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Research article

Targeted analysis for the detection of phenolics and authentication of Albanian wines using LC-DAD/ESI–MS/MS combined with chemometric tools

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ABSTRACT

In recent years, Albania has seen a significant increase in wine production, which can be attributed to the growing interest in the diversity of native grape varieties. Among the most popular grape varieties are Kallmet, Shesh i zi (ShiZ), Shesh i bardhë (ShiB), and Cerruje, which are known for their distinctive wines as well as the planted area. A study was conducted to investigate the influence of the territory and vintage on phenolic compounds of single-variety wines from these grape varieties. Liquid chromatography identified and quantified thirty-one phenolic compounds, sub-grouped into flavonoids and non-flavonoids, with diode-array detection coupled to electrospray ionization tandem mass spectrometry (LC–DAD–ESI/MS^n). Within the red wines group, the ShiZ variety wine presented the highest phenolic content (1037 mg/L), followed by Kallmet cv. (539 mg/L); conversely, in the white wine group, the ShiB wines (699 mg/L) were distinguished from the Cerruje variety. Gallic acid was the main phenolic compound, followed by procyanidin B3. ShiB and ShiZ had the highest levels, at 215 and 136 mg/L, respectively. Among flavanols, (+)-catechin was found in the highest levels, with the maximum in Kallmet cv. red wine (58.9 mg/L), followed by (-)-epicatechin (29.1 mg/L). The ShiB wine had the highest content of flavonols, with quercetin-3-O-glucuronide and quercetin-3-O-glucoside as the main contributors. The highest quantity of stilbenoids belonged to Kallmet red wine (1.59 mg/L). Applying Principal Component Analysis (PCA) in red and white wine groups made a good separation possible according to variety and region. However, a separation according to vintage year was not successful.

1. Introduction

Wine is an alcoholic beverage of great commercial value and cultural significance [1,2]. Several factors influence the quality of

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wine, including grape variety, terroir, viticultural practices, winemaking techniques, and aging conditions [3,4,][5]] [][3–5][]. Although wine is a complex mixture, two minor constituents, phenolic compounds and volatile aroma compounds, determine wine's diversity [6]. Phenolic compounds are secondary metabolites produced in grape berries, and their content is significantly affected by oenological and storage practices, which play essential roles in determining the aroma, color, bitterness, and astringency of wine [7,8,9,][10]] [][7–10][]. Studies have shown that grape variety and vintage significantly affect wine phenolic content and profile [7,11,][12]] [][7,11,12][]. Chemically, they are grouped into two broad classes: nonflavonoids and flavonoids, with the first class comprising hydroxycinnamic acids, hydroxybenzoic acids, stilbenes, and volatile phenols. The second class, flavonoids, includes flavan-3-ols, flavonols, and anthocyanins, which contribute to the organoleptic characteristics of wines [13,14]. In young red wines, anthocyanins are responsible for their intense red color, while chemical reactions that occur during wine maturation lead to a change in color [2,8].

Flavan-3-ols may be found in several structural forms, including monomers, oligomers, and polymers, and are present in grape seeds, stems, and skins, with (+)-catechin and (-)-epicatechin as the primary monomers. Also, according to Jordao and Ricardo-da-Silva (2019) [9], polymers and oligomers are either proanthocyanidins or condensed tannins. Many processed foods contain wine, chocolate, fruits, flowers, and plant seeds [15]. The sensory qualities of red wine, including its color and texture, are influenced by proanthocyanidins [9,16]. Copigmentation activities involving flavan-3-ols and anthocyanins contribute to the unique color of the wine. Oligomeric proanthocyanidins are more common than polymeric ones, and hardly 10 % of all proanthocyanidins are flavan-3-ol monomers [17]. Red wine aging or flavanol involvement in oxidative browning reactions can be influenced by interactions with anthocyanin-flavanol or other condensation processes [15,18]. According to Kontoudakis et al. (2011) [3], one analytical approach that might be used to verify the validity of varietal wines is their anthocyanin fingerprints.

Hydroxybenzoic and hydroxycinnamic acids are compounds that have health-promoting properties and play an important role in the sensory attributes of wine [1,19]. During the fermentation process of wine, nonesterified structures are produced as hydrolysis products. Precursors of oxidizing reactions can lead to the browning of white wines and may produce a bitter taste [5]. From a taxonomic perspective, polyphenols are also crucial. The genetic control of some flavonoid classes, such as anthocyanins, affects their distribution among grape cultivars [20,21].

Wine phenolics exert several health benefits, including antioxidant, anti-aging, anti-inflammatory, antibacterial, antiviral, antifungal, antiproliferative, and antithrombotic properties. Moreover, they positively affect the composition and functionality of human microbiota, cardiovascular diseases, cancer, obesity, neurodegenerative diseases, diabetes, allergies, and osteoporosis [2,22,23,][24]] [][2,22–24][]. Among the many ways they improve human health are regulating inflammation and the immune system, lowering blood sugar and cholesterol levels, controlling metabolism, and even warding off cancer [15,25].

Wine is easily adulterated; consequently, the authenticity of wine contributes to consumer protection and defends producers from unfair competition. As such, ensuring the authenticity of wine is crucial for safeguarding both consumers and producers through investigating the phenolic classes [10,26,][27]] [][10,26,27][]. Authenticity is closely tied to factors like grape variety, terroir, and vintage, with certain regions and countries known for producing wines of superior quality and subsequent higher retail value. Researchers have utilized unsupervised exploratory principal component analysis (PCA) and cluster analysis techniques to assess authenticity. Additionally, discriminant techniques like linear discriminant analysis (LDA), partial least squares-discriminant analysis (PLS-DA), and k-nearest neighbor (KNN) have been employed in authentication studies, as noted by Kamiloglu (2018) [28]. By using these rigorous methods, we can protect consumers and defend the integrity of the wine industry).

Albania, a Mediterranean country, has a thriving agricultural sector focusing on olive, vine, and other plants native to this region. In recent years, olive oil and wine production have grown significantly, contributing to the country's sustainable development [27,29]. The country boasts unique grape varieties, including Kallmet, Shesh i zi (ShiZ), and Shesh i bardhë (ShiB), which have been cultivated for a long time and are the most important in terms of the planted area [30–32]. The Shesh i zi grape cultivar is known for its elegant and aromatic qualities, while Kallmet is renowned for its bold and robust flavor. Another grape variety, Cerruje, grown in the inland regions of northern Albania, has shown potential as a promising wine-producing local variety. Understanding the specific qualities of these mono-varietal wines is crucial in appreciating and promoting Albanian wine diversity.

This study aimed to accurately and comprehensively identify phenolic compounds in Albanian mono-varietal white and red wines made from native grape varieties using LC-DAD-ESI/MS^n analysis. It also aimed to evaluate the impact of different vine zones and vintages.

2. Materials and methods

2.1. Chemicals

HPLC-grade methanol, acetonitrile, and formic acid (Merck, Darmstadt, Germany) were used after filtration through a 0.45-μm pore-size membrane. Chemical standards procyanidin B1, B2, B3, B4, resveratrol, and protocatechuic acid were purchased from Extrasynthese (Genay, France). Caffeic acid (331-39-5), caftaric acid (67879-58-7), coutaric acid (27174-07-8), (+)-catechin (154-23-4) and (−)-epicatechin (490-46-0), fertaric acid ferulic acid, gallic acid(149-91-7), gallocatechin, isorhamnetin-3-O-glucoside, kaempferol-3-O-glucoside, *p*-coumaric acid (501-98-4), quercetin (849061-97-8), quercetin-3-O-glucoside (482-35-9) and quercetin-3-O−galactoside standards were purchased from Sigma Aldrich Chemical Co. (St. Louis, MO, USA).

Table 1
Mono-variety wine samples according to county and district divisions.

Grape Variety	Acronym	Berry color	Wine type	County	District
Kallmet		blue	red	Lezha	Lezha
				Mirdita	Lezha
Shesh i zi	ShiZ	blue	red	Kavaja	Tirana
Shesh i bardhë	ShiB	yellow	white	Kavaja	Tirana
				Tirana	Tirana
Cerruje		yellow	white	Mati	Dibra

Table 2
Long-term weather variables for wine terroirs in the study (1990–2020).

County	Köppen and Geiger classification	Average annual temperatures (°C)	Average annual precipitation (mm)	Annual sunny hours (h)
Durrësi	Csa	15.9	1245	3491.5
Kavaja	Csa	15.7	1245	3489.9
Tirana	Csa	14.8	1136	3447.4
Lezha	Csa	14.6	1288	3435.8
Mirdita	Cfa	13.2	1338	3163.7
Mati	Cfa	12.2	1484	3122.1

(**Source:** [34].

Table 3
Method specifications on wine phenolics identification with LC−ESI−MS/MS (negative ionization mode).

Peak	Compounds	Abbreviation	t_R (min)	UV λ_{max} (nm)	$[M - H]^-$ (*m/z*)	MS/MS (*m/z*)
Hydroxy benzoic acids and flavanols						
1	Gallic acid	GA	14.13	276	169	125
2	3-O-galloyl quinic acid	3-G_Qui_A	14.71	274	343	191, 169, 125
3	Protocatechuic acid-O-hexoside	PC_A-hex	17.25	296	315	153
4	Gallocatechin	Gcat	18.37	274	305	179, 125
5	Protocatechuic acid	PC_A	20.55	294	153	109
6	Epigallocatechin	EpiGCat	25.10	274	305	179, 125
7	Procyanidin B3	B3	23.64	279	577	559, 425, 289
8	Procyanidin B1	B1	29.53	279	577	559, 425, 289
9	Catechin	Cat	30.97	280	289	245, 175
10	Procyanidin B2	B2	33.86	280	577	559, 425, 289
11	Epicatechin	Ecat	37.56	280	289	245, 175
12	Procyanidin B4	B4	42.93	280	577	559, 425, 289
13	Ethyl gallate	etGal	44,39	277	197	169, 125
Phenolic acids						
14	2-S-glutathionyl-caffeoyl-tartaric acid	2-S-glt_CaTa_A	18.89	330	616	484, 440, 272
15	*cis*-Caftaric acid	c-Caf_A	21.94	328	311	179, 149, 135
16	*trans*-Caftaric acid	t-Caf_A	24.18	328	311	179, 149, 135
17	*cis*-Coutaric acid	c-Cou_A	31.11	310	295	163, 149
18	*trans*-Coutaric acid	t-Cou_A	32.70	314	295	163
19	*cis*-Fertaric acid	c-Fer_A	34.83	322	325	193, 149
20	*trans*-Caffeic acid	t-Caf_A	35.83	323	179	135
21	*trans*-Fertaric acid	t-Fer_A	36.16	328	325	193, 149
22	p-Coumaric acid	p-Cou_A	45.94	310	163	119
Flavonols						
23	Quercetin-3-O-galactoside	Que-3-gal	47.80	360	463	301
24	Quercetin-3-O-glucoside	Que-3-glu	48.14	360	463	397, 301
25	Quercetin-3-O-glucuronide	Que-3-glcn	48.49	355	477	301, 133
26	Isorhamnetin-3-O-glucoside	Iso-3-glu	52.32	356	477	315, 301, 300, 299
27	Quercetin	Que	63.38	355	301	151
Stilbenoids						
28	*cis*-Piceid	c-Pic	47.46		389	227
29	*trans*-Piceid	t-Pic	53.29		389	227
30	*cis*-Resveratrol	c-Res	59.4		227	185, 159
31	*trans*-Resveratrol	t-Res	64.34		227	185, 159

Table 4
Kallmet and Shesh i zi red wines according to vine zones and vintages (Mean ± Std, mg/L).

Peak	Compound	Kallmet						Shesh i zi (ShiZ)		
		Mirdita			Lezha			Kavaja		Mean ± Std
	Hydroxybenzoic ac. & flavanols	2019	2020	Mean ± Std	2019	2020	Mean ± Std	2019	2020	
1	Gallic acid	175.14 ± 4.78^{a}	204.95 ± 4.96^{b}	190.05 ± 17.67	245.28 ± 1.60	270.82 ± 0.82^{d}	258.05 ± 14.78	548.02 ± 1.72^{f}	500.59 ± 1.52^{e}	524.31 ± 27.42
2	3-O-galloylquinic acid	18.52 ± 2.89^{b}	23.59 ± 0.97^{c}	21.06 ± 3.42	13.77 ± 1.00^{a}	14.32 ± 0.09^{ab}	14.05 ± 0.66	157.45 ± 3.09^{e}	132.02 ± 0.81^{d}	144.73 ± 14.79
3	Protocatechuic ac-O-hexoside	4.18 ± 1.34^{a}	5.13 ± 0.09^{a}	4.65 ± 0.95	2.59 ± 3.26^{a}	5.14 ± 0.14^{a}	3.86 ± 2.39	35.46 ± 4.73^{b}	2.89 ± 0.08^{a}	19.18 ± 31.94
4	Gallocatechin	5.38 ± 0.01^{a}	6.92 ± 0.02^{ab}	6.15 ± 0.89	5.25 ± 0.08^{a}	8.10 ± 0.08^{ab}	6.68 ± 1.6	9.91 ± 3.23^{c}	5.36 ± 0.06^{a}	7.63 ± 3.22
5	Protocatechuic acid	6.84 ± 0.04^{d}	4.51 ± 0.02^{b}	5.68 ± 1.34	7.74 ± 0.02^{e}	6.53 ± 0.07^{c}	7.14 ± 0.70	12.30 ± 0.03^{f}	2.38 ± 0.02^{a}	7.34 ± 5.73
6	Epigallocatechin	1.09 ± 0.00^{a}	1.40 ± 0.01^{b}	1.24 ± 0.18	1.04 ± 0.01^{a}	1.66 ± 0.01^{c}	1.35 ± 0.35	12.42 ± 0.08^{e}	8.88 ± 0.06^{d}	10.65 ± 2.04
7	Procyanidin B3	7.67 ± 0.32^{b}	0.87 ± 0.08^{a}	4.27 ± 3.93	6.78 ± 0.01^{b}	26.16 ± 0.02^{c}	16.47 ± 11.19	136.30 ± 1.57^{e}	97.12 ± 0.08^{d}	116.71 ± 22.63
8	Procyanidin B1	4.51 ± 0.11^{b}	5.24 ± 0.28^{c}	4.88 ± 0.45	2.72 ± 0.00^{a}	16.51 ± 0.14^{f}	9.61 ± 7.96	12.77 ± 0.01^{d}	13.83 ± 0.12^{e}	13.30 ± 0.61
9	Catechin	30.46 ± 0.82^{cd}	25.01 ± 2.14^{bc}	27.74 ± 3.41	58.91 ± 0.30^{e}	41.29 ± 0.92^{d}	50.10 ± 10.19	16.32 ± 11.73^{ab}	10.52 ± 4.68^{a}	13.42 ± 8.02
10	Procyanidin B2	12.44 ± 0.07^{c}	11.91 ± 0.04^{b}	12.17 ± 0.31	19.19 ± 0.05^{d}	28.00 ± 0.29^{f}	23.60 ± 5.09	24.59 ± 0.07^{e}	4.75 ± 0.05^{a}	14.67 ± 11.46
11	Epicatechin	13.45 ± 1.49^{c}	10.05 ± 0.14^{b}	11.75 ± 2.15	17.66 ± 0.06^{d}	22.66 ± 0.34^{e}	20.16 ± 2.89	6.49 ± 0.02^{a}	6.54 ± 0.10^{a}	6.51 ± 0.07
12	Procyanidin B4	2.52 ± 0.02^{a}	3.08 ± 0.03^{b}	2.80 ± 0.32	6.38 ± 0.02^{d}	7.64 ± 0.05^{e}	7.01 ± 0.72	9.10 ± 0.03^{f}	5.67 ± 0.04^{c}	7.38 ± 1.98
13	Ethyl gallate	27.82 ± 1.40^{c}	18.43 ± 0.27^{b}	23.13 ± 5.48	34.15 ± 0.83^{d}	44.94 ± 0.18^{e}	39.54 ± 6.25	12.66 ± 0.07^{a}	11.63 ± 0.04^{a}	12.14 ± 0.60
	©Hydroxybenzoic ac. & flavanols	**310.01 ± 5.23^{a}**	**321.10 ± 8.23^{a}**	**315.55 ± 8.52**	**421.46 ± 5.09^{b}**	**493.77 ± 2.38^{c}**	**457.62 ± 41.87**	**993.78 ± 23.23^{e}**	**802.18 ± 6.92^{d}**	**897.98 ± 111.50**
Phenolic acids										
14	2-S-glutathionyl-caffeoyltartaric ac.	2.28 ± 0.54^{ab}	1.80 ± 0.09^{a}	2.04 ± 0.42	1.34 ± 0.19^{a}	2.88 ± 0.10^{bc}	2.11 ± 0.90	4.80 ± 0.69^{d}	3.69 ± 0.13^{c}	4.24 ± 0.76
15	*cis*-Caftaric acid	1.00 ± 0.45^{a}	0.75 ± 0.23^{a}	0.88 ± 0.32	1.02 ± 0.08^{a}	0.86 ± 0.18^{a}	0.94 ± 0.15	0.61 ± 0.05^{a}	1.23 ± 0.26^{a}	0.92 ± 0.39
16	*trans*-Caftaric acid	34.77 ± 1.99^{d}	36.00 ± 2.79^{d}	35.38 ± 2.10	19.82 ± 0.41^{a}	20.32 ± 0.48^{a}	20.07 ± 0.46	28.28 ± 0.59^{c}	23.99 ± 0.56^{b}	26.13 ± 2.52
17	*cis*-Coutaric acid	2.04 ± 0.16^{b}	1.54 ± 0.02^{a}	1.79 ± 0.31	2.54 ± 0.35^{c}	1.71 ± 0.11^{ab}	2.13 ± 0.52	1.25 ± 0.17^{a}	1.56 ± 0.10^{a}	1.41 ± 0.21
18	*trans*-Coutaric acid	7.44 ± 0.02^{c}	7.60 ± 1.05^{c}	7.52 ± 0.61	3.84 ± 0.13^{b}	3.99 ± 0.08^{b}	3.91 ± 0.12	3.71 ± 0.12^{b}	2.48 ± 0.05^{a}	3.10 ± 0.71
19	*cis*-Fertaric acid	3.27 ± 0.02^{e}	2.77 ± 0.00^{d}	3.02 ± 0.29	2.31 ± 0.02^{c}	2.12 ± 0.00^{b}	2.21 ± 0.11	–	0.50 ± 0.00^{a}	0.25 ± 0.29
20	*trans*-Caffeic acid	3.32 ± 0.00^{d}	3.10 ± 0.01^{c}	3.21 ± 0.13	3.58 ± 0.02^{e}	3.14 ± 0.04^{c}	3.36 ± 0.26	0.09 ± 0.00^{a}	0.50 ± 0.01^{b}	0.30 ± 0.24
21	*trans*-Fertaric acid	2.69 ± 0.00^{e}	2.45 ± 0.00^{c}	2.57 ± 0.14	3.15 ± 0.00^{f}	2.38 ± 0.01^{b}	2.77 ± 0.44	2.59 ± 0.00^{d}	1.79 ± 0.01^{a}	2.19 ± 0.46
22	p-Coumaric acid	1.48 ± 0.01^{e}	1.46 ± 0.00^{d}	1.47 ± 0.01	1.28 ± 0.00^{c}	3.13 ± 0.02^{f}	2.20 ± 1.07	0.41 ± 0.00^{b}	0.26 ± 0.00^{a}	0.33 ± 0.08
	Total Phenolic acids	**58.30 ± 2.78^{c}**	**57.48 ± 3.95^{c}**	**57.89 ± 2.83**	**38.88 ± 0.21^{ab}**	**40.54 ± 0.94^{ab}**	**39.71 ± 1.11**	**41.74 ± 1.03^{b}**	**36.01 ± 1.10^{a}**	**38.87 ± 3.42**
Flavonols										
23	Quercetin-3-O-galactoside	1.09 ± 0.01^{e}	0.83 ± 0.03^{d}	0.96 ± 0.15	0.21 ± 0.00^{a}	1.62 ± 0.07^{f}	0.91 ± 0.82	0.50 ± 0.01^{c}	0.39 ± 0.02^{b}	0.44 ± 0.07
24	Quercetin-3-O-glucoside	0.93 ± 0.00^{f}	0.73 ± 0.00^{e}	0.83 ± 0.11	0.25 ± 0.00^{a}	0.27 ± 0.00^{b}	0.26 ± 0.01	0.35 ± 0.00^{c}	0.40 ± 0.00^{d}	0.38 ± 0.03
25	Quercetin-3-O-glucuronide	3.01 ± 0.01^{d}	3.02 ± 0.02^{d}	3.01 ± 0.01	0.56 ± 0.00^{a}	0.56 ± 0.00^{a}	0.56 ± 0.00	0.64 ± 0.00^{b}	1.62 ± 0.00^{c}	1.13 ± 0.56
26	Isorhamnetin-3-O-glucoside	0.31 ± 0.00^{d}	0.39 ± 0.01^{e}	0.35 ± 0.04	0.17 ± 0.00^{b}	0.08 ± 0.00^{a}	0.13 ± 0.06	0.08 ± 0.00^{a}	0.20 ± 0.00^{c}	0.14 ± 0.07
27	Quercetin	0.66 ± 0.02^{d}	0.44 ± 0.01^{c}	0.55 ± 0.13	0.20 ± 0.00^{a}	0.83 ± 0.04^{e}	0.52 ± 0.36	0.25 ± 0.01^{b}	0.19 ± 0.01^{a}	0.22 ± 0.03

(*continued on next page*)

Table 4 (*continued*)

Peak	Compound	Kallmet						Shesh i zi (ShiZ)		
		Mirdita			Lezha			Kavaja		Mean ± Std
	Hydroxybenzoic ac. & flavanols	2019	2020	Mean ± Std	2019	2020	Mean ± Std	2019	2020	
	Total Flavonols	**6.00 ± 0.02^{f}**	**5.40 ± 0.08^{e}**	**5.70 ± 0.35**	**1.39 ± 0.01^{a}**	**3.36 ± 0.11^{d}**	**2.37 ± 1.14**	**1.82 ± 0.01^{b}**	**2.81 ± 0.03^{c}**	**2.31 ± 0.57**
Stilbenoids										
28	*cis*-Piceid	0.31 ± 0.00^{a}	0.43 ± 0.00^{b}	0.37 ± 0.07	0.31 ± 0.01^{a}	0.76 ± 0.01^{c}	0.54 ± 0.26	–	–	0.00 ± 0.00
29	*trans*-Piceid	0.45 ± 0.00^{c}	0.48 ± 0.00^{d}	0.46 ± 0.02	0.28 ± 0.00^{b}	0.78 ± 0.01^{e}	0.53 ± 0.29	0.03 ± 0.00^{a}	0.04 ± 0.00^{a}	0.04 ± 0.01
30	*cis*-Resveratrol	0.01 ± 0.00^{a}	0.01 ± 0.00^{a}	0.01 ± 0.00	0.01 ± 0.00^{a}	–	0.01 ± 0.00	0.01 ± 0.00^{a}	–	0.01 ± 0.01
31	*trans*-Resveratrol	0.09 ± 0.00^{d}	0.12 ± 0.00^{e}	0.11 ± 0.01	0.08 ± 0.00^{c}	0.05 ± 0.00^{b}	0.06 ± 0.02	0.14 ± 0.00^{f}	0.04 ± 0.00^{a}	0.09 ± 0.06
	Total Stilbenoids	**0.87 ± 0.01^{d}**	**1.04 ± 0.00^{e}**	**0.95 ± 0.10**	**0.68 ± 0.01^{c}**	**1.59 ± 0.02^{f}**	**$1.13 \pm$** 0.53	**0.19 ± 0.00^{b}**	**0.09 ± 0.00^{a}**	**0.14 ± 0.06**
	Total Phenolics	**375.18 ± 2.46^{a}**	**385.11 ± 4.36^{b}**	**380.10 ± 6.38**	**462.41 ± 5.30^{c}**	**539.26 ± 3.24^{d}**	**500.83** $\pm$ 44.51	**1037.53 ± 24.28^{f}**	**841.08 ± 7.99^{e}**	**939.31 ± 114.38**

Different letters (a-f) in the same row show statistical differences ($p < 0.05$).

2.2. Wine sampling

The study examined wine samples supplied from local wineries belonging to two vintages, 2019 and 2020, stored in their original bottles in a cool, dark environment at 4 °C until analysis. Red wines, Kallmet and Shesh I zi, and white wines, Shesh I bardhë and Cerruje, were considered distinguished native grape varieties (Table 1). Based on the Köppen and Geiger climate classification system, the Kavaja, Lezha, and Tirana counties are categorized as *Csa*. In contrast, Mati and Mirdita counties fall under the *Cfa* category [33], as shown in Table 2.

2.3. Liquid chromatography-tandem mass spectrometry analysis

High-performance liquid chromatography equipment (Agilent 1260 HPLC; Agilent Tech., Palo Alto, California, USA) and a diode array detector (G1351D 1260 DAD VL) were used to conduct the analysis. The analytical method developed by Kelebek and coauthors employing LC-DAD-ESI-MS/MS in negative ionization mode (Table 3) was applied to analyze the phenolic compounds [35,36]. Previously, wine samples were filtered with a filter membrane of 0.45-μm pore size and injected into the LC system. A binary pump (G1312 B, 1260 Bin pump), a degasser (G1322 A, 1260 Degasser), and an autosampler (G1367 E, 1260 HIP ALS) comprised the working system. A reverse-phase C-18 column (Phenomenex Luna) with dimensions of 5 μm and 4.6 × 250 mm (Torrance, California, USA) was employed. Two mobile phases were utilized as solvent A (water/formic acid; 99:1 v/v) and solvent B (acetonitrile/solvent A; 60:40 v/v). The Agilent 6430 LC-MS/MS spectrometer was used to analyze the compounds with an ESI source. ESI-MS detection was carried out in negative ion mode under optimized conditions. Quantification of the compounds was achieved using the external standard method with authentic standards. The phenolic contents were calculated based on the method available by Sonmezdag et al. (2019) [37]. The calibration curves of the standard phenolic compounds, whose compound names and CAS numbers were given in the chemicals section, were utilized to determine the amount of each phenolic compound. However, since it was infeasible to provide a standard substance for all compounds, calibration curves prepared with structurally comparable chemicals were used to quantify them. The calibration procedure to structurally similar chemical compounds was employed in the case of the reference compound absence by considering the molecular weight correction factor. Since Fertaric acid is similar to ferulic acid, kaempferol-3-O-glucoside to kaempferol, quercetin-3-O-galactoside to quercetin, and Protocatechuic acid-O-hexoside to protocatechuic acid, the calibration procedure for structurally similar chemical compounds was applied to these compounds. Commercial standard concentrations generally found in extracts (nearly 1–100 mg/L) and regression values (r2) greater than 0.995 were applied to obtain standard curves. The limit of quantification (LOQ) and limit of detection (LOD) were computed by utilizing S/N ratio values (signal-to-noise) of 10 and 3, respectively.

2.4. Wine phenolics screening

Thirty-one phenolic compounds, flavonoids, and nonflavonoids were identified and quantified by liquid chromatography with diode-array detection coupled to electrospray ionization tandem mass spectrometry (LC–DAD–ESI/MS^{n}). Method specification and compound retention times, specific UV absorption, molecular ion, and characteristic pattern of fragmentation are presented in Table 3. They are subgrouped into 'hydroxybenzoic acids and flavanols', 'phenolic acids,' 'Flavonols', and 'stilbenoids' (Tables 4 and 5). Mean values and standard deviation of three replicates to specific wine phenolics, as well as total content according to subgroup, region, and

Table 5
Phenolic compounds in *Shib* and *Cerruje* wines, according to vine zones and vintage (Mean ± Stdev, mg/L).

Peak	Compounds	Shesh i bardhë (ShiB)					Cerruje
		Kavaja			Tirana	Mean ± Stdev	Mati
	Hydroxybenzoic ac. & Flavanols	2019	2020	Mean ± Stdev	2020		2020
1	Gallic acid	221.44 ± 5.36[c]	215.82 ± 14.20[c]	218.63 ± 1.30	182.97 ± 1.99[b]	206.74 ± 19.80	50.77 ± 0.26[a]
2	3-O-galloyl quinic acid	20.41 ± 0.84[b]	16.54 ± 2.58[b]	18.47 ± 2.31	16.82 ± 0.15[b]	17.92 ± 2.28	1.35 ± 0.01[a]
3	Protocatechuic acid-O-hexoside	3.13 ± 0.05[a]	4.00 ± 1.28[ab]	3.56 ± 0.64	5.39 ± 0.26[b]	4.17 ± 1.18	4.41 ± 0.07[ab]
4	Gallocatechin	12.82 ± 0.05[c]	12.22 ± 0.03[b]	12.52 ± 0.40	7.23 ± 0.05[a]	10.76 ± 2.74	–
5	Protocatechuic acid	12.24 ± 0.05[c]	6.59 ± 0.04[b]	9.42 ± 3.97	19.12 ± 0.09[d]	12.65 ± 5.61	5.36 ± 0.25[a]
6	Epigallocatechin	20.96 ± 0.11[c]	18.44 ± 0.02[b]	19.70 ± 1.73	12.83 ± 0.02[a]	17.41 ± 3.72	–
7	Procyanidin B3	208.83 ± 6.42[c]	215.23 ± 8.92[c]	212.03 ± 7.73	142.90 ± 5.48[b]	188.99 ± 36.23	2.13 ± 0.04[a]
8	Procyanidin B1	16.39 ± 0.86[a]	21.85 ± 0.51[b]	19.12 ± 4.29	17.44 ± 0.16[a]	18.56 ± 2.63	–
9	Catechin	26.13 ± 2.24[b]	25.89 ± 0.70[b]	26.01 ± 0.95	54.76 ± 0.24[c]	35.59 ± 14.89	6.53 ± 0.21[a]
10	Procyanidin B2	24.48 ± 0.09[c]	13.19 ± 0.08[b]	18.84 ± 7.94	38.24 ± 0.18[d]	25.31 ± 11.22	3.43 ± 0.03[a]
11	Epicatechin	17.48 ± 0.24[b]	14.86 ± 1.65[b]	16.17 ± 1.97	29.15 ± 2.31[c]	20.50 ± 6.92	3.19 ± 0.06[a]
12	Procyanidin B4	5.99 ± 0.06[a]	7.36 ± 0.07[b]	6.68 ± 0.99	26.84 ± 0.09[c]	13.40 ± 10.43	–
13	Ethyl gallate	34.97 ± 0.28[c]	26.25 ± 0.84[b]	30.61 ± 6.03	54.98 ± 0.63[d]	38.73 ± 13.18	6.07 ± 0.06[a]
	©Hydroxybenzoic ac. & flavanols	**625.27 ± 16.16[b]**	**598.23 ± 6.52[b]**	**611.75 ± 11.04**	**608.68 ± 9.87[b]**	**610.73 ± 15.13**	**83.23 ± 0.86[a]**
Phenolic acids							
14	2-S-glutathionyl-caffeoyl Tartaric acid	1.97 ± 0.10[b]	2.03 ± 0.48[b]	2.00 ± 0.09	3.67 ± 0.24[c]	2.56 ± 0.90	0.03 ± 0.01[a]
15	*cis*-Caftaric acid	0.89 ± 0.27[a]	1.06 ± 0.47[a]	0.97 ± 0.02	0.96 ± 0.08[a]	0.97 ± 0.26	0.73 ± 0.01[a]
16	*trans*-Caftaric acid	43.37 ± 3.36[b]	43.03 ± 2.47[b]	43.20 ± 1.92	23.42 ± 0.28[a]	36.61 ± 10.38	20.93 ± 0.62[a]
17	*cis*-Coutaric acid	1.00 ± 0.01[a]	1.42 ± 0.11[b]	1.21 ± 0.30	2.56 ± 0.27[c]	1.66 ± 0.73	2.68 ± 0.01[c]
18	*trans*-Coutaric acid	5.98 ± 0.82[b]	6.84 ± 0.02[bc]	6.41 ± 0.20	7.43 ± 0.03[c]	6.75 ± 0.75	4.55 ± 0.01[a]
19	*cis*-Fertaric acid	5.42 ± 0.00[d]	0.51 ± 0.00[a]	2.97 ± 3.47	0.54 ± 0.00[b]	2.16 ± 2.53	0.64 ± 0.01[c]
20	*trans*-Caffeic acid	3.15 ± 0.01[c]	3.39 ± 0.00[d]	3.27 ± 0.17	2.03 ± 0.00[b]	2.85 ± 0.65	0.51 ± 0.01[a]
21	*trans*-Fertaric acid	4.90 ± 0.00[d]	4.46 ± 0.00[c]	4.68 ± 0.31	2.51 ± 0.00[a]	3.96 ± 1.14	2.87 ± 0.01[b]
22	*p*-Coumaric acid	1.38 ± 0.00[c]	1.31 ± 0.01[b]	1.34 ± 0.05	1.72 ± 0.01[d]	1.47 ± 0.20	0.40 ± 0.01[a]
	Total Phenolic acids	**68.05 ± 4.33[c]**	**64.05 ± 3.29[c]**	**66.05 ± 5.00**	**44.84 ± 0.89[b]**	**58.98 ± 11.37**	**33.34 ± 0.64[a]**
Flavonols							
23	Quercetin-3-O-galactoside	0.63 ± 0.02[c]	0.32 ± 0.00[a]	0.48 ± 0.21	1.60 ± 0.00[d]	0.85 ± 0.60	0.39 ± 0.01[b]
24	Quercetin-3-O-glucoside	0.91 ± 0.01[b]	1.51 ± 0.00[c]	1.21 ± 0.43	6.21 ± 0.01[d]	2.88 ± 2.60	0.34 ± 0.01[a]
25	Quercetin-3-O-glucuronide	3.27 ± 0.02[b]	3.45 ± 0.01[c]	3.36 ± 0.14	10.89 ± 0.01[d]	5.87 ± 3.89	1.21 ± 0.01[a]
26	Isorhamnetin-3-O-glucoside	0.42 ± 0.01[b]	0.87 ± 0.00[c]	0.64 ± 0.32	2.20 ± 0.01[d]	1.16 ± 0.83	0.13 ± 0.00[a]
27	Quercetin	0.32 ± 0.01[b]	0.36 ± 0.01[b]	0.34 ± 0.03	2.49 ± 0.02[c]	1.06 ± 1.11	0.23 ± 0.01[a]
	Total Flavonols	**5.55 ± 0.08[b]**	**6.51 ± 0.02[c]**	**6.03 ± 0.72**	**23.40 ± 0.05[d]**	**11.82 ± 8.98**	**2.31 ± 0.05[a]**
Stilbenoids							
28	***cis*-Piceid**	**0.07 ± 0.00[a]**	**0.06 ± 0.00[a]**	**0.06 ± 0.00**	**0.08 ± 0.00[a]**	**0.07 ± 0.01**	**-**
29	*trans*-Piceid	0.70 ± 0.00[a]	0.68 ± 0.01[a]	0.69 ± 0.01	0.88 ± 0.01[a]	0.75 ± 0.10	–
30	*cis*-Resveratrol	0.01 ± 0.00[a]	0.01 ± 0.00[a]	0.01 ± 0.00	0.01 ± 0.00[a]	0.01 ± 0.00	–
31	*trans*-Resveratrol	0.12 ± 0.00[a]	0.10 ± 0.00[a]	0.11 ± 0.01	0.07 ± 0.00[a]	0.10 ± 0.02	–
	Total Stilbenoids	**0.90 ± 0.00[a]**	**0.86 ± 0.01[a]**	**0.88 ± 0.03**	**1.04 ± 0.01[a]**	**0.93 ± 0.08**	**-**
	Total amount	**699.78 ± 11.91[c]**	**669.65 ± 3.24[b]**	**684.71 ± 15.35**	**677.96 ± 9.01[b]**	**682.46 ± 15.50**	**118.88 ± 0.26[a]**

Different letters (a-d) in the same row show statistical differences ($p < 0.05$).

vintage, are elaborated in this study.

2.5. Statistical analysis

The results obtained in the study were compared with the international literature and subjected to one-way ANOVA analysis using the SPSS statistics program (version 22, SPSS Inc., Chicago, IL, USA). The differences between the means were compared using Duncan's comparison tests. Principal component analysis (PCA) was conducted by Xlstate 2023 software according to vintage, wine region, and grape variety. Mono-variety comparisons according to wine color are discussed in the study with the results were evaluated in a biplot.

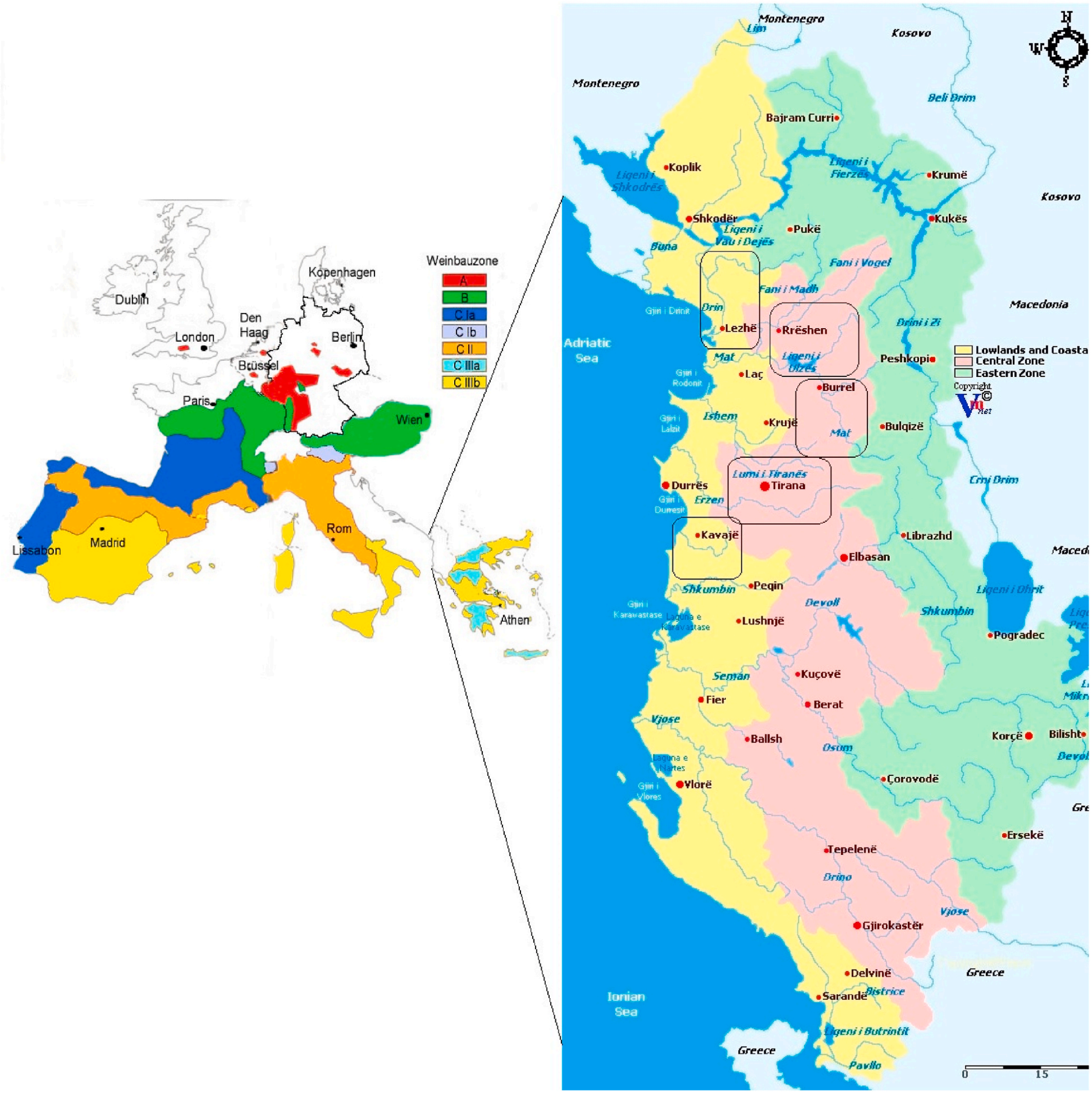

Fig. 1. Albanian wine regions according to the Wineandvinesearch and European wine region classification [39].

3. Results and DISCUSSIONS

3.1. Albanian climate regions and vine zones

Albania has diverse climatic zones due to its mountainous geography, which runs north-south. The updated Köppen and Geiger climate classification system categorizes the country's climate into CSA and CFA, but some regions own microclimate conditions. The wine production regions are organized based on administrative units and districts. In contrast, according to its climate characteristics and EU regulation on wine-growing regions, as compared to the case of the country, wine cultivation and wine production are classified into three zones [38]. The first zone (C IIIa) covers lowland and coastal areas along the Adriatic and Ionian seas, with altitudes up to 400 m above sea level (asl). The second zone (C IIIb) includes pre-mountainous regions between 400 and 800 m. The third zone (C II) comprises more mountainous eastern areas with elevations over 800 m. This study analyzed Albanian mono-variety wines made from local grape varieties Kallmet, Shesh i zi, Shesh i bardhë, and Cerruje in two consecutive vintages, 2019 and 2020. The coastal vine zone (CIIIa) includes Kavaja, Tirana, and Lezha counties. Meanwhile, Mirdita and Mati belong to the inland vine zone, CIIIb (Fig. 1).

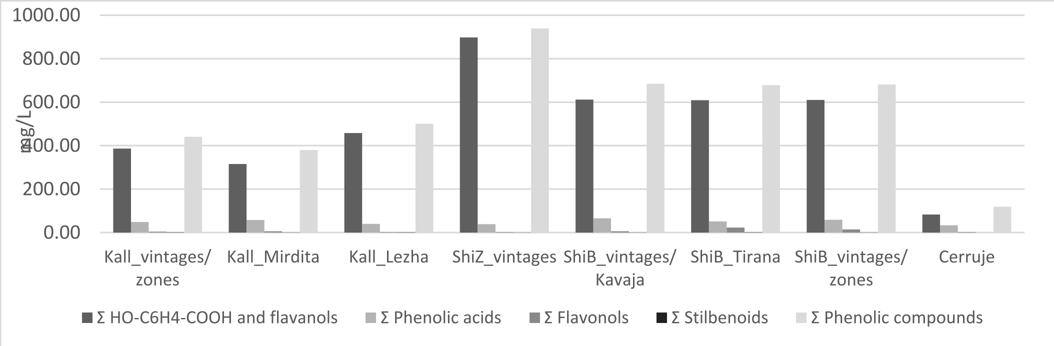

Fig. 2. Phenolic classes amount according to grape cultivars, vintage, and wine zones. (Kall_vintage/zone: Kallmet wine mean value for vintage and two vintages).

Kavaja County is characterized by a mild, warm, and temperate climate, with over 3000 h of sunshine yearly (as shown in Table 1). The area is dominated by vineyards growing ShiZ and ShiB grape varieties, situated on hilly terrain up to 200 m above sea level. Meanwhile, the Kallmet variety is commonly found in Northwest regions, including Lezha and Mirdita counties [31]. Among the earliest indigenous grape varieties, Kallmet has been a popular red wine grape variety. Originating in the regions actually the north-west Albania, it has grown in Hungary, Croatia, Austria, and Romania since the Roman Empire. Kallmet cv. produce a red grape berry. When fully ripe, the fruit is medium in size (about 10–12 mm in diameter), round or elliptical. Its skin is a reddish-purple hue and a thick layer of wax, and the pulp is solid and juicy and has a nice mix of color and flavor. it grows on light, porous soils with good drainage [30]. The Cerruje variety is typically grown in the IIIb vine zone in northern Albania, where the climate provides 2500–3000 h of sunshine per year.

3.2. Total phenolics in red and white wines

Understanding the composition and levels of phenolic compounds in wine is essential for assessing its quality and authenticity. The phenolic content in mono-variety red wines, Kallmet and Shiz, and white wines, Shib and Cerruje, was evaluated as total phenolic compounds (TPC). The *Kallmet* red wines were studied based on wine zones, Lezha and Mirdita, and 2019 and 2020 vintages. Kallmet wines for the 2020 vintage revealed the highest levels, while according to wine zones, the highest TPC was found in Lezha county Kallmet wines (539.47 mg/L) versus 385.11 mg/L, with those from Mirdita county. The influence of vintage was significant, with a 2020 vintage of 462.41 mg/L, compared with the 2019 vintage of 539.47 mg/L in the case of Lezha County. Central Albania, including the Tirana district, is classified in the *Csa* climatic zone. Red wines from the *Shiz* variety, originating in this area, revealed TPC values (939.31 mg/L) much higher than *Kallmet* wine, 539.26 mg/L. TPC belonging to wines from the 2019 vintage resulted in a higher amount, 1037.53 mg/L, compared with the 2020 vintage (841.08 mg/L), indicating the influence of vintage on ShiZ red wines. TPC in *Shib* white wines (682.46 mg/L) was much higher than that in *Cerruje* white wine (118.88 mg/L) (Table 5, and Fig. 2). It is concluded that ShiZ red wine had the highest TPC levels in the studied Albanian wines.

3.3. Phenolic acids

The 'hydroxybenzoic acids and flavanols' cluster constitutes the leading group in both studied red wines, in *Kallmet* wine, accounting for up to 87.8 % of total phenolic compounds. At the same time, a difference between Mirdita (83.0 %) and Lezha (91.4 %) wine zones was observed in this cluster, mainly due to higher gallic acid amounts. It was found that hydroxybenzoic acids constitute 64 % of TPC in *Kallmet* wine, with no significant difference between the two vine zones. Gallic acid was found in up to 47.4 % of the total phenolic compounds from both regions and vintage, comprising the most abundant phenolic compound. Gallic acid (GA) is a hydrolysis product of condensed and hydrolyzable tannins, chemically classified as gallate esters [40]. A significant difference in the Kallmet wines was found in GA (LOD-LOQ: 1.89–6.30 μg/mL, R^2: 0.995), mean values among Lezha (258.05 ± 14.78 mg/L) and Mirdita (190.05 ± 17.67 mg/L) vine zones. Catechin (LOD-LOQ: 0.11–0.37 μg/mL, R^2: 0.995) was identified as the second compound contributing to this cluster, in higher amounts in Kallmet wines from the Lezha vine zone (50.10 ± 10.19 mg/L) compared with Mirdita (27.74 ± 3.41 mg/L). Ethyl gallate ester (31.33 ± 10.33 mg/L) was the third phenolic compound among hydroxybenzoic acids, with significant differences among the two vine zones, Lezha (39.54 ± 6.25 mg/L) versus Mirdita (23.13 ± 5.48 mg/L) referring mean values from two vintages, respectively ($p < 0.05$).

Regarding *Shesh i zi* red wine, the 'hydroxybenzoic acids and flavan-3-ols' cluster reached up to 95.6 % of total phenolic compounds from the 2019 vintage. The wine quality and authenticity assessment was evaluated by estimating hydroxybenzoic acids (containing seven carbon atoms) and hydroxycinnamic acids (nine carbon atoms, phenylpropanoid derivatives) since these families constitute primary phenolic acids. The hydroxybenzoic acid group constituted the highest level (75.51 %) of TPC, and the highest value was found compared to the other wine phenolics in this study. The difference between the two vintages, 993.78 ± 23.23 mg/L and 802.12 ± 6.92 mg/L, was observed with the 2019 and 2020 vintages, respectively. There is a similarity among Kallmet and Shiz red wines regarding the phenolic compounds present in highest levels, with gallic acid (55.8 %) to the total phenolics for both vintages, mean value (524.31 ± 27.42 mg/L). In contrast, the second phenolic compound from this group was the 3-O-galloyl quinic acid (144.73 ± 14.79 mg/L) found in both vintages, values much higher than their level in *Kallmet* wine (17.55 mg/L).

Hydroxybenzoic acids in *Shesh i bardhë* white wine were found to have the lowest percentage (26.99 %) compared with other analyzed wines in this study (Tables 4 and 5). The GA was found at the highest level in both vintages compared with other phenolic compounds, 206.74 ± 19.80 mg/L. Also, the GA content in ShiB wines from Kavaja county was higher than in Tirana county; the *Cerruje* white wine presented lower phenolic compounds compared with the ShiB white wine.

Essential nonflavonoids in wine include hydroxycinnamic acid, stilbenoids, and hydroxybenzoic acid. The primary structural component of the group is (E)-3-phenyl prop-2-enoic acid, more commonly known as cinnamic acid. According to Waterhouse, Sacks, and Jeffery (2016) [40], tartaric acid esters of caffeic, coumaric, and ferulic acids are mainly extracted from grape berries. In the analyzed wines phenolic acids were found as the second group. Among the phenolic acids found in Kallmet red wine (11.08 %), Mirdita has a significantly higher concentration (15.23 %) than Lezha (7.93 %), and this is true for both vintages. In both vintages of Kallmet wines, *trans*-caftaric acid (LOD-LOQ: 0.25–76 μg/mL, R^2: 0.999) was the most significant phenolic acid, with a concentration of 27.73 ± 8.31 mg/L. There were substantial variances between Lezha (20.07 ± 0.46 mg/L) and Mirdita (35.38 ± 2.10 mg/L), but there was no difference between the vintages in either county. The second phenolic acid, *trans*-coutaric acid (LOD-LOQ: 0.049–0.14 μg/mL, R2: 0.995), has the same trend for both areas as *trans*-caftaric acid (5.72 ± 1.97 mg/L). The *trans*-caftaric acid (27.73 ± 8.31 mg/L) was found in higher concentrations compared to the *cis*-caftaric acid (0.91 ± 0.24 mg/L), among the tartaric acid esters of the phenolic acids. There is a similar pattern in the *trans*-caftaric acid amounts in analyzed red wines with data presented in a review paper by Clarke et al. (2022) [41]. Other tartaric acid esters, such as p-coumaric acid (1.84 ± 0.80 mg/L) and *trans*-coutaric acid (5.72 ± 1.97 mg/L), were significantly higher than nonesterified phenolic acids.

Similarly, phenolic acids (4.1 %) formed the second group in the ShiZ red wines. The *trans*-caftaric acid revealed the highest concentration 26.13 ± 2.52 mg/L, accounted for 67.22 % of the total phenolic acids group. *trans*-coutaric acid and *trans*-fertaric acid, with concentrations of 3.10 ± 0.71 mg/L and 2.19 ± 0.46 mg/L, respectively, followed. These values are comparable with data published in the review paper from Clark et al. (2022) [41]. The phenolic acid group (48.80 ± 9.92 mg/L), in Kallmet red wine and 38.87 ± 3.42 mg/L, in ShiZ red wine, which is larger than their respective contributions to the total quantity of phenolic compounds.

The second group of phenolic compounds detected in white wines from Shesh i bardhë cv. (6.61 %) was phenolic acids (58.98 ± 11.37 mg/L), followed by flavonols (3.45 %) and stilbenoids (0.15 %). The two vine zones, Kavaja (66.05 ± 5.00 mg/L) and Tirana (44.84 ± 0.89 mg/L) showed a significant disparity in total phenolic acids. Shib white wines had the highest quantities of *trans*-caftaric acid, measured at 36.61 ± 10.38 mg/L. There were significant variations throughout the vine zones, with the mean values in Kavaja and Tirana being 43.20 ± 1.92 mg/L and 23.42 ± 0.28 mg/L, respectively. When compared with ShiB white wines, phenolic acids comprised in Cerruje white wine account for 28.04 % of the total, much higher than the percentage of phenolic acids in the other wines in this research. These values are comparable with caftaric acid mean values in white wines (36.76 mg/L) [42], comparable to Silvaner (40.2 mg/L), and higher compared to Rieslaner (28.4 mg/L), Müller-Thurgau (19.9 mg/L) or Traminer (21.1 mg/L) German white wines [43].

3.4. Procyanidins and flavan-3-ol monomers

Tannins are flavonoids that comprise two different classes: hydrolyzable tannins comprise gallotannins (gallic acid derivatives] together with ellagitannins (ellagic acid derivatives), and condensed tannins, called proanthocyanidins, indicating flavan-3-ol oligomer structures, or polymers. Their presence influences wine's taste, bitterness, astringency, and color [5].

In Kallmet red wines, catechin (LOD-LOQ: 0.11–0.37 μg/mL, R^2: 0.995), was found as the second phenolic component in the cluster of hydroxybenzoic acid and flavanols (38.92 ± 13.87 mg/L). The mean values of this compound differed significantly between the vine zones of Mirdita (27.74 ± 3.41 mg/L) and Lezha (50.10 ± 10.19 mg/L). The calculated mean concentration of procyanidins B3, B1, B2, and B4 in Kallmet wine was 40.41 ± 25.21 mg/L. Mirdita and Lezha, two vine zones, had 2.5 times varying concentrations of 24.12 and 56.69 mg/L, respectively.

The total phenolic acids in Shesh i zi red wine were influenced mainly by GA and two other phenolic compounds, 3-O-galloyl quinic acid and procyanidin B3. Regarding procyanidins, the average value was 152.07 ± 36.69 mg/L for B3, B1, B2, and B4. At the same time, 2019 had a variation of 182.76 ± 1.68 mg/L, while 2020 had a variation of 121.37 mg/L. Compared to Kallmet wine, which had a catechin level of 38.92 ± 13.87 mg/L, ShiZ red wine had a lower catechin content of 13.42 ± 8.02 mg/L.

The second phenolic ingredient in Shesh i bardhë white wines was procyanidin B3, with a concentration of 188.99 ± 36.23 mg/L. Shib wines from Kavaja had a concentration of 212.03 ± 7.73 mg/L, while those from Tirana had a concentration of 142.90 ± 5.48 mg/L. These wines had a mean value of 246.25 ± 14.75 mg/L for procyanidins B3, B1, B2, and B4. On the other hand, the Cerruje white wine had significantly lower levels of these chemicals, 5.56 ± 0.06 mg/L, when added together. Cerruje wine has the highest concentration of procyanidin B2, measuring 3.43 ± 0.03 mg/L.

The results of the study on the flavan-3-ol monomers, epicatechin (LOD- LOQ:0.13–0.47 μg/mL, R^2: 0.995), and catechin (LOD-LOQ: 0.11–0.37 μg/mL, R^2: 0.995), in red and white wines show that the average catechin levels were 38.92 ± 13.87 mg/L in Kallmet, with the highest recorded in Lezha county at 50.10 ± 10.19 mg/L. The amounts of catechin in the Shesh i zi wines were significantly lower, at 13.42 ± 8.02 mg/L. Epicatechin levels followed a similar trend, reaching their peak in the Lezha grape zone (20.16 ± 2.89 mg/L) and the highest average levels in Kallmet wines (15.95 ± 5.08 mg/L). In comparison to Kallmet wines, the concentrations of catechin (13.42 ± 8.02 mg/L) and epicatechin (6.51 ± 0.07 mg/L) found in Shiz red wines were much lower. No change was noticed when looking at the findings of Shib wine based on vintage. On the other hand, the total catechin and epicatechin levels were significantly different in Kavaja county (40.75 ± 0.95 mg/L) and Tirana (83.92 ± 2.07 mg/L). Catechin (6.53 ± 0.21 mg/L) and epicatechin (3.19 ± 0.06 mg/L) were the only flavan-3-ol monomers found in Cerruje white wines, which had low quantities. Of all the flavan-3-ols, including proanthocyanidins in all their forms, 64.92 % were catechin and epicatechin. Their total in ShiB white wines was similarly low at 25.47 percent. Kallmet wines had a low proportion of proanthocyanidin dimers to total flavan-3-ols; the 2020 vintage from Lezha County had the greatest proportion, at 51.52 %. But in Shiz red wine, they hit a peak, with 80.38 percent coming from the 2019 harvest. According to Jordao and Ricardo da Silva (2019) [9], the amounts of proanthocyanidin and flavonoids in grape berries can be influenced by various variables, including climate, geography, and vintage.

Comparison of flavan-3-ol monomers in *Kallmet* wines, catechin (38.92 ± 13.87 mg/L), and epicatechin (15.95 ± 5.08 mg/L), with wines from international grape cultivars, such as Cabernet Sauvignon, Syrah [44], Merlot [45], and Nero D'Avola [46], indicate that Kallmet wine presented similar values with Cabernet Sauvignon, catechin (38.6 ± 8.9 mg/L), epicatechin (16.7 ± 3.9 mg/L), meanwhile compared to Syrah wines, lower values were found for both catechin (43.0 ± 8.3 mg/L) and epicatechin (51.9 ± 22.6 mg/L) [44]. Compared with Merlot wines, higher catechin amounts (27 mg/L) and similar values referring to epicatechin (19 mg/L) were analyzed [45]. Catechin and epicatechin in the Kallmet wines presented a reverse contribution, respectively, compared with Nero D'Avola wine, catechin (25 mg/L), and epicatechin (32 mg/L) [46].

Shesh i zi red wines were characterized by lower levels of catechin (13.42 ± 8.02 mg/L) and epicatechin (6.51 ± 0.07 mg/L) compared to Merlot wines from Spain [45], Nero D'Avola wine from Sicily [46], and Cabernet Sauvignon, and Syrah wines [44]. Compared with Greek red wines from local cultivars were found different patterns for flavanols catechin (30–40 mg/L), and epicatechin (20–45 mg/L) [47], the Albanian wines were characterized by higher amounts of catechin compared to epicatechin.

The flavan-3-ol monomers in *Shib* white wines, catechin (35.59 ± 14.89 mg/L) and epicatechin (20.50 ± 6.92 mg/L), were found at higher levels wine compared with catechin amount in white wines from Croatia Traminer (1.3 mg/L) and Peljesac (4.1 mg/L), with the second belonging to the coastal region of Dalmatia, geographically close to regions in our study [48], Czech white wines, respectively catechin (4.68–17.69 mg/L) and epicatechin (3.16–12.62 mg/L) [42] but were considerably different from other German white wine, such as catechin amounts in Reislaner, (10.9 mg/L), Silvaner (26.3 mg/L), and epicatechin Müller-Thurgau (12.3 mg/L) and Silvaner (10.3 mg/L). The same authors found that catechin (0.3–102 mg/L and epicatechin (0.3–53.3 mg/L) levels were much higher in Müller-Thurgau wines after fermentation in the presence of skin grape [43] and also confirmed by other publications on the effect of wine fermentation in the presence of skin berry [49].

Cerruje white wines, the catechin (6.53 ± 0.21 mg/L) and epicatechin (3.19 ± 0.06 mg/L) amounts were found comparable to Czech white wines Chardonnay (7.76 mg/L) and (4.11 mg/L), respectively to catechin and epicatechin [Lampir and Pavlousek, 2013], and Müller Thurgau (7.53 mg/L) and (4.77 mg/L). The catechin amount in Shib white wine was comparable with Greek white wines (11.8–40 mg/L) identified as the main flavanol, while not valid for the *Cerruje* white wine [47]. Finally, the flavan-3-ol monomers and oligomers contributing to the total phenolics according to the wine were *Kallmet* wine from the Mirdita (18.70 %), *Kallmet* wine from the Lezha (26.85 %), *Shiz* (20.07 %), *Shib* (48.37 %) and *Cerruje* (12.85 %) wine.

3.5. Flavonols

Flavonols are UV sunscreen compounds and the most diverse nonpolymeric flavonoids isolated in berry skin and wines [13,40]. Their main glycosylated forms in wines are 3-O-glucosides and 3-O-glucuronides. Red wines have higher amounts than white wines due to their main isolation in the grape skin [50]. The bound flavonol glycosides identified in the studied Albanian wines were quercetin-3-O-galactoside, quercetin-3-O-glucoside, quercetin-3-O-glucuronide, and isorhamnetin-3-O-glucoside. The bound quercetin amounts fall in the range of published data for red wines [40,51]. Shib white wine revealed the highest levels of total flavonols (11.82 ± 8.98 mg/L). Both red wines, Kallmet and Shiz, presented lower levels compared to Shib white wine. The wine zone influence was higher than vintage in the case of Shib white wines, Tirana (23.40 ± 0.05 mg/L) versus Kavaja (6.03 ± 8.98 mg/L). This influence was also presented in Kallmet red wines, with Mirdita county showing the highest amount, 5.70 ± 0.35 mg/L, compared with Lezha (2.37 ± 1.14 mg/L). The only aglycon flavonol identified was quercetin. The highest quercetin level (2.49 ± 0.02 mg/L) was found in Shib white wines from Tirana county; the interval range in the white wines varied from 0.0 to 2.05 mg/L, while the quercetin levels in both red wines, Kallmet and Shiz, were found in lower level than the interval range of red wines, 3.49–37.36 mg/L [40]. Meanwhile, flavonol glycosides, quercetin-3-O-galactoside, quercetin-3-O-glucoside, quercetin-3-O-glucuronide, and isorhamnetin-3-O-glucoside in *Shib* white wines, show levels fall in the interval proposed in white wines. According to Waterhouse et al. (2016) [40], the red wine interval to the detected flavonol glucosides are: quercetin-3-O-galactoside (n.d.-6.0 mg/L), quercetin-3-O-glucoside (n.d.-14.0 mg/L), quercetin-3-O-glucuronide (n.d.-113.0 mg/L) and isorhamnetin-3-O-glucoside (n.d-4.0 mg/L). Due to the huge discrepancy in the interval of red wines, the glycosylated flavonols fall within the proposed range in the analyzed red wines. Meanwhile, there is the exception in both white wines *Shib* and *Cerruje,* where in contrast to the flavonols range, according to Waterhouse and coauthors (2016) [40], quercetin-3-O-galactoside, quercetin-3-O-glucoside, quercetin-3-O-glucuronide, and isorhamnetin-3-O-glucoside, these flavonols were detected. This is in contrast to common knowledge and to recent investigations, which reported for isorhamnetin-3-O-glucoside in white wines 0.35 mg/L and for red wines 3.21 mg/L, as well as related to bound Quercetin in white wines 0.86 mg/L and red wines 5.81 mg/L [52].

Flavonols in *Kallmet* wine were found at levels of 4.04 ± 1.94 mg/L, with higher values in wines from the Mirdita (5.70 ± 0.35 mg/L) than in wines from the Lezha (2.37 ± 1.14 mg/L). *Shesh i zi* red wine flavonols were 2.31 ± 0.57 mg/L, lower than *Kallmet* wines, 5.70 ± 0.35 mg/L. The highest amount (2.81 ± 0.03 mg/L) belonged to the 2020 vintage. Flavonol glycosides in *Shesh i bardhë* and *Cerruje* white wine presented the lowest percentage compared with other phenolic compound groups, hydroxybenzoic acid, flavan-3-ol, and phenolic acids, except stilbenoids. Total flavonols in *Shesh i bardhë* wine from the Kavaja, 6.03 ± 0.72 mg/L, were lower

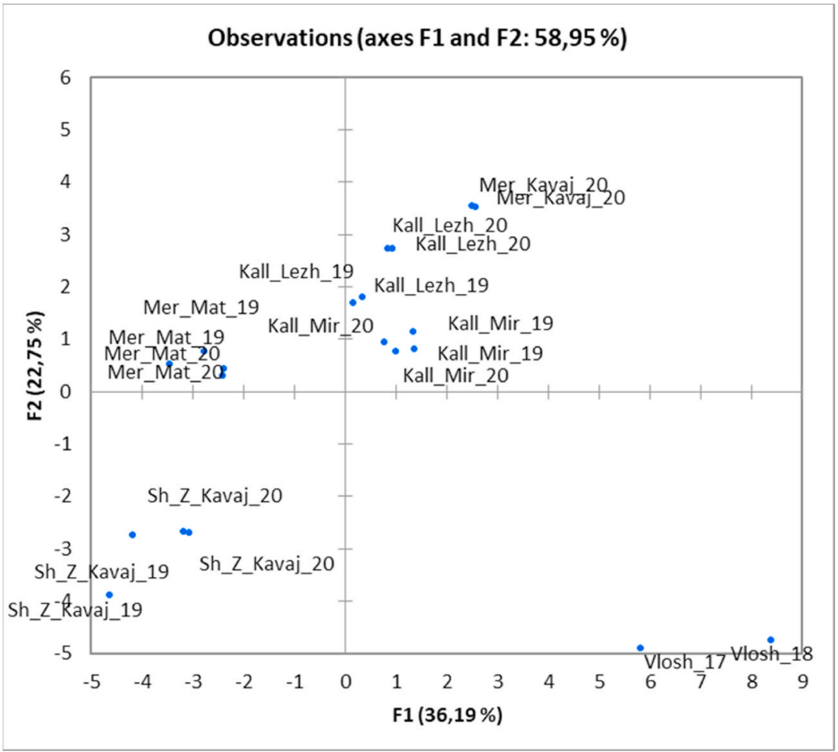

Fig. 3. Biplot square phenolic compounds (axes F1 and F2 in total 58.95 %) in single-variety red wines.

compared with ShiB wines originating from the Tirana vine zone (23.40 ± 0.05 mg/L).

3.6. Stilbenoids pattern in red and white wines

Resveratrol, produced in grape berry skin, exists in *cis*- and *trans*-forms, with the second isomer being more biologically active. Resveratrol exhibits antioxidant, cardioprotective, chemopreventive, anti-inflammatory, and estrogenic properties [53]. Both *cis*-/-*trans*-isomers and their glucosides, *cis*-piceid and *trans*-piceid, are found in wines. *Trans*-resveratrol biosynthesis in grape skin indicates that red wines have higher amounts than white wines.

Trans-resveratrol, *cis*-resveratrol, *trans*-piceid, and *cis*-piceid were identified in all four studied wines. According to the total stilbenoids amount in *Kallmet* red wine (1.04 ± 0.36 mg/L) was found to be the highest concentration, followed by Shib (0.93 ± 0.08 mg/L), while the Shiz was characterized by low levels (0.14 ± 0.06 mg/L). A difference was observed between the two vintages and zone in the case of Kallmet red wines, with higher levels from the 2020 vintage, and Lezha (1.59 ± 0.02 mg/L) higher than Mirdita (1.04 ± 0.01 mg/L) from this vintage. Conversely, in the 2020 vintage, in 2019, the difference favors the Mirdita wine zone, although it is much more pronounced (0.68 versus 0.87 mg/L). Both *cis*- and *trans*-piceid, two resveratrol glucosides, were identified as the main stilbenoids in all four analyzed wines. The highest levels belonged to *trans*-piceid, reaching up to 0.78 ± 0.01 mg/L in the Kallmet wines from the Lezha and 2020 vintage and Shib white wines (0.75 ± 0.10 mg/L). In a previous publication by Peçuli et al. (2018) [32], the stilbenoids amount in Kallmet wines were higher compared with our findings, respectively *trans*-resveratrol (0.3–4.3 mg/L), *cis*-resveratrol (0.3–2.8 mg/L). According to the literature, when compared with wines from North Macedonia, the stilbenoids amounts were analyzed in lower levels, e.g., *trans*-piceid in *Vranac* wine (2.24 ± 0.08 mg/L) and *trans*-resveratrol in Merlot wine (1.49 ± 0.06 mg/L) [54]. The total stilbenoids in *Shesh i bardhë* wine was 0.93 ± 0.08 mg/L for both vintage and vine zones, much higher than according to the literature over the total stilbenoids in white wines reaching up to 0.5 mg/L [55]. A much lower level of resveratrol was found when compared with Austrian wines, which reached up to 17.7 mg/L in Pinot noir, as well as compared with the higher average amount (7.6 mg/L) to Blaufränkisch [56]. In the case of studied wines, the proposal of wine consumption as an important source of resveratrol indicates that they do not constitute an important dietary source, even in the case of ShiB white wines. The results on the stilbenoid profiles found that *trans*-piceid, the *trans*-resveratrol glucoside, was at the highest level, 0.88 ± 0.01 mg/L, in the 2020 vintage of the Shib, originated from Tirana vine zone. *Cerruje* white wines revealed no presence of resveratrol and other stilbenoids.

3.7. Chemometric processing of wine phenolics

Principal component analysis (PCA) was utilized to better explain the phenolic composition of analyzed wines. PCA can reduce the dimensionality of such datasets, increase interpretability, and minimize information loss.

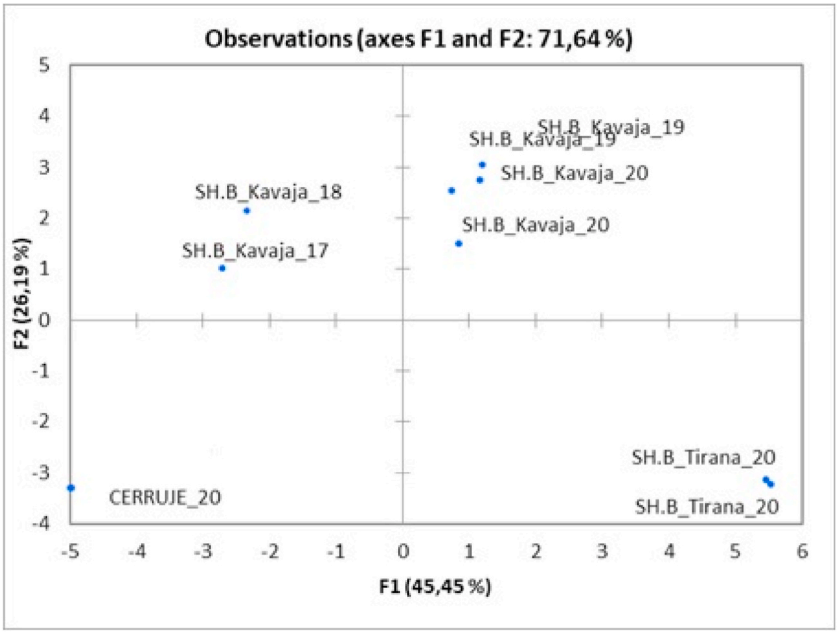

Fig. 4. Biplot square (F1 and F2: 71.64 %) for white wines according to vintage and terroir.

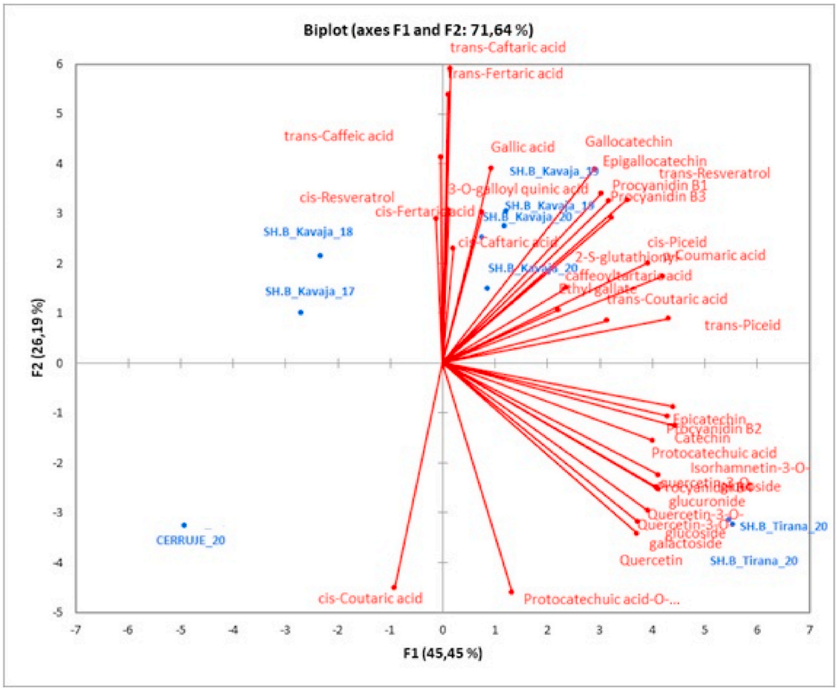

Fig. 5. Biplot square (F1 and F2: 71.64 %) of phenolic compounds in white wines group according to variety and vintage.

PCA of red wines, including the Vlosh data from a previous publication [Topi et al., 2021], is presented in Fig. 3. The plot indicates that the first two F2 (22.75 %) and F1 (36.19 %) biplot components (F1 and F2) account for 58.95 % of the information needed regarding differences in red wines according to vine zone and vintage. The variety is the main factor that gives a good separation, with *Vlosh* and *Shesh i zi* wines showing the best differentiation and *Shesh i zi* with *Kallmet* red wines. The flavonoids isorhamnetin-3-glucoside, quercetin-3-O-glucornide, quercetin-3-O-galactoside, and procyanidin B4 contribute more to the first principal component (F1). In contrast, F2 was the main contributor to nonflavonoids: epicatechin, ethyl gallate, and procyanidin B2, and on the opposite side, protocatechuic acid and procyanidin B1.

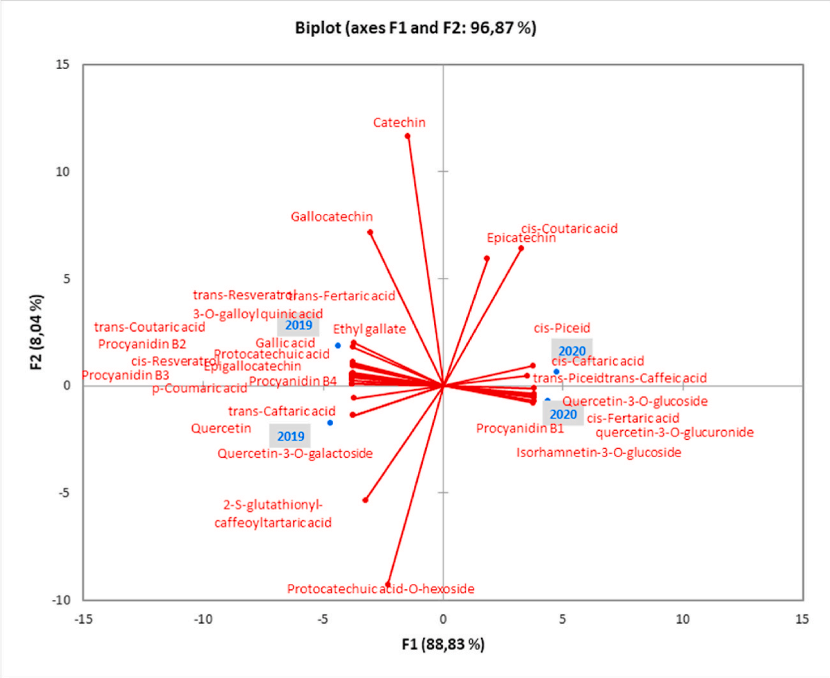

Fig. 6. Biplot square (F1 and F2: 96.87 %) of phenolics in *Shesh i zi* red wine according to vintage.

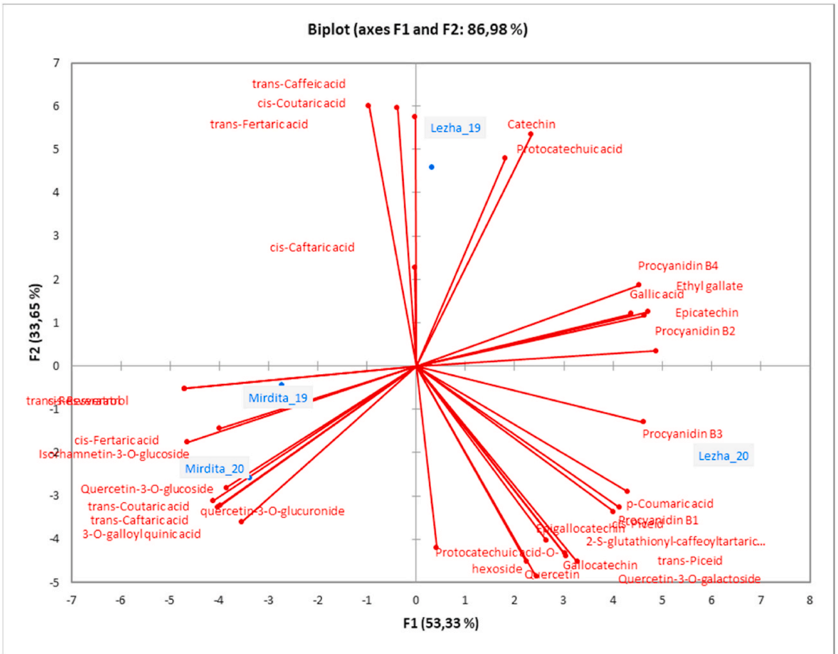

Fig. 7. Biplot square (F1 and F2: 86.98 %) for wine phenolics in *Kallmet* red wine according to the terroir and vintage.

The study discriminated against white wines, including variety, terroir, and vintage (Fig. 4). The biplot square indicates that the first two biplot components (F1 and F2) account for 71.64 % of the information needed regarding differences in white wines. These data present results with higher confidence compared to red wines.

Referring to the specific phenolics, the white wines' biplot components (F1 and F2: 71.64 %) values indicate a good correlation in the case of *Shesh i bardhë* wines (Fig. 5). Shib wine from the Tirana vine zone was mainly correlated with phenolic compounds belonging to flavonols, hydroxybenzoic acid, and flavonols. In contrast, the Kavaja county wines had phenolic acids, stilbenoids, and specific compounds from hydroxybenzoic acid and flavanols subgroups in the case of Shib wines. Data from a previous publication by Topi and coauthors (2022) [27] were introduced to perform discrimination analysis.

According to two vintages, PCA on Shesh i zi red wine, indicates that F1 and F2 contribute 96.87 %. *Cis*- and *trans*-piceid, procyanidin B1, *trans*-caffeic acid, quercetin 3-O-glucoside, and quercetin-3-O-glucuronide served as F1 to the *Sheshi i zi* wine samples of the 2019 vintage (Fig. 6). Meanwhile, the F1 to 2019 vintage may serve three other procyanidins, B2, B3, and B4, together with gallic acid.

Kallmet red wine analyzed according to the terroir and vintage indicates good discrimination between F1 and F2: 86.98 % (Fig. 7). Procyanidin B2 and B3 are good PC1 discriminators for *Kallmet* wine samples originating in the Lezha vine zone and 2020 vintage. Cis and *trans*-resveratrol, together with *cis*-fertaric acid and isorhametin-3-O-glucoside, may serve as a marker of the *Kallmet* wines that originate from Mirdita terroir, referring to F1 (53.33 %),. Discrimination of *Kallmet* wine from the Lezha region to the 2019 vintage is discriminated according to F2 (33.65 %) according to *trans*-caffeic acid, *cis*-coutaric acid, *trans*-fertaric acid, protocatechuic acid, and catechin.

4. Conclusions

This study aimed to authenticate Albanian wines by analyzing the phenolic chemicals found in four local grape cultivars: Shesh i zi, Kallmet, Shesh i bardhë, and Cerruje. The research covered two vintages in a row and varied vine zones. Thirty-one flavonoids and nonflavonoids were found in the wine samples by LC-DAD-ESI-MSn analysis. The results show that the higher amounts of phenolic compounds identify the Shesh i Zi and Shesh i bardhë grape varieties from Central Albania. Meanwhile, Kallmet red wine had greater quantities of resveratrol than the other wines in our study. The most prevalent phenolic component, gallic acid, was found in ShiZ red wine at the highest concentration. Although all the wines contained flavan-3-ol monomers, catechin, and epicatechin, the ShiB wine from Kavaja County had the highest concentrations. Procyanidin dimers (B1, B2, B3, and B4) are discernible at the most concentrated levels in ShiB white wines. Among red wines, ShiZ wines are known to contain the most anthocyanidins. When subjected to principal component analysis, wine samples from several grape kinds and those from the same variety but different counties showed discriminating solid results. They may improve their chances of competing in the international wine market by promoting native varietals, which increases genetic diversity.

CRediT authorship contribution statement

Dritan Topi: Writing – original draft, Resources, Project administration, Formal analysis, Conceptualization. **Ardiana Topi:** Visualization, Software, Data curation. **Gamze Guclu:** Writing – original draft, Resources, Methodology, Formal analysis. **Serkan Selli:** Writing – review & editing, Supervision, Conceptualization. **Turkan Uzlasir:** Writing – review & editing, Validation, Methodology, Investigation, Data curation, Conceptualization. **Hasim Kelebek:** Writing – review & editing, Validation, Supervision, Investigation, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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