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Anthocyanin profiles of pomace skins of international and indigenous grape varietety determined by UHPLC-MS/MS OrbiTrap

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1 INTRODUCTION

During the winemaking production, a significant amount of different by-products is generated, which can be used as a rich source of valuable phenolic compounds, primarily anthocyanins.

2 AIM

The aim of this study was to determine anthocyanin profiles of oven dried non-fermented grape pomace skins (GPS) of international (**Merlot**) and autochthonous (**Prokupac**) grape varieties.

3 MATERIAL AND METHODS

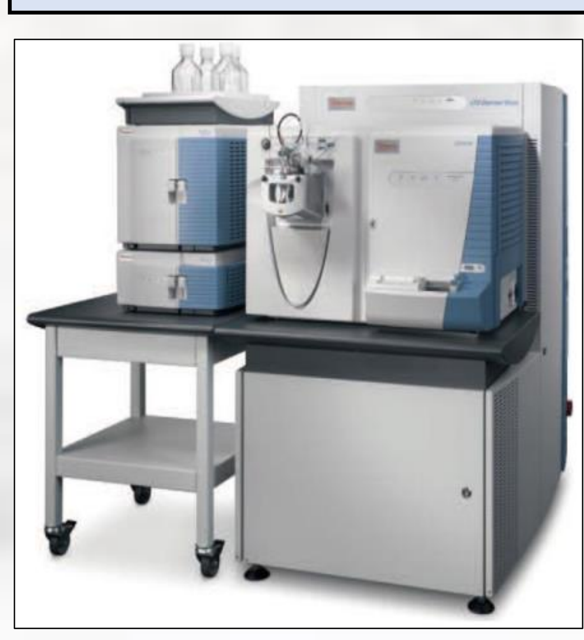
Anthocyanins were extracted from GPS with acidified methanol (MeOH) and aqueous ethanol (50:50 v/v, EtOH), evaporated to dryness, reconstituted in milliQ water and further analysed by UHPLC-MS/MS OrbiTrap.

Anthocyanin have been identified based on retention times, molecular masses of the molecular ions ($[M-H]^+$), individual MS^2, MS^3 and MS^4 fragment ions and data from the literature.

PROKUPAC

MERLOT

GRAPE SKINS



UHPLC-MS/MS OrbiTrap

ANTHOCYANIN ANALYSIS

4 RESULTS AND DISCUSSION

Both GPS extracts of international Merlot wine variety had a significantly higher content of total (6.95-9.97 times) and individual anthocyanins, in comparison to the GPS extracts of the autochthonous Prokupac variety. Further, the content of total and individual anthocyanins were significantly higher in the MeOH extracts, probably due to the increased stability of anthocyanins in an acidic environment. In total, thirteen anthocyanin derivatives were identified in all analysed GPS extracts, primarily malvidin derivatives for both varieties (70.8-81.4% of total quantified anthocyanins); which is in agreement with literature data. Malvidin, peonidin and petunidin glucoside were predominantly quantified in MeOH extracts of Merlot (142.79, 53.30 and 43.28 mg/kg DM), while other glucosides were detected in traces. Methanolic and aqueous extracts originated from Merlot variety, contained various acetyl, caffeoyl and coumaroyl derivatives of anthocyanins found in significant amounts, primarily malvidin-3-O-(6"-acetyl)hexoside (100.82 and 112.98 mg/kg DM) and malvidin-3-O-(6"-p-coumaroyl)hexoside (9.47-145.96 mg/kg DM).

COMPOUNDS (mg/kg DW)	PROKUPAC		MERLOT	
	methanol	ethanol	methanol	ethanol
MALVIDIN DERIVATIVES				
Malvidin 3-O-glucoside[a]	18.90	5.89	142.79	30.27
Malvidin-3,5-di-O-glucoside[a]	0.39	0.21	1.84	0.62
Malvidin-3-O-hexoside-acetaldehidyde[b]	/	/	2.88	1.58
Malvidin-3-O-(6"-acetyl)hexoside[b]	4.50	6.18	112.98	100.82
Malvidin-3-O-(6"-caffeoyl)hexoside[b]	/	/	18.81	3.12
Malvidin-3-O-(6"-p-coumaroyl)hexoside[b]	12.81	8.15	48.89	9.47
PEONIDIN DERIVATIVES				
Peonidin-3-O-glucoside[a]	9.55	2.77	53.30	10.19
Peonidin-3-O-(6"-acetyl)hexoside[b]	/	/	9.55	6.88
Peonidin-3-O-(6"-p-coumaroyl)hexoside[b]	/	2.15	9.98	1.54
DELPHINIDIN DERIVATIVES				
Delphinidin-3-O-glucoside[a]	/	0.46	9.91	1.75
PETUNIDIN DERIVATIVES				
Petunidin-3-O-hexoside[b]	/	/	43.28	6.86
Petunidin-3-O-(6"-acetyl)hexoside[b]	/	/	5.38	5.61
CYANIDIN DERIVATIVES				
Cyanidin-3-O-glucoside[a]	0.29	/	3.72	0.61
TOTAL	46.44	25.80	463.31	179.31

a Quantified using corresponding standards; **b** Expressed as malvidin 3-O-glucoside equivalents.

5 CONCLUSION

Based on data, GPS can be a good source of anthocyanins (primarlly from Merlot variety), potential natural colorants and functional additives in the food industry.

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