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Doctoral Dissertation

A comprehensive study on postharvest dehydration of grapes destined for the production of 'Commandaria' dessert wine: a protected designation of origin (PDO) product

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ABSTRACT

Grapes' sun-dried process is one of the most critical steps in the production of 'Commandaria', a dessert wine that is exclusively produced in Cyprus from must obtained from grapes of the two indigenous *Cypriot cultivars (Vitis vinifera* L.), namely 'Mavro' (red skin) and 'Xynisteri' (white skin). Despite its significant economic importance, no data regarding the primary and secondary metabolites of the aforementioned cultivars exist. In view of this, the current dissertation was composed of three interrelated, yet complementary, experiments.

Initially, the effect of traditional sun drying process on the qualitative attributes and phenolic profile of 'Mavro' and 'Xynisteri' musts was dissected. Musts were analyzed at harvest and at the end of the sun-drying process that corresponds to *ca.* 30 – 40% water loss. Results highlighted significant differences in chemical composition of the must before and after the sun-drying process. Except for the increase of soluble solids content, a significant increment in glucose, fructose, titratable acidity, total phenols and total flavonoids contents was recorded due to condensation effect. Moreover, forty and forty two phenolic compounds were identified by LC-DAD-qTOF-MS in 'Xynisteri and 'Mavro' grape must, respectively. Results also indicated significant changes in the phenolic composition of the obtained musts. In particular, the increase in the concentration of hydroxybenzoic acids group was higher than the condensation effect for both cultivars. Furthermore, dehydration led to a six-fold increment of hydroxycinnamic acid content in both cultivars. Intriguingly, the concentration of some hydroxycinnamic acids, such as caffeic acid dihexoside and fertaric acid isomer went descending. Although the degradation of the internal side of the skin facilitate extractability from the skins to the grape pulp and therefore to the grape must, the sun-drying process may also induce stilbene and lignans synthesis production. A significant effect of dehydration on the postharvest biosynthesis of three groups of flavonoids (flavonols, flavan-3-ols, flavanonols), was also observed.

Thereafter, the effect of traditional sun-drying method on the phenolic composition, oenological parameters, aroma potential and browning compounds of 'Xynisteri' musts was compared to that of four alternative dehydration methods [(a) multiple horizontal wires (MHW), (b) multiple vertical pallets (MVP), (c) low greenhouse (LGH) and (d) hot-air dryer treatment (HAD)]. LGH and HAD treatments,

led to a significant reduction of the dehydration period. Soluble solid contents were used to monitor the progress of dehydration process; no changes among the examined dehydration methods in reducing sugar composition were found. Notably, HAD method led to a dramatic rise of titratable acidity (3.2-fold), which was obviously not related only to the condensation effect. Furthermore, all dehydration methods concentrated total bound volatiles and induced the formation of brown pigments. Based on the Folin-Ciocalteu index, only HAD and LGH methods induced a significant increase in total phenolic content in dehydrated grape musts. Subsequently, forty phenolic compounds were identified and quantified by LC-DAD-qTOF-MS. Results showed significant effects of dehydration methods that vary according to the different groups of phenolic compounds considered. Similarly to Folin-Ciocalteu index, HAD and LGH methods increased significantly the phenolic content in grape musts, whereas MHW and MVP methods increased it slightly higher than the dehydration factor. Flavonols, flavan-3-ols and flavanonols were the most affected polyphenolic groups. A significant increment of hydroxybenzoic and hydroxycinnamic acids, the predominant groups of phenolic compounds found in 'Xynisteri' grapes, was monitored. Taking into consideration that HAD method cannot exploited under the existing legal framework, LGH showed the greatest potential for the production of high quality sun-drying grapes, as it led to appreciably higher phenolic and aroma potential and lower concentration of brown pigments and melanoidins, compared to the other methods used. Furthermore, LGH protects the grapes against several factors such as rodents, birds, insects and rain incidents over the drying period. However, the further development of the LGH system (i.e. use of a ventilation system, multiple racks and inclined north wall reflection) is recommended as future perspective, with the aim to achieve the optimum quality of the dehydrated grapes and subsequently its end-product.

Finally, the effect of leaf removal application at veraison stage on the composition of must obtained from fresh and dehydrated grapes of both cultivars was evaluated. Leaf removal led to a reduction of soluble solids, titratable acidity, aroma potential and most of the phenolic groups of musts of both cultivars. Dehydration led to a significant increase of the aforementioned parameters in both cultivars, being more pronounced in cv. 'Mavro'. Furthermore, thirty-three phenolic compounds were identified and quantified by LC-DAD-qTOF-MS in 'Mavro' and thirty in 'Xynisteri' musts obtained from all treatments applied. Interestingly, leaf removal indicated

differential response in the dehydrated product of the examined cultivars. A significant decrease of phenolic compounds in ‘Xynisteri’ must (from 66.73 to 44.15 mg L^{-1}) was monitored, while ‘Mavro’ must registered similar values of phenolic compounds, but with different distribution among phenolic groups. Interestingly, flavonols and flavan-3-ols that present great health-promoting properties, showed higher concentrations in must from defoliated dehydrated ‘Mavro’ grape. However, the efficacy of leaf removal in successive developmental stages and different intensities is recommended as a future perspective, with the aim to achieve the optimum technological and phenolic maturity of the grapes destined for ‘Commandaria’ production.

Overall, this study sheds some light in the substantial changes that occur in specific metabolites during sun-drying and provides useful insights regarding the use of other dehydration methods and the application of leaf removal as preharvest treatment. In particular, from the three aforementioned experiments, forty-three discrete phenolic compounds were identified, revealing the polyphenolic fingerprint of the two predominant indigenous grape cultivars. Moreover, results highlighted significant differences in chemical composition of the must before and after the dehydration and indicated that changes in the phenolic composition of the obtained must were not only correlated with the dehydration effect, but both synthesis and degradation reactions occurred. In addition, results showed significant effects of dehydration methods; Low greenhouse showed the greatest potential for the production of high quality dehydrated ‘Xynisteri’ must. Moreover, leaf removal significantly affected chemical composition of the must of fresh grapes, but registering different responses based on the cultivar considered regarding dehydrated grape composition.

Keywords: *Vitis vinifera*, autochthonous cultivars, ‘Xynisteri’, ‘Mavro’, leaf removal, grape ripening, postharvest dehydration, sun-drying, sweet dessert wine, Commandaria, phenolic compounds, aroma potential, bound volatiles, melanoidins, LC-DAD-qTOF-MS