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Oil Content and Oil Quality Properties of Some Grape Seeds

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Abstract: In the present study, the oil contents and some oil quality properties of seeds taken from 18 grape cultivars were examined. The results showed that the oil concentration of seeds ranged from 11.6 to 19.6%. Grape seeds were rich in oleic and linoleic acids, ranging from 17.8 to 26.5% and 60.1 to 70.1%, respectively. The degree of unsaturation in the grape seed oil was over 86%, and the average concentration of total tocopherol in oil was around 454 mg/kg. The results indicate that grape seed oil could be an important source for production of an edible vegetable oil and lowering wine production costs.

Key Words: grape seed, oil content, fatty acid composition, degree of unsaturation, total tocopherol content

Bazı Üzüm Çekirdeklerinin Yağ İçeriği ve Yağ Kalite Özellikleri

Özet: Sunulan araştırmada, 18 üzüm çeşidinden alınan çekirdeklerin yağ içeriği ve yağ kalite özellikleri incelenmiştir. Sonuçlar çekirdeklerin yağ içeriklerinin %11,6 ile 19,6 arasında değiştiğini göstermiştir. Üzüm çekirdekleri, oranları sırasıyla %17,8 -26,5 ve %60,1-70,1 arasında değişen oleik ve linoleik asitlerce zengindir.Üzüm çekirdeği yağının doymamışlık derecesi %86'nın üzerindedir, ve bu yağda ortalama toplam tokoferol (Vitamin E) içeriği 454 mg/kg dolayındadır. Bu sonuçlar, üzüm çekirdeklerindeki yağın yenilebilir bitkisel yağ olarak kullanılması ve şarap üretim masraflarının düşürülmesi bakımından önemli bir kaynak olabileceğini göstermiştir.

Anahtar Sözcükler: Üzüm çekirdeği, yağ içeriği, yağ asitleri kompozisyonu, doymamışlık derecesi, toplam tokoferol içeriği

Introduction

Grapes are one of the fruit crops grown widely in many areas of the world and 46% of the fresh grapes produced are accounted for in wine production (Anonymous, 1999).

During winemaking, large quantities of pomace are produced as a by-product (Ohnishi et al., 1990). In general, the pomace is not economically utilized except locally. However, the use of pomace in the food industry can create some opportunities to lower production costs and to create a new food source for human consumption. Grape seeds, which comprise 20 to 26% of the pomace (Kamel et al., 1985), have a high protein content (Ohnishi et al., 1990). They also have 10 to 20% oil (Schuster, 1992) with high vitamin E content, which has very important effects on human health. Grape seed oil mainly consists of triglycerides (TG), which are rich in unsaturated fatty acids, such as oleic and linoleic acids, compared to other oil-rich seeds (Barron et al., 1988).

The poly-unsaturated fatty acids such as linoleic and linolenic acids are essential for the human metabolism because of the lack of enzymes responsible for synthesis of these fatty acids. For this reason, they must be taken from daily foods. It was reported that grape seed oil is rich in linoleic acid (Barron et al., 1988; Schuster, 1992), and so its oil can be used as a source of edible vegetable oil (Ohnishi et al., 1990).

In this research, the seeds of 12 wine grape and six table grape cultivars (to compare with the first group of cultivars) were examined for oil content and some oil quality properties such as fatty acid composition, degree of unsaturation and total tocopherol content.

Materials and Methods

Materials

The seeds of 12 wine and six table grape cultivars were used in the present study. The grapes were collected at harvesting time from the experimental vineyard of the Agricultural Faculty of Ankara University (Ankara, Turkey) in 1998. The seeds from the grapes were dried at 70ºC for 72 h and used for the analyses mentioned below. All the cultivars and their main characteristics are presented in Table 1.

Methods

Oil content, fatty acid composition and total tocopherol content in oil (Vitamin E) were analyzed at the Institute of Plant Science and Plant Breeding-I of Justus Liebig University in Giessen, Germany, in 1998. Methylation of the fatty acids and total tocopherol analysis were performed as described by Marquard (1987) and Linow and Pohl (1970).

Analysis of oil content: Oil contents of 2 g dried intact grape seeds were determined by using nuclear magnetic resonance (NMR) (New Port Analyzer Magnet Type 10, Oxford Instruments Deutschland GmbH, Wiesbaden, Germany).

Analysis of fatty acids: Fatty acids of the grape seed oil were analyzed using gas chromatography (GC) (Carlo Erba GC Model 600) with a flame ionization detector (FID) and a Permabond FFAP stainless steel column (60 m x 0.25 mm, Thermo Quest Germany, Egelsbach, Germany). Esterification of the fatty acids was performed using the method given by Marquard (1987). According to this method, 20 dried grape seeds were homogenized with 400 ml iso-octane/iso-propanol (9:1, v:v) and the upper phase was removed and put into 2 ml sodium methylate (5 g sodium methylate: 800 ml methanol: 200 ml iso-octane). After orbital shaking and then waiting for 30 min, 0.7 ml of iso-octane was added to the mixture. Then 0.5µl of upper phase containing fatty acid methyl esters (FAME) was injected into the column of GC. The operation conditions of GC were chosen as follows:

Detector temperature: 240ºC

Injector temperature: 250ºC

Table 1. Main characteristics of the grape cultivars used in the study.

Cultivars	Origin	Color	Productivity	Time of Maturity	Number of seeds
Wine					
Alicante Bouschet	France	Black	High	Medium	1-2
Boğazkere	Turkey	Black	High	Medium	2-3
Clairette	France	Green-Yellow	Medium	Medium	1-2
Emir	Turkey	Green-Yellow	High	Medium	2-3
Hasandede	Turkey	Green-Yellow	High	Medium	2-3
Muscat of Hamburg*	Germany	Black	High	Medium	2-3
Kalecik karası	Turkey	Black	High	Medium	1-2
Karasakız	Turkey	Black	High	Medium	2-3
Narince	Turkey	Green-Yellow	High	Late	2-3
Öküzgözü	Turkey	Black	Medium	Very late	2-3
Pinot noir	France	Black	Low	Medium	1-2
Riesling	Germany	Green-Yellow	Medium	Medium	1-2
Table					
Alphonse Lavallée	Belgium	Black-Purple	Very high	Medium	3-4
Amasya beyazı	Turkey	Green-Yellow	Medium	Medium	2-3
Cardinal	USA	Red	Very high	Early	2-4
Çavuş	Turkey	Green-Yellow	High	Mid-early	1-3
Gül üzümü	Turkey	Pink	Low	Mid-early	1-2
Razakı	Turkey	Green-Yellow	High	Medium	2-4

*Muscat of Hamburg is also used as a table grape

Column temperature: from 120ºC (3 min hold) to 200°C at 3ºC/min (6 min hold)

Split ratio: 50:1 ml/h

Carrier gas: Helium

Palmitic (C16:0), stearic (C18:0), oleic (C18:1), linoleic (C18:2), linolenic (C18:3) and eicosenoic (C20:1) acids were determined by computing integrator. Peaks were integrated by a Shimadzu C-R3A computing integrator which was calibrated with a reference methyl-ester fatty acid obtained from the Institute of Plant Science and Plant Breeding-I Laboratories, Inc. Degrees of unsaturation were calculated by addition of the unsaturated fatty acids.

Analysis of total tocopherol: 200 ml of pure oil was obtained from dried grape seeds by means of a mechanical press machine. A series of concentrations (0, 25, 50, 100, 150, 200 and 250 µg/0.2 ml in ethyl acetate) of DL-α-tocopherol were prepared for a standard curve. Before spectrophotometric analysis, 1 ml of α- ά- diphenyl- β-picrylhydranyl (DPPH) solution (20 mg DPPH in 50 ml ethyl acetate) was put into each of the tubes containing DL-α-tocopherol series. The values were monitored with a spectrophotometer set (PYE Unicam SP 8-300 UV/VIS, Pye Unicam/Philips Analytical, Kassel, Germany) at an excitation wavelength of 522 nm. The amount of total tocopherol was calculated by comparing the peak areas of the standard curve (Linow and Pohl, 1970).

Analyses of correlation coefficients were performed using the MSTATC package on a personal computer (Anonymous,1989).

Results and Discussion

The oil contents and some oil quality properties of grape seeds obtained from 18 grape cultivars are given in Table 2.

Oil Content

As shown in Table 2, the oil contents of the grape seeds ranged from 11.6 to 19.6% (v/w). These results were similar to those obtained by Ohnishi et al. (1990) and Schuster (1992). They reported that the seeds of

Table 2. Oil contents and some oil quality properties of some grape seeds.

Cultivars	Oil content (%)(v/w)	Fatty acid composition (%)(v/w)						Degree of unsaturation (%)	Total tocopherol in oil (mg/kg)
		Palmitic	Stearic	Oleic	Linoleic	Linolenic	Eicosenoic		
Wine									
Alicante Bouschet	16.2±0.63	8.3±0.32	5.1±0.11	25.5±0.54	60.1±3.06	0.51±0.04	0.49±0.02	86.6±3.23	357±9.96
Boğazkere	17.6±0.55	7.1±0.19	5.1±0.19	23.9±1.55	62.9±2.49	0.40±0.03	0.65±0.03	87.8±1.72	456±9.76
Clairette	17.5±0.72	8.1±0.18	4.2±0.14	20.7±0.86	66.2±3.52	0.43±0.02	0.42±0.01	87.7±2.77	438±8.16
Emir	15.3±0.50	8.6±0.35	4.7±0.13	17.8±1.08	68.1±4.20	0.53±0.03	0.34±0.01	86.7±5.30	486±23.66
Hasandede	16.5±0.80	8.6±0.27	4.5±0.26	18.7±0.87	67.5±6.74	0.35±0.02	0.35±0.01	86.8±7.13	480±14.80
Muscat of Hamburg	19.1±0.64	6.5±0.11	4.3±0.27	18.3±0.93	70.1±4.98	0.33±0.01	0.48±0.03	89.3±5.02	401±11.04
Kalecik karası	13.1±0.47	9.0±0.50	4.0±0.27	22.2±1.34	62.9±4.05	0.87±0.03	0.97±0.05	87.0±5.44	578±27.65
Karasakız	18.0±0.46	7.9±0.32	5.4±0.48	19.2±0.53	66.7±6.10	0.39±0.02	0.51±0.04	86.8±6.24	386±8.93
Narince	14.7±0.48	8.4±0.30	3.5±0.15	18.7±1.35	68.8±6.15	0.53±0.03	0.12±0.01	88.1±7.50	458±22.51
Öküzgözü	19.6±0.59	8.6±0.13	4.3±0.19	20.1±1.11	66.3±3.94	0.42±0.02	0.32±0.02	87.2±5.00	542±15.98
Pinot noir	17.8±0.88	9.0±0.28	3.5±0.16	22.6±1.06	64.9±4.36	0.00±0.00	0.00±0.00	87.5±4.73	408±15.70
Riesling	16.0±0.23	9.0±0.25	4.5±0.28	22.2±1.12	63.4±5.07	0.38±0.02	0.47±0.03	86.5±6.20	364±14.25
Table									
Alphonse Lavallée	16.2±0.59	8.5±0.41	4.0±0.23	20.5±1.01	66.1±2.52	0.42±0.03	0.51±0.04	87.5±2.92	512±17.25
Amasya beyazı	18.1±0.54	7.7±0.45	4.8±0.19	22.1±0.95	64.1±3.75	0.75±0.05	0.45±0.03	87.4±4.04	449±18.15
Cardinal	16.7±0.38	8.3±0.24	4.3±0.30	19.4±1.32	67.2±4.62	0.39±0.02	0.35±0.01	87.4±5.77	556±22.39
Çavuş	11.6±0.38	7.6±0.21	4.2±0.14	26.5±1.31	60.7±2.64	0.37±0.02	0.76±0.03	88.3±3.25	572±30.61
Gül üzümü	18.0±0.77	8.5±0.35	7.3±0.27	19.6±0.90	64.4±3.52	0.31±0.01	0.00±0.00	84.2±3.44	398±18.65
Razakı	14.5±0.41	9.7±0.28	6.0±0.29	21.1±1.20	62.7±5.27	0.50±0.02	0.09±0.01	84.4±6.41	328±10.96

different grape cultivars contained 9.9 to 20.0% oil. The grape cultivars used in the present study differed in their oil content. The highest oil content was found in the cultivar Öküzgözü, a very late-ripening wine cultivar, and the lowest oil content was obtained from the cultivar Çavuş, a mid-early ripening table grape cultivar. This result leads us to the suggestion that there may be a relationship between the oil content and the time of maturity. However, this relationship was not the only valid factor as there were some exceptions in Cardinal (early-ripening cultivar) and Gül üzümü (mid-early ripening cultivar) the oil concentrations were 16.7 and 18.0%, respectively, while the late ripening cultivar Narince contained only 14.7% oil (Table 2). Ohnishi et al. (1990) explained that oil content differences among the cultivars are related to the maturity of the grape seeds.

Fatty Acid Composition

Fatty acid concentrations of the cultivars had the following range: 6.5 to 9.7% for palmitic, 3.5 to 7.3% for stearic, 17.8 to 26.5% for oleic, 60.1 to 70.1% for linoleic. Other fatty acids present in small quantities were linolenic (0.00 to 0.87%) and eicosenoic acid (0.00 to 0.97%) (Table 2). Eicosenoic acid was not determined in the oil of the cultivars Pinot noir and Gül üzümü. Linolenic acid was not found in the oil of Pinot noir.

As reported previously (Barron et al., 1988; Schuster, 1992), grape seed oil contained mainly palmitic, stearic, oleic, and linoleic acids. Ohnishi et al. (1990) reported that the ranges of fatty acids in the seeds of five grape cultivars were 6.7 to 8.9% for palmitic, 1.1 to 5.3% for stearic, 9.7 to 17.5% for oleic, 69.2 to 80.5% for linoleic and less than 0.1% for palmitoleic and linolenic acids. These results showed that the ratios of the fatty acids have less variability. The fatty acid composition of the grape seed oil is placed among the oils of safflower, sunflower, soybean, maize, cotton seed, poppy and tabacco, which are linoleic type (Weiss, 1983). As reported previously (Ohnishi et al., 1990), the fatty acid composition of grape seed oil was similar to that of sunflower oil. Sunflower oil generally comprises 60% linoleic, 25% oleic, 8% palmitic and 5% stearic acid (Weiss, 1983). The fatty acid composition of grape seed oil is very close to that of sunflower oil. The other important similarity between the two oils is TG (triglyceride) composition. The principal TG species in grape seeds were found to be LLL (trilinolein), OLL (oleo-dilinolein) and PLL (palmito-dilinolein), which were 80% in total. It was also reported that LLL, OLL and PLL were predominant in sunflower oil, their proportions being 36%, 23% and 12%, respectively (Barron et al., 1988; Ohnishi et al., 1990).

The degree of unsaturation in the grape seed oil (Table 2) was over 86%, coming from unsaturated fatty acids. High levels of unsaturation play an important role in lowering high blood cholestrol and also in the treatment of atherosclerosis (Axtell, 1981).

Poly-unsaturated fatty acids such as linoleic and linolenic are essential for the human body because they cannot be synthesized in the body. From this point of view, grape seed oil, very rich in linoleic acid, may be a valuable source of dieatery fat. Grape seed oil was rather poor in linolenic acid. Low levels of linolenic acid are desired in edible oils, because high levels of this fatty acid can cause unfavorable odor and taste in oil. Furthermore, since linolenic acid is simply oxidized due to having three double bonds on its hydrocarbon chain, the stability or shelf-life of an oil rich in linolenic acid would be too short. Because of its low quantities of linolenic acid, grape seed oil also has advantages in terms of human health and the shelf-life of the oil.

Total Tocopherol Content in Oil

Tocopherols are the most powerful natural fat-soluble antioxidants (Vitamin E). They exist in four forms of homologues: α (5,7,8- trimethyltocol), β (5,8-dimethyltocol), γ (7,8-dimethyltocol) and δ (8-methyltocol). The a form has the highest vitamin activity and the lowest antioxidant property in comparison with the δ form (Demirun et al., 1996). Lipid oxidation remains a major problem in the food industry. Oils with a high tocopherol content can be used in applications where a high level of antioxidant protection is needed (Haumann, 1990; Demirun et al., 1996). In the seed oils of grape cultivars, the concentrations of total tocopherols ranged between 328 mg/kg (Razakı) and 578 mg/kg (Kalecik karası), with an average of 454 mg/kg (Table 2). The value of total tocopherol found in grape seed oil was not higher than that found in soybean oil (860 mg/kg) and sunflower oil (880 mg/kg), but was close to that found in cotton seed oil (560 mg/kg) and higher than that in sesame oil (387 mg/kg) (Demirun, 1986; Fukuda et al., 1986; Shahidi et al., 1997).

Table 3. The comparison of wine and table grape seeds with respect to oil contents and some oil quality properties.

Cultivars	Oil content (%)(v/w)	Fatty acid composition (%)(v/w)						Degree of unsaturation (%)	Total tocopherol in oil (mg/kg)
		Palmitic	Stearic	Oleic	Linoleic	Linolenic	Eicosenoic		
Wine grape	16.77±1.86	8.25±0.79	4.42±0.60	20.82±2.46	65.66±2.90	0.43±0.20	0.43±0.20	87.34±0.81	446.19±68.38
Table grape	15.82±2.47	8.38±0.74	5.09±1.29	21.54±2.62	64.19±2.34	0.46±0.16	0.36±0.28	86.54±1.76	469.24±95.46

In the present study, it was also observed that there were no clear differences between wine cultivars and table grape cultivars with respect to oil contents, fatty acid compositions, degrees of unsaturation and total tocopherol contents (Table 3).

Correlations Between Oil Content and Oil Quality Properties

The simple correlation coefficients among the oil content, fatty acids and total tocopherol content of the grape seeds are given in Table 4.

Oil content showed positive correlations with stearic and linoleic acids, but negative correlations with palmitic, oleic, linolenic and eicosenoic acids. These correlations were not statistically significant. It was reported that in sesame seeds, oil content gave strong negative and positive correlations with oleic and linoleic acids, respectively (Reheja et al., 1989; Baydar and Turgut, 1994). The most remarkable correlation among the fatty acids was found between oleic and linoleic acid, which are primary fatty acids in grape seed oil. A statistically significant negative correlation was found between oleic and linoleic acid (r =-0.903), which was also found in seeds of the sunflower, soybean, rape, peanut, sesame, safflower etc. (Weiss, 1983).

The correlation coefficient between oil content and total tocopherol content was negative (r =-0.316). In addition, the average total tocopherol content of sunflower oil was shown to be negatively correlated with oil content (Linow and Pohl, 1970). Total tocopherol content of grape seed oil was negatively correlated with palmitic and stearic acids, but positively correlated with other fatty acids (Table 4).

Conclusion

The results of this research showed that grape seeds which are by-products of the pomace obtained after the wine-making process can be used as an edible oil source. The quality properties of fatty acids are markedly dependent on their degree of saturation. Unsaturated fatty acids have a lower melting point than saturated fatty acids. Mammals lack the enzymes needed to produce polyunsaturates, and therefore, polyunsaturated fatty acids must be supplied through external sources (Stryer, 1988). Lowering the linolenic acid content has been a research goal of plant breeders to improve the flavor quality and oxidative stability of vegetable oils. Decreasing the linolenic acid and increasing the oleic acid have been found to give greater frying stability. Linolenic acid having 3 double bonds is undesirable because it is readily oxidized and oxidation products are believed to be the cause of off-flavor in the oils (Warner et al., 1997). Having a high level of linoleic acid increased the importance of grape seed oil in the particular treatment of high cholesterol and atherosclerosis, and, also, having a low level of linolenic acid increased the oxidative stability, taste and odor quality of the oil. Total tocopherol content in grape seed oil was found to be an average of 454 mg/kg.

All these quality characteristics of grape seed oil were similar to those of sunflower oil, which is one of the most commonly produced and consumed oils in the world. Today, grape seeds have only been extracted on a small scale to obtain edible vegetable oils in Europe. However, grape seeds as a large by-product can be evaluated both to produce high quality oil and to lower the wine production costs.

Table 4. Correlations between oil content and oil quality properties.

	Fatty Acids						Total Tocopherol
	Palmitic	Stearic	Oleic	Linoleic	Linolenic	Eicosenoic	
Oil content	-0.322	0.181	-0.382	0.428	-0.360	-0.362	-0.316
Palmitic		0.065	-0.069	-0.206	0.077	-0.367	-0.094
Stearic			-0.044	-0.286	0.016	-0.266	-0.478*
Oleic				-0.903**	0.038	0.424	0.026
Linoleic					-0.172	-0.317	0.090
Linolenic						0.518*	0.275
Eicosenoic							0.480*

* P< 0.05 ** P<0.01

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