STILBENOID CHEMISTRY FROM WINE AND THE GENUS *VITIS*, A REVIEW

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Abstract

Stilbenoids are of great interest on account of their many promising biological activities, especially in regards to prevention and potential treatment of many chronic diseases associated with aging. The simple stilbenoid monomer, *E*-resveratrol, has received the most attention due to early *in vitro* and *in vivo* biological activities in anti-aging assays. Since *Vitis vinifera*, primarily in the form of wine, is a major dietary source of these compounds, there is a tremendous amount of research on resveratrol in wine and grapes. Relatively few biological studies have been performed on other stilbenoids from *Vitis*, primarily due to the lack of commercial sources of many of these compounds. The diverse stilbenoids from this economically important genus are an untapped source of health promoting compounds and because of this, numerous efforts for isolation, identification and quantification of additional stilbenoids have been ongoing. Additionally, due to their role as phytoalexins, stilbenoids play an important role in the defense against pathogens. Therefore, the compounds produced by highly resistant strains are of great interest for the development of resistant crops, natural spray reagents, and as new dietary supplements or pharmaceuticals. Since closely related species are likely to have similar metabolic pathways, a more thorough understanding of the chemical diversity of stilbenoids within *Vitis* is useful in this endeavor. In this review, we focus on stilbenoids found in the *Vitis* genus with the aim of aiding future stilbenoid chemistry, particularly in *V. vinifera* and wine. Additionally, we discuss the efforts to quantify stilbenoids in *Vitis*, with a focus on non-resveratrol stilbenoid compounds.

Key words: oligostilbenoid, resveratrol, *Vitis*, *Vitis vinifera*, wine

Résumé

Les stilbénoïdes présentent un grand intérêt en raison de leurs nombreuses activités biologiques prometteuses, en particulier dans la prévention et le traitement de diverses maladies chroniques liées au vieillissement. Le *E*-resvératrol, monomère stilbénique, a suscité beaucoup d'intérêt de par ses activités biologiques *in vitro* et *in vivo*. Une des principales sources alimentaires en stilbénoïdes est *Vitis vinifera*, principalement sous forme de vin. De nombreux travaux de recherche ont été menés sur le resvératrol dans le vin et le raisin. À ce jour, relativement peu d'études ont été réalisées sur les stilbènes du genre *Vitis* autre que le resvératrol, principalement en raison de leur absence de commercialisation. Ce genre est une source inexploitée de stilbénoïdes d'intérêt potentiel pour la santé et c'est pourquoi de nombreux efforts pour l'isolement, l'identification et la quantification d'autres stilbénoïdes sont en cours. Comme les espèces proches sont susceptibles de présenter des voies métaboliques similaires, une meilleure connaissance de la diversité chimique du genre *Vitis* peut être utile dans cette tâche. Nous avons effectué une revue bibliographie des stilbénoïdes de ce genre économiquement important afin de promouvoir la chimie des stilbénoïdes du vin et des espèces de *Vitis*, plus particulièrement *V. vinifera*. En outre, nous abordons la quantification et la distribution de tous ces stilbénoïdes.

Mots clés: oligostilbénoïde, resvératrol, *Vitis*, *Vitis vinifera*, vin

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INTRODUCTION

Epidemiological studies have attributed moderate consumption of red wine to numerous health benefits such as the prevention of age-related diseases, including some cancers, neurodegenerative diseases, and most strongly, cardiovascular diseases (Anstey *et al*., 2009 ; Chao *et al*., 2008 ; Larrieu *et al*., 2004 ; Orgogozo *et al*., 1997 ; Renaud and de Lorgeril, 1992 ; Wang *et al*., 2006). What accounts for such activity ? A single glass of wine contains the fermented extract of 100 to 140 grape berries, which produces, depending on variety and vinification methods, up to 500 mg of polyphenolic compounds (Lopez *et al*., 2001 ; Stervbo *et al*., 2007 ; Waterhouse and Teissedre, 1997). These polyphenols include a number of known beneficial compounds, the majority being flavonoids, such as anthocyanins and tannins, phenolic acids and stilbenoids. While many of these compounds are found in widely consumed fruits and vegetables, wine is the dominant dietary source of stilbenoids.

Stilbenoids have received considerable attention due to their promising biological activities. The stilbenoid monomer, resveratrol **(1)**, 3,5,4'-trihydroxy-*trans*-stilbene, in particular, has undergone extensive biological testing. Both in vitro and in vivo animal studies of resveratrol have demonstrated promising activities in regards to disease prevention, progression, and treatment (Baur and Sinclair, 2006 ; Howitz *et al*., 2003 ; Jang *et al*., 1997 ; Pezzuto, 2011). Due to these biological activities, it has been concluded that resveratrol could be part of the explanation for the French Paradox and other epidemiological studies supporting the moderate consumption of red wine for the prevention of diseases such as cardiovascular disease (Renaud and de Lorgeril, 1992 ; Renaud *et al*., 1998 ; Sun *et al*., 2002). Since the numerous biological activities reported for resveratrol are outside the scope of this article, we refer the reader to existing biologically focused reviews (Anekonda, 2006 ; Bishayee, 2009 ; Szkudelska and Szkudelski, 2010). More recently, promising biological activities have been shown with other stilbenoids found in *Vitis* species, including piceatannol **(2)**, piceid **(3)**, pterostilbene **(4)**, scirpusin A **(5)**, vaticanol C, α-viniferin **(6)**, and vitisin A **(7)**. These activities include mechanisms related to the prevention of cancers, neurological diseases, and cardiovascular diseases (Chung *et al*., 2010 ; Joseph *et al*., 2008 ; Oshima *et al*., 1995b ; Richard *et al*., 2011 ; Shibata *et al*., 2007 ; Son *et al*., 2010 ; Tsukamoto *et al*., 2010), demonstrating potential health benefits of additional stilbenoids, many of which are known constituents of wine.

As phytoalexins, stilbenoids are induced by infections and mechanical stress, such as that caused by UV damage or insects. Their production affords protection against many *Vitis* pathogens, such as *Plasmopara viticola* (Bavaresco and Fregoni, 2001). Stilbenoids are, therefore, of great interest due to their activity against many devastating vine diseases and pests. Multiple avenues to exploit this activity are being investigated. One potential use of stilbenoids is as a naturally occurring pesticide for non-resistant species, such as *Vitis vinifera* L., the major wine grape. Such usage could reduce reliance on traditional pesticides. In addition to producing stilbenoid rich products such as natural spray reagents, wine, or dietary supplements, another avenue of research involves the use of known induction mechanisms to promote disease resistance (Cantos *et al*., 2003). There is also interest in selectively breeding high stilbenoid producing *Vitis* species by crossing *V. vinifera* with disease resistant, wild *Vitis* (Malacarne *et al*., 2011).

In all, a more thorough knowledge of the chemistry and biology of these molecules can provide multiple health, environmental, and economic benefits. In this review we summarize the current knowledge of stilbenoids found in the *Vitis* genus in addition to recent data on stilbenoid quantitation in *Vitis* and wine.

STILBENOIDS IN THE *VITIS* GENUS

Over 1000 stilbenoids have been structurally characterized throughout the plant kingdom and their distribution and structural variations have been reviewed (Cichewicz and Kouzi, 2002 ; Lin and Yao, 2006 ; Shen *et al*., 2009 ; Sotheeswaran and Pasupathy, 1993). They are found in a number of plant families, including Celastraceae, Cyperaceae, Dipterocarpaceae, Fabaceae, Gnetaceae, Iridaceae, Moraceae, Paeoniaceae and Vitaceae. The Vitaceae family encompasses approximately 900 species within 14 to 17 genera, primarily in tropical regions (Keller, 2010 ; Soejima and Wen, 2006). Of these genera, stilbenoids have been found primarily in only five, the *Ampelopsis*, *Cissus*, *Cyphostemma*, *Parthenocissus* and *Vitis* genera. Due to their economic importance as the major table and wine making grape around the world, the species in the *Vitis* genus have been studied the most. Species from *Vitis* also have a long history of use as medicinal plants, particularly *V. amurensis*, *V. coignetiae*, and *V. vinifera*, the later also being used by the modern nutraceutical and cosmeceutical industries. *Vitis* has, until recently, been divided into two subgenera, the Euvitis and the Muscadinia. Muscadinia is composed of three American species, including the species formerly known as *V. rotundifolia*, the most important economic species of Muscadinia. Due to differences in chromosome number and other characteristics, Muscadinia is now considered its own genus and *V. rotundifolia* is now named *Muscadinia rotundifolia* (Michx.) Small (Bouquet *et al*., 2008 ; Keller, 2010 ; Péros *et al*., 2011). Since it is still of interest in the wine industry, we included this species in our review.

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Within *Vitis*, stilbenoids have been identified in around 20 species, including hybrid species, of the approximate 60 to 70 species found in *Vitis*. In table 1, we have listed the *Vitis* species and the specific plant parts the stilbenoids were isolated from. The remaining two-thirds of the *Vitis* species most likely contain stilbenoids, but have yet to be examined for these compounds. Despite this lack of research in all *Vitis* species, approximately 100 stilbenoid monomers, dimers, and oligomers have been found, and nearly 20 are known constituents of wine.

STILBENOID PRODUCTION

The metabolism of stilbenoids and regulatory interactions are complex and not all mechanisms are currently understood. However, we do know that stilbenoids are downstream secondary metabolic products of the phenylpropanoid pathway and diverge from the flavonoid pathway through the stilbene synthase (STS) enzymes. According to recent analysis of the grapevine genome, there is an estimated 20 to 40 STS genes, many of which have shown to be expressed when exposed to biotic stress (Chong *et al*., 2009).

Since a number of stilbenoids are induced by infections and have antifungal activity, they are considered to be phytoalexins. Comparisons between disease resistant and susceptible *Vitis* species have shown that disease resistant species produce stilbenoids more readily and in higher concentration when exposed to pathogens such as downy mildew, *Plasmopara viticola*, and gray mold, *Botrytis cinerea* (Bavaresco *et al*., 1997 ; Bavaresco and Fregoni, 2001 ; Pezet *et al*., 2004). Stilbenoid production can also be induced by abiotic stress such as UV irradiation, mechanical injury, and certain chemicals (Bavaresco and Fregoni, 2001 ; Bavaresco *et al*., 2009). In fact, the major stilbenoids from *V. vinifera* were first identified in leaves after induction by abiotic and biotic stresses (Langcake and Pryce, 1976 ; Langcake and Pryce, 1977a ; Langcake and Pryce, 1977b ; Langcake and McCarthy, 1979 ; Langcake, 1981). The production of stilbenoids is highly variable among the different plant parts in regards to types produced, concentrations, and response to outside stimuli. For example, resveratrol is induced in both leaves and berries in response to external stimuli, but is constitutively expressed and accumulated in stems and roots where it, along with other stilbenoids, are believed to protect against wood rot. Other stilbenoids, such as piceid, have been shown to be constitutively expressed in various tissues, including berries (Gatto *et al*., 2008).

Due to their biological activities, both in the plant and in humans, the possibility to artificially manipulate stilbenoid levels is of great interest. Research into post-

Table 1. *Vitis* species and plant part where stilbenoids have been reported. References are found in Table 2.

[a]Plant Species	Plant Part(s) Studied
Muscadinia rotundifolia (Michx.) Small (previously *V. rotundifolia* Michx.)	Berries and wine
V. acerifolia Raf. (reported as *V. longii*)	Roots
V. amurensis Rupr.	Leaves, stems and roots
V. berlandieri Planch.	Roots
V. betulifolia Diels & Gilg	Stems
V. chunganensis Hu	Whole plant
V. cinerea (Engelm.) Engelm. ex Millard	Roots
V. coignetiae Pulliat ex Planch.	Berries, leaves, stems, and whole plant
V. davidii (Rom. Caill.) Foëx	Stems
V. flexuosa Thunb.	Stems
V. heyneana Roem. & Schult. (also includes *V. pentagona* Diels & Gilg)	Stems
V. labrusca L. (Concord grape)	Berries, stems, leaves and wine
V. riparia Michx.	Leaves and roots
V. riparia x *V. berlandieri* SO4 (Oppenheim selection no. 4)	Roots
V. rupestris Scheele	Roots
V. solonis longii	Roots
V. solonis richter	Roots
V. thunbergii Sieb. & Zucc.	Roots and stems
V. vinifera L.	Berries, cell suspension cultures, leaves, roots, stems and wine
V. wilsoniae H. J. Veitch	Stems

[a]This table is to meant to provide an up-to-date survey of which *Vitis* species stilbenoids have been reported from. In these studies, many different clones, cultivars, and hybrids have been used, particularly with *V. vinifera*. This information can be found in the original manuscript, however, in many studies, this information was lacking.

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harvest abiotic stresses, such as UV irradiation and ozone treatment, is currently ongoing for the production of high-stilbenoid containing wines and grape-derived products (Cantos *et al*., 2003 ; Gonzalez-Barrio *et al*., 2006 ; Guerrero *et al*., 2010). Efforts are also being made to utilize stilbenoid induction as natural pesticides through known elicitors, such as ethephon and methyl jasmonate (Belhadj *et al*., 2008a ; Belhadj *et al*., 2008b ; Faurie *et al*., 2009). This research could lead ways to safely induce naturally occurring stilbenoids on an industrial scale or use them as spray reagents against disease, which could help reduce or eliminate the need for the currently used pesticides.

STRUCTURAL DIVERSITY OF *VITIS* STILBENOIDS

Structural variations in stilbenoids typically involve stilbenoid monomer polymerization, glycosylation, prenylation, methoxylation, and various hydroxylation patterns. There have been several attempts to delineate and improve the classification of these various derivatives (Lin and Yao, 2006 ; Shen *et al*., 2009 ; Sotheeswaran and Pasupathy, 1993). The proposed classification initially separates the monomers from the oligomers. Oligomers undergo further classifications based on their monomer unit composition and heterogeneous coupling, i. e. resveratrol **(1)**, piceatannol **(2)**, gnetol (2,3', 5',6-tetrahydroxy-*trans*-stilbene), isorhapontigenin (3,4', 5-trihydroxy-3'-methoxy-*trans*-stilbene), and oxyresveratrol. These are further separated into groups with oxygen containing heterocycles (group A), such as ε-viniferin **(8)**, or those without (group B), such as pallidol **(9)**. The few remaining compounds that do not fit within this scheme are assigned to a small miscellaneous category. Resveratrol is the predominant monomer subunit in *Vitis*, with multiple patterns of oligomerization and glycosylation. The resveratrol dimer, ε-viniferin **(8)**, is considered the major oligomer intermediate in *Vitis* species.

In order to better understand the chemical diversity of stilbenoids in *Vitis* species, we have delineated the known stilbenoid compounds with their plant name and part, including those found in wine, in Table 2. Of the approximately 100 stilbenoids identified in *Vitis*, 18 are monomers. These are primarily methoxylated and glycosylated derivatives of resveratrol and piceatannol along with their *Z* (c*is*) and *E* (*trans*) isomers. A large portion of these monomers are glycosides, many of which were isolated and identified in *V. vinifera* cell culture studies, a method developed in our laboratory for further biological studies and potential industrial production of these compounds (Krisa *et al*., 1999 ; Waffo-Téguo *et al*., 1996a). Seventeen of these 18 monomers have been identified in parts of the *V. vinifera* vine or in cell cultures, while only nine are currently known in wine. Among these is the more unusual 2,4,6-trihydroxyphenanthrene 2-*O*-glucoside **(10)**, isolated from a Riesling wine (Baderschneider and Winterhalter, 2000). There are 35 reported dimers in *Vitis*, 24 having been identified in *V. vinifera* and its cell cultures, and nine in wine. The dimers found in wine are mostly resveratrol dimers, derivatives of viniferin and pallidol, with ε-viniferin **(8)** being the most common.

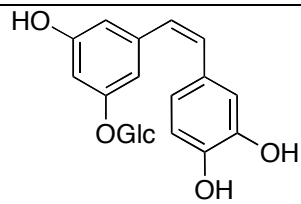
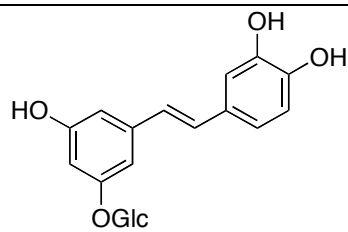
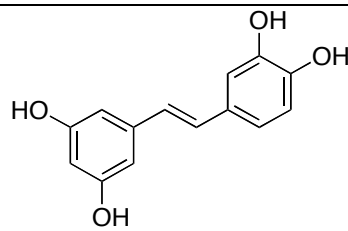
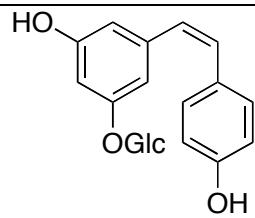
There are 16 known trimers in *Vitis* species. Six of these trimers have been reported in various *V. vinifera* plant parts, including the roots, leaves, and stems, although, to date, none of these have been reported in wine. The presence of trimers, based on molecular weight using HPLC-MS-MS, has, however, been suggested in grapes treated with UV light and ozone (Gonzalez-Barrio *et al*., 2006). Additionally, there are a total of 26 known tetramers, including a tetramer breakdown product, (-)-*viniferal* **(11)**. While only one of these compounds, hopeaphenol **(12)**, has been reported in wine, 14 others are known *V. vinifera* plant part constituents. Finally, there are two known *Vitis* stilbenoid pentamers and one hexamer, none of which have been found in wine or any *V. vinifera* plant part.

Several notable points exist in the literature, relating to stilbenoid nomenclature and structure, which complicate matters of identification and classification. There are a number of instances where common names given to particular stilbenoids can lead to confusion. In 2009, two independent research groups published the isolation and identification of two new different stilbenoid dimers, one from *V. vinifera* stembark and one from *V. thunbergii* roots. These groups published concurrently and chose the same name for their newly identified compounds, vitisinol E **(13,14)** (Chiou *et al*., 2009 ; Choi *et al*., 2009). The opposite situation occurred in 1999, when two groups isolated the same stilbenoid dimer but gave it two different common names, amurensin H and viniferifuran **(15)** (Huang *et al*., 1999a ; Ito *et al*., 1999). Another area of confusion with nomenclature comes from the use of the common name "vitisin" », which refers to either the well-characterized pyranoanthocyanin pigments in wine, vitisin A and B, or to a series of stilbenoid oligomers, vitisins A through E.

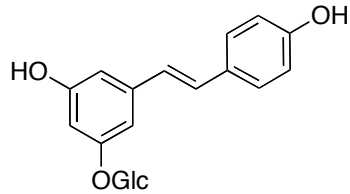
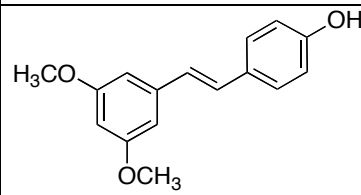
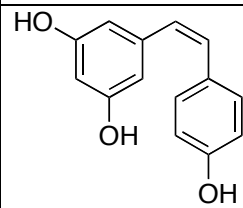
Another potential point of confusion lies in the structure and naming of the ε-viniferins. The compound itself is a simple resveratrol dimer, however, there are two stereochemical centers, at positions 7a and 8a on the dihydrofuran ring, allowing for four potential stereoisomers (see compound 8 in Table 2 for numbering). The *trans* configuration of the two hydrogens in this saturated ring system, meaning one alpha and one beta hydrogen, is most common in *Vitis*.

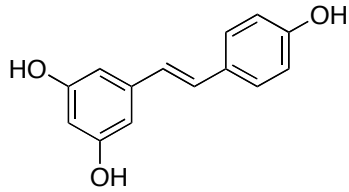
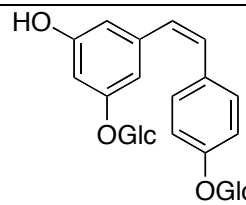
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Table 2. Compounds reported in *Vitis* species.

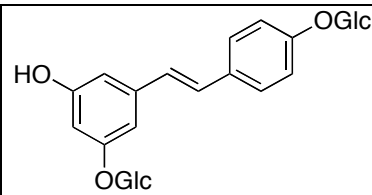
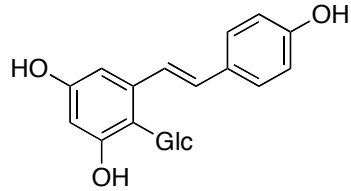
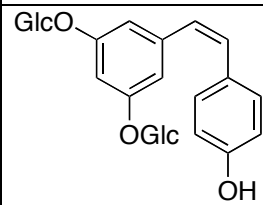
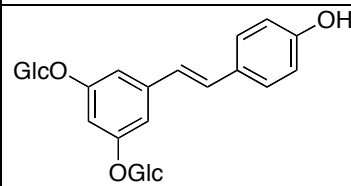
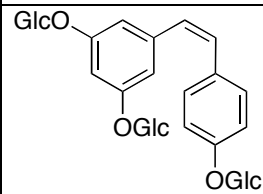
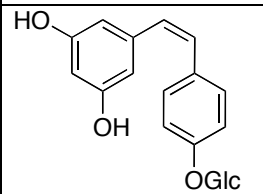
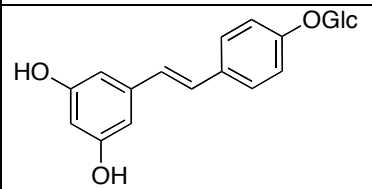
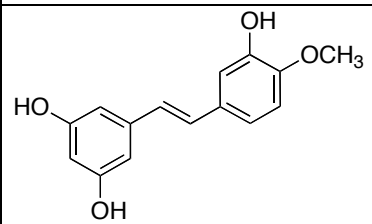
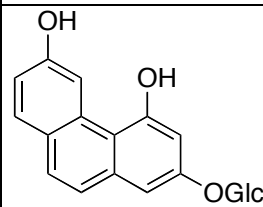
Monomers				
Compound Name	**[a]Structure**	**M.W.**	**Plant Name and Part**	**[b]References**
Z-Astringin		406.38	*V. vinifera* cell suspension cultures and wine	(Buiarelli *et al.*, 2007; Waffo-Téguo *et al.*, 1998)
E-Astringin (**18**)		406.38	*V. coignetiae* berries *V. vinifera* cell suspension cultures, and red and white wine	(Buiarelli *et al.*, 2007; Carando *et al.*, 1999; Kim *et al.*, 2009; Krisa *et al.*, 1999; Naugler *et al.*, 2007; Ribeiro de Lima *et al.*, 1999; Vitrac *et al.*, 2002; Vitrac *et al.*, 2005; Waffo-Téguo *et al.*, 1996a; Waffo-Téguo *et al.*, 1998)
E-Piceatannol (astringinin) (**2**)		244.24	*V. amurensis* leaves and stems *V. coignetiae* berries *V. vinifera* stems, berries, and wine	(Bavaresco *et al.*, 2002; Buiarelli *et al.*, 2007; Delaunay *et al.*, 2002; Ha *et al.*, 2009b; Kim *et al.*, 2009; Kulesh *et al.*, 2006; Zga *et al.*, 2009)
Z-Piceid		390.38	*V. labrusca* berries *M. rotundifolia* berries *V. vinifera* berries, leaves, cell cultures and red and white wine	(Adrian *et al.*, 2000; Baderschneider and Winterhalter, 2000; Buiarelli *et al.*, 2007; Krisa *et al.*, 1999; Larronde *et al.*, 2005; Leblanc *et al.*, 2008; Mattivi *et al.*, 1995; Naugler *et al.*, 2007; Pezet *et al.*, 2003; Ribeiro de Lima *et al.*, 1999; Santamaria *et al.*, 2010; Vitrac *et al.*, 2001; Vitrac *et al.*, 2002; Waffo-Téguo *et al.*, 1998)

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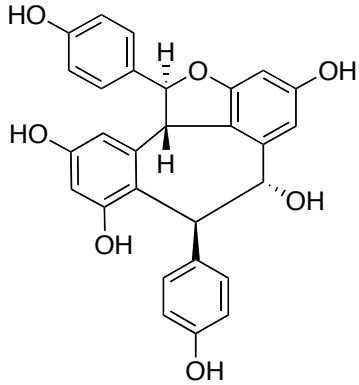
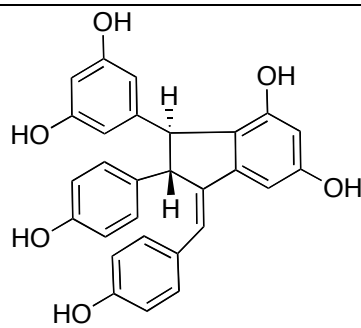
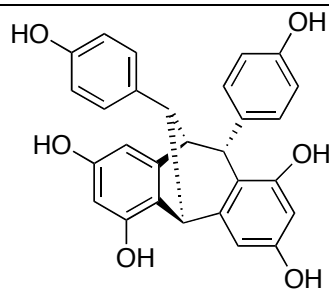
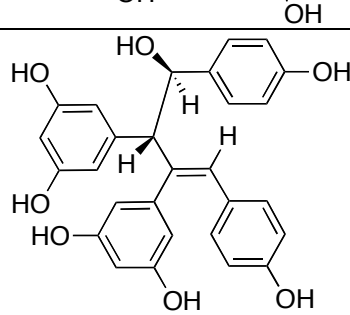
E-Piceid (**3**)		390.38	*V. amurensis* leaves and stems *V. coignetiae* berries *V. labrusca* berries *M. rotundifolia* berries *V. vinifera* berries, cell suspension cultures, leaves, stems and red and white wine	(Adrian *et al.*, 2000; Baderschneider and Winterhalter, 2000; Buiarelli *et al.*, 2007; Guebailia *et al.*, 2006; Ha *et al.*, 2009a; Ha *et al.*, 2009b; Jean-Denis *et al.*, 2006; Kim *et al.*, 2009; Krisa *et al.*, 1999; Landrault *et al.*, 2002; Larronde *et al.*, 2005; Leblanc *et al.*, 2008; Mattivi *et al.*, 1995; Naugler *et al.*, 2007; Ribeiro de Lima *et al.*, 1999; Santamaria *et al.*, 2010; Vitrac *et al.*, 2001; Vitrac *et al.*, 2002; Vitrac *et al.*, 2005; Waffo-Téguo *et al.*, 1996a; Waffo-Téguo *et al.*, 1996b; Waffo-Téguo *et al.*, 1998; Waterhouse and Lamuela-Raventós, 1994; Yan *et al.*, 2001)
E-Pterostilbene (**4**)		256.30	*V. coignetiae* berries *V. vinifera* leaves and berries	(Adrian *et al.*, 2000; Kim *et al.*, 2009; Langcake *et al.*, 1979; Pezet and Pont, 1988; Pezet *et al.*, 2003)
Z-Resveratrol		228.24	*V. labrusca* wine *M. rotundifolia* wine *V. vinifera* leaves, stems, cell suspension cultures and red and white wine	(Buiarelli *et al.*, 2007; Delaunay *et al.*, 2002; Jeandet *et al.*, 1995; Krisa *et al.*, 1999; Lamikanra *et al.*, 1996; Mattivi *et al.*, 1995; Naugler *et al.*, 2007; Pezet *et al.*, 2003; Ribeiro de Lima *et al.*, 1999; Vitrac *et al.*, 2001; Vitrac *et al.*, 2002; Vitrac *et al.*, 2005)

E-Resveratrol (**1**)		228.24	*V. amurensis* leaves, stems, and roots *V. betulifolia* stems *V. chunganensis* whole plant *V. coignetiae* berries and leaves *V. davidii* stems *V. labrusca* berries, leaves, stems, and wine *V. pentagona* stems *V. riparia* leaves *V. riparia* x *V. berlandieri* roots *M. rotundifolia* berries and wine *V. thunbergii* stems *V. vinifera* berries, cell suspension cultures, stems, leaves, and red and white wine	(Adrian *et al.*, 2000; Amico *et al.*, 2009; Baderschneider and Winterhalter, 2000; Barjot *et al.*, 2007; Bisson *et al.*, 2011; Buiarelli *et al.*, 2007; Dourtoglou *et al.*, 1999; Ector *et al.*, 1996; Gambuti *et al.*, 2004; Gerogiannaki-Christopoulou *et al.*, 2006; Guebailia *et al.*, 2006; Ha *et al.*, 2009a; Ha *et al.*, 2009b; He *et al.*, 2009; Huang and Lin, 1999; Jean-Denis *et al.*, 2006; Jeandet *et al.*, 1991; Jeandet *et al.*, 1995; Krisa *et al.*, 1999; Kulesh *et al.*, 2006; Lamikanra *et al.*, 1996; Landrault *et al.*, 2002; Langcake and Pryce, 1976; Langcake, 1981; Leblanc *et al.*, 2008; Li *et al.*, 1996; Li *et al.*, 1998a; Lou *et al.*, 2004; Mattivi *et al.*, 1995; Naugler *et al.*, 2007; Pezet *et al.*, 2003; Ribeiro de Lima *et al.*, 1999; Siemann and Creasy, 1992; Vitrac *et al.*, 2001; Vitrac *et al.*, 2002; Vitrac *et al.*, 2005; Wang *et al.*, 2011; Waterhouse and Lamuela-Raventós, 1994)
Z-Resveratrol-3,4'-*O*-*β*-diglucoside		552.52	*V. vinifera* cell suspension cultures	(Decendit *et al.*, 2002; Larronde *et al.*, 2005)

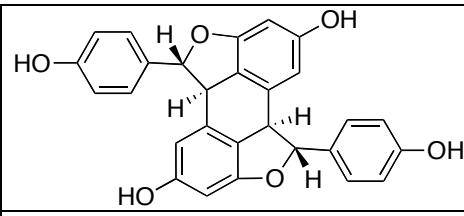
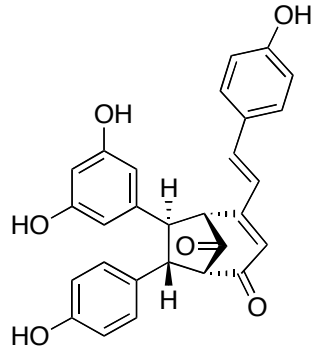
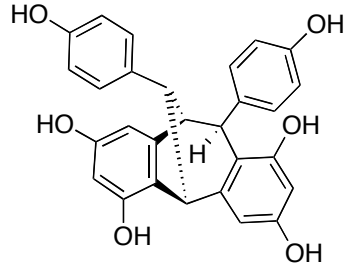
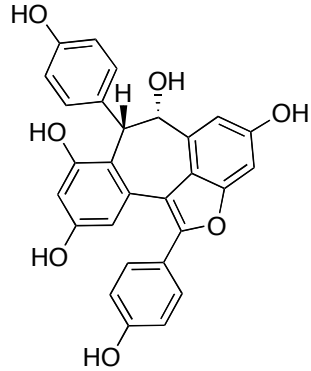
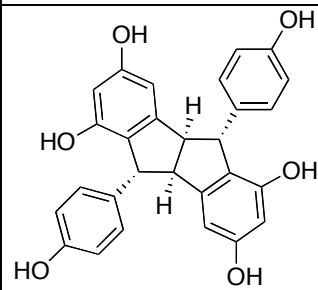
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E-Resveratrol-3,4′-*O*-*β*-diglucoside (mulberroside E)		552.52	*V. vinifera* cell suspension cultures	(Decendit *et al.*, 2002; Larronde *et al.*, 2005)
E-Resveratrol 2-*C*-glucoside		390.38	*V. vinifera* stems and wine, Riesling	(Baderschneider and Winterhalter, 2000; Yan *et al.*, 2001)
Z-Resveratrol 3,5-*O*-*β*-diglucoside		552.52	*V. vinifera* cell suspension cultures	(Larronde *et al.*, 2005)
E-Resveratrol 3,5-*O*-*β*-diglucoside		552.52	*V. vinifera* cell suspension cultures	(Larronde *et al.*, 2005)
Z-Resveratrol 3,5,4'-*O*-*β*-triglucoside		714.67	*V. vinifera* cell suspension cultures	(Larronde *et al.*, 2005)
Z-Resveratroloside		390.38	*V. vinifera* cell suspension cultures	(Krisa *et al.*, 1999; Waffo-Téguo *et al.*, 1998)
E-Resveratroloside		390.38	*V. vinifera* cell suspension cultures	(Krisa *et al.*, 1999; Waffo-Téguo *et al.*, 1998)
E-Rhapontigenin		258.27	*V. coignetiae* berries	(Adrian *et al.*, 2000)
2,4,6-Trihydroxyphenanthrene 2-*O*-glucoside (**10**)		388.37	*V. vinifera* wine, Riesling	(Baderschneider and Winterhalter, 2000)

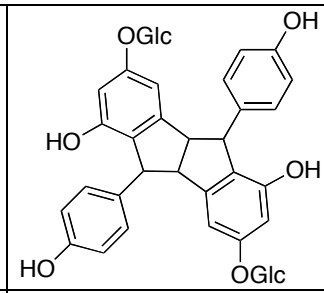
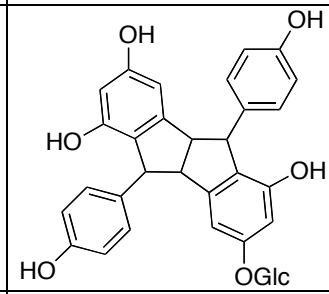
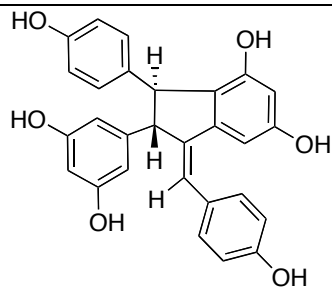
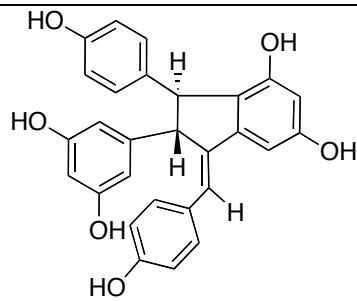
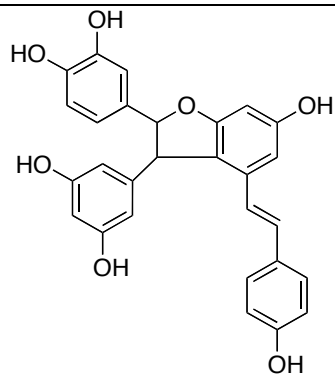
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Dimers				
Compound Name	**[a]Structure**	**M.W.**	**Plant Name and Part**	**[b]References**
(+)-Ampelopsin A		470.47	*V. amurensis* leaves, stems, and roots *V. betulifolia* stems *V. coignetiae* whole plant *V. heyneana* stems *V. thunbergii* roots and stems (var. *taiwaniana*) *V. vinifera* stems	(Chen and Wang, 2009; Chiou *et al.*, 2009; Ha *et al.*, 2009a; Ha *et al.*, 2009b; Huang and Lin, 1999; Kulesh *et al.*, 2006; Li *et al.*, 1996; Li *et al.*, 1998b; Lou *et al.*, 2004; Oshima *et al.*, 1995b; Reniero *et al.*, 1996; Wang *et al.*, 2011; Yan *et al.*, 2001; Zga *et al.*, 2009)
Ampelopsin D		454.47	*V. amurensis* roots *V. vinifera* leaves	(Huang and Lin, 1999; Mattivi *et al.*, 2011)
(+)-Ampelopsin F		454.47	*V. amurensis* leaves and stems *V. coignetiae* whole plant *V. thunbergii* roots *V. vinifera* stems	(Chiou *et al.*, 2009; Ha *et al.*, 2009a; Ha *et al.*, 2009b; Oshima *et al.*, 1995b; Yan *et al.*, 2001)
Amurensin A		472.49	*V. amurensis* roots	(Huang and Lin, 1999)

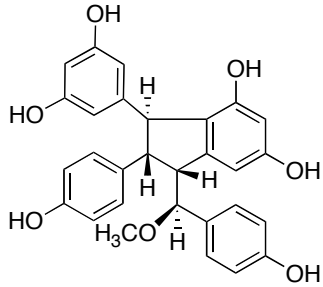
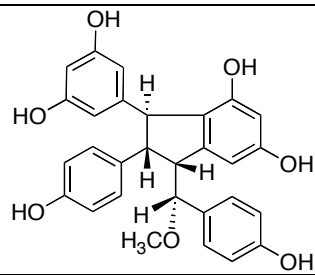
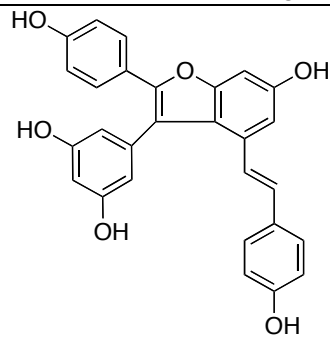
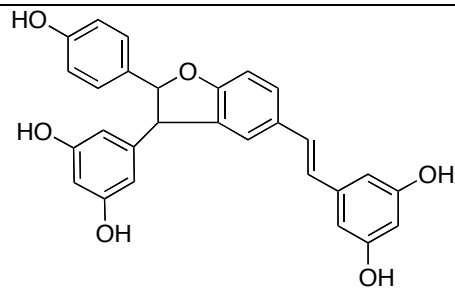
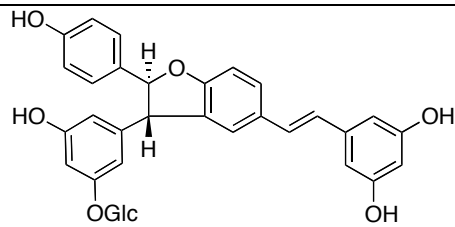
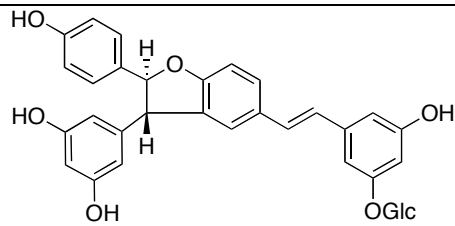
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Betulifol A		452.45	*V. betulifolia* stems	(Li *et al.*, 1998b)
Gnetin A		454.47	*V. flexuosa* stems *V. wilsoniae* stems	(Li *et al.*, 1998c; Li *et al.*, 1998d)
Isoampelopsin F		454.47	*V. amurensis* stems	(Kulesh *et al.*, 2006)
(-)-Malibatol A		468.45	*V. vinifera* stems	(Yan *et al.*, 2001)
Pallidol (**9**)		454.47	[c]*V. amurensis* stems *V. vinifera* cell suspension cultures, leaves, stems and red wine (Bergerac)	(Delaunay *et al.*, 2002; Guebailia *et al.*, 2006; Kulesh *et al.*, 2006; Landrault *et al.*, 2002; Mattivi *et al.*, 2011; Naugler *et al.*, 2007; Vitrac *et al.*, 2001; Vitrac *et al.*, 2002; Waffo-Téguo *et al.*, 2001)

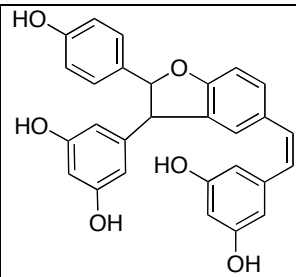
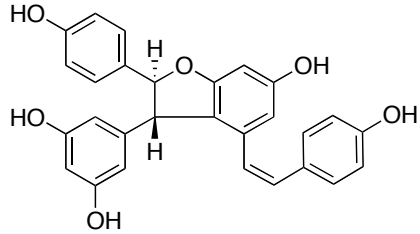
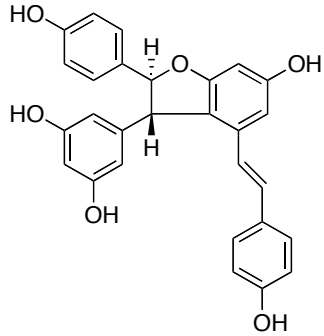
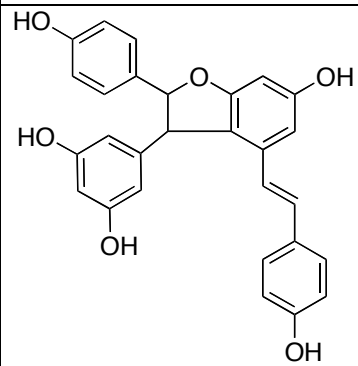
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Pallidol 3,3″-diglucoside		778.75	*V. vinifera* wine, Riesling	(Baderschneider and Winterhalter, 2000)
Pallidol 3-*O*-glucoside		616.61	*V. vinifera* wine, Riesling	(Baderschneider and Winterhalter, 2000)
Parthenocissin A		454.47	*V. vinifera* wine, red Bergerac	(Vitrac *et al.*, 2001)
Quadrangularin A		454.47	*V. vinifera* leaves	(Mattivi *et al.*, 2011)
Scirpusin A (**5**)		470.47	*V. vinifera* stems	(Kong *et al.*, 2010)

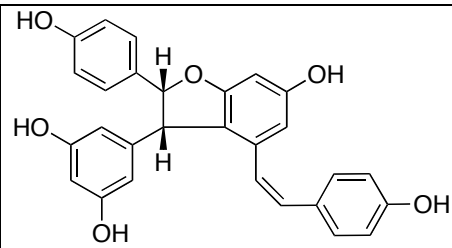
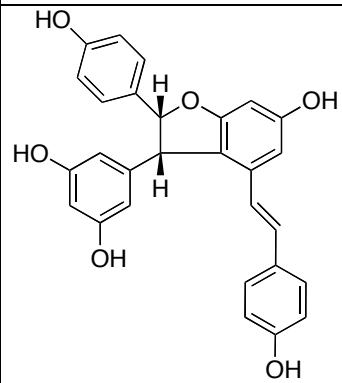
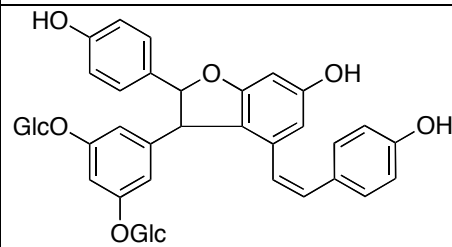
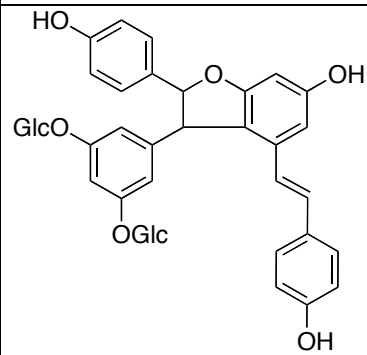
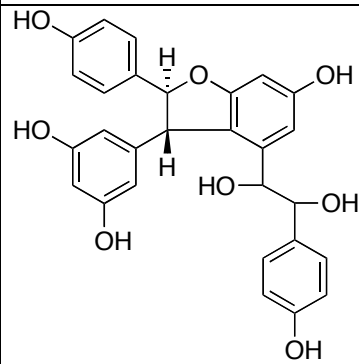
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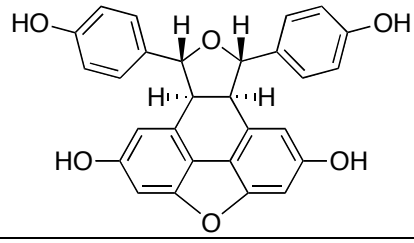
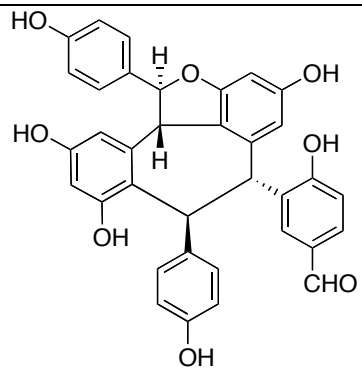
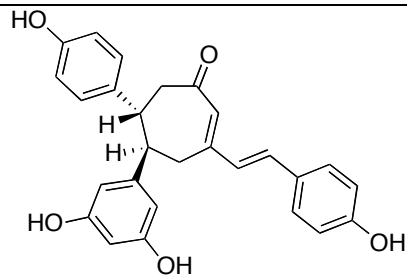
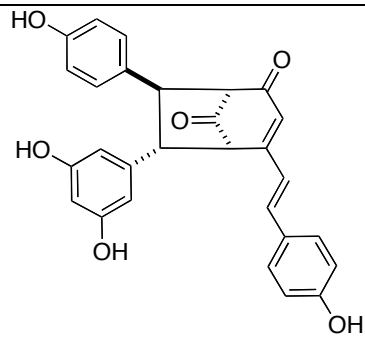
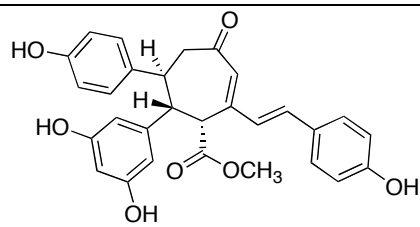
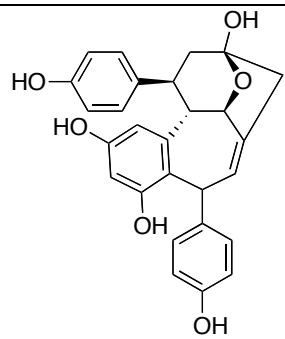
(+)-Viniferether A		486.51	*V. vinifera* roots	(Fujii *et al.*, 2005)
(+)-Viniferether B		486.51	*V. vinifera* roots	(Fujii *et al.*, 2005)
Viniferifuran (**15**) (Amurensin H)		452.45	*V. amurensis* roots *V. thunbergii* roots *V. vinifera* stems	(Chiou *et al.*, 2009; Huang *et al.*, 1999a; Ito *et al.*, 1999)
E-*δ*-Viniferin (**19**) (*E*-Resveratrol dehydrodimer)		454.47	*V. vinifera* cell suspension cultures, leaves, and wine	(Breuil *et al.*, 1998; Jean-Denis *et al.*, 2006; Pezet *et al.*, 2003; Vitrac *et al.*, 2005; Waffo-Téguo *et al.*, 2001)
E-*δ*-Viniferin 11-*O*-*β*-D-glucopyranoside (resveratrol dehydrodimer 11-*O*-*β*-D-glucopyranoside)		616.61	*V. vinifera* cell suspension cultures	(Waffo-Téguo *et al.*, 2001)
E-*δ*-Viniferin 11′-*O*-*β*-D-glucopyranoside (*E*-Resveratrol dehydrodimer 11′-*O*-*β*-D-glucopyranoside)		616.61	*V. vinifera* cell suspension cultures	(Waffo-Téguo *et al.*, 2001)

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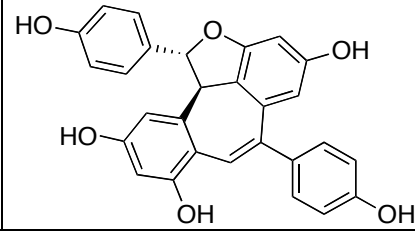
Z-*δ*-Viniferin		454.47	*V. vinifera* leaves after UV-irradiation	(Pezet *et al.*, 2003)
Z-*ε*-Viniferin		454.47	*V. vinifera* leaves and wine	(Amira-Guebailia *et al.*, 2009; Mattivi *et al.*, 2011; Pezet *et al.*, 2003)
(+)-*E*-*ε*-Viniferin		454.47	*V. heyneana* stems *V. vinifera* stems and leaves	(Huang and Lin, 1999; Ito and Niwa, 1996; Li *et al.*, 1996; Mattivi *et al.*, 2011)
E-*ε*-Viniferin (**8**)		454.47	*V. amurensis* leaves, stems, and roots *V. berlandieri* roots *V. betulifolia* stems *V. chunganensis* whole plant *V. cinerea roots* *V. coignetiae* whole plant *V. davidii* stems *V. flexuosa* stems *V. longii* roots *V. riparia* leaves and roots *V. riparia* x *V. berlandieri* roots *V. rupestris* roots *V. solonis longii* roots *V. solonis richter* roots *V. thunbergii* roots and stems (var. *taiwaniana*) *V. vinifera* leaves, roots, stems, and red wine *V. wilsoniae* stems	(Amico *et al.*, 2009; Amira-Guebailia *et al.*, 2009; Barjot *et al.*, 2007; Bisson *et al.*, 2011; Chiou *et al.*, 2009; Guebailia *et al.*, 2006; Ha *et al.*, 2009b; He *et al.*, 2009; Huang *et al.*, 2005; Jean-Denis *et al.*, 2006; Kulesh *et al.*, 2006; Landrault *et al.*, 2002; Langcake and Pryce, 1977a; Langcake, 1981; Li *et al.*, 1998a; Li *et al.*, 1998b; Li *et al.*, 1998c; Li *et al.*, 1998d; Mattivi and Reniero, 1992; Oshima *et al.*, 1995b; Ourtoule *et al.*, 1996; Pezet *et al.*, 2003; Vitrac *et al.*, 2005; Wang *et al.*, 2011; Yan *et al.*, 2001; Zga *et al.*, 2009)

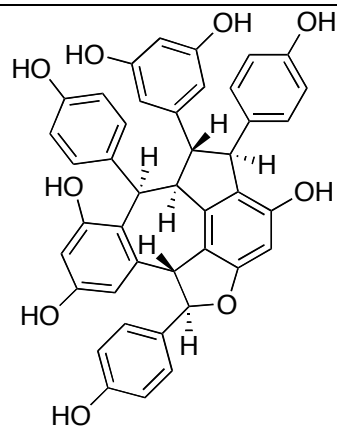
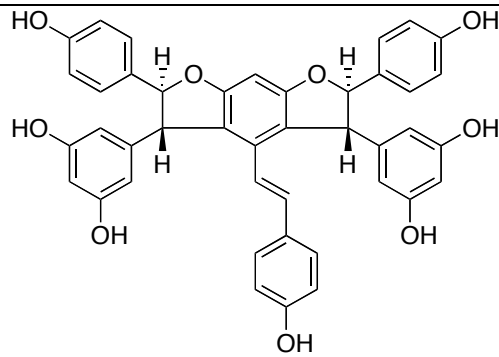
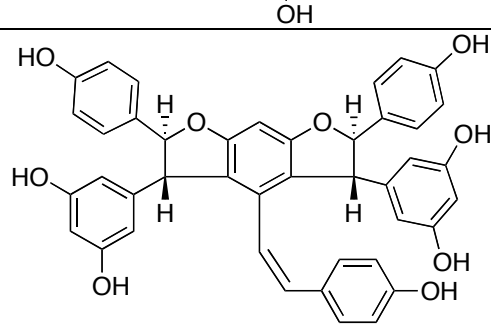
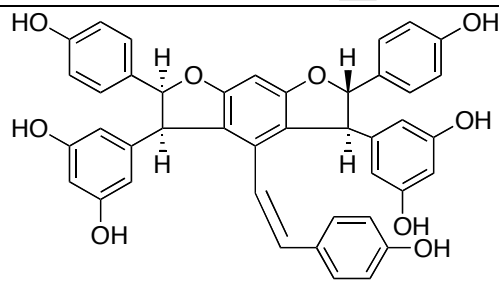
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Z-*ω*-Viniferin (7a,8a-*cis*-*Z*-*ε*-viniferin **17**)		454.47	*V. vinifera* leaves	(Mattivi *et al.*, 2011)
E-*ω*-Viniferin (7a,8a-*cis*-*E*-*ε*-viniferin **16**)		454.47	*V. vinifera* leaves	(Mattivi *et al.*, 2011)
Z-*ε*-Viniferin diglucoside		778.75	*V. vinifera* wine, Riesling	(Baderschneider and Winterhalter, 2000)
E-*ε*-Viniferin diglucoside		778.75	*V. vinifera* wine, Riesling	(Baderschneider and Winterhalter, 2000)
ε-Viniferin diol (Betulifol B)		488.49	*V. betulifolia* stems *V. coignetiae* stems	(Li *et al.*, 1998b; Oshima *et al.*, 1995a)

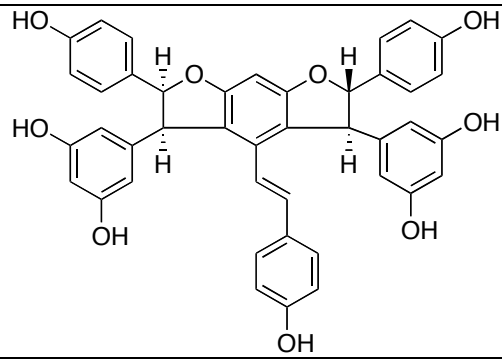
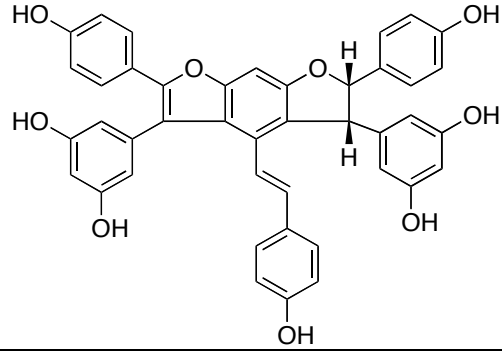
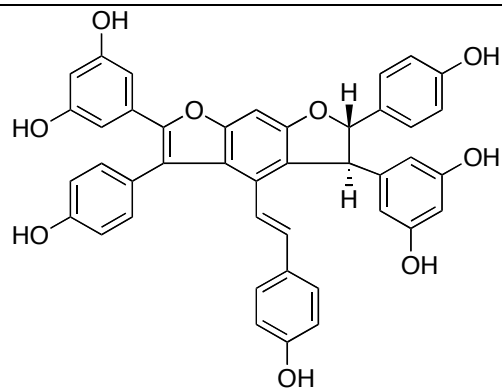
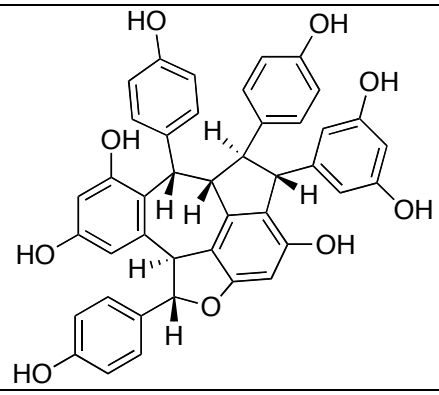
Vitisinol A		452.45	*V. thunbergii* roots	(Huang *et al.*, 2005)
Vitisinol B		574.58	*V. thunbergii* roots	(Huang *et al.*, 2005)
Vitisinol C		428.48	*V. thunbergii* roots	(Huang *et al.*, 2005)
Vitisinol D		454.47	*V. thunbergii* roots	(Huang *et al.*, 2005)
(+)-Vitisinol E (**13**)		486.51	*V. vinifera* stembark	(Choi *et al.*, 2009)
Vitisinol E (**14**)		444.48	*V. thunbergii* roots	(Chiou *et al.*, 2009)

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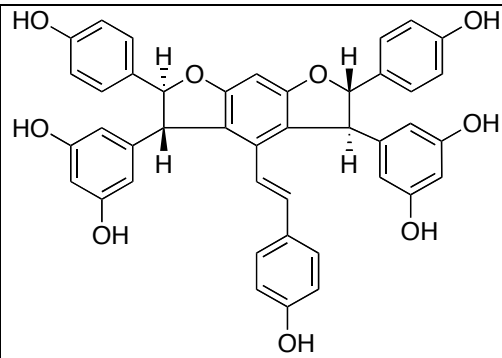
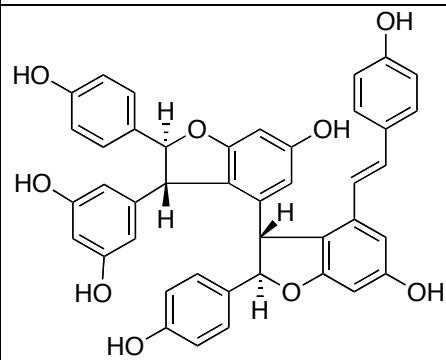
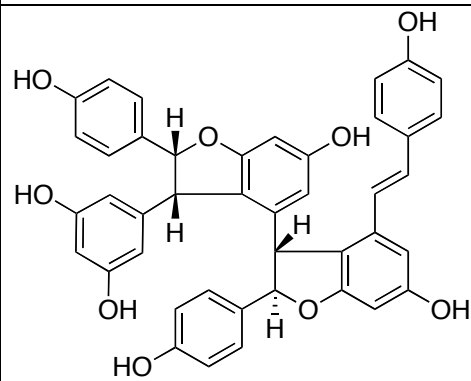
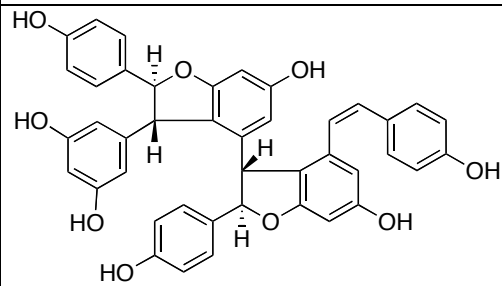
Vitisinol G		452.45	*V. thunbergii* roots	(Chiou *et al.*, 2009)

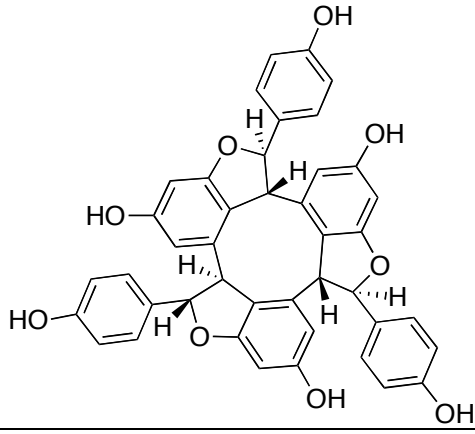
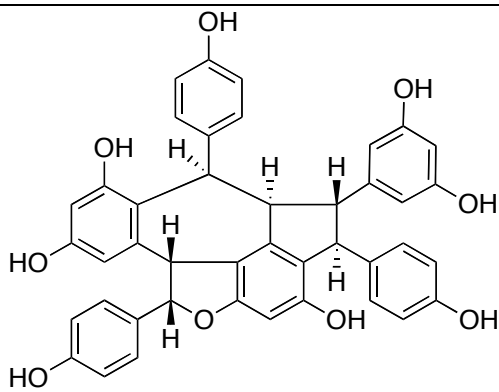
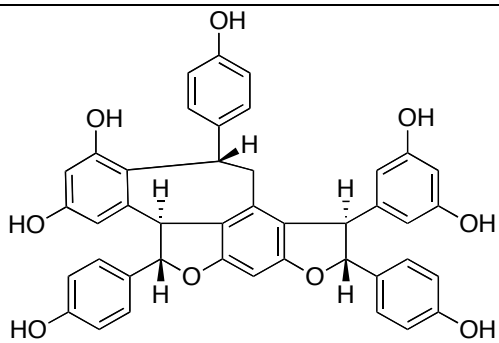
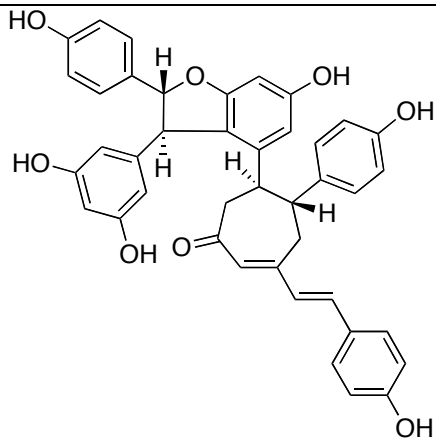
Trimers				
Compound Name	**[a]Structure**	**M.W.**	**Plant Name and Part**	**[b]References**
Ampelopsin C		680.70	*V. betulifolia* stems *V. coignetiae* whole plant *V. davidii* stems *V. heyneana* stems *V. thunbergii* roots and stems (var. *taiwaniana*)	(Chiou *et al.*, 2009; Huang *et al.*, 2005; Li *et al.*, 1996; Li *et al.*, 1998a; Li *et al.*, 1998b; Oshima *et al.*, 1995b; Wang *et al.*, 2011)
Ampelopsin E		680.70	*V. amurensis* roots *V. davidii* stems *V. wilsoniae* stems	(Huang and Lin, 1999; Li *et al.*, 1998a; Li *et al.*, 1998d)
Z-Ampelopsin E		680.70	*V. thunbergii* roots	(Chiou *et al.*, 2009)
Z-Amurensin B		680.70	*V. amurensis* leaves and stems	(Ha *et al.*, 2009a)

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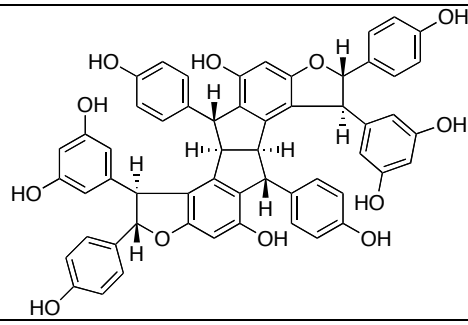
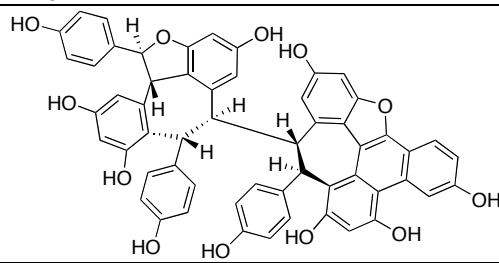
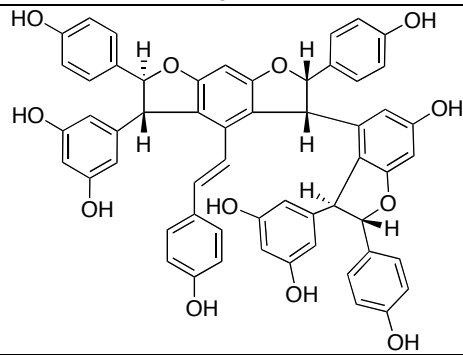
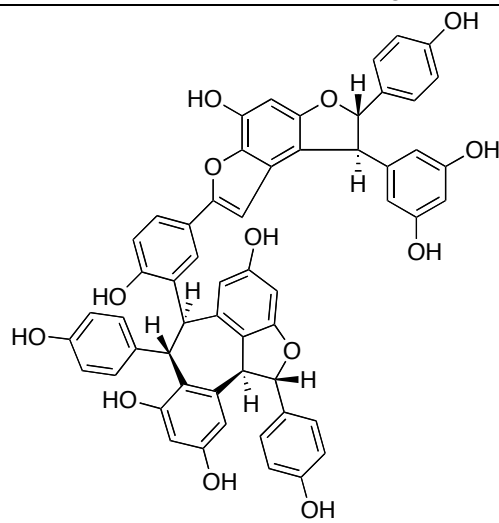
E-Amurensin B		680.70	*V. amurensis* leaves, stems, and roots *V. chunganensis* whole plant	(Ha *et al.*, 2009a; Ha *et al.*, 2009b; He *et al.*, 2009; Huang and Lin, 1999)
Amurensin C		678.68	*V. amurensis* roots	(Huang *et al.*, 2000)
Amurensin D		678.68	*V. amurensis* roots	(Huang *et al.*, 2000)
Amurensin G		680.70	*V. amurensis* leaves, stems, and roots *V. chunganensis* whole plant	(Ha *et al.*, 2009b; He *et al.*, 2009; Huang *et al.*, 1999b)

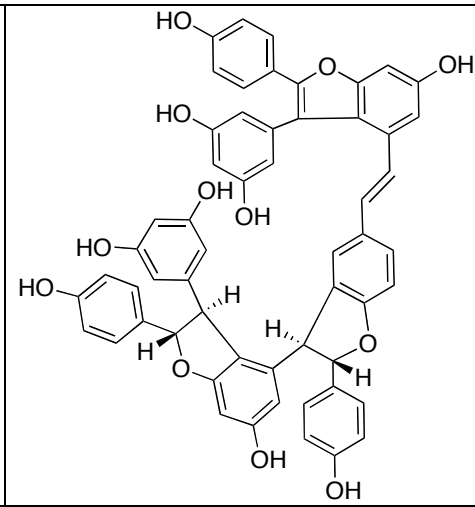
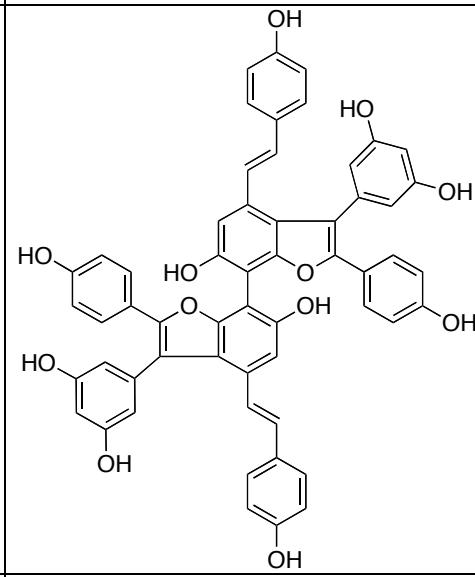
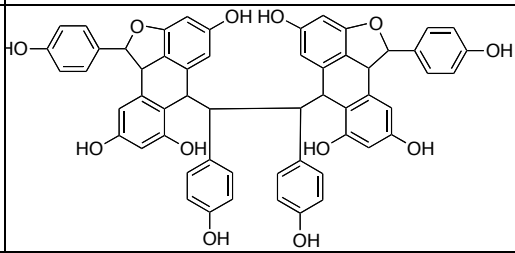
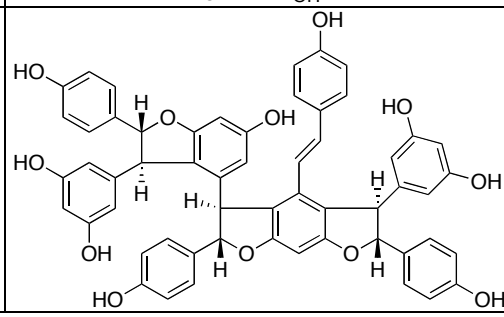
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Gnetin H		680.70	*V. amurensis* leaves and stems *V. berlandieri* roots *V. chunganensis* whole plant *V. cinerea* roots *V. longii* roots *V. riparia* roots *V. rupestris* roots *V. solonis longii* roots *V. solonis richter* roots *V. vinifera* roots	(Ha *et al.*, 2009a; Ha *et al.*, 2009b; He *et al.*, 2009; Mattivi and Reniero, 1992)
E-trans-Miyabenol C		680.70	*V. vinifera* leaves and stems	(Barjot *et al.*, 2007; Mattivi *et al.*, 2011)
E-cis-Miyabenol C		680.70	*V. vinifera* leaves	(Mattivi *et al.*, 2011)
Z-trans-Miyabenol C		680.70	*V. vinifera* leaves	(Mattivi *et al.*, 2011)

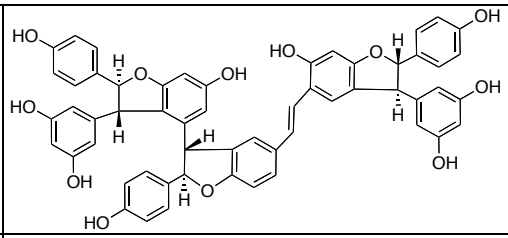
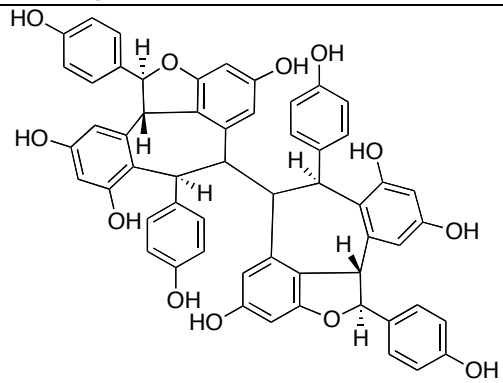
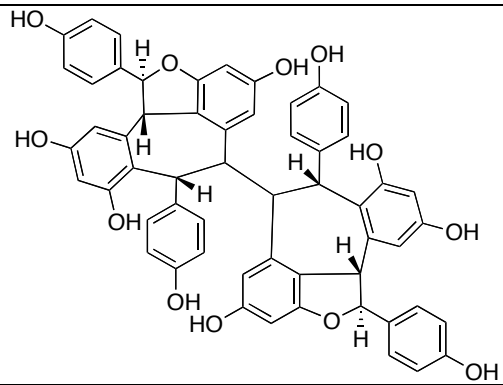
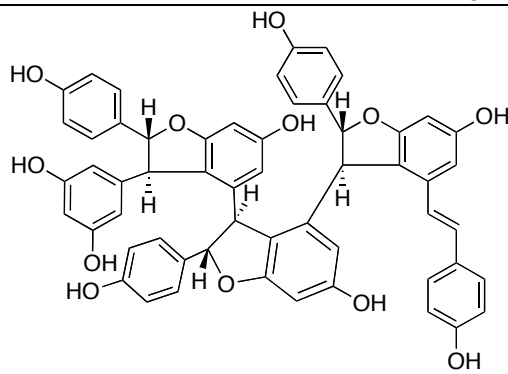
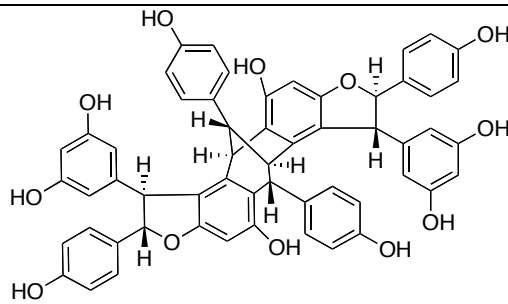
α-Viniferin (**6**)		678.68	*V. riparia* leaves *V. vinifera* leaves	(Langcake, 1981; Mattivi *et al.*, 2011; Pryce and Langcake, 1977)
(+)-Viniferol D		680.70	*V. vinifera* stems	(Takaya *et al.*, 2003)
Vitisin E		680.70	*V. coignetiae* stems	(Shinoda *et al.*, 1997)
Vitisinol F		654.70	*V. thunbergii* roots	(Chiou *et al.*, 2009)

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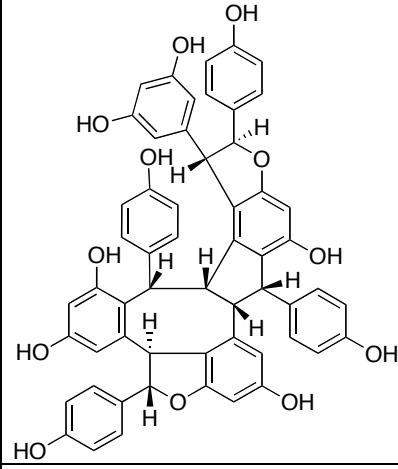
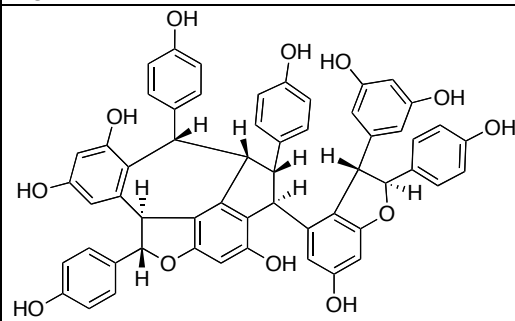
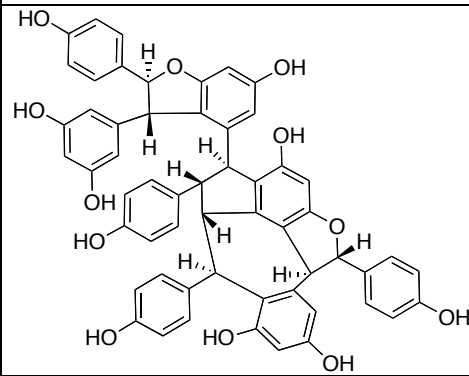
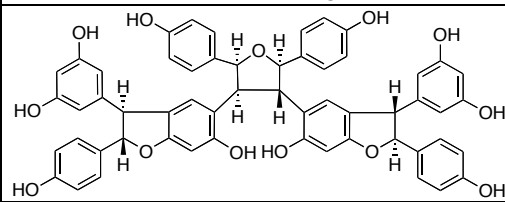
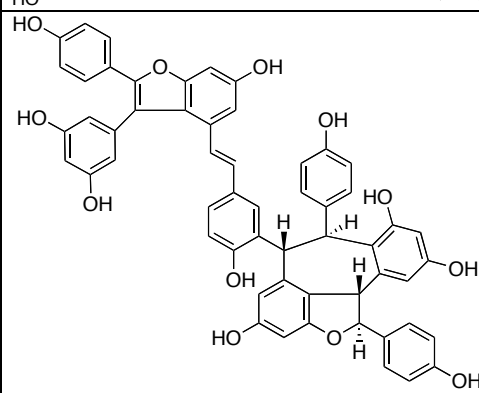
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Compound Name	**[a]Structure**	**M.W.**	**Plant Name and Part**	**[b]References**
Ampelopsin H		906.93	*V. vinifera* leaves	(Mattivi *et al.*, 2011)
Amurensin I		902.89	*V. amurensis* roots	(Huang *et al.*, 2001)
Amurensin J		906.93	*V. amurensis* roots	(Huang *et al.*, 2001)
Amurensin K		920.91	*V. amurensis* roots	(Huang *et al.*, 2001)

Amurensin L		904.91	*V. amurensis* roots	(Huang *et al.*, 2001)
Amurensin M		902.89	*V. amurensis* roots	(Huang *et al.*, 2001)
Davidol A (hypothesized structure)		906.93	*V. davidii* stems	(Li *et al.*, 1998a)
Flexuosol A		906.93	*V. flexuosa* stems	(Li *et al.*, 1998c)

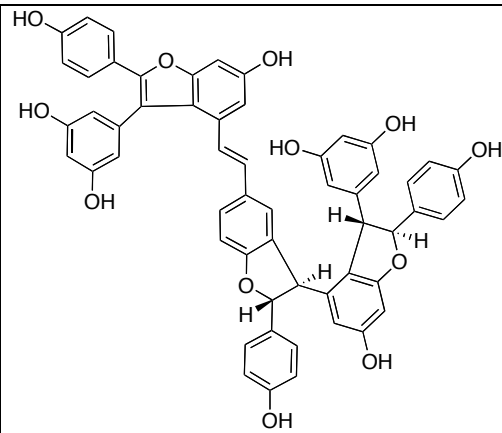
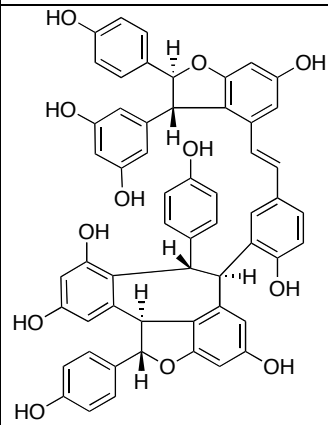
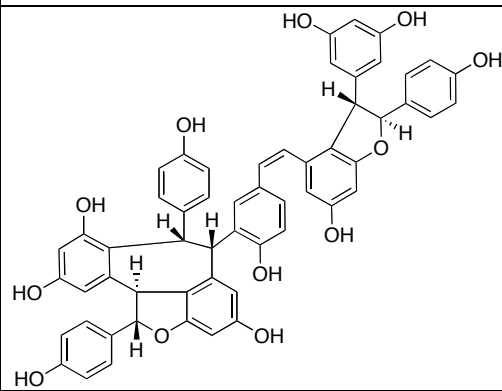
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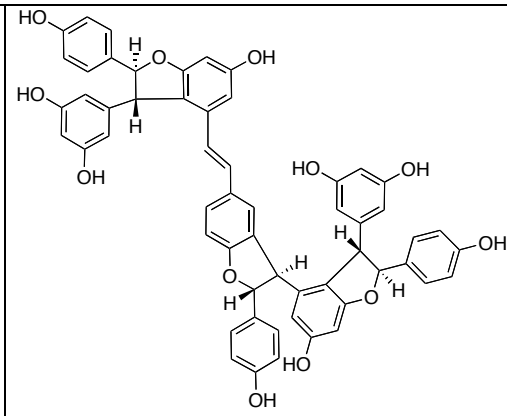
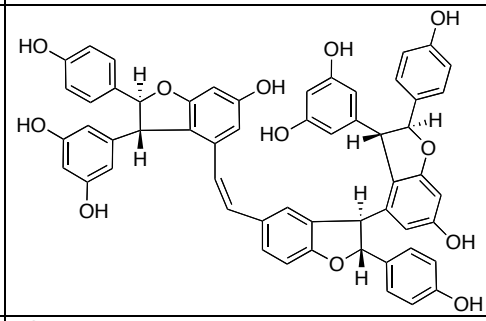
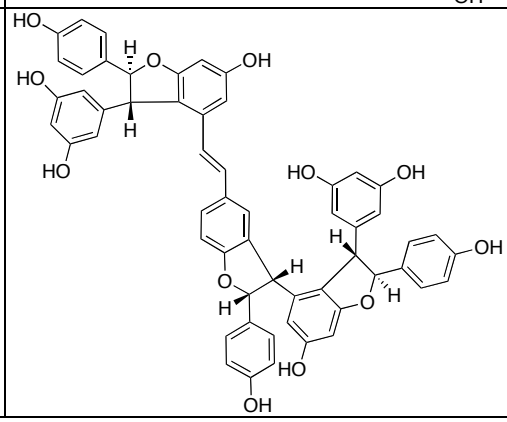
Heyneanol A		906.93	*V. amurensis* roots *V. betulifolia* stems *V. heyneana* stems	(Huang *et al.*, 2001; Jang *et al.*, 2007; Li *et al.*, 1996; Li *et al.*, 1998b; Li *et al.*, 2000)
Hopeaphenol (**12**)		906.93	*V. amurensis* roots *V. betulifolia* stems *V. chunganensis* whole plant *V. flexuosa* stems *V. vinifera* leaves, stems, roots, and red wine	(Guebailia *et al.*, 2006; He *et al.*, 2009; Huang *et al.*, 2001; Ito *et al.*, 1997; Li *et al.*, 1998b; Li *et al.*, 1998c; Reniero *et al.*, 1996; Yan *et al.*, 2001)
Isohopeaphenol		906.93	*V. amurensis* roots *V. vinifera* leaves and stems	(Huang *et al.*, 2001; Ito *et al.*, 1997; Mattivi *et al.*, 2011; Yan *et al.*, 2001)
Miyabenol A		922.92	*V. thunbergii* roots	(Chiou *et al.*, 2009; Huang *et al.*, 2005)
Vaticanol C isomer (tentative structure)		906.93	*V. vinifera* leaves	(Mattivi *et al.*, 2011)

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(+)-Viniferol A		906.93	*V. vinifera* stems	(Yan *et al.*, 2001)
(+)-Viniferol B		906.93	*V. vinifera* stems	(Yan *et al.*, 2002)
(+)-Viniferol C		906.93	*V. vinifera* stems	(Yan *et al.*, 2002)
(+)-Viniferol E		924.94	*V. vinifera* roots	(Fujii *et al.*, 2005)
(+)-Vitisifuran A		904.91	*V. amurensis* roots *V. vinifera* stems	(Huang *et al.*, 2001; Ito *et al.*, 1999)

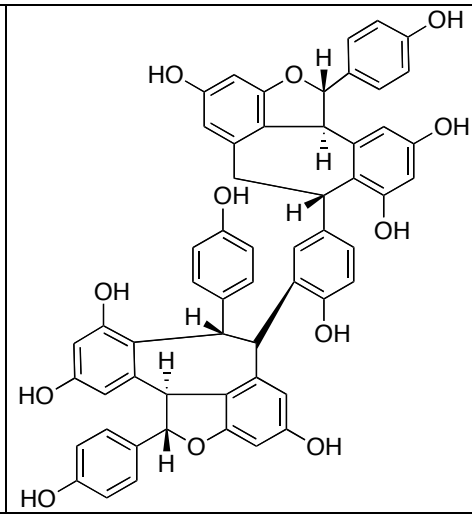
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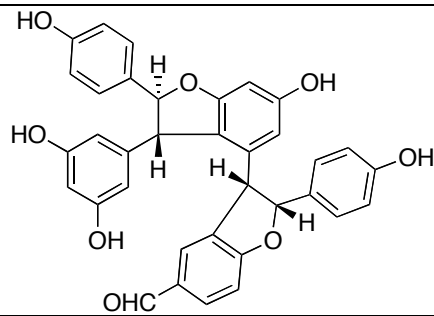
(-)-Vitisifuran B		904.91	*V. vinifera* stems	(Ito *et al.*, 1999)
Vitisin A (*r*-2-Viniferin) (**7**)		906.93	*V. amurensis* leaves, roots, and stems *V. betulifolia* stems *V. chunganensis* whole plant *V. coignetiae* stems and whole plant *V. davidii* stems *V. flexuosa* stems *V. thunbergii* roots and stems *V. vinifera* stems *V. wilsoniae* stems	(Chen and Wang, 2009; Chiou *et al.*, 2009; Ha *et al.*, 2009b; He *et al.*, 2009; Huang *et al.*, 2001; Huang *et al.*, 2005; Ito *et al.*, 1998; Jang *et al.*, 2007; Korhammer *et al.*, 1995; Li *et al.*, 1998a; Li *et al.*, 1998b; Li *et al.*, 1998c; Li *et al.*, 1998d; Oshima *et al.*, 1993; Oshima *et al.*, 1995b; Wang *et al.*, 2011; Yan *et al.*, 2001)
Z-Vitisin A		906.93	*V. coignetiae* stems and whole plant	(Ito *et al.*, 1998; Oshima *et al.*, 1993; Oshima *et al.*, 1995b)

E-Vitisin B (r-Viniferin)		906.93	*V. amurensis* roots *V. berlandieri* roots [d]*V. riparia* x *V. berlandieri* roots *V. cinerea* roots *V. coignetiae* stems *V. longii* roots *V. riparia* roots *V. rupestris* roots *V. solonis longii* roots *V. solonis richter* roots *V. thunbergii* var. *taiwaniana* stems and roots *V. vinifera* stems and roots	([d]Bisson *et al.*, 2011; Chen and Wang, 2009; Ito and Niwa, 1996; Korhammer *et al.*, 1995; Lou *et al.*, 2004; Mattivi and Reniero, 1992; Oshima *et al.*, 1995a; Wang *et al.*, 2011; Zga *et al.*, 2009)
Z-Vitisin B		906.93	*V. amurensis* roots *V. coignetiae* stems	(Lou *et al.*, 2004; Oshima *et al.*, 1995a)
E-Vitisin C		906.93	*V. thunbergii* roots *V. vinifera* stems	(Huang *et al.*, 2005; Ito and Niwa, 1996)

However, a recent study found the *cis* configuration in downy mildew infected *V. vinifera* leaves, meaning both hydrogens arein the alpha or both in the beta position (Mattivi *et al*., 2011). This naming of *cis* and *trans* conformation for these hydrogens is an area of confusion when dealing with stilbenoids, which often contain a *trans* (*E*) or *cis* (*Z*) double bond as well. The *E*/*Z* nomenclature, for the *trans* and *cis* double bond, respectively, is more precise, yet less commonly used in stilbenoid literature. The study by Mattivi *et al*. (2011) illustrates this problem, where both the *trans*-ε-viniferin and the *cis*-dihydrobenzofuran form were isolated with both *cis* (*Z*) and *trans* (*E*)-double bond configurations. The authors named these two *cis*-dihydrobenzofuran forms, *E*-ω-viniferin **(16)** and *Z*-ω-viniferin **(17)**, despite having the same planar structure as ε-viniferin, while other authors have referred to this compound as 7a, 8a-*cis*-ε-viniferin (Huang *et al*., 2000 ; Lin and Yao, 2006 ; Mattivi *et al*., 2011). It should also be noted that in the relative conformation, the difference between the *cis*-dihydrobenzofuran form and the *trans*-dihydrobenzofuran form can be determined by comparison of their NMR

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Vitisin D		906.93	*V. coignetiae* stems	(Shinoda *et al.*, 1997)

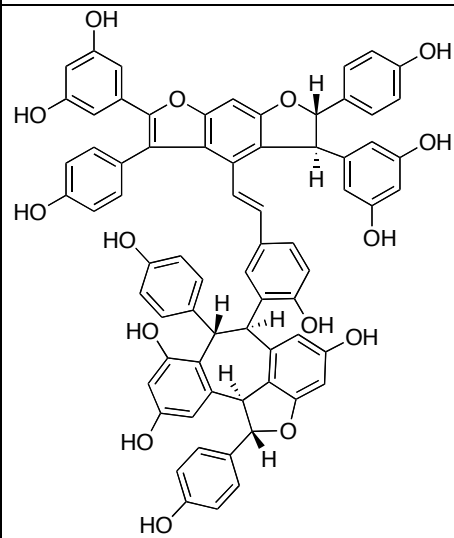
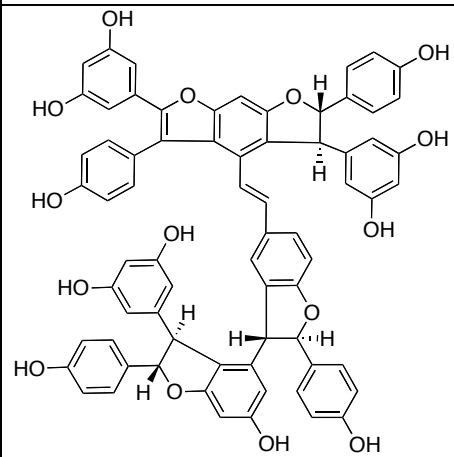
Breakdown Product from Tetramer				
Compound Name	**[a]Structure**	**M.W.**	**Plant Name and Part**	**[b]References**
(-)-Viniferal (**11**)		574.58	*V. thunbergii* roots *V. vinifera* stems	(Chiou *et al.*, 2009; Huang *et al.*, 2005; Ito and Niwa, 1996)

data. Determining the absolute configuration, however, is more challenging, i. e. the difference between (+) and (-)-*ε*-viniferin. For known compounds, their $[\alpha]_D$ values can be compared with the literature. Currently, only the (+)-*ε*-viniferin form has been proven to be in Vitaceae, whereas (-)-*ε*-viniferin can be found in other plant families (Lin and Yao, 2006). Nevertheless, there have been isolated reports of (-)-*ε*-viniferin in *Vitis*, though the complete spectroscopic data set was not provided (Amico *et al*., 2009; Kulesh *et al*., 2006). A careful discussion on the difficulties in determining the relative and absolute configurations of the viniferins and other stilbenoids, is provided in the publication by Mattivi *et al*. (2011). Due to the difficulties in assigning absolute configurations to stilbenoid oligomers, many compounds have been reported with only their relative configurations assigned. However, since (+)-*ε*-viniferin is considered a major stilbenoid intermediate for larger oligomers, the structures containing viniferin moieties are normally presented as containing the same configuration when not otherwise determined. In the reports of many complex oligomers, only the relative configuration has been assigned.

QUANTIFICATION OF STILBENOIDS

1 Quantification methods

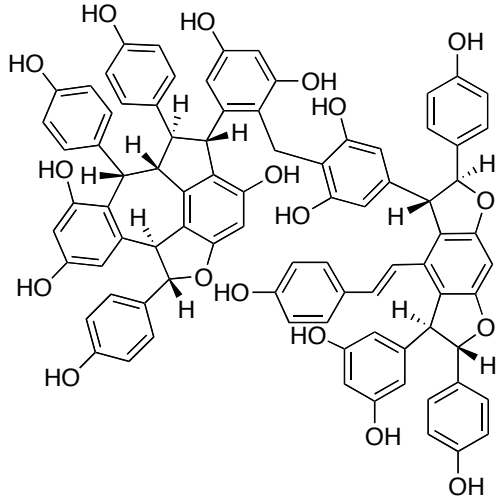
Numerous techniques have been used for the quantification of stilbenoids with varying degrees of success. The primary techniques used include liquid chromatography with ultraviolet detection (LC-UV), LC-fluorescence detection, gas chromatography-mass spectrometry (GC-MS) and LC-MS, in conjunction with numerous sample preparation techniques, see Table 3. The majority of the initial studies utilized GC-MS, however, this method has drawbacks, such as derivation requirements and destruction of oligomers and glycosides prior to detection. These properties have a tendency to promote artificially high aglycone monomer levels and *E* to *Z*-isomer conversions (Flamini, 2003; Soleas *et al*., 1997). While HPLC-UV analysis does not have the same problems as GC-MS, other problems such as lack of baseline resolution, leading to overestimation of individual stilbenoid levels, may exist, along with poor sensitivity. More selective techniques such as fluorescence detection

Pentamers				
Compound Name	**[a]Structure**	**M.W.**	**Plant Name and Part**	**[b]References**
Amurensin E		1132.14	*V. amurensis* roots	(Huang *et al.*, 2000)
Amurensin F		1132.14	*V. amurensis* roots	(Huang *et al.*, 2000)

can help overcome these drawbacks, whereas the high selectivity of LC-MS techniques can eliminate this problem. However, matrix effects offer a particular challenge in the quantitation of individual compounds in complex samples such as wine. This may be overcome by sample cleaning techniques such as solid phase extraction (SPE), sample dilution, selective extraction, or use of stable isotopes (Careri *et al*., 2004 ; Stark *et al*., 2011 ; Zotou and Frangi, 2008). The comparison of LC-UV with LC-MS-MS has shown the later to have higher sensitivity and selectivity (Careri *et al*., 2004).

We have compiled quantitation studies of stilbenoids in *Vitis* species, including wine, in Table 3. While useful, comparison between quantitation studies has some drawbacks since additional, non-detector variables exist, particularly when comparing solid materials such as grape skins or stems. One important problem may involve incomplete extraction due to poor solvent choice. Comparisons of multiple solvent extraction efficiencies have shown that 50 to 60 % ethanol in water was more effective for *E*-resveratrol and *E*-ε-viniferin extraction in vine canes than a wide-range of other solvent systems and ratios tested (Karacabey and Mazza, 2008 ; Rayne *et al*., 2008). In another study, comparing extraction rates of solvents with grape skins, a different set of solvents was tested and acidified methanol was shown to be most effective for resveratrol and piceid extraction (Sun *et al*., 2006). Higher temperatures and ultrasonication also improve extraction efficiencies, but decomposition or isomer conversion may occur more readily. Therefore, differences between studies may represent differences in extraction efficiencies or changes occurring during the extraction procedures. Additionally, there are variations in the preparation of plant material that need to be considered when comparing mul≤tiple studies. Some

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Hexamer				
Compound Name	**[a]Structure**	**M.W.**	**Plant Name and Part**	**[b]References**
Chunganenol		1372.40	*V. chunganensis* whole plant	(He *et al.*, 2009)

[a]Many reports of previously isolated known compounds were not confirmed using all spectroscopic techniques required for unambiguous assignments. We included these to have a more complete list where stilbenoids have been identified. Additionally, due to the challenge of assigning absolute stereochemistry to complex oligomers, only the relative configuration was reported in some cases. We drew the structures as reported, but these may only reflect relative configurations. In the case of common compounds such as *E*-ε-viniferin, we attempted to differentiate between reports where the configuration was determined from those where only the planar structure was determined.
[b]All or most of the spectroscopic information can be found in underlined references.
[c]This report of pallidol from *V. amurensis* (Kulesh *et al*., 2006) has recently been disputed due to discrepancies in NMR data (Mattivi *et al*., 2011).
[d]This report of vitisin B had an error in the original publication, the name of the structure was erroneously given as vitisin C.

researchers have used the fresh weight of the plant material whereas others have used the dry weight, making comparison between these studies difficult. Using the fresh weight for quantitation studies may also be complicated by amount of rainfall or lack of rainfall levels immediately prior to collection. Due to the role of stilbenoids as phytoalexins, quantitation of stilbenoids has been performed on different parts of infected grapevines. However, even within these studies, variations exist in sample material. For example, some studies examined only the infected parts of the leaves and others extracted the entire leaf that showed some degree of infection. We have therefore attempted to include all relevant information available in Table 2.

2 Quantitation results

A tremendous effort has been made to quantify levels of stilbenoids in wine of multiple varieties, vintages, terroir, and growth conditions. Since the initial quantitation of resveratrol in wine by Siemann and Creasy in 1992, the quest to find which variables may produce wines with high concentrations has been ongoing (Siemann and Creasy, 1992). While *E*-resveratrol concentrations have been the most widely reported, efforts to quantify its isomer, *Z*-resveratrol, in addition to their glycosides, *Z*- and *E*-piceid, have become more common. The majority of research has been performed on wine made from different cultivars of *V. vinifera*, including comparisons of wines made in different years, geographic locations, micro-climates, and using different methods of vinification, see Table 3 (Bavaresco, 2003 ; Moreno-Labanda *et al*., 2004). A 2007 review by Stervbo *et al*. summarized the findings from 31 papers on the quantitation of *E*-resveratrol levels in a total of 511 individual monovarietal red wines, including 21 different varieties from 18 regions around the world. Not all of these studies examined *Z*-resveratrol and the piceids, but the authors included these data when available. The overall levels of *E*-resveratrol ranged from undetectable levels to 14.3 mg/l, with an average of 1.9 mg/L. In this review no variety or region was found to be clearly superior. Interestingly, varieties such as Pinot noir tend to have higher levels, though this higher level was not ubiquitous with every Pinot noir tested. No distinct trends were observed with *Z*-resveratrol, which ranged from undetectable levels to 5.1 mg/L, averaging 1.0 mg/L. The piceid isomers, which were typically higher than resveratrol levels, averaged 5.4 and 1.4 mg/L for *E*- and *Z*-piceid, respectively. A slight trend appeared when

Table 3 - Summary of recent quantitation studies of different stilbenoids, in *Vitis* species.

Plant Species	Compound	Plant Part, Variety/Origin, Concentration, Method of Quantitation	[a]Wine Concentrations, in mg/L (Averages, when available, and sample size)	References
V. amurensis	*E*-Resveratrol	**Stems**, average of data from *V. amurensis* and *V. amurensis* x *V. vinifera*, HPLC-UV: 889.7±62.2 mg/kg fw		(Zhang *et al.*, 2011)
V. davidii	*E*-Resveratrol	**Stems**, HPLC-UV: 1048.9±137.9 mg/kg fw		(Zhang *et al.*, 2011)
V. labrusca	*Z*-Resveratrol	**Wine**, GC-MS	1.5-4.0 (2.8, n=2)	(Lamikanra *et al.*, 1996)
	E-Resveratrol	**Leaves**, mg/g dw, HPLC-UV: 0.714±0.01 (organic) 0.062±0.003 (conventional)		(Dani *et al.*, 2010)
		[c]**Berry skins**, HPLC-UV: 9.3 mg/kg dw		(Waterhouse and Lamuela-Raventós, 1994)
		Wine, GC-MS	1.1-2.7 (1.9, n=2)	(Lamikanra *et al.*, 1996)
	Piceid	[c]**Berry skins**, HPLC-UV: ND		(Waterhouse and Lamuela-Raventós, 1994)
V. pentagona	*E*-Resveratrol	**Stems**, Chinese, different regions evaluated, HPLC-UV: 700.6±64.9-838.8±30.9 mg/kg fw		(Zhang *et al.*, 2011)
M. rotundifolia (muscadine)	*Z*-Resveratrol	**Wine**, American, GC-MS: Noble Muscadine Muscadine port	9.2-31.9 (21.14, n=5) 3.3, n=1 (port)	(Lamikanra *et al.*, 1996)
	E-Resveratrol	**Berries**, American, HPLC-UV, µg/100 g fw: **Bronze-skinned**: **Berries**: 860.7±145.4 **Berries without seeds**: 601.7±146.6 **Seeds**: 259.0±39.6 **Dark-skinned**: **Berries**: 1481.0±290.1 **Berries without seeds**: 1134.0±232.5 **Seeds**: 347.02	0.7 (bronze-skinned) 1.1 (dark-skinned)	(Ector *et al.*, 1996)
		Wine, American, GC-MS: Noble Muscadine Muscadine port	4.9-13.4 (9.1, n=5) 3.6, n=1 (port)	(Lamikanra *et al.*, 1996)
V. vinifera (plus hybrid species as indicated)	Ampelopsin D + quadrangularin A (quantified as mixture)	**Leaves**, *P. viticola* infected, averaged over 3 years, 6 days post-infection, µg/g fw: F1 genotype 21/103: 21.4 (20.9 SD) F1 genotype 21/74: 192.5 (329.5 SD)		(Vrhovsek *et al.*, 2011)
	Ampelopsin H + vaticanol-C-like isomer (quantified as mixture)	**Leaves**, *P. viticola* infected, averaged over 3 years, 6 days post-infection, µg/g fw: F1 genotype 21/103: 143.6 (150.6 SD) F1 genotype 21/74: 33.3 (41.7 SD)		(Vrhovsek *et al.*, 2011)

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	E-Astringin	**Wine**, French (Bergerac), red and white, LC with fluorescence detection	Red: ND-38.1 (6.3, n=19) White: ND-8.5 (1.4, n=30)	(Vitrac *et al.*, 2002)
		Wine, Brazilian, HPLC-UV: Cabernet Franc: 25.72 (n=1) Cabernet Sauvignon: ND (n=1) Tannat: ND (n=1) Merlot: ND–23.12 (7.37, n=6)	ND-25.7 (n=9)	(Vitrac *et al.*, 2005)
		Wine, Canadian, HPLC-UV: French hybrid varieties: Baco Noir: 0.16-0.18 (n=2) Leon Millot/Lucie Kuhlmann: 0.10-0.22 (n=2) Marechal Foch: 0.04-0.35 (0.21, n=4) Lucie Kuhlmann: 0.16 (n=1) Leon Millot: 0.10-0.17 (n=2) de Chaunac: 0.30 (n=1) *V. vinifera* varieties: Zweigelt/Cabernet: 0.04 (n=1) Pinot Noir/Cabernet: 0.12 (n=1) Pinot Noir: 0.06 (n=1)	0.04-0.35 (0.15, n=15)	(Naugler *et al.*, 2007)
		Wine, Italian, LC-MS-MS: Red: Barbara: ND (n=2) Cesanese+Sangiovese+Merlot+Montepulciano: ND Sangiovese: ND-0.51 (n=2) Montepulciano: ND (n=3) Lambrusco: ND-0.72 (n=2) Nero d'Avola: ND Merlot: 0.70 Nero d'Avola+Nerello+Mascalese+Pignatello: 0.72 Aglianico: 1.83 Sangiovese+Ciliegiolo+Canaiolo: 0.88 Cannonau: 0.50 Primitivo: 0.51 Negroamaro: 0.72 Syrah: 0.62 White: Chardonnay (60%): ND Pinot Grigio: ND Sauvignon Blanc (60%)+Grechetto: ND	Red: ND-1.8 (n=19) White: ND (n=3)	(Buiarelli *et al.*, 2007)
		Wine, Portuguese and French, HPLC-UV: Red: Portuguese, monovarietal: ND-35.9 (10.4, n=34) Portuguese, blended: ND-24.8 (10.3, n=5) French: 2.5-26.1 (13.1, n=7) White: Portuguese, monovarietal: ND-15.6 (5.8, n=50) Portuguese, blended: 2.4-11.3 (5.5, n=9) Portuguese, fortified: ND-13.4 (8.0, n=15)	Red: ND-35.9 (n=46) White: ND-15.6 (n=74)	(Ribeiro de Lima *et al.*, 1999)
	Z-Astringin	**Wine**, Italian, LC-MS-MS: Red: Barbara: ND (n=2) Cesanese+Sangiovese+Merlot+Montepulciano: ND Sangiovese: ND (n=2) Montepulciano: ND-0.55 (n=3) Lambrusco: ND-1.32 (n=2)	Red: ND-1.6 (n=19) White: ND (n=3)	(Buiarelli *et al.*, 2007)

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		Nero d'Avola: ND Merlot: trace Nero d'Avola+Nerello+Mascalese+Pignatello: ND Aglianico: 1.59 Sangiovese+Ciliegiolo+Canaiolo: ND Cannonau: ND Primitivo: 0.51 Negroamaro: ND Syrah: ND White: Chardonnay (60%): ND Pinot Grigio: ND Sauvignon Blanc (60%)+Grechetto: ND		
	Hopeaphenol	**Wine**, French (Burgundy), Pinot Noir, UPLC-UV	trace (n=4)	(Boutegrabet *et al.*, 2011)
		Wine, North African, HPLC-UV: Monovarietal red: Merlot: 2.1 Cabernet Sauvignon: 1.48 [d]Blended red: Cuvée du Président: ND Amjad: 0.34 Guerrouane: 2.68 Sidi-Brahim: 0.61 Terrale: ND	ND-2.7 (n=7)	(Guebailia *et al.*, 2006)
	Isohopeaphenol	**Leaves**, *P. viticola* infected, averaged over 3 years, 6 days post-infection, µg/g fw: F1 genotype 21/103: 1214.8 (1948.5 SD) F1 genotype 21/74: 112.2 (139.7 SD)		(Vrhovsek *et al.*, 2011)
	Z + *E*-miyabenol C (quantified as mixture)	**Leaves**, *P. viticola* infected, averaged over 3 years, 6 days post-infection, µg/g fw: F1 genotype 21/103: 42.5 (41.9 SD) F1 genotype 21/74: 21.5 (25.8 SD)		(Vrhovsek *et al.*, 2011)
	E-*cis*-miyabenol C	**Leaves**, *P. viticola* infected, averaged over 3 years, 6 days post-infection, µg/g fw: F1 genotype 21/103: 45.5 (43.4 SD) F1 genotype 21/74: 27.0 (35.8 SD)		(Vrhovsek *et al.*, 2011)
	Pallidol	**Wine**, French (Bergerac), red, LC with fluorescence detection	0.5-4.8 (2.5±0.2, n=19)	(Vitrac *et al.*, 2002)
		Wine, North African, HPLC-UV: Monovarietal red: Merlot: 4.1 Cabernet Sauvignon: 3.54 [d]Blended red: Cuvée du Président: 0.2 Amjad: 0.35 Guerrouane: 4.63 Sidi-Brahim: 5.34 Terrale: 7.0 Gris d'Algérie: ND Monovarietal white: Muscat: 9.20	Red: ND-7.0 (n=8) White: 9.2 (n=1)	(Guebailia *et al.*, 2006)

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		Wine, Canadian, HPLC-UV: French hybrid varieties: Baco Noir: 0.14-0.26 (n=2) Leon Millot/Lucie Kuhlmann: 0.28-0.38 (n=2) Marechal Foch: 0.06-0.32 (0.22, n=4) Lucie Kuhlmann: 0.16 (n=1) Leon Millot: 0.09-0.40 (n=2) de Chaunac: 0.36 (n=1) *V. vinifera* varieties: Zweigelt/Cabernet: 0.11 (n=1) Pinot Noir/Cabernet: 0.24 (n=1) Pinot Noir: 0.19 (n=1)	0.06-0.4 (0.2, n=15)	(Naugler *et al.*, 2007)
		Wine, French, HPLC-UV: Red: Cabernet Sauvignon: ND-2.22 (n=3) Merlot: ND (n=1) Tempranillo: ND (n=1) Egiodola: 1.33 (n=1) Rosé: Syrah: 0.38 (n=1) White: Chardonnay: ND-0.30 (n=3) Sauvignon: ND (n=2) Viognier: ND (n=1) Sémillon, botrytized sweet wine: ND (n=8)	Red: ND-2.2 (n=6) Rosé: 0.4 (n=1) White: ND-0.3 (n=6) Sweet white, botrytized: ND (n=8)	(Landrault *et al.*, 2002)
		Leaves, *P. viticola* infected, averaged over 3 years, 6 days post-infection, µg/g fw: F1 genotype 21/103: 22.5 (19.8 SD) F1 genotype 21/74: 24.7 (29.8 SD)		(Vrhovsek *et al.*, 2011)
	E-Piceatannol	**Wine**, Italian, LC-MS-MS: Red: Barbara: 0.88-1.80 (n=2) Cesanese+Sangiovese+Merlot+Montepulciano: 1.53 Sangiovese: 0.56-0.80 (n=2) Montepulciano 0.93-5.22 (2.39, n=3) Lambrusco: 0.59-0.67 (n=2) Nero d'Avola: 1.42 Merlot: 1.21 Nero d'Avola+Nerello+Mascalese+Pignatello: 0.91 Aglianico: 1.34 Sangiovese+Ciliegiolo+Canaiolo: 0.64 Cannonau: 0.54 Primitivo: 0.75 Negroamaro: trace Syrah: trace White: Chardonnay (60%): ND Pinot Grigio: ND Sauvignon Blanc (60%)+Grechetto: ND	Red: trace-5.2 (n=19) White: ND (n=3)	(Buiarelli *et al.*, 2007)
		Berries without seeds, HPLC-UV: Cabernet Sauvignon: 0.052 mg/kg fw		(Bavaresco *et al.*, 2002)
		Mourvèdre (Monastrell), Spanish, HPLC-UV with MS identification, pre and post UV-C irradiation for stilbenoids induction: Solids in mg/kg fw (n=3): **Berries**: 0.78±0.1 (1.63±0.2, post UV-C) **Stems**: 4.68±0.46 (5.33±1.8, post UV-C) **Skins**: 0.38±0.2 (0.62±0.2, post UV-C) **Pomace**: 0.13±0.1 (0.16±0.03, post UV-C)	0.2, no UV-C irradiation 0.3 after UV-C irradiation	(Cantos *et al.*, 2003)

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		Lees: 0.54±0.05 (1.14±0.3, post UV-C) Liquid in mg/L: **Must** before pressing 0d: 0.04±0.003 (0.12±0.03, post UV-C) **Must** before pressing 10d: 0.23±0.02 (0.41±0.01, post UV-C) **Must**: 0.10±0.04 (0.22±0.05, post UV-C) **Racked wine**: 0.21±0.03 (0.30±0.01, post UV-C) **Clarified wine**: 0.25±0.04 (0.31±0.03, post UV-C) **Final wine**: 0.21±0.04 (0.31±0.04, post UV-C)		
	Z-Piceid	**Wine**, French (Burgundy), Pinot Noir, UPLC-UV	2.4-8.9 (n=4)	(Boutegrabet *et al.*, 2011)
		Wine, French (Bergerac), red and white, LC with fluorescence detection	Red: ND-24.1 (n=19) White: ND-0.9 (n=30)	(Vitrac *et al.*, 2002)
		Wine, American, HPLC-UV with MS confirmation: Cabernet Sauvignon: ND-5.15 (n=12) Merlot: ND-3.36 (n=9) Chardonnay: ND-1.89 (n=14) Riesling: ND (n=7)	Red: ND-5.2 (n=21) White: ND-1.89 (n=21)	(Lee and Rennaker, 2007)
		Wine, Italian, LC-MS-MS: Red: Barbara: 18.93-21.01 (n=2) Cesanese+Sangiovese+Merlot+Montepulciano: 15.70 Sangiovese: 2.77-17.02 (n=2) Montepulciano: 18.24-38.47 (28.51, n=3) Lambrusco: 7.40-16.26 (n=2) Nero d'Avola: 18.78 Merlot: 3.81 Nero d'Avola+Nerello+Mascalese+Pignatello: 6.10 Aglianico: 37.17 Sangiovese+Ciliegiolo+Canaiolo: 10.38 Cannonau: 3.43 Primitivo: 11.27 Negroamaro: 10.45 Syrah: 3.08 White: Chardonnay (60%): 1.59 Pinot Grigio: 0.82 Sauvignon Blanc (60%)+Grechetto: 6.35	Red: 2.8-38.5 (15.22, n=19) White: 0.82-6.35 (2.92, n=3)	(Buiarelli *et al.*, 2007)
		Wine, Portuguese and French, HPLC-UV: Red: Portuguese, monovarietal: ND-17.9 (n=34) Portuguese, blended: ND-8.1 (n=5) French: ND-5.3 (n=7) White: Portuguese, monovarietal: ND-4.0 (n=50) Portuguese, blended: ND-2.8 (n=9) Portuguese, fortified: ND-3.9 (n=15)	Red: ND-17.9 (n=46) White: ND-4.0 (n=74)	(Ribeiro de Lima *et al.*, 1999)

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		Wine, Spanish, Mourvèdre (Monastrell), HPLC-UV: Young: ND-7.24 (n=21) Oak-aged: ND-5.36 (n=12) Sweet: ND (n=3) Organic: 3.72-11.40 (6.5, n=3) Aged Organic: 3.49 (n=1) e"Doble" Pasta: 4.52-14.80 (8.5, n=5)	ND-14.80 (n=45)	(Moreno-Labanda *et al.*, 2004)
		Berry skins, French, with varying degrees of *B. cinerea* infection, 24 and 48 hours after UV light treatment, HPLC with fluorescence detection, mg/kg fw: Gamay: Noninfected: 6.7 (UV, 24h=5.8, 48h=16.4) Highly infected: 0 (UV, 24h=0, 48h=0) Moderately infected: 9.4 (UV, 24h=7.0, 48h=7.9) Mildly infected: 11.9 (UV, 24h=7.2, 48h=13.6) Chardonnay: Noninfected: 5.0 (UV, 24h=3.0, 48h=5.0) Highly infected: 0.1 (UV, 24h=0, 48h=0) Moderately infected: 10.0 (UV, 24h=12.1, 48h=6.0) Mildly infected: 9.6 (UV, 24h=0.4, 48h=6.9) Pinot Noir: ND in any level of infection		(Adrian *et al.*, 2000)
		Leaves, Chasselas, infected with *P. viticola* for 7 days or 72 hours after UV-C irradiation, mg/g fw: *P. viticola*: 12.85±1.34 UV irradiated: 1.69±0.11 Control: ND		(Pezet *et al.*, 2003)
	E-Piceid	Pinot Gris, Welschriesling, Chardonnay, André, Blauer Portugieser, Saint Laurent from South Moravia, Czech Republic, fungus infected vines, HPLC-UV, mg/kg: **Leaves**: 11.3-58.4 dw 18.5-60.9 dw (infected) **Berries**: 0.6-2.9 frozen 1.5-6.3 frozen (infected) **Stems**: 12.1-24.2 dw **Shoots**: 12.6-99.7 dw		(Balík *et al.*, 2008)
		Wine, French (Burgundy), Pinot Noir, UPLC-UV	ND-14.27 (n=4)	(Boutegrabet *et al.*, 2011)
		Wine, French (Bergerac), red and white, LC with fluorescence detection	Red: 0.1-26.0 (6.2, n=19) White: ND-2.9 (0.5, n=30)	(Vitrac *et al.*, 2002)
		Wine, Brazilian, HPLC-UV: Cabernet Franc: ND (n=1) Cabernet Sauvignon: ND-7.43 (n=4) Tannat: ND (n=1) Merlot: 5.3-19.53 (13.1, n=6)	ND-19.5 (n=12)	(Vitrac *et al.*, 2005)

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		Wine, North African, HPLC-UV: Monovarietal red: Merlot: 14.0 Cabernet Sauvignon: 9.37 [d]Blended red: Cuvée du Président: 45.0 Amjad: 38.6 Guerrouane: 15.0 Sidi-Brahim: 17.6 Terrale: 10.0	9.4-45.0 (n=7)	(Guebailia *et al.*, 2006)
		Wine, American, HPLC-UV with MS confirmation, mg (expressed as *E*-resveratrol)/l: Cabernet Sauvignon: ND-6.48 (1.65, n=12) Chardonnay: ND-1.91 (0.14, n=14) Merlot: ND-4.58 (2.45, n=9) Riesling: ND-1.45 (0.49, n=7)	ND-6.5 (n=21) White: ND-1.9 (n=21)	(Lee and Rennaker, 2007)
		Wine, Canadian, (total piceid), HPLC-UV: French hybrid varieties: Baco Noir: 3.57-3.95 (n=2) Leon Millot/Lucie Kuhlmann: 2.36-2.84 (n=2) Marechal Foch: 0.64-2.88 (1.92, n=4) Lucie Kuhlmann: 1.64 (n =1) Leon Millot: 0.96-1.13 (n=2) de Chaunac: 7.02 (n=1) *V. vinifera* varieties: Zweigelt/Cabernet: 1.29 (n=1) Pinot Noir/Cabernet: 1.56 (n=1) Pinot Noir: 1.72 (n=1)	0.64-7.0 (n=15)	(Naugler *et al.*, 2007)
		Wine, Italian, LC-MS-MS: Red: Barbara: 3.81-5.81 (n=2) Cesanese+Sangiovese+Merlot+Montepulciano: 9.31 Sangiovese: 0.49-4.45 (n=2) Montepulciano: 6.78-7.32 (6.97, n=3) Lambrusco: 1.55-4.12 (n=2) Nero d'Avola: 3.23 Merlot: 0.75 Nero d'Avola+Nerello+Mascalese+Pignatello: 1.53 Aglianico: 4.96 Sangiovese+Ciliegiolo+Canaiolo: 3.68 Cannonau: 0.77 Primitivo: 2.50 Negroamaro: 2.69 Syrah: 0.48 White: Chardonnay (60%): trace Pinot Grigio: trace Sauvignon Blanc (60%)+Grechetto: 0.47	Red: 0.5-9.3 (3.7, n=19) White: trace-0.5 (n=3)	(Buiarelli *et al.*, 2007)
		Wine, Portuguese and French, HPLC-UV: Red: Portuguese, monovarietal: ND-50.8 (11.8, n=34) Portuguese, blended: ND-17.1 (8.0, n=5) French: 3.1-32.8 (13.0, n=7) White: Portuguese monovarietal: ND-5.8 (2.6, n=50) Portuguese, blended: 1.2-4.7 (2.9, n=9) Portuguese, fortified: 1.6-7.0 (4.5, n=15)	Red: ND-50.8 (11.6, n=46) White: ND-7.0 (3.0, n=74)	(Ribeiro de Lima *et al.*, 1999)

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		Wine, Spanish, Mourvèdre (Monastrell), HPLC-UV: Young: 1.19-17.09 (8.66, n=21) Oak-aged: 6.03-17.24 (9.61, n=12) Sweet: ND-6.00 (3.5, n=3) Organic: 5.83-16.88 (11.43, n=3) Aged Organic: 4.15 (n=1) [e]Doble Pasta: 13.07-29.24 (18.80, n=5)	ND-29.2 (n=45)	(Moreno-Labanda *et al.*, 2004)
		Berries, Italian and South African, without seeds, HPLC-UV, mg/kg dw: Italian: Primitivo: 30.7±0.9 Negroamaro: 4.14±0.02 Susumaniello: 150.3±4.6 Uva di Troia: 15.3±0.5 Malvasia Nera: 98.0±2.0 Aglianico: 75.7±1.9 Cesanese: 12.05±0.02 Merlot: 26.3±0.43 Moscato: ND South African: Alphonse Lavallée: 24.1±0.5		(Nicoletti *et al.*, 2008)
		Berries, Cabernet Sauvignon, without seeds, HPLC-UV, mg/kg fw: 0.097		(Bavaresco *et al.*, 2002)
		[c]**Berry skins**, HPLC-UV, mg/kg dw: Syrah: 2.8 (n=1) Pinot Noir: 7.1-187 (86.8, n=3)		(Waterhouse and Lamuela-Raventós, 1994)
		Berry skins, French, with varying degrees of *B. cinerea* infection, 24 and 48 hours after UV light treatment, HPLC with fluorescence detection, mg/kg fw: Gamay: Noninfected: 37.7 (UV, 24h=79.7, 48h=75.4) Highly infected: 0 (UV, 24h=4.3, 48h=0) Moderately infected: 35.5 (UV, 24h=30.2, 48h=57.2) Mildly infected: 77.9 (UV, 24h=33.5, 48h=60.4) Chardonnay: Noninfected: 26.2 (UV, 24h=46.5, 48h=13.4) Highly infected: 0 (UV, 24h=0, 48h=0) Moderately infected: 70.2 (UV, 24h=57.5, 48h=19.8) Mildly infected: 41.4 (UV, 24h=73.3, 48h=43.9) Pinot Noir: Noninfected: 0 (UV, 24h=0, 48h=0) Highly infected: 0 (UV, 24h=0, 48h=0) Moderately infected: 0 (UV, 24h=0, 48h=0) Mildly infected: 0 (UV, 24h=0, 48h=0)		(Adrian *et al.*, 2000)
		Leaves, Chasselas, infected with *P. viticola* for 7 days or 72 hours after UV-C irradiation, mg/g fw: *P. viticola*: 64.93±0.95 UV irradiated: 18.74±3.69 Control: ND		(Pezet *et al.*, 2003)

		Leaves, *P. viticola* infected, averaged over 3 years, 6 days post-infection, µg/g fw: F1 genotype 21/103: 5.2 (2.5 SD) F1 genotype 21/74: 5.1 (1.4 SD)		(Vrhovsek *et al.*, 2011)
	Pterostilbene	**Berry skins**, French, with varying degrees of *Botrytis cinerea* infection, 24 and 48 hours after UV light treatment, HPLC with fluorescence detection, mg/kg fw: Gamay: Noninfected: 0 (UV, 24h=0.5, 48h=1.4) Highly infected: 0.2 (UV, 24h=0, 48h=0) Moderately infected: 1.5 (UV, 24h=0, 48h=1.4) Mildly infected: 1.3 (UV, 24h=0.8, 48h=1.9) Chardonnay: Noninfected: 0 (UV, 24h=1.0, 48h=0) Highly infected: 0.2 (UV, 24h=0, 48h=0) Moderately infected: 4.7 (UV, 24h=1.8, 48h=2.5) Mildly infected: 0.2 (UV, 24h=1.5, 48h=20.0) Pinot Noir: Noninfected: 0 (UV, 24h=3.0, 48h=0) Highly infected: 0 (UV, 24h=0, 48h=0) Moderately infected: 0 (UV, 24h=0, 48h=1.1) Mildly infected: 0 (UV, 24h=0, 48h=1.3)		(Adrian *et al.*, 2000)
		Leaves, Chasselas, infected with *P. viticola* for 7 days or 72 hours after UV-C irradiation, mg/g fw: *P. viticola*: 5.14±0.46 UV irradiated: ND Control: ND		(Pezet *et al.*, 2003)
	Z-Resveratrol	Bohemian and Moravian grapevines, HPLC with electrochemical detection, mg/kg dw: **Leaves:** Red varieties: Cabernet Sauvignon: 1.30 Pinot Noir: 1.20 Laurot: 1.60 Tintet: trace Neronet: trace Merlot: 3.00 White varieties: Erilon: 2.20 Rubikon: 2.60 Hibernal: 1.30 **Rachis**: Red varieties: Cabernet Sauvignon: trace Pinot Noir: trace Laurot: 2.00 Tintet: 6.80 Neronet: 2.30 Merlot: 1.80 White varieties: Erilon: 9.90 Rubikon: trace Hibernal: 3.40 **Berries**, red and white: Cabernet Sauvignon, Pinot Noir, Laurot, Tintet, Neronet, Merlot, Erilon, Rubikon, Hibernal: trace		(Melzoch *et al.*, 2001)

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		Wine, French (Bergerac), red and white, LC with fluorescence detection	Red: ND-0.9 (0.1, n=19) White: ND-0.1 (0.03, n=30)	(Vitrac *et al.*, 2002)
		Wine, Brazilian, HPLC-UV: Cabernet Franc: 8.43 (n=1) Cabernet Sauvignon: 1.7-7.02 (3.98, n=4) Tannat: 1.91 (n=1) Merlot: 4.9-23.23 (15.45, n=6)	1.7-23.2 (9.9, n=12)	(Vitrac *et al.*, 2005)
		Wine, American, HPLC-UV with MS confirmation: Cabernet Sauvignon: ND-trace (n=12) Chardonnay: ND (n=14) Merlot: ND-trace (n=9) Riesling: ND (n=7)	Red and white: ND-trace (n=42)	(Lee and Rennaker, 2007)
		Wine, Canadian, LC-fluorescence detection: French hybrid varieties: Baco Noir: 0.80-3.68 (n=2) Leon Millot/Lucie Kuhlmann: 1.17-1.92 (n=2) Marechal Foch: 0.65-1.76 (1.04, n=4) Lucie Kuhlmann: 0.68 (n=1) Leon Millot: 0.37-0.38 (n=2) de Chaunac: 0.41 (n=1) *V. vinifera* varieties: Zweigelt/Cabernet: 0.44 (n=1) Pinot Noir/Cabernet: 0.45 (n=1) Pinot Noir: 0.58 (n=1)	0.37-3.7 (0.9, n=15)	(Naugler *et al.*, 2007)
		Wine, Italian, LC-MS-MS: Red: Barbara: 0.48-0.76 (n=2) Cesanese+Sangiovese+Merlot+Montepulciano: trace Sangiovese: 0.82-1.58 (n=2) Montepulciano: trace-4.93 (n=3) Lambrusco: trace-0.76 (n=2) Nero d'Avola: 1.85 Merlot: 2.09 Nero d'Avola+Nerello+Mascalese+Pignatello: 0.89 Aglianico: 1.59 Sangiovese+Ciliegiolo+Canaiolo: 1.50 Cannonau: 0.83 Primitivo: 1.00 Negroamaro: 0.82 Syrah: 0.91 White: Chardonnay (60%): trace Pinot Grigio: trace Sauvignon Blanc (60%)+Grechetto: 0.52	Red: trace-4.9 (n=19) White: trace-0.5 (n=3)	(Buiarelli *et al.*, 2007)
		Wine, world-wide, SIDA-UPLC-Quan-TOF-MS: Dornfelder aged in barrel, 2005: 0.41±0.02 Dornfelder, 2005: trace Bordeaux, 2003 (Côtes de Castillon): 4.88±0.14 Bordeaux, 2007 (Graves): 11.97±0.23 Spaetburgunder (Pinot Noir), 2008: trace Merlot, 2009: trace Zinfandel, 2007: trace Zinfandel, 2008: trace Shiraz, 2009: trace Cabernet Sauvignon, 2006: trace Cabernet Sauvignon, 2008: trace Barbera, 2005: 0.47±0.02	trace-12.0 (n=14)	(Stark *et al.*, 2011)

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		Lemberger, 2008: 0.78±0.05 Bardolino, 2009: 0.28±0.04		
		Wine, Spanish, HPLC with fluorimetric detection	Red: ND-0.23 (0.06, n=24) White: ND-0.2 (0.11, n=24)	(Feijóo *et al.*, 2008)
		[b]**Berries**, Spanish, HPLC with fluorescence detection, picked once a week for three weeks prior to ripeness, for three years, in mg/L: Mencia grape skins: 1st week: ND-0.18 (n=9, 3 each year) 2nd week: ND-0.28 (n=9, 3 each year) 3rd week: ND-0.17 (n=9, 3 each year) Mencia grape seeds: ND for each week Albarello grape skins: 1st week: ND-0.37 (n=9, 3 each year) 2nd week: 0.04-0.23 (0.11, n=9, 3 each year) 3rd week: 0.06-0.21 (0.13, n=9, 3 each year) Albarello grape seeds: ND for each week Merenzao grape skins: 1st week: ND-0.18 (n=9, 3 each year) 2nd week: 0.05-0.13 (0.08, n=9, 3 each year) 3rd week: 0.15-0.16 (0.15, n=6, 3 each year for two years) Merenzao grape seeds: ND for each week		(Moreno *et al.*, 2008)
		Leaves, Chasselas, infected with *P. viticola* for 7 days or 72 hours after UV-C irradiation, mg/g fw: *P. viticola*: 6.45±2.09 UV irradiated: 0.32±0.09 Control: ND		(Pezet *et al.*, 2003)
	E-Resveratrol	Pinot Gris, Welschriesling, Chardonnay, André, Blauer Portugieser, Saint Laurent from South Moravia, Czech Republic, fungus infected vines, HPLC-UV, mg/kg: **Leaves**: 2.5-10.3 dw 3.7-20.9 dw (infected) **Berries**: 0.3-2.3 frozen 0.7-12.1 frozen (infected) **Stems**: 16.3-276.1 dw **Shoots**: 3.7-15.6 dw		(Balík *et al.*, 2008)
		Wine, French (Bergerac), red and white, LC with fluorescence detection	Red: 0.9-3.8 (2.3, n=19) White: ND-0.2 (n=30)	(Vitrac *et al.*, 2002)
		Bohemian and Moravian grapevines, HPLC with electrochemical detection, mg/kg dw: **Leaves**: Red varieties: Cabernet Sauvignon: 5.00 Pinot Noir: 1.60 Laurot: 4.40		(Melzoch *et al.*, 2001)

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		Tintet: 3.60 Neronet: 9.90 Merlot: 7.10 White varieties: Erilon: 44.20 Rubikon: 14.60 Hibernal: 5.40 **Rachis**: Red varieties: Cabernet Sauvignon: 7.00 Pinot Noir: 13.00 Laurot: 15.00 Tintet: 440.00 Neronet: 209.00 Merlot: 15.00 White varieties: Erilon: 482.00 Rubikon: 6.00 Hibernal: 63.00 **Berries**: Red varieties: Cabernet Sauvignon: 0.72 Pinot Noir: 2.34 Laurot: 5.80 Tintet: 0.30 Neronet: 0.70 Merlot: 0.70 White varieties: Erilon: 0.44 Rubikon: 0.20 Hibernal: 0.32		
		Wine, French (Burgundy), Pinot noir, UPLC-UV	0.53-5.08 (n=4)	(Boutegrabet *et al.*, 2011)
		Wine, American, HPLC-UV with MS confirmation: Cabernet Sauvignon: ND-3.07 (1.45, n=12) Chardonnay: ND-trace (n=13) Merlot: ND-2.13 (1.40, n=9) Riesling: ND-1.16 (0.17, n=7)	Red: ND-3.07 (n=21) White: ND-1.16 (n=20)	(Lee and Rennaker, 2007)
		Wine, North African, HPLC-UV: Monovarietal red: Merlot: 3.4 Cabernet Sauvignon: 2.2 [d]Blended red: Cuvée du Président: 3.2 Amjad: 2.5 Guerrouane: ND Sidi-Brahim: 3.45 Terrale: ND	ND-3.45 (n=7)	(Guebailia *et al.*, 2006)
		Stems, multiple cultivars, HPLC-UV: 664.7-1,751.6 mg/kg fw		(Zhang *et al.*, 2011)
		Stems, Pinot Noir, HPLC-UV: 3.45±0.04 mg/g dw		(Rayne *et al.*, 2008)
		Stems, LC-UV quantitation with LC-MS detection, mg/g dw: Hasaine Sladki: 3.2±0.5 (n=16) Zilga: 2.1±0.3 (n=16) Yubilei Novgoroda: 1.1±0.3 (n=16)		(Püssa *et al.*, 2006)

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		Stems, Estonian, LC-UV quantitation with LC-MS detection, mg/g dw: *V. vinifera* cv., not specified: 1.2-2.8 Hasaine Sladki: 0.3-4.7 Marechal Joffre: 0.1-1.6 Zilga: 0.1-1.1 ES 12-7-98: 0.1-2.4 Jubilei Novgoroda: 2.9		(Aaviksaar *et al.*, 2003)
		Wine, Canadian (Nova Scotia), HPLC-fluorescence detection: French hybrid varieties: Baco Noir: 0.85-0.90 (n=2) Leon Millot/Lucie Kuhlmann: 1.17-1.92 (n=2) Marechal Foch: 0.15-4.55 (1.7, n=4) Lucie Kuhlmann: 0.93 (n=1) Leon Millot: 0.49-0.75 (n=2) de Chaunac: 0.65 (n=1) *V. vinifera* varieties: Zweigelt/Cabernet: 0.56 (n=1) Pinot Noir/Cabernet: 0.56 (n=1) Pinot Noir: 0.62 (n=1)	0.15-4.5 (1.1, n=15)	(Naugler *et al.*, 2007)
		Wine, Greek, HPLC-UV: Red: Agiorgitico: 1.21±0.63 Xinimavro: 0.70±0.48 Kalambaki: 0.49±1.35 Negosca: 0.35±0.24 Mantilaria: 1.99±1.11 Kotsifali: 1.33±1.32 [d]Cabernet: 0.74±0.51 Fokiano: 0.99±1.29 Romeiko: 1.16±1.04 Verzami: 0.74±1.17 Liatiko: 0.46±0.11 Mavrodafni: 0.52±0.19 Mavro Mesenikola: 0.97±0.32 White: Savatiano: 0.57±0.32 Athiri: 0.54±0.63 Roditis: 0.02±0.11 Muscat of Alexandria: 0.02±0.53 Moschofilero: 0.01±0.39 Asyritco: 0.42±0.21 Robolla: 0.11±0.57 Muscat of Samos: 0.01±0.01 Moschoudi: 0.09±0.09 Vilana: 0.21±0.04 Malagouzia: 0.31±0.15 Malvazia: 0.30±0.18 Monembasia: 0.23±0.54 Batiki: 0.37±0.21 Debina: 0.12±0.03 Opsimos Soufliou: 0.43±0.07 Voidomatis: 0.27±0.04 Soultanina: 0.12±0.02	Red: 0.35-1.3 (0.9, n=13) White: 0.01-0.57 (0.23, n=18)	(Gerogiannaki-Christopoulou *et al.*, 2006)
		Wine, Italian, LC-MS-MS: Red: Barbera: 0.87-1.74 (n=2) Cesanese+Sangiovese+Merlot+Montepulciano: 1.46 Sangiovese: 0.67-1.39 (1.0, n=2) Montepulciano: 1.30-3.39 (2.3, n=3) Lambrusco: 0.63-0.96 (0.8, n=2)	Red: trace-3.4 (n=19) White: trace	(Buiarelli *et al.*, 2007)

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		Nero d'Avola: 1.25 Merlot: 2.24 Nero d'Avola+Nerello+Mascalese+Pignatello: 1.93 Aglianico: 1.69 Sangiovese+Ciliegiolo+Canaiolo: 2.19 Cannonau: 1.06 Primitivo: 0.82 Negroamaro: 0.63 Syrah: trace White: Chardonnay (60%): trace Pinot Grigio: trace Sauvignon Blanc (60%)+Grechetto: trace		
		Wine, world-wide, SIDA-UPLC-Quan-TOF-MS: Dornfelder aged in barrel, 2005: 1.26±0.04 Dornfelder, 2005: 0.61±0.02 Bordeaux, 2003 (Côtes de Castillon): 5.14±0.09 Bordeaux, 2007 (Graves): 9.04±0.14 Spaetburgunder (Pinot Noir), 2008: 2.10±0.04 Merlot, 2009: 0.93±0.04 Zinfandel, 2007: 0.75±0.02 Zinfandel, 2008: 0.64±0.02 Shiraz, 2009: 0.61±0.02 Cabernet Sauvignon, 2006: 0.79±0.02 Cabernet Sauvignon, 2008: 0.59±0.02 Barbera, 2005: 1.25±0.05 Lemberger, 2008: 3.24±0.10 Bardolino, 2009: 0.90±0.04	0.6-9.0 (2.0, n=14)	(Stark *et al.*, 2011)
		Wine, Spanish, HPLC with fluorimetric detection	Red: 0.06-36.1 (12.7, n=24) White: 0.65-8.0 (2.51, n=24)	(Feijóo *et al.*, 2008)
		Berries, Italian and South African, without seeds, mg/kg dw: Italian: Primitivo: 13.9±0.4 Negroamaro: 3.6±0.01 Susumaniello: 63.0±0.9 Uva di Troia: 4.60±0.06 Malvasia Nera: 48.5±1.0 Aglianico: 61.1±0.8 Cesanese: 8.16±0.02 Merlot: 9.2±0.2 Moscato: 3.89±0.01 South African: Alphonse Lavallée: 20.0±0.60		(Nicoletti *et al.*, 2008)
		Berries, Cabernet Sauvignon, without seeds, mg/kg fw: 0.297		(Bavaresco *et al.*, 2002)
		[b]**Berries**, Spanish, HPLC with fluorescence detection, picked once a week for three weeks prior to ripeness, for three years, in mg/L: Mencia grape skins: 1st week: 6.23-21.07 (15.2, n=9, 3 each year) 2nd week: 4.99-18.35 (11.4, n=9, 3 each year) 3rd week: 5.47-21.97 (11.9, n=9, 3 each year) Mencia grape seeds: 1st week: 0.94-2.01 (1.59, n=9, 3 each year) 2nd week: 0.33-1.59 (0.87, n=9, 3 each year) 3rd week: 0.71-1.87 (1.20, n=9, 3 each year) Albarello grape skins:		(Moreno *et al.*, 2008)

		1st week: 0.23-0.46 (0.35, n=9, 3 each year) 2nd week: 0.38-1.71 (0.98, n=9, 3 each year) 3rd week: 0.56-2.56 (1.27, n=9, 3 each year) Albarello grape seeds: 1st week: 0.47-0.68 (0.61, n=9, 3 each year) 2nd week: 0.78-1.10 (0.91, n=9, 3 each year) 3rd week: 0.41-1.26 (0.74, n=9, 3 each year) Merenzao grape skins: 1st week: 0.33-0.73 (0.53, n=9, 3 each year) 2nd week: 0.50-1.71 (0.91, n=9, 3 each year) 3rd week: 0.84-1.51 (1.18, n=6, 3 each year for two years) Merenzao grape seeds: 1st week: 0.37-0.53 (0.47, n=9, 3 each year) 2nd week: 0.43-0.55 (0.47, n=9, 3 each year) 3rd week: 0.47-0.48 (0.47, n=6, 3 each year for two years)		
		[c]**Berry skins**, mg/kg dw: Syrah: 11.3 (n=1) Pinot Noir: ND-78.5 (n=3)		(Waterhouse and Lamuela-Raventós, 1994)
		Stems, Turkish table grapes, HPLC-UV, mg/kg dw: Alphonse Lavallée: 2.20±0.52 Atasarisi: 2.18±0.42 Cardinal: 2.56±0.32 Hafizali: 0.95±0.08 Horoz Karasi: 3.94±0.21 Isabella: 2.96±0.26 Italia: 1.42±0.14 Sultani Çekirdeksiz: 1.42±0.32 Tekirdağ Çekirdeksiz: 2.62±0.36 Trakya İlkeren: 1.88±0.24		(Çetin *et al.*, 2011)
		Mourvèdre (Monastrell), Spanish, HPLC-UV with MS identification, pre and post UV-C irradiation for stilbenoids induction: Solids in mg/kg fw (n=3)**:** **Berries**: 3.18±0.1 (8.13±1.7, post UV-C) **Stems**: 49.60±4.7 (56.40±9.7, post UV-C) **Skins**: 3.16±1.1 (8.9±0.5, post UV-C) **Pomace**: 0.18±0.05 (0.34±0.01, post UV-C) **Lees**: 0.29±0.03 (0.59±0.2, post UV-C) Liquid in mg/L: **Must** before pressing 0d: 0.08±0.02 (0.25±0.1, post UV-C) **Must** before pressing 10d: 0.12±0.02 (0.23±0.01, post UV-C) **Must**: 0.06±0.02 (0.14±0.02, post UV-C) **Racked wine**: 0.062±0.01 (0.17±0.02, post UV-C) **Clarified wine**: 0.11±0.007 (0.17±0.01, post UV-C)	0.09, no UV-C irradiation 0.19, after UV-C irradiation	(Cantos *et al.*, 2003)
		Berry skins, French, with varying degrees of *B. cinerea* infection, 24 and 48 hours after UV light treatment, HPLC with fluorescence detection, mg/kg fw: Gamay: Noninfected: 5.7 (UV, 24h=15.9, 48h=91.4) Highly infected: 0.7 (UV, 24h=2.7, 48h=0) Moderately infected: 9.4 (UV, 24h=51.0, 48h=56.5)		(Adrian *et al.*, 2000)

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		Mildly infected: 3.4 (UV, 24h=51.8, 48h=66.1) Chardonnay: Noninfected: 6.7 (UV, 24h=37.2, 48h=122.9) Highly infected: 0.7 (UV, 24h=0.3, 48h=3.4) Moderately infected: 48.0 (UV, 24h=77.8, 48h=71.7) Mildly infected: 21.8 (UV, 24h=25.1, 48h=47.4) Pinot Noir: Noninfected: 0 (UV, 24h=33.3, 48h=30.2) Highly infected: 1.8 (UV, 24h=0, 48h=0) Moderately infected: 11.4 (UV, 24h=14.7, 48h=24.7) Mildly infected: 0 (UV, 24h=13.9, 48h=24.4)		
		Leaves, Chasselas, infected with *P. viticola* for 7 days or 72 hours after UV-C irradiation, mg/g fw: *P. viticola*: 50.0±8.5 UV irradiated: 337.5±27.5 Control: 0.3±0.02		(Pezet *et al.*, 2003)
		Wine, Portuguese, red sorted by wine region, HPLC-UV: Vinhos Verdes: 0.20-8.59 (2.71±1.8, n=23) Bairrada: 2.98-5.42 (3.30±0.8, n=7) Ribatejo: 0.34-6.96 (2.60±1.6, n=39) Douro: 0.05-4.93 (2.21±1.5, n=13) Dão: 0.23-5.92 (3.42±1.8, n=7) Beira Interior: 0.23-10.87 (3.50±1.9, n=83) Alentejo: 0.77-2.80 (1.62±0.7, n=7)	0.05-10.9 (2.9, n=179)	(Paulo *et al.*, 2011)
		Leaves, *P. viticola* infected, averaged over 3 years, 6 days post-infection, µg/g fw: F1 genotype 21/103: 11.0 (4.1 SD) F1 genotype 21/74: 11.7 (8.9 SD)		(Vrhovsek *et al.*, 2011)
	α-Viniferin	**Leaves**, *P. viticola* infected, averaged over 3 years, 6 days post-infection, µg/g fw: F1 genotype 21/103: 44.0 (48.1 SD) F1 genotype 21/74: 12.8 (14.9 SD)		(Vrhovsek *et al.*, 2011)
	ε-Viniferin	**Wine**, French (Burgundy), Pinot Noir, concentration not given, UPLC-UV		(Boutegrabet *et al.*, 2011)
		Wine, Brazilian, HPLC-UV: Cabernet Franc: 1.85 (n=1) Cabernet Sauvignon: 0.58-2.19 (1.39, n=4) Tannat: 0.64 (n=1) Merlot: 0.19-4.32 (2.58, n=6)	0.19-4.3 (2.0, n=12)	(Vitrac *et al.*, 2005)
		Wine, North African, HPLC-UV**:** Monovarietal red: Merlot: 1.2±0.05 Cabernet Sauvignon: 0.69±0.08 [d]Blended red: Ksar: 0.49±0.08 Cuvée du Président: ND Amjad: 0.20±0.04 Guerrouane: ND Sidi-Brahim: ND Terrale: ND Gris d'Algérie: ND Monovarietal white: Muscat: ND	Red: ND-1.2 (n=9) White: ND (n=1)	(Guebailia *et al.*, 2006)
		Wine, French, HPLC-UV: Red: Cabernet Sauvignon: 0.1-1.63 (1.03, n=3) Merlot: 0.53 (n=1)	Red: 0.1-1.6 (0.81, n=6) Rosé: ND (n=1) White: ND (n=6)	(Landrault *et al.*, 2002)

		Tempranillo: 0.13 (n=1) Egiodola: 1.12 (n=1) Rosé: Syrah: ND (n=1) White: Chardonnay: ND (n=3) Sauvignon: ND (n=2) Viognier: ND (n=1) Sémillon, botrytized sweet wine: 0.08-0.17 (0.12, n=8)	Sweet white, botrytized: 0.08-0.17 (0.12, n=8)	
		Stems, Estonian, LC-UV quantitation with LC-MS detection, mg/g dw: *V. vinifera* cv., not specified: ≤0.1-1.1 Hasaine Sladki: <0.1-1.5 Marechal Joffre: <0.1-0.3 Zilga: <0.1-0.5 ES 12-7-98: 1.1 Jubilei Novgoroda: 1.0		(Aaviksaar *et al.*, 2003)
		Stems, LC-UV quantitation with LC-MS detection, mg/g dw: Hasaine Sladki: 1.7±0.3 (n=16) Zilga: 1.2±0.3 (n=16) Yubilei Novgoroda: 0.7±0.2 (n=16)		(Püssa *et al.*, 2006)
		Stems, Pinot Noir, HPLC-UV: 1.30±0.07 mg/g dw		(Rayne *et al.*, 2008)
		Stems, Pinot Noir, HPLC-UV: 2.03 mg/g dw		(Karacabey and Mazza, 2008)
		Mourvèdre (Monastrell), Spanish, HPLC-UV with MS identification, pre and post UV-C irradiation: Solids in mg/kg fw (n=3): **Berries**: 6.37±0.4 (11.00±2.4, post UV-C) **Stems**: 11.70±4.5 (9.70±4.6, post UV-C) **Skins**: 6.52±2.8 (9.60±2.5, post UV-C) **Pomace**: 2.20±0.02 (2.91±0.4, post UV-C) **Lees**: 0.25±0.02 (0.28±0.0, post UV-C)		(Cantos *et al.*, 2003)
		Berry skins, French, with varying degrees of *B. cinerea* infection, 24 and 48 hours after UV light treatment, HPLC with fluorescence detection, mg/kg fw: Gamay: Noninfected: 8.5 (UV, 24h=16.4, 48h=43.8) Highly infected: 0 (UV, 24h=1.5, 48h=0) Moderately infected: 15.6 (UV, 24h=19.0, 48h=43.2) Mildly infected: 13 (UV, 24h=14.9, 48h=47.5) Chardonnay: Noninfected: 2.2 (UV, 24h=6.4, 48h=12.6) Highly infected: 3 (UV, 24h=2.2, 48h=2.9) Moderately infected: 12.2 (UV, 24h=19.8, 48h=27.9) Mildly infected: 4.6 (UV, 24h=4.9, 48h=23.6) Pinot Noir: Noninfected: 0 (UV, 24h=2.5, 48h=3.0) Highly infected: 5.9 (UV, 24h=0, 48h=0) Moderately infected: 13.1 (UV, 24h=20.0, 48h=22.9) Mildly infected: 0 (UV, 24h=9.5, 48h=38.4)		(Adrian *et al.*, 2000)

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		Leaves, Chasselas, infected with *P. viticola* for 7 days or 72 hours after UV-C irradiation, mg/g fw: *P. viticola*: 86.81±18.12 UV irradiated: 8.63±1.45 Control: ND		(Pezet *et al.*, 2003)
		Leaves, *P. viticola* infected, averaged over 3 years, 6 days post-infection, µg/g fw: F1 genotype 21/103: 32.3 (30.7 SD) F1 genotype 21/74: 15.6 (20.8 SD)		(Vrhovsek *et al.*, 2011)
	Z-*ε*-Viniferin	**Wine**, North African, HPLC-UV: Monovarietal red: Merlot: 0.30±0.03 Cabernet Sauvignon: 0.35±0.04 [d]Blended red: Ksar: 0.38±0.06 Cuvée du Président: 0.22±0.06 Amjad: 0.20±0.05 Guerrouane: 1.12±0.09 Sidi-Brahim: ND Terrale: 0.13±0.05 Gris d'Algérie: 0.10±0.02 Monovarietal white: Muscat: 0.38±0.08	Red: ND-1.12 (n=9) White: 0.38±0.08	(Amira-Guebailia *et al.*, 2009)
		Leaves, Chasselas, infected with *P. viticola* for 7 days or 72 hours after UV-C irradiation, mg/g fw: *P. viticola*: 7.31±1.08 UV irradiated: ND Control: ND		(Pezet *et al.*, 2003)
	E-*δ*-Viniferin	**Wine**, Brazilian, HPLC-UV: Cabernet Franc: ND (n=1) Cabernet Sauvignon: ND-6.06 (5.52, n=4) Tannat: ND (n=1) Merlot: ND-22.41 (10.94, n=6)	ND-22.4 (n=12)	(Vitrac *et al.*, 2005)
		Leaves, Chasselas, infected with *P. viticola* for 7 days or 72 hours after UV-C irradiation, mg/g fw: *P. viticola*: 155.68±20.36 UV irradiated: 165.71±18.42 Control: 2.04±0.43		(Pezet *et al.*, 2003)
	Z-*δ*-Viniferin	**Leaves**, Chasselas, infected with *P. viticola* for 7 days or 72 hours after UV-C irradiation, mg/g fw: *P. viticola*: ND UV irradiated: 3.42±0.72 Control: ND		(Pezet *et al.*, 2003)
	Z + *E*-*ω*-Viniferin (quantified as mixture)	**Leaves**, *P. viticola* infected, averaged over 3 years, 6 days post-infection, µg/g fw: F1 genotype 21/103: 40.2 (40.9 SD) F1 genotype 21/74: 22.5 (32.7 SD)		(Vrhovsek *et al.*, 2011)

[a]Red wine unless otherwise specified. [b]Units are based on weight of skins and seeds from 50 grapes, macerated with 50 ml of MeOH. [c]Recovery for piceid was 73% and for resveratrol was 37%, based on spiking/recovery study. [d]Variety used was not specified further. fw=fresh weight, dw=dry weight, ND=none detected, SD=standard deviation, trace=compound found, but not in quantifiable concentrations. « Doble pasta » was made from additional solids from rosé production.

looking at latitude in the northern hemisphere, where more northern locations contained higher resveratrol content. One example of this is the higher concentrations in Canadian red wines than those found in Greece or Japan. The authors also looked to see if a trend was apparent with thick and thin skinned grapes. This was also ambiguous, since levels between thin and thick varied unpredictably (Stervbo *et al*., 2007).

Additional efforts to quantify resveratrol in wine have occurred, which we included in Table 3. In addition to examining wine samples, studies have quantified

stilbenoids in separate plant parts, the berries themselves, and wine during the vinification process in order to gain a better understanding of the stilbenoid level dynamics. For example, in a study by Gatto *et al*. (2008), the *E*-resveratrol and *Z*- and *E*-piceid levels were examined in 78 *V. vinifera* white and red grape varieties grown in the same research station in three different years. This study controlled for influences such as climate variability and differences in vinification methods by studying the berries directly, allowing genetic influences and ripening phases on stilbenoid levels to be examined. The authors evaluated the grapes at three different time points to determine the levels of the three different stilbenoids at veraison, at technological ripeness, and at a post-ripening phase, 20 days later. They simultaneously monitored genetic expression between high and low resveratrol producers. The authors demonstrated that in high resveratrol producers, such as Pinot noir, Tarrango, Franconia, Alicante Bouquette, and Carmenere, there was stilbenoid accumulation in the berries throughout development. Both *E*- and *Z*-piceid were constitutively expressed, whereas resveratrol was confirmed to be an inducible stilbenoid (Gatto *et al*., 2008). They also supported the reoccurring finding that Pinot noir is one of the varieties with higher levels of resveratrol (Lamuela-Raventos *et al*., 1997 ; Melzoch *et al*., 2001). In another recent study, 186 Portuguese red wines of different varieties and vintages were evaluated for their *E*- and *Z*-resveratrol content using HPLC-UV. *E*-resveratrol levels ranged from 0.05 to 10.9 mg/L, while the concentrations of *Z*-resveratrol ranged from 0.04 to 8.7 mg/L. The identity of all the varieties tested was not provided, since many were blended wines, but wine made from Touriga Nacional variety in the Beira Interior denomination of origin contained the highest resveratrol content (Paulo *et al*., 2011).

Most studies have not been able to single out a wine variety with consistently higher stilbenoid levels, with the possible exception of Pinot noir, which many studies have shown to have the highest average, and a lesser known variety, Mencia. In a recent study focusing on resveratrol isomers, involving wines from 5 different Galician Controlled Denomination of Origin regions in Northwestern Spain, the Mencia variety from Valdeorras had one of the highest *E*-resveratrol concentrations currently known. In one monovarietal wine sample, the *E*-resveratrol concentration was 36.1 mg/L. Mencia containing wines from Ribeira Sacra also contained high levels, up to 31.4 mg/L. However, the Mencia grown in Ribeiro CDO were much lower, with levels ranging from 2.5 to 5.8 mg/L. The concentration of *Z*-resveratrol in all wines was very low, with a maximum *Z*-resveratrol concentration of 0.25 mg/L (Feijóo *et al*., 2008). The relatively high concentration of resveratrol in Mencia berries was also demonstrated in a study comparing the *E*- and *Z*-resveratrol concentration in the berries of Mencia, Albarello and Merenzao grapes. In this study, Mencia berry skins had approximately 10 times the concentrations of *E*-resveratrol than the other two varieties tested (Moreno *et al*., 2008). These high levels of *E*-resveratrol in Mencia wine and grapes warrant further investigation. It would also be interesting to determine if the levels of other stilbenoids were also high in this variety or if this monomer dominates.

The main purpose of these quantitation studies has generally been to determine the amount of these biologically important molecules in wines and grapes currently being consumed. Additional studies have aimed at determining which factors, such as specific vinification processes, variety used, and location, may contribute to higher levels. However, this has proved challenging since stilbenoid content varies significantly in wines, even the same types of wine produced in the same region can contain nontrivial differences. Numerous studies have found that stilbenoid levels in grapes and leaves are influenced by a number of factors, including genetic, nutritional, climatic, disease status, altitude, and latitude (Bavaresco, 2003 ; Bavaresco *et al*., 2007 ; Deluc *et al*., 2011 ; Tinttunen and Lehtonen, 2001). For example, since resveratrol is induced in berries, levels of disease pressure in the vineyard may influence resveratrol levels. This relationship is not linear however, as a small amount of disease pressure increases stilbenoid production, while highly infected berries have lower levels (Adrian *et al*., 2000). Similar non-linearity has been seen in resveratrol levels and increasing altitudes (Bavaresco *et al*., 2007). In other studies, incubation of resveratrol and pterostilbene with *Botrytis cinerea*, the causative organism of gray mold, showed oxidative dimerization of both compounds, demonstrating disease status may also influence overall stilbenoid profiles (Breuil *et al*., 1998 ; Breuil *et al*., 1999). Controlled studies using *P. viticola* infected leaves showed high year-to-year variability of a number of stilbenoids, demonstrating a need for multi-year studies (Vrhovsek *et al*., 2011). These factors, that play a role in stilbenoid synthesis, have been reviewed and updated by Bavaresco *et al*. (Bavaresco and Fregoni, 2001 ; Bavaresco *et al*., 2009). Other factors such as influence of phylloxera resistant rootstock have yet to be evaluated. Furthermore, the process of vinification has influences on wine stilbenoids, both qualitatively and quantitatively. Known influential factors include maceration and fermentation time and temperature, yeast and bacteria used for alcoholic and malolactic fermentation, and post-processsing factors such as wine bottle aging (Monagas *et al*., 2005 ; Poussier *et al*., 2003 ; Vitrac *et al*., 2005).

To further complicate matters, there is an observable, dynamic relationship between the resveratrol monomers with their corresponding glycosides and oligomers. For

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example, a study involving the UV irradiation of leaf discs showed resveratrol levels peaking at 18 hours, then decreasing as ε-viniferin levels increased, peaking at 36 hours (Langcake and Pryce, 1977b). This gradual accumulation of viniferins after exogenous induction has been confirmed in grape skins as well (Gonzalez-Barrio *et al*., 2006). During the wine making process itself, glycoside levels typically fall while monomer levels rise. This is due to the alcoholic and, to a lesser extent, the malolactic fermentation processes, causing a decrease in glycoside levels via deglycosylation reactions, in addition to increases in extraction efficiency of the aglycones from the grape skins as alcohol levels increase (Bavaresco *et al*., 1999 ; Vian *et al*., 2005 ; Vrhovsek *et al*., 1997). However, as seen in the review article by Stervbo *et al*. (2007), many wines still contain high levels of glycosides and low levels of aglycones. In the 2005 study by Vitrac *et al*., a 1999 Brazilian Merlot contained 23 mg/L of *E*-astringin, a glycoside of piceatannol, and no detectable quantities of *E*-resveratrol (Vitrac *et al*., 2005). This suggests that in studies where only the levels of resveratrol aglycones in wines have been determined, a substantial amount of glycosides may exist, however the reason is not known (Goldberg *et al*., 1995 ; Waterhouse and Lamuela-Raventós, 1994). In another example, wine made from Cabernet Franc has been reported in several studies to have one of the lowest levels of *E*-resveratrol when compared to others such as Pinot noir, Cabernet-Sauvignon, and Merlot (Gatto *et al*., 2008 ; Nikfardjam *et al*., 2006). However, in a study comparing several Merlot and Cabernet-Sauvignon wines with a Cabernet Franc, *E*-astringin (18) was highest in Cabernet Franc, at a concentration of 23.1 mg/L, which made its overall stilbenoids quantity comparable to the other wines (Vitrac *et al*., 2005). This demonstrates the usefulness of quantifying a greater range of stilbenoids in wine when trying to determine stilbenoid levels.

So far, of the 19 currently known stilbenoids in wine, 12 have been quantified in at least one study, as referenced in Table 3. These compounds include the *E* and *Z* forms of astringin, piceid, resveratrol, and ε-viniferin, in addition to hopeaphenol, pallidol, *E*-piceatannol, and *E*-δ-viniferin (19). The piceatannol glycoside, *E*-astringin, was quantified in wines from France, Brazil, Canada, Italy, and Portugal, where levels ranged from undetectable to 38.1 mg/L, in a French Bergerac wine. Its isomer, *Z*-astringin was quantified in a number of Italian wines where it was found to have levels up to 1.3 mg/L, similar to *E*-astringin levels which ranged from undetectable to 1.8 mg/L. Several dimers, including pallidol, *Z*- and *E*-ε-viniferin, and *Z*- and *E*-δ-viniferin were also examined, of these, δ-viniferin was found to have the highest levels, 22.4 mg/L in a Brazilian Merlot. The only known tetramer to be unambiguously identified in wine, hopeaphenol, was quantified in Pinot noir wines from Burgundy and a range of North African wines, with concentrations up to 2.1 mg/L. Taken together, these studies show that the range of concentrations among and between these compounds in different wines varies significantly, from below detectable levels to tens of mg/mL, see Table 3 for references.

In addition to studies involving the quantitation of stilbenoids in wine and berries, there is a growing interest in evaluating the stilbenoids in other parts of the grapevine. Since roots, stems, canes, and rachis are a byproduct of the wine industry, they are an untapped source of these biologically active molecules (Bisson *et al*., 2011 ; Rayne *et al*., 2008 ; Zhang *et al*., 2011). A recent comparison of *V. vinifera* plant parts, examining resveratrol levels in the shoot tips, petiole, leaves, stem phloem, stem xylem, and roots demonstrated highest levels in the stem phloem, axillary bud, and roots (Wang *et al*., 2010). Additionally, *Vitis* species other than *V. vinifera* have different stilbenoid profiles and may be rich sources of biologically active stilbenoids. For example, in our laboratory, we found the roots of a phylloxera resistant grapevine rootstock, *V. riparia* x *V. berlandieri* SO4A, had significant levels of the stilbenoid tetramer, *E*-vitisin B. The levels of stilbenoids in stems and roots also appear to be seasonally dependent. For example, a 2002 study comparing the concentrations of ε-viniferin and *E*-resveratrol in the stems showed that there were significantly higher levels of these two compounds in October than in July and January (Aaviksaar *et al*., 2003). Plant part, variety, and disease pressure can influence the type and quantity of stilbenoids found.

CONCLUSION

We have reviewed the current state of *Vitis* stilbenoid chemistry and show that it is a very active area of research. Eighteen of the approximately 60 species in *Vitis* have at least one reported phytochemical study with a current total of around 100 known stilbenoids. The most studied *Vitis* species is the primary wine producing species, *V. vinifera*, followed by other minor species used for wine, species used as phylloxera resistant rootstock for *V. vinifera*, and species used as medicinal plants. Sixty-one stilbenoids have been identified in various plant tissues, cell cultures, and wine of *V. vinifera* with only 19 currently known constituents of wine. The isolation and structure elucidation of stilbenoids is not trivial, particularly as the determination of absolute configurations becomes more difficult as oligomer sizes and complexities increase.

Due to the interest in the health promoting and antifungal properties of stilbenoids, we summarized recent studies pertaining to their quantitation in different plant parts and wine. The majority of studies have focused on resveratrol and piceid levels, with more recent research

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quantifying additional monomers, dimers and complex oligomers. The metabolic pathways for stilbenoid synthesis are complex and the relationship between stilbenoids is dynamic since they are influenced by multiple environmental and genetic factors. Wine presents an even more complex case as viticultural and vinification techniques may vary widely between varieties and regions. Therefore, studies quantifying only a small number of stilbenoids may be misleading in regards to overall stilbenoid content.

The multiple techniques for quantitation studies, pertaining to the plant preparation, extraction, and experimental methods, vary considerably in the literature, complicating comparisons between studies. A uniform examination of plant material, including wine, using validated, rigorous methods for a complete stilbenoid profile will provide useful information in regards to stilbenoid levels and allow better comparisons between *Vitis* species and varieties.

A more thorough understanding of the stilbenoid profile within individual economically valuable *Vitis* species, in addition to wine, will be extremely valuable in elucidating their biological importance, both in humans and the plants themselves. Since the majority of stilbenoids, particularly those found in wine, have not undergone extensive biological testing, some may be found to have an even greater biological importance as they become known and available for testing. An increased knowledge of stilbenoids found in *Vitis* will facilitate this endeavor.

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