

Phenolic Compounds, Fatty Acid Compositions and Antioxidant Activity of Commercial Cold-Pressed Grape Seed (*Vitis vinifera*) Oils From Turkey

Zeliha Ustun-Argon

Abstract— Grapes (*Vitis vinifera*) are one of the largest fruit crops in the world and its consumed both as fresh fruits or processed products such as wine, jam, juice, grape seed extract, oil, vinegar. Grape seed oil is one of the most important by-product of grape juice and wine processes due to its beneficial health effects, flavor and special characteristics for food applications. Different samples of cold pressed grape seed oil from Turkey have been evaluated for fatty acid compositions and the samples found rich in polyunsaturated and monounsaturated fatty acids. Phenolic components determined with LC-QTOF-MS have identified with Metlin_Metabolomic database and 26-77 different components were defined for five different samples. DPPH scavenging activities were determined as 31.00-45.31%.

Index Terms— Cold press, DPPH radical scavenging, Fatty acid composition, Grape seed oil, LC-QTOF-MS, Phenolics, *Vitis vinifera*

1 INTRODUCTION

In recent years, improving and maintaining health by changing life styles, eating habits and using nutraceuticals has become more popular. Therefore dietary properties of nonconventional foods for alternative usages have been developed by novel researches. And products are launched in the market to support the metabolism for managing or treating diseases and to promote well-being. Grapes (*Vitis vinifera*) are one of the largest fruit crops in the world and its consumed both as fresh fruits or processed products such as wine, jam, juice, grape seed extract, vinegar, jelly, grape seed oil and dried grapes [1]. After the wine and grape juice production processes there is a great amount of pomace which is 20-26% of the grape fruit. Grape seeds are rich in carbohydrates (60%-70%), fatty acids (13%-19%), proteins (11%), and antioxidants. Tocopherols and tocotrienols belong to the vitamin E family and are well known with antioxidant, anti-inflammatory, and antithrombotic effects in grape seeds [2]. Grape seed oil is a valuable product which can be obtained from the grape juice and wine process as a by-product [3]. Grapeseed oil is one of the most commonly preferred gourmet oil with its unique light and nutty flavor. It is used successfully in frying due to its high smoke point also has been chosen for baking, marinades, salad dressings purposes. In addition to the food applications, grape seed is also important for cosmeceutical, supplements, pharmaceutical and personal care products owing to bioactive components, antioxidants, fatty acids and high amount of nutrients in its content [4], [5], [6], [7], [8].

Grape seeds contain approximately 8-15% (w/w) of oil

and cold pressed oil is rich with unsaturated fatty acids (UFAs) such as linoleic acid (72-76%) and oleic acid (12-20%) [9], [10], [11]. Grape seed oil with its fatty acid composition and antioxidants has an important role in inhibition of cardiovascular diseases, prevention of thrombosis, oxidation of low-density lipoproteins, cholesterol serum level reductions, regulation of autonomic nerve [12]. Additionally, high content of tannins in grape seed oil cause higher stability against peroxidations [11]. Cold pressed extracted grape seed oils tend to have more antioxidant and significant level of phytochemicals, and aroma compounds since the process does not include any heat or chemical applications. Therefore it is preferred for supplements and a healthy diet. In addition, the stability properties of cold pressed oils which include peroxide value and an oxidative stability index support a longer shelf life for the oil [13], [14], [15], [16],[17], [18].

Free radicals play an important role in health problems such as cardiovascular diseases with the major effect on lipid peroxidation. The mechanism of antioxidant products is related with removal of free radicals. This is important for edible oils which are defined as antioxidants, as the oils lower the low density lipoprotein levels and oxidative stress and support reduction of inflammation with some diseases [19], [20], [21].

In the present study, mostly preferred cold pressed grape seed oils in the Turkish market have been evaluated. The samples have been analysed for their fatty acids compositions (FAME), phenolic profiles and DPPH radical scavenging activities. Since the measuring instruments' performances have been improved, the authenticity and characterization of the conventional and unconventional oils were able to detected extensively [22]. With this respect the analysis has been completed by using advanced instruments, such as LC-Q-TOF-MS, GC-MS to be able to see the differences between different

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brandnames. This study also aimed to determine the trends in components of the grape seed oils by applying principal component (PCA) analysis.

2 MATERIAL AND METHOD

2.1 Material

Cold pressed grape seed oil samples have been chosen from amongst the mostly known brandnames. Samples have been bought from the pharmacies and natural supplements shops.

2.2 Chemicals

All the reagents were obtained from J.T. Baker, and Sigma-Aldrich and they are either chromatographic or analytical grade. Millipore ultrapure water (Type I) was used for all analysis.

2.3 Fatty acid methyl esters (FAME) analysis

The method to determine fatty acid composition was COI/T.20/Doc. No 33 for olive oils [23]. The standard for retention time to identify the fatty acids was A 37 component mixture of FAME (Supelco). The quantitative analysis was completed with the area ratio of the relevant peak. The instrument was An Agilent 6890 GC-FID system. The column was a Supelco 2560 capillary column (100 m x 0.25 mm ID x 0.2 µm) with 1:100 split ratio, injection and detector temperatures were 250°C and 260°C, respectively. The oven temperature is held at 140°C for 1 min and then, increased to 240°C at a rate of 4°C/min and hold for 5 min.

2.4 Phenolics

An HPLC Agilent 1260 Infinity series (Agilent Technologies, Santa Clara, CA, USA) equipped with a the double pump, degasser, automatic sample dispenser was used for chromatographic separation. Compound separations completed by using Poroshell 120 EC-C18 (3.0x50 mm, particle size 2.7 µm) (Agilent) column. The gradient washing (elution) steps given in the table. Mobile phase A was the mixture of 0.1% formic acid and water and mobile phase B was the acetonitrile. The column temperature was 35 ° C, 3 µL sample was injected and the flow rate was arranged as 0.4 mL/min.

The Agilent 6550 iFunnel high resolution Accurate Mass QTOF-MS is used for MS analysis. The instrument equipped with Agilent Dual Jet Stream which is able to operate in positive ion electrospray ionization (Dual AJS ESI) interface. The drying gas temperature was 290 ° C ; gas flow of desiccant was 14.0 L / min; nebulizer gas pressure was 35 psi; sheath gas temperature was 400 ° C; the sheath nitrogen gas flow was at 12 L/min. Mass spectra were recorded in the negative ionization mode in a mass range of 50-1700 m/z.

MassHunter Workstation software was used for Integration and data detailing were performed using the station. Agilent METLIN Metabolomix database, library and full mass personal com-posite database and library (METLIN_AM_PCDL) have been used to identify analytes. Positive and negative modes are conducted in the same conditions.

2.5 DPPH Free Radical-Scavenging Assay

The free radical scavenging activity was determined by the DPPH assay spectrophotometrically [24]. Shortly, the extract was taken as 1.0 mL and mixed with DPPH (1.0 mL and 0.8 mmol/L). After shaking the mix left for 30 min. At the end of the time the absorbance was measured at 517 nm against a reagent blank for 5% solution. Gallic acid and BHT used as standards. Analysis have been repeated for three times. The inhibition percentage for sceaevnging DPPH radical it was calculated with the following equation;

$$\text{DPPH radical scavenging effect (\%)} = \frac{(\text{A control} - \text{A sample})}{(\text{A control})} \times 100$$

A Control : The initial concentration of the DPPH

A Sample : The remaining concentration of DPPH's absorbance in the presence of the extract and positive controls.

TABLE 1
 ELLUTION STEPS

Time (min)	Mobile phase
0	% 5 B
8	% 15 B
10	% 20 B
13	% 25 B
18	% 30 B
20	% 45 B
24	% 60 B
27	% 80 B
30	% 90 B
32	% 5 B
3	Conditioning cycle

2.6 Data Analysis

The multivariate data matrix is evaluated with fatty acid methyl esters, phenolics and DPPH radical scavenging activity of the chosen samples. Results are given means±SD for triplicate analysis. Chemometric methods, PCA (Ward’s algorithmic method) are used to classify and characterize the grape seeds oil samples. Multivariate analysis completed with Minitab 15 Statistical Software. Prior to the chemometric analysis, data and auto scaled variables were standardized. For visualization of PCA results Scores and loading plots are used. Score plots and loading plots provided a clear relevance between principal groupings and observations and indicated the significance of each variable for the results. The plots are used to explain the correlation between variables and cluster observations also.

3 RESULTS AND DISCUSSION

3.1 Fatty Acid Composition

The main fatty acids in the grape seed oil samples found as linoleic, oleic, palmitic and stearic acid with 32.12-66.06%, 19.81-41.73%, 6.46-8.19%, 2.17-5.02% respectively. Linoleic acid value was the highest in sample A and the lowest in sample D (Table 2). Sample B found the richest with the oleic acid while sample A and C have the lowest values. Sample A found with the highest essential fatty acids (EFAs) (66.23%) and polyunsaturated fatty acids (PUFAs) (66.62%), Sample B was the richest with monounsaturated fatty acids (MUFAs) (44.18%) and saturated fatty acids (SFAs) (16.53%). Linolenic acid amount in Sample D and oleic acid in Sample B unusually higher than the values in the literature. This extraordinary values can explain with addition of other oils which are rich with linolenic acid or oleic acid to the grape seed oil. The results show accordance with other studies which are reported the fatty acids as linoleic acid (61.3-74.6), oleic acid (12.7-20.9), palmitic acid (6.3-11.6), stearic acid (3.6-5.4) and linolenic acid (0.3-1.8) [4], [7], [9], [10], [11], [25], [26]. The slight differences in the value of fatty acids can be explained variations between the grape varieties, extraction processes and storage conditions. In addition, oleic-linoleic acid rate can change with the climatic conditions [15], [27], [28].

3.2 Phenolics

Polyphenol components are known with their important antioxidant and antimicrobial roles in a wide range of biological activities. These compounds are responsible for the stability of the oils by preventing oxidation. Phenolics also contribute the nutritional value improvements and edible oils quality [29], [30], [31]. Amounts of phenolic compounds and their compositions are very effective for biological activities [30], [32]. In this study phenolic components have been determined with LC-QTOF-MS and have been identified with Metlin_Metabolomic databases. According to the results Sample A contains 77 different components which is highest amount amongs other samples. Sample B, C, D and E contain 26, 74, 59 and 53 different components respectively (Table 3). These results, in our knowledge, are the widest range of iden-

tification for grape seed oils. Different studies mentioned about vanillic, p-coumaric, ferulic, catechin, procyanidin B1, trans-resveratrol, epicatechin, and sinapic phenolic compounds in the grape seed oil [29], [27]. Total phenolic content (TPC) of Muscadine, Concord, Ruby red, Chardonnay varieties found as 0.44,0.80,0.16 and 0.23 mf GAE/g respectively [4]. Other studies found the TPC between 10.68-115 g/kg for different varieties [15], [30], [29]. Since the phenolics can indicate the antioxidant activities, cold pressed grape seed oil with its phenolic compounds can be raw material or an ingredient in different daily diet products, natural cosmetics or nutraceuticals.

TABLE 2
FATTY ACID COMPOSITIONS

FATTY ACIDS	A	B	C	D	E
Myristic	0.07±0.001	5.62±0.007	0.06±0.001	0.05±0.001	0.06±0.001
Palmitic	8.13±0.003	7.24±0.002	8.19±0.003	6.46±0.002	7.46±0.001
Palmitoleic	0.13±0.002	0.16±0.001	0.17±0.003	0.10±0.001	0.15±0.001
Heptadecanoic	0.08±0.001	0.05±0.002	0.07±0.001	0.07±0.000	0.05±0.001
Stearic	4.96±0.022	2.17±0.001	4.97±0.003	5.02±0.001	4.06±0.002
Oleic	19.81±0.017	41.73±0.041	19.81±0.013	22.38±0.002	26.70±0.002
Linoleic	66.06±0.013	34.68±0.004	65.25±0.044	32.13±0.001	59.82±0.002
Linolenic	0.17±0.001	3.76±0.003	0.74±0.001	32.83±0.004	0.29±0.001
Behenic	0.04±0.000	0.39±0.003	0.04±0.001	0.15±0.001	0.43±0.000
EFAs	66,23	38,44	65,99	64,96	60,11
Linoleic/ Linolenic Ratio	66,66	39,71	66,53	65,24	60,80
PUFAs	20,01	44,18	20,24	22,76	27,08
MUFAs	13,30	16,53	13,35	12,00	12,19
SFAs	5,01	2,40	4,98	5,43	4,99
PUFA/SFA	66,23	38,44	65,99	64,96	60,11

TABLE 3
PHENOLICS CONTENT OF GRAPE SEED OIL

METLIN-NEGATIVE						
Name	Formula	Sample				
		A	B	C	D	E
α-Linolenic Acid	C ₁₈ H ₃₀ O ₂	+		+	+	+
Δ ² -cis-Hexadecenoic Acid	C ₁₆ H ₃₀ O ₂		+	+		
Traumatic Acid	C ₁₂ H ₂₀ O ₄	+		+		
Sucrose	C ₁₂ H ₂₂ O ₁₁	+	+	+		
Stearidonic Acid	C ₁₈ H ₂₈ O ₂	+		+	+	+
Stearic acid	C ₁₈ H ₃₆ O ₂	+		+	+	+
Urocanic acid	C ₆ H ₆ N ₂ O ₂					+
trans-EKODE-(E)-Ib	C ₁₈ H ₃₀ O ₄					+
Ricinoleic acid	C ₁₈ H ₃₄ O ₃		+			
Methyl N-(a-methylbutyryl)glycine	C ₉ H ₁₆ O ₄		+			
Elaidic Acid	C ₁₈ H ₃₄ O ₂		+	+	+	
Quercetin	C ₁₅ H ₁₀ O ₇	+			+	
Pyrocatechol	C ₆ H ₆ O ₂	+				
Pinocembrin	C ₁₅ H ₁₂ O ₄	+		+	+	+
Petroselinic acid	C ₁₈ H ₃₄ O ₂	+				+
Methyl N-(a-methylbutyryl)glycine	C ₉ H ₁₆ O ₄	+		+	+	+
m-Coumaric acid	C ₉ H ₈ O ₃	+		+	+	
Matairesinol	C ₂₀ H ₂₂ O ₆	+	+	+		
Luteolin	C ₁₅ H ₁₀ O ₆	+	+	+	+	
Kaempferol	C ₁₅ H ₁₀ O ₆	+		+	+	+
Genkwanin	C ₁₆ H ₁₂ O ₅					+
Isosteviol	C ₂₀ H ₃₀ O ₃				+	+
Hieracin	C ₁₅ H ₁₀ O ₇	+		+	+	+
Hexadecanedioic acid	C ₁₆ H ₃₀ O ₄			+		
Gallic acid	C ₇ H ₆ O ₅	+			+	
Ethyl-p-coumarate	C ₁₁ H ₁₂ O ₃	+		+	+	+
Dihydroxyphenylacetic acid	C ₈ H ₈ O ₄				+	
DL-b-Hydroxycaprylic acid	C ₈ H ₁₆ O ₃	+		+	+	
Diosmetin	C ₁₆ H ₁₂ O ₆	+		+	+	
D-(+)-3-Phenyllactic acid	C ₉ H ₁₀ O ₃	+		+		
Apigenin	C ₁₅ H ₁₀ O ₅					+
Absciscic Acid (cis,trans)	C ₁₅ H ₂₀ O ₄					+
Corosolic acid	C ₃₀ H ₄₈ O ₄	+		+	+	+
cis-9,10-Epoxystearic acid	C ₁₈ H ₃₄ O ₃	+		+	+	+
Betulonic acid	C ₃₀ H ₄₆ O ₃	+		+		
Betulinic Acid	C ₃₀ H ₄₈ O ₃	+	+	+	+	+
Absciscic Acid (cis,trans)	C ₁₅ H ₂₀ O ₄	+		+		

TABLE 3

METLIN-NEGATIVE						
Name	Formula	Sample				
		A	B	C	D	E
9-Thiastearic Acid	C ₁₇ H ₃₄ O ₂ S					+
9-OxoOTrE	C ₁₈ H ₂₈ O ₃	+		+	+	+
9-OxoODE	C ₁₈ H ₃₀ O ₃	+	+	+	+	+
(+)9-HODE	C ₁₈ H ₃₂ O ₃					+
9,10-DiHOME	C ₁₈ H ₃₄ O ₄		+			
9(E),11(E)-Conjugated Lino-leic Acid	C ₁₈ H ₃₂ O ₂	+	+	+		+
4-Nitrophenol	C ₆ H ₅ NO ₃	+		+		
4Hydroxybenzaldehyde	C ₇ H ₆ O ₂	+		+	+	+
4-Hydroxy-3-methoxy cinnamaldehyde	C ₁₀ H ₁₀ O ₃			+		
4-formyl Indole	C ₉ H ₇ NO	+	+	+	+	+
3-Hydroxycapric acid	C ₁₀ H ₂₀ O ₃	+		+		
3-hydroxy-tetradecanoic acid	C ₁₄ H ₂₈ O ₃			+		
3,4-Dihydroxybenzoic acid	C ₇ H ₆ O ₄	+				
3,4-Dihydroxy-benzaldehyde	C ₇ H ₆ O ₃	+	+	+		
2,2'-(3-methylCyclohexane-1,1diacetic acid	C ₁₁ H ₁₈ O ₄					+
2-Pyrimidine	C ₆ H ₆ N ₂ O ₂	+		+	+	+
Acetic Acid						
2-Hydroxy-hexadecanoic acid	C ₁₆ H ₃₂ O ₃	+	+	+		+
2-Hexyldecanoic acid	C ₁₆ H ₃₂ O ₂	+	+	+	+	+
2-Hydroxycinnamic acid	C ₉ H ₈ O ₃			+		
2-Hydroxymyristic Acid	C ₁₄ H ₂₈ O ₃					+
1-Palmitoyl Lysophosphatidic Acid	C ₁₉ H ₃₉ O ₇ P	+				
1-Oleoyl Lysophosphatidic Acid	C ₂₁ H ₄₁ O ₇ P	+				
18α-Glycyrrhetic Acid	C ₃₀ H ₄₆ O ₄	+		+		
16-hydroxy hexadecanoic acid	C ₁₆ H ₃₂ O ₃	+		+	+	+
13,14-dihydro Prostaglandin F1α	C ₂₀ H ₃₈ O ₅	+		+		
13(S)-HODE	C ₁₈ H ₃₂ O ₃			+		
13(S)-HOTrE	C ₁₈ H ₃₀ O ₃	+			+	+
13(R)-HODE	C ₁₈ H ₃₂ O ₃				+	+
(+)-Naringenin	C ₁₅ H ₁₂ O ₅	+		+	+	+
(+)12,13-DiHOME	C ₁₈ H ₃₄ O ₄	+		+		+

TABLE 3
PHENOLICS CONTENT OF GRAPE SEED OIL

METLIN-POSITIVE						
Name	Formula	Sample				
		A	B	C	D	E
Phthalic acid Mono-2-ethylhexyl Ester	C ₁₆ H ₂₂ O ₄	+				
Tetramethylpyrazine	C ₈ H ₁₂ N ₂			+		
Sucrose	C ₁₂ H ₂₂ O ₁₁				+	+
U-74389G	C ₃₇ H ₅₀ N ₆ O ₂	+		+		
Stearidonic Acid	C ₁₈ H ₂₈ O ₂	+		+	+	+
Stearamide	C ₁₈ H ₃₇ NO	+	+	+	+	+
Quercetin	C ₁₅ H ₁₀ O ₇			+	+	
Quercetin 3-methyl ether	C ₁₆ H ₁₂ O ₇	+		+	+	
Prostaglandin D2 methyl ester	C ₂₁ H ₃₄ O ₅				+	
PGF2α methyl ester	C ₂₁ H ₃₆ O ₅	+		+	+	+
PGF1α Alcohol	C ₂₀ H ₃₈ O ₄	+		+	+	+
Omega-3 Arachidonic Acid	C ₂₀ H ₃₂ O ₂	+		+		
O-2545	C ₂₆ H ₃₆ N ₂ O ₂	+	+	+	+	+
MG(18:2(9Z,12Z)/0:0/0:0)	C ₂₁ H ₃₈ O ₄	+	+	+	+	+
MG(18:1(9Z)/0:0/0:0)	C ₂₁ H ₄₀ O ₄		+		+	+
Luteolin	C ₁₅ H ₁₀ O ₆	+		+	+	
Linoleoyl Ethanolamide	C ₂₀ H ₃₇ NO ₂	+		+	+	
Linoelaidic Acid	C ₁₈ H ₃₂ O ₂				+	
Linoleic Acid ethyl ester	C ₂₀ H ₃₆ O ₂	+		+		
Niacin (Nicotinic acid)	C ₆ H ₅ NO ₂					+
Hepoxilin A3	C ₂₀ H ₃₂ O ₄			+		
Herbacetin	C ₁₅ H ₁₀ O ₇	+				
Ethyl-p-coumarate	C ₁₁ H ₁₂ O ₃	+		+		
Ethyl syringate	C ₁₁ H ₁₄ O ₅	+	+	+		+
Enoxolone	C ₃₀ H ₄₆ O ₄	+		+	+	+
Dioctyl phthalate	C ₂₄ H ₃₈ O ₄				+	
Dehydrocholic acid	C ₂₄ H ₃₄ O ₅					+
Methyl linolenate	C ₁₉ H ₃₂ O ₂				+	
N,N'-Dicyclohexylurea	C ₁₃ H ₂₄ N ₂ O		+			
Dehydrocholic acid	C ₂₄ H ₃₄ O ₅		+			
1-Monopalmitin	C ₁₉ H ₃₈ O ₄		+			
2-Linoleoyl Glycerol	C ₂₁ H ₃₈ O ₄			+		
2,3-dinor Prostaglandin E1	C ₁₈ H ₃₀ O ₅			+	+	

TABLE 3

METLIN-POSITIVE						
Name	Formula	Sample				
		A	B	C	D	E
9(Z),11(E),13(E)-Octadecatrienoic Acid ethyl ester	C ₂₀ H ₃₄ O ₂	+		+	+	+
8-iso-PGF2β	C ₂₀ H ₃₄ O ₅	+				
8-iso Prostaglandin F1β	C ₂₀ H ₃₆ O ₅	+		+	+	
8-iso Misoprostol	C ₂₂ H ₃₈ O ₅	+				
4-Hydroxy-3-methoxycinnamaldehyde	C ₁₀ H ₁₀ O ₃	+	+	+		+
4-formyl Indole	C ₉ H ₇ NO	+				
3-methoxy Prostaglandin F1α	C ₂₁ H ₃₈ O ₆	+		+	+	+
1-Monopalmitin	C ₁₉ H ₃₈ O ₄	+		+	+	+
19(R)-hydroxy-PGF1α	C ₂₀ H ₃₆ O ₆	+		+	+	
19(R)-hydroxy-PGE1	C ₂₀ H ₃₄ O ₆	+				
15(R)-PGE1	C ₂₀ H ₃₄ O ₅	+				
11β-Prostaglandin F1β	C ₂₀ H ₃₆ O ₅	+		+	+	+
15(R),19(R)-hydroxy Prostaglandin E1	C ₂₀ H ₃₄ O ₆				+	
11-deoxy-PGF1β	C ₂₀ H ₃₆ O ₄	+		+	+	+
11-deoxy-PGE1	C ₂₀ H ₃₄ O ₄	+		+		
13-OxoODE	C ₁₈ H ₃₀ O ₃			+	+	+

3.3 DPPH Radical Scavenging Activity

DPPH radical scavenging activity method is preferred to assess the kinetical and thermodynamical properties of antioxidant-radical reaction with its stable properties for determination of antioxidant's radical scavenging capacities [33]. In this study sample A found with the highest antioxidant activity while sample D with the lowest rate (Table 4). The results are generally higher than the Casoni et al's [27] study which is found the radical scavenger activity for hemp seed oil 41.90±1.11%. Studies for different grape varieties found between 0.07-1.11 mmol TE/g [4], oxidative stability at 98 °C, 6.38-9.36 h [26], and 0.09-1.16 mg/kg [15]. The results can be accepted in medium scale when its compared with the other plants oil. Among these oils while antioxidant activity of pumpkin seed oil (65.3±3.1%), rapeseed oil (51.2±4.1%) were found higher than grape seed oil, anise (12.52 ± 0.66%), white mustard (7.39 ± 0.29%), caraway (8.81 ± 0.41%), coriander (4.96 ± 0.22%) seed oils had lower values than our samples. Our results were similar with the antioxidant activity of nutmeg and hemp seed oil which are 31.69 ± 1.27% and 38.24-51.23% respectively [18], [34].

The results show that these seed oils can protect the

DNA, proteins and membrane lipids against free radicals activity. Therefore seed oils with high content of antioxidants can be used with different purposes in foods, cosmeceuticals and nutraceuticals [33].

TABLE 4
DPPH RADICAL SCAVENGING ACTIVITY

Sample	Antioxidant Activity (%)
A	45.31±0.116
B	36.24±0.578
C	36.68±1.99
D	31.00±0.349
E	42.19±0.116

3.4 Principal Component (PCA) Analysis

Results of positive and negative mod evaluated separately according to LC-QTOF-MS databases. Sample A and Sample C are separated from other oils and clustered. Sample B, D and E located in different zones. PC1 has 43.94 % effect for positive mode while PC2's effect was 26.44%. Effective parameters for separation can be seen in a loading plot.

In positive mod, Sample B was separated with the effect of Phthalic acid Mono-2-ethylhexyl Ester, 4-Hydroxy-3-methoxy cinnamaldehyde and ethyl syringate. Sample E was separated with the effect of dehydrocholic acid, niacin, sucrose, prostaglandin D2 methyl ester, methyl linolenate and linoelaidic acid.

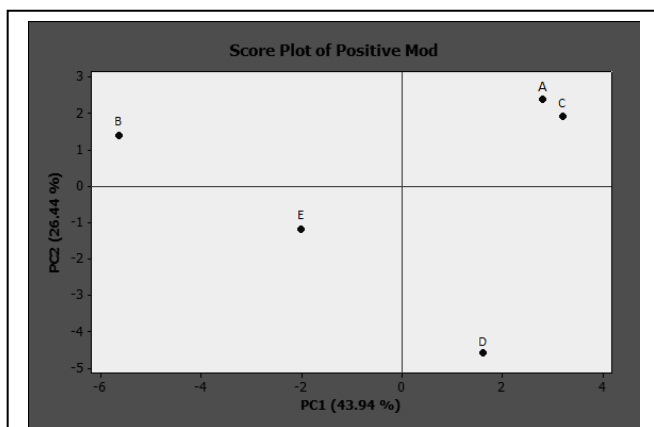


Fig. 1. Score plot of positive mod grape seed oil

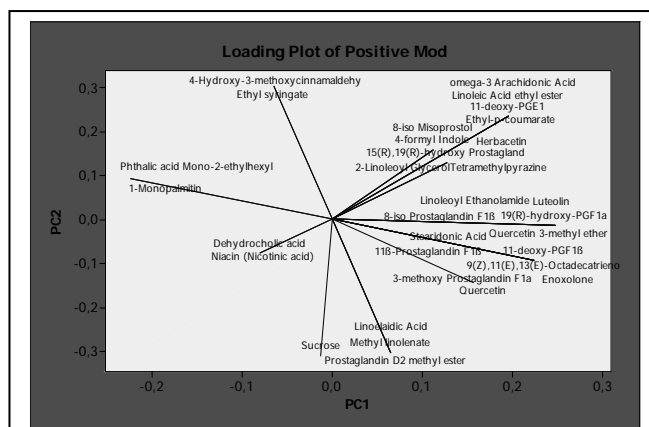


Fig. 2 Loading plot of positive mod grape seed oil

According to database scanning in negative mod, Sample A clustered with Sample C while Sample D clustered with Sample E. Sample B is separated from other samples. The effect of PC1 and PC2 were approximately 70%.

Ricinoleic acid, methyl N-(α-methylbutyryl)glycine, elaidic acid were effective for separation of Sample B. Abscisic acid, isosteviol, apigenin, 9-thiastearic acid, urocanic acid, dihydroxyphenylacetic acid, 2 hydroxymyristic acid, m-coumaric acid components were effective for separation of Sample E and sample D.

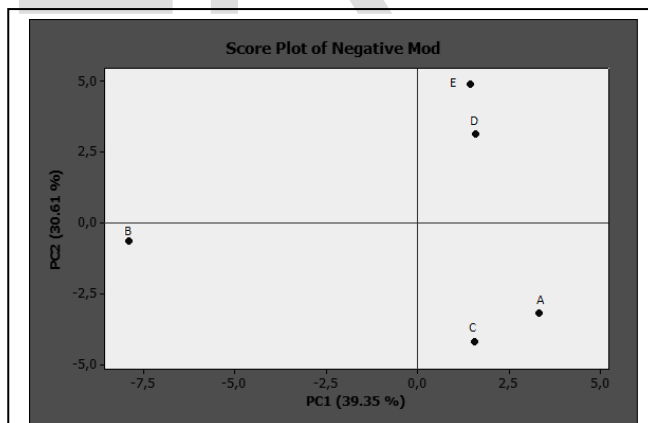


Fig. 3. Score plot of negative mod grape seed oil

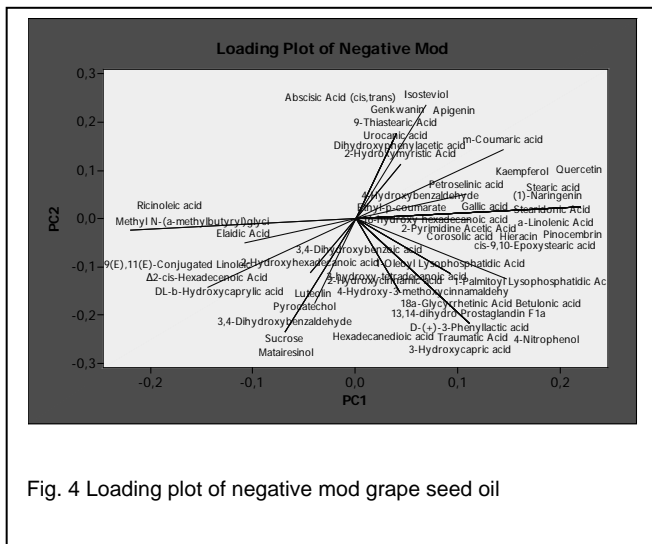


Fig. 4 Loading plot of negative mod grape seed oil

4 CONCLUSION

In the present study, mostly preferred cold pressed grape seed oils in the Turkish market have been evaluated for their antioxidant capacity, phenolic components and fatty acid methyl esters. According to the fatty acid compositions, the cold pressed grape seed oil samples from Turkish market found rich with PUFA and MUFA. These fatty acids are accepted as an important component for a healthy life style and support treatments. Phenolic components also were found in very wide range therefore grape seed oil can be preferred especially in supplements and cosmeceuticals formulations with its antioxidant effect. The results from the DPPH radical scavenging activity analysis support the antioxidant characteristic of grape seed oil for health studies. The results of this research with deeper components analysis may provide a basis for improvements of novel ingredients for natural food and pharmaceuticals.

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