.68	10.00	9.57	9.40	9.04	8.56	7.81	7.21
5	Mv-3-*O*-glc	53.37	52.61	67.17	78.65	88.14	88.53	84.17	84.01	74.39	70.77	73.58	74.49	68.69	73.25	70.45	68.65	64.55	60.88	56.61	53.43	50.22	45.41	37.03
6	Dp-3-*O*-(6-ac)-glc	0.45	0.90	1.68	1.30	2.00	2.18	1.80	1.93	0.92	0.86	0.88	0.81	0.77	1.59	0.71	1.60	1.54	1.54	1.53	1.54	1.50	1.31	1.40
7	Pt-3-*O*-(6-ac)-glc	0.70	1.42	2.69	2.15	2.50	2.65	2.44	2.58	1.89	1.85	1.87	1.87	1.79	2.63	1.93	2.90	2.86	3.01	2.98	3.17	3.19	3.02	2.50
8	Pn-3-*O*-(6-ac)-glc	0.50	0.80	1.68	1.26	1.56	1.68	1.56	1.71	1.30	1.31	1.29	1.33	1.25	1.86	1.36	2.07	2.10	2.20	2.24	2.35	2.32	2.23	2.43
9	Mv-3-*O*-(6-ac)-glc	3.15	3.50	5.85	6.85	7.82	7.87	7.60	7.54	6.50	6.17	6.34	6.45	5.70	6.93	6.11	6.84	6.53	6.45	6.13	6.25	6.07	5.56	5.47
10	Mv-3-*O*-(6-caff)-glc	0.32	0.64	1.67	1.24	1.62	1.65	1.69	1.84	1.33	1.36	1.39	1.41	1.31	2.11	1.44	2.32	2.29	2.44	2.45	2.64	2.68	2.57	3.01
11	Pt-3-*O*-(6-*p*-coum)-glc	0.89	1.23	2.59	2.94	3.60	3.65	3.57	3.57	2.98	2.85	2.95	3.01	2.58	3.40	2.63	3.24	3.11	3.09	3.00	3.12	3.06	2.83	2.98
12	Pn-3-*O*-(6-*p*-coum)-glc	4.13	4.35	8.77	12.03	15.49	15.93	15.92	15.83	13.53	13.06	12.97	13.37	11.55	13.95	10.95	12.63	11.72	11.38	10.66	10.89	10.29	9.20	8.69
13	Mv-3-*O*-(6-*p*-coum)-glc	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Table S9. Results of the chromatic coordinates obtained for wine of Mendavia 2018.

Tank 01

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	39.93	29.47	35.57	61.19	42.02	-5.29	-0.13	42.4
1	54.82	44.31	51.88	72.43	35.35	-4.47	-0.13	35.6
3	34.97	23.19	27.70	55.26	51.40	-4.44	-0.09	51.6
4	34.57	22.66	28.17	54.73	52.34	-6.10	-0.12	52.7
5	39.08	27.90	31.36	59.80	45.38	-2.01	-0.04	45.4
6	37.22	26.19	29.59	58.22	46.19	-2.18	-0.05	46.2
7	36.41	25.65	28.25	57.71	45.71	-1.07	-0.02	45.7
10	42.43	30.80	35.07	62.34	44.76	-2.65	-0.06	44.8
15	34.19	22.91	26.79	54.98	49.89	-3.53	-0.07	50.0
18	34.42	24.65	26.52	56.73	43.18	-0.08	0.00	43.2
20	39.34	28.60	31.68	60.42	43.49	-1.38	-0.03	43.5
24	35.12	25.00	26.75	57.07	44.11	0.14	0.00	44.1
28	41.88	31.94	34.57	63.30	38.98	-0.36	-0.01	39.0
33	41.61	33.31	36.54	64.41	33.35	-0.99	-0.03	33.4
52	44.13	35.35	37.30	66.02	33.95	0.82	0.02	34.0
61	35.79	27.98	29.70	59.87	34.33	0.49	0.01	34.3

Tank 02

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	45.11	33.94	41.18	64.91	41.54	-5.79	-0.14	41.9
1	58.56	49.52	57.41	75.78	30.19	-4.09	-0.13	30.5
3	43.59	32.42	37.79	63.68	42.41	-3.82	-0.09	42.6
4	31.26	19.33	23.83	51.08	56.29	-5.44	-0.10	56.6
5	41.94	29.90	34.26	61.57	46.62	-2.93	-0.06	46.7
6	41.02	29.50	33.50	61.22	45.29	-2.50	-0.06	45.4
7	40.25	28.48	31.91	60.32	46.79	-1.87	-0.04	46.8
10	43.45	32.12	36.71	63.44	43.04	-2.87	-0.07	43.1
15	34.77	24.04	27.49	56.12	46.99	-2.64	-0.06	47.1
18	37.05	26.75	28.79	58.74	43.39	-0.10	0.00	43.4
20	36.03	25.60	28.11	57.65	44.67	-0.95	-0.02	44.7
24	34.01	24.09	25.76	56.18	44.16	0.18	0.00	44.2
28	40.89	31.08	33.54	62.58	39.07	-0.22	-0.01	39.1
33	42.39	33.69	36.47	64.72	34.40	-0.37	-0.01	34.4
52	44.52	35.64	37.41	66.25	34.09	1.08	0.03	34.1
61	39.87	31.35	34.13	62.80	34.91	-0.63	-0.02	34.9

Tank 03

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	43.02	30.83	37.88	62.36	46.43	-6.21	-0.13	46.8
1	62.42	53.71	61.43	78.29	28.50	-3.45	-0.12	28.7
3	40.10	27.96	32.90	59.85	48.33	-4.05	-0.08	48.5
4	29.77	18.60	23.14	50.22	54.41	-5.74	-0.11	54.7
5	45.58	33.78	38.51	64.78	43.47	-2.81	-0.06	43.6
6	44.63	33.08	37.27	64.23	43.10	-2.22	-0.05	43.2
7	41.51	29.94	33.40	61.60	45.16	-1.71	-0.04	45.2
10	45.33	33.44	38.30	64.51	43.93	-3.03	-0.07	44.0
15	37.58	25.57	29.98	57.63	49.88	-3.77	-0.08	50.0
18	39.31	28.87	31.00	60.67	42.35	0.00	0.00	42.3
20	40.19	29.74	32.97	61.42	41.85	-1.43	-0.03	41.9
24	35.40	25.87	27.87	57.91	41.44	-0.13	0.00	41.4
28	43.69	34.75	37.53	65.56	34.65	-0.26	-0.01	34.6
33	44.18	36.30	39.28	66.75	30.93	-0.36	-0.01	30.9
52	45.01	36.69	38.80	67.04	32.09	0.73	0.02	32.1
61	42.43	33.39	35.95	64.47	35.58	-0.13	0.00	35.6

Tank 04

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	51.23	41.05	47.87	70.21	35.63	-4.14	-0.12	35.9
1	62.10	52.58	60.88	77.63	30.62	-4.11	-0.13	30.9
3	40.82	28.60	33.87	60.43	48.12	-4.38	-0.09	48.3
4	27.78	16.94	20.96	48.19	55.40	-5.35	-0.10	55.7
5	36.03	25.02	27.80	57.09	47.11	-1.44	-0.03	47.1
6	38.03	26.60	30.08	58.60	47.16	-2.23	-0.05	47.2
7	41.05	29.21	31.94	60.97	46.50	-0.80	-0.02	46.5
10	44.61	31.86	37.05	63.22	47.39	-3.69	-0.08	47.5
15	30.50	19.47	22.57	51.23	52.81	-3.01	-0.06	52.9
18	33.37	23.18	25.06	55.26	45.84	-0.28	-0.01	45.8
20	30.27	20.41	22.88	52.30	47.34	-1.70	-0.04	47.4
24	28.73	19.83	21.23	51.64	44.25	0.11	0.00	44.2
28	34.91	25.86	28.08	57.91	39.78	-0.47	-0.01	39.8
33	38.25	29.42	31.69	61.15	36.87	-0.14	0.00	36.9
52	39.55	30.46	31.91	62.05	37.17	1.11	0.03	37.2
61	33.87	25.10	26.42	57.17	39.35	0.84	0.02	39.4

Tank 05

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	46.90	34.29	41.69	65.19	45.43	-5.91	-0.13	45.8
1	56.03	45.39	52.60	73.15	35.31	-3.95	-0.11	35.5
3	47.24	34.34	40.56	65.23	46.23	-4.51	-0.10	46.5
4	37.20	24.07	28.51	56.16	55.01	-4.13	-0.07	55.2
5	39.96	27.79	31.69	59.69	48.58	-2.65	-0.05	48.6
6	40.90	28.58	32.23	60.41	48.41	-2.17	-0.04	48.5
7	39.71	27.77	31.00	59.68	47.87	-1.70	-0.04	47.9
10	39.79	27.90	31.86	59.79	47.64	-2.72	-0.06	47.7
15	34.13	22.72	26.87	54.78	50.58	-3.99	-0.08	50.7
18	36.77	26.06	29.16	58.10	45.24	-1.76	-0.04	45.3
20	39.67	28.64	32.50	60.46	44.37	-2.46	-0.06	44.4
24	38.99	28.00	31.00	59.89	44.69	-1.34	-0.03	44.7
28	42.44	32.76	36.44	63.97	37.77	-1.62	-0.04	37.8
33	48.94	39.03	43.42	68.77	35.68	-1.73	-0.05	35.7
52	44.90	36.14	39.59	66.63	33.55	-0.94	-0.03	33.6
61	40.63	31.91	34.77	63.27	35.25	-0.67	-0.02	35.3

Tank 06

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	43.31	31.09	38.30	62.58	46.34	-6.35	-0.14	46.8
1	55.10	43.69	51.75	72.02	37.82	-5.04	-0.13	38.2
3	49.52	36.95	43.92	67.24	43.87	-4.94	-0.11	44.1
4	33.57	21.43	25.63	53.42	54.48	-4.37	-0.08	54.7
5	41.02	28.61	32.84	60.43	48.68	-2.96	-0.06	48.8
6	40.53	28.67	32.76	60.49	46.93	-2.75	-0.06	47.0
7	34.17	25.32	35.77	57.38	39.50	-12.12	-0.30	41.3
10	42.66	30.37	35.35	61.97	47.05	-3.67	-0.08	47.2
15	39.43	26.91	31.67	58.89	50.37	-4.01	-0.08	50.5
18	39.80	28.66	31.70	60.48	44.69	-1.31	-0.03	44.7
20	42.73	31.20	35.10	62.68	44.21	-2.12	-0.05	44.3
24	35.68	25.19	27.67	57.26	45.19	-0.97	-0.02	45.2
28	43.79	33.60	37.13	64.65	38.87	-1.33	-0.03	38.9
33	42.20	32.81	36.43	64.01	36.90	-1.55	-0.04	36.9
52	44.10	34.65	36.95	65.48	36.19	0.33	0.01	36.2
61	35.67	28.32	30.14	60.18	32.60	0.39	0.01	32.6

Tank 07

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	37.83	26.12	31.94	58.15	48.46	-5.65	-0.12	48.8
1	50.99	39.40	46.54	69.04	40.03	-4.73	-0.12	40.3
3	49.15	36.64	43.85	67.00	43.87	-5.27	-0.12	44.2
4	29.31	18.09	21.58	49.60	55.30	-4.04	-0.07	55.4
5	38.56	26.17	29.96	58.20	50.61	-2.76	-0.05	50.7
6	47.04	34.81	39.75	65.60	44.11	-2.92	-0.07	44.2
7	36.07	26.99	37.75	58.96	39.17	-11.91	-0.30	40.9
10	41.74	29.39	33.94	61.12	47.93	-3.26	-0.07	48.0
15	34.77	23.62	27.85	55.71	48.78	-3.90	-0.08	48.9
18	39.07	28.07	30.82	59.95	44.68	-0.97	-0.02	44.7
20	36.96	25.97	29.44	58.01	46.23	-2.33	-0.05	46.3
24	40.41	29.21	31.84	60.97	44.51	-0.66	-0.01	44.5
28	40.88	31.35	34.67	62.80	38.06	-1.34	-0.04	38.1
33	44.85	35.27	38.75	65.96	36.28	-1.07	-0.03	36.3
52	44.39	34.73	37.78	65.53	36.78	-0.62	-0.02	36.8
61	49.32	39.79	42.58	69.32	34.35	0.16	0.00	34.4

Tank 08

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	55.00	44.51	52.33	72.57	35.22	-4.68	-0.13	35.5
1	48.55	37.04	44.23	67.31	40.92	-5.17	-0.13	41.2
3	47.82	35.03	41.20	65.77	45.50	-4.33	-0.09	45.7
4	31.21	19.30	23.04	51.04	56.26	-4.14	-0.07	56.4
5	40.43	27.85	31.91	59.75	49.79	-2.85	-0.06	49.9
6	41.99	29.56	33.41	61.27	48.02	-2.29	-0.05	48.1
7	37.66	28.78	39.63	60.59	37.42	-11.41	-0.30	39.1
10	43.35	31.20	35.67	62.68	46.04	-2.85	-0.06	46.1
15	38.00	25.69	30.28	57.74	50.77	-4.01	-0.08	50.9
18	36.82	26.49	28.91	58.50	43.67	-0.70	-0.02	43.7
20	39.35	28.55	32.06	60.38	43.72	-1.98	-0.05	43.8
24	35.75	25.69	28.18	57.74	43.36	-0.90	-0.02	43.4
28	40.50	31.08	34.15	62.58	37.84	-1.04	-0.03	37.9
33	47.25	37.42	40.61	67.59	36.07	-0.50	-0.01	36.1
52	44.74	35.53	38.60	66.16	35.11	-0.54	-0.02	35.1
61	44.58	34.78	36.90	65.57	37.16	0.56	0.02	37.2

Tank 09

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	53.53	43.40	48.03	71.83	34.68	-1.53	-0.04	34.7
1	49.92	39.20	45.94	68.90	37.78	-4.32	-0.11	38.0
3	47.93	34.93	41.47	65.69	46.15	-4.80	-0.10	46.4
4	32.69	20.28	24.13	52.15	56.83	-4.09	-0.07	57.0
5	36.83	24.34	27.88	56.43	52.63	-2.72	-0.05	52.7
6	43.63	31.05	35.43	62.55	47.44	-2.77	-0.06	47.5
7	31.10	22.20	31.83	54.24	42.06	-12.24	-0.28	43.8
10	37.73	26.61	30.64	58.61	46.15	-3.03	-0.07	46.3
15	38.41	26.23	30.44	58.26	49.88	-3.36	-0.07	50.0
18	36.98	25.85	27.58	57.90	46.79	0.27	0.01	46.8
20	39.83	27.87	31.29	59.77	47.85	-1.95	-0.04	47.9
24	38.99	27.59	29.88	59.52	46.30	-0.37	-0.01	46.3
28	44.73	33.66	37.01	64.69	41.41	-1.10	-0.03	41.4
33	43.37	33.97	37.14	64.94	36.36	-0.83	-0.02	36.4
52	44.84	35.66	38.30	66.26	34.99	-0.01	0.00	35.0
61	40.08	30.64	32.92	62.21	38.14	-0.01	0.00	38.1

Tank 10

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	54.68	45.21	50.96	73.03	32.41	-2.50	-0.08	32.5
1	48.31	37.31	43.46	67.51	39.38	-3.95	-0.10	39.6
3	41.82	29.56	35.40	61.28	47.50	-4.93	-0.10	47.8
4	33.37	20.86	24.59	52.80	56.45	-3.75	-0.07	56.6
5	38.43	25.59	29.25	57.64	52.60	-2.68	-0.05	52.7
6	40.81	28.77	32.47	60.57	47.44	-2.21	-0.05	47.5
7	32.11	23.06	32.58	55.13	41.91	-11.76	-0.27	43.5
10	39.47	27.45	31.35	59.38	48.36	-2.69	-0.06	48.4
15	40.04	27.64	31.58	59.56	49.43	-2.73	-0.06	49.5
18	35.84	25.29	27.05	57.36	45.33	0.16	0.00	45.3
20	38.86	27.23	30.04	59.18	47.32	-1.18	-0.02	47.3
24	35.04	24.30	25.76	56.38	46.81	0.53	0.01	46.8
28	42.94	31.77	34.38	63.16	42.78	-0.35	-0.01	42.8
33	39.46	30.32	32.92	61.93	37.41	-0.49	-0.01	37.4
52	45.05	35.73	37.41	66.31	35.37	1.18	0.03	35.4
61	38.74	29.42	31.04	61.15	38.48	0.78	0.02	38.5

Tank 11

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	56.19	47.88	52.92	74.75	28.83	-1.52	-0.05	28.9
1	46.04	35.46	41.83	66.11	39.07	-4.51	-0.11	39.3
3	46.18	33.78	39.84	64.79	45.15	-4.42	-0.10	45.4
4	34.27	21.87	25.82	53.89	54.92	-3.87	-0.07	55.1
5	41.80	28.71	32.69	60.53	50.66	-2.61	-0.05	50.7
6	40.39	28.34	32.05	60.19	47.76	-2.28	-0.05	47.8
7	33.36	24.20	34.10	56.29	41.38	-11.82	-0.28	43.0
10	39.69	28.24	32.02	60.10	45.99	-2.41	-0.05	46.0
15	40.03	27.85	31.94	59.76	48.53	-2.89	-0.06	48.6
18	37.58	26.89	28.65	58.87	44.55	0.33	0.01	44.6
20	42.65	30.49	33.83	62.08	46.57	-1.48	-0.03	46.6
24	37.42	26.65	28.79	58.65	45.00	-0.27	-0.01	45.0
28	43.52	33.02	36.10	64.18	40.07	-0.82	-0.02	40.1
33	44.92	35.37	38.51	66.03	36.17	-0.66	-0.02	36.2
52	49.01	39.23	41.76	68.92	35.24	0.43	0.01	35.2
61	44.69	35.04	37.46	65.78	36.60	0.21	0.01	36.6

Tank 12

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	55.00	45.91	51.13	73.49	31.25	-1.88	-0.06	31.3
1	56.51	45.90	52.76	73.48	35.07	-3.55	-0.10	35.3
3	39.52	26.88	32.36	58.86	50.80	-5.01	-0.10	51.1
4	33.18	21.17	24.87	53.13	54.36	-3.63	-0.07	54.5
5	39.59	26.76	30.48	58.75	51.50	-2.56	-0.05	51.6
6	37.12	24.96	28.18	57.04	50.94	-2.12	-0.04	51.0
7	31.85	22.32	32.12	54.36	44.27	-12.44	-0.27	46.0
10	40.12	27.86	31.74	59.77	48.78	-2.60	-0.05	48.8
15	38.35	26.30	29.94	58.32	49.42	-2.51	-0.05	49.5
18	35.12	24.50	26.37	56.59	46.21	-0.09	0.00	46.2
20	37.36	25.75	28.70	57.80	48.46	-1.59	-0.03	48.5
24	35.40	24.65	26.22	56.73	46.52	0.39	0.01	46.5
28	36.84	26.56	29.35	58.56	43.43	-1.24	-0.03	43.4
33	42.54	32.53	35.18	63.78	38.90	-0.33	-0.01	38.9
52	42.09	32.04	33.87	63.37	39.27	0.71	0.02	39.3
61	45.42	35.66	37.49	66.26	36.64	1.00	0.03	36.7

Tank 13

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	57.92	47.72	54.23	74.65	33.51	-2.98	-0.09	33.6
1	53.77	42.56	49.35	71.25	37.76	-3.90	-0.10	38.0
3	42.53	29.01	34.49	60.79	51.74	-4.58	-0.09	51.9
4	38.78	25.07	29.11	57.15	55.84	-3.32	-0.06	55.9
5	41.75	28.20	32.20	60.07	52.51	-2.72	-0.05	52.6
6	42.95	30.21	34.29	61.83	48.49	-2.50	-0.05	48.6
7	33.64	23.62	34.53	55.71	44.87	-13.39	-0.29	46.8
10	41.12	28.43	32.67	60.28	49.68	-2.99	-0.06	49.8
15	40.41	28.02	32.14	59.90	49.10	-2.91	-0.06	49.2
18	37.86	26.72	29.20	58.72	46.13	-0.75	-0.02	46.1
20	42.45	30.00	33.51	61.66	47.77	-1.76	-0.04	47.8
24	35.38	24.65	26.85	56.73	46.44	-0.59	-0.01	46.4
28	41.94	31.20	34.38	62.67	41.85	-1.18	-0.03	41.9
33	43.82	33.10	36.62	64.24	40.70	-1.38	-0.03	40.7
52	40.67	30.52	32.74	62.10	40.41	0.05	0.00	40.4
61	42.17	32.28	34.33	63.57	38.66	0.44	0.01	38.7

Tank 14

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	51.26	41.07	47.06	70.23	35.63	-3.25	-0.09	35.8
1	48.86	36.79	43.45	67.12	42.56	-4.61	-0.11	42.8
3	46.63	33.43	40.10	64.51	47.65	-5.21	-0.11	47.9
4	38.78	25.07	29.11	57.15	55.84	-3.32	-0.06	55.9
5	43.03	29.37	33.67	61.11	51.87	-2.92	-0.06	52.0
6	40.62	28.16	31.98	60.04	49.17	-2.47	-0.05	49.2
7	32.18	22.46	32.84	54.51	44.81	-13.18	-0.29	46.7
10	42.70	30.18	34.65	61.81	47.86	-3.03	-0.06	48.0
15	41.25	28.57	33.05	60.40	49.54	-3.31	-0.07	49.7
18	40.72	29.35	31.78	61.09	44.93	-0.38	-0.01	44.9
20	42.00	30.78	34.73	62.32	43.55	-2.25	-0.05	43.6
24	43.55	31.63	34.11	63.03	45.13	-0.20	0.00	45.1
28	41.34	30.48	33.80	62.06	42.64	-1.46	-0.03	42.7
33	44.28	33.96	37.53	64.93	39.07	-1.34	-0.03	39.1
52	48.75	38.20	40.89	68.16	37.76	0.15	0.00	37.8
61	44.32	34.42	36.69	65.29	37.61	0.34	0.01	37.6

Tank 15

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	54.23	43.45	49.77	71.86	36.31	-3.29	-0.09	36.5
1	52.51	40.61	46.76	69.90	40.33	-3.49	-0.09	40.5
3	43.88	30.10	35.82	61.74	51.63	-4.67	-0.09	51.8
4	40.47	26.50	30.74	58.51	55.27	-3.35	-0.06	55.4
5	40.32	27.95	32.26	59.84	49.08	-3.19	-0.06	49.2
6	42.76	29.67	34.24	61.37	49.95	-3.25	-0.06	50.1
7	34.51	24.75	35.87	56.83	43.05	-13.19	-0.30	45.0
10	44.89	31.96	36.70	63.31	47.81	-3.09	-0.06	47.9
15	43.03	30.48	35.53	62.07	47.75	-3.74	-0.08	47.9
18	40.95	29.51	32.23	61.23	45.04	-0.74	-0.02	45.0
20	40.95	29.53	33.29	61.25	44.96	-2.17	-0.05	45.0
24	39.75	28.62	30.87	60.44	44.71	-0.20	0.00	44.7
28	42.65	31.71	35.03	63.10	42.14	-1.29	-0.03	42.2
33	45.98	35.55	39.23	66.18	38.62	-1.29	-0.03	38.6
52	45.65	35.98	38.27	66.50	36.26	0.44	0.01	36.3
61	51.53	42.09	44.62	70.93	33.31	0.65	0.02	33.3

continued

Table S9. Results of the chromatic coordinates obtained for wine of Mendavia 2018.

Tank 16

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	49.73	38.10	43.14	68.09	40.75	-2.60	-0.06	40.8
1	48.92	38.13	44.19	68.11	38.44	-3.74	-0.10	38.6
3	45.52	31.93	38.38	63.28	49.76	-5.24	-0.10	50.0
4	35.46	22.22	25.22	54.26	57.36	-2.25	-0.04	57.4
5	39.29	26.33	30.35	58.35	52.28	-3.06	-0.06	52.4
6	41.45	29.24	33.61	60.99	47.60	-3.04	-0.06	47.7
7	32.25	22.39	32.91	54.43	45.40	-13.41	-0.29	47.3
10	42.00	28.91	33.39	60.70	50.54	-3.25	-0.06	50.6
15	40.05	27.40	32.16	59.35	50.36	-3.90	-0.08	50.5
18	40.60	28.83	31.14	60.63	46.57	-0.27	-0.01	46.6
20	44.52	32.40	36.44	63.67	45.20	-2.13	-0.05	45.2
24	37.19	25.97	27.85	58.01	46.99	0.05	0.00	47.0
28	38.84	28.05	31.11	59.94	44.00	-1.41	-0.03	44.0
33	42.02	31.48	34.81	62.91	41.09	-1.35	-0.03	41.1
52	42.95	32.75	34.87	63.96	39.33	0.40	0.01	39.3
61	46.55	35.65	37.77	66.25	39.88	0.63	0.02	39.9

Tank 17

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	55.22	46.29	50.91	73.73	30.76	-1.24	-0.04	30.8
1	60.22	51.61	58.21	77.05	28.71	-2.65	-0.09	28.8
3	40.64	27.83	33.50	59.73	50.54	-5.08	-0.10	50.8
4	40.65	26.82	31.60	58.81	54.56	-4.06	-0.07	54.7
5	41.81	29.53	34.01	61.25	47.57	-3.13	-0.07	47.7
6	44.25	31.81	35.65	63.18	46.54	-1.97	-0.04	46.6
7	35.93	26.41	37.36	58.43	40.99	-12.35	-0.29	42.8
10	43.27	30.79	35.40	62.33	47.32	-3.12	-0.07	47.4
15	42.78	29.86	34.62	61.54	49.28	-3.45	-0.07	49.4
18	42.74	31.28	33.67	62.75	43.93	-0.10	0.00	43.9
20	42.00	30.84	34.62	62.37	43.34	-2.02	-0.05	43.4
24	39.75	28.79	30.81	60.60	44.04	0.16	0.00	44.0
28	43.31	32.98	36.42	64.15	39.58	-1.29	-0.03	39.6
33	49.12	38.79	42.84	68.60	36.91	-1.37	-0.04	36.9
52	47.03	38.02	40.79	68.04	33.54	0.05	0.00	33.5
61	48.43	38.90	41.37	68.68	34.66	0.47	0.01	34.7

Tank 18

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	61.85	54.40	58.29	78.70	25.45	0.12	0.00	25.5
1	50.41	41.04	47.84	70.20	33.48	-4.13	-0.12	33.7
3	47.14	33.49	40.10	64.56	48.87	-5.13	-0.10	49.1
4	36.21	24.01	28.28	56.10	51.98	-3.89	-0.07	52.1
5	41.09	28.81	33.19	60.61	48.12	-3.12	-0.06	48.2
6	41.85	30.49	34.19	62.07	44.17	-1.96	-0.04	44.2
7	35.16	25.67	36.27	57.72	41.43	-12.18	-0.29	43.2
10	45.89	33.33	38.15	64.43	45.86	-2.98	-0.06	46.0
15	42.39	30.06	34.91	61.70	47.39	-3.56	-0.07	47.5
18	40.21	29.22	31.59	60.97	43.88	-0.31	-0.01	43.9
20	40.47	28.66	32.37	60.48	46.80	-2.24	-0.05	46.8
24	42.09	30.43	32.55	62.02	45.09	0.17	0.00	45.1
28	40.59	30.66	33.69	62.22	39.68	-1.04	-0.03	39.7
33	46.54	36.61	40.12	66.98	36.70	-0.97	-0.03	36.7
52	48.87	39.59	41.95	69.17	33.75	0.65	0.02	33.8
61	48.53	39.31	41.86	68.97	33.68	0.40	0.01	33.7

Tank 19

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	55.00	46.36	50.70	73.78	30.02	-0.95	-0.03	30.0
1	54.24	43.49	50.53	71.89	36.22	-4.03	-0.11	36.4
3	45.25	31.62	38.10	63.03	50.06	-5.32	-0.11	50.3
4	36.07	23.66	28.14	55.75	53.01	-4.27	-0.08	53.2
5	45.63	33.06	37.58	64.21	46.08	-2.65	-0.06	46.2
6	42.92	30.28	34.01	61.90	48.15	-2.02	-0.04	48.2
7	34.35	24.92	35.52	57.00	41.78	-12.45	-0.29	43.6
10	44.64	32.16	36.92	63.47	46.40	-3.09	-0.07	46.5
15	41.36	28.92	33.34	60.71	48.55	-3.17	-0.07	48.7
18	41.14	30.07	32.00	61.72	43.55	0.41	0.01	43.6
20	42.92	32.16	35.87	63.47	41.33	-1.75	-0.04	41.4
24	43.71	32.51	34.20	63.76	42.45	0.94	0.02	42.5
28	45.01	34.99	38.24	65.74	37.69	-0.83	-0.02	37.7
33	46.07	36.37	39.64	66.80	36.19	-0.71	-0.02	36.2
52	50.78	41.74	44.06	70.69	32.36	0.85	0.03	32.4
61	50.64	41.50	43.90	70.53	32.70	0.76	0.02	32.7

Tank 20

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	54.94	45.71	50.05	73.36	31.66	-1.01	-0.03	31.7
1	45.25	35.30	41.80	65.98	37.34	-4.68	-0.12	37.6
3	49.02	36.22	43.02	66.69	44.87	-4.88	-0.11	45.1
4	35.35	23.00	27.30	55.08	53.50	-4.15	-0.08	53.7
5	39.21	27.19	31.41	59.15	48.57	-3.19	-0.07	48.7
6	45.02	33.08	37.63	64.23	44.26	-2.68	-0.06	44.3
7	36.12	26.05	37.40	58.08	43.14	-12.99	-0.29	45.0
10	37.91	27.05	30.96	59.02	44.96	-2.78	-0.06	45.1
15	38.12	25.98	30.33	58.02	49.97	-3.60	-0.07	50.1
18	38.44	28.56	30.92	60.39	40.80	-0.37	-0.01	40.8
20	42.35	31.25	35.07	62.72	42.89	-2.01	-0.05	42.9
24	38.79	28.19	29.86	60.06	43.33	0.60	0.01	43.3
28	44.97	33.95	37.12	64.93	41.10	-0.84	-0.02	41.1
33	43.25	33.67	36.90	64.70	37.04	-0.95	-0.03	37.1
52	47.96	38.29	40.50	68.23	35.31	0.73	0.02	35.3
61	44.85	35.97	38.04	66.49	33.99	0.71	0.02	34.0

Tank 21

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	50.60	40.57	46.37	69.87	35.42	-3.12	-0.09	35.6
1	48.82	37.77	43.84	67.85	39.30	-3.80	-0.10	39.5
3	50.45	37.21	44.54	67.43	45.52	-5.30	-0.12	45.8
4	43.51	29.62	34.86	61.32	52.35	-4.13	-0.08	52.5
5	44.56	31.06	36.30	62.55	50.13	-3.89	-0.08	50.3
6	42.31	29.81	33.70	61.49	48.05	-2.30	-0.05	48.1
7	36.20	26.24	37.78	58.27	42.60	-13.15	-0.30	44.6
10	46.53	33.74	38.46	64.75	46.29	-2.80	-0.06	46.4
15	48.22	35.85	41.16	66.41	43.90	-3.21	-0.07	44.0
18	41.92	30.84	33.62	62.37	43.10	-0.69	-0.02	43.1
20	45.18	33.42	37.66	64.50	43.56	-2.26	-0.05	43.6
24	46.24	34.47	37.38	65.34	42.96	-0.46	-0.01	43.0
28	47.83	37.06	41.54	67.33	38.84	-2.06	-0.05	38.9
33	49.17	38.92	43.37	68.69	36.63	-1.81	-0.05	36.7
52	50.49	40.33	43.83	69.70	35.85	-0.60	-0.02	35.9
61	50.31	41.26	44.42	70.36	32.54	-0.12	0.00	32.5

Tank 22

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	42.70	30.36	36.10	61.97	47.17	-4.64	-0.10	47.4
1	56.73	45.02	52.65	72.90	38.10	-4.43	-0.12	38.4
3	44.24	30.78	36.87	62.32	50.19	-5.00	-0.10	50.4
4	41.68	28.12	33.00	####	52.58	-3.93	-0.07	52.7
5	44.23	30.76	35.78	62.30	50.24	-3.65	-0.07	50.4
6	42.36	29.97	33.97	61.63	47.62	-2.43	-0.05	47.7
7	32.73	23.86	34.37	55.95	40.61	-12.76	-0.30	42.6
10	44.50	32.56	37.26	63.80	44.58	-2.94	-0.07	44.7
15	46.66	34.45	39.87	65.32	44.21	-3.54	-0.08	44.4
18	43.96	32.26	35.69	63.56	44.03	-1.37	-0.03	44.1
20	46.07	34.32	38.77	65.22	42.99	-2.38	-0.06	43.1
24	43.52	32.31	35.25	63.60	42.59	-0.72	-0.02	42.6
28	46.83	35.81	39.99	66.38	40.16	-1.86	-0.05	40.2
33	50.09	39.47	43.71	69.09	37.41	-1.52	-0.04	37.4
52	53.94	44.47	47.31	72.54	32.62	0.47	0.01	32.6
61	50.85	41.83	44.80	70.75	32.28	0.13	0.00	32.3

Tank 23

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	49.92	38.32	44.90	68.25	40.58	-4.29	-0.11	40.8
1	54.95	43.78	50.67	72.08	37.18	-3.84	-0.10	37.4
3	43.54	29.43	34.84	61.16	53.16	-4.39	-0.08	53.3
4	39.59	26.69	31.35	58.69	51.77	-3.90	-0.08	51.9
5	44.31	30.70	35.92	62.26	50.68	-3.90	-0.08	50.8
6	42.34	29.84	33.87	61.52	48.03	-2.49	-0.05	48.1
7	35.78	25.72	37.37	57.77	43.34	-13.49	-0.30	45.4
10	45.50	33.02	38.02	64.18	45.85	-3.26	-0.07	46.0
15	42.62	30.49	35.20	62.08	46.47	-3.29	-0.07	46.6
18	42.40	30.94	33.79	62.46	44.15	-0.75	-0.02	44.2
20	44.43	32.38	36.55	63.66	45.00	-2.30	-0.05	45.1
24	43.24	31.35	34.12	62.81	45.16	-0.60	-0.01	45.2
28	47.64	36.57	40.21	66.95	39.93	-1.13	-0.03	39.9
33	49.00	37.90	42.27	67.94	39.40	-1.84	-0.05	39.4
52	49.12	39.99	42.40	69.46	33.19	0.61	0.02	33.2
61	44.67	35.79	38.21	66.36	34.06	0.28	0.01	34.1

Tank 24

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	48.18	37.18	41.82	67.41	39.46	-2.24	-0.06	39.5
1	52.07	40.49	47.58	69.81	39.56	-4.52	-0.11	39.8
3	49.66	36.51	43.02	66.91	45.66	-4.49	-0.10	45.9
4	40.73	27.44	32.49	59.38	52.35	-4.31	-0.08	52.5
5	45.38	31.87	37.40	63.23	49.57	-4.11	-0.08	49.7
6	40.86	28.76	32.75	60.57	47.61	-2.61	-0.05	47.7
7	38.35	28.61	40.93	60.43	40.30	-13.23	-0.32	42.4
10	38.12	27.51	32.17	59.44	43.86	-3.75	-0.09	44.0
15	47.14	34.79	39.93	65.59	44.41	-3.14	-0.07	44.5
18	42.82	31.31	34.69	62.77	44.09	-1.42	-0.03	44.1
20	45.50	33.52	37.99	64.58	44.11	-2.52	-0.06	44.2
24	44.76	32.84	35.72	64.03	44.32	-0.58	-0.01	44.3
28	45.77	34.66	38.69	65.48	40.98	-1.82	-0.04	41.0
33	49.87	38.92	43.24	68.69	38.54	-1.67	-0.04	38.6
52	50.32	40.50	43.53	69.82	34.88	-0.05	0.00	34.9
61	53.04	43.66	46.45	72.00	32.65	0.48	0.01	32.6

Table S10. Results of the chromatic coordinates obtained for wine of Alfaro 2019.

Tank 02

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	67.63	62.10	69.96	82.97	20.13	-2.74	-0.14	20.32
1	64.43	56.82	65.25	80.08	25.45	-3.75	-0.15	25.72
3	53.59	43.94	50.95	72.19	33.28	-3.94	-0.12	33.51
4	57.01	48.04	54.51	74.85	30.38	-2.90	-0.10	30.52
5	50.80	42.16	48.36	70.98	31.16	-3.34	-0.11	31.34
6	54.59	44.69	52.78	72.69	33.66	-4.92	-0.15	34.02
7	53.43	44.78	51.59	72.75	30.44	-3.63	-0.12	30.65
8	52.40	44.48	50.29	72.55	28.65	-2.65	-0.09	28.77
10	59.88	51.66	57.68	77.08	27.78	-2.10	-0.08	27.85
11	59.38	52.28	56.28	77.45	24.96	-0.13	-0.01	24.96
12	57.10	49.51	55.18	75.77	26.65	-1.98	-0.07	26.73
13	52.50	45.58	49.89	73.27	25.79	-0.98	-0.04	25.81
25	54.75	47.08	48.90	74.24	27.36	1.73	0.06	27.41
26	52.53	43.65	47.00	71.99	31.35	-0.14	0.00	31.35
31	52.07	44.65	46.32	72.66	27.27	1.75	0.06	27.33
34	52.74	46.25	46.64	73.71	24.51	3.21	0.13	24.72
38	56.07	49.73	50.86	75.90	23.54	2.56	0.11	23.67
45	57.14	52.35	52.79	77.49	19.32	3.35	0.17	19.61
48	50.47	45.60	46.35	73.28	20.37	2.78	0.14	20.56
52	49.04	44.12	44.38	72.31	20.70	3.28	0.16	20.96
53	49.75	44.97	45.41	72.87	20.19	3.11	0.15	20.43

Tank 03

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	68.32	63.41	70.15	83.66	18.69	-1.71	-0.09	18.77
1	59.14	50.81	57.81	76.57	28.20	-3.10	-0.11	28.37
3	47.40	37.42	44.57	67.59	36.49	-5.06	-0.14	36.84
4	60.78	51.77	58.39	77.14	29.64	-2.65	-0.09	29.76
5	52.28	42.85	49.71	71.45	33.04	-3.94	-0.12	33.27
6	56.27	46.44	54.54	73.83	32.96	-4.68	-0.14	33.29
7	51.81	42.97	49.37	71.53	31.46	-3.44	-0.11	31.65
8	54.21	46.18	51.91	73.66	28.49	-2.38	-0.08	28.58
10	57.27	49.08	54.65	75.50	28.25	-1.93	-0.07	28.32
11	57.01	50.18	53.95	76.18	24.67	-0.07	0.00	24.67
12	60.62	53.21	58.89	78.00	25.56	-1.63	-0.06	25.62
13	55.06	47.84	52.12	74.72	26.08	-0.76	-0.03	26.10
25	53.33	46.37	47.50	73.79	25.69	2.41	0.09	25.81
26	50.74	41.81	44.45	70.74	32.05	0.49	0.02	32.06
31	51.44	43.44	43.90	71.86	29.10	3.04	0.10	29.26
34	53.27	46.59	46.59	73.93	24.94	3.64	0.14	25.20
38	52.36	45.93	45.91	73.50	24.42	3.64	0.15	24.69
45	58.62	53.54	53.79	78.19	19.93	3.56	0.18	20.25
48	50.17	45.12	45.86	72.97	20.90	2.78	0.13	21.08
52	49.56	44.62	44.81	72.64	20.69	3.37	0.16	20.96
53	56.51	51.34	51.84	76.88	20.40	3.25	0.16	20.65

Tank 04

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	67.31	60.61	67.93	82.17	22.89	-2.44	-0.11	23.02
1	58.12	50.16	57.12	76.17	27.44	-3.14	-0.11	27.62
3	52.81	41.69	50.09	70.65	37.85	-5.70	-0.15	38.28
4	56.78	47.90	54.46	74.76	30.23	-3.01	-0.10	30.38
5	51.08	41.61	48.50	70.60	33.55	-4.14	-0.12	33.80
6	53.86	43.80	52.12	72.09	34.38	-5.29	-0.15	34.78
7	52.79	43.93	50.01	72.18	31.23	-2.99	-0.10	31.37
8	53.60	46.42	51.77	73.81	26.28	-1.97	-0.07	26.35
10	58.47	50.47	56.10	76.36	27.48	-1.84	-0.07	27.55
11	60.54	53.39	57.47	78.11	24.90	-0.13	-0.01	24.90
12	60.01	53.13	58.80	77.95	24.32	-1.64	-0.07	24.37
13	52.86	45.29	49.79	73.08	27.53	-1.21	-0.04	27.56
25	52.94	45.61	46.37	73.29	26.82	2.78	0.10	26.96
26	44.60	36.01	38.97	66.52	33.12	-0.37	-0.01	33.13
31	51.47	44.21	44.87	72.37	26.96	2.84	0.11	27.11
34	49.07	42.53	42.60	71.23	25.43	3.45	0.13	25.66
38	50.74	44.37	44.48	72.47	24.58	3.45	0.14	24.82
45	56.59	51.39	51.79	76.91	20.48	3.35	0.16	20.75
48	50.76	45.61	46.14	73.29	21.08	3.04	0.14	21.30
52	46.36	41.82	41.56	70.75	19.99	3.81	0.19	20.35
53	51.28	46.10	46.39	73.61	21.11	3.32	0.16	21.37

Tank 05

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	67.53	60.72	69.24	82.23	23.11	-3.43	-0.15	23.36
1	51.64	39.26	46.88	68.94	42.21	-5.28	-0.12	42.54
3	43.36	29.57	36.36	61.28	52.11	-6.15	-0.12	52.47
4	49.81	35.81	43.26	66.37	48.39	-5.69	-0.12	48.72
5	44.61	31.94	38.90	63.29	47.10	-5.86	-0.12	47.46
6	45.19	32.28	39.84	63.58	47.55	-6.51	-0.14	47.99
7	46.23	33.26	40.48	64.37	47.09	-5.91	-0.12	47.46
8	48.04	35.83	43.18	66.39	43.47	-5.57	-0.13	43.83
10	49.16	36.84	43.82	67.16	43.21	-4.97	-0.11	43.50
11	47.30	35.84	41.72	66.40	41.38	-3.87	-0.09	41.56
12	46.60	35.04	41.94	65.78	42.08	-5.20	-0.12	42.40
13	44.74	33.02	39.02	64.18	43.65	-4.48	-0.10	43.88
25	48.00	36.94	41.53	67.23	39.73	-2.21	-0.06	39.79
26	43.32	31.73	36.58	63.12	44.05	-3.27	-0.07	44.17
31	43.08	32.60	36.54	63.83	40.28	-1.99	-0.05	40.32
34	45.55	34.78	37.98	65.58	39.94	-0.79	-0.02	39.95
38	44.65	34.32	37.65	65.21	38.92	-1.00	-0.03	38.93
45	45.07	35.40	38.64	66.06	36.51	-0.77	-0.02	36.52
48	47.85	38.29	41.67	68.23	34.98	-0.65	-0.02	34.99
52	40.52	32.39	35.02	63.66	33.23	-0.31	-0.01	33.23
53	45.65	37.11	40.32	67.36	32.59	-0.57	-0.02	32.59

Tank 06

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	56.29	49.50	54.05	75.76	24.69	-0.89	-0.04	24.71
1	55.46	43.53	51.68	71.91	39.21	-5.16	-0.13	39.55
3	44.15	31.34	38.52	62.79	47.91	-6.26	-0.13	48.31
4	53.28	39.39	47.57	69.03	46.07	-5.85	-0.13	46.44
5	47.64	35.01	42.44	65.75	45.10	-5.81	-0.13	45.47
6	46.62	33.07	40.96	64.22	48.86	-6.73	-0.14	49.32
7	48.84	35.51	43.34	66.14	46.74	-6.18	-0.13	47.15
8	48.13	36.21	43.73	66.68	42.44	-5.69	-0.13	42.82
10	50.59	38.14	45.41	68.13	42.92	-5.07	-0.12	43.22
11	47.85	36.63	42.62	67.00	40.32	-3.88	-0.10	40.51
12	49.52	38.73	46.11	68.55	38.17	-5.11	-0.13	38.51
13	47.08	37.01	43.42	67.28	36.93	-4.31	-0.12	37.18
25	45.33	34.68	38.54	65.50	39.65	-1.61	-0.04	39.68
26	44.17	33.48	37.56	64.55	40.39	-2.03	-0.05	40.44
31	45.83	34.99	38.54	65.74	40.05	-1.19	-0.03	40.07
34	44.94	34.64	37.68	65.47	38.69	-0.60	-0.02	38.70
38	44.05	34.30	37.34	65.20	37.23	-0.64	-0.02	37.24
45	45.95	36.39	39.86	66.82	35.74	-0.94	-0.03	35.76
48	47.01	37.94	41.34	67.98	33.76	-0.71	-0.02	33.76
52	46.71	38.10	40.56	68.09	32.42	0.41	0.01	32.43
53	48.14	39.82	42.94	69.34	31.01	-0.21	-0.01	31.01

Tank 07

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	71.45	64.68	73.65	84.32	22.57	-3.41	-0.15	22.82
1	45.72	32.46	38.76	63.72	48.45	-4.96	-0.10	48.70
3	48.04	34.14	41.83	65.07	49.14	-6.28	-0.13	49.54
4	51.84	38.60	46.04	68.46	44.78	-5.19	-0.12	45.08
5	47.50	35.93	42.94	66.46	41.65	-5.16	-0.12	41.97
6	44.26	32.45	39.65	63.72	44.25	-6.04	-0.14	44.66
7	47.37	35.85	43.23	66.41	41.51	-5.59	-0.13	41.89
8	44.98	33.30	40.42	64.40	43.38	-5.78	-0.13	43.77
10	54.75	43.35	50.70	71.79	37.94	-4.37	-0.11	38.19
11	50.99	40.33	46.45	69.71	37.17	-3.49	-0.09	37.33
12	53.59	43.05	50.85	71.59	35.83	-4.87	-0.14	36.16
13	46.49	34.96	40.95	65.72	42.01	-4.14	-0.10	42.21
25	50.27	40.08	44.08	69.53	36.01	-1.18	-0.03	36.03
26	52.35	41.58	46.44	70.58	36.98	-1.96	-0.05	37.03
31	51.58	40.65	44.51	69.93	37.77	-0.96	-0.03	37.78
34	48.91	39.29	42.59	68.96	34.80	-0.47	-0.01	34.80
38	50.82	40.83	44.34	70.06	35.20	-0.56	-0.02	35.20
45	53.28	44.53	48.25	72.58	30.78	-0.46	-0.01	30.79
48	52.79	43.88	47.50	72.15	31.36	-0.41	-0.01	31.37
52	52.38	44.09	47.13	72.29	29.70	0.23	0.01	29.70
53	52.06	44.19	47.21	72.36	28.58	0.26	0.01	28.58

Tank 08

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	65.00	57.88	65.98	80.67	24.16	-3.35	-0.14	24.40
1	44.89	33.09	40.28	64.24	43.85	-5.90	-0.13	44.24
3	41.99	29.36	36.18	61.09	48.81	-6.24	-0.13	49.21
4	48.57	35.27	42.20	65.96	46.78	-5.20	-0.11	47.07
5	49.00	37.21	44.24	67.43	41.59	-4.96	-0.12	41.89
6	48.29	37.34	45.00	67.53	39.23	-5.65	-0.14	39.64
7	46.83	34.35	41.58	65.24	45.06	-5.71	-0.13	45.42
8	49.18	38.36	45.55	68.28	38.44	-4.96	-0.13	38.76
10	50.93	38.87	45.78	68.65	41.54	-4.57	-0.11	41.79
11	49.71	37.37	43.06	67.55	43.02	-3.43	-0.08	43.16
12	51.41	39.54	47.01	69.14	40.71	-5.06	-0.12	41.03
13	44.91	33.59	39.40	64.63	42.18	-4.15	-0.10	42.38
25	46.29	35.63	39.55	66.24	39.22	-1.57	-0.04	39.25
26	46.40	35.19	39.54	65.90	41.00	-2.14	-0.05	41.05
31	45.54	34.27	37.72	65.18	41.67	-1.15	-0.03	41.68
34	44.02	33.49	36.25	64.55	39.94	-0.38	-0.01	39.94
38	40.27	30.42	33.03	62.01	39.56	-0.51	-0.01	39.57
45	44.36	35.04	38.11	65.78	35.64	-0.59	-0.02	35.64
48	47.62	37.92	41.33	67.96	35.52	-0.71	-0.02	35.53
52	46.06	37.47	40.10	67.63	32.58	0.16	0.00	32.58
53	43.38	35.15	37.76	65.87	32.39	-0.01	0.00	32.39

Tank 09

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	74.57	68.70	76.33	86.36	20.32	-2.02	-0.10	20.42
1	49.74	40.92	46.98	70.12	32.04	-3.35	-0.10	32.22
3	47.39	35.39	42.86	66.05	43.11	-5.79	-0.13	43.50
4	48.52	37.63	43.87	67.75	38.92	-4.01	-0.10	39.13
5	47.79	37.85	43.93	67.91	36.22	-3.79	-0.10	36.42
6	48.29	37.34	45.00	67.53	39.23	-5.65	-0.14	39.64
7	50.11	39.45	46.43	69.08	37.51	-4.55	-0.12	37.78
8	50.28	39.89	46.39	69.39	36.63	-3.97	-0.11	36.85
10	51.99	41.83	47.93	70.76	35.29	-3.27	-0.09	35.44
11	52.93	43.93	48.76	72.18	31.59	-1.70	-0.05	31.64
12	54.14	45.34	51.78	73.12	30.68	-3.19	-0.10	30.85
13	48.39	39.36	44.19	69.01	33.12	-2.19	-0.07	33.19
25	48.81	39.70	41.89	69.26	33.23	0.86	0.03	33.24
26	47.57	38.23	41.22	68.19	34.42	-0.20	-0.01	34.42
31	50.72	41.74	43.79	70.69	32.21	1.15	0.04	32.23
34	50.03	41.66	42.94	70.64	30.59	2.03	0.07	30.66
38	51.93	44.34	46.02	72.46	27.79	1.72	0.06	27.84
45	52.89	45.37	47.88	73.14	27.35	0.89	0.03	27.37
48	49.62	42.32	44.72	71.09	27.53	0.80	0.03	27.54
52	47.21	40.61	42.42	69.90	26.03	1.35	0.05	26.06
53	51.55	43.79	45.76	72.09	28.39	1.38	0.05	28.42

Tank 10

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	61.97	53.90	61.92	78.40	27.00	-3.71	-0.14	27.25
1	51.32	43.35	49.28	71.79	29.06	-2.90	-0.10	29.20
3	50.03	38.05	45.45	68.06	41.72	-5.24	-0.12	42.05
4	52.46	41.23	48.15	70.33	38.32	-4.23	-0.11	38.56
5	48.91	37.53	44.14	67.67	40.32	-4.44	-0.11	40.57
6	46.14	35.69	43.10	66.28	38.62	-5.67	-0.15	39.03
7	48.36	37.51	44.30	67.66	38.88	-4.64	-0.12	39.15
8	47.46	37.25	43.38	67.47	37.22	-3.94	-0.11	37.43
10	51.51	41.71	47.73	70.67	34.40	-3.20	-0.09	34.54
11	56.71	47.96	52.69	74.80	29.90	-1.20	-0.04	29.92
12	52.44	43.40	49.84	71.83	31.83	-3.43	-0.11	32.01
13	48.19	38.94	43.88	68.71	33.88	-2.36	-0.07	33.96
25	49.62	40.50	42.75	69.82	32.98	0.84	0.03	32.99
26	48.03	38.45	41.53	68.35	34.99	-0.29	-0.01	34.99
31	47.41	38.51	40.20	68.40	33.07	1.37	0.04	33.10
34	48.37	39.99	41.32	69.46	31.12	1.88	0.06	31.18
38	45.17	37.54	39.01	67.68	29.80	1.57	0.05	29.84
45	48.10	41.14	42.94	70.27	26.89	1.40	0.05	26.92
48	46.04	38.87	40.61	68.65	28.08	1.33	0.05	28.11
52	47.45	40.46	41.65	69.80	27.14	2.07	0.08	27.22
53	48.92	41.55	43.45	70.56	27.90	1.32	0.05	27.93

Tank 11

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	68.92	61.91	69.43	82.86	23.41	-2.49	-0.11	23.54
1	59.89	51.03	58.91	76.69	29.44	-3.91	-0.13	29.70
3	49.92	38.77	46.05	68.59	39.14	-4.98	-0.13	39.46
4	52.24	40.64	47.50	69.92	39.53	-4.24	-0.11	39.76
5	49.54	37.80	44.31	67.88	41.18	-4.28	-0.10	41.40
6	37.09	23.56	28.25	55.64	56.86	-4.63	-0.08	57.05
7	48.96	38.16	45.10	68.14	38.45	-4.71	-0.12	38.74
8	46.73	36.87	42.94	67.18	36.40	-3.94	-0.11	36.61
10	49.24	39.32	45.34	68.98	35.60	-3.53	-0.10	35.78
11	48.37	39.86	44.51	69.37	31.52	-1.93	-0.06	31.58
12	51.69	43.38	49.68	71.81	29.93	-3.29	-0.11	30.11
13	49.80	40.62	45.37	69.91	33.09	-1.95	-0.06	33.14
25	44.11	35.47	37.52	66.11	33.49	0.71	0.02	33.49
26	47.46	37.66	40.39	67.77	35.88	0.06	0.00	35.88
31	47.54	38.67	40.03	68.51	32.94	1.76	0.05	32.98
34	46.37	38.13	39.29	68.12	31.35	1.98	0.06	31.41
38	48.13	40.49	41.91	69.82	28.93	1.80	0.06	28.98
45	47.58	40.70	42.35	69.96	26.80	1.55	0.06	26.84
48	46.47	39.75	41.46	69.29	26.57	1.41	0.05	26.61
52	44.22	37.72	39.26	67.81	26.50	1.50	0.06	26.54
53	49.55	41.91	43.83	70.81	28.54	1.31	0.05	28.57

Tank 12

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	60.25	51.99	59.65	77.28	27.80	-3.59	-0.13	28.03
1	53.50	44.12	51.91	72.31	32.52	-4.71	-0.14	32.86
3	43.44	31.95	39.22	63.30	43.63	-6.23	-0.14	44.07
4	47.80	36.62	43.18	66.99	40.22	-4.54	-0.11	40.47
5	42.89	32.20	37.59	63.51	41.10	-3.87	-0.09	41.29
6	40.52	26.76	32.10	58.75	54.40	-4.85	-0.09	54.61
7	44.54	34.81	40.68	65.60	36.93	-4.02	-0.11	37.15
8	47.99	37.74	43.59	67.83	37.13	-3.55	-0.10	37.30
10	47.31	36.89	42.47	67.19	37.98	-3.37	-0.09	38.13
11	46.82	38.43	42.25	68.33	31.69	-1.15	-0.04	31.71
12	46.19	37.67	43.31	67.77	32.32	-3.33	-0.10	32.49
13	45.53	36.20	40.66	66.67	35.18	-2.15	-0.06	35.25
25	48.05	38.41	40.40	68.32	35.17	1.00	0.03	35.18
26	44.06	35.07	37.16	65.80	34.68	0.63	0.02	34.69
31	42.98	34.41	35.47	65.28	33.72	1.89	0.06	33.78
34	44.64	36.53	37.28	66.92	31.52	2.40	0.08	31.61
38	43.40	35.55	36.93	66.18	31.12	1.55	0.05	31.15
45	42.23	36.15	37.48	66.64	25.63	1.67	0.06	25.68
48	38.45	32.36	33.73	63.64	26.81	1.36	0.05	26.84
52	41.24	34.79	35.43	65.59	27.16	2.46	0.09	27.27
53	42.11	35.22	36.81	65.92	28.37	1.27	0.04	28.40

Tank 13

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	66.15	59.34	66.92	81.48	23.29	-2.77	-0.12	23.45
1	53.49	39.84	47.42	69.35	45.24	-5.14	-0.11	45.53
3	38.20	24.97	29.93	57.05	54.44	-4.70	-0.09	54.64
4	39.97	26.47	31.51	58.48	53.87	-4.48	-0.08	54.05
5	40.31	26.87	31.95	58.85	53.30	-4.45	-0.08	53.48
6	43.25	32.80	38.87	64.00	40.08	-4.61	-0.11	40.35
7	43.80	30.12	36.26	61.76	51.35	-5.21	-0.10	51.61
8	44.43	30.87	37.24	62.39	50.44	-5.35	-0.11	50.72
10	46.78	32.36	38.44	63.64	51.81	-4.70	-0.09	52.03
11	43.64	30.82	36.06	62.35	48.31	-3.92	-0.08	48.47
12	46.88	33.51	40.52	64.57	48.06	-5.61	-0.12	48.39
13	42.36	29.58	34.82	61.29	49.09	-4.15	-0.08	49.26
25	44.53	32.16	36.38	63.48	46.08	-2.39	-0.05	46.14
26	43.28	31.22	35.53	62.69	45.77	-2.65	-0.06	45.84
31	44.25	31.51	35.12	62.94	47.58	-1.70	-0.04	47.61
34	40.88	29.45	32.57	61.18	45.05	-1.31	-0.03	45.07
38	41.44	30.04	33.18	61.69	44.58	-1.27	-0.03	44.60
45	41.84	29.77	32.72	61.45	46.79	-1.04	-0.02	46.80
48	40.00	28.82	31.57	60.62	44.73	-0.88	-0.02	44.74
52	39.28	28.25	30.53	60.12	44.64	-0.28	-0.01	44.65
53	37.24	26.43	28.90	58.45	45.25	-0.77	-0.02	45.26

Tank 14

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	61.24	53.59	59.70	78.22	26.07	-2.00	-0.08	26.14
1	42.02	28.51	33.66	60.34	52.11	-4.23	-0.08	52.28
3	43.87	29.50	35.62	61.22	53.86	-5.30	-0.10	54.12
4	42.75	28.11	33.32	59.99	55.83	-4.37	-0.08	56.00
5	36.86	23.70	27.71	55.79	55.47	-3.55	-0.06	55.59
6	46.19	34.44	41.44	65.31	42.96	-5.42	-0.13	43.30
7	38.26	25.36	30.45	57.42	53.00	-4.80	-0.09	53.22
8	42.74	29.29	35.21	61.03	51.32	-5.10	-0.10	51.57
10	41.73	28.01	33.01	59.90	53.17	-4.11	-0.08	53.33
11	40.84	27.80	31.77	59.71	51.27	-2.74	-0.05	51.34
12	40.39	28.31	34.16	60.17	47.91	-5.21	-0.11	48.19
13	39.89	27.41	31.98	59.35	49.87	-3.65	-0.07	50.01
25	41.24	29.12	32.54	60.89	47.40	-1.77	-0.04	47.44
26	43.14	30.68	34.30	62.24	47.34	-1.82	-0.04	47.37
31	39.64	27.76	30.52	59.67	47.66	-1.02	-0.02	47.68
34	36.27	25.23	27.36	57.30	47.00	-0.41	-0.01	47.00
38	36.97	25.68	27.83	57.73	47.49	-0.39	-0.01	47.49
45	37.91	27.11	29.31	59.08	44.74	-0.30	-0.01	44.75
48	35.89	25.04	26.93	57.12	46.51	-0.07	0.00	46.51
52	36.51	26.12	27.76	58.15	44.11	0.44	0.01	44.11
53	36.81	25.97	28.16	58.00	45.74	-0.42	-0.01	45.74

Tank 15

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	55.47	47.15	54.31	74.29	29.00	-3.68	-0.13	29.23
1	42.59	28.97	34.23	60.75	52.08	-4.29	-0.08	52.26
3	37.92	24.27	28.83	56.36	56.49	-4.27	-0.08	56.65
4	38.25	24.94	29.38	57.01	54.72	-3.95	-0.07	54.86
5	43.73	29.67	35.19	61.37	52.80	-4.50	-0.09	53.00
6	47.16	35.95	43.22	66.48	40.63	-5.45	-0.13	40.99
7	44.45	30.28	36.47	61.89	52.67	-5.25	-0.10	52.93
8	39.28	26.68	32.11	58.67	50.85	-4.99	-0.10	51.10
10	40.31	27.18	32.00	59.14	52.09	-4.05	-0.08	52.24
11	40.46	27.56	31.89	59.49	51.05	-3.28	-0.06	51.15
12	42.67	30.37	36.48	61.97	47.07	-5.11	-0.11	47.34
13	42.18	29.60	34.63	61.31	48.43	-3.85	-0.08	48.58
25	40.24	28.05	31.20	59.94	48.42	-1.54	-0.03	48.44
26	41.48	29.38	32.90	61.12	47.15	-1.86	-0.04	47.19
31	39.42	27.73	30.72	59.64	47.13	-1.37	-0.03	47.15
34	36.40	25.12	27.34	57.20	47.86	-0.56	-0.01	47.87
38	39.33	27.45	30.09	59.39	47.92	-0.89	-0.02	47.93
45	37.95	26.79	29.25	58.78	46.15	-0.72	-0.02	46.15
48	37.57	26.85	29.59	58.84	44.65	-1.11	-0.02	44.67
52	40.44	29.53	31.81	61.25	43.38	-0.14	0.00	43.38
53	39.05	27.93	30.68	59.82	45.18	-0.99	-0.02	45.19

Tank 16

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	58.72	49.20	55.74	75.58	31.46	-2.84	-0.09	31.59
1	47.05	33.78	40.42	64.79	47.59	-5.11	-0.11	47.87
3	41.96	27.46	32.85	59.40	56.01	-4.77	-0.08	56.21
4	42.64	27.87	32.78	59.77	56.49	-4.03	-0.07	56.63
5	38.31	25.16	29.53	57.23	54.01	-3.80	-0.07	54.14
6	47.13	36.00	43.19	66.52	40.37	-5.36	-0.13	40.73
7	43.39	29.88	35.68	61.55	51.01	-4.81	-0.09	51.23
8	41.50	28.35	34.03	60.21	51.15	-4.96	-0.10	51.39
10	43.23	29.24	34.35	60.99	52.94	-4.04	-0.08	53.10
11	40.33	27.60	31.71	59.53	50.44	-2.96	-0.06	50.53
12	43.64	30.50	36.55	62.08	49.48	-5.02	-0.10	49.73
13	41.16	28.41	33.03	60.25	49.90	-3.54	-0.07	50.03
25	40.36	29.53	33.55	61.25	43.14	-2.53	-0.06	43.21
26	40.01	28.15	31.61	60.02	47.33	-1.98	-0.04	47.37
31	38.85	26.97	29.66	58.95	48.31	-1.02	-0.02	48.32
34	38.24	27.01	29.44	58.99	46.20	-0.63	-0.01	46.21
38	38.38	26.80	29.31	58.78	47.52	-0.80	-0.02	47.52
45	36.42	25.53	27.40	57.59	46.23	0.04	0.00	46.23
48	38.54	27.26	29.40	59.22	46.18	-0.18	0.00	46.18
52	35.80	25.60	27.11	57.65	43.90	0.59	0.01	43.91
53	34.92	24.28	25.91	56.36	46.47	0.25	0.01	46.47

continued

Table S10. Results of the chromatic coordinates obtained for wine of Alfaro 2019.

Tank 17

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	67.73	61.09	69.19	82.43	22.70	-3.04	-0.13	22.90
1	59.34	51.62	60.03	77.05	26.57	-4.32	-0.16	26.91
3	49.53	38.91	46.53	68.68	37.66	-5.34	-0.14	38.03
4	50.90	40.64	46.85	69.92	35.99	-3.55	-0.10	36.17
5	50.76	41.14	46.90	70.28	34.09	-2.99	-0.09	34.23
6	49.36	36.91	44.71	67.21	43.55	-5.88	-0.13	43.94
7	51.89	42.98	48.85	71.54	31.63	-2.88	-0.09	31.76
8	52.76	44.25	50.02	72.39	30.24	-2.63	-0.09	30.35
10	52.09	43.69	49.13	72.02	30.08	-2.35	-0.08	30.17
11	50.94	42.80	46.29	71.42	29.66	-0.36	-0.01	29.66
12	55.79	48.19	53.96	74.95	26.95	-2.20	-0.08	27.04
13	54.02	46.39	50.30	73.80	27.43	-0.50	-0.02	27.43
25	52.87	44.60	46.04	72.63	29.51	2.00	0.07	29.58
26	46.91	39.35	40.71	69.00	29.05	1.80	0.06	29.11
31	49.52	42.05	42.53	70.90	28.05	2.96	0.11	28.21
34	50.42	43.58	43.99	71.95	26.01	3.09	0.12	26.19
38	53.78	47.19	47.15	74.31	24.59	3.70	0.15	24.87
45	53.63	48.51	48.43	75.15	20.62	3.77	0.18	20.96
48	53.88	48.53	48.76	75.16	21.21	3.44	0.16	21.49
52	52.78	47.24	47.22	74.34	21.88	3.68	0.17	22.19
53	51.00	45.38	45.99	73.14	22.39	2.94	0.13	22.59

Tank 18

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	68.86	62.79	70.56	83.33	21.25	-2.61	-0.12	21.41
1	47.02	38.53	44.25	68.41	31.92	-3.29	-0.10	32.09
3	47.51	36.61	44.03	66.99	39.43	-5.51	-0.14	39.81
4	54.68	44.00	50.78	72.23	35.86	-3.70	-0.10	36.05
5	47.68	37.58	43.45	67.71	36.76	-3.60	-0.10	36.94
6	47.79	35.31	42.75	65.99	44.51	-5.77	-0.13	44.89
7	50.85	41.42	46.78	70.47	33.49	-2.53	-0.08	33.59
8	53.53	45.81	50.93	73.42	27.81	-1.80	-0.06	27.87
10	57.54	48.57	54.28	75.19	30.26	-2.10	-0.07	30.34
11	50.44	42.94	46.55	71.51	27.91	-0.48	-0.02	27.91
12	54.88	47.11	52.62	74.26	27.64	-2.05	-0.07	27.72
13	55.68	47.72	51.64	74.65	27.96	-0.40	-0.01	27.96
25	50.27	42.12	43.30	70.95	29.87	2.15	0.07	29.95
26	50.27	42.12	43.30	70.95	29.87	2.15	0.07	29.95
31	51.16	43.34	43.58	71.79	28.64	3.28	0.11	28.83
34	51.98	44.90	44.68	72.83	26.32	3.83	0.14	26.60
38	51.31	44.78	44.74	72.75	24.89	3.64	0.15	25.16
45	52.56	47.16	47.19	74.29	21.54	3.61	0.17	21.84
48	52.06	46.17	46.31	73.66	22.96	3.47	0.15	23.22
52	49.72	44.67	44.86	72.68	20.96	3.38	0.16	21.23
53	50.00	44.27	44.96	72.41	22.86	2.82	0.12	23.03

Tank 19

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	62.97	56.60	63.68	79.95	22.63	-2.59	-0.11	22.77
1	56.89	48.94	56.87	75.41	27.69	-4.20	-0.15	28.00
3	50.84	40.82	47.74	70.05	35.28	-4.28	-0.12	35.53
4	52.11	42.17	48.34	70.99	34.59	-3.30	-0.10	34.75
5	47.93	38.28	43.58	68.23	35.25	-2.85	-0.08	35.37
6	51.81	41.48	48.42	70.51	35.88	-4.21	-0.12	36.13
7	52.54	43.55	48.43	71.93	31.68	-1.78	-0.06	31.73
8	50.21	42.16	47.08	70.98	29.58	-1.97	-0.07	29.65
10	52.92	44.73	49.91	72.71	29.26	-1.96	-0.07	29.33
11	51.62	44.13	47.55	72.32	27.58	-0.17	-0.01	27.58
12	55.45	48.35	54.11	75.05	25.67	-2.17	-0.08	25.76
13	52.42	45.17	48.73	73.00	26.74	-0.25	-0.01	26.74
25	52.22	44.28	45.72	72.42	28.72	1.99	0.07	28.79
26	49.00	41.17	42.67	70.29	29.27	1.75	0.06	29.32
31	48.24	40.98	41.57	70.16	27.76	2.80	0.10	27.90
34	53.00	46.01	46.47	73.55	25.87	3.12	0.12	26.05
38	55.58	49.13	49.21	75.53	23.93	3.61	0.15	24.20
45	56.12	50.94	51.00	76.64	20.47	3.69	0.18	20.79
48	57.30	51.56	51.64	77.02	21.78	3.68	0.17	22.09
52	50.75	45.37	45.49	73.13	21.75	3.47	0.16	22.03
53	52.80	47.46	48.17	74.48	21.34	2.90	0.14	21.53

Tank 20

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	54.69	48.41	52.00	75.08	23.61	-0.02	0.00	23.61
1	54.13	46.16	52.97	73.65	28.36	-3.45	-0.12	28.57
3	55.00	44.78	51.69	72.75	34.44	-3.73	-0.11	34.65
4	51.34	41.97	47.46	70.85	33.16	-2.60	-0.08	33.26
5	46.46	37.59	42.42	67.72	33.34	-2.41	-0.07	33.43
6	45.40	32.77	39.89	63.97	46.44	-5.89	-0.13	46.81
7	51.19	42.24	46.95	71.03	31.98	-1.74	-0.05	32.02
8	55.00	47.13	51.96	74.28	27.86	-1.36	-0.05	27.89
10	56.22	47.57	53.10	74.55	29.73	-2.04	-0.07	29.80
11	54.45	46.95	50.34	74.16	26.98	0.07	0.00	26.98
12	55.30	48.67	53.91	75.25	24.42	-1.63	-0.07	24.47
13	54.69	47.69	51.53	74.63	25.56	-0.32	-0.01	25.56
25	51.52	44.07	45.19	72.28	27.50	2.32	0.08	27.60
26	51.01	43.38	44.71	71.81	28.15	2.05	0.07	28.22
31	52.52	45.49	45.89	73.21	26.10	3.16	0.12	26.29
34	50.68	44.16	44.24	72.34	24.99	3.49	0.14	25.23
38	52.80	46.80	46.74	74.06	23.15	3.72	0.16	23.45
45	51.40	46.40	46.18	73.80	20.60	3.86	0.19	20.96
48	54.02	48.58	48.60	75.19	21.43	3.66	0.17	21.74
52	50.87	45.83	45.85	73.44	20.77	3.60	0.17	21.08
53	51.78	46.55	47.05	73.90	21.18	3.10	0.15	21.41

Tank 21

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	70.10	63.90	71.86	83.91	21.45	-2.67	-0.12	21.62
1	50.93	37.29	45.31	67.50	46.52	-6.05	-0.13	46.91
3	46.48	32.93	40.06	64.10	48.97	-5.87	-0.12	49.32
4	48.08	34.28	41.17	65.19	48.75	-5.31	-0.11	49.03
5	46.07	33.45	40.32	64.53	45.98	-5.45	-0.12	46.30
6	54.04	44.85	51.49	72.79	31.81	-3.45	-0.11	32.00
7	46.68	34.21	40.97	65.13	45.10	-5.18	-0.11	45.40
8	49.15	37.97	45.06	68.00	39.58	-4.90	-0.12	39.88
10	49.96	38.16	45.22	68.14	41.17	-4.84	-0.12	41.45
11	45.98	35.01	40.73	65.75	40.43	-3.82	-0.09	40.61
12	48.24	37.37	44.60	67.56	38.98	-5.16	-0.13	39.32
13	49.22	37.71	44.28	67.81	40.60	-4.37	-0.11	40.83
25	50.67	39.14	43.74	68.85	39.98	-1.95	-0.05	40.03
26	50.23	38.64	43.42	68.49	40.39	-2.23	-0.06	40.45
31	48.38	37.36	41.30	67.55	39.42	-1.39	-0.04	39.45
34	47.35	36.42	40.04	66.84	39.60	-1.12	-0.03	39.62
38	48.02	37.37	40.83	67.55	38.40	-0.84	-0.02	38.41
45	45.59	36.32	39.46	66.76	34.96	-0.56	-0.02	34.97
48	50.73	40.76	44.34	70.01	35.16	-0.64	-0.02	35.16
52	47.51	38.11	41.21	68.10	34.63	-0.34	-0.01	34.64
53	45.40	36.04	39.10	66.55	35.34	-0.49	-0.01	35.34

Tank 22

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	61.66	55.32	60.14	79.23	22.71	-0.67	-0.03	22.72
1	49.13	36.11	43.74	66.60	45.52	-5.84	-0.13	45.90
3	50.02	36.38	44.31	66.81	47.07	-6.13	-0.13	47.47
4	45.86	33.03	39.74	64.19	46.83	-5.34	-0.11	47.13
5	46.26	33.17	39.49	64.30	47.48	-4.83	-0.10	47.73
6	50.33	41.99	48.04	70.86	30.41	-3.20	-0.10	30.58
7	47.25	35.81	42.34	66.37	41.34	-4.64	-0.11	41.60
8	48.00	36.82	43.51	67.14	40.13	-4.66	-0.12	40.40
10	50.22	38.55	45.67	68.42	40.64	-4.84	-0.12	40.93
11	48.42	37.53	43.48	67.67	39.00	-3.70	-0.09	39.17
12	50.32	39.33	46.61	68.99	38.46	-4.90	-0.13	38.77
13	50.42	39.27	45.69	68.95	38.91	-3.96	-0.10	39.11
25	49.32	38.81	42.96	68.61	37.40	-1.49	-0.04	37.43
26	43.83	34.10	38.04	65.04	37.29	-1.79	-0.05	37.33
31	46.84	36.28	39.69	66.74	38.64	-0.89	-0.02	38.65
34	45.95	36.03	39.04	66.54	36.95	-0.43	-0.01	36.96
38	48.24	38.06	41.09	68.06	36.81	-0.26	-0.01	36.81
45	47.68	38.15	41.04	68.13	34.97	-0.09	0.00	34.97
48	47.32	37.70	40.45	67.80	35.41	0.03	0.00	35.41
52	46.59	37.98	40.45	68.01	32.44	0.40	0.01	32.45
53	48.14	38.93	41.85	68.70	33.78	-0.05	0.00	33.78

Tank 23

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	62.92	56.76	63.48	80.05	22.12	-2.26	-0.10	22.24
1	45.30	31.85	37.57	63.22	49.39	-4.34	-0.09	49.58
3	45.19	32.14	39.15	63.46	48.04	-5.87	-0.12	48.40
4	48.93	35.01	42.04	65.76	48.63	-5.35	-0.11	48.92
5	45.81	32.60	38.88	63.83	48.24	-4.90	-0.10	48.48
6	50.24	40.94	47.06	70.13	33.32	-3.41	-0.10	33.49
7	45.91	33.49	40.21	64.56	45.37	-5.26	-0.12	45.67
8	48.28	36.77	43.50	67.10	41.05	-4.70	-0.11	41.32
10	49.82	37.74	44.85	67.83	42.13	-4.97	-0.12	42.42
11	49.18	38.33	44.16	68.26	38.52	-3.45	-0.09	38.68
12	48.71	37.91	45.14	67.96	38.55	-5.07	-0.13	38.89
13	50.14	39.01	45.66	68.76	38.98	-4.26	-0.11	39.21
25	50.06	39.00	43.39	68.75	38.78	-1.73	-0.04	38.82
26	47.88	36.83	41.38	67.15	39.75	-2.18	-0.05	39.81
31	48.81	38.11	41.90	68.10	38.19	-1.14	-0.03	38.21
34	47.44	37.58	41.23	67.71	36.13	-1.05	-0.03	36.14
38	48.43	38.45	42.07	68.35	36.07	-0.91	-0.03	36.08
45	50.29	40.64	44.17	69.92	34.37	-0.60	-0.02	34.37
48	50.00	40.69	44.22	69.96	33.43	-0.59	-0.02	33.43
52	45.51	37.34	40.27	67.53	31.40	-0.20	-0.01	31.40
53	46.40	37.95	41.29	67.98	32.01	-0.64	-0.02	32.01

Tank 24

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	63.33	56.44	64.25	79.86	23.85	-3.25	-0.14	24.07
1	55.64	42.37	50.92	71.12	43.07	-5.75	-0.13	43.45
3	45.79	33.06	40.37	64.21	46.53	-6.05	-0.13	46.92
4	50.04	37.06	44.16	67.32	44.90	-5.07	-0.11	45.19
5	45.71	33.49	39.82	64.56	44.82	-4.79	-0.11	45.08
6	46.42	33.78	40.59	64.79	45.84	-5.31	-0.12	46.14
7	49.38	38.51	45.29	68.39	38.51	-4.48	-0.12	38.77
8	51.52	40.23	47.26	69.63	38.88	-4.49	-0.11	39.14
10	54.11	42.05	49.12	70.91	40.12	-4.26	-0.11	40.35
11	48.15	37.17	42.60	67.40	39.41	-3.15	-0.08	39.53
12	49.93	39.21	46.36	68.91	37.78	-4.77	-0.13	38.08
13	51.02	40.06	46.51	69.51	38.08	-3.89	-0.10	38.28
25	49.61	39.16	43.20	68.87	37.08	-1.32	-0.04	37.10
26	50.82	40.61	44.25	69.90	35.88	-0.73	-0.02	35.89
31	47.95	37.54	40.60	67.68	37.67	-0.35	-0.01	37.67
34	46.61	36.56	39.55	66.95	37.07	-0.36	-0.01	37.07
38	46.39	36.57	39.49	66.95	36.42	-0.26	-0.01	36.42
45	47.28	38.46	41.34	68.36	32.87	-0.05	0.00	32.87
48	47.05	38.23	41.16	68.19	32.97	-0.14	0.00	32.97
52	50.38	41.72	44.29	70.67	31.37	0.57	0.02	31.38
53	48.95	40.14	42.97	69.57	32.26	0.16	0.00	32.26

Table S11. Results of the chromatic coordinates obtained for wine of Alfaro 2019.

Tank 01

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	68.91	60.67	67.84	82.20	26.23	-2.30	-0.09	26.34
1	67.27	57.04	63.14	80.20	31.26	-1.68	-0.05	31.30
2	53.41	42.74	47.85	71.38	36.29	-2.12	-0.06	36.35
4	42.20	31.29	34.88	62.75	42.31	-1.71	-0.04	42.34
5	47.81	36.30	41.40	66.75	41.28	-2.90	-0.07	41.38
6	49.75	37.80	43.53	67.87	41.74	-3.41	-0.08	41.88
7	47.46	35.43	40.71	66.08	43.19	-3.23	-0.07	43.31
8	50.57	38.74	44.55	68.56	41.00	-3.38	-0.08	41.14
11	47.58	36.09	41.41	66.59	41.33	-3.19	-0.08	41.45
12	49.97	38.42	43.71	68.33	40.38	-2.83	-0.07	40.48
13	47.42	35.67	40.28	66.27	42.26	-2.40	-0.06	42.33
14	48.86	37.29	42.50	67.50	40.94	-2.88	-0.07	41.04
15	55.93	44.92	49.85	72.84	36.39	-1.69	-0.05	36.43
19	49.86	38.59	42.91	68.45	39.54	-1.70	-0.04	39.58
21	50.51	39.56	43.21	69.16	38.25	-0.83	-0.02	38.26
25	45.26	35.30	38.34	65.98	37.38	-0.54	-0.01	37.39
28	45.51	35.96	38.96	66.49	35.93	-0.43	-0.01	35.93
32	53.56	43.99	46.04	72.22	33.05	1.29	0.04	33.08
35	49.89	42.26	44.06	71.05	28.41	1.47	0.05	28.45
39	53.99	46.99	49.10	74.18	25.69	1.41	0.05	25.73
42	46.19	40.38	42.08	69.74	23.84	1.47	0.06	23.89
46	47.35	40.81	42.72	70.04	25.81	1.25	0.05	25.84
60	40.71	35.34	37.35	66.01	23.68	0.75	0.03	23.70

Tank 02

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	69.58	61.76	68.57	82.79	25.19	-1.90	-0.08	25.26
1	67.31	56.40	62.50	79.84	32.90	-1.74	-0.05	32.95
2	53.51	42.96	47.68	71.53	35.89	-1.66	-0.05	35.93
4	42.22	31.36	34.99	62.81	42.09	-1.74	-0.04	42.13
5	51.60	39.63	44.97	69.20	40.96	-2.73	-0.07	41.05
6	50.49	38.98	44.97	68.74	40.00	-3.53	-0.09	40.15
7	47.15	35.75	41.38	66.33	41.26	-3.60	-0.09	41.41
8	49.64	38.28	43.78	68.22	39.93	-3.09	-0.08	40.05
11	50.75	39.75	45.08	69.29	38.32	-2.70	-0.07	38.42
12	51.59	40.58	46.07	69.88	38.03	-2.78	-0.07	38.13
13	49.20	38.67	43.03	68.52	37.49	-1.73	-0.05	37.53
14	53.07	41.67	47.00	70.64	38.58	-2.46	-0.06	38.66
15	52.84	42.02	46.72	70.89	36.93	-1.74	-0.05	36.97
19	47.77	36.65	40.87	67.02	40.00	-1.80	-0.05	40.04
21	51.83	41.05	44.61	70.21	37.19	-0.58	-0.02	37.20
25	45.49	35.68	38.84	66.27	36.77	-0.65	-0.02	36.77
28	51.38	41.65	44.95	70.63	34.22	-0.25	-0.01	34.22
32	59.22	49.80	52.80	75.95	31.07	0.67	0.02	31.08
35	53.17	45.72	48.37	73.36	27.12	0.76	0.03	27.13
39	58.30	50.40	52.92	76.31	27.25	1.19	0.04	27.28
42	47.75	41.65	43.86	70.63	24.39	0.96	0.04	24.41
46	50.00	43.28	45.32	71.75	25.73	1.26	0.05	25.76
60	44.54	38.68	40.91	68.52	24.37	0.73	0.03	24.38

Tank 03

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	68.25	58.63	66.46	81.09	29.63	-3.05	-0.10	29.78
1	59.25	48.58	55.48	75.19	34.39	-3.25	-0.09	34.54
2	48.58	37.74	42.36	67.83	38.77	-2.15	-0.06	38.83
4	42.20	31.25	34.94	62.71	42.46	-1.84	-0.04	42.50
5	47.49	35.84	40.52	66.40	41.90	-2.46	-0.06	41.97
6	52.69	40.63	46.38	69.92	40.71	-3.05	-0.07	40.83
7	45.42	34.14	39.22	65.07	41.76	-3.18	-0.08	41.88
8	48.31	37.01	42.16	67.29	40.34	-2.86	-0.07	40.44
11	46.63	35.89	40.43	66.43	39.33	-2.29	-0.06	39.39
12	53.31	41.84	46.95	70.76	38.68	-2.21	-0.06	38.75
13	48.98	37.88	41.79	67.93	39.40	-1.30	-0.03	39.42
14	48.70	37.72	42.42	67.81	39.17	-2.25	-0.06	39.23
15	52.02	42.14	46.27	70.97	34.44	-1.11	-0.03	34.46
19	46.65	36.38	39.79	66.81	37.77	-0.87	-0.02	37.78
21	53.27	42.28	45.21	71.06	37.29	0.21	0.01	37.29
25	45.28	35.54	37.48	66.16	36.65	0.85	0.02	36.66
28	46.68	36.38	39.60	66.81	37.87	-0.65	-0.02	37.88
32	48.49	39.23	41.60	68.92	33.82	0.61	0.02	33.82
35	49.97	40.94	43.29	70.14	32.59	0.77	0.02	32.59
39	53.12	45.51	47.27	73.23	27.58	1.69	0.06	27.63
42	46.20	40.38	42.00	69.74	23.87	1.56	0.07	23.92
46	49.73	43.23	44.67	71.71	25.16	1.93	0.08	25.23
60	45.70	39.25	40.77	68.93	25.93	1.61	0.06	25.98

Tank 04

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	70.73	61.55	69.68	82.68	28.12	-3.02	-0.11	28.28
1	64.52	53.58	60.14	78.21	33.68	-2.42	-0.07	33.76
2	47.26	35.90	40.58	66.44	41.06	-2.45	-0.06	41.14
4	40.55	29.43	32.96	61.16	44.12	-1.87	-0.04	44.16
5	47.63	35.58	40.26	66.20	43.16	-2.50	-0.06	43.23
6	49.13	37.01	42.89	67.28	42.62	-3.70	-0.09	42.78
7	39.18	28.45	33.40	60.29	43.57	-3.96	-0.09	43.75
8	44.35	32.81	37.89	64.01	43.24	-3.38	-0.08	43.37
11	48.56	37.04	42.40	67.31	40.93	-3.09	-0.08	41.05
12	50.42	39.40	44.76	69.04	38.51	-2.77	-0.07	38.61
13	46.65	35.24	39.94	65.93	41.54	-2.57	-0.06	41.62
14	45.74	34.71	39.93	65.52	40.74	-3.27	-0.08	40.87
15	48.25	37.08	41.79	67.33	39.98	-2.34	-0.06	40.05
19	47.81	35.84	40.92	66.40	42.78	-2.93	-0.07	42.89
21	48.85	38.18	42.02	68.15	38.11	-1.19	-0.03	38.13
25	41.77	32.84	36.48	64.03	35.48	-1.56	-0.04	35.51
28	38.44	30.67	34.28	62.23	32.85	-1.81	-0.06	32.90
32	50.81	42.86	46.51	71.46	29.14	-0.53	-0.02	29.14
35	44.15	37.22	40.96	67.44	27.87	-1.18	-0.04	27.89
39	52.20	45.14	47.93	72.98	26.23	0.57	0.02	26.24
42	46.38	40.28	42.98	69.67	24.69	0.32	0.01	24.70
46	50.23	42.97	45.48	71.54	27.24	0.73	0.03	27.25
60	33.48	28.12	30.66	60.00	25.79	-0.67	-0.03	25.80

Tank 05

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	64.83	52.81	60.05	77.77	36.31	-3.11	-0.09	36.44
1	47.76	33.09	35.72	64.24	51.98	-0.24	0.00	51.98
2	38.04	24.85	25.64	56.93	54.42	1.66	0.03	54.45
4	33.38	20.42	19.92	52.31	58.59	3.72	0.06	58.71
5	34.97	21.12	19.90	53.08	60.81	5.08	0.08	61.02
6	36.88	22.89	22.77	54.96	59.11	3.08	0.05	59.19
7	33.32	20.24	19.84	52.10	59.29	3.51	0.06	59.40
8	37.49	22.84	22.57	54.90	61.34	3.34	0.05	61.43
11	36.76	22.64	22.98	54.69	59.85	2.26	0.04	59.89
12	39.97	25.48	27.28	57.54	57.92	0.13	0.00	57.92
13	36.31	22.49	24.49	54.55	59.01	-0.56	-0.01	59.01
14	36.43	22.50	24.46	54.56	59.36	-0.50	-0.01	59.36
15	38.78	24.02	25.31	56.11	60.33	0.78	0.01	60.33
19	36.42	22.25	23.43	54.29	60.47	0.78	0.01	60.47
21	39.70	24.99	26.73	57.06	59.14	0.15	0.00	59.14
25	32.27	20.10	21.37	51.95	56.17	0.40	0.01	56.17
28	37.73	24.12	25.95	56.20	56.52	-0.08	0.00	56.52
32	38.51	24.41	25.64	56.49	57.80	0.90	0.02	57.81
35	35.80	22.20	22.38	54.24	58.62	2.53	0.04	58.67
39	36.41	23.32	24.13	55.40	55.68	1.50	0.03	55.70
42	34.52	22.28	23.46	54.32	53.89	0.79	0.01	53.90
46	32.13	20.29	20.64	52.16	54.78	2.10	0.04	54.82
60	34.59	22.30	22.48	54.35	54.02	2.53	0.05	54.08

Tank 06

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	74.49	62.79	71.09	83.33	33.18	-3.04	-0.09	33.32
1	50.07	34.96	37.73	65.72	51.89	-0.24	0.00	51.89
2	37.98	24.76	25.44	56.84	54.58	1.83	0.03	54.61
4	36.81	23.20	23.65	55.28	57.49	2.12	0.04	57.53
5	38.52	23.69	22.95	55.78	60.90	4.19	0.07	61.04
6	37.06	23.08	23.05	55.16	58.85	2.93	0.05	58.93
7	35.05	21.44	21.17	53.42	59.60	3.29	0.06	59.69
8	36.11	22.44	22.94	54.49	58.57	1.97	0.03	58.61
11	36.26	22.63	23.23	54.68	58.23	1.80	0.03	58.26
12	39.12	24.66	26.22	56.74	58.67	0.41	0.01	58.68
13	38.38	23.86	25.97	55.95	59.74	-0.56	-0.01	59.75
14	33.99	21.12	23.31	53.08	57.39	-1.09	-0.02	57.40
15	36.94	23.25	25.17	55.34	57.70	-0.32	-0.01	57.70
19	39.55	24.98	26.91	57.06	58.67	-0.14	0.00	58.67
21	40.17	25.71	28.10	57.76	57.58	-0.76	-0.01	57.58
25	34.03	20.89	21.86	52.83	58.61	1.02	0.02	58.62
28	36.10	22.68	23.86	54.74	57.47	0.83	0.01	57.47
32	41.49	26.19	27.51	58.22	59.69	0.93	0.02	59.70
35	34.44	21.46	21.79	53.45	57.38	2.22	0.04	57.42
39	36.57	23.10	23.42	55.17	57.19	2.32	0.04	57.24
42	35.83	23.00	24.15	55.07	55.15	0.91	0.02	55.16
46	29.96	18.81	19.33	50.47	54.04	1.67	0.03	54.07
60	33.75	21.64	22.16	53.64	54.15	1.89	0.03	54.18

Tank 07

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	68.55	56.75	64.40	80.04	34.78	-3.07	-0.09	34.92
1	46.91	31.73	33.62	63.12	54.42	0.61	0.01	54.42
2	39.81	25.75	26.23	57.80	56.30	2.22	0.04	56.34
4	31.51	19.22	18.78	50.94	57.79	3.57	0.06	57.90
5	34.05	20.63	19.63	52.54	59.97	4.65	0.08	60.15
6	37.52	23.34	23.14	55.42	59.21	3.24	0.05	59.30
7	33.61	20.15	19.18	52.01	60.71	4.63	0.08	60.89
8	37.56	23.04	22.81	55.11	60.69	3.28	0.05	60.77
11	37.53	23.11	23.07	55.19	60.26	2.96	0.05	60.33
12	40.35	25.61	27.12	57.67	58.52	0.59	0.01	58.52
13	36.03	22.18	23.91	54.22	59.45	-0.15	0.00	59.45
14	37.62	23.21	25.13	55.28	60.14	-0.34	-0.01	60.14
15	34.71	21.88	23.59	53.90	56.35	-0.15	0.00	56.35
19	37.60	22.93	23.69	55.00	61.31	1.56	0.03	61.33
21	41.05	26.05	28.09	58.08	58.93	-0.19	0.00	58.93
25	34.03	20.89	21.86	52.83	58.61	1.02	0.02	58.62
28	32.80	19.99	20.59	51.82	58.65	1.61	0.03	58.67
32	37.36	23.18	24.05	55.26	59.40	1.41	0.02	59.42
35	33.17	20.53	20.64	52.43	57.33	2.56	0.04	57.39
39	35.51	22.39	22.77	54.44	56.77	2.19	0.04	56.81
42	34.95	22.31	23.34	54.36	55.22	1.06	0.02	55.23
46	30.82	19.35	19.70	51.10	54.57	2.04	0.04	54.61
60	32.58	20.74	20.82	52.66	54.22	2.62	0.05	54.29

Tank 08

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	66.73	54.16	61.03	78.55	37.19	-2.65	-0.07	37.28
1	53.76	37.42	40.38	67.59	53.51	-0.23	0.00	53.51
2	40.33	26.33	27.18	58.35	55.56	1.68	0.03	55.59
4	35.50	22.12	22.09	54.16	57.94	2.90	0.05	58.02
5	35.64	22.60	23.09	54.65	56.29	2.00	0.04	56.33
6	37.07	22.73	21.85	54.80	60.43	4.42	0.07	60.59
7	31.31	18.90	18.42	50.57	58.66	3.65	0.06	58.77
8	37.33	22.96	22.98	55.03	60.29	2.83	0.05	60.36
11	36.23	22.49	22.83	54.54	58.75	2.24	0.04	58.79
12	41.03	25.75	27.00	57.80	60.09	1.00	0.02	60.09
13	38.46	23.76	25.43	55.85	60.43	0.14	0.00	60.43
14	37.78	23.45	25.47	55.54	59.55	-0.47	-0.01	59.56
15	40.62	25.48	27.04	57.54	59.95	0.49	0.01	59.95
19	37.00	22.53	23.30	54.58	61.12	1.51	0.02	61.14
21	41.19	26.38	28.47	58.40	57.97	-0.21	0.00	57.97
25	33.79	20.93	21.99	52.87	57.63	0.85	0.01	57.64
28	31.52	19.34	19.92	51.08	57.23	1.60	0.03	57.25
32	38.47	24.15	24.99	56.23	58.79	1.52	0.03	58.81
35	35.34	22.12	22.11	54.15	57.46	2.86	0.05	57.53
39	37.02	23.48	23.54	55.57	56.94	2.80	0.05	57.01
42	35.36	22.81	23.60	54.87	54.41	1.50	0.03	54.43
46	32.09	20.25	20.41	52.12	54.82	2.45	0.04	54.87
60	33.10	21.20	20.99	53.16	53.94	3.18	0.06	54.03

Tank 09

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	66.58	57.49	65.09	80.45	28.66	-2.96	-0.10	28.82
1	66.77	55.18	61.65	79.14	34.73	-2.19	-0.06	34.79
2	50.53	40.28	44.77	69.67	36.08	-1.70	-0.05	36.12
4	45.15	33.04	36.36	64.19	44.80	-1.14	-0.03	44.81
5	50.03	38.07	43.13	68.07	41.65	-2.61	-0.06	41.73
6	51.49	39.75	45.38	69.29	40.26	-3.02	-0.07	40.37
7	44.61	33.47	38.06	64.54	41.72	-2.68	-0.06	41.80
8	48.30	37.28	42.76	67.48	39.47	-3.21	-0.08	39.60
11	49.22	37.83	42.62	67.90	40.20	-2.32	-0.06	40.27
12	51.95	40.92	46.37	70.12	37.91	-2.69	-0.07	38.01
13	47.92	37.00	40.84	67.28	39.31	-1.33	-0.03	39.33
14	47.66	37.31	41.82	67.51	37.57	-2.06	-0.05	37.63
15	54.00	43.43	47.17	71.84	35.80	-0.58	-0.02	35.80
19	51.87	40.82	44.57	70.05	38.01	-0.82	-0.02	38.02
21	54.05	42.83	45.97	71.44	37.66	0.02	0.00	37.66
25	46.68	35.84	38.95	66.39	39.66	-0.57	-0.01	39.67
28	48.80	38.05	41.29	68.06	38.36	-0.50	-0.01	38.37
32	55.41	44.57	47.42	72.61	36.09	0.47	0.01	36.10
35	48.17	39.86	42.40	69.37	30.99	0.46	0.01	31.00
39	55.23	47.93	50.33	74.78	26.24	1.17	0.04	26.27
42	52.17	45.25	47.35	73.06	25.85	1.32	0.05	25.88
46	50.48	43.46	45.46	71.87	26.51	1.31	0.05	26.54
60	49.16	41.93	43.86	70.82	27.43	1.31	0.05	27.46

Tank 10

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	71.62	61.52	69.29	82.66	30.09	-2.73	-0.09	30.22
1	70.17	58.22	64.81	80.86	34.75	-2.02	-0.06	34.81
2	53.60	42.57	46.74	71.26	37.30	-1.12	-0.03	37.31
4	43.32	31.55	34.55	62.97	44.68	-0.89	-0.02	44.69
5	49.31	37.44	42.29	67.61	41.70	-2.44	-0.06	41.78
6	51.37	39.37	44.87	69.02	41.17	-2.95	-0.07	41.27
7	46.11	34.51	39.14	65.37	42.46	-2.59	-0.06	42.53
8	51.50	39.51	44.78	69.12	41.06	-2.66	-0.06	41.14
11	49.20	37.86	42.39	67.91	40.07	-2.03	-0.05	40.13
12	50.63	39.62	44.73	69.20	38.39	-2.47	-0.06	38.47
13	49.18	37.45	41.12	67.62	41.31	-1.06	-0.03	41.33
14	51.09	39.81	44.12	69.34	39.03	-1.56	-0.04	39.06
15	51.07	39.86	43.79	69.37	38.81	-1.13	-0.03	38.83
19	53.02	41.03	45.32	70.20	40.37	-1.40	-0.03	40.39
21	54.35	42.94	45.72	71.51	38.11	0.43	0.01	38.11
25	43.65	33.44	35.42	64.51	39.02	0.63	0.02	39.03
28	43.57	33.31	35.74	64.41	39.21	0.04	0.00	39.21
32	56.02	44.72	47.23	72.71	37.17	0.85	0.02	37.18
35	45.97	37.19	39.06	67.42	33.22	1.07	0.03	33.24
39	50.37	42.09	43.71	70.93	30.23	1.66	0.05	30.28
42	50.54	43.37	44.93	71.80	26.93	1.80	0.07	26.99
46	48.67	41.26	42.49	70.36	28.12	2.06	0.07	28.19
60	43.22	36.45	38.15	66.86	27.62	1.22	0.04	27.65

Tank 11

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	67.96	58.19	65.28	80.84	30.02	-2.45	-0.08	30.12
1	63.23	51.42	57.13	76.93	36.26	-1.83	-0.05	36.30
2	51.50	40.41	44.34	69.76	38.28	-1.07	-0.03	38.29
4	45.91	33.73	37.27	64.75	44.55	-1.33	-0.03	44.57
5	48.53	36.98	41.63	67.26	41.06	-2.28	-0.06	41.13
6	50.34	38.36	43.78	68.28	41.56	-2.98	-0.07	41.66
7	49.59	38.03	42.87	68.05	40.57	-2.36	-0.06	40.64
8	49.96	37.54	42.38	67.68	43.13	-2.42	-0.06	43.20
11	49.62	38.36	42.84	68.29	39.59	-1.91	-0.05	39.64
12	50.91	39.82	44.83	69.34	38.53	-2.33	-0.06	38.60
13	48.56	37.22	40.63	67.44	40.34	-0.79	-0.02	40.35
14	51.92	40.27	44.71	69.66	39.83	-1.65	-0.04	39.87
15	48.43	36.83	40.36	67.15	41.29	-0.98	-0.02	41.30
19	49.72	37.89	41.22	67.94	41.37	-0.63	-0.02	41.37
21	49.62	39.28	41.82	68.95	36.72	0.42	0.01	36.73
25	43.76	34.03	36.37	64.98	37.33	0.21	0.01	37.33
28	43.27	33.97	36.72	64.94	36.08	-0.31	-0.01	36.08
32	50.61	41.15	43.40	70.28	33.67	0.89	0.03	33.68
35	52.42	43.17	45.25	71.67	32.46	1.22	0.04	32.48
39	53.27	45.25	46.96	73.06	28.70	1.74	0.06	28.75
42	49.44	42.76	44.15	71.39	25.73	1.96	0.08	25.80
46	48.13	41.46	42.83	70.50	26.02	1.90	0.07	26.09
60	48.01	40.92	42.05	70.12	27.32	2.16	0.08	27.40

Tank 12

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	61.18	51.93	58.47	77.24	30.15	-2.56	-0.08	30.26
1	60.34	47.05	52.68	74.22	41.18	-2.19	-0.05	41.24
2	53.55	42.44	46.55	71.17	37.54	-1.07	-0.03	37.56
4	47.05	34.59	38.10	65.43	44.85	-1.20	-0.03	44.87
5	53.41	41.09	45.80	70.24	41.18	-1.86	-0.05	41.22
6	52.12	40.18	45.56	69.60	40.60	-2.69	-0.07	40.69
7	46.33	34.70	39.29	65.51	42.47	-2.51	-0.06	42.54
8	45.05	34.00	38.36	64.96	41.17	-2.32	-0.06	41.24
11	47.15	36.38	40.57	66.81	39.19	-1.81	-0.05	39.23
12	49.40	38.38	43.11	68.30	38.95	-2.20	-0.06	39.01
13	49.56	37.73	40.87	67.82	41.48	-0.43	-0.01	41.48
14	51.85	40.07	44.29	69.52	40.24	-1.43	-0.04	40.27
15	48.27	36.68	40.22	67.04	41.31	-1.00	-0.02	41.33
19	50.56	38.70	42.22	68.53	41.07	-0.78	-0.02	41.07
21	52.86	41.15	43.78	70.28	39.59	0.47	0.01	39.59
25	42.51	32.84	34.92	64.03	37.71	0.45	0.01	37.71
28	35.87	22.75	23.64	54.82	56.37	1.34	0.02	56.37
32	49.83	39.76	41.35	69.30	35.84	1.55	0.04	35.87
35	51.05	42.45	44.09	71.18	30.97	1.66	0.05	31.02
39	53.25	45.34	46.95	73.12	28.40	1.85	0.07	28.46
42	48.00	40.88	42.47	70.09	27.40	1.63	0.06	27.45
46	49.58	42.14	43.70	70.97	27.94	1.74	0.06	28.00
60	43.46	36.36	37.85	66.79	28.64	1.47	0.05	28.67

continued

Table S11. Results of the chromatic coordinates obtained for wine of Alfaro 2019.

Tank 13

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	56.98	42.16	46.62	70.98	47.01	-1.47	-0.03	47.03
1	50.83	35.27	37.37	65.96	52.89	0.63	0.01	52.89
2	39.37	25.44	25.88	57.50	56.19	2.26	0.04	56.24
4	34.31	21.15	20.66	53.11	58.41	3.69	0.06	58.52
5	38.72	24.38	24.61	56.46	58.61	2.55	0.04	58.67
6	39.17	24.85	25.07	56.93	58.00	2.60	0.04	58.05
7	35.44	22.07	21.94	54.10	58.02	3.06	0.05	58.10
8	37.21	23.61	24.48	55.69	57.03	1.43	0.03	57.05
11	36.47	22.87	23.27	54.94	57.85	2.18	0.04	57.89
12	38.02	24.28	25.80	56.37	56.76	0.44	0.01	56.77
13	37.55	23.36	25.03	55.44	59.25	0.08	0.00	59.25
14	40.59	25.62	27.60	57.68	59.24	-0.13	0.00	59.24
15	39.39	24.94	26.55	57.02	58.33	0.36	0.01	58.33
19	38.08	24.07	25.57	56.16	57.87	0.44	0.01	57.87
21	43.45	28.12	30.35	59.99	57.92	-0.23	0.00	57.92
25	35.30	22.14	23.18	54.18	57.17	1.03	0.02	57.18
28	32.84	20.58	21.47	52.49	55.92	1.14	0.02	55.93
32	37.90	23.88	24.44	55.96	58.11	1.97	0.03	58.15
35	37.64	24.21	24.54	56.29	55.85	2.37	0.04	55.90
39	39.69	25.71	26.23	57.76	56.08	2.16	0.04	56.12
42	37.00	23.95	24.74	56.04	54.84	1.60	0.03	54.86
46	37.59	24.38	24.65	56.47	54.92	2.48	0.05	54.97
60	35.88	23.61	23.65	55.70	52.60	2.83	0.05	52.68

Tank 14

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	60.75	44.64	49.64	72.65	48.91	-1.79	-0.04	48.95
1	50.48	35.08	37.20	65.81	52.61	0.58	0.01	52.62
2	37.73	24.39	24.76	56.48	55.37	2.31	0.04	55.42
4	32.59	20.21	20.10	52.07	56.84	2.95	0.05	56.92
5	37.86	23.21	22.32	55.29	60.89	4.45	0.07	61.05
6	33.92	20.80	20.10	52.73	58.68	4.10	0.07	58.83
7	35.40	21.69	21.11	53.70	59.60	3.87	0.06	59.73
8	39.15	24.93	25.70	57.01	57.62	1.70	0.03	57.64
11	36.66	23.01	23.29	55.08	57.85	2.40	0.04	57.90
12	40.39	25.77	27.27	57.82	58.01	0.62	0.01	58.01
13	35.35	21.83	23.36	53.84	58.81	0.14	0.00	58.81
14	39.60	24.91	26.77	56.98	59.13	-0.04	0.00	59.13
15	38.76	24.30	25.47	56.39	59.07	1.01	0.02	59.07
19	37.22	23.37	24.47	55.45	58.14	1.03	0.02	58.14
21	42.61	27.52	29.55	59.45	57.75	0.00	0.00	57.75
25	36.10	22.53	23.31	54.59	58.13	1.50	0.03	58.15
28	33.62	20.95	21.45	52.90	56.92	1.88	0.03	56.95
32	39.81	25.58	26.58	57.64	56.97	1.39	0.02	56.98
35	39.89	25.86	26.34	57.90	56.09	2.22	0.04	56.13
39	37.18	23.96	24.30	56.05	55.43	2.35	0.04	55.48
42	35.31	22.61	22.76	54.67	55.10	2.60	0.05	55.16
46	34.01	21.74	21.57	53.75	54.60	3.13	0.06	54.69
60	33.75	21.81	21.30	53.83	53.36	3.76	0.07	53.49

Tank 15

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	59.88	43.86	48.55	72.13	49.07	-1.55	-0.03	49.09
1	50.01	34.83	37.31	65.61	52.18	0.11	0.00	52.18
2	41.75	27.30	28.42	59.25	56.02	1.33	0.02	56.03
4	33.60	21.05	21.32	53.01	56.35	2.31	0.04	56.39
5	35.44	21.37	19.81	53.35	61.23	5.71	0.09	61.49
6	35.98	22.27	21.48	54.31	58.92	4.26	0.07	59.07
7	35.82	21.81	20.77	53.83	60.46	4.73	0.08	60.64
8	39.10	24.43	24.31	56.51	59.60	3.13	0.05	59.68
11	37.12	23.08	22.97	55.16	59.05	3.07	0.05	59.13
12	39.89	25.33	26.35	57.39	58.28	1.33	0.02	58.30
13	38.66	24.20	25.96	56.29	59.14	0.06	0.00	59.14
14	38.14	23.61	24.80	55.70	60.02	0.91	0.02	60.03
15	38.32	23.77	24.69	55.86	59.92	1.37	0.02	59.94
19	36.97	22.82	23.58	54.88	59.74	1.55	0.03	59.76
21	39.63	25.15	26.57	57.22	58.21	0.69	0.01	58.22
25	33.63	20.95	21.76	52.90	56.97	1.32	0.02	56.99
28	33.93	21.41	22.03	53.39	55.88	1.69	0.03	55.91
32	40.55	25.79	26.48	57.84	58.44	1.89	0.03	58.47
35	34.82	21.92	21.61	53.95	56.57	3.40	0.06	56.67
39	37.92	24.75	25.09	56.83	54.45	2.38	0.04	54.50
42	34.97	22.42	22.47	54.47	54.80	2.76	0.05	54.87
46	36.34	23.22	22.80	55.30	55.87	3.60	0.06	55.99
60	31.97	20.36	19.46	52.25	53.83	4.49	0.08	54.02

Tank 16

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	54.67	39.63	43.45	69.21	48.87	-1.02	-0.02	48.88
1	47.89	33.04	35.19	64.20	52.50	0.38	0.01	52.51
2	39.44	25.04	24.98	57.12	58.06	3.06	0.05	58.14
4	36.21	22.77	22.91	54.84	57.41	2.63	0.05	57.47
5	36.05	22.26	21.80	54.30	59.20	3.67	0.06	59.31
6	36.43	22.52	21.93	54.57	59.31	3.89	0.07	59.44
7	38.09	23.66	23.47	55.74	59.70	3.21	0.05	59.79
8	38.09	23.66	23.47	55.74	59.70	3.21	0.05	59.79
11	36.80	23.03	23.18	55.10	58.23	2.61	0.04	58.29
12	38.53	24.42	25.54	56.51	57.79	1.10	0.02	57.80
13	36.76	22.52	23.49	54.57	60.39	1.16	0.02	60.40
14	39.56	24.51	25.89	56.60	60.71	0.69	0.01	60.72
15	35.78	22.27	23.28	54.32	58.21	1.09	0.02	58.22
19	35.73	21.99	22.62	54.02	59.33	1.72	0.03	59.36
21	40.80	25.83	27.14	57.87	59.05	0.92	0.02	59.06
25	35.71	22.13	22.63	54.17	58.61	1.95	0.03	58.64
28	50.46	40.89	43.30	70.10	34.08	0.68	0.02	34.09
32	39.47	25.27	26.16	57.34	57.21	1.53	0.03	57.23
35	36.49	22.85	22.40	54.92	58.00	3.66	0.06	58.11
39	36.74	23.31	23.00	55.39	56.78	3.42	0.06	56.88
42	34.27	21.87	21.98	53.89	54.90	2.64	0.05	54.96
46	34.72	22.34	22.25	54.39	54.30	3.00	0.06	54.39
60	34.90	22.41	21.69	54.45	54.63	4.13	0.08	54.79

Tank 17

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	69.97	61.20	69.00	82.49	27.30	-2.78	-0.10	27.44
1	64.62	54.63	61.25	78.83	31.27	-2.37	-0.08	31.36
2	48.52	38.12	42.76	68.11	37.37	-2.12	-0.06	37.43
4	46.15	34.44	38.17	65.31	42.83	-1.49	-0.03	42.85
5	51.31	39.23	44.59	68.92	41.42	-2.80	-0.07	41.51
6	49.86	38.64	44.18	68.49	39.39	-3.09	-0.08	39.51
7	44.99	33.69	38.32	64.72	42.06	-2.69	-0.06	42.15
8	51.14	39.75	45.18	69.29	39.35	-2.81	-0.07	39.45
11	50.71	39.51	44.30	69.12	38.95	-2.13	-0.05	39.00
12	53.42	41.98	47.36	70.85	38.56	-2.49	-0.06	38.64
13	47.63	36.29	40.19	66.74	40.81	-1.48	-0.04	40.84
14	51.74	40.41	44.99	69.76	38.93	-1.80	-0.05	38.97
15	52.61	41.25	45.32	70.35	38.65	-1.14	-0.03	38.66
19	51.76	40.36	44.08	69.73	39.12	-0.84	-0.02	39.13
21	52.89	42.17	44.89	70.99	36.61	0.44	0.01	36.61
25	44.00	34.28	36.47	65.18	37.16	0.44	0.01	37.17
28	48.40	38.52	40.82	68.40	35.80	0.63	0.02	35.80
32	55.71	46.22	48.45	73.69	32.19	1.24	0.04	32.21
35	53.98	45.99	48.02	73.54	28.44	1.43	0.05	28.48
39	56.33	48.92	50.83	75.40	26.33	1.72	0.07	26.39
42	53.33	47.09	48.01	74.24	23.74	2.66	0.11	23.89
46	47.89	41.65	42.69	70.63	24.78	2.30	0.09	24.88
60	48.05	41.38	43.03	70.44	26.04	1.58	0.06	26.08

Tank 18

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	69.31	59.25	67.44	81.43	30.44	-3.29	-0.11	30.61
1	59.97	50.12	56.29	76.14	32.03	-2.40	-0.07	32.12
2	49.92	38.95	43.33	68.72	38.56	-1.72	-0.04	38.60
4	45.17	33.27	36.91	64.38	44.06	-1.52	-0.03	44.08
5	49.17	37.75	42.86	67.83	40.35	-2.71	-0.07	40.44
6	53.22	41.51	47.61	70.53	39.45	-3.32	-0.08	39.59
7	46.88	35.30	40.24	65.98	41.98	-2.85	-0.07	42.08
8	49.66	38.53	43.84	68.41	39.19	-2.83	-0.07	39.29
11	51.97	40.58	45.44	69.88	39.02	-2.09	-0.05	39.07
12	55.15	44.06	49.20	72.27	36.91	-2.00	-0.05	36.97
13	48.83	37.24	41.22	67.46	41.04	-1.46	-0.04	41.07
14	54.15	42.74	47.50	71.38	38.19	-1.74	-0.05	38.23
15	50.55	39.80	43.71	69.32	37.64	-1.11	-0.03	37.66
19	52.46	41.36	44.97	70.43	37.92	-0.62	-0.02	37.92
21	51.90	41.47	43.91	70.50	36.15	0.69	0.02	36.16
25	42.59	33.37	35.40	64.46	36.09	0.57	0.02	36.10
28	45.94	35.55	37.60	66.17	38.52	0.71	0.02	38.52
32	54.56	44.92	46.95	72.84	32.93	1.38	0.04	32.96
35	53.55	44.95	47.05	72.86	30.29	1.30	0.04	30.31
39	54.27	46.74	48.27	74.02	27.10	2.00	0.07	27.17
42	53.26	46.45	47.58	73.84	25.31	2.42	0.10	25.42
46	51.44	44.66	45.41	72.66	25.60	2.75	0.11	25.75
60	44.14	37.60	38.97	67.72	26.63	1.69	0.06	26.68

Tank 19

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	65.11	55.66	63.29	79.42	29.83	-3.17	-0.11	29.99
1	67.30	55.97	62.46	79.60	33.94	-2.13	-0.06	34.01
2	50.61	39.77	44.30	69.31	37.88	-1.80	-0.05	37.92
4	45.04	33.04	36.26	64.19	44.44	-1.00	-0.02	44.46
5	48.32	36.42	41.13	66.84	42.29	-2.41	-0.06	42.35
6	49.00	37.87	43.69	67.93	39.49	-3.50	-0.09	39.64
7	48.18	36.61	41.28	66.99	41.27	-2.35	-0.06	41.34
8	50.24	38.79	43.61	68.60	39.94	-2.24	-0.06	40.00
11	50.51	39.30	43.75	68.97	39.05	-1.76	-0.05	39.09
12	53.32	42.39	47.24	71.14	37.10	-1.87	-0.05	37.15
13	46.66	35.77	39.35	66.35	39.81	-1.14	-0.03	39.82
14	51.93	41.16	45.23	70.29	37.15	-1.15	-0.03	37.16
15	54.57	43.43	47.10	71.85	37.24	-0.50	-0.01	37.24
19	51.70	40.36	43.65	69.73	38.97	-0.35	-0.01	38.97
21	50.87	40.12	42.44	69.55	37.50	0.74	0.02	37.51
25	47.66	37.51	39.49	67.66	36.92	0.95	0.03	36.93
28	45.63	35.84	38.10	66.40	36.64	0.49	0.01	36.64
32	56.91	46.81	48.73	74.07	33.53	1.59	0.05	33.57
35	53.72	44.95	46.88	72.86	30.71	1.49	0.05	30.75
39	56.76	48.84	50.25	75.35	27.63	2.23	0.08	27.72
42	54.62	48.07	48.86	74.87	24.35	2.84	0.12	24.52
46	53.39	46.66	47.45	73.97	25.07	2.79	0.11	25.22
60	45.39	38.93	40.12	68.70	26.03	1.99	0.08	26.11

Tank 20

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	65.04	55.03	62.50	79.06	31.20	-3.09	-0.10	31.35
1	67.72	56.86	63.59	80.10	32.70	-2.26	-0.07	32.78
2	51.24	41.16	45.78	70.29	35.35	-1.76	-0.05	35.39
4	43.55	32.26	35.99	63.56	42.84	-1.76	-0.04	42.88
5	53.07	41.14	46.28	70.27	40.19	-2.33	-0.06	40.25
6	50.28	38.14	44.04	68.12	42.09	-3.56	-0.08	42.24
7	46.19	35.18	39.90	65.89	40.45	-2.59	-0.06	40.53
8	52.53	40.92	46.01	70.12	39.41	-2.29	-0.06	39.48
11	47.27	36.58	41.22	66.96	38.88	-2.32	-0.06	38.95
12	52.14	41.55	46.39	70.56	36.53	-1.95	-0.05	36.58
13	49.73	38.29	42.02	68.24	40.13	-1.05	-0.03	40.15
14	52.43	41.53	45.52	70.54	37.35	-1.03	-0.03	37.37
15	49.55	39.08	42.68	68.81	37.17	-0.83	-0.02	37.18
19	51.19	39.97	43.44	69.45	38.79	-0.59	-0.02	38.80
21	54.53	43.79	46.13	72.09	36.11	0.96	0.03	36.12
25	48.01	37.80	40.02	67.88	36.98	0.69	0.02	36.99
28	45.16	35.36	37.53	66.03	36.89	0.55	0.01	36.89
32	54.99	44.85	46.90	72.79	34.23	1.35	0.04	34.26
35	51.29	42.42	44.35	71.16	31.71	1.33	0.04	31.74
39	54.10	46.55	48.13	73.90	27.17	1.94	0.07	27.24
42	52.32	46.10	47.61	73.61	23.85	1.99	0.08	23.93
46	46.82	41.14	42.15	70.27	23.33	2.31	0.10	23.45
60	45.72	39.50	40.92	69.11	25.20	1.75	0.07	25.26

Tank 21

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	55.99	41.81	47.15	70.74	45.57	-2.46	-0.05	45.64
1	49.53	34.67	38.12	65.49	51.40	-1.11	-0.02	51.41
2	41.78	28.27	30.43	60.13	52.33	-0.11	0.00	52.33
4	34.68	21.34	21.20	53.32	58.77	3.06	0.05	58.85
5	37.06	23.16	23.43	55.24	58.49	2.43	0.04	58.54
6	35.67	21.96	21.85	53.98	59.29	3.03	0.05	59.37
7	40.64	26.05	27.25	58.08	57.67	1.10	0.02	57.68
8	38.48	24.17	24.94	56.26	58.72	1.65	0.03	58.75
11	37.01	23.37	24.22	55.46	57.40	1.45	0.03	57.42
12	39.80	25.77	27.87	57.82	56.18	-0.30	-0.01	56.18
13	37.39	23.59	26.01	55.67	57.73	-1.10	-0.02	57.74
14	36.63	23.10	25.35	55.17	57.38	-0.90	-0.02	57.39
15	40.55	25.98	28.11	58.02	57.63	-0.32	-0.01	57.64
19	40.59	25.88	27.94	57.92	58.18	-0.22	0.00	58.18
21	43.84	30.64	34.89	62.20	49.54	-2.66	-0.05	49.61
25	36.76	23.64	25.57	55.72	55.43	-0.30	-0.01	55.43
28	39.85	26.16	28.30	58.19	54.71	-0.31	-0.01	54.71
32	39.34	25.27	26.40	57.33	56.80	1.16	0.02	56.82
35	37.53	24.05	24.71	56.14	56.15	1.82	0.03	56.18
39	37.14	24.22	25.08	56.31	54.16	1.51	0.03	54.19
42	36.44	24.02	25.33	56.10	52.71	0.74	0.01	52.72
46	38.21	25.06	25.88	57.13	54.08	1.63	0.03	54.10
60	34.12	22.80	23.37	54.86	50.19	1.87	0.04	50.22

Tank 22

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	54.98	41.38	47.03	70.44	44.33	-2.84	-0.06	44.42
1	52.99	37.22	40.82	67.44	52.18	-1.02	-0.02	52.19
2	38.29	24.64	25.40	56.72	56.10	1.69	0.03	56.12
4	35.41	22.78	24.37	54.85	54.70	0.15	0.00	54.70
5	33.30	20.30	20.04	52.18	58.89	3.25	0.06	58.98
6	37.86	23.47	23.65	55.55	59.78	2.58	0.04	59.83
7	36.59	22.72	23.17	54.78	58.93	2.08	0.04	58.97
8	40.37	25.55	26.66	57.61	58.84	1.21	0.02	58.85
11	38.94	24.82	26.22	56.90	57.43	0.69	0.01	57.44
12	40.82	26.30	28.41	58.32	57.20	-0.25	0.00	57.20
13	35.47	21.97	23.92	54.00	58.56	-0.55	-0.01	58.57
14	38.68	24.38	26.87	56.47	58.45	-1.09	-0.02	58.46
15	38.78	24.51	26.34	56.59	58.24	-0.04	0.00	58.24
19	38.41	24.26	26.13	56.34	58.12	-0.13	0.00	58.12
21	40.17	25.86	28.11	57.90	56.99	-0.53	-0.01	56.99
25	36.22	23.34	24.89	55.43	54.92	0.29	0.01	54.93
28	32.00	20.12	21.30	51.97	55.11	0.56	0.01	55.11
32	40.24	26.29	28.18	58.31	55.43	0.08	0.00	55.43
35	36.13	23.41	24.31	55.50	54.30	1.38	0.03	54.32
39	40.75	26.83	27.47	58.82	54.82	2.04	0.04	54.86
42	34.28	22.24	23.01	54.28	53.27	1.49	0.03	53.29
46	34.07	22.23	22.46	54.27	52.57	2.44	0.05	52.63
60	31.00	20.27	20.14	52.14	50.70	3.01	0.06	50.79

Tank 23

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	58.77	43.09	48.28	71.61	48.65	-2.16	-0.04	48.70
1	49.69	34.42	37.53	65.30	52.70	-0.71	-0.01	52.70
2	36.30	23.35	24.19	55.43	55.15	1.47	0.03	55.17
4	-1.59	-0.74	1.18	-38.59	-30.67	-83.46	-1.92	88.92
5	35.38	22.19	22.59	54.23	57.25	2.14	0.04	57.29
6	35.01	21.03	19.90	52.98	61.37	4.91	0.08	61.57
7	34.37	20.91	20.53	52.85	59.73	3.49	0.06	59.83
8	34.87	21.48	21.50	53.48	58.77	2.79	0.05	58.84
11	35.32	21.85	22.20	53.87	58.59	2.20	0.04	58.63
12	37.26	23.22	24.08	55.29	58.92	1.41	0.02	58.94
13	34.85	21.14	22.49	53.10	60.27	0.38	0.01	60.27
14	34.82	21.65	23.46	53.66	57.80	-0.35	-0.01	57.80
15	36.39	22.50	23.61	54.56	59.24	0.94	0.02	59.25
19	39.28	24.69	26.09	56.77	59.05	0.66	0.01	59.06
21	37.96	23.90	25.40	55.99	58.23	0.43	0.01	58.23
25	34.88	21.80	22.71	53.81	57.35	1.21	0.02	57.36
28	34.04	21.23	21.88	53.20	57.07	1.63	0.03	57.10
32	36.89	23.50	24.21	55.58	56.47	1.69	0.03	56.50
35	37.29	23.84	24.28	55.93	56.26	2.17	0.04	56.30
39	37.44	24.05	24.21	56.14	55.88	2.65	0.05	55.94
42	33.61	21.60	22.07	53.60	53.82	1.98	0.04	53.85
46	39.89	26.88	27.68	58.86	51.98	1.78	0.03	52.01
60	34.61	22.76	22.75	54.83	52.04	2.89	0.06	52.12

Tank 24

Time (days)	X	Y	Z	L*	a*	b*	H*	C*
0	63.61	50.55	57.02	76.41	39.39	-2.64	-0.07	39.48
1	56.28	40.74	44.87	70.00	49.51	-1.25	-0.03	49.53
2	41.86	27.64	28.81	59.56	55.02	1.28	0.02	55.03
4	39.52	25.74	27.24	57.79	55.41	0.62	0.01	55.42
5	43.13	27.98	29.32	59.87	57.51	1.06	0.02	57.52
6	41.18	26.06	26.47	58.09	59.28	2.34	0.04	59.32
7	40.90	26.04	26.96	58.07	58.48	1.54	0.03	58.50
8	42.65	27.66	29.33	59.58	57.32	0.54	0.01	57.32
11	42.39	27.56	29.20	59.49	56.95	0.58	0.01	56.96
12	43.25	28.65	31.60	60.47	55.25	-1.18	-0.02	55.26
13	40.89	26.36	29.32	58.38	57.15	-1.52	-0.03	57.17
14	42.92	27.70	30.82	59.62	57.94	-1.54	-0.03	57.96
15	46.58	31.65	35.32	63.05	53.77	-1.75	-0.03	53.80
19	43.91	28.68	31.52	60.50	57.09	-1.03	-0.02	57.10
21	43.07	28.46	31.40	60.30	55.46	-1.19	-0.02	55.47
25	40.91	26.63	28.81	58.63	56.12	-0.32	-0.01	56.12
28	41.21	27.04	28.85	59.01	55.41	0.28	0.01	55.42
32	46.80	31.31	33.80	62.77	55.61	-0.24	0.00	55.61
35	40.50	27.00	28.41	58.98	53.38	0.87	0.02	53.38
39	41.30	27.51	28.66	59.45	53.81	1.32	0.02	53.82
42	38.07	25.44	26.78	57.51	52.02	0.85	0.02	52.03
46	38.77	26.07	27.10	58.10	51.72	1.37	0.03	51.74
60	37.45	25.52	26.01	57.58	49.71	2.18	0.04	49.75

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