

Evolution of *trans*- and *cis*-resveratrol content in red grapes (*Vitis vinifera* L. cv Mencía, Albarello and Merenzao) during ripening

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Abstract Concentrations of *cis*- and *trans*-resveratrol were analyzed in grapes from three red Galician varieties (Mencía, Albarello and Merenzao). Free resveratrol was quantified using a HPLC method (binary gradient) with fluorescence detection. The grapes were sampled weekly during the last 3 weeks before the optimal stage of maturation and the three parts were separated (skin, pulp and seed). These compounds are absent in pulp in all the grapes and the varieties, and the content in skin and seed varied according to the variety (Mencía > Albarello > Merenzao) and the vintage (1999 > 2001 > 2000). The results obtained from the grapes (7–24 mg/L) indicated that the wines elaborated from Mencía variety could be present with important amounts of *trans*-resveratrol.

Keywords *cis*-resveratrol · *trans*-resveratrol · Grape · Red varieties · HPLC · Fluorescence detection

Introduction

Phenolic compounds, especially flavonoids and stilbenes have been recognized as being responsible for several beneficial physiological effects owing to their potent antioxidant and anti-inflammatory properties [1–4]. Several epidemiological studies carried out before the French paradox [5] have shown that moderated alcoholic consumption, mainly red wine [6] had health benefits, due to its supposed protective effects against cardiovascular

diseases [7–10], inhibition of platelet aggregation [11] and cancer [12–14].

Resveratrol (3,4',5-trihydroxystilbene) and its derivatives (glycosides and oligomers) have been identified in a number of different plants or food [15], but the most important source are the grape and related products. *Trans* isomer is considered a phytoalexin for its role on human health and it is synthesized in the plant in response to external aggressions, such as fungal infection, UV irradiation, humidity, etc. [16–20]. The isomer *trans* is primarily located in the skin and it is absent in the pulp [21, 22] while *cis*-resveratrol, produced by UV irradiation on *trans*-resveratrol [23, 24], is typically at lower concentrations and is often less biologically active than the *trans* isomer.

Grapes contain a variable amount of *trans*-resveratrol depending on factors such as grape cultivar, vintage, fungal infection, environmental conditions, etc. [25–31]. Their extraction from grapes during wine-making is also influenced by the employment of skin contact of commercial or endogenous enzymes, the yeast strain, etc. [32–35], and during wine-aging [36]. Red wine seems to be the main dietary source of this compound, because it is present in much higher levels in red than in white grape and wines.

The resveratrol content in Galician red grapes has not been determined until the present time. The present work represents an approach to this subject through a study of the evolution of *cis*- and *trans*-resveratrol concentration during the last 3 weeks of maturation of grapes from Mencía, Albarello and Merenzao varieties. These berries were picked in vineyards from the Certified Brand of Origin “Ribeira Sacra” (NW Spain), which is a wine producing area of 1,235 hectares situated in the centre of Galicia (NW Spain), equivalent to 5.2% of the total ground dedicated to grape production in this region. Fundamentally, the CBO “Ribeira Sacra” produces red wines (principally from the

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Mencía, Brancellao and Merenzao varieties), although some white wines from the varieties Albariño, Loureira, Treixadura, Godello, Dona Branca and Torrontés are also produced. Mencía is the most representative of the three red wine varieties [37]. The variety Merenzao (María Ordoña or Bastard) is grown in Portugal, Spain, the Argentine and Australia [37], and the variety Brancellao, also known as Alvarello, Albarello, Alvarelhao or Bancelho [37], is grown in Galicia and Portugal. The grapes from the three varieties were sampled during three consecutive years (1999–2001) and the determination was carried out in the different parts of grapes (skin, pulp and seed).

Materials and methods

Reagents

Pure resveratrol (*trans*-3,4',5-trihydroxystilbene) was purchased from Sigma Chemical Co. and stock solution (100 mg/L) was prepared by dissolving 10.00 mg of the commercial product, without previous purification, in 100 mL of methanol. Stock solution of *cis*-resveratrol was prepared by UV irradiation (sunlight) of *trans*-resveratrol for 3 days (total conversion). They were kept in dark bottles at 4 °C.

The calibration curves of *trans*-resveratrol and *cis*-resveratrol were obtained by plotting the peak area of each standard against concentration, in the ranges 0.01–25 mg/L and 0.1–2 mg/L, respectively. The number of calibration points was nine for *trans*-resveratrol and seven for *cis*-resveratrol. Each calibration point was the mean of three independent measurements.

Acetonitrile and acetic acid were of liquid chromatographic grade (Merck). Doubly distilled water was purified using a Milli-Q system. The solvents were filtered (0.45 µm, Gelman) and degassed by purging with helium gas.

HPLC analysis

Analysis were performed, in triplicate, on a Lichrocart (250 × 4 mm, 5 µm) preceded by a guard column of Lichrospher 100RP (4 × 4 mm, 5 µm). A Waters system comprising two pumps (model 510), an automated injector (model 717 plus), a fluorescence detector (model 474) and a software Millennium-32 was used. For fluorimetric detection, maximum excitation wavelength was measured at 270 nm and emission at 372 nm [23]. The two isomers of resveratrol were eluted with a binary gradient comprising 6% acetic acid (solvent A) and acetic acid/acetonitrile/water (5:30:65, v/v/v) (solvent B) according to the following program: linear gradient elution from 80% A and 20%

B to 0% A and 100% B within 40 min and maintained for 20 min. This was followed by a 5 min equilibrium period with the initial conditions prior to injection of the next sample. The flow rate was 0.3 mL/min and the injection volume was 20 µL. Under these chromatographic conditions, retention times were 32 min and 41 min for *trans*- and *cis*-resveratrol, respectively.

Sample grapes

Grape berries from Mencía, Albarello and Merenzao varieties cultivated in vineyards from Certified Brand of Origin “Ribeira Sacra”—NW Spain—were harvested weekly in the last 3 weeks of maturation from the 1999, 2000 and 2001 vintages. Fifty berries of each variety were picked randomly, weighed in the laboratory, (Table 1), and sepa-

Table 1 Weight (in g) of grapes from the three Galician grape varieties

Year	Sampling	Total weight	Skin	Seeds	Pulp
Mencía grapes					
1999	1st week	73,860	16,170	5,410	52,280
	2nd week	81,580	15,040	4,990	61,550
	3rd week	82,060	16,410	7,480	58,170
2000	1st week	101,950	14,350	5,530	82,070
	2nd week	100,910	14,560	5,900	80,450
	3rd week	89,370	15,700	6,760	66,910
2001	1st week	52,959	20,838	6,030	26,091
	2nd week	57,500	18,223	6,250	33,027
	3rd week	56,953	18,323	4,030	34,600
Albarello grapes					
1999	1st week	64,660	9,500	5,870	49,290
	2nd week	67,470	11,980	5,520	49,970
	3rd week	66,800	13,210	6,040	47,550
2000	1st week	54,340	7,880	6,640	39,820
	2nd week	64,680	9,080	5,430	50,170
	3rd week	79,970	10,950	7,800	61,220
2001	1st week	81,317	11,195	8,034	62,088
	2nd week	95,835	15,900	9,358	70,577
	3rd week	75,674	15,226	5,770	54,678
Merenzao grapes					
1999	1st week	78,190	12,270	6,130	59,790
	2nd week	95,780	12,200	5,360	78,220
	3rd week	94,200	13,420	6,980	73,800
2000	1st week	71,630	9,280	7,750	54,600
	2nd week	79,960	11,270	7,980	60,710
	3rd week	–	–	–	–
2001	1st week	63,062	11,807	5,270	45,985
	2nd week	93,604	17,427	8,490	67,687
	3rd week	78,629	17,787	5,880	54,962

rated into the three fractions (skin, pulp and seed), which were crushed in 50 mL of methanol using an Ultra Turrax. They were enclosed in amber glass, protected by aluminium foil and stored in the dark at 4 °C until the analysis. All samples were filtered only through a 0.20 µm membrane filter (Gelman) before injection into the HPLC system.

During sample preparation, the extracts were constantly protected from the light to avoid photochemical isomerization of *trans*-resveratrol to the *cis* form.

Statistics

The concentration of the two isomers of resveratrol was reported as mean content ± SD of three replicates. Significance of overall differences was evaluated by performing Student's *t* test (probability of 95%).

Results and discussion

The content of resveratrol (*trans* and *cis*) in the skin and seeds of the three varieties of red grapes that were studied

(Mencía, Albarello and Merenza) in three harvests (1999, 2000 and 2001) during ripening, are shown in Tables 2, 3, 4. Neither of these two compounds was found in the pulp.

Content in resveratrol found in the variety Mencía

The concentration found in the grape skins in the year 2000 was about three or four times less in most of the samples, than in the other two years (Table 2). The exception was found in the third sampling of 2001, which, even though still the lowest of these two years (9.23 mg/L), continued to be higher than any of the contents found in the year 2000 (6.23 mg/L in the first sampling; 4.99 mg/L in the second and 5.47 mg/L in the sampling previous to harvesting).

On comparing the values obtained from the three samplings of grapes from each harvest, it was observed that these values were significantly different from each other. Although, between the first and second week of ripening, there was a decrease in the content of resveratrol in all of the 3 years analysed. Afterwards, in the last sampling taken at harvest-time, this behaviour was not repeated. In 2001, the content of resveratrol continued to decrease, reaching

Table 2 Content in *trans*- and *cis*-resveratrol in Mencía grapes during three harvests

	<i>trans</i> -resveratrol			<i>cis</i> -resveratrol		
	1999	2000	2001	1999	2000	2001
Skin						
1st week	17.32 ± 0.56	6.23 ± 0.15	21.07 ± 0.30	nd	0.18 ± 0.01	nd
2nd week	10.92 ± 0.17	4.99 ± 0.06	18.35 ± 0.19	0.28 ± 0.02	nd	nd
3rd week	21.97 ± 0.08	5.47 ± 0.06	9.23 ± 0.04	nd	0.17 ± 0.02	nd
Seed						
1st week	2.01 ± 0.01	1.82 ± 0.01	0.94 ± 0.01	nd	nd	nd
2nd week	1.59 ± 0.05	0.70 ± 0.03	0.33 ± 0.01	nd	nd	nd
3rd week	1.87 ± 0.07	1.03 ± 0.05	0.71 ± 0.01	nd	nd	nd
Pulp						
All weeks	nd	nd	nd	nd	nd	nd

Mean values ± SD (*n* = 3) expressed in mg/L
nd not detected

Table 3 Content in *trans*- and *cis*-resveratrol in Albarello grapes during three harvests

	<i>trans</i> -resveratrol			<i>cis</i> -resveratrol		
	1999	2000	2001	1999	2000	2001
Skin						
1st week	0.37 ± 0.01	0.23 ± 0.02	0.46 ± 0.02	0.04 ± 0.004	nd	0.37 ± 0.01
2nd week	1.71 ± 0.09	0.38 ± 0.02	0.84 ± 0.06	0.23 ± 0.015	0.04 ± 0.001	0.05 ± 0.001
3rd week	2.56 ± 0.14	0.68 ± 0.01	0.56 ± 0.05	0.06 ± 0.002	0.12 ± 0.01	0.21 ± 0.01
Seed						
1st week	0.67 ± 0.05	0.47 ± 0.05	0.68 ± 0.05	nd	nd	nd
2nd week	1.10 ± 0.03	0.84 ± 0.01	0.78 ± 0.04	nd	nd	nd
3rd week	1.26 ± 0.08	0.54 ± 0.04	0.41 ± 0.02	nd	nd	nd
Pulp						
All weeks	nd	nd	nd	nd	nd	nd

Mean values ± SD (*n* = 3) expressed in mg/L
nd not detected

Table 4 Content in *trans*- and *cis*-resveratrol in Merenzao grapes during three harvests

	<i>trans</i> -resveratrol			<i>cis</i> -resveratrol		
	1999	2000	2001	1999	2000	2001
Skin						
1st week	0.54 ± 0.04	0.73 ± 0.01	0.33 ± 0.03	nd	0.18 ± 0.01	0.05 ± 0.003
2nd week	1.71 ± 0.05	0.52 ± 0.01	0.50 ± 0.02	0.05 ± 0.002	0.13 ± 0.01	0.05 ± 0.002
3rd week	1.51 ± 0.16	***	0.84 ± 0.04	0.15 ± 0.01	***	0.16 ± 0.009
Seed						
1st week	0.37 ± 0.02	0.50 ± 0.02	0.53 ± 0.03	nd	nd	nd
2nd week	0.43 ± 0.02	0.43 ± 0.04	0.55 ± 0.04	nd	nd	nd
3rd week	0.48 ± 0.04	***	0.47 ± 0.04	nd	***	nd
Pulp						
All weeks	nd	nd	nd	nd	nd	nd

*** Grapes from 2000 vintage were not sampled
 Mean values ± SD ($n = 3$)
 expressed in mg/L
 nd not detected

9.23 mg/L. In the year 2000, it increased almost imperceptively to 5.47 mg/L and in 1999, contrarily, increased to 21.97 mg/L, which was even higher than in the first sampling.

Few studies exist that have been performed on samples of grapes. However, if the actual study is compared to that carried out by Cantos et al. [38] using red grapes of the variety Monastrell (Mourvèdre), the *trans*-resveratrol determined in the skins showed a value of 8.90 µg/L. This was one thousand times lower than that obtained for the variety Mencía.

With respect to the seeds (Table 2), the concentration of *trans*-resveratrol was much lower, when compared to that of the skins, given that the highest value found in the seeds (2.01 mg/L) was less than half the lowest content found in the skins (4.99 mg/L). In addition, the concentrations of this compound obtained in 1999 are higher than those of the year 2000 and, in turn, these were higher than those found in 2001. However, the behaviour of this compound was similar in the different samplings of all three harvests. That is, in the first sampling of each of the years, the concentrations obtained (2.01 mg/L in 1999; 1.82 mg/L in 2000; 0.94 mg/L in 2001) are higher than those corresponding to the second sampling (1.59 mg/L in 1999; 0.70 mg/L in 2000; 0.33 mg/L in 2001). In turn, the latter are lower than those found during harvest-week (1.87 mg/L in 1999; 1.03 mg/L in 2000; 0.71 mg/L in 2001), although they are never higher than the concentrations obtained in the first week sampled.

The *cis*-resveratrol has not been detected in any of the seed samples and, in the skins (Table 2), was only detected in three samples corresponding to the second sampling of 1999 (0.28 mg/L) and those corresponding to the first (0.18 mg/L) and third sampling (0.17 mg/L) of the year 2000. From the skin samples in which this isomer of resveratrol was detected, it could be observed that the berries from the second week of 1999 showed the highest content

of the *cis* isomer and the lowest concentration of the other isomer, *trans*-resveratrol. On the contrary, the skin samples from the year 2000 (first and third weeks), were those that showed the highest concentration of the two isomers.

Content in resveratrol found in the variety Albarello

The variety Albarello or Brancellao is not very common and, in fact, the samples collected for this study were taken from a mountainous zone, contrarily to the other two varieties, which were taken from the bottom of a valley. This could have influenced the content of resveratrol, due to the higher humidity of the valley-floor.

The content of *trans*-resveratrol in the grape skins of Albarello (Table 3) was five or six times less than that obtained from the variety Mencía. During the process of ripening in 1999 and 2000, the grapes followed the same behaviour. In both harvests, the content in this compound increased from the time the grape was formed (0.37 mg/L in 1999 and 0.23 mg/L in 2000) until it was harvested (2.56 mg/L in 1999 and 0.68 mg/L in the year 2000). However, in 2001, this tendency was broken. During the last week, a decrease was produced in the concentration of *trans*-resveratrol, from 0.84 mg/L detected in the second week to 0.56 mg/L shown at harvest. This was contrary to the behaviour of grapes of the variety Mencía although, in both cases, the concentration of *trans*-resveratrol was always higher at harvest-time than in the first week of sampling.

In the case of the seeds (Table 3), behaviour was similar to that of the skin. From the first to the second sampling, an increase of *trans*-resveratrol in the three years studied was confirmed. However, in the last sampling of each year, behaviour was not the same. In 1999, the concentration of *trans*-resveratrol continued to increase until it reached 1.26 mg/L. This was contrary to the behaviour of the other 2 years, in which the content was lower, even lower than

the content shown in the first sampling of these 2 years. In the year 2000, it decreased from 0.84 to 0.54 mg/L and in 2001, the content of *trans*-resveratrol increased from the first sampling (0.68 mg/L) to the second (0.78 mg/L), but then decreased in the last week before the harvest (0.41 mg/L).

None of the samples of seeds from Albarello grapes analysed showed the presence of *cis*-resveratrol (Table 3), while almost all the samples of skin from this variety contained this compound. This was the reverse of the variety Mencía where, in most cases, the isomer *cis* was not detected in any of the samples (either in skin or in seeds). In general, the content of *cis*-resveratrol varied in an interval from 0.04 to 0.36 mg/L. These amounts are similar to those determined in skins from the variety Mencía, which did not go beyond 0.28 mg/L. In the last sampling of each year, it can be seen that exactly the opposite occurred with *cis*-resveratrol than with the isomer *trans*-resveratrol, as the sample collected in 1999 had the highest concentration of *trans*-resveratrol, followed firstly by the year 2000 and then by the year 2001, which had the lowest content. In the case of the isomer *cis*, the year 2001 showed the highest concentration (0.21 mg/L), followed by the year 2000 with a slightly lower concentration (0.12 mg/L) and, lastly, by the sample from 1999 with a much lower concentration (0.06 mg/L).

Content in resveratrol found in the variety Merenzao

This variety was harvested earlier than expected in the year 2000 and so the third sampling of this variety was not performed.

The concentrations of *trans*-resveratrol in the grape skins of the variety Merenzao (Table 4) varied significantly during the 3 years analyzed and did not follow the same tendency. In 2001, the samples showed a progressive increase from the time the grape was formed until harvest-time (0.33 mg/L in the first week, 0.50 mg/L in the second and 0.84 mg/L in the last week). A significant increase from the first sampling (0.54 mg/L) to the second (1.71 mg/L) was also produced in 1999, but at harvest-time the concentration of *trans*-resveratrol had decreased slightly (1.51 mg/L). In the year 2000, despite the fact that no grapes were available from the last week of maturing, the behaviour of this variety was very different to that of the previous and following year. The content in resveratrol decreased slightly from the first sampling (0.73 mg/L) to the second (0.52 mg/L), which could be due to an anomalous degree of ripeness, because the weight of the grapes was lower than the berries from the other vintages and varieties studied. The contents determined in the seeds (Table 4) show different tendencies in each year. In 1999, the concentration of *trans*-resveratrol in seeds increased from the first to the third sampling (0.37, 0.43 and 0.48 mg/L respectively). The

grapes from the year 2000 had the same concentration in the first 2 weeks (0.53 and 0.55 mg/L), although this decreased slightly at harvest-time (0.47 mg/L).

The *cis*-resveratrol was only detected in the skins (Table 4) and its content in the samples collected during the year 2000 reflect a behaviour contrary to that registered in the other 2 years. In 1999, the isomer *cis* was not detected in the first sampling. In the second sampling, the content of *cis*-resveratrol was detected, although at a very low level (0.05 mg/L). This level was triplicated in the grapes sampled at harvest-time (0.15 mg/L).

In 2001, the concentration of this isomer was the same in the first and second sampling (0.05 mg/L) and then increased during the week before harvest to 0.16 mg/L. With respect to the year 2000, and despite the fact that it was not possible to analyse samples from the third week, the concentration of *cis*-resveratrol decreased slightly, the same as the isomer *trans*, from 0.18 mg/L obtained in the first sampling to 0.13 mg/L of the second sampling.

Total content in resveratrol found in red Galician varieties

The total concentrations of resveratrol in both skins and seeds of the three varieties at the date closest to harvest-time are shown in Figs. 1, 2, 3. This could be considered as the concentration of resveratrol that will potentially be transferred to the wine, although this transfer would not be 100% of this compound. This is because, in some studies, it is shown that the employment of some vinification techniques as well as the type of yeast used [39], the use of clarifiers [40], malolactic fermentation, the use of β -glycosidase [41, 42], etc., significantly influence the content of *cis*- and *trans*-resveratrol. Thus, for example, the concentration of resveratrol increases in the wine when a pre-fermentation maceration is performed [43]. In some cases, and depending on the variety of grape used, fermentation and aging influence the result differently. In fact, during the

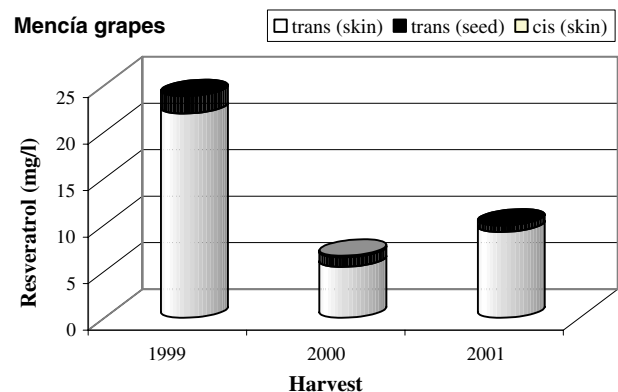


Fig. 1 Total concentration of resveratrol in Mencía grapes previous to harvesting

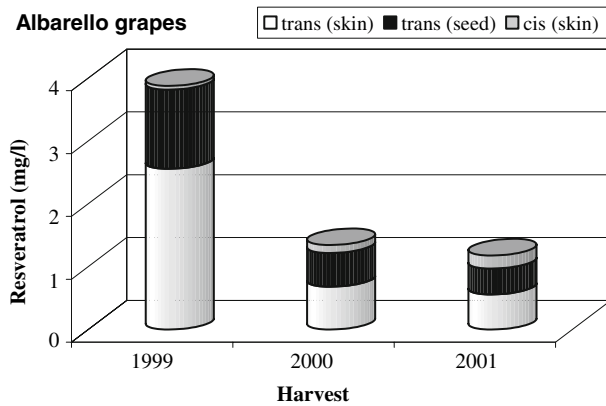


Fig. 2 Total concentration of resveratrol in Albarello grapes previous to harvesting

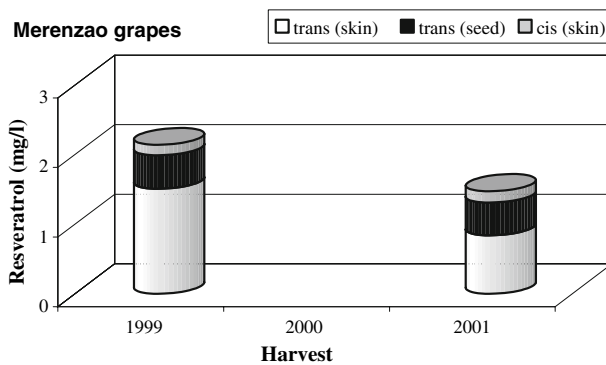


Fig. 3 Total concentration of resveratrol in Merenzao grapes previous to harvesting (Grapes from 2000 were not sampled in the last week)

alcoholic fermentation, the concentration of *trans*- and *cis*-resveratrol increases. However, during aging, behaviour is not uniform, as in some varieties such as Mourvèdre, the content in resveratrol is maintained over various years, but in other cases, the content of this compound decreases during this period [36, 44].

In Fig. 1, it can be seen that the total content of resveratrol in the variety Mencía was higher in 1999 (23.84 mg/L) in both the skins and seeds, although in this year the isomer *cis*-resveratrol was not detected in the last sampling. In the year 2000, the total content of resveratrol (6.67 mg/L) was about four times less than in 1999, but *cis*-resveratrol was present, and in the grapes harvested in the year 2001, the content of resveratrol was 9.94 mg/L. The contribution from the seeds was very low and the isomer *cis* was not detected at all.

In general, in the total content of resveratrol found in the variety Albarello (Fig. 2) and also in the variety Mencía, there was a notable difference in the concentration of resveratrol of the grapes from 1999 (3.88 mg/L) with respect to the following years. The concentration in the following years of this compound was lower (1.34 mg/L in the year

2000 and 1.18 mg/L in the year 2001). With relation to the total content of resveratrol in the final sampling of this variety, the concentration of the isomer *trans* in the skin and pips of the grape at harvest-time was higher in 1999 than in the year 2000, which was lower than in 2001. However, in the case of the isomer *cis*, exactly the opposite occurred. The sample that showed the lowest content of *trans*-resveratrol (2001) was the one that showed the highest concentration of *cis*-resveratrol, followed by the year 2000 and lastly by 1999, which had the lowest concentration of *cis* even though it showed the highest content of the isomer *trans*.

Finally, of the three varieties studied in this work, the Merenzao grapes (Fig. 3) are the ones that showed the lowest concentrations of these isomers at harvest-time, although it must be remembered that the data relative to the samples of the year 2000 are missing and so comprehensive generalisations cannot be made. However, in general and independently of the isomer and the grape fraction, it could be said that the behaviour of this variety was the same in both 1999 and the year 2001.

Comparison of the content in resveratrol with grapes of other varieties

As shown previously, on the basis of the content in resveratrol of either the isomer *cis* or the isomer *trans*, it is not possible to conclude that a uniform behaviour exists during the 3 years that they were evaluated, either between the three red Galician grape varieties analysed or within each of the varieties individually. The climate of the CBO “Ribeira Sacra” is characterised by a continental climate, although, in winter, the climate could be considered as more typical of the Atlantic region. It has an annual rainfall of 700–900 mm and an average temperature of 13.2–13.9 °C, but varied according to the different areas and as significant differences existed between the different concentrations determined, they could be justified by the different climatic conditions that existed in each of the years sampled [30]. Evidently, the study of the same varieties should be continued over a longer period, but using samples taken from vines planted in different types of soil, climate, production techniques, etc. Thus, it would be possible to extrapolate the average content that might be shown by the grapes of each of these varieties and, consequently, of the wine. However, the variety Mencía was much richer in this compound (about nine times) than the other two *Vitis vinifera*, which show approximate average values of around 1.20 mg/kg of grape, although in any one of the three, much higher levels have been determined in the first year evaluated.

On the other hand, even though the concentrations of resveratrol in different varieties of wines are reflected in the bibliography, very few studies are available referring to the

content of resveratrol in grapes. The levels that have been published for different varieties are shown in Table 5. It can be seen that any of the three Galician varieties would have a much higher concentration, expressed in mg/L, than the variety Monastrell, both with respect to the skin and to the total of the grape [38]. When compared to the white variety Palomino [30], Mencía does show much higher contents in the skin, but similar or slightly lower levels have also been determined in Albarello and Merenzao grapes. However, given that this compound is present at its highest concentrations in the skin, it is frequently expressed as mg/kg skin. The average value shown by the variety Mencía (37 mg/kg skin) would place it among the poorest of the varieties analysed by Pascual-Martí et al. [45] in this compound, excelling only the variety Chardonnay. The other two Galician varieties, with contents of 5 and 4 mg/kg skin for Albarello and Merenzao, respectively, are far from the values published for these varieties. If we express the contents as mg resveratrol/kg grape, these last two Galician varieties show values similar to those determined in Korean [46], Chinese [47], Estonian [48] and Spanish varieties [29]. Thus, the variety Mencía would be much richer in this compound, excepting the Chinese variety Hongkemisi.

Conclusions

The concentrations of resveratrol in three varieties of red grapes (Mencía, Albarello and Merenzao) from the CBO “Ribeira Sacra” and in their three fractions (skins, seeds and pulp), during ripening in three consecutive years, highlights the fact that Mencía shows contents of resveratrol that are much higher than were found in the other two varieties in 1999, 2000 and 2001. This content was from six to nine times higher in all the samplings than in Albarello and Merenzao, despite being collected in the same area, while Merenzao shows, in general, a lower concentration in all of the 3 years.

It was also established that the highest content of resveratrol, both in the isomer *trans* and in the isomer *cis*, was found in the skin of the grapes, independent of the variety. Neither of the two isomers was detected in the pulp from any of the three *Vitis viniferas* analysed.

When the data from the three harvests analysed are compared, the grapes harvested during 1999, above all in the case of Mencía, show the highest concentrations of resveratrol, followed by the samples from 2001 and, finally those harvested in the year 2000.

Table 5 Comparison of average contents in resveratrol in some variety of grapes

Variety	mg/kg skin	mg/L	nmol/grape	mg/kg grape
Mencía	17.42–66.94	5.47–21.97	29.22–104.45	3.73–14.53
Albarello	1.84–9.69	0.56–2.56	5.17–16.99	0.84–2.90
Merenzao	2.36–5.63	0.84–1.51	6.46–9.37	0.94–1.13
Monastrell skin ^a	–	0.00890	–	–
Monastrell grape ^a	–	0.00813	–	–
Palomino must ^b	–	–	nd–2.9	–
Palomino skin ^b	–	–	13.5–14.5	–
Boval ^c	75	–	–	–
Mazuelo ^c	52	–	–	–
Tempranillo ^c	171	–	–	–
Monastrell ^c	61	–	–	–
Chadornnay ^c	36	–	–	–
Cabernet ^c	49	–	–	–
Korean grapes ^d	–	–	–	4–8
Suosuo ^e	–	–	–	0.9850
Hongkemisi ^e	–	–	–	154.159
Hasaine sladki ^f	–	–	–	3.2
Zilga ^f	–	–	–	2.1
Tempranillo ^g	–	–	–	2.92
Tinto mazuelo ^h	71.2	–	–	–
Cabernet ^h	52.3	–	–	–
Boval ^h	80.3	–	–	–
Merlot ^h	21.5	–	–	–
Tempranillo ^h	174.0	–	–	–

nd not detected

^a Cantos et al. [38]; ^bRoldán et al. [30]; ^cPascual-Martí et al. [45]; ^dCho et al. [46]; ^eXiang et al. [47]; ^fPüssa et al. [48]; ^gPiñeiro et al. [29]; ^hChafer et al. [25]

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