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Shikimic acid concentration in white wines produced with different processing protocols from fungus-resistant grapes growing in the Alps

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Summary

Shikimic acid (SHA) has been used for years as variety marker in fraud control, especially for 'Pinot Noir', 'Pinot Gris' and 'Pinot Blanc' with very low amounts. Until now no data for the hybrid grapes 'Bronner', 'Helios', 'Johanniter', 'Muscaris', 'Solaris' and 'Souvignier Gris' from the Viticultural Institute of Freiburg (Germany) were published. These white varieties with resistance against downy and powdery mildew are increasingly planted in some Alpine Italian regions. Data obtained from white wines of different vintages and vineyards in Trentino by HPLC showed that 'Johanniter' had the highest average content of SHA, while 'Solaris' and 'Muscaris' had much lower levels. These data are compared with previously published data for Italian wines of 19 white varieties and new data for 'Müller-Thurgau' and 'Yellow Muscat' wines.

For a subset of 10 grape batches the influence of four different winemaking protocols on the amount of SHA was investigated. Increasing levels were found in the expected order from direct pressing to pressing of crushed-destemmed grapes (+28 %), short maceration of crushed-destemmed grapes before pressing (+37 %) and a 7-day skin-contact fermentation (+107 %).

K e y w o r d s : fungus-resistant grapes; 'Müller Thurgau'; shikimate; winemaking technique; 'Yellow Muscat'.

Introduction

(3*R*,4*S*,5*R*)-3,4,5-trihydroxycyclohex-1-ene-1-carboxylic acid (CAS Number 000138-59-0), common name shikimic acid (SHA), synthetized from phosphoenolpyruvate and erythrose-4-phosphate by the activity of 4 enzymes, is an important compound participating in various metabolic pathways in plants producing aromatic amino acids, flavonoids, phenylpropanoids, indole and derivatives (Haslam 1993). The name of this acid seems to derive from a Japanese word indicating the flower/fruit of *Illicium anisatum* (Eykman 1881), but *Liquidambar styraciflua* is considered an interesting renewable source for its industrial extraction (Enrich *et al*. 2008). Also, this molecule can be synthesised by using properly engineered *E.coli* (Krämer *et al*. 2003, Johansson *et al*. 2005).

According to the International Agency for Research on Cancer Monographs on the evaluation of carcinogenic risks to humans, SHA is classified into the group 3; exactly the high concentration of SHA in the edible young fronds of *Pteridium esculentum* - a tree fern of the order Cyatheales - is at the basis of the recommended roasting treatment to reduce acid level before eating (Evans and Osman 1974, IARC Monographs 1987). Moreover, the SHA presence in various tissues and organs from several plants - *e.g.* those belonging to the genera *Illicium, Hypericum* and *Liquidambar* - justifies their traditional use in popular medicine. The therapeutic activity of SHA alone is a vexed question (Giovannini *et al*. 2008), but nowadays, in association with other compounds, it is used for the production of Tamiflu®, a drug that became popular in 2003 when several countries ran the risk of a new bird flu pandemic.

In enology, many simple phenols are used as markers for botanical origin traceability or ascertaining the use of specific products (Fernández de Simón *et al*. 2014, Chinnici *et al*. 2015, Malacarne *et al*. 2016), but SHA has risen to the headlines for some years as a variety correspondence marker (Symonds and Cantagrel 1982, Etievant *et al*. 1989, Holbach *et al*. 2001). This, mainly because Pinot wines proved to be characterised by low contents of this compound, just few milligrams per litre approximately, unlike other *Vitis vinifera* white varieties (Pisoni 2001, Versini et al. 2003), as in the case of 'Chardonnay' wine which can contain a few tens. However, a survey of 98 commercial 'Chardonnay' wines (Otteneder 2008) showed a rather large shikimate concentration distribution, related - almost partially - with the possible blends executed or executable according to the existing different designations of origin (DO) or types of product. Commercially, a maximum acceptable level of 20 $mg \cdot L^{-1}$ has become common for 'Pinot Gris' transactions just taking into account the blending edge allowed by the DOs.

The variety discrimination ability of SHA - satisfactory by itself in some cases - can be favoured by the concomitant analysis of other parameters in grapes (Tamborra and Esti 2010) and wines (Chabreyrie *et al*. 2008). In the latter, for instance, the ratio of acylated anthocyanins (malvin and peonin) to the corresponding *p*-cumarate forms proved to be useful, as it was observed in South American wines where 'Cabernet Sauvignon' was distinguishable from 'Merlot' and 'Carménère' (von Baer *et al*. 2005) for

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its higher values of both SHA concentration and acylated/*p*-cumarate ratio. More recently, Tamborra *et al*. (2014) confirmed the typically high concentration values of 'Cabernet' and highlighted that mono-variety red wines of Italian cultivars grown in Southern ranges can have a rather low concentration of SHA (*e.g*. 'Primitivo', 'Negroamaro'). Moreover, the same authors proved that agronomic variables - such as different farming systems and water supplies - only caused limited changes, while ripening determined a slightly decreasing trend. By contrast, the treatment with glyphosate seems to impact noteworthy; in fact, this herbicide interferes with the accumulation and enzymatic metabolisation of shikimate (Steinrücken and Amrhein 1980, Vivancos *et al*. 2011) and some wine grape hybrids seem to be slightly less injured compared to *vinifera* grapes (Mohseni-Moghadam *et al*. 2016).

As regards the effect of winemaking technique, it has been known for years that SHA increases during carbonic maceration (Flanzy *et al*. 1981) but acid and basic hydrolysis or glycosidase treatments have no effect, thus proving that in wine SHA is present in its free form only (Tamborra *et al*. 2014). Generally, SHA concentration is not modified from juice to wine during white fermentation (Pisoni 2001), but some increases have been observed in long-lasting skin-contact fermentations (Tamborra *et al*. 2014). Hypothetically, the reason could be the presence of some bacterial contamination since, for instance, an unusual bacteria strain, *Citrobacter freundii*, has been found to be able to produce SHA under fermentation conditions (Tripathi *et al*. 2013).

SHA levels from 3 to 36 $mg \cdot L^{-1}$ and from 4 to 34 $mg \cdot L^{-1}$ have been respectively found in red and white wines produced on semi-industrial scale with 12 grape varieties native to Romania (Niculaua *et al*. 2009). A survey on mono-variety white wines from Abruzzo (Italy) reported values ranging from 8 to 60 $mg \cdot L^{-1}$, confirming 'Chardonnay' among the SHA richest cultivars (Carinci 2014), irrespective of harvest year.

In this survey we investigated the concentration of shikimic acid in white wines produced in Trentino Alto-Adige, an Italian Region in the Alps, from fungus-resistant grape varieties recently authorised for wines without designation of protected geographic origin. To the best of our knowledge, this is the first investigation involving SHA content in wines produced from these varieties.

Material and Methods

G r a p e s : The following white-fruited fungus-resistant grape varieties created since the late "Sixties" at the Grape Breeding Institute in Freiburg, Germany, were used: 'Bronner' (entry in the Italian National Register for Wine Grapes: 27/03/2009; registration code: 416; G.U. 146, 26/06/2009), 'Helios' (10/07/2013; 468; G.U. 186, 09/08/2013), 'Johanniter' (10/07/2013; 469; G.U. 186, 09/08/2013), 'Muscaris' (20/10/2014; 495; G.U. 258, 11/06/2014), 'Solaris' (10/07/2013; 471; G.U. 186, 09/08/2013), 'Souvignier Gris' (20/10/2014; 96; G.U. 285, 11/06/2014). They might enter the National Register following the Reg. UE 1308/2013. Further information about these varieties can be found at the site of the Italian ministry in charge (http://catalogoviti.politicheagricole.it/catalogo.php) and in the *Vitis* International Variety Catalogue (http://www.vivc.de). Moreover, 'Aromera' samples, a variety obtained by InnoVitis (Marlengo, BZ, Italy; http://www.innovitis.eu/tl_files/InnoVitis/pdf/Datenblaetter%20italienisch/Aromera.pdf) were also used. 'Aromera' parents are not declared and it was not yet included either in the *Vitis* International Variety Catalogue or in the above mentioned Italian register.

Grapes were harvested, depending on climatic condition of the year and with an adequate leaf coverage, at the time when a clear slowdown of soluble solids accumulation (expressed as °Brix) between 2 subsequent sampling was measured, after passing a minimum potential alcohol strength of 11 % vol., avoiding any berry withering.

W i n e m a k i n g : Single fungus-resistant variety wines were produced in semi-industrial scale at the E. Mach Foundation Experimental Winery (San Michele all'Adige, Italy) in the harvest years and according to the winemaking protocols reported in Tab. 1. In addition to the "control" protocol used for all grape samples, characterized by the pressing of crushed-destemmed grapes, other 2 protocols dealing with processing options commonly used for white wines were applied on a reduced number of samples. Specifically, direct pressing (DP) of uncrushed grapes and short maceration (MAC; 12 °C x 4 h) of crushed-destemmed grapes before pressing were applied. Moreover, a fourth protocol traditionally made for young reds, was carried out: a 7-day skin-contact fermentation (7DSK) of crushed-destemmed grapes, punching down the cap twice a day for 4 d, then 1 per day, devatting at day 7, and assembling free-run and press wine. A crusher-destemmer Ares 15 (OMAC s.r.l., Corridonia, MC, Italy) and a Hydropress (Speidel GmbH., Ofterdingen, Germany) were used, applying 3 pressing cycles (5 min x 3.5 bar). All musts were supplemented with 35 $mg \cdot L^{-1}$ sulfur dioxide. The white-processed grape juices were settled at 10 °C x 24 h before fermentation at 18-20 °C. Lalvin EC-1118 yeast strain (20 $g \cdot 100\ L^{-1}$; Lallemand Inc., Montreal, Canada) was used irrespective of the winemaking protocol. At fermentation completion, all wines were racked, sulphited and maintained at 4 °C to avoid malolactic fermentation until analysis, carried out 1-2 months later. No other chemicals, clarifying or fining agents and supplementations were used in juice and wine.

A n a l y s i s : The HPLC determination of shikimic acid was carried out according to the OIV-MA-AS313-17:R 2004 method (OIV 2004), using a C_{18} reverse-phase column (Merck LiChroCART® 125-3 Purospher® RP 18e, 5 µm; working at room temperature) coupled with a cationic exchange column (Biorad Aminex® HPX-87H, 300 x 7.8 mm; working at 65 °C), and detection at 210 nm. The basic composition of wine was measured by a WineScan SO2 (Foss, Hillerød, Denmark), accurately aligned with official methods.

Statistical data treatment was performed using the procedures of STATISTICA v. 8.0 package (StatSoft Inc., Tulsa, OK).

Table 1

Wine samples displayed per cultivar, vintage year and vinification protocol. (Legend: A = 'Aromera', B = 'Bronner', H = 'Helios', J = 'Johanniter', M = 'Muscaris', S = 'Solaris', SG = 'Souvignier Gris'; 4 = 2014, 5 = 2015, 6 = 2016; Control = pressing of crushed-destemmed grapes; DP = direct pressing of uncrushed grapes; MAC = 4-h pre-fermentation maceration; 7DSK = 7-day skin contact fermentation)

Plot	Trelli-sing	m a.s.l.	A	B	H	J	M	S	SG	A	B	H	J	M	S	SG
			Control							DP						
P01	Guyot	250		4							4					
P02	Guyot	180		5-6		5-6	5-6	5-6								
P03	Guyot	200	6	5-6	5-6	4-5-6	5-6	5-6	5-6							
P04	Pergola	900						5							5	
P05	Guyot	700						5								
P06	Pergola	210				5										
P07	Pergola	200				5										
P08	Pergola	190	5-6	5-6	5-6	5-6	5-6	5-6	5-6					5	5	5
P09	Guyot	550	5	5-6	5-6		5-6	5-6	5-6			5			5	5
P10	Pergola	450		4							4					
P11	Guyot	480		4							4					
Plot	**Trelli-sing**	**m a.s.l.**	**A**	**B**	**H**	**J**	**M**	**S**	**SG**	**A**	**B**	**H**	**J**	**M**	**S**	**SG**
			MAC							7DSK						
P01	Guyot	250		4							4					
P02	Guyot	180														
P03	Guyot	200														
P04	Pergola	900						5							5	
P05	Guyot	700														
P06	Pergola	210				5							5			
P07	Pergola	200														
P08	Pergola	190		5			5	5	5		5			5	5	5
P09	Guyot	550			5			5	5			5			5	5
P10	Pergola	450		4							4					
P11	Guyot	480		4							4					

Results and Discussion

Shikimic acid in *vinifera* wines: The SHA concentration variability in genuine Italian *Vitis vinifera* white wines is shown in Fig. 1 as reference. In this figure, data from the literature (Versini *et al.* 2003, Carinci 2014) were integrated with our more recent unpublished data mainly regarding 'Müller Thurgau' (vintage years 2012, 2013 and 2014) and 'Yellow Muscat' (2015 and 2016) wines produced on semi-industrial scale using grapes collected in Trentino (Italy) in different plots and belonging to different clones. These grapes were processed according the above mentioned "control" winemaking protocol. SHA concentration in wine of both those varieties, previously not investigated, lies in intermediate position among that of the other *vinifera* wines. Concentrations' distribution observed in *vinifera* white wines, on the basis of the whole data set, is shown by the box plot in Fig. 2; median value is 20.0 mg·L^{-1} and only one sample was over 62 mg·L^{-1}, reaching a maximum of 95.5 mg·L^{-1}.

Shikimic acid in the wines of fungus-resistant grapes: The shikimic acid concentration in the white-processed wines (control, DP, MAC) obtained with resistant grapes is presented in Fig. 3 displayed *per* variety. The distribution and the number of samples *per* variety and year suggested the use of a non-parametric statistical approach to support discussion. In addition, only differences between variety wines with Multiple Comparisons *p* values below 0.0001 in the Kruskal-Wallis test were highlighted; these were found for 'Johanniter' *vs* 'Muscaris' and 'Solaris'. Lower significance levels ($p < 0.05$) were found for 'Johanniter' *vs* 'Aromera' and 'Helios', as well as for 'Bronner' *vs* 'Muscaris' and 'Solaris'. Finally, 'Solaris' and 'Muscaris' seemed really to be characterised by low SHA, considering that even the corresponding red-processed wines had concentration close to or below 15 mg·L^{-1} (see next chapter). The composition of the white-processed wines is given in Tab. 2 just to present the basic characteristics of the available sample that, in its minimum pH and maximum acidic level, felt the effect of the difficult climatic conditions of 2014 vintage year, particularly for 'Bronner' that confirms its well known marked acidity (Basler *et al.* 2002). The minimum alcohol degree naturally reached by Solaris proved the variety ability to adequately accumulate sugars also when grown in the Alps at a remarkable altitude, about 900 m a.s.l.

Effect of winemaking protocol: For a subset of 10 grape batches (Tab. 1; 'Bronner', N = 3; 'So-

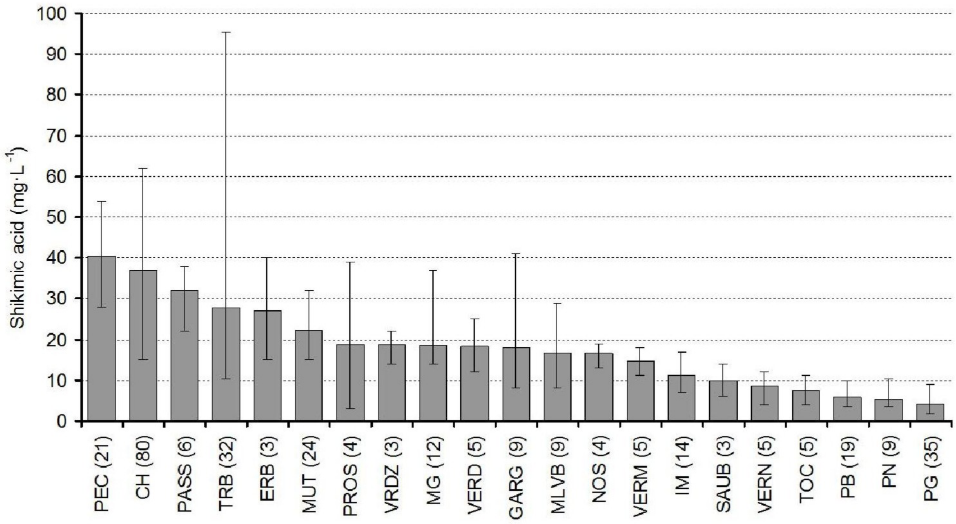

Fig. 1: Mean, minimum and maximum concentration values of shikimic acid in Italian monovarietal white wines from *Vitis vinifera* grapes. The Figure integrates data from the literature (Versini *et al*. 2003, Carinci 2014) with our more recent unpublished data. (Legenda: PEC = 'Pecorino', CH = 'Chardonnay', PASS = 'Passerina', TRB = 'Trebbiano', ERB = 'Erbaluce', MUT = 'Müller-Thurgau', MG = 'Yellow Muscat', PROS = 'Prosecco', VRDZ = 'Verduzzo', VERD = 'Verdicchio', GARG = 'Garganega', MLVB = 'Malvasia Bianca,' NOS = 'Nosiola', VERM = 'Vermentino', IM = 'Manzoni Bianco', SAUB = 'Sauvignon Blanc', VERN = 'Vernaccia', TOC = 'Tocai', PB = 'Pinot Blanc', PN = 'Pinot Noir', PG = 'Pinot Gris').

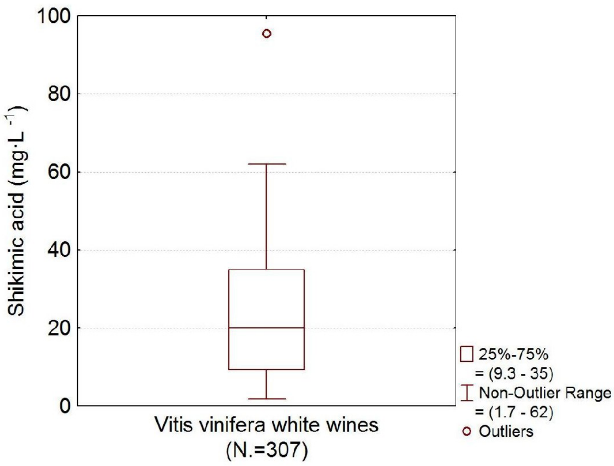

Fig. 2: Shikimic acid concentration in the *Vitis vinifera* white wines reported in Fig. 1.

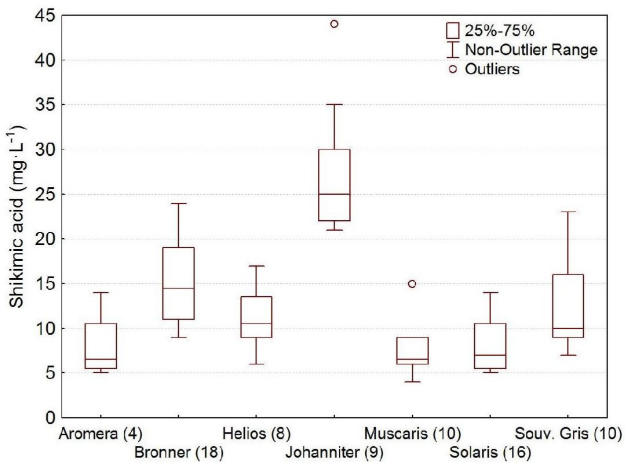

Fig. 3: Box plot of the shikimic acid concentration in single variety white wines. Number of samples in brackets.

laris', 3; 'Muscaris', 1; 'Helios', 1; 'Souvignier Gris', 2) it was possible to carry out all the 4 winemaking protocols described above: DP, control, MAC and 7DSK which represent in this order a hypothetical increase of extractions from the skins. Statistically analysing the concentration of SHA, significant differences were found between white- and red-processed wines (Fig. 4; Anova, sources of variance: grape batch and winemaking treatment; Tukey's HSD test, $p < 0.05$). Although not statistically significant, an increasing trend of the mean values can be observed within the white-processed wines, consistent with expected extraction phenomena. Compared to DP treatment, representing the typical grape processing in the case of base-for-sparkling wines, the increases of the mean values are 28 %, 37 % and 107 % respectively for control, MAC and 7DSK. In the light of the increasing application of old winemaking techniques (*e.g.* long skin-contact fermentations in amphoras) in white wine production, these data suggest attention in using shikimic acid as sole variety marker.

Conclusions

In this survey it for the first time the shikimic acid concentration in wines obtained from fungus-resistant grapes were evaluated, which are more and more planted in some northern and mountainous Italian regions thanks to their interesting oenological performances associated with a potentially higher sustainability, related to the lower need of treatments against fungi. Secondly, the shikimic acid concentration variability caused in wine by the winemaking options related to skin management was described and, finally, the shikimic acid concentration in *Vitis vinifera* 'Müller Thurgau' and 'Yellow Muscat' gen-

Table 2

Basic composition of the white-processed wine samples

Variety (No. of samples)		Alcohol (% vol)	pH	Titratable acidity (g·L^{-1})
Aromera (4)	Min	11.4	3.14	5.1
	Median	12.9	3.25	5.7
	Max	14.0	3.41	7.1
Bronner (18)	Min	11.0	2.57	4.3
	Median	12.1	2.95	7.5
	Max	14.1	3.37	10.8
Helios (8)	Min	11.7	2.95	4.7
	Median	12.7	3.14	6.7
	Max	13.5	3.30	7.6
Johanniter (9)	Min	10.2	2.84	5.0
	Median	10.8	3.03	7.5
	Max	13.3	3.58	8.5
Muscaris (1)	Min	11.8	2.74	4.2
	Median	14.6	3.18	6.4
	Max	15.4	3.53	9.8
Solaris 16	Min	12.5	2.73	5.9
	Median	15.0	3.14	6.6
	Max	16.7	3.27	8.9
Souvignier Gris (10)	Min	11.7	2.77	5.2
	Median	12.9	3.04	7.1
	Max	14.9	3.34	10.0

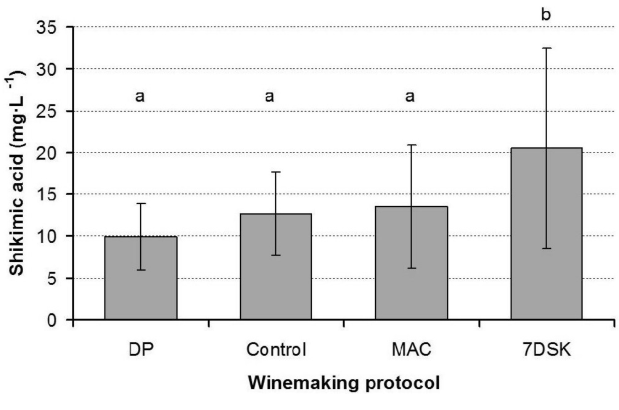

Fig. 4: Concentration of shikimic acid (mean ± standard deviation, N. = 10) in wines according to the winemaking protocol applied.

uine wines, not yet investigated, was evaluated.The SHA concentration values found suggest that some white resistant variety wines could be used in blend with traditional *vinifera* wines without designation of protected geographic origin - *e.g.* 'Solaris' in 'Pinot Gris', or 'Muscaris' in 'Yellow Muscat' - in full compliance with the variety percentages already defined by law (usually less than 15 %), without impacting the possibility of using SHA as a tool for ascertaining the main variety declared on the label. This aspect is of major relevance in problematic contexts for cultivation, like Alpine areas and sharply sloped vineyards where, in addition, the use of resistant grapes - thanks to the lower number of treatments - can indirectly reduce the risk of fatal accidents for farmers.

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