Grapevine Cane Extracts

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Grapevine canes are viticulture waste that is usually discarded without any further use. However, recent studies have shown that they contain significant concentrations of healthpromoting compounds, such as stilbenes, secondary metabolites of plants produced as a response to biotic and abiotic stress from fungal disease or dryness. Stilbenes have been associated with antioxidant, anti-inflammatory, and anti-microbial properties and they have been tested as potential treatments of cardiovascular and neurological diseases, and even cancer, with promising results.

Stilbenes have been described in the different genus of the Vitaceae family, the Vitis genera being one of the most widely studied due to its important applications and economic impact around the world.

This entry presents an in-depth study of the composition and concentration of stilbenes in grapevine canes. The results show that the concentration of stilbenes in grapevine canes is highly influenced by the Vitis genus and cultivar aspects (growing conditions, ultraviolet radiation, fungal attack, etc.). Different methods for extracting stilbenes from grapevine canes have been reviewed, and the extraction conditions have also been studied, underlining the advantages and disadvantages of each technique. After the stilbenes were extracted, they were analyzed to determine the stilbene composition and concentration. Analytical techniques have been employed with this aim, in most cases using liquid chromatography, coupled with others such as mass spectrometry and/or nuclear magnetic resonance to achieve the individual quantification. Finally, stilbene extracts may be applied in multiple fields based on their properties. The five most relevant are preservative, antifungal, insecticide, and biostimulant applications. The current state-of-the-art of the above applications and their prospects are discussed.

Keywords: grapevine cane extract ; stilbenes ; grapevine ; extraction ; antioxidant ; preservative ; biostimulant ; antifungal ; bioplaguicide

1. Introduction

Wine production is an important part of agriculture and the beverage industry worldwide. In fact, according to the latest officially-recorded data from the Organisation Internationale de la Vigne et du Vin (OIV), the global consumption of wine in 2016 was 24,144,400,000 L [1].

Winemaking is a multistage process producing a huge amount of organic and inorganic waste, which is usually discarded, or used as compost or animal food. New uses have been proposed in recent years, including its transformation into chemicals, bioproducts, dyes, etc. [2][3][4][5]. However, its biochemical conversion is an time-consuming and costly process and a large area of the vineyard is required to generate a worthwhile amount of fuel, chemicals, etc. [6][7] —the reason why these alternatives have not already been incorporated in most vineyards.

It is possible to distinguish two main categories of winery waste: that generated during the collection and that resulting from the winemaking process. During winemaking—in the first stage for white wines and after alcoholic fermentation for reds—must/wine is crushed in a pneumatic press, producing a solid residue known as *pomace*. The amount of pomace generated depends on the grape variety, the cultivation conditions, and the pressing conditions used, but many researchers have concluded that pomace represents around 20–30% of grape weight [8][9]. Lees are another kind of winemaking waste. They consist of yeast biomass, undissolved carbohydrates of cellulosic nature, lignin, proteins, phenolic compounds, tartrates acid salts and fruit skins, grains, and seeds in suspension [10] produced in the tanks during the alcoholic fermentation process. Wine lees are usually at a concentration of 5% *v/v* [6] and they are distilled to recover ethanol or elaborate distilled beverages [11].

In the collection process, the major by-products of vineyards are *grapevine canes* (also called stems, shoots, or stalks), with an average production of around 2–5 tons per hectare and year [12]. Grapevine canes are rich in lignin, cellulose, nitrogen, and potassium—the reason why they are highly composted in the field or burned [13]. However, they also present high contents of interesting compounds such as polyphenols, proteins, and stilbenes [14]. Stilbenes are an interesting

family of non-flavonoid polyphenols that belong to the phenylpropanoid group. They are produced by plants in response to biotic and abiotic stresses [15]. The *trans (t)* or *cis* (*c*) ethene double bond and the different radicals that can bond to phenyl structures mean that stilbenes constitute a huge and varied group of molecules [15][16][17]. This family is composed of monomers and oligomers. Monomers are modified by the different radicals and steric configurations of the molecules, whereas oligomers correspond to varied condensation from the resveratrol monomer (dimer, trimer, etc.) or to monomer hydroxylation, methylation, and glycosylation processes.

Several researchers have reported the important health-related properties of these compounds. Stilbenes have shown positive results in the treatment of cancer, decreasing cancer cell proliferation in some cases [18][19][20][21]. Some stilbene compounds have exhibited a decisive role as chemoprevention agents, inhibiting tumor initiation, tumor promotion, and the progression of malignant cells in breast [22], bladder [23], colon [24], and gastric [25] cancers, and even leukemia [26].

Furthermore, stilbenes present significant anti-inflammatory activity in the brain, which represents crucial progress in the treatment of neurodegenerative diseases such as Alzheimer's [27][28][29]. Stilbenes' potential anti-inflammatory activity is based on the inhibition of enzymes that activate cytokines [30]. These results have important cardioprotective applications, which have been suggested in the so-called "French paradox," which explains the low incidence of coronary heart disease among French people consuming a diet rich in saturated fats but with a high consumption of wine (a source of stilbenes) [31][32].

Finally, studies of resveratrol (the most relevant stilbene) have reported increases in the maximum lifespans of *Saccharomyces cerevisiae*, *Caenorhabditis elegans* [33][34][35][36], the fruit fly *Drosophila melanogaster*, and the honey bee *Apis mellifera* [35][37][38]. Regarding mammals, a dietary supplement with resveratrol was supplied to obese mice, the results showing that their lifespan was longer and healthier compared with the control mice [39].

Thus, stilbenes show important health benefits that could be applied in a variety of fields, such as agriculture, cosmetics, nutraceuticals, and medicine [40][41][42][43][44][45]. Grapevine canes are a rich stilbene source that is usually discarded. For this reason, recent studies have investigated the process for extracting stilbenes from grapevine canes, and the influences of the *Vitis* species and climate conditions on stilbene content. Besides, multiple analytical techniques have identified and quantified stilbenes from these grapevine cane extracts.

2. Grapevine Cane Extract Analysis

Once grapevine cane extracts have been obtained by the selected methodology, it is necessary to analyze them to determine the exact stilbene composition. To that end, many analytical techniques are described in detail below.

2.1. High-Pressure Liquid Chromatography (HPLC)

One of the most widely used methodologies for the detection and quantification of stilbenes in grapevine cane extracts is high-pressure liquid chromatography (HPLC) coupled to a photodiode array detector (DAD) and a fluorescence detector (FLD).

Soural et al. [46] (Analysis 1, Table 1) used HPLC to quantify different stilbenes in grapevine canes from *Vitis Vinifera*. To this end, they used a C18 column; as the mobile phase A the authors selected 5% acetonitrile in pure water + 0.1% *o*-phosphoric acid, and as phase B 80% acetonitrile in water + 0.1% *o*-phosphoric acid. The DAD wavelengths employed were 220 and 315 nm and the scanning range was 190–600 nm, whereas the FLD detector used an excitation wavelength of 315 nm, an emission wavelength of 395 nm, and emission scanning in the range of 300–600 nm. This methodology was applied by Zachová et al. [47] to quantify stilbenes in the Cabernet Moravia variety.

Table 1. Analytical techniques used to identify stilbenes in grapevine cane samples.

	Analysis	Identified Compounds from Grapevine Cane	References
HPLC–DAD/FLD	1	*t*-Resveratrol, *t*-ε-Viniferin and r2-Viniferin	[46][47]
	2	*t*-Resveratrol and *t*-ε-Viniferin	[48]
	3	*t*-Resveratrol (306 nm), *t*-Piceid (304 nm), *t*-Piceatannol (323 nm), Ampelopsin A (208 nm), Hopeaphenol (282 nm), r-Viniferin (326 nm), r2-viniferin (328 nm) and *t*-ε-Viniferin (323 nm)	[49]
	4	Hopeaphenol, Isohopeaphenol and Ampelopsin A (280 nm); *t*-Resveratrol (306 nm); *t*-Piceid, Piceatannol, *t*-ε-Viniferin, r-Viniferin and *t*-ω-Viniferin (320 nm)	[50][51]
	5	*t*-Resveratrol and *t*-Piceatannol	[52]
LC–MS	6	*t*-ε-Viniferin ($C_{28}H_{22}O_6$): $C_{28}H_{22}O_6^+$ (*m/z* 455.1482), $C_{28}H_{21}O_5^+$(*m/z* 437.1373), $C_{22}H_{17}O_5^+$ (*m/z* 361.0740), and $C_{13}H_{11}O_3^+$ (*m/z* 215.0709) and r2-viniferin ($C_{56}H_{42}O_{12}$): $C_{56}H_{42}O_{12}^+$ (*m/z* 907.2745), $C_{35}H_{27}O_7^+$ (*m/z* 559.1709), $C_{28}H_{21}O_6^+$ (*m/z* 453.1339), $C_{22}H_{17}O_5^+$ (*m/z* 361.1038), and $C_{13}H_{11}O_3^+$ (*m/z* 215.0690)	[46]
	7	α-Viniferin $C_{24}H_{30}O_9$ (*m/z* 677.1812), Resveratrol trimer A $C_{42}H_{32}O_9$ (*m/z* 679.1964), Resveratrol trimer B $C_{42}H_{32}O_9$ (*m/z* 679.1968), Resveratrol tetramer A $C_{56}H_{42}O_{12}$ (*m/z* 905.2598) and Resveratrol tetramer B $C_{56}H_{42}O_{12}$ (*m/z* 905.2612).	[53]
HPLC–DAD-FLD–MS/MS	8	*t*-Piceid (DAD λ_{max} = 304 - 315 nm, FLD $\lambda_{Exc\text{-}Emis}$ = 330 - 374 nm, *m/z* 389), Ampelopsin A (DAD λ_{max} = 280 nm, FLD $\lambda_{Exc\text{-}Emis}$ = 230 - 320 nm, *m/z* 469), *t*-Piceatannol (DAD λ_{max} = 324 nm, FLD $\lambda_{Exc\text{-}Emis}$ = 330 - 374 nm, *m/z* 243), Pallidol (DAD λ_{max} = 280 nm, *m/z* 253), *t*-Resveratrol (DAD λ_{max} = 306 nm, FLD $\lambda_{Exc\text{-}Emis}$ = 330 - 374 nm, *m/z* 227), Hopeaphenol (DAD λ_{max} = 280 nm, FLD $\lambda_{Exc\text{-}Emis}$ = 230 - 320 nm, *m/z* 905), *t*-ε-Viniferin (DAD λ_{max} = 324 nm, FLD $\lambda_{Exc\text{-}Emis}$ = 330 - 374 nm, *m/z* 453), *t*-δ-Viniferin (DAD λ_{max} = 324 nm, FLD $\lambda_{Exc\text{-}Emis}$ = 330 - 374 nm, *m/z* 453), *t*-ω-Viniferin (DAD λ_{max} = 324 nm, FLD $\lambda_{Exc\text{-}Emis}$ = 330 - 374 nm, *m/z* 453) and r-Viniferin (DAD λ_{max} = 326 nm, FLD $\lambda_{Exc\text{-}Emis}$ = 330 - 374 nm, *m/z* 905).	[54]
HPLC–DAD–ESI–MS/MS	9	*t*-Piceid (λ_{max} = 304 - 315 nm, *m/z* 389), Ampelopsin A (λ_{max} = 280 nm, *m/z* 469), *t*-Piceatannol (λ_{max} = 323 - 303 nm, *m/z* 243), *t*-Resveratrol (λ_{max} = 304 - 316 nm, *m/z* 227) and *t*-ε-Viniferin (λ_{max} = 308 - 322 nm, *m/z* 453)	[55]
	10	Ampelopsin A (*m/z* 469), Hopeaphenol (*m/z* 905), Piceatannol (*m/z* 243), Resveratrol (*m/z* 227), r2-Viniferin (*m/z* 905), Miyabenol C (*m/z* 679), *t*-ε-Viniferin (*m/z* 453) and r-Viniferin (*m/z* 905)	[48]
	11	*t*-Resveratrol (*m/z* 227), *t*-Piceid (*m/z* 389), *t*-Piceatannol (*m/z* 243), Ampelopsin A (*m/z* 469), Hopeaphenol (*m/z* 906), r-Viniferin (*m/z* 906), r2-viniferin (*m/z* 906) and *t*-ε-Viniferin (*m/z* 453)	[49]
UHPLC–DAD/ESI–Q-TOF	12	*t*-Resveratrol, *t*-Piceid, *t*-Piceatannol, Ampelopsin A, Ampelopsin F, Pallidol, *t*-Parthenocissin A, Miyabenol C, Ampelopsin E, Viniferol E, Ampelopsin H, Hopeaphenol, Isohopeaphenol, r-Viniferin, r2-viniferin, *t*-ω-Viniferin, and *t*-ε-Viniferin	[56]

	Analysis	Identified Compounds from Grapevine Cane	References
HPLC–NMR	13	***t*-Piceatannol: ^{1}H-NMR δ (ppm) 7.00 (1H, d, *J* = 2.0 Hz, H-2), 6.93 (1H, d, *J* = 16.4 Hz, H-7), 6.88 (1H, dd, *J* = 2.0, 8.4 Hz, H-6) 6.80 (1H, d, *J* = 16.4 Hz, H-8), 6.77 (1H, d, *J* = 8.4, H-5), 6.45 (2H, d, *J* = 2.1 Hz, H-10,14), 6.14 (1H, t, *J* = 2.1 Hz, H-12)** ***t*-Resveratrol: ^{1}H-NMR δ (ppm) 7.36 (2H, d, *J* = 8.5 Hz, H-2,6), 6.99 (1H, d, *J* = 16.4 Hz, H-7), 6.82 (1H, d, *J* = 16.4 Hz, H-8), 6.76 (2H, d, *J* = 8.5, H-3,5), 6.44 (2H, d, *J* = 2.1 Hz, H-10,14), 6.13 (1H, t, *J* = 2.1 Hz, H-12)** **Hopeaphenol: ^{1}H-NMR δ (ppm) 7.07 (2H, d, *J* = 8.5 Hz, H-2b,6b), 6.79 (2H, d, *J* = 8.5 Hz, H-2a,6a), 6.76 (2H, d, *J* = 8.5 Hz, H-3b,5b), 6.56 (2H, d, *J* = 8.5 Hz, H-3a,5a), 6.39 (1H, brs, H-12b), 6.19 (1H, brs, H-14b), 5.73 (1H, d, *J* = 12.2 Hz, H-7b), 5.72 (1H, brs, H-12a), 5.42 (1H, d, brs, H-14a), 4.85 (1H, brs, H-7a), 4.08 (1H, d, *J* = 12.2 Hz, H-8b), 3.76 (1H, brs, H-8a)** **Isohopeaphenol: ^{1}H-NMR δ (ppm) 7.46 (2H, d, *J* = 8.4 Hz, H-2a,6a), 6.95 (2H, d, *J* = 8.4 Hz, H-3a,5a), 6.30 (2H, d, *J* = 8.4 Hz, H-2b,6b), 6.23 (2H, d, J = 8.4, H-3b,5b), 6.22 (1H, brs, H-12a), 6.01 (1H, brs, H-14a), 5.80 (1H, d, brs, H-12b), 5.51 (1H, d, J = 10.8 Hz, H-7a), 5.31 (1H, d, brs, H-14b), 5.27 (1H, d, J = 10.8 Hz, H-8a), 4.77 (1H, brs, H-7b), 3.23 (1H, brs, H-8b)** ***t*-ε-Viniferin: ^{1}H-NMR δ (ppm) 7.14 (2H, d, *J* = 8.3 Hz, H-2a,6a), 7.11 (2H, d, *J* = 8.3 Hz, H-2b,6b), 6.87 (1H, d, *J* = 16.4, H-7b), 6.76 (2H, d, *J* = 8.5 Hz, H-3a,5a), 6.69 (2H, d, *J* = 8.8 Hz, H-3b,5b), 6.62 (1H, d, *J* = 1.8, H-14b), 6.59 (1H, d, *J* = 16.4 Hz, H-8b), 6.28 (1H, d, *J* = 1.8 Hz, H-12b), 6.12 (2H, d, *J* = 2.01 Hz, H-10a,14a), 6.09 (1H, t, *J* = 2.1 Hz, H-12a), 5.39 (1H, d, *J* = 5.7 Hz, H-7a), 4.45 (1H, d, *J* = 5.7 Hz, H-8a)** ***t*-ω-Viniferin: ^{1}H-NMR δ (ppm) 7.14 (2H, d, *J* = 8.4 Hz, H-2b,6b), 6.95 (2H, d, *J* = 8.4 Hz, H 2a,6a), 6.90 (1H, d, *J* = 16.4 Hz, H-7b), 6.69 (2H, d, *J* = 8.4 Hz, H-3b,5b), 6.63 (1H, brs, H-14b), 6.61 (1H, d, *J* = 16.4 Hz, H-8b), 6.55 (2H, d, *J* = 8.4 Hz, H-3a,5a), 6.32 (1H, d, brs, H-12b), 5.84 (1H, d, *J* = 8.5 Hz, H-7a), 5.83 (1H, brs, H-12a), 5.70 (2H, brs, H-10a,14a), 4.64 (1H, d, *J* = 8.5 Hz, H-8a)** **r-Viniferin: ^{1}H-NMR δ (ppm) 7.15 (2H, d, *J* = 8.5 Hz, H-2a,6a), 7.13 (2H, d, *J* = 8.5 Hz, H-2d,6d), 7.05 (1H, brd, *J* = 8.2 Hz,-H-6b), 6.79 (2H, d, *J* = 8.4 Hz, H-3a,5a),6.77 (2H, d, *J* = 8.4 Hz, H-3d,5d), 6.73 (1H, d, *J* = 16.4 Hz, H-8b), 6.73 (1H, d, brs, H-2b), 6.72 (1H, d, *J* = 8.2 H-5b), 6.60 (2H, d, *J* = 8.5 Hz, H-2c,6c), 6.56 (1H, d, *J* = 1.8, H-14b), 6.52 (2H, d, *J* = 8.5 Hz, H-3c,5c), 6.30 (1H, d, *J* = 1.8, H-12b), 6.27 (1H, d, *J* = 1.8, H-12c), 6.08 (2H, d, *J* = 1.8 Hz, H-10d,14d), 6.06 (1H, brs, H-12d), 6.05 (1H, d, *J* = 1.8, H-14c), 5.96 (1H, t, *J* = 1.8, H-12a), 5.90 (2H, d, *J* = 1.8 Hz, H-10a,14a), 5.45 (1H, d, J = 5.0 Hz, H-7c), 5.39 (1H, d, *J* = 5.6 Hz, H-7d), 5.33 (1H, d, *J* = 5.6 Hz, H-7a), 4.41 (1H, d, *J* = 5.6 Hz, H-8a), 4.41 (1H, d, *J* = 5.6 Hz, H-8d), 4.21 (1H, d, *J* = 5.0 Hz, H-8c)**	[57]

Ewald et al. [48] (Analysis 2, Table 1) used the same solid–liquid extraction methodology as Vergara et al. to obtain stilbene rich extracts, but for the identification and quantification the authors selected an HPLC-ESI-MS/MS system. For the quantification, a method with HPLC–DAD was performed. The column was C18 at 25 °C, whereas the mobile phases consisted of 1% aqueous acetic acid (*v*/*v*) (A) and methanol (B). The wavelengths selected in the DAD system were 306 and 324 nm for the quantification of *t*-resveratrol and *t*-ε-viniferin respectively.

Gorena et al. [49] (Analysis 3, Table 1) suggested the use of HPLC–DAD for the quantification of stilbenes from grapevine canes of different *Vitis vinifera* varieties. The wavelengths selected in the DAD system were 280 and 306 nm. The identification was performed with an HPLC–DAD–ESI–MS/MS system.

Guerrero et al. [51] (Analysis 4, Table 1) used an HPLC with DAD in full scan mode. The wavelengths used were 280 and 320 nm. This methodology was used by Piñeiro et al. [50] to quantify four stilbenes (*t*-resveratrol, *t*-piceid, piceatannol, and *t*-ε-viniferin) extracted with the microwave-assisted technique.

Billet et al. [52] (Analysis 5, Table 1) suggested HPLC–DAD for the identification and quantification of two stilbenes in grapevine canes from the Pinot noir variety. Quantification was based on pure standards of *t*-resveratrol and *t*-piceatannol with full scans.

The HPLC technique has been used to identify and quantify different stilbenes in grapevine cane extracts. However, their quantification is highly related to the standard preparation, since few of them are commercially available. For this reason, to ensure the correct identification and quantification, HPLC is usually coupled to other analytical techniques such as mass spectrometry (MS) or nuclear magnetic resonance (NMR).

2.2. Liquid Chromatography–Mass Spectrometry (LC–MS)

Soural et al. (Analysis 6, Table 1) [46] used HPLC–MS for the identification of *t*-ε-viniferin and r2-viniferin in grapevine canes. To this end, the mass system was equipped with an electrospray (ESI), atmospheric pressure chemical (APCI), and atmospheric pressure photo ionization (APPI) sources and a photodiode array. The APCI capillary temperature was 275 °C, APCI vaporizer temperature 400 °C, sheath gas flow 58 L/min, auxiliary gas flow 10 L/min, source voltage 6 kV, source current 5 µA, and capillary voltage 10 V.

Rodríguez-Cabo et al. [53] (Analysis 7, Table 1) proposed the use of LC separation. The authors injected the samples into a quadrupole time-of-flight mass spectrometry (QToF-MS) system operated at 2 GHz and using HS ($[M-H]^-$) mode for the quantification. The LC-QTOF-MS library and previously published data from wine extracts were used for the identification and quantification of the stilbenes.

Sáez et al. [54] (Analysis 8, Table 1) proposed the use of an HPLC system coupled in series to a DAD, an FLD, and a triple-quadrupole mass spectrometer for the identification of stilbenes in grapevine canes. Detection using DAD was performed at 306 and 280 nm, and for FLD the excitation and emission wavelengths were 330 and 374 nm for the stilbenoids. The mass spectrometer used electrospray ionization in negative mode. The source temperature selected was 450 °C, the nebulizer gas pressure was 2.7 bar, and the auxiliary gas pressure 3.4 bar. The *m/z* mass range was set to 100–1200.

Vergara et al. [55] (Analysis 9, Table 1) used HPLC–DAD–ESI–MS/MS for the identification and quantification of stilbenes in grapevine cane extracts from different *Vitis vinifera* varieties. Mass spectrometry was in negative ionization mode, with a drying temperature of 450 °C, ion spray voltage of –4000V, nebulizer gas at 40 psi, and auxiliary gas at 50 psi. The scan range was *m/z* 100–1200.

Ewald et al. [48] (Analysis 10, Table 1) used HPLC–DAD–ESI–MS/MS for the identification of stilbenes in Pinot noir grapevine canes. Mass spectra were recorded in negative ionization mode with a capillary voltage set at 3500 V, the endplate at –500 V, and the capillary exit at −115.0 V. The drying gas was nitrogen at 330 °C and the nebulizer pressure was set to 50 psi, the target mass at *m/z* 400, and the scan range from *m/z* 100 to 3000.

Gorena et al. [49] (Analysis 11, Table 1) selected the HPLC–DAD–ESI–MS/MS system for the identification of stilbenes from grapevine canes from different varieties of *Vitis Vinifera*. Regarding the ESI–MS/MS system, a negative ionization mode was selected with a drying temperature of 450 °C. The nebulizer gas pressure was 40 psi and the auxiliary gas pressure was 50 psi. Finally, the scan range was 100–1200 *m/z*.

Gabaston et al. (Analysis 12, Table 1) [56] selected a UHPLC–DAD/ESI–Q-TOF system. Mass spectrometry analyses were carried out in negative mode, and the drying gas used was nitrogen at 9 L/min at 300 °C with a nebulizer pressure of 25 psi. The sheath gas flow and temperature were set to 11 L/min and 350 °C. The capillary voltage was 4000 V.

2.3. Liquid Chromatography–Nuclear Magnetic Resonance (LC–NMR)

NMR is the main technique used for the structural identification of unknown compounds. Coupling with liquid chromatography using different modes allows for the direct analysis of complex extracts [58]. This technique has been successfully applied to grapevine products such as berries [59] and wines [60]. HPLC–NMR was also applied to identify and quantify stilbenes in grapevine cane extracts [57]. Soural et al. [46] used HPLC coupled to a 500 MHz spectrometer equipped with an HCN triple resonance microflow probe to separate and analyze stilbenes from grapevine canes. ^{1}H-NMR spectra were collected in on-flow mode. Complete structural elucidation was performed in the stop-flow mode using 2D-NMR spectra. Using this method, *t*-ε-viniferin and r-viniferin were identified in grapevine canes. Similarly, Lambert et al. [57] identified and quantified nine stilbenes and two flavonols using a combination of LC–MS, LC–NMR, and NMR analysis. In this study, seven stilbenes (*t*-piceatannol, *t*-resveratrol, hopeaphenol, isohopeaphenol, *t*-ε-viniferin, ω-viniferin, r-viniferin) were directly identified using LC–NMR in stop-flow mode or by multi-trapping on a FOXY collector connected to the NMR probe before analysis (Analysis 13, Table 1).

In conclusion, grapevine cane extracts were generally analyzed by liquid chromatography coupled to different detectors: UV–Vis, photodiode array (DAD), fluorescence (FLD), and mass and NMR spectroscopies. Initially, the stilbenes were mainly identified by a classical purification and identification process using MS and NMR spectroscopies. UV–Vis or fluorescence detectors were used for quantification, the latter being more specific. Mass spectroscopy allowed the direct identification of the stilbenes in different matrices, with a high sensitivity and specificity in comparison to UV–Vis or fluorescence spectroscopy. Finally, LC–NMR spectrometry was successfully developed for stilbene analysis. Although NMR is less sensitive than mass spectroscopy, it allows the unambiguous identification of each compound, for instance, among isomers.

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